Tracing cosmic magnetic fields using molecules

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Abstract

Understanding the magnetic field strength and morphology of astrophysical regions is of great importance to understand their dynamics. There exist a number of methods astronomers can employ to trace magnetic field structures, and each have their own limitations. This thesis focuses on tracing magnetic field using molecules.

A promising technique to trace the magnetic field morphology around evolved stars, or on the smallest scales of star forming regions, is (sub-)millimeter spectral line polarization observations. Line (linear) polarization can either arise in association with maser radiative transfer, or alternatively, molecular lines polarize through the Goldreich-Kylafis effect. In both cases, the polarization angle traces the magnetic field with a 90-degree ambiguity. In order to remove this ambiguity, and to estimate the observational viability of particular line polarization measurements, polarized line radiative transfer needs to be employed. This thesis contributes to this field in that it presents a three-dimensional polarized line radiative transfer tool: PORTAL. PORTAL simulates the emergence of thermal molecular line polarization in astrophysical objects of arbitrary geometry and magnetic field morphology. Also, this thesis introduces a novel polarization mechanism: collisional polarization. Which provides the possibility of directly detecting ambipolar diffusion in disks through the polarization of molecular ions.

Some molecules occur as masers. Masers occur naturally in specific astrophysical regions, which are often associated with highly dynamical events. Their emission is characterized by narrow lines and high brightness temperatures, and is often associated with polarization. The polarization of masers contains information on the magnetic field strength and direction of the regions they occur in. Many maser polarization observations have been performed over the last 30 years. However, one requires versatile maser polarization models that can aide in the interpretation of these observations. This thesis contributes to the study of maser polarization by presenting a modeling program called CHAMP (CHARacterizing Maser Polarization) that simulates the polarization of masers of arbitrarily high maser saturation and high angular momentum.

Methanol masers occur exclusively in association with high-mass star forming regions. They trace specific regions there, and may teach us about the magnetic field structures in the densest regions. There have been many polarization observations of methanol, but proper interpretation of them has not been possible because the molecular properties associated with its magnetic field interactions have been unknown. This thesis presents the first quantum chemical models of methanols magnetic field interactions. With them, we re-interpret the many previous methanol maser polarization observations and conclude that magnetic fields are dynamically important to the process of high-mass star formation.
Keywords: magnetic field – stars: formation – stars: evolved – stars: massive – masers – polarization
Research contributions

This thesis is based on the work contained in the following papers:

• B. Lankhaar, W.H.T. Vlemmings, G. Surcis, H.J. van Langevelde, G.C. Groenenboom, A. van der Avoird:  
  *Characterization of methanol as a magnetic field tracer in star-forming regions.*  

• B. Lankhaar, W.H.T. Vlemmings:  
  *Characterizing maser polarization: effects of saturation, anisotropic pumping and hyperfine structure.*  

• B. Lankhaar, W.H.T. Vlemmings:  
  *PORTAL: Three-dimensional polarized (sub) millimeter line radiative transfer.*  

• B. Lankhaar, W.H.T. Vlemmings:  
  *Collisional polarization of molecular ions: a signpost of ambipolar diffusion.*  

• B. Lankhaar, W.H.T. Vlemmings, P. Bjerkeli:  
  *Spectral line polarization in protoplanetary disks*  
  Manuscript intended for submission to Astronomy & Astrophysics.

Other publications not included in this thesis

• B. Lankhaar, G.C. Groenenboom, A. van der Avoird:  
  *Hyperfine interactions and internal rotation in methanol.*  

• D. Dall'Olio, W. H. T. Vlemmings, G. Surcis, H. Beuther, B. Lankhaar, M. V. Persson, A. M. S. Richards, and E. Varenius:  
  *Methanol masers reveal the magnetic field of the high mass protostar IRAS 18089-1732*  

  *The shock-heated atmosphere of an asymptotic giant branch star resolved by ALMA.*  

• R. Larsson, B. Lankhaar, P. Eriksson:  
  *Updated Zeeman effect splitting coefficients for molecular oxygen in planetary applications.*  
Detection of highly excited OH towards AGB stars - A new probe of shocked gas in the extended atmospheres.

• W. H. T. Vlemmings, B. Lankhaar, P. Cazzoletti, C. Ceccobello, D. Dall’Olio, E. F. van Dishoeck, S. Facchini, E. M. L. Humphreys, M. V. Persson, L. Testi, J. P. Williams
Stringent limits on the magnetic field strength in the disc of TW Hya. ALMA observations of CN polarisation.

• R. Larsson, B. Lankhaar:
Zeeman effect splitting coefficients for ClO, OH and NO in some Earth atmosphere applications.

• D. Dall’Olio, W. H. T. Vlemmings, B. Lankhaar and G. Surcis:
Polarization properties of methanol masers.
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Introduction

1.1 Astrophysical magnetic fields

Magnetic fields are ubiquitous in the universe. They are important to many astrophysical processes. In this thesis, we are interested in processes associated with magnetic fields in cosmic media. Particularly, we describe methods to trace magnetic fields using molecular line emission. In this section, we review the stages of the stellar evolution process, with particular emphasis on star formation and the post-main sequence phase.

Human intuition about magnetism is based on the magnetic fields that are associated with currents. Once the source of magnetism is removed, the magnetic field quickly diffuses away. Magnetic fields are only found in association with their source, which requires a constant operation in order for the magnetic field to be sustained. Indeed, on earth we are surrounded by air, which is an effective insulator. Magnetic fields that are not sustained are rapidly diffused through the process of Ohmic diffusion.

Once we leave the Earth’s atmosphere we eventually find ourselves in the interstellar medium (ISM), where the gas is dilute and electrons roam almost freely. In such diffuse gases, particle collisions happen so infrequently that they can be considered effective—almost perfect—conductors (Alfvén 1963). Here, electric fields are restored almost instantaneously, and magnetic fields—once generated—are ‘frozen’ into the gas. Because of these properties—even though it is only partially ionized—the interstellar medium can be considered a plasma (Parker 2019).

We linger on the statement that the magnetic field is frozen into the gas of a perfect conductor. We can show this to be the case if we note the induction
\[
\frac{\partial B}{\partial t} = \eta \nabla^2 B + \nabla \times (v \times B) \tag{1.1}
\]

where \( B \) is the magnetic field, \( \eta \) is the magnetic diffusivity of the medium, and \( v \) is the bulk motion. The relative importance of both terms in the induction equation can be estimated as \( \eta \nabla^2 B \sim \eta B/L^2 \) and \( \nabla \times (v \times B) \sim VB/L \), where \( L \) is the characteristic length scale and \( V \) the characteristic velocity. The ratio between them is the magnetic Reynolds number: \( R_m = LV/\eta \) and captures the relative importance of magnetic diffusion. In most astrophysical plasmas, because of their large scales and low densities, \( R_m \gg 1 \), and it is appropriate to ignore the diffusion term in the induction equation \( [\text{Shu} \ 1991a, \ \text{Choudhuri} \ 1998] \). It can be shown that the convective derivative of the magnetic flux vanishes, \( \frac{d\Phi_B}{dt} = 0 \), if there is no magnetic diffusion (infinite electric conductivity). This constitutes Alfvén’s theorem, which states that the magnetic field passing through a surface moving with the fluid is conserved \( \text{(Alfvén} \ 1942) \)

\[
\int_S dS \cdot B = \text{constant.} \tag{1.2}
\]

An important implication of Alfvén’s theorem is that converging gas flows have an associated increase in their magnetic field, which is why it is sometimes referred to as the flux-freezing theorem. The flux-freezing theorem is central to the progression and dynamics of astrophysical processes. To a good approximation, the flux-freezing theorem holds for almost all processes in the ISM \( \text{(Kulsrud} \ 2020) \). Still, non-ideal magneto-hydrodynamical (MHD) effects are important to the progression of star formation through, for instance, ambipolar diffusion \( \text{(Mouschovias \ & Ciolek} \ 1999) \). Or, on cloud scales, super-Alfvénic turbulence tends to twist magnetic field lines, thus gradually lowering the characteristic length scale, \( L \), up to a point where non-ideal magnetic reconnection events may occur \( \text{(Parker} \ 1957, \ \text{Lazarian \ & Vishniac} \ 1999) \).

In this thesis, we focus on cosmic media; particularly, on the star-formation process in the ISM, and the shedding of evolved stellar atmospheres leading to a circumstellar medium (CSM). In the star formation process, a diffuse gas cloud collapses under its own weight to form stars which accrete the collapsing gas \( \text{(Shu} \ 1977) \). The gas cloud from the outset is endowed with a magnetic field that permeates the entire galaxy \( \text{(Beck} \ 2016, \ \text{Crutcher} \ 2012) \). The geometry of the collapse process and its relation to the magnetic field, combined with the flux-freezing theorem predicts a relation between the gas (number) density and the magnetic-field strength, often captured in the so-called power law: \( B \propto n^{\kappa} \); where the constant \( \kappa \) is different for models with dynamically important magnetic fields \( \text{(Crutcher} \ 2012) \).

But, for there to be flux-freezing in astrophysical processes, we need to establish that there exists a magnetic field in the first place, because later on,
when studying the star-formation process in the next section, we take this as a
given. Radio synchrotron observations of other spiral-galaxies generally reveal
magnetic-field strengths of the order of $\sim 10 \mu G$ (Beck 2016). The magnetic
fields are stronger in central starburst regions and weaker in between the spiral
arms, consistent with the correlation between density and magnetic-field strength.
The sustenance of the galactic magnetic field is thought to be achieved through
galactic-scale dynamo action (Widrow 2002). The galactic magnetic field threads
the ISM that makes up part of the galaxy and where star formation takes place. In
the next section, we study the formation of stars. We will lay particular emphasis
on the role of magnetic fields in the star-formation process.

1.1.1 Star formation

Part of this thesis will be focussing on the role of magnetic fields in star formation.
The formation of stars is thought to occur in giant molecular clouds. Giant molec-
ular clouds are divided up in regions of higher density that are self-gravitating
clumps. These clumps contain a number of cores of still greater density, which
are also self-gravitating. Each core is likely to eventually form a star or a multi-
ple system (Draine 2010). In order for a star to form, the core must collapse
under its own gravity. If we balance the stabilizing thermal gas pressure with the
cores’ self-gravity, we can derive the core-mass above which the cloud will collapse
under its own mass: the Jeans mass (Jeans 1902). The Jeans mass is a function
of the density and the gas temperature. A lot of cores are observed to be more
massive than the Jeans mass, while still not dynamically collapsing. Such cores
require additional stabilizing forces, often hypothesized to be found in turbulence
or magnetic fields (Tan et al. 2014).

The turbulent pressure can be estimated from line-profile measurements
of molecular lines in the dense cores (Elmegreen & Scalo 2004). Turbulence is
seen to be present and dynamically important for the more massive core$^1$, while
lower mass cores are relatively unaffected by it (Tan et al. 2014). Magnetic fields
permeate the entire galaxy, and thus also the dense cores. The question is if
the magnetic field is strong enough to be of importance to the gas dynamics.
The relative importance of the magnetic field to the gravitational collapse of the
cloud is often estimated through a mass-to-flux ratio. A high mass-to-flux ratio
means that gravity is stronger than the stabilizing magnetic field: the cloud is

$^1$In this section, we discuss the formation of massive stars within the Core Accretion model. The core
accretion model of massive star formation can be roughly thought of as a scaled-up version of low-mass
star formation, where turbulent gas motion provides for an additional stabilization. There exist other
hypotheses of massive star formation processes, of which the most important is Competitive Accretion.
In the picture of competitive accretion, massive pre-stellar cores move through a self gravitating clump
and accretes mass within a certain accretion radius, that is determined by the core mass. Massive star
formation through competitive accretion leads naturally to the stellar IMF, but begins to have problems
when stellar feedback and magnetic fields are being included.
magnetically supercritical, while a low mass-to-flux ratio means that the cloud is supported by a stabilizing magnetic field: the cloud is magnetically subcritical.

In a magnetically regulated process of star formation, clouds are supported by a magnetic field that threads them. Initially, the cloud is magnetically subcritical. The magnetic field does only work on the charged part of the medium, which transfers the support to the neutral medium via collisions. Since collisions happen rather infrequently, the neutral medium does not fully capture the support of the magnetic field and slips, quasi-statically, with an approximate constant velocity, inwards through gravitational contraction. This process is called ambipolar diffusion. The magnetic field is frozen to the charged medium, while the contracting neutral medium holds all the mass. So, through this contraction, the mass-to-flux ratio slowly increases to being supercritical and a dynamic collapse ensues (Mouschovias & Ciolek 1999). For solar mass stars, the magnetically regulated core collapse leads to an initial-core-mass function distribution that is in very good agreement with the initial-core-mass function derived from observations (Kunz & Mouschovias 2009). However, more massive cores are only viable through additional stabilizing turbulence (Tan et al. 2014). Still, magnetic regulation of the collapse process of massive cores can happen through ambipolar diffusion.

Numerical simulations of magnetically regulated collapse, predict that in the dynamical collapse stage, from about $10^5$ cm$^{-3}$, the magnetic-field strength holds a relation to the number density of $B \propto n_{H_2}^{0.47}$ (Mouschovias & Ciolek 1999). In the dynamical collapse phase, the mass-to-flux ratio is 2 – 3 times the critical mass-to-flux ratio. In magnetically regulated star formation, the contraction of matter is along the magnetic field lines, and infall will be associated with a disk-like structure that is oriented perpendicular to the magnetic field. Additionally, the magnetic field is pinched in the perpendicular direction because of the (albeit approximate) flux-freezing of the magnetic field, and yields an hour-glass shape. Models where the magnetic field does not have a regulatory role and the collapse is randomly oriented with respect to the magnetic field, predict that the magnetic field scales $B \propto n_{H_2}^{0.66}$ (Crutcher 2012).

Direct observations of the magnetic field in star-forming regions suggest that the magnetic field scales with the density as $B \propto n_{H_2}^{0.65}$, while most molecular clouds are generally slightly supercritical (Crutcher et al. 2010). This results implies that magnetic fields do not fully regulate the progression of star formation, and that magnetic fields are only part of the story of the onset of star formation. Turbulence plays an additional, and possibly dominant, role. Still, turbulence is observed to be sub- or trans-Alfvénic, suggesting that magnetic fields are important to the dynamics of turbulence. Additionally, on the smaller scales of star formation magnetic fields are important to a range of processes, whose feedback to the cloud-scale affects the generation and maintenance of turbulent processes (Krumholz & Federrath 2019).

We move on to the smaller scales of star formation, and follow the material
that collapses towards the centre of a core. The collapsing core is from the outset endowed with a small net rotation \( \text{(Krumholz} \) \( \text{2015)} \). When the mass of the core is infalling, nature requires that angular momentum be conserved. Therefore, matter that is infalling will increase its rotational energy, and through this, form a disk-like structure. In the centre of the disk (and the collapsing region), a protostar has had time to form. In order for mass to accrete onto the protostar, angular momentum has to be transported outwards. This can occur through viscous tension, provided the viscosity of the disk gas is amplified by turbulence \( \text{(Pringle} \) \( \text{1981)} \). The turbulence in turn can form through instabilities such as the magneto-rotational instability \( \text{(Balbus} \& \text{Hawley} \text{1991)} \). Other means of angular momentum transport are magnetic tensions between the toroidal and radial part of the magnetic field, or the formation of an outflow structure. Outflows that are bipolar in structure are often seen in association with accretion disks, and they are thought to be launched by magnetic fields \( \text{(Blandford} \& \text{Payne} \text{1982; Shu et al.} \text{2000; Bjerke} \text{li et al.} \text{2016)} \).

The accretion onto the protostar lessens with time and demands on the fast removal of angular momentum are diminished. The outflow dies out and—for the lower mass stars—a quasi-stationary disk forms in which the dust has time to coagulate and increase in size, while the gravitational contraction of the protostar has raised the temperature there enough to drive hydrogen nuclear fusion, which takes over as the main-energy source of the protostar. The star has thus entered its ‘main-sequence’. The persistent luminosity of the star blows away most of the disk material that has accrued over the star-formation process, while possible planet- and comet-sized objects remain to revolve around it.

1.1.2 The outflows of evolved stars

The magnetic field that made up the collapsing core from the beginning is partially transferred to the central star through its coupling to the gas. It should be said though that processes such as ambipolar diffusion and Ohmic dissipation have weakened the magnetic field further. Still, all stars on the main-sequence are thought to be associated with a magnetic field \( \text{(Berdyugina} \text{2008)} \). Some of the magnetized stars are characterized by a magnetic field that is relatively stable over time. These are believed to host a magnetic field that is the remnant of the ISM magnetic field, amplified by the contraction \( \text{(Braithwaite} \& \text{Spruit} \text{2004)} \). While other stars, such as our Sun, have a magnetic field that is highly variable over time. Such magnetic fields have to be sustained by a stellar dynamo, likely driven by stellar rotation in combination with convection \( \text{(Parker} \text{1953)} \).

When solar-type main-sequence star runs out of hydrogen in its core, it expands and cools down in its evolution along the red giant branch (RGB). While the outer layers of an RGB star cool down, gravitational contraction heats up its core further up to the point when it becomes hot enough to fuse helium. After
exhausting the central helium, the stellar envelope expands for a second time, and
the star goes over to evolve along the asymptotic giant branch (AGB) (Habing
& Olofsson 2013). The expansion of the star weakens the magnetic-field strength
because of flux-freezing. Additionally, the stellar evolution processes likely have an
impact on the stellar dynamo-action, and the magnetic field changes accordingly.
Few direct observations exist of AGB stellar surface magnetic fields (Vlemmings
2018). The usual method of Zeeman-Doppler imaging is not sensitive enough for
the (in comparison to main-sequence stars) weaker magnetic fields of AGB stars
(see Eq. (3.35)).

The atmosphere of the AGB star is slowly shedding a stellar wind, thus
forming a circumstellar medium. In the extended atmosphere of AGB-type stars,
the relatively low temperature allows for certain molecules to adhere in complexes
that are generally referred to as dust (Gail & Sedlmayr 2014). Momentum carried
by the light that luminates from the central star is transferred to the dust through
its broad-band absorption or scattering. This drives a strong stellar wind that
results in significant mass loss of the AGB star (Lamers et al. 1999). A magnetic
field could have a significant impact on the wind-formation in AGB stellar atmos-
pheres. For instance, Alfvén waves could add to the acceleration of the wind
(Falceta-Gonçalves & Jatenco-Pereira 2002), or they can create cool spots on the
stellar surface so that dust could form more easily there (Soker 1998; Vlemmings
2018). As to the internal stellar structure, magnetic fields affect nuclear fusion
processes, through MHD-induced internal mixing, that can significantly impact
the stellar yields (Trippella et al. 2016).

The loss of stellar mass in the AGB phase is an important feature of the
galactic gaseous life-cycle as it enriches the ISM with the elements produced
through the stars’ life, as well as providing seeds for dust production in the ISM
(Habing & Olofsson 2013). The high mass-loss of the AGB star limits its lifetime
to about $10^6$ yr. After losing essentially all of its envelope, the star starts heating
up, while maintaining approximately the same luminosity. It has now entered the
post-AGB phase. The stellar wind in the post-AGB phase is characterized by a
lower mass loss, but is associated with large outflow velocities, which are sometimes
bipolar in their geometry (Van Winckel 2003). The stellar wind from the AGB
phase has built an envelope of gas and into which the post-AGB wind crashes. If
the conditions are suitable, the envelope gas is ionized and emits as a Planetary
Nebula (Kwok et al. 1978). Planetary Nebulae manifest elaborate geometries that
require equally elaborate wind expulsion mechanisms to be explained (Balick &
Frank 2002). Magnetic fields might play an important role here, too (Nordhaus
et al. 2007; Balick & Frank 2002).
1.2 Observations of cosmic magnetic fields

Cosmic magnetic fields have been observed in a variety of ways. We review the range of methods that astronomers employ to measure both the strength and morphology of magnetic field structures in astrophysical objects.

On the galactic scale, radio astronomers have identified that a significant part of the emission in the radio part of the spectrum is due to synchrotron emission. Synchrotron radiation is produced by highly energetic electrons traveling in a path that is curved with respect to the magnetic field (Shu 1991b). Synchrotron radiation has a characteristic intensity-frequency relation and can be identified through a broad spectral analysis; its emission is also partially polarized (Rybicki & Lightman 2008) and may reveal the properties of the magnetic field that gave rise to the emission.

On smaller scales, of the order of molecular clouds, we require different mechanisms to trace magnetic fields, since the high-energetic electrons are not present. Galactic molecular clouds span rather large angular scales, and for a global analysis, single-dish observations will have the appropriate angular resolution. Molecular clouds can be traced through the observation of molecular lines, typically in the radio to the submillimeter region of the spectrum. Alternatively, the interstellar dust that makes up about a percent of the molecular cloud mass may be observed, typically in the infrared part of the spectrum.

Some molecular emission lines may be used as tracers of the magnetic-field strength. Those molecules that have unpaired electrons—paramagnetic molecules—exhibit particularly strong Zeeman effects (section 3.2.2). Zeeman effects can be seen in the circular polarization of spectral lines, and are sensitive to the line-of-sight magnetic field (Crutcher & Kemball 2019). Molecular lines can also be used as tracers of the magnetic field morphology. Through the so-called Goldreich-Kylafis (GK) effect (section 4.3), rotational lines tend to be linearly polarized in the direction parallel or perpendicular to the magnetic field, provided that an anisotropic velocity gradient as well as relatively low densities characterize the emission region (Goldreich & Kylafis 1981).

Most notable polarized dust continuum observations of molecular clouds come from the Planck space telescope, that mapped dust emission in the far-infrared (FIR) region of the spectrum (Ade et al. 2015), the air-borne observatory SOFIA, that can go up to mid-IR frequencies (e.g. Chuss et al. 2019) and ALMA (Hull & Zhang 2019). Tracing cloud structures through polarized observations, they show the dust emission to be significantly polarized. This is believed to occur through the Radiative Torque Alignment (RAT) mechanism, where an anisotropic radiation field ‘spins up’ (non-spherical) dust particles to precess around the magnetic field axis (Lazarian & Hoang 2007). Thus, on average, the dust particles are
aligned with the magnetic field and their polarized emission traces the magnetic field structure. The magnetic-field strength can be estimated by comparing the scatter in the dust polarization angles to the turbulence—where the turbulence is gauged by co-spatial line-profile measurements. The comparison gives an indication of the ratio of turbulent and magnetic energy; and thus is a gauge for the magnetic field strength (Davis Jr & Greenstein 1951; Chandrasekhar & Fermi 1953; Houde et al. 2009). This method is referred to as the Chandrasekhar-Fermi method, and gives an order-of-magnitude estimate of the magnetic-field strength.

We need yet better angular resolution to trace smaller scales of star formation; closer to the protostar. (Sub-)millimeter observations using the Atacama Large Millimeter/submillimeter Array (ALMA) interferometer may be employed for this. Tracing magnetic fields in the (sub)millimeter regime close ($\lesssim 100$ AU) to the protostar has proven more difficult using dust polarization observations. In these warmer regions, where a clear disk geometry has manifested in the gas (and dust) structure, and an intricate radiation morphology is present, alternative alignment mechanisms may determine the spinning properties of the dust (Kataoka et al. 2015, 2017; Stephens et al. 2017). This gives rise to polarized emission that does not trace the magnetic field structure. Such polarized dust emission maps may be used to trace other properties of these small-scale star-forming regions, but for magnetic field morphology measurements, we have to defer to spectral line polarization measurements. It can be shown that GK polarization does trace the magnetic field, also in these regions (see Chapter 3). However, the polarization mechanism of molecular spectral lines in the complicated star-forming geometries cannot be viably modeled through the large velocity gradient (LVG) approximation that characterizes the standard GK effect (see section 4.3). Rather, three-dimensional modeling of the polarized radiation transport is required. This is what we present in paper III of this thesis.

When the star-formation process is done and the star enters its main-sequence, its magnetic field can be gauged through Zeeman-Doppler imaging of atomic line transitions in the optical (Semel 1989). In particular, such measurements of the Sun have yielded magnetic field maps of high resolution, that show a very complicated—but approximately dipolar—magnetic field structure of the Sun’s surface. Also, magnetic fields are closely related to many processes on the Sun’s surface that are associated with its mass-loss (Choudhuri 1998). Typical solar surface magnetic-field strengths are on the order of $\sim G$, while the magnetic fields of sunspots can go up to $\sim kG$ field strengths (Zwaan 1987).

After their main sequence evolution, solar-type stars eventually enter the AGB phase, which is partially characterized by a strong mass loss through a stellar wind. Optical observations of the stellar surface are often obscured, and the magnetic field has weakened because of the stellar expansion, so Zeeman-Doppler imaging is of limited utility. Close to the stellar surface, SiO masers are excited in rotational lines at millimeter and submillimeter wavelengths, and show partic-
ularly high degrees of polarization, both circular and linear \cite{Cotton2004}. The polarization might trace the magnetic field morphology and strength, but a better understanding of the excitation mechanism, and how it pertains to SiO masers’ polarization properties is required to draw definitive conclusions (see also Paper II). Outflows that are seen in some AGB and post-AGB objects, are associated with maser-lines from \textit{H}_2\textit{O} and OH \cite{Gray2012}. These maser-lines can be studied for magnetic field signatures in their polarization properties \cite{Vlemmings2005, Vlemmings2006, Rudnitski2010}. Thermal lines are significantly affected by the central stellar emission and may be polarized \cite{Morris1985}. This also requires proper three-dimensional radiative transfer modeling to be interpreted (Paper III and Vlemmings et al. in prep.).

\subsection*{1.3 Motivation of this thesis}

In this introduction, we have stressed the importance of magnetic fields to all the stages of stellar evolution, and the difficulties of measuring them, particularly on the smallest scales of star-formation processes and in the vicinity of evolved stellar objects, that lose much of their mass in a stellar wind. We contend that tracing magnetic fields in these regions through the polarization of molecular lines is a viable and promising method. We briefly outline the contributions that this thesis makes in this endeavor.

To trace the densest regions of the ISM, close to stellar objects, interferometers with high angular resolution are required. Of these, the most recent and advanced is the ALMA telescope. ALMA has recently commissioned full polarization capabilities, allowing for the observation of these star-forming regions at the smallest scales while utilizing the polarization capabilities to give information on the magnetic field.

Alternatively, masers have been traditionally used as probes in the denser parts of (high-mass) star-forming regions, where they are often associated with accretion flows and feedback processes. Masers have also been used as tracers of the gas close to the AGB stellar surface of AGB stars, in regions before the dust condensates, and in the (bipolar) outflows of some AGB/post-AGB objects. Masers radiate optimally in the radio to millimeter/submillimeter part of the spectrum, and they are particularly suited to high-resolution imaging through Very Long Baseline Interferometry (VLBI).

As significant strides have been made in developing polarized interferometry capabilities to observe astrophysical processes on the smallest scales, the development of radiative transfer modeling tools to interpret the polarized signals from these regions has been lacking. In this thesis we present such tools, both for thermal line emission in (sub)millimeter spectral lines (Paper III, V), as well as for
one-dimensional maser propagation through a medium permeated by a magnetic field (Paper II).

We dedicate particular attention to the molecular physics of the Zeeman effect of a particular maser species that traces dense regions of high-mass star-forming regions: methanol (CH$_3$OH). Over the years, many maser polarization observations of this species have been performed (e.g. Vlemmings et al. [2011]), but a rigorous model for its complicated Zeeman effect has never been presented. Paper I presents a first-principles model of methanols Zeeman effect, that also takes into account the effects of torsional motion of the OH-group with respect to the CH$_3$ group.

We have at many points in this introduction stressed the importance of ambipolar diffusion in the star-formation process. Still, telescope observations have not been able to show the presence of this process through direct observation (Yen et al. [2018]). In Paper IV, we present a hypothesis, that the presence of an ambipolar diffusion induced drift-velocity gives rise to a partial alignment of molecular ions, because their collisions with the main collision partner H$_2$ have a preferential direction. We show that on the smallest scales of star formation, within $\sim 100$ AU of the accreting protostar, this process will give rise to detectable polarization in the emission, that traces the magnetic field direction, as well as provide direct evidence for the process of ambipolar diffusion.
Chapter 2

Light

The senses of the astronomer are limited. Astronomers are almost exclusively bound to inferring the properties of night-sky objects from the electromagnetic radiation they emit. Modern astronomers can also enlist high-energy particles and even gravitational waves as sources of information; but still, most of astrophysics is based on the observation of light. The earliest astronomers had to limit themselves to observation of electromagnetic radiation in the visible spectrum, but nowadays also the radio, infrared, UV and X-ray part of the electromagnetic spectrum have become available for astronomical observations as well.

In this chapter, we revisit the properties of light. To fully appreciate the work contained in this thesis, we lay particular emphasis on two properties of light: coherence and polarization. In most astronomical observations, both the coherence and polarization properties of light are ignored. Coherence might be an important factor in the transfer of radiation in masers, while the polarization properties of light are indicative of a particular alignment of the emitting region. In the following section, we introduce the radiative transfer equation and define the specific intensity of light. After that, we relate this to the polarization properties of light. We end this chapter by discussing the use of light in this thesis.

2.1 Radiative transfer equation

From the definition of how light is measured, we describe some of its properties and introduce the radiative transfer equation that characterizes the transport of radiation in astrophysical media.

When we measure light, we measure the total energy of the light ray, $dE$, that passes per unit area, $dA$, per unit time, $dt$, per unit frequency, $d\nu$, and per unit
solid angle, $d\Omega$ (Chandrasekhar 2013)

$$I_\nu = \frac{dE}{dAdtd\nu d\Omega}. \quad (2.1)$$

The quantity, $I_\nu$, is called the specific intensity. It can be related to the density of states in phases space, $N = dN/dV_x dV_p$, where $N$ is the number of photons, and $V_x$ and $V_p$ represent the volume in physical and momentum space. By using $dE = h\nu dN$, $dV_p = (h/c)^3 \nu^2 d\Omega d\nu$ and $dV_x = c dt dA$, we have the density of states (Thorne & Blandford 2017)

$$N = \frac{c^2 I_\nu}{h^4 \nu^3}. \quad (2.2)$$

Assuming that the (bosonic) photons are in statistical equilibrium, at some temperature, $T$, we have the standard bosonic distribution function (Landau et al. 1980)

$$N_{s.e.} = \frac{2}{h^3} \frac{1}{e^{h\nu/kT} - 1}, \quad (2.3)$$

where the factor 2 comes from the photon energy degeneracy. A photon gas that is in thermal equilibrium, thus has a specific intensity

$$B_\nu(T) = \frac{h^4 \nu^3}{c^2} N_{s.e.} = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}, \quad (2.4)$$

which is the Planck function.

Now, we consider a ray of light moving through some medium. The changes to the specific intensity can be described by the convective derivative (Shu 1991b)

$$\frac{1}{c} \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) I_\nu = \text{sources} - \text{sinks},$$

$$\left( \frac{\partial}{\partial ct} + \mathbf{n} \cdot \nabla \right) I_\nu = \epsilon_\nu - \kappa_\nu I_\nu, \quad (2.5a)$$

where $c$ and $\mathbf{n}$ are the speed and direction of the light ray, $\epsilon_\nu$ is the emissivity of the medium and $\kappa_\nu$ is the absorption coefficient of the medium. In this thesis, we are predominantly interested in the interaction of light with molecules. We present the appropriate absorption and emissivity coefficients for a molecular medium in section 4.1. At the frequencies that we are interested in in this thesis, it is safe
to ignore scattering of radiation in the radiative transfer. One can compute the propagation of the specific intensity of a ray of light (in the Lagrangian frame) as

\[
\frac{d}{ds}I_\nu = \epsilon_\nu - \kappa_\nu I_\nu,
\]
\[
\frac{d}{d\tau_\nu}I_\nu = S_\nu - I_\nu,
\]

(2.5b)

where we define \(\tau_\nu\) as the optical depth; and \(S_\nu = \epsilon_\nu/\kappa_\nu\) is the source function. For a medium in thermal equilibrium \(S_\nu \rightarrow B_\nu(T)\); so that under optically thick conditions, the specific intensity will converge to \(I_\nu \rightarrow B_\nu(T)\), thermal radiation.

### 2.2 Polarization and coherence properties of light

Up to now, we upheld a fluid-like description of electromagnetic radiation—as particles traveling through a medium of sources and sinks. To appreciate more deeply some of the properties of light that will interest us, we will take a step back and consider the light as oscillating electric and magnetic fields. While doing this, we dedicate particular attention to the polarization and coherence properties of light.

To start off, we note the Maxwell Equations ([Jackson](1998))

\[
\nabla \cdot E = 4\pi \rho_e, \quad \nabla \cdot B = 0, \\
\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t}, \quad \nabla \times B = \frac{4\pi}{c} j_e + \frac{1}{c} \frac{\partial E}{\partial t},
\]

(2.6)

that relate the electric and magnetic fields, \(E\) and \(B\) to each other, and the current density, \(j_e\) and charge density \(\rho_e\). In a vacuum, the charge density and electric current are both zero: \(\rho_e = 0\) and \(j_e = 0\). Then, under vacuum conditions, the following wave equations can be derived from the Maxwell equations

\[
\left(\frac{\partial^2}{\partial t^2} - \frac{1}{c^2} \frac{\partial^2}{\partial z^2}\right) E = 0,
\]

(2.7a)

\[
\left(\frac{\partial^2}{\partial t^2} - \frac{1}{c^2} \frac{\partial^2}{\partial z^2}\right) B = 0,
\]

(2.7b)

which has the general solution propagating in the \(\pm z\) directions ([Shu](1991b))

\[
E = E_+ (z - ct) + E_- (z + ct),
\]

(2.8a)

\[
B = B_+ (z - ct) + B_- (z + ct),
\]

(2.8b)
\[ \nabla \cdot \mathbf{E} = \nabla \cdot \mathbf{B} = 0 \] implies \( z \cdot \mathbf{E}_\pm = z \cdot \mathbf{B}_\pm = 0 \), and we have the electric and magnetic field components of the electromagnetic wave perpendicular to each other: \( \mathbf{B}_\pm = \pm z \times \mathbf{E}_\pm \). We posed the solution to the Maxwell equations in vacuum, Eq. (2.8), generally, but for our purposes it leads to better insight if we specify our solution to a monochromatic wave with frequency, \( \nu \), propagating in the \(+z\) direction. The solution for the electric field then, is trivially (Shu 1991b)

\[ \mathbf{E}_\nu(z - ct) = \text{Re} \left( \left( \hat{e}_x \hat{E}_x + \hat{e}_y \hat{E}_y \right) e^{2\pi i \nu (z/c - t)} \right), \]  (2.9)

where \( \hat{e}_x,y \) are the complex electric field amplitudes of the \( x \) and \( y \)-components of the radiation field.

It may be noted in the description of the monochromatic wave traveling in the \( \hat{z} \)-direction, that four variable factors describe the properties of the traveling EM-wave (the amplitudes \( \hat{E}_x,y \) and their phases \( \phi_{x,y} \)). This may be contrasted to our earlier fluid-like description of light, where only the specific intensity, \( I_{\nu} \), was used to describe a ray of light. Indeed, if we had only been concerned with the total energy flux of the electromagnetic wave, the total energy flux density

\[ I_{\nu} = \frac{c}{8\pi} \left( |\hat{E}_x|^2 + |\hat{E}_y|^2 \right), \]  (2.10a)

is the only parameter of interest. However, directional properties of light may also be detected, and are conveniently described as the Stokes polarization parameters

\[ Q_{\nu} = \frac{c}{8\pi} \left( |\hat{E}_x|^2 - |\hat{E}_y|^2 \right), \]  (2.10b)

\[ U_{\nu} = \frac{c}{4\pi} \text{Re} \left( \hat{E}_x \hat{E}_y^* \right), \]  (2.10c)

\[ V_{\nu} = \frac{c}{4\pi} \text{Im} \left( \hat{E}_x \hat{E}_y^* \right). \]  (2.10d)

These additional Stokes parameters hold information about the directional properties of the radiation. In this thesis, we will endeavor to obtain information of the preferential alignment of molecules in astrophysical environments due to—mainly—magnetic fields. Aligned molecules emit preferentially oriented radiation, which is reflected in the \( Q \), \( U \) - and \( V \)-components of the Stokes parameters.

The Stokes parameters that we derived from a monochromatic single wave are fully polarized,

\[ I_{\nu}^2 = Q_{\nu}^2 + U_{\nu}^2 + V_{\nu}^2. \]  (2.11)

However, in reality, and particularly in astrophysical context, the light that is observed is an ensemble of many EM-waves. These EM-waves are caught by a
detector over a period of time, and the Stokes parameters are measured as a time-average

\[ I = \frac{c}{8\pi} \left( \langle |\tilde{E}_x|^2 \rangle + |\tilde{E}_y|^2 \rangle \right), \]  
\[ Q = \frac{c}{8\pi} \left( \langle |\tilde{E}_x|^2 \rangle - |\tilde{E}_y|^2 \rangle \right), \]  
\[ U = \frac{c}{4\pi} \text{Re} \left[ \langle \tilde{E}_x \tilde{E}_y^* \rangle \right], \]  
\[ V = \frac{c}{4\pi} \text{Im} \left[ \langle \tilde{E}_x \tilde{E}_y^* \rangle \right], \]

which relaxes the condition (Chandrasekhar 2013)

\[ I^2 \geq Q^2 + U^2 + V^2, \]

and also allows for partially polarized light. The time average \( \langle \tilde{E}_p \tilde{E}_p^* \rangle \) includes all EM waves, with arbitrary frequencies. We can relate the time-dependent electric field to its frequency components through a Fourier decomposition

\[ \tilde{E}_p = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d(2\pi \nu) \tilde{E}_p(\nu) e^{-2\pi i \nu (t-z/c)}, \]

For non-coherent light, it may be shown that (Elitzur 1992)

\[ \langle \tilde{E}_p(\nu) \tilde{E}_p^*(\nu') \rangle = \langle \tilde{E}_p(\nu) \tilde{E}_p^*(\nu) \rangle \delta(\nu - \nu'), \]

which allows for the formulation of the Stokes parameters per frequency; and in the same dimension as the specific intensity.

Coherence is said to be present in radiation if the phases of ensembles of EM waves of different frequency (temporal coherence) or position (spatial coherence) are linked. When light is temporally coherent, the statistically random average we take in Eq. (2.15) no longer applies, which has deep consequences for matter-radiation interactions. Since we are interested in maser radiation in this thesis, it is necessary to linger on the coherence properties of EM radiation of astrophysical masers. In particular because the laboratory counterpart of the astrophysical maser—as well as laboratory lasers—possess a high degree of coherence in their radiation.

For this discussion, it is worth pointing out one important difference between laboratory and astrophysical masers. In order for maser radiation to build up, one needs a long column of population inverted particles (the maser medium). Since laboratories are generally confined to scales of the order of meters or less, this presents a challenge. Experimentalists circumvent this problem by placing on either side of the maser medium a mirror, which reflects back and forth the maser radiation, thereby increasing the maser path length with some orders of magnitude,
but also enhancing the spatial and temporal coherence of the maser radiation due to interference effects.

This is in contrast to masers on astrophysical scales, where maser path lengths are sufficiently long to lead to significant amplification of radiation by way of stimulated emission. Because of the large path lengths ($\ell/\lambda \sim 10^{14}$), maser radiation is only spatially coherent for rays that propagate on within small angles $\Delta \Omega \ll \lambda/\ell$ (Elitzur 1992), which is well below the maser beaming angles (see chapter 4) of $\Delta \Omega = 10^{-4} - 10^{-2}$ that are inferred from observations. Temporal coherence only manifests in astrophysical masers when stimulated emission events are occurring at a higher rate, $R$, than statistical fluctuations in the maser radiation, represented by its line-width (in angular frequency units), $\Delta \omega$. However, such high rates of stimulated emission are not observed for astrophysical masers (Elitzur 1992; Gray 2012). It has been suggested that coherence effects in astrophysical maser radiation give rise to the pulsed nature of some of the periodic masers through global superradiant states (Dicke 1954) in a very thin slice of velocity-space (Rajabi & Houde 2020). One critical difference between theories of superradiance and maser theory is their assumed lifetimes of the states participating in the maser/superradiant transition.

Observations of the temporal coherence properties of astrophysical maser radiation are necessary to determine the coherent nature of the stimulated emission processes in population inverted regions. Considering that most maser sources are relatively long-lived, and that their decay-rates—obtained from line-profile observations and maser excitation modeling—are too high for significant temporal coherence to build up, we assume throughout this thesis that astrophysical maser emission is non-coherent.

2.3 The use of light in this thesis

We opened this thesis by highlighting the importance of magnetic fields in astrophysical processes. It is very difficult to observe magnetic fields in astrophysical regions directly. Magnetic fields do not leave a trace in the emission of radiation when one only observes the total intensity of the light emerging from these regions. Instead, the polarization of light has to be analyzed to obtain information on the directional properties of the region of interest. In this thesis, we characterize the polarization properties of light that emerges from molecular lines that are affected by magnetic fields.

In the (sub)millimeter regime, relevant to the ALMA (Atacama Large (sub)Millimetre Array) telescope, emission comes predominantly from molecules—in the form of line-emission—and dust—in the form of continuum emission. Magnetic fields indirectly work on both molecules and dust and tend to partially align part of the
populations of these species. A consequence of this is that the (sub)millimeter light emission coming from these partially aligned species also has a preferred direction for the oscillating electric field: the emission is partially polarized. The direction of polarization is indicative of the magnetic field direction; and by studying the polarization of radiation, one can infer the magnetic field morphology of the region under study.

Dust polarization has proven itself to be a very useful tool to study the magnetic field morphology of astrophysical star forming regions on molecular cloud scales. However, going to smaller scales of star formation—in the direct vicinity of forming protostars—the alignment of dust is affected through other mechanisms, and dust-polarization therefore does not trace magnetic field morphologies faithfully. Also, in atmospheres of evolved stars, dust formation is ongoing, but dust emission is too diffuse to be viably used for polarization analysis.

To study magnetic fields in these regions, we thus have to resort to the observation of molecular line polarization. However, while significant strides have been made in developing polarized interferometry capabilities to observe astrophysical processes on the smallest angular scales, theories of molecular line polarization are based on approximations that are not applicable to, for instance, the small-scale regions of star-formation or evolved stellar envelopes. Part of this thesis focuses on developing new theoretical tools that are to be used in conjunction with polarized interferometry of molecular line emission, to obtain accurate information on the magnetic field morphology of the astrophysical regions they are excited in.

A special case of line emission, ‘masing’, is found in some regions (see section 4.2). Masers (Microwave Amplified by Stimulated Emission of Radiation), because of their highly ‘beamed’ geometry, are in good approximation described by one-dimensional propagation. The almost one-dimensional propagation in conjunction with a magnetic field results in partial alignment of the maser medium, which emits polarized emission that traces the magnetic field direction. Furthermore, masers, because of their extreme brightness temperatures and narrow line profiles, can also be used to infer magnetic field strength through direct observations of the splitting of the emission lines through the Zeeman effect. In this thesis, we develop a theoretical quantum-chemical model to quantify Zeeman splitting effects for methanol (Paper I): a non-rigid rotor system with a complicated hyperfine structure, and we present a radiative transfer program, that characterizes the maser polarization profile for masers at arbitrary magnetic field strength, direction and maser brightness temperature; and investigates alternative ways to produce maser polarization (Paper II).
Molecules

Much of the material that exists between the stars, the interstellar medium (ISM), is found in molecular form. In this chapter, we review the molecular physics that is relevant to radio astronomy. Because it is the main theme of this thesis, we dedicate extra attention to effects that can lead to the alignment of molecular species, and thus to the polarization in the radiation that emerges from ISM regions.

In the following section, we review the basic molecular physics of isolated molecules. Thereafter, we describe the interaction of isolated molecules with magnetic—both internal and external—and electric fields. In the final section, we linger on the directional nature of molecular interactions with external electric and magnetic fields; this will serve as a preamble to the next chapter.

3.1 Basic molecular physics

Molecules in the ISM spend the vast majority of their time as isolated particles. To describe the dynamics of individual molecules, we consider the motions of the electrons and nuclei that make up a molecule. We identify three types of molecular motion: electronic, vibrational and rotational motions. To a reasonable approximation, these types of motion can be studied in isolation. In this section, we review the (quantum-mechanical) description of internal dynamics of molecules.

Densities in the ISM are exceedingly low. In the cold neutral medium, the number of H$_2$ molecules found in a cubic centimeter, the number density, is on the order of $10^4$ cm$^{-3}$. But in sites of ongoing dynamical events, such as accretion, number densities can rise to higher values. Typical mean-free paths of molecules in the ISM are

$$ l_{\text{mfp}} = 10^{10} \left( \frac{\sigma}{1 \text{ A}^2} \right)^{-1} \left( \frac{n_{\text{H}_2}}{10^6 \text{ cm}^{-3}} \right)^{-1} \text{ cm}, $$

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where $\sigma$ is the collisional cross-section. For a species in the ISM with a typical thermal velocity of $\sim 1 \text{ km/s}$, this would mean that it would take about a day before that species interacts with another constituent of the ISM. When we furthermore consider that this interaction takes about a picosecond, it is clear that we can consider the molecular constituents of the ISM as individual particles, with their associated properties unperturbed by the interaction with other particles of the ISM.

The physics of isolated molecules is most effectively described by considering the motion of the electrons and nuclei that they consist of. We will start our discussion by considering the motion of the electrons that make up a molecule. We consider a poly-atomic molecule with $N_n$ nuclei and $N_e$ electrons. The coordinates of nucleus, $\alpha$, are $r_\alpha$ and have an associated mass $m_\alpha$ and charge $Z_\alpha e$, where $e$ is the elementary charge. We let the coordinates of electron, $i$, be $r_i$, and all electrons have mass $m_e$ and charge $-e$. The Hamiltonian of this system is the sum of the electron- and nuclear-motion energies and the attractive and repulsive Coulomb-energies (Szabo & Ostlund 2012)

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_\alpha \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 - \sum_{i\alpha} \frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{i\alpha}} + \sum_{ij} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 r_{\alpha\beta}},$$

(3.1)

where $\varepsilon_0$ is the vacuum permittivity and $r_{ij}$ is a short-hand notation for the distance between the vectors $|r_i - r_j|$. The motion of the nuclei and electrons are not strictly separated according to this general molecular Hamiltonian. But considering that the motion of the nuclei is much slower than that of the electrons, the nuclear and electronic motion can be separated through the Born-Oppenheimer approximation (Born & Oppenheimer 1927).

In our discussion of the structure of molecules, we assume the electronic structure to be ‘closed-shell’: that is, there are no unpaired electrons. It is certainly possible to perform calculations to the electronic structure of ‘open-shell’ molecules, but we will refrain from such a discussion in this thesis. This will also simplify our coming discussion on the nuclear motions of molecules, because spectral fine-structure that is introduced by interactions with the unpaired electrons can be neglected (Brown & Carrington 2003). For the purposes of this thesis, where we consider the alignment of molecules, and considering that most astrophysical molecules are closed-shell, these approximations will do. However, open-shell molecules are extremely important in tracing magnetic field strengths in astrophysical regions, as the unpaired electrons give rise to a paramagnetic Zeeman effect that is 3 orders of magnitude greater than the Zeeman effects we will be considering in this thesis (Crutcher & Kemball 2019). The resulting spectral decoupling of the circularly polarized transitions can be directly observed already for weak magnetic fields, and has provided astronomers with solid information on magnetic field strengths in astrophysical regions (Crutcher 2012).
3.1.1 Electronic motion

We assume that the nuclei are stationary on the timescale of electronic motion and thus separate the molecular Hamiltonian in a kinetic nuclear part, and an electronic part,

\[ \hat{H}_{\text{el}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{ia} \frac{Z_a e^2}{4\pi\epsilon_0 r_{ia}} + \sum_{ij} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{\alpha\beta} Z_\alpha Z_\beta e^2, \]  

(3.2)

\[ \hat{H}_{\text{nuc}} = -\sum_\alpha \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2. \]  

(3.3)

We will consider the nuclear Hamiltonian at a later stage. Now, we will briefly consider the electronic part of the molecular Hamiltonian.

It is beyond the scope of this thesis to work out the full methodology behind solving the molecular electronic Hamiltonian. It will however be helpful if we consider briefly and qualitatively the steps modern quantum chemists take to find the solution to \( \hat{H}_{\text{el}} \). First, it has to be conceded that finding the ‘exact’ solution to the time-independent Schrödinger equation,

\[ \hat{H}_{\text{el}} \psi_{\text{el}}(\{r_i\}; \{r_\alpha\}) = E_{\text{el}} \psi_{\text{el}}(\{r_i\}; \{r_\alpha\}), \]  

(3.4)

is not possible considering the two-particle interaction term contained in the electron-electron Coulomb repulsion (Szabo & Ostlund 2012). To solve the eigenvalue problem, we have to work around the two-particle operator while keeping the problem tractable. First, we define a basis of wave functions within which the solution of the eigenvalue problem is going to be sought. These basis functions are based on the hydrogen-atom-like orbitals that are the solutions of the electronic Hamiltonian of an hydrogen-like-atom (Helgaker et al. 2014). The orbital functions are tweaked in order to be conveniently integrated and they are specific to each nucleus. The basis can be infinitely big but is truncated to make solving Eq. (3.4) feasible. The total eigenfunctions \( \psi_{\text{el}} \) are described as Slater determinants of the basis functions to make sure that the fermionic requirement of anti-symmetry is fulfilled.

But even inside the truncated basis it is not possible to directly solve Eq. (3.4) due to the two-particle operator of the electron-electron Coulomb repulsion term. To reduce this term to a one-electron operator, one employs the mean-field approximation: the electron-electron interaction between the individual electrons is approximated by those electrons interacting instead with a ‘mean-field’ (Szabo & Ostlund 2012). The ‘mean-field’ is initially constructed from a ‘guess’, which is typically derived from the solution of Eq. (3.4) neglecting electron-electron interactions. The mean-field is subsequently used in constructing the ‘Fock-operator’—the one-electron operator containing the electronic motion and (mean-field) Coulomb interactions—which is then inserted in the ‘Roothaan’-equations to find a new wave function (Roothaan 1951). The associated energy of
the new wave function is guaranteed to be lower through the variational principle, and thus constitutes a ‘better’ solution to the system at hand. In this way, the wave function is iteratively updated until convergence is attained. The eventual wave function constitutes the ‘Hartree-Fock’ solution to Eq. (3.4).

Modern quantum chemical techniques exist to further improve the Hartree-Fock solution to the system. Techniques such as the coupled-cluster or configuration interaction method mitigate the error that has been introduced through the mean-field approximation (Bartlett & Musiał 2007). Full configuration interaction finds the ‘exact’ solution to Eq. (3.4) within a certain basis, but is generally very expensive. Coupled cluster techniques are usually considered to be the most cost-effective, but one compromises the variational principle with this technique. The solution to Eq. (3.4) yields the ‘electronic energy’ and the ‘electronic wave function’ of the molecule. We note that the electronic energy is a function of the nuclear coordinates. The minimal electronic energy (as a function of the nuclear coordinates) defines the molecular geometry, or rather, the equilibrium coordinates. The electronic wave function defines how the (indistinguishable) electrons are distributed through the molecule according to the probability density. We will keep this in mind when we will consider the interactions between the electrons and external (and internally induced) magnetic fields.

3.1.2 Nuclear motion

We now return to the total molecular Hamiltonian that also includes the nuclear motion. Considering the nuclear motion to be far slower than electronic motions, we note

\[
\hat{H} = \hat{H}_{\text{nuc}} + \langle \hat{H}_e(\{r_\alpha\}) \rangle = \sum_\alpha \frac{\hat{p}_\alpha^2}{2m_\alpha} + V(\{r_\alpha\}),
\]

(3.5)

where we note the nuclear kinetic energy in terms of momentum operators, \(\hat{p}_\alpha\) and where we from now on will consider the electronic energy—that is a function of the nuclear coordinates—as a potential field through which the nuclei move. The nuclear coordinates associated with the minimal electronic energy we call the equilibrium coordinates and refer to these as \(\{r_\alpha^{(0)}\}\). We set the electronic potential energy at these points to zero. We furthermore define the coordinates \(\{r_\alpha\}\) in terms of displacements from the equilibrium coordinates (Wilson et al. 1980)

\[
r_\alpha = r_\alpha^{(0)} + d_\alpha,
\]

(3.6)
and we represent the potential energy by the first two terms of its Taylor-expansion, in accordance with the harmonic approximation,

\[ V(\{r_\alpha\}) \approx \frac{1}{2} \sum_{\alpha\beta} d_\alpha \cdot \frac{\partial^2 V}{\partial d_\alpha \partial d_\beta} \bigg|_{d_\alpha=d_\beta=0} d_\beta, \quad (3.7) \]

where we have been able to set the first-order term to zero because \( V(\{r_\alpha^{(0)}\}) \) is a minimum. We re-state the nuclear Hamiltonian in the harmonic approximation

\[ \hat{H}_{\text{nuc}} = \sum_\alpha \frac{\hat{p}_\alpha^2}{2m_\alpha} + \frac{1}{2} \sum_{\alpha\beta} d_\alpha \cdot \frac{\partial^2 V}{\partial d_\alpha \partial d_\beta} \bigg|_{d_\alpha=d_\beta=0} d_\beta. \quad (3.8) \]

This Hamiltonian can be represented as a sum of uncoupled harmonic oscillators in the ‘normal coordinate’ system, \( \{Q_i, i = 1, 2, \ldots, 3N_\alpha\} \), in which the second-order potential operator is diagonalized (Papousek & Aliev 1982)

\[ \hat{H}_{\text{nuc}} = \sum_i \left( \hat{p}_i^2 + \lambda_i \hat{Q}_i^2 \right), \quad (3.9) \]

where the terms \( \lambda_i \) are the eigenvalues of the harmonic potential matrix and they are related to the harmonic frequencies: \( \omega_i = \lambda_i^2 \), and the momentum operators are formulated with respect to the transformed coordinates (Papousek & Aliev 1982). The normal-coordinates correspond to vibrational modes: we give the vibrational modes of water with the associated harmonic frequencies in Fig. (3.1). The first six eigenvalues of the harmonic potential matrix are zero if the electronic potential is invariant under rotation and translation operations. The first three normal modes can be set to zero by requiring

\[ \sum_\alpha m_\alpha r_\alpha = 0, \quad (3.10a) \]

which corresponds to using a center of mass frame; the first three modes thus correspond to the translational modes. The next three normal modes are the rotational modes and are set to zero by requiring

\[ \sum_\alpha m_\alpha r_\alpha^{(0)} \times d_\alpha = 0. \quad (3.10b) \]

Equations (3.10) define an axis system in which coupling between translational and vibrational motion is removed, and coupling between rotation and vibration is minimized. The conditions of Eqs. (3.10) are the Eckart conditions (Eckart 1935).

We return to the nuclear Hamiltonian of Eq. (3.9) and discard the translation and rotation modes for the moment to be left with the vibrational Hamiltonian. In the ‘normal coordinate’ system, we recognize that the vibrational Hamiltonian
Figure 3.1: Vibrational normal modes of water. Mode $v_1 (Q_1)$ corresponds to the symmetric stretch and has an harmonic frequency of $3657 \text{ cm}^{-1}$, $v_2 (Q_2)$ corresponds to the symmetric bend and has an harmonic frequency of $\sim 1595 \text{ cm}^{-1}$ and $v_3 (Q_3)$ corresponds to the symmetric bend and has an harmonic frequency of $\sim 3756 \text{ cm}^{-1}$.

is the sum of $3N_{\alpha} - 6$ (uncoupled) quantum harmonic oscillator Hamiltonians

$$\hat{H}_i = \hat{P}_i^2 + \sqrt{\omega_i} \hat{Q}_i^2,$$

(3.11)

that have associated eigenvalues, $\hbar \omega_i (v_i + \frac{1}{2})$, dependent on the vibrational quantum number, $v_i$ of mode $i$. Eigenfunctions are the Hermite functions of the normal coordinates. When higher-order terms of the electronic potential, $V(\{r_{\alpha}\})$ are re-introduced, coupling between the normal modes will be present.

Vibrationally excited states and transitions will be important later in analyzing the alignment of molecules because they provide strong alignment potential for molecules close to strong sources of radiation. Also, when discerning molecular electromagnetic properties, it will be important to keep the internal motion of the nuclei in the electronic potential field in mind.

In our discussion of the vibrational structure of the molecule, we have considered the molecule to be stationary, and have captured all the rotational displacements in the normal modes 4 to 6. We will now investigate these modes as the proper rotation of the molecule. It will be too involved to start the derivation of the rotational Hamiltonian in a quantum-mechanical framework; but it will suffice for our purposes to consider rotational motion from a classical perspective. We will later refer to the proper way to transform the classical rotational Hamiltonian to a quantum-mechanical one.

The molecular rotation is not through an electronic potential field, and the energy consists only of the kinetic energy \cite{Flygare1978}

$$T_{\text{rot}} = \frac{1}{2} \sum_{\alpha} m_{\alpha}(\dot{r}_{\alpha})^2$$

(3.12)

\footnote{A linear molecule has $3N_{\alpha} - 5$ vibrational modes, because rotation about the molecular axis cannot be observed.}
of the rotation. We only take into account the motion of the nuclei as they carry nearly all of the molecules mass and thus kinetic energy. The velocity of a rotating object is \( \dot{r}_\alpha = \omega \times r_\alpha \), where \( \omega \) is the angular velocity. Using this relation in the expression for the rotational kinetic energy yields

\[
T_{\text{rot}} = \frac{1}{2} \omega \cdot \left[ \sum_\alpha m_\alpha \left( r_\alpha^2 1 - r_\alpha \otimes r_\alpha \right) \right] \omega, \tag{3.13}
\]

where the part in brackets is commonly referred to as the inertiatensor: \( I \). The angular momentum, \( J = \frac{\partial T}{\partial \omega} \), can be evaluated from the rotational kinetic energy, giving \( J = I \omega \), so that

\[
T_{\text{rot}} = H_{\text{rot}} = \frac{1}{2} J \cdot I^{-1} J.
\]

The relation between this classical Hamiltonian and the quantum-mechanical one turns out to be trivial \( \text{[Podolsky 1928]} \)

\[
\hat{H}_{\text{rot}} = \frac{1}{2} \hat{\mathbf{P}} \cdot \mathbf{I}^{-1} \hat{\mathbf{P}} = A \hat{\mathbf{P}}_a + B \hat{\mathbf{P}}_b + C \hat{\mathbf{P}}_c, \tag{3.14}
\]

where \( \hat{\mathbf{P}} \) is the body-fixed angular momentum operator fulfilling the anomalous commutation relations \( \text{[Brink & Satchler 1993]} \). The constants \( A = \frac{1}{2I_{aa}}, B = \frac{1}{2I_{bb}} \) and \( C = \frac{1}{2I_{cc}} \) are the rotational constants and are defined with respect to the principal axis frame within which the inertia-tensor is diagonal and where the axes are chosen so that \( A \geq B \geq C \) \( \text{[Flygare 1978]} \). The eigenfunctions of the angular momentum operators are

\[
\hat{\mathbf{P}}^2 |JKM\rangle = \hbar^2 J(J+1) |JKM\rangle, \tag{3.15a}
\]
\[
\hat{\mathbf{P}}_a |JKM\rangle = \hbar K |JKM\rangle, \tag{3.15b}
\]

where the operators fulfill the anomalous commutation relations \( \text{[Brink & Satchler 1993]} \). The quantum number \( M \) is associated with the space-fixed angular momentum operator, \( \hat{\mathbf{J}} \),

\[
\hat{\mathbf{J}}^2 |JKM\rangle = \hbar^2 J(J+1) |JKM\rangle, \tag{3.15c}
\]
\[
\hat{\mathbf{J}}_a |JKM\rangle = \hbar M |JKM\rangle, \tag{3.15d}
\]

whose operators fulfill the usual commutation relations \( \text{[Brink & Satchler 1993]} \). The space-fixed angular momentum operators will become important when the influence of external fields is considered. In the cases of very symmetrical molecules, \( A = B = C \), and the eigenvalues to the rotational Hamiltonian (rotational energies) are simply

\[
E_J = \hbar^2 BJ(J+1)
\]
and the eigenfunctions $|JKM\rangle$ are degenerate for all $K$ within $J$. These types of molecules are called spherical tops. It turns out that spherical tops share the energy-structure with linear molecules on the ground of negligible angular momentum along the interatomic axis. Molecules that have cylindrical symmetry have $A \neq B = C$ (prolate) or $A = B \neq C$ (oblate) are called symmetric tops and have rotational energies (here, only for a prolate)

\[ E_{J|K|} = \hbar^2 B K^2 + \hbar^2 (A - B)J(J + 1), \]

and the $|J(\pm K)M\rangle$ eigenstates are degenerate. Asymmetric tops, with $A \neq B \neq C$ have no good $K$ quantum-number. Eigenfunctions and rotational energies have to be found by setting up $\hat{H}_{\text{rot}}$ in a basis of Eq. (3.15) for a specific $J$ ($J$ is a good quantum number) and diagonalized. Diagonalization yields the eigenfunctions as a linear combination of $|JKM\rangle$ functions and the eigenvalues are the rotational energies. Eigenstates of asymmetric top molecules are usually denoted as $J_{K_a,K_c}$, referring to the projection on both the $a$ (prolate) and $c$ (oblate) projection axes.

At high rotational energies, centrifugal forces become important and start to affect the positions of the nuclei in the molecule. This has consequences for both the vibrational and the rotational structure, as equilibrium positions of the nuclei are altered. It is common to incorporate the effects of centrifugal (and other, such as Coriolis) forces as additional terms in a total Hamiltonian that depends on a lot of parameters. Such an extended Hamiltonian can be fitted to the observed spectrum of a particular molecule and return an accurate energy spectrum.

Concluding this section on the internal dynamics of molecules, we point out that internal torsional motion through a relatively weak potential field can influence the rotational dynamics of a molecule deeply (Lin & Swalen 1959). In this thesis, a lot of attention is dedicated to methanol, whose OH-group can rotate along the C–O-axis with respect to the CH$_3$-group through a relatively weak potential field, where the threefold torsional barrier is 373 cm$^{-1}$ (Xu & Lovas 1997). When a molecule is torsionally active, the rotational dynamics cannot be considered in isolation from the internal nuclear motion and a rotation-torsion Hamiltonian has to be set-up and solved in order to properly model the rotational dynamics (Wilson et al. 1980). We perform such calculations in Paper I; where we study the electrodynamics and interactions with an external magnetic field of the torsionally active molecule methanol.
3.2 Molecular electrodynamics

In the previous section, we reviewed the internal dynamics of isolated molecules. The nuclei and electrons that make up the molecule are charged particles and their motion is therefore associated with electric and magnetic fields. In this section we review the electrodynamics relevant to the motion of charges in molecules. Both how it affects the energy structure, through (hyper)fine interactions and Zeeman effects, but also how different energy states can interact through a dipole moment that two states span.

3.2.1 Molecular electromagnetic properties

Molecular dipole moment

The nuclei and electrons that make up the molecule are all charged particles. If the charged particles are not evenly distributed, they yield multipole moments of the system. Classically, the dipole moment is given by (Jackson 1998)

\[ \mu(r) = \int d^3 r' \rho(r')[r-r'] = \sum_j q_j(r_j-r), \]

(3.16)

where \( \rho(r) \) is the charge density at position \( r \) and we consider the particles, \( j \), that make up the molecule as point particles with charge \( q_j \). Earlier, we had already discussed that within the Born-Oppenheimer approximation, the nuclei are stationary with respect to the electron motion. With this in mind, we first compute the expectation value of the dipole moment with respect to the electronic motions

\[ \mu^{el}(r, \{r_\alpha\}) = e \sum_\alpha Z_\alpha(r_\alpha-r) - e \sum_j \int d^3 r_j |\psi^{el}(r, \{r_\alpha\}, \{r_i\})|^2(r_j-r) \]

(3.17)

where we denote the probability density function of the electron cloud by \( |\psi^{el}|^2 \).

We recognize from Eq. (3.17) that for molecules such as homonuclear diatoms (H\_2, O\_2) or highly symmetric molecules such as CH\_4, the dipole moment vanishes.

In formulating the molecular dipole moment, we have thus far assumed the nuclear-coordinates to be stationary and given. Indeed, the electronic dipole moment is a function of the nuclear coordinates: \( \mu^{el}(\{r_\alpha\}) \). In our discussion on the vibrational structure of molecules, we have seen that molecules vibrate around
the equilibrium configuration, \( \{ r_\alpha^{(0)} \} \), along the vibrational normal modes. To obtain the dipole moment for a particular vibrational state, we thus have to weigh the dipole moment over the vibrational modes

\[
\langle \mu_{\text{el}} \rangle_{v_1, v_2, \ldots, v_n} = \int d^3r_1 \int d^3r_2 \cdots \int d^3r_n |\Psi_{v_1, v_2, \ldots, v_n}^\text{vib}(\{ r_\alpha \})|^2 \mu(\{ r_\alpha \}),
\]

where \( \Psi_{v_1, v_2, \ldots, v_n}^\text{vib} \) denotes the vibrational wave function of the \((v_1, v_2, \ldots, v_n)\) vibrational state. The molecular dipole moment of the vibrational ground state will mostly have the character of the dipole moment at the equilibrium configuration.

Finally, we recognize that the molecule is rotating according to its associated rotational state: \(|J_{K_a, K_c}\rangle\). Evaluating the dipole-operator for a specific rotational state,

\[
\langle J_{K_a, K_c} | \langle \mu_{\text{el}} \rangle_{v_1, v_2, \ldots, v_n} | J_{K_a, K_c} \rangle = 0,
\]

it becomes clear that, indeed, molecules do not possess any dipole moment in a particular rovibronic state \((\text{Klemperer et al. 1993})\). It is only between different rovibronic states that molecules can possess a dipole moment. This will be an important insight when discussing the interaction of molecules with electromagnetic fields.

**Molecular magnetic moment**

The classical expression for a magnetic moment for a set of moving point charges is \((\text{Jackson 1998})\)

\[
m = \frac{1}{2} \int d^3r \, r \times j(r) = \frac{1}{2} \sum_j q_j (r_j \times v_j).
\]

The magnetic moment is generated by the charged particles and their different motions. In the case of closed-shell molecules, the orbital currents from the electrons in the same orbit with counter-spin cancel each other out. Also, when we compare the vibrational motion to the rotational motion of the molecule, we recognize that the rotational motion is far greater, and thus the rotational contribution to the magnetic moment dwarfs the vibrational contribution \((\text{Moss & Perry 1973})\). For simplicity, we will assume in this discussion the molecule to be in the vibrational ground state, at the equilibrium geometry. If the motion of the molecule only comes from the molecular rotation: \(v_j = \omega \times r_j\), then

\[
m = \frac{1}{2} \sum_j q_j r_j \times \omega \times r_j = \mu_N \left[ \frac{1}{\mu_N} \sum_j \frac{q_j}{2} \left( r_j^2 1 - r_j \otimes r_j \right) I^{-1} \right] J,
\]

\[28\]
where we used the relation between the angular velocity and the angular momentum, and consolidated the characteristically weighed charge distribution of the molecule in the dimensionless rotational g-tensor, \( g \), which is the entity between brackets. The charged particles that make up the molecule all contribute to the magnetic moment, depending on their velocity and charge. Because the electron cloud and nuclear positions are not the same, this results in a net magnetic moment due to the molecular rotation. In a full quantum mechanical derivation of the rotational magnetic moment, one also takes into account the mixing in of paramagnetic electronic energy levels due to the rotation. This effect contributes to the total magnetic moment. For detailed calculations, see \textit{Flygare} (1978) and \textit{Sauer} (2011). Note that the magnetic moment can be non-zero for a single rotational state, but is also present between different rotational states.

\textbf{Hyperfine structure}

In the previous section we outlined how the motions of the charged particles that make up a molecule give rise to a magnetic moment. The magnetic moment from the molecular rotation was given at the centre-of-mass of the molecule. Besides this rotational magnetic moment, it is the case that some nuclei possess internal magnetic moments on account of their “nuclear spin”. The magnetic moment of a nucleus, \( K \) is proportional to the nuclear spin, \( I_K \) and the ‘nuclear g-factor’, \( g_K \):

\[
m_K = \mu_N g_K I_K. \quad (3.22)
\]

When we consider the interaction of a the rotational magnetic moment, \( m \), located at the origin, and the magnetic moment of a nucleus, \( m_K \) at position, \( r \), we have the Hamiltonian of this ‘spin-rotation’ interaction

\[
H_{SR}^K = -\frac{\mu_0}{4\pi r^3} [3(m_K \cdot \hat{r})(\hat{r} \cdot m) - m_K \cdot m]
= I_K \cdot \left[ \frac{\mu_0 \mu_0^2 g_K}{4\pi r^3} (1 - 3 \hat{r} \otimes \hat{r}) g \right] J
= I_K \cdot M_K J, \quad (3.23)
\]

where \( \mu_0 \) stands for the magnetic constant. As before, we contained the interactions in a tensor which is called the spin-rotation tensor, \( M_K \).

It should be noted that in our (semi-)classical model of the spin-rotation interaction, the spin-rotation tensor in our formulation does not fully capture the quantum mechanical intricacies of the spin-rotation interactions. More detailed derivations are given in \textit{Sauer} (2011) and \textit{Flygare} (1978), where special attention is given to the quantum chemical methodology behind computing this tensor from the electronic structure. For our discussion, it is sufficient to note that the nuclear-spin magnetic moment interacts with the molecular rotation via a rank-2 tensor, which
is calculable from ab-initio methods. The classical expressions for the nuclear-spin and the rotational angular momentum we have employed so far, can be shown to transform to their quantum-mechanical counterparts: \( \mathbf{I}_K \rightarrow \hat{\mathbf{I}}_K, \mathbf{J} \rightarrow \hat{\mathbf{J}} \).

The total spin-rotation interaction Hamiltonian is obtained by summing the spin-rotation interaction of all nuclei, \( K \), that have non-zero nuclear spin

\[
\hat{H}_{SR} = \sum_k \hat{\mathbf{I}}_K \cdot \mathbf{M}_K \hat{\mathbf{J}}.
\]  (3.24)

If there are multiple nuclei with nuclear spin, \( K \) and \( L \), which are separated by \( \mathbf{r}_{KL} = \mathbf{r}_K - \mathbf{r}_L \), then the energy of the interaction of these magnetic moments is

\[
\hat{H}_{SS}^{KL} = -\frac{\mu_0}{4\pi r_{KL}^3} \left[ 3(\mathbf{m}_K \cdot \hat{\mathbf{r}}_{KL})(\hat{\mathbf{r}}_{KL} \cdot \mathbf{m}_L) - \mathbf{m}_K \cdot \mathbf{m}_L \right]
= \hat{\mathbf{I}}_K \cdot \left[ \frac{\mu_0 \mu_K^2 g_K g_L}{4\pi r_{KL}^3} (1 - 3\hat{\mathbf{r}}_{KL} \otimes \hat{\mathbf{r}}_{KL}) \right] \hat{\mathbf{I}}_L
= \hat{\mathbf{I}}_K \cdot \mathbf{D}_{KL} \hat{\mathbf{I}}_L.
\]  (3.25)

It can be shown that the spin-spin interaction tensor, \( \mathbf{D}_{KL} \), is a traceless tensor with only irreducible rank-2 components.

A third hyperfine interaction for closed-shell molecules is only present for nuclei with nuclear spin \( I \geq 1 \), which we denote as \( K' \), and is called the quadrupole interaction

\[
\hat{H}_Q = \sum_{K'} \hat{\mathbf{I}}_{K'} \cdot \mathbf{Q}_{K'} \hat{\mathbf{I}}_{K'}.
\]  (3.26)

Quadrupole interactions arise on account of the electric field gradient at the nucleus. They are often an order of magnitude stronger than spin-rotation and spin-spin interactions and dominate the hyperfine structure of a molecule like HCN to such an extent that astronomers frequently ignore its hyperfine interactions involving the H-atom.

The quadrupole, spin-rotation and spin-spin interactions make up the hyperfine Hamiltonian

\[
\hat{H}_{hyp} = \hat{H}_Q + \hat{H}_{SR} + \hat{H}_{SS},
\]  (3.27)

and have to be added to the total molecular Hamiltonian to obtain its proper energy. Because hyperfine interaction energies are dwarfed even by rotational energies, it is common to consider the hyperfine Hamiltonian as a perturbation on the rotational structure of the molecule. To obtain matrix-elements of \( \hat{H}_{hyp} \), rotational eigenfunctions, \( |J_{K_a, K_c}\rangle \), have to be expanded with the nuclear-spin wave functions: \( |I_1 M_1\rangle |I_2 M_2\rangle \cdots |I_N M_N\rangle \). Usually, the rotation-hyperfine wave function is kept tractable by utilizing symmetry properties of the molecule and angular momentum techniques.
3.2.2 Interaction of molecules with external fields

We have discussed the electronic, vibrational and rotational structure of the molecule and have laid out how electromagnetic interactions arise as a consequence of this structure. An electric dipole moment arises through an asymmetric distribution of charges, and magnetic moments arise through the differential rotation velocities of the charged particles that make up the molecule. We have studied the internal electromagnetic interactions, but now we will study how electric dipole moments and magnetic dipole moments interact with external electric and magnetic fields.

Magnetic fields

We have seen earlier that the differential motion of the charged particles that make up a molecule introduces a magnetic moment which is proportional to its rotational angular momentum

\[ \hat{m}_\text{rot} = \mu_N g \hat{J}, \]

(3.28)

where \( g \) is the so called rotational g-tensor, and \( \hat{J} \) the rotational angular momentum. Additionally, the nuclei with nuclear spin possess an intrinsic magnetic moment

\[ \hat{m}_1 = \mu_N \sum_K g_K \hat{I}_K, \]

(3.29)

where the sum over \( K \) runs over all nuclei with non-zero nuclear spin, \( g_K \) is the associated nuclear g-factor and \( \hat{I}_K \) nuclear spin angular momentum. The rotational and nuclear-spin magnetic momenta make up the total magnetic moment of a closed-shell molecule. These are commonly known as non-paramagnetic molecules. Molecules that have unpaired electrons, paramagnetic molecules, possess additional magnetic momenta due to electron spin and electronic orbital momentum. The electronic magnetic momenta are proportional to the Bohr magneton and are accordingly 3 orders of magnitude stronger than non-paramagnetic momenta (Brown & Carrington 2003).

An external magnetic field interacts with the magnetic moment as (Flygare 1978)

\[ \hat{H}_B = \hat{H}_{BR} + \hat{H}_{BI} = -\hat{m}_\text{rot} \cdot \mathbf{B} - \hat{m}_1 \cdot \mathbf{B}, \]

(3.30)

giving rise to the rotational and nuclear spin Zeeman effects. Under astrophysical conditions relevant to molecular radio and (sub)millimeter astronomy, Zeeman interactions (~ kHz/G) are way smaller than rotational interactions (~ 100 GHz). Since furthermore the external magnetic field is constant and non-oscillatory, we
only need to bother with perturbative elements. For the rotational Zeeman interactions, these are

\[ \langle jm|\hat{H}_{BR}|jm'\rangle = \mu_N ||g||\langle jm|B \cdot \hat{J}|jm'\rangle = \mu_N ||g|| B m \delta_{mm'}, \tag{3.31} \]

if we choose the magnetic sublevels to be oriented with respect to the magnetic field direction. The reduced g-tensor, ||g||, is a constant in the case we are dealing with a linear molecule or spherical top, but is specific to the rotational state for asymmetric tops: ||g|| = \( g_{j_{K_a,K_c}} \). The matrix-elements of the nuclear spin Zeeman effects have to be taken in a basis which is extended with the nuclear spin wave functions \( |i_K\rangle \).

An interesting and useful manifestation of the Zeeman effect in (astrophysical) spectra of molecular lines is through the spectral decoupling of right- and left-circularly polarized radiation. Radiative transitions between two states may be associated with a change in magnetic quantum number of \( \Delta m = 0 \), which are the \( \pi^0 \) transitions and are linearly polarized, or \( \Delta m = \pm 1 \), which are the \( \sigma^\pm \) transitions and are left- and right-handedly circularly polarized. For a transition between two rotational levels, \( |j_1m_1\rangle \) and \( |j_2m_2\rangle \), with associated rotational g-factors \( g_1 \) and \( g_2 \), we have the transition frequency

\[ \omega(j_1,m_1;j_2,m_2) = \omega_0 - \frac{\mu_N}{\hbar} \left[ g_1 m_1 - g_2 m_2 \right], \tag{3.32} \]

slightly displaced from the line-centre, \( \omega_0 \), by the Zeeman-shifts. The average (weighed over the line-strengths) displacement of the circularly polarized transitions is \( \Delta \omega(\sigma^\pm) = \pm \frac{\mu_N}{\hbar} \bar{g}B, \) \( \tag{3.33} \)

where

\[ \bar{g} = \frac{g_1 + g_2}{2} + \frac{g_1 - g_2}{4} \left[ j_1(j_1 + 1) - j_2(j_2 + 1) \right]; \]

so for diatomic molecules simply \( \bar{g} = g \). The circular polarization of the radiation is given in the Stokes-V profile. We give an example of a Zeeman-split spectral line in Fig. (3.2). The maximum polarization fraction of the Stokes-V profile can be analytically evaluated to be

\[ p_V^{\text{max}}(\%) \approx 0.33 \bar{g} \left( \frac{\Delta v_{\text{FWHM}}}{1 \text{ km/s}} \right)^{-1} \left( \frac{\nu_0}{100 \text{ GHz}} \right)^{-1} \left( \frac{B}{1 \text{ G}} \right), \tag{3.34} \]

for non-paramagnetic molecules, while it is

\[ p_V^{\text{max}}(\%) \approx 0.61 \bar{g} \left( \frac{\Delta v_{\text{FWHM}}}{1 \text{ km/s}} \right)^{-1} \left( \frac{\nu_0}{100 \text{ GHz}} \right)^{-1} \left( \frac{B}{1 \text{ mG}} \right), \tag{3.35} \]
Figure 3.2: Spectral decoupling of the different type of transitions ($\sigma^{\pm}$ and $\pi$). We have plotted the $\sigma^+$- (red), $\sigma^-$- (blue) and $\pi$- (black) -transitions within a $j = 5 \rightarrow j' = 6$-transition, with a certain Zeeman splitting, that is smaller than the (Gaussian) broadening of the line. Straight lines in the figure demarcate the individual $m \rightarrow m'$-transitions. The different $\sigma^{\pm}$-transitions are spectrally decoupled, depending on the strength of the Zeeman effect. $\sigma^{\pm}$-transitions show an asymmetric spectrum, but do note that the total intensity, $\sigma^+ + \sigma^-$, is symmetric.

for paramagnetic molecules. The maximum polarization fraction estimate is accurate up to polarization fractions of $\sim 10%$. The transition g-factor, $\tilde{g}$, generally takes the value of $\sim 0.1$. Indeed, as we can infer from Eq. (3.34), it is difficult to observe the Zeeman splitting of non-paramagnetic spectral lines directly. Only masers, with their extreme brightness and narrow velocity profiles present us with Zeeman profiles that are within the observational sensitivity limits. But, for thermal line-emission, non-paramagnetic Zeeman effects are unobservable under regular astrophysical conditions. Zeeman effects in non-paramagnetic molecules will however manifest through other secondary effects, as they force the molecule to precess along the magnetic field axis, and therefore endow it with a preferred orientation (Degl’Innocenti & Landolfi 2006; Goldreich & Kylafis 1981). In the next section, we will see how that can lead to the partial linear polarization of radiation that emerges from such molecules.

**Electromagnetic radiation**

In the following, we consider the interaction of electromagnetic (EM) radiation with a molecule. The interaction is dominated by the interaction of the oscillating electric field and the dipole moment; interactions between the oscillating magnetic field and the magnetic moment are some orders of magnitude weaker and are generally ignored.

We have already seen that the dipole moment of a certain molecular state...
is zero. Indeed, only dipole moments between states are non-zero. Conversely, the electric field of EM radiation is oscillatory. Both these properties result in that dipole-EM radiation interactions result in a transition between two states, provided the transition dipole moment is non-zero and the radiation is resonant with the transition frequency.

The dipole moment and the EM-wave are both vectors, but the direction-dependent properties of their interaction are often ignored. Because we are particularly interested in directional properties through the alignment of molecules and polarization of radiation, we dedicate extra attention to it. We consider a transition between two molecular rotational levels $j_1 = 0 \rightarrow j_2 = 1$, where the magnetic sublevels are oriented along the magnetic field, $B$. This molecule is interacting with the electric field part of an EM wave (see chapter 2)

$$E(r, t) = \text{Re} \left( \hat{\mathcal{E}}_+ e^{i k r - i \omega t} \hat{e}_+ + \hat{\mathcal{E}}_- e^{i k r - i \omega t} \hat{e}_- \right), \quad (3.36)$$

where $k$ is the EM-wave number and direction, and $\hat{e}_\pm$ are the unit polarization directions, $\hat{e}_\pm = \mp \frac{1}{\sqrt{2}} (\hat{e}_j \pm i \hat{e}_\perp)$, chosen with respect to parallel and perpendicular projected magnetic field directions on the plane of the sky. The complex amplitude of the electric field part of the EM-wave is given by $\hat{\mathcal{E}}_\pm$, and is oscillating with a frequency $\omega$. The interaction between the electric field and the dipole moment, placed at $r = 0$, is

$$\hat{V}(t) = - E(t) \cdot \hat{\mu}$$

$$= \frac{1}{2} \left[ \hat{\mathcal{E}}_+ e^{i \omega t} + \hat{\mathcal{E}}_- e^{-i \omega t} \right] \hat{\mu}_+ + \frac{1}{2} \left[ \hat{\mathcal{E}}_+^* e^{i \omega t} + \hat{\mathcal{E}}_-^* e^{-i \omega t} \right] \hat{\mu}_-. \quad (3.37)$$

Now, we consider the transition rate from the ground state level, $|j_1 m_1\rangle = |00\rangle$, to an excited state level, $|j_2 m_2\rangle = |1m\rangle$, where $m = 0$ or $m = \pm 1$ and the transition frequency is $\omega_0$. States are denoted by their total angular momentum $j$ and magnetic sublevel $m$. To compute the transition rate from an oscillatory perturbation as Eq. (3.37), we use Fermi’s Golden rule

$$\Gamma_m = \frac{2 \pi}{\hbar^2} | \langle 1m| \hat{\mathcal{E}}_+^* \mu_+ + \hat{\mathcal{E}}_-^* \mu_-|00\rangle |^2 \delta(\omega - \omega_0), \quad (3.38)$$

where we have invoked the rotating wave approximation and set the fast-rotating $(2\omega)$ elements zero.

Before working out the matrix elements of Eq. (3.38), we should linger on the elements $\mu_\pm$ of the dipole moment. We note that these elements arose out of the in-product with the electric field; and thus refer to an axis system related to the radiation direction. This is in contrast to the eigenfunctions, $|jm\rangle$ of the transition levels, which are related to the magnetic field direction. Thus, when we consider the matrix elements, we have to first rotate these elements back from the
radiation field frame (RF) to the magnetic field frame (MF)

\[ \mu_{\pm}^{RF} = \sum_{m} D_{\pm m}^{(1)}(\chi \theta \phi) \mu_{m}^{MF}, \quad (3.39) \]

where \( D_{qm}^{(1)}(\chi \theta \phi) \) is the Wigner D-matrix element for a rotation described by the Euler angles, \((\chi \theta \phi)\), that relate the propagation direction and the magnetic field direction. After rotating the dipole-vector to the proper frame, we can take the matrix elements

\[ \langle 1m | \mu_{m'}^{MF} | 00 \rangle = ||\mu|| \frac{1 \pm \cos \theta}{2\sqrt{3}}, \quad (3.40a) \]

\[ \langle 1| \mu_{\pm}^{RF} | 00 \rangle = i||\mu|| \frac{\sin \theta}{\sqrt{6}}, \quad (3.40b) \]

which are only non-zero for \( m' = m \). In Eq. (3.40), we used the Wigner-Eckart theorem in the Racah-Wigner convention (Racah 1942; Wigner 1951) and \( C_{m''}^{j'' j' m} \) represents a Clebsch-Gordan coefficient. Putting Eqs. (3.39) and (3.40) together we obtain for the dipole matrix-elements (Deguchi & Watson 1990)

\[ \langle 10 | \mu_{\pm}^{RF} | 00 \rangle = \pm ||\mu|| \frac{1 \pm \cos \theta}{2\sqrt{3}}, \quad (3.41a) \]

\[ \langle 11 | \mu_{\pm}^{RF} | 00 \rangle = i||\mu|| \frac{\sin \theta}{\sqrt{6}}, \quad (3.41b) \]

both of which are dependent on the angle between the magnetic field and the radiation: \( \cos \theta = \hat{k} \cdot \hat{b} \). Using Eqs. (3.41) in Eq. (3.38), we find the rates of absorption to \( m = 0 \) and \( m = 1 \) to be

\[ \Gamma_0 = B_{j_1 \rightarrow j_2} \sin^2 \theta \frac{I + Q}{2} \delta(\omega - \omega_0), \quad (3.42a) \]

\[ \Gamma_1 = \frac{B_{j_1 \rightarrow j_2}}{2} \left( \frac{I - Q}{2} + \frac{I + Q}{2} \cos^2 \theta \right) \delta(\omega - \omega_0), \quad (3.42b) \]

where we defined \( B_{j_1 \rightarrow j_2} = \frac{8\pi^2||\mu||}{3\hbar^2c(2j_2+1)} \) as the Einstein B-coefficient of absorption and we can relate the Stokes parameters \( I \) and \( Q \) to the electric field amplitudes as

\[ I = \frac{c}{8\pi} \left( \tilde{E}_+^* \tilde{E}_+ + \tilde{E}_-^* \tilde{E}_- \right), \quad (3.43a) \]

\[ Q = \frac{c}{8\pi} \left( \tilde{E}_+^* \tilde{E}_- + \tilde{E}_-^* \tilde{E}_+ \right). \quad (3.43b) \]

If we now generalize these absorption rates to astrophysical conditions, where radiation can come from any direction, \( \Omega \), and where the molecular absorbers are distributed over a velocity profile, \( \phi_\nu \), we note the rate of absorption from \( |00\rangle \) to \( |10\rangle \) and \( |1 \pm 1\rangle \) as (Goldreich & Kylafis 1981)

\[ R_0 = B_{j_1 \rightarrow j_2} \int d\nu \phi_\nu \int \frac{d\Omega}{4\pi} \sin^2 \theta I_{||}(\nu, \Omega), \quad (3.44a) \]

\[ R_\pm = \frac{B_{j_1 \rightarrow j_2}}{2} \int d\nu \phi_\nu \int \frac{d\Omega}{4\pi} \left( I_{\perp}(\nu, \Omega) + I_{||}(\nu, \Omega) \cos^2 \theta \right), \quad (3.44b) \]
where we defined $I_{\parallel,\perp} = (I \pm Q)/2$ as the radiation parallel and perpendicular to the magnetic field direction projected on the plane of the sky. One should make particular note, that the total rate of absorption from $j_1 \rightarrow j_2$, 

$$R = R_- + R_0 + R_+ = B_{j_1 \rightarrow j_2} \int d\nu \phi_\nu \int \frac{d\Omega}{4\pi} I(\nu, \Omega)$$  \hspace{1cm} (3.45)$$

has no particular weighing with respect to the incoming radiation direction. Thus, it is only the relative alignment of the molecular states that is a function of the anisotropic illumination of the molecules.

Suppose we consider the case that unidirectional unpolarized light, that is directed with an angle $\Theta$ with respect to the magnetic field, is shone on an ensemble of molecules at the transition frequency of the $0 \rightarrow 1$ transition. Now, the absorption rate of the $|00\rangle \rightarrow |10\rangle$, $R_0$, will be different to the absorption rate to the $|00\rangle \rightarrow |1 \pm 1\rangle$ transitions:

$$\frac{R_0}{R} = \frac{\sin^2 \Theta}{2},$$  \hspace{1cm} (3.46a)$$

$$\frac{R_\pm}{R} = \frac{1 + \cos^2 \Theta}{4},$$  \hspace{1cm} (3.46b)$$

and thus will result in the differential population of the $m = 0$ and $m = \pm 1$ levels of the $j = 1$ state. In practice, this means that the molecular states are partially aligned, as the differential population of the magnetic sublevels translates to a propensity to be found in some preferred direction with respect to the magnetic field. In the following section, we give an intuitive introduction to molecular alignment by connecting it to a classical picture of alignment. This will prepare us for the next chapter, where we consider the interaction of radiation and molecules—and its relation to the alignment of molecules under astrophysical conditions—in more detail.

### 3.3 Modeling the alignment of molecules

Alignment is said to be present when the molecules have propensity to be found in some preferred direction. In this section, we lay briefly a connection between the classical description of alignment, and its representation for a quantized rotational level. The quantum mechanical representation becomes equivalent to the classical description for rotational angular momentum $j \rightarrow \infty$. Because of their attractive symmetry properties, we represent the alignment properties of molecules in terms of irreducible tensor elements.

First, we consider a collection of $N$ classical molecules under the influence of a
magnetic field. Due to the magnetic field, the molecule precesses around the magnetic field axis with a rate of $\sim s^{-1}$ for a mG magnetic field. Under ISM conditions, the precession rate is therefore far greater than any other interaction rate, so after each interaction event, the molecule will re-orient itself with respect to the magnetic field axis and precess around it with an angle $\theta$. We will find $n(\theta)d\theta$ molecules precessing with an angle, $\theta$, around the magnetic field axis. We can expand $n(\theta)$ in terms of Legendre polynomials

$$n(\theta) = n_0 P_0(\cos \theta) + n_1 P_1(\cos \theta) + n_2 P_2(\cos \theta) + \cdots.$$  \hspace{1cm} (3.47)

Using the orthogonality of the Legendre polynomials, the elements $n_k$ are

$$n_k = \frac{[k]}{2} \int_{-1}^{1} d\cos \theta \ n(\theta)P_k(\cos \theta), \hspace{1cm} (3.48)$$

where $[k]$ is a short-hand notation for $2k + 1$. It is easy to see that $n_0 = N$, the total number of molecules. The other elements that have $k = \text{even}$ are related to the orientation of the molecules, while the $k = \text{odd}$ populations are related to the alignment \cite{Blum1981}. We proceed to introduce the notation of orientations and alignments in terms of irreducible tensor elements. It is convenient to work in terms of irreducible tensor elements, because of the symmetry properties and convenient rotation properties of these elements.

We note the irreducible tensor element, $\rho^k_q$, of rank-$k$ and projection $q$. In this introduction we are only interested in the case of a strong magnetic field, where only the $q = 0$ term survives, as the $q \neq 0$ terms average out to 0 due to the fast magnetic precession. The irreducible tensor elements are related to the expansion elements $n_k$ by \cite{Blum1981}

$$\rho^k_j(j \rightarrow \infty) = \frac{1}{\sqrt{4\pi[k]}} n_k. \hspace{1cm} (3.49)$$

We note that in the distribution $n(\theta)$ we have assumed a continuum of states that can adopt the orientation, $\theta$. This is akin to assuming a 'classical distribution' of the angular momentum vectors. The assumption of classical rotation becomes exact when $j \rightarrow \infty$. For smaller, finite, $j$, quantum effects play a role and this has to be accounted for in the representation of the irreducible tensor elements. The quantum states of a rotating molecule are $|jm\rangle$ \cite[see section 3.1]{Blum1981}. The probability of finding part of the $N$ molecules in the $|jm\rangle$ state is obtained by taking the matrix element over the density operator, $\hat{\rho}$,

$$\rho_{mm}(j) = \langle jm|\hat{\rho}|jm\rangle. \hspace{1cm} (3.50)$$

Off diagonal elements of the density-matrix, $\langle jm|\hat{\rho}|jm'\rangle$, are called coherence elements. In analogy to the classical case, for a molecule in a strong magnetic field,
only the diagonal $\rho_{mm}(j)$ elements are non-zero (it is exceedingly likely to find a molecule precessing with respect to the magnetic field). The quantum-state irreducible tensor elements of rank $k$ and projection $q$, are defined as

$$\rho_{q}^{k}(j) = \sum_{mm'} (-1)^{j-m}[k]^{1/2} \left( \begin{array}{ccc} j & j & k \\ m & -m' & q \end{array} \right) \rho_{mm'}(j), \quad (3.51)$$

where the entity demarcated by round brackets is called a Wigner 3j-symbol. Comparing the orientation $\rho_{0}^{1}$ and the alignment $\rho_{0}^{2}$ for the classical and the quantum case

$$\rho_{0}^{1}(\infty) = \sqrt{\frac{3}{4\pi}} \int_{-1}^{1} d\cos\theta \ n(\theta) \cos\theta, \quad (3.52a)$$

$$\rho_{0}^{1}(j) = \sqrt{\frac{3}{[j]j(j+1)}} \sum_{m} m\rho_{mm}, \quad (3.52b)$$

$$\rho_{0}^{2}(\infty) = \sqrt{\frac{5}{4\pi}} \int_{-1}^{1} d\cos\theta \ n(\theta) \frac{3\cos^{2}\theta - 1}{2}, \quad (3.52c)$$

$$\rho_{0}^{2}(j) = \sqrt{\frac{5}{(2j+3)(j+1)(2j+1)j(j-1)}} \sum_{m} [3m^{2} - j(j+1)]\rho_{mm}. \quad (3.52d)$$

In particular, note the relation between the projection quantum number, $m$, normalized with the length of the angular momentum vector, $\sqrt{j(j+1)}$, to the projection on the magnetic axis, $\cos\theta$, in the classical description. In the classical limit, $2j+1 \to 4\pi$, which makes that in the limit of $j \to \infty$, these two descriptions converge.

Next chapter, we make thankful use of the formalism of molecular density states in terms of their irreducible tensor elements. This is particularly useful when treating the generation of partially polarized radiation. Just as is the case for aligned dust, an ensemble of aligned molecules tend to emit partially polarized radiation.
Chapter 4

Light & Molecules

In the preceding chapters of this thesis we have studied the nuclear motion and electronic structure of molecules. We have seen how electric and magnetic fields can interact with these molecules and we reviewed some of the appropriate molecular physics required to conveniently compute the interaction terms. We have also studied the properties of light and dedicated particular attention to its polarization properties.

In this chapter we combine these results from previous chapters and study the interaction of light with molecules. In particular, the interaction of radio to (sub)millimeter radiation with molecules in the ISM provides for an interesting problem, because in these regions, the radiative interactions are of the same order as the collisional interactions, making a comprehensive excitation analysis necessary.

An additional effect that significant radiative interactions have on the molecular populations, is that if the interacting radiation field is anisotropic, this results in the partial alignment of the interacting molecules. Already in the case of weak magnetic fields, this alignment is with respect to the magnetic field direction and results in polarized radiation signals that trace the magnetic field morphology of the region in which the molecules are excited.

In light of these observations, we discuss maser polarization and the GK effect. Maser polarization provides a simple system of dominant radiative interactions because of the effects of strong amplification of the radiation through stimulated emission processes. In terms of polarization analysis, its simple (approximately) one-dimensional geometry makes it a good system to analyze analytically. After our discussion of maser polarization, we move on to thermal line polarization through an anisotropic velocity gradient in the LVG approximation. We end this chapter by discussing the general full 3D radiative transfer and excitation modeling, and outline a method to incorporate this into an alignment and polarization analysis.
4.1 Molecular excitation analysis

The population of the energy-levels of molecules is determined by balancing the radiative and collisional excitations and de-excitations. In particular, in astrophysical regions, the rates of collisional and radiative interactions are often comparable. A comprehensive analysis needs to be made to evaluate the excitation of a particular molecule embedded in an astrophysical region. Because radiative interactions are important, this has to be done in conjunction with evaluating the transfer of radiation.

When a system is equilibrated with a heat bath of temperature, $T$, statistical mechanics tells us that the probability of finding the system in a state, $i$, with energy $\epsilon_i$, is (Thorne & Blandford 2017)

$$p_i \propto e^{-\epsilon_i/kT}, \quad (4.1)$$

where $k$ is known as the Boltzmann constant. Thus, the ratio of probabilities between two states, $i$ and $j$,

$$\frac{p_j}{p_i} = e^{-\frac{(\epsilon_j-\epsilon_i)}{kT}} \quad (4.2)$$

depends only on the states' energy and the temperature. If we suppose that the system is an ensemble of molecules, with discrete energy levels, and that $\epsilon_j > \epsilon_i$, then Eq. (4.2) shows, that thermal equilibrium requires $p_j < p_i$; the upper energy level is less populated than the lower energy level.

It is rare for a system to be in thermal equilibrium in astrophysics. If we focus on the ISM, it is usually the low densities of these regions that make thermal equilibrium unattainable. Molecular gas in the ISM consists mostly of H$_2$ that acts as a heat bath. But under conditions of low densities, the coupling of a certain molecular species to the H$_2$ heat bath via collisions is weak. If a molecule, for instance CO, would be left to itself, it would gradually relax to its lowest energy configuration through the emission of radiation. Therefore, only when the rate of collisions with H$_2$ is much higher than the rate of radiative relaxation can thermal equilibrium be attained. Usually, however, in the ISM, radiative rates are of the order of the heat-exchanging collisions.

When we have to consider radiative effects as a feature of the molecular excitation, it is not only radiative relaxation we have to take into account. Indeed, when a molecule relaxes radiatively from state $j$ to state $i$, this relaxation is associated with the emission of a photon of energy $(\epsilon_j - \epsilon_i)$. Obviously, this photon is resonant with the transition $j \rightarrow i$, and it is thus a possibility that this...
photon is subsequently absorbed again by another molecule in the same region.
Alternatively, the photon is lost to the (local) ensemble of molecules when it is
not absorbed. Thus, to keep track of the energy-level population of a molecular
ensemble in conjunction with the collisional coupling of it with the H$_2$ heat bath.
We model the transfer of radiation of frequency, $\nu$, close to the resonant frequency
$\nu_{ij}$, through a molecular medium using the radiative transfer equation (see also
section 2.1)
\[
d\frac{d}{ds}I_\nu = -\kappa_\nu I_\nu + \epsilon_\nu,
\]
(4.3)
where the opacity includes absorption and stimulated emission \[\text{(Rybicki & Light-
man 2008)}\]
\[
\kappa_\nu = \frac{h\nu}{4\pi} B_{ij} (n_i - \frac{g_j}{g_i} n_j) \phi_\nu,
\]
(4.4)
where $n_i$ and $n_j$ are the number densities of the lower and upper level and $g_i$ and
$g_j$ its degeneracies. The Einstein B-coefficient is $B_{ij}$, and is defined in Eq. (3.42).
The line profile, $\phi_\nu$, is centered around the resonance frequency and usually takes
the form of a Doppler profile
\[
\phi_\nu = \frac{1}{\sqrt{\pi b_\nu}} e^{-\left(\frac{\nu - \nu_0}{b_\nu}\right)^2},
\]
(4.5)
where $b_\nu$ is the Doppler b-parameter in frequency units. The emissivity of the
medium is \[\text{(Rybicki & Lightman 2008)}\]
\[
\epsilon_\nu = \frac{h\nu}{4\pi} A_{ji} n_j \phi_\nu,
\]
(4.6)
where the Einstein A-coefficient, $A_{ji}$, is defined below. When the levels are Boltz-
mann distributed according to a certain temperature, $T$, the ratio $\epsilon_\nu/\kappa_\nu \rightarrow B_\nu(T)$
becomes the Planck function.
Returning to the interaction of molecular matter with radiation, we invoked
three processes relevant to the molecular excitation and transfer of radiation: (i)
spontaneous emission, where a molecule spontaneously relaxes from upper state
$j$ to lower state $i$, while emitting a photon of frequency $(\epsilon_j - \epsilon_i)/h$ in a random
direction, (ii) absorption, where a molecule absorbs a photon of frequency $(\epsilon_j -\epsilon_i)/h$, while exciting the molecule from state $i$ to state $j$, (iii) stimulated emission,
where a molecule under the influence of a photon of frequency $(\epsilon_j - \epsilon_i)/h$ emits an
additional such photon, in the same direction, while relaxing from upper state $j$ to
lower state $i$. The rate of spontaneous emission is only determined by molecular
properties, and is specific to the transition \( j \rightarrow i \), and is denoted, \( A_{ji} \). The symbol \( A_{ji} \) is the Einstein-A coefficient

\[
R_{\text{spont}}^{j \rightarrow i} = A_{ji}.
\]

The rate of absorption and the rate of stimulated emission are determined by molecular properties and the strength of the radiation field. The rate of absorption is

\[
R_{\text{abs}}^{i \rightarrow j} = B_{ij} \bar{J}_{ij},
\]

where \( B_{ij} \) is the Einstein-B coefficient of absorption and \( J_{ij} \) is specific intensity, integrated over all directions, and resonant with the \( i \rightarrow j \) transition of the molecular ensemble

\[
\bar{J}_{ij} = \int d\nu \int \frac{d\Omega}{4\pi} I_\nu \phi_\nu.
\]

The rate of stimulated emission is

\[
R_{\text{stim}}^{j \rightarrow i} = B_{ji} \bar{J}_{ij}
\]

where \( B_{ji} \) is the Einstein-B coefficient of stimulated emission. Transitions between levels \( i \) and \( j \) due to inelastic collisions are denoted \( C_{ij} \). Arguments of detailed balance relate collisional excitation and de-excitation rates by

\[
C_{ij}/C_{ji} = \frac{g_i g_j e^{-\epsilon_j - \epsilon_i/kT}}{g_i g_j}.
\]

We note the change in the population of level \( i \) as a function of radiative and collisional events (van der Tak et al. 2007)

\[
\dot{n}_i = \sum_{j>i} \left[ R_{\text{spont}}^{j \rightarrow i} + R_{\text{stim}}^{j \rightarrow i} + C_{ji} \right] n_j + \sum_{j<i} \left[ R_{\text{abs}}^{i \rightarrow j} + C_{ij} \right] n_j + n_i \sum_{j<i} \left[ R_{\text{abs}}^{i \rightarrow j} + C_{ij} \right] + n_i \sum_{j>i} \left[ R_{\text{abs}}^{j \rightarrow i} + C_{ij} \right]
\]

\[
= \sum_{j \neq i} n_j P_{ji} - n_i \sum_{j \neq i} P_{ij}.
\]

So that we can define

\[
P_{ij} = \begin{cases} 
A_{ij} + B_{ij} \bar{J}_{ij} + C_{ij}, & \text{if } i > j \\
B_{ij} \bar{J}_{ij} + C_{ij}, & \text{if } j > i.
\end{cases}
\]

It is easy to see that when the collisional rates far exceed the radiative rates, i.e. when the coupling to the \( \text{H}_2 \) heat-bath is strong, we obtain Boltzmann distributed level number densities. When radiative rates are higher or in the order of collisional rates, we have to solve Eqs. (4.3) and (4.8) together. This is one of the main problems that radiative transfer models try to solve.
Suppose we want to determine the molecular excitation (here written as a vector with elements \(n_i\), \(\mathbf{n}(r)\) as a function of the position \(r\), given a certain model for the temperature \(T(r)\), hydrogen number density, \(n_{H_2}(r)\), velocity structure \(\mathbf{v}(r)\) and molecular abundance \(x_{\text{mol}}(r)\). The radiation field at a specific point \(r_0\), \(I_\nu(r_0, \Omega)\) is a function of the excitation, \(\mathbf{n}(r)\), of the entire system, while the excitation at point \(r_0\), \(\mathbf{n}(r_0)\), is a function of the specific intensity at that point, because it determines the rates absorption and stimulated emission. Additionally, one has to consider the contribution of the co-spatial dust to the radiative transfer of Eq. (4.3). It may be clear that radiative problems can rapidly become prohibitively complex.

We will come back to solving the radiative transfer equations for complex physical systems in section 4.4. Before that, we comment on an approximation that reduces the complexity of the radiative transfer problem greatly: the Sobolev approximation (Sobolev 1957; Ossenkopf 1997). In the Sobolev approximation, we consider a system with a velocity gradient in direction \(\hat{\mathbf{r}}\), \(dv/\hat{\mathbf{r}} = dv/ds\), which is the same in all directions. At a later stage, we consider the Sobolev approximation for a plane-parallel system. If a velocity gradient is present, the radiation that is resonant with a certain transition is confined to a region of the order of the Sobolev length

\[
s_0 = \frac{b}{dv/\hat{\mathbf{r}}},
\]

where \(b\) is the Doppler-b parameter, representing the width of a line in velocity-space. For strong gradients, we note that the Sobolev length is small. At small enough Sobolev lengths, we can consider the molecular excitation to be constant throughout the region characterized by the Sobolev length. The line-profile of a certain transition

\[
\phi_\nu = \frac{c}{\nu} \phi_\nu = \frac{1}{\sqrt{\pi}b} e^{-\left(v/b\right)^2}
= \frac{1}{\sqrt{\pi}b} e^{-\left(|dv/ds|s/b\right)^2},
\]

(4.11)

can be related to the distance \(s\) along the line-of-sight. If we restate Eq. (4.3) by factorizing \(\kappa_\nu = k_{ij} \phi_\nu\), we obtain

\[
\frac{dI_\nu}{ds} = -k_{ij} \phi_\nu [I_\nu - S_\nu].
\]

(4.12)

The solution of this radiative transfer equation can be inserted into the expression
for \( \tilde{J}_{ij} \)

\[
\tilde{J}_{ij} = \int \frac{d\Omega}{4\pi} \int d\nu \phi_{\nu} I_{\nu} \\
= \int \frac{d\Omega}{4\pi} \left[ S_{ij} - (S_{ij} - I_{ij}^{(0)}) \frac{1 - e^{-\tau_{ij}}}{\tau_{ij}} \right],
\]

(4.13)

where \( \tau_{ij} = \int ds \phi_{\nu} k_{ij} = c k_{ij} / \nu_{ij} (dv/ds) \) and \( I_{ij}^{(0)} \) is the background radiation field for the \( i \rightarrow j \) transition. It may be noted that \( \tilde{J}_{ij} \) has become a function of the populations of the number densities of the levels associated with the transition \( i \rightarrow j \). Thus, by inserting \( \tilde{J}_{ij}(n_i, n_j) \) into the set of equations of Eq. (4.8), we are left with a problem of the type

\[
0 = Q(n)n,
\]

which can be solved using root-finding algorithms such as the Newton-Raphson method. It is worth noting that for high optical depths, the solution of Eq. (4.8) returns the Boltzmann distribution. This may be expected, because photons do not escape the Sobolev region in this limit. The excitation of molecules departs from simple Boltzmann statistics at low densities, where the collisional coupling to \( H_2 \) is weak, and finite optical depths, where the molecular ensemble is effectively ‘cooled’ through the loss of photons. The departure from Boltzmann statistics sometimes leads to a situation, where an upper level \( j \) is higher populated than a lower level \( i \): population inversion. Population inversion gives rise to a ‘negative opacity’ (see Eq. (4.4)), which has profound effects on the radiative transfer: the molecule is said to be ‘masing’.

4.2 Masers

A peculiar case of the interaction of radiation and matter occurs when the population of two states are inverted, the higher energy level is more populated than the lower energy level. When this is the case, we speak of masers. Masers are characterized by the exponential amplification of (resonant) radiation and a highly beamed (almost one-dimensional) geometry. The radiative transfer of such systems can be viably simplified, and they form the most basic systems where polarization of the radiation arises through the alignment of the molecular states by directional radiative interactions.

When the conditions are such that population inversion is produced between two (usually rotational) molecular energy levels, we speak of a MASER (Microwave Amplified by Stimulated Emission of Radiation). Maser refers to the radiative transfer, where the process of stimulated emission is more likely than absorption,
so that a resonant radiation field gets amplified instead of attenuated. In this section, we discuss briefly the radiative transfer of masers, including an important feature of the radiative transfer, namely ‘maser beaming’. We will lay particular emphasis on a consequence of maser beaming, which we show to be the partial polarization of radiation.

4.2.1 Radiative transfer

Suppose we study a transition between upper level \(a\) and lower level \(b\). We write out the rate of change of the \(a\)'th and the \(b\)'th level populations. In accordance to Eq. (4.8), we may note the rate of change as

\[
\dot{n}_a = \sum_{i \neq a,b} P_{ai} n_i - n_a \sum_{i \neq a,b} P_{ia} + n_b P_{ba} - n_a P_{ab} = \lambda_a - n_a \gamma_a + [B_{ba} \bar{J}_{ba} + C_{ba}] n_b - [A_{ab} + B_{ab} \bar{J}_{ab} + C_{ab}] n_a \quad (4.14a)
\]

\[
\dot{n}_b = \lambda_b - n_b \gamma_b - [B_{ba} \bar{J}_{ba} + C_{ba}] n_b + [A_{ab} + B_{ab} \bar{J}_{ab} + C_{ab}] n_a. \quad (4.14b)
\]

We call all other levels that are not participating in the transition between \(a\) and \(b\) the ‘reservoir’. Note that we have consolidated the radiative and collisional interactions with the reservoir in the pumping-rates: \(\lambda_a\) and \(\lambda_b\), and the decay-rates: \(\gamma_a\) and \(\gamma_b\). The decay rate of state \(a\), \(\gamma_a\), encapsulates all absorption and collisional excitations of state \(a\) to higher states, and all spontaneous and stimulated emissions, and collisional de-excitations, of state \(a\) to lower states. The pumping rate of state \(a\), \(\lambda_a\), includes all absorption and collisional excitations to state \(a\) from lower states to state \(a\), and all spontaneous and stimulated emissions, and collisional de-excitations, from higher states to state \(a\).

If we suppose that \(\lambda_a/\gamma_a > \lambda_b/\gamma_b\), then the upper level is consistently higher populated than the lower \(n_a > g_b n_b/g_a\). In this case of ‘population inversion’, we recognize in the radiative transfer equation, Eq. (4.3), that the rate of stimulated emission is higher than absorption. Because of this, the transition has a negative optical depth, and thus the radiative transfer is characterized by the exponential amplification of radiation.

Because of the exponential amplification of maser radiation, the radiation field will be mainly comprised of those maser-rays that have the longest coherent path-length. This effect is called maser beaming. For an interferometer observing a maser source, maser beaming means that only a fraction of the source is effectively visible: the maser appears a lot smaller than it actually is. A local effect of maser beaming is, if one follows the local radiation transfer in the maser cloud, that it is the rays with the longest path-length, that subtend a small solid angle, that dominate the local radiation field resonant with the maser transition. So we can approximate the radiation that interacts with the maser transition to be
approximately one-dimensional \cite{Gray2012,Elitzur1992}

\[ \bar{J}_{ab} = \Delta \Omega \int dv \, \phi_v I(\nu_j[1 - v/c], \Omega_0), \]

(4.15)

where \( \Omega_0 \) is the direction of the maser and \( \Delta \Omega \) is the beaming angle. The symbol \( \phi_v \) denotes the velocity-distribution for the maser-states. Because of the strong radiation field, the rates of absorption and stimulated emission for a maser-line are far greater than the spontaneous emission rate and the collision rate. We can therefore neglect the effects of spontaneous emission and collisions on the populations, and we arrive at the simplified evolution equations

\[ \dot{n}_a = \lambda_a - n_a \gamma_a - B_{ab} \bar{J}_{ab} \left[ n_a - \frac{g_a}{g_b} n_b \right] , \]

(4.16a)

\[ \dot{n}_b = \lambda_b - n_b \gamma_b + B_{ab} \bar{J}_{ab} \left[ n_a - \frac{g_a}{g_b} n_b \right] . \]

(4.16b)

If the decay rates for the upper and lower level are the same \( \gamma_a \simeq \gamma_b \), we can easily compute the population inversion, \( \Delta n = n_a - g_a n_b / g_b \), under steady-state conditions as

\[ \Delta n = \frac{\Delta \lambda}{\gamma + 2B_{ab} \bar{J}_{ab}} = \frac{\Delta n_0}{1 + \frac{J_{sat}}{J_{sat}}}, \]

(4.17)

where \( \Delta n_0 = \Delta \lambda / \gamma \) is the population inversion at weak maser fields, and \( J_{sat} = \gamma / 2B_{ab} \) is the saturation intensity.

The population (inversion) is a function of the velocity. The velocity distribution is taken to be a Doppler profile in the case of an unsaturated maser \( \bar{J}_{ab} \ll J_{sat} \), while under conditions of maser saturation, the profile will be affected by the radiation field. Similarly, the radiation spectrum quickly departs from the Doppler profile that characterizes thermal lines. Because of the exponential amplification of radiation, the spectrum is narrowed, as on-resonance radiation is amplified more strongly. In a rigorous analysis, the velocity-dependent population inversion and the frequency-dependent intensity are comprehensively analyzed.

In this elementary derivation, we assume that the population inversion and the intensity assume rectangular profiles of width \( \Delta v \) and \( \Delta \nu = \frac{\nu_0}{c} \Delta v \),

\[ \Delta n(v) = \frac{\Delta n}{\Delta v} , \quad \text{for} \quad -\Delta v/2 \leq v \leq \Delta v/2, \]

(4.18a)

\[ I_\nu = I , \quad \text{for} \quad \nu_0 - \Delta \nu/2 \leq \nu \leq \nu_0 + \Delta \nu/2. \]

(4.18b)

The radiative transfer can then be noted

\[ \frac{d}{ds} I = \frac{h \nu_0}{4\pi} B_{ab} \Delta n I, \]

(4.19)
where we furthermore ignored the contribution of the spontaneous emission. The term for the population inversion can be related to the maser brightness using Eq. (4.17). The resonant radiation field interacting with the maser transition can be trivially evaluated from Eqs. (4.15) and (4.18): \( J_{ab} = \Delta \Omega I \). If we define the opacity at weak maser fields \( \kappa_0 = \frac{h\nu_0}{4\pi B_{ab} \Delta n_0} \), then we can re-state the radiative transfer equation as

\[
\left[ 1 + \frac{\Delta \Omega I}{J_{\text{sat}}} \right] d (\ln I) = \kappa_0 ds. \tag{4.20}
\]

It is interesting to consider this differential equation in the limits of weak, unsaturated masers, and the strong, saturated masers. For an unsaturated maser, where the maser brightness is weak compared to the saturation intensity, we note that the solution to Eq. (4.20) becomes

\[
I = I_0 e^{\kappa_0 s}, \quad \text{for } \Delta \Omega I / J_{\text{sat}} \to 0, \tag{4.21}
\]

which is simply exponential growth of the maser intensity. As a result, the maser brightness will rapidly increase, and the maser will saturate. In the strongly saturated regime, the maser brightness temperature is far greater than the saturation intensity and the equation of radiative transfer

\[
\frac{d (\Delta \Omega I)}{d (\kappa_0 s)} = J_{\text{sat}}, \quad \text{for } \Delta \Omega I / J_{\text{sat}} \gg 1 \tag{4.22}
\]

is an equation describing linear growth of the maser intensity.

### 4.2.2 Maser polarization

In order for polarization to emerge in the maser radiation, we require the maser states to be partially aligned. Alignment is said to be present when the molecules have propensity to be found in some preferred direction.

In the coming derivation, we consider the interaction of the maser molecules with the magnetic field to be dominant: the magnetic field determines the symmetry axis of the molecules. This means that the magnetic precession rate, \( g\Omega (\sim s^{-1}/mG) \), is far higher than rates of stimulated emission, collisions, or spontaneous emission events. In the case of a dominant magnetic field, the molecule will have ample time to re-orient itself around the magnetic field after each (stimulated emission) interaction event. That means that the alignment of a single molecule can be described by only the angle its angular momentum vector makes with the magnetic field direction around which the molecule precesses (see also section 3.3).

In paper II, we show the proper theory and modeling of maser polarization that relaxes the assumption of a dominant magnetic field.

Suppose we have a maser radiation field that is partially polarized. Just as before, we consider it to have a rectangular velocity profile, and that it is strongly
beamed. We let $I$ be the total intensity of the radiation field on resonance with the maser transition $a \rightarrow b$, while $Q$ is its polarized intensity. The polarized intensity is defined $Q = I_\parallel - I_\perp$: positive $Q$ describes polarization parallel to the projected magnetic field direction. The angle that the propagation direction makes with the magnetic field is $\hat{k} \cdot \hat{b} = \cos \theta$. Because we are interested in describing the directional properties of both the radiation and the maser states, we use the irreducible tensor formalism that is introduced in section 3.3. The relevant radiation field irreducible tensor elements are (Degl’Innocenti & Landolfi 2006)

$$\bar{J}_0^0 = \int d\nu \, \phi_\nu \int d\Omega' \, I(\nu, \Omega')$$
$$= \Delta \Omega \bar{I} = \bar{J}_{ab}, \quad (4.23a)$$

$$\bar{J}_0^2 = \int d\nu \, \phi_\nu \int d\Omega' \left[ \frac{3 \cos^2 \theta' - 1}{2 \sqrt{2}} I(\nu, \Omega') - \frac{3 \sin^2 \theta'}{2 \sqrt{2}} Q(\nu, \Omega') \right]$$
$$= \Delta \Omega \left[ \frac{3 \cos^2 \theta - 1}{2 \sqrt{2}} I - \frac{3 \sin^2 \theta}{2 \sqrt{2}} Q \right]. \quad (4.23b)$$

Noting the radiation field in terms of their irreducible tensor elements provides an easy link to the molecular states formulated as irreducible tensor elements (see section 3.3). The irreducible tensor elements of molecular states are denoted as, $\rho^k_q(j_i)$, where $k$ is the irreducible tensor element and $q$ its projection, $i$ refers to either the upper maser state $a$ or the lower state $b$. We consider the case of a strong magnetic field, so that $\rho^k_q(j_i) = 0$ if $q \neq 0$, and we keep ourselves to a $j_a = 1 \rightarrow j_b = 0$ transition. In this case, the lower state, $b$, cannot be aligned and only has isotropic elements of $k = 0$, while the upper state, $a$, has an isotropic element of $k = 0$ and an alignment element of $k = 2$.

In order for polarized emission to emerge, we require the maser states to be partially aligned. Because of the condition of a strong magnetic field, this alignment is either parallel or perpendicular to the magnetic field direction, and therefore, polarization is generated either parallel or perpendicular to the magnetic field direction, projected onto the plane of the sky. If we intend to model the emergent maser polarization fraction, it is incumbent to model the relative alignment of the maser states. Just as in section 4.1 on the relative populations of molecular states, we model the relative alignment of the maser states through analyzing the rates of excitation and de-excitation to and from the states of interest. Since we are speaking about a maser, we are mostly interested in the absorption and stimulated emission events between the maser states. We follow the relative alignment of the $j_a = 1$ maser state, $\rho_0^0(j_a)$: the rate of change of this state is

$$\dot{\rho}_0^0(j_a) = -B_{ab} \left[ J_0^0 \rho_0^0(j_a) + J_0^0 \rho_0^0(j_a) \right] + \frac{1}{\sqrt{3}} B_{ba} \bar{J}_0^0 \rho_0^0(j_b) - \gamma \rho_0^0(j_a)$$
$$= 0, \quad (4.24)$$

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where $\gamma$ is the maser decay rate (see Eq. (4.16)). We divide Eq. (4.24) by $B_{ab}J_0^0$ and rearrange to obtain an expression for the relative alignment of the $j_a = 1$ maser state

$$\rho_0^2(j_a = 1) = -\frac{\delta_0^2}{\sqrt{3}} \frac{\Delta n}{1 + \frac{\Delta n}{\bar{J}_{ab}}}$$

(4.25)

where $\Delta n = n_a - 3n_b = \sqrt{3}[\rho_0^0(j_a) - \sqrt{3}\rho_0^0(j_b)]$ and we have defined the relative anisotropy of the radiation field

$$\delta_0^2 = \frac{J_0^2}{J_0^0} = \left[ \frac{3\cos^2 \theta - 1}{2\sqrt{2}} - \frac{3\sin^2 \theta Q}{2\sqrt{2} I} \right].$$

(4.26)

It is interesting to note that in case of an unsaturated maser, $J_{sat} \gg \bar{J}_{ab}$, then the relative alignment of the maser state is absent: $\rho_0^2(j_a = 1) \to 0$. Only in saturated masers, where $\bar{J}_{ab}$ is on the order of, or greater than, the saturation intensity will the radiation field be able to partially align the maser states. In the limit of a highly saturated maser, the alignment of the $j_a = 1$ tends to

$$\rho_0^2(j_a = 1) \approx -\frac{\delta_0^2}{\sqrt{3}} \Delta n.$$  

(4.27)

We proceed our analysis and keep ourselves to the highly saturated maser regime. When we do not consider polarization, the line-opacity is given by (see Eq. (4.4))

$$\kappa_\nu = \frac{h\nu}{4\pi B_{ab} \Delta n \phi_\nu}.$$  

(4.28)

But when the emitting entity is partially aligned, the opacity expressions have to be augmented; and also pertain to the radiation polarization

$$\kappa_I/\kappa_\nu = 1 + \sqrt{3}\rho_0^2(j_a = 1) \frac{3\cos^2 \theta - 1}{2\sqrt{2}},$$

(4.29a)

$$\kappa_Q/\kappa_\nu = \sqrt{3}\rho_0^2(j_a = 1) \frac{3\sin^2 \theta}{2\sqrt{2}}.$$  

(4.29b)

We can fill in our expression for the relative alignment of the maser state from Eq. (4.27), and find that the polarized opacity

$$\kappa_Q/\kappa_\nu = -\delta_0^2 \frac{3\sin^2 \theta}{2\sqrt{2}},$$

(4.30)

depends only on the relative alignment of the radiation field (Eq. 4.26) and the maser propagation angle $\theta$. In order for the polarization fraction to converge, we require $\kappa_Q \to 0$, which puts a constraint on the polarization fraction

$$\frac{Q}{I} = -\frac{3\sin^2 \theta - 2}{3\sin^2 \theta}.$$
This polarization fraction is unphysical for $\sin^2 \theta < 1/3$ since $|Q/I| > 1$. Under these circumstances, polarization is produced until $|Q/I| \to 1$. We thus have the polarization fraction of a highly saturated maser in the strong magnetic field limit ($\Delta \omega \gg g\Omega \gg R \gg \gamma$):

$$Q/I = \begin{cases} \frac{-3\sin^2 \theta - 2}{3\sin^2 \theta}, & \text{for } \sin^2 \theta \geq \frac{1}{3} \\ 1, & \text{for } \sin^2 \theta < \frac{1}{3} \end{cases}$$

(4.31)

which is the classic result of Goldreich et al. (1973).

4.3 Goldreich-Kylafis effect

In previous sections, we discussed excitation modeling within the (isotropic) large-velocity gradient approximation and the alignment of molecular quantum states via directional radiation in masers. Goldreich & Kylafis (1981) combined both these features when considering the (polarized) excitation modeling of a system with an anisotropic large velocity gradient. In this section, we summarize the main physical arguments that lead to the so-called Goldreich-Kylafis (GK) effect.

In section 4.1, we considered the large velocity gradient approximation to solve the radiative transfer and molecular excitation analysis of a non-LTE system. In that discussion, we considered the velocity gradient to be isotropic, but in this section, we consider the more general case of anisotropic velocity gradient. An anisotropic geometry results in an anisotropic radiation field; in section 3.2.2 we showed that anisotropic radiative excitation differentially excites magnetic sublevels, thus leading to the partial alignment of the molecular states.

Because we expect alignment in the molecular states, it cannot be excluded that the radiation is partially polarized. Thus, we need to employ a complete description of the relevant radiation field by including also its partial polarization. We follow Goldreich & Kylafis (1981), and represent the radiation field in terms of their parallel and perpendicular polarized components

$$I_{||,\perp}(\nu, \Omega) = \frac{1}{2} (I(\nu, \Omega) \pm Q(\nu, \Omega)),$$

(4.32)

where the components are with reference to the magnetic field projection on the plane of the sky. We consider a transition between ground state level $j = 0$, and an excited state $j = 1$. In Eqs. (3.42), we computed the radiative interaction rates of absorption transitions $|00 \rangle \to |10 \rangle$ and $|00 \rangle \to |1\pm \rangle$ to be

$$R_0 = B_{01} \int d\nu \phi_\nu \int \frac{d\Omega}{4\pi} \sin^2 \theta I_{||}(\nu, \Omega),$$

(4.33a)

$$R_{\pm} = B_{01} \frac{1}{2} \int d\nu \phi_\nu \int \frac{d\Omega}{4\pi} \left( I_{\perp}(\nu, \Omega) + I_{||}(\nu, \Omega) \cos^2 \theta \right).$$

(4.33b)
We use these radiative rates to formulate the rate equations of the populations of the excited state magnetic sublevels \( n_0 \) and \( n_\pm \), to be

\[
\dot{n}_0 = -A_{10}n_0 + R_0(n_g - n_0) + C(n_be^{-h\nu_0/kT} - n_0), \\
\dot{n}_\pm = -A_{10}n_\pm + R_\pm(n_g - n_\pm) + C(n_be^{-h\nu_0/kT} - n_\pm), \\
2n_\pm + n_0 + n_g = \text{constant},
\]

(4.34a, 4.34b, 4.34c)

We formulated these equations in terms of \( I_{||,\perp} \), instead of the Stokes parameters, because in the case of a constant magnetic field, the radiative transfer of these components can be solved independent from each other.

Because of the anisotropic velocity gradient, the Sobolev length, \( s_0(\Omega) \), is in turn a function of the direction. By using the LVG approximation, the profile averaged specific intensity can be solved. Following the same procedure as we did leading up to Eq. (4.13), we obtain

\[
\int d\Omega \int d\nu \phi_\nu I_{||,\perp}(\nu, \Omega) = \int d\Omega \int d\Omega \left[ S_{||,\perp}(\Omega) - (S_{||,\perp}(\Omega) - \frac{1}{2}I(0)) \frac{1 - e^{-\tau_{||,\perp}(\Omega)}}{\tau_{||,\perp}(\Omega)} \right],
\]

(4.35a)

where

\[
\tau_{||,\perp}(\Omega) = \left( \frac{c}{\nu_0} \right) \frac{s_0(\Omega)}{b} k_{||,\perp}(\Omega).
\]

(4.35b)

If we adopt for the geometry of the velocity gradient a plane parallel slab, where the magnetic field is oriented along the velocity-gradient, \( dv/ds \). We note that the Sobolev length is

\[
s_0(\Omega) = \frac{b}{dv_r/dv} = \frac{b}{dv/ds \cos^2 \theta} = s_0/ \cos^2 \theta,
\]

where \( \cos \theta \) is the projection of the ray-tracing direction on the magnetic field axis. If the velocity gradient is in the directions perpendicular to the magnetic field: \( s_0(\Omega) = s_0/ \sin^2 \theta \). For completeness, the direction dependent propagation coefficients and source functions can be derived to be

\[
k_{||} = \frac{h\nu_0}{4\pi} B_{01}(n_b - n_\pm \cos^2 \theta - n_0 \sin^2 \theta), \\
k_{\perp} = \frac{h\nu_0}{4\pi} B_{01}(n_b - n_\pm), \\
S_{||} = \frac{h\nu_0^3}{c^2} \frac{n_\pm \cos^2 \theta + n_0 \sin^2 \theta}{n_b - n_\pm \cos^2 \theta - n_0 \sin^2 \theta}, \\
S_{\perp} = \frac{h\nu_0^3}{c^2} \frac{n_0 - n_\pm}{n_b - n_\pm}.
\]

(4.36a, 4.36b, 4.36c, 4.36d)
With Eqs. (4.34-4.36), we have obtained a set of equations that can be solved through root-finding methods such as the Newton-Rhapson method. These equations have been first formulated and solved by Goldreich & Kylafis [1981]. They yield the polarization fraction as a function of the ratio of radiative to collisional interactions, captured in $A_{10}/C$, and the average optical depth, $\tau$. For $\tau \sim 1$, polarization fractions are greatest, because at these optical depths, anisotropy in the radiation field best manifests itself. Also, high collisional rates tend to quench the polarization, as the isotropic collisional term in the rate equations de-polarizes the molecular states. In Fig. (4.1) we plot the predicted polarization fraction by the GK model for different ratios $A_{10}/C$ and a range of optical depths. In the same figure, we plot the predicted polarization fractions in case of an unpolarized, but anisotropic radiation field. At low polarization fractions, the two methods converge. This will prove an important insight when modeling the polarization and alignment of radiation and molecular states in more complex geometries, while also including the extensive modeling of a large portion of the rotation-vibration energy-levels of a particular molecule.

4.4 Polarization in a complex geometry

With ever increasing computational power, the comprehensive excitation analysis of molecules in complex astrophysical systems has become viable. We discuss the numerical schemes that allow for the excitation modeling of complex systems. Because the full (polarized) radiative transfer analysis of such systems is still prohibitively complex, we discuss the anisotropic intensity approximation that allows for the polarized excitation analysis of molecular quantum states in a complex geometry, while using the converged output of regular isotropic excitation modeling of these systems.

Up to now, we have discussed radiative transfer and molecular excitation problems in idealized geometries. For maser radiative transfer, we assumed the beaming angle so small that approximating it as one-dimensional propagation is warranted, while for regular molecular excitation, we only discussed the case of geometries with a large (and constant) velocity gradients. The large velocity gradient was invoked so that we could approximate the molecular excitation as being constant in the region, while the constant velocity gradient allowed us to simplify the radiative transfer considerably, and set up a set of coupled equations that can be solved via a root-finding algorithm.

The approximations of one-dimensional propagation or LVG lose their quality when studying astrophysical objects with complex geometries, such as evolved stellar envelopes or protoplanetary disks. Further, with the advent of large interferometers, such objects have been resolved to AU scales, and the interpretation
Figure 4.1: Comparison of the polarization fraction computed through the GK method (solid line) and through the radiation anisotropy approximation (dotted line). For more details on the simulation parameters, see Goldreich & Kylafis (1981). We consider a $J = 1 - 0$ transition at 100 GHz, with a strong magnetic field along the $\hat{z}$-axis and a velocity gradient of $10^{-9}$ s$^{-1}$ in the $xy$-plane. We consider a temperature $T = 10$ K. Three ratios for the collision-radiative rates are considered and denoted inside the figure. The polarization fraction is computed for a ray traveling along the $\hat{x}$-axis.
of molecular emission from these regions cannot be reasonably interpreted using simplified molecular excitation schemes. Indeed, in the last decades, large improvements have been made in non-local non-LTE analyses of the excitation of molecular lines in complex geometries.

In the numerical work presented in this thesis, when analyzing the non-local (isotropic) molecular excitation in complex geometries, we use the LIme Modeling Engine (LIME), developed by Brinch & Hogerheijde (2010). LIME treats the radiative transfer in a complex geometry that is defined by a density, temperature, velocity and abundance structure. The region is studied, by dividing it up in a (large) number of randomly distributed cells, where the random distribution is density-weighed. The cells are connected by performing a Delaunay triangulation, from which the Voronoi diagram define the cells that are neighboring and connected. The radiative transfer equations are solved, together with the molecular excitation, in a Monte-Carlo scheme, that is sped-up by the Accelerated Lambda Iteration algorithm (Rybicki & Hummer 1991).

Typical numbers of grid-cells for LIME are 100,000, while the molecular excitation per cell includes about 40 rotational levels. Molecules with hyperfine structure, low-lying vibrational levels, or asymmetric rotors require a drastically increased dimensionality of the energy-structure to enable a proper excitation analysis. Thus, the dimensionality of the global excitation analysis is high even without paying attention to molecular alignment and polarized radiation. In paper III, we outline how a polarized excitation analysis can be attained at reasonable computational cost anyway, using two main approximations: (i) the anisotropic intensity approximation, and (ii) the strong magnetic field approximation.

We have seen in our discussion of the polarization of maser radiation, that the relative anisotropy of the radiation field, that quantifies the partial alignment of molecular states due to radiative interactions, is (for one-dimensional propagation)

\[
\delta_0^2 = \frac{\bar{J}_2^2}{\bar{J}_0^2} = \left[ \frac{3 \cos^2 \theta - 1}{2 \sqrt{2}} - \frac{3 \sin^2 \theta Q}{2 \sqrt{2} I} \right],
\]

and has a part that is dependent on the polarization fraction of the radiation field, \(p_l = Q/I\). However, from both earlier modeling of GK effects (see Fig. (4.1)), and linear polarization observations of thermal lines, we know that polarization fractions rarely exceed magnitudes of a couple of percents. At these low polarization fractions, it is safe to ignore the contribution of the polarized emission to the anisotropy of the radiation field, and we formulate the radiation field irreducible tensor elements within the anisotropic intensity approximation as

\[
\bar{J}_0^0 = \int d\nu \phi_\nu \int d\Omega I(\nu, \Omega),
\]

\[
\bar{J}_0^2 = \int d\nu \phi_\nu \int d\Omega \frac{3 \cos^2 \theta - 1}{2 \sqrt{2}} I(\nu, \Omega).
\]
If we use this approximation for obtaining the irreducible tensor elements of the radiation field, they can be obtained for a complex three-dimensional geometry from the solution of a radiative transfer engine such as LIME. Having acquired the irreducible tensor elements of the radiation field at every transition, the relative alignment of the molecular states can be computed and used to ray-trace a polarized image of the region of interest. This is the method we employ in PORTAL, which we present in Paper III, and use to analyze the emergence of polarization from different molecular lines in protoplanetary disks in Paper V.
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Paper I

Characterization of methanol as a magnetic field tracer in star-forming regions


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Characterization of methanol as a magnetic field tracer in star-forming regions

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Magnetic fields play an important role during star formation1. Direct magnetic field strength observations have proven particularly challenging in the extremely dynamic protostellar phase2. Because of their occurrence in the densest parts of star-forming regions, masers, through polarization observations, are the main source of magnetic field strength and morphology measurements around protostars3. Of all maser species, methanol is one of the strongest and most abundant tracers of gas around high-mass protostellar disks and in outflows. However, as experimental determination of the magnetic characteristics of methanol has remained largely unsuccessful4, a robust magnetic field strength analysis of these regions could hitherto not be performed. Here, we report a quantitative theoretical model of the magnetic properties of methanol, including the complicated hyperfine structure that results from its internal rotation5. We show that the large range in values of the Landé g factors of the hyperfine components of each maser line lead to conclusions that differ substantially from the current interpretation based on a single effective g factor. These conclusions are more consistent with other observations5,6 and confirm the presence of dynamically important magnetic fields around protostars. Additionally, our calculations show that (nonlinear) Zeeman effects must be taken into account to further enhance the accuracy of cosmological electron-to-proton mass ratio determinations using methanol7,8.

The presence of a magnetic field within an astrophysical maser produces partially polarized radiation. Linear polarization provides information on the magnetic field direction, while the magnetic field strength can be determined by comparing the field-induced frequency shifts between left- and right-circularly polarized maser emission. Extraction of the relevant information from polarized maser spectra requires knowledge of the Zeeman parameters that describe the response of the maser molecule/atom to a magnetic field. These Zeeman parameters are known for maser molecules such as hydroxide (OH), water and silicon monoxide, but not for methanol (CH$_3$OH).

Various torsion–rotation transitions of methanol have been observed as astrophysical masers. It has long been known that these transitions have a hyperfine structure, but only recently has an accurate model of this structure been presented9. It was shown that the so-called torsional motion of methanol about the carbon–oxygen (C–O) bond drastically complicates the hyperfine interactions and that ‘spin–torsion’ terms occur in addition to the usual ‘spin–rotation’ and spin–spin coupling terms. The magnetic moments that produce the hyperfine structure also interact with an external magnetic field, that is, a Zeeman effect. Here, we extend the model of methanol’s hyperfine structure with the Zeeman interactions. We quantitatively determine all of the relevant coupling parameters, including effects from the torsional motion, by quantum chemical ab initio calculations and an estimate of the torsional Zeeman effect based on experimental results10. With this model, we can determine the Zeeman splitting of the hyperfine states within all the known methanol maser transitions. Zeeman interactions are usually described in a first-order approximation by the Landé g factor. In methanol, each torsion–rotation transition is actually split into a number of transitions between individual hyperfine levels of the upper and lower torsion–rotation states (Fig. 1). The Landé g factors calculated for the different hyperfine transitions differ strongly, and although these transitions cannot be individually resolved in the observed maser spectra, we show that this is important for the interpretation of the measured polarization effects. Furthermore, we find that, in several cases, the energy gaps between hyperfine levels are so small that hyperfine states with different total angular momenta F get mixed even by a weak magnetic field. In such cases, the first-order approximation for the Zeeman interactions breaks down, and the Zeeman splittings depend nonlinearly on the magnetic field strength (Fig. 2). Also, the Einstein A coefficients of transitions between two hyperfine levels become magnetic-field-dependent quantities in these cases (Supplementary Fig. 2). This behaviour has not previously been seen in Zeeman interactions for non-paramagnetic molecules, and is therefore not accounted for in current maser polarization theory11,12.

To apply our results to maser polarization measurements, we must consider hyperfine-specific effects in the maser action. The individual hyperfine lines are not spectrally resolved, but the maser action can favour specific hyperfine transitions by the following mechanisms: (1) varying radiative rates for stimulated emission (see the Einstein coefficients of the various hyperfine components within a torsion–rotation line (Supplementary Information)); (2) kinematic effects, when there are two maser clouds along the line of sight with different velocities, such that a hyperfine transition in the foreground cloud amplifies emission from a different hyperfine transition in the background cloud13; (3) population inversion of the levels involved in maser action is preceded by collisional and radiative de-excitation of higher torsion–rotation levels14, with rate coefficients that are hyperfine-state specific15. The last effect has been overlooked in current maser excitation models14, and thus no quantitative information is available. To obtain a qualitative understanding, we consider the relative hyperfine-specific collisional and...
Until now, methanol maser circular-polarization observations7,8 have supported the conclusion that within a torsion–rotation transition the various hyperfine components or by any of the other components, the derived magnetic field strength would be higher. Including all hyperfine components would result in an average $\Delta g_f \approx 0.17\, \text{mg}^{-1}$ and an average $\langle B \rangle \approx 80\, \text{mg}$. This is considerably larger than expected based on OH masers observed at similar densities7,8. The results based on the $F=3 \rightarrow 4$ transition are in good agreement with OH maser polarization observations5,6 as well as with the extrapolated magnetic field versus density relation $B \propto n^{1/2}$ (refs7,23). This indicates, as already suggested by linear polarization studies2,25,26, that methanol masers probe the large-scale magnetic field around massive protostars. Reversing, extending the magnetic field versus density relation by almost two orders of magnitude in density provides important constraints on the theory of massive star formation, because it implies that the magnetic energy density remains important up to densities of $n_H \approx 10^9\, \text{cm}^{-3}$. The conclusions are also supported by a more specific study of Cepheus A HW2 (ref.23 and Fig. 3), where our reinterpretation confirms a slightly supercritical maser region, giving rise to magnetically regulated accretion towards the disk of Cepheus A HW2.

Polarization observations of class I methanol masers in the outflows of massive star-forming regions have been made for the $36\, \text{GHz}(7_{05}A_2 \rightarrow 6_{06}A_1)$ and $44\, \text{GHz}(7_{05}A_2 \rightarrow 6_{06}A_1)$ torsion–rotation transitions. Because the magnetic characteristics of methanol were not known, (hyperfine-unspecific) estimates of the Zeeman parameters were used. In the following, we re-analyse some of the observations, using our calculated Zeeman parameters (Table 1). We take into account that within a torsion–rotation transition the various hyperfine transitions have different Landé $g$ factors (Supplementary Tables 1–18) and that the maser action can be hyperfine-state specific.

We begin with the circular-polarization observations of class II methanol masers at $6.7\, \text{GHz}$, occurring in protostellar disks. We assume that the transition with the largest Einstein coefficient for stimulated emission, the $F=3 \rightarrow 4$ transition (see Fig. 1 and Supplementary Table 3), will be favoured and that the maser action is limited to this transition. Then, the Zeeman-splitting coefficient $\alpha_L$ (related to the Landé $g$ factor $g_L$ as $\alpha_L = \mu_B g_L n_H^2$, with $\mu_B$ being the magnetic moment of the maser transition) will be $\alpha_L = -1.135\, \text{Hz} \cdot \text{mg}^{-1}$, which is ten times larger than the value currently used for magnetic field estimates19,20. In the methanol maser regions probed by these class II masers, with an $H_2$ number density of $n_{H_2} \approx 10^9\, \text{cm}^{-3}$ (ref.17), application of our new results to a large sample of maser observations indicates an average field strength $\langle |B| \rangle \approx 12\, \text{mg}$. If, instead of the $F=3 \rightarrow 4$ hyperfine transition, the polarization is caused by a combination of hyperfine components or by any of the other components, the derived magnetic field strength would be higher. Including all hyperfine components would result in an average $\Delta g_f \approx 0.17\, \text{mg}^{-1}$ and an average $\langle |B| \rangle \approx 80\, \text{mg}$. This is considerably larger than expected based on OH masers observed at similar densities7,8. The results based on the $F=3 \rightarrow 4$ transition are in good agreement with OH maser polarization observations5,6 as well as with the extrapolated magnetic field versus density relation $B \propto n^{1/2}$ (refs7,23). This indicates, as already suggested by linear polarization studies2,25,26, that methanol masers probe the large-scale magnetic field around massive protostars. Reversing, extending the magnetic field versus density relation by almost two orders of magnitude in density provides important constraints on the theory of massive star formation, because it implies that the magnetic energy density remains important up to densities of $n_H \approx 10^9\, \text{cm}^{-3}$. The conclusions are also supported by a more specific study of Cepheus A HW2 (ref.23 and Fig. 3), where our reinterpretation confirms a slightly supercritical maser region, giving rise to magnetically regulated accretion towards the disk of Cepheus A HW2.

Polarization observations of class I methanol masers in the outflows of massive star-forming regions have been made for the $36\, \text{GHz}$ and $44\, \text{GHz}$ torsion–rotation transitions. In both lines, the individual hyperfine transitions are clustered in two groups, giving rise to a doublet structure in the spectra7. Considering kinematic effects favouring one of the two peaks, and selecting from this peak the transition with the largest coefficient for stimulated emission, we assume that
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with the observations. We thus suggest that class I methanol maser polarization) imply an average line-of-sight magnetic field strength of several tens of mG, to be compared to the result from other masers along the line of sight (Fig. 3).

Our results also suggest an explanation for a surprising feature observed in both class II (6.7 GHz) and class I (44 GHz) masers. Observations have shown reversals in the sign of polarization over areas of small angular extent in the sky (fig. 3 (6.7 GHz) and fig. 2 (44 GHz) in ref. 39). Such reversals have usually been interpreted as a change in field direction. However, reversals on au-scales would be surprising if one considers the agreement between the fields probed by methanol masers and dust emission32. A more plausible explanation favoured by our results is that in the masers with opposite signs of polarization, the masing process itself is due to the dominance of different hyperfine transitions. If we assume for the 6.7 GHz spectrum that for the oppositely polarized maser the $F = 7 \rightarrow 8$ hyperfine transition is favoured by kinematic effects, instead of the $F = 3 \rightarrow 4$ transition for the other masers, we find a magnetic field comparable to the result from other masers along the line of sight (Fig. 3).

For the 44 GHz maser, if we assume the $F = 8 \rightarrow 7$ transition to be favoured for the oppositely polarized maser instead of the $F = 5 \rightarrow 4$ transition for the other maser, we also get Zeeman-splitting coefficients with opposite signs, and we find similar magnetic fields of $\sim 50 \text{ mG}$ from both masers composing the signal. We thus find that an alternative preferred hyperfine transition in the maser action is able to explain opposite circular polarization along the line of sight, and we obtain magnetic fields comparable to the results from other masers that trace similar areas around the protostar.

Our model is also important for the study of methanol maser absorption in red-shifted cosmological sources. Methanol’s high sensitivity to variation of the electron-to-proton mass ratio in the torsion–rotation structure is enhanced by its torsional motion1. Extragalactic absorption measurements of the $3 \rightarrow 1E \rightarrow 20E$ (12.2 GHz) transition have been used to provide the strongest constraints on the time variation of the electron-to-proton mass ratio9,10. Recently, measurements with a high spatial resolution have been able to selectively observe methanol absorption in an extragalactic cold cloud33. Hyperfine effects shift the centre of torsion–rotation lines, which is an effect not accounted for in the current torsion–rotation fitting Hamiltonian31 from which the parameters are used in determination of the sensitivity coefficients31,32. Also, in cold extragalactic regions, temperature broadening effects are smaller than the hyperfine splittings, which could be resolved with a sufficiently high spectral resolution. Furthermore, in regions with strong magnetic fields ($> 30 \text{ mG}$), this structure will be affected by Zeeman effects. These effects should be included in the error-accounting of the constraints to the time variation of the electron-to-proton mass ratio11.

Theoretical modelling of (nonlinear) Zeeman effects for other molecular species such as hydrogen cyanide (HCN) and formaldehyde (H$_2$CO) can also be done according to the theory presented here. The same care should be taken in the assessment of Zeeman effects in radical species, where the magnetic field can mix fine-structure states, which is analogous to hyperfine mixing. This will be particularly important for thioxoethenylidene (CCS)37,38, for which the Zeeman characteristics are still poorly known, but which will be one of the prime molecules for Zeeman studies with the Square Kilometre Array.

Methods

We theoretically modelled the response of methanol to weak magnetic fields by the addition of magnetic field (Zeeman) interactions to the model for methanol’s hyperfine structure from Lankhaar et al.6. Here, we briefly revisit methanol’s hyperfine structure and describe the relevant Zeeman interactions. Next, we detail the computational methods used to obtain the molecule-specific coupling parameters. Finally, we describe the methods used to compute the magnetic-field-dependent spectrum of methanol.

Hyperfine structure

The elucidation of methanol’s hyperfine structure has been a challenge. The CH$_3$ group in methanol can easily rotate with respect to the OH group, which leads to an extension of the usual rigid-rotor hyperfine Hamiltonian with nuclear spin–torsion interactions31. In contrast with the nuclear spin–rotation

Fig. 3 | Total intensity and circular-polarization ($V$) spectra of the 6.7 GHz ($S_{12}A_2 \rightarrow 6_0A_3$) methanol masers around the disk of the high-mass protostar Cepheus A HW232. Total intensity is flux density in Jy = $10^{-26} \text{ W m}^{-2} \text{ Hz}^{-1}$. The velocity is defined with respect to the local standard of rest, $V_{\odot}$. The spectra (solid) were observed with the Effelsberg 100 m telescope. They originate from methanol masers with different velocities along the same line of sight and can be approximated by ten Gaussian peaks (dashed, total intensity). If we assume that a single hyperfine component is dominant, our calculations (dashed, circular polarization) imply an average line-of-sight magnetic field strength of $B_0 = 7.7 \pm 1.0 \text{ mG}$. The field strengths (in mG) extracted from the individual components, with errors of $\sim 20\%$ s.d., are indicated in the figure for each Gaussian. These correspond to a total magnetic field strength of $\beta = 26 \text{ mG}$. In one of the peaks, the maser radiation is oppositely polarized with respect to the other peaks, which suggests a reverse magnetic field.

However, this could be due to pumping of a different hyperfine component with a different Landé $g$ factor. If this argument holds, the field strengths and the mass of the region where the magnetic field is probed would be $\beta = 0.2$, showing the dominance of the magnetic field. The recalculated mass to magnetic flux ratio compared with the critical ratio is 1.5.

the $F = 3 \rightarrow 2$ (36 GHz) and $F = 5 \rightarrow 4$ (44 GHz) hyperfine lines are favoured and that the maser action is limited to these transitions. Then, the Zeeman-splitting coefficients of the maser transitions will be $\alpha_{1} = -0.704 \text{ Hz mG}^{-1}$ for the 36 GHz line and $\alpha_{2} = -0.920 \text{ Hz mG}^{-1}$ for the 44 GHz line (Supplementary Tables 10 and 4). The observed class I methanol masers are expected to occur in shocked regions of the outflows at densities of an order of magnitude lower than class II masers34. The Zeeman splitting of the 36 GHz and 44 GHz lines was found to be of the order of several tens of hertz$^{34,35}$. Using our analysis, this would indicate magnetic field strengths of $20–75 \text{ mG}$. Because class I masers are shock excited, shock compression is expected to increase the magnetic field strength. For the outflow velocities in the class I maser regions, a preshock magnetic field as observed in the OH maser regions ($\sim 5 \text{ mG}$) will be amplified to $> 20 \text{ mG}$, consistent with the observations. We thus suggest that class I methanol maser polarization observations provide important information on the shock conditions of protostellar outflows.

Theoretical resolution

$\beta = 20$ for the 44 GHz line and $\beta = 0.2$ for the 36 GHz line. We thus find that the critical ratio is 1.5.
coupling parameters, for which the ab initio calculated values have recently been experimentally confirmed\(^1\), the torsional hyperfine coupling parameters cannot be obtained from quantum chemical ab initio calculations\(^2\). Experiments probing the hyperfine structure of methanol have proven difficult to interpret, because the hyperfine transitions cannot be individually resolved. Lankhaar et al.\(^1\) revised the derivation of a Hamiltonian that includes the torsional hyperfine interactions, and obtained the coupling parameters in this Hamiltonian from both ab initio calculations and experimental data\(^3\). The hyperfine spectra of methanol calculated from this Hamiltonian agree well with the spectra observed for several torsion–rotation states of both A symmetry and E symmetry. In our present calculations of the Zeeman interactions of methanol in external magnetic fields, we start from this hyperfine Hamiltonian. For a detailed description, see Lankhaar et al.\(^1\).

Zeeman Hamiltonian. Zeeman interactions are governed by the same magnetic moments that determine the hyperfine structure, interacting with an external magnetic field \(B\). For a closed-shell diamagnetic molecule such as methanol, three contributions are important: the overall rotation term, the internal rotation term or torsional term and the nuclear spin term. The most abundant \(^1\)C and \(^1\)O nuclei have spin zero, so the nuclear spin of methanol (CH\(_3\)OH) comes from the three protons in the CH\(_3\) group and the proton in the OH group. As derived in appendix A of Lankhaar et al.\(^1\) for the corresponding hyperfine Hamiltonian, the rotational Zeeman Hamiltonian

\[
\hat{H}_{\text{Zeeman}} = -\mu_B B \cdot \mathbf{g}(\gamma) \hat{J} + \mu_B B \cdot \mathbf{g}(\gamma) \hat{\rho} \cdot \hat{I}.
\]

(1)

depends not only on the overall rotation angular momentum \(\hat{J}\), but also on the torsional angular momentum \(\hat{I}\). The unit vector \(\mathbf{g}(\gamma)\) defines the direction of the internal rotation axis in the principal-axes frame of the molecule, and \(\rho = \Gamma^{-1/2}\Gamma^*\), where \(\Gamma\) is the total inertial tensor and \(\Gamma^*\) is the inertia tensor of the CH\(_3\) group. The dimensionless factor \(\rho\) depends on the ratio of the moments of inertia of the OH frame and the rotating CH\(_3\) top about the torsional axis \(\gamma\).

In addition, we must account for torsional Zeeman effects. Similarly to the torsional hyperfine Hamiltonian \(\hat{H}_{\text{hf}}\) in Lankhaar et al.\(^1\), the torsional Zeeman Hamiltonian

\[
\hat{H}_{\text{Zeeman}} = -\mu_B B \cdot \mathbf{g}(\gamma) \hat{I}
\]

(2)

with the coupling vector \(b(\gamma)\), not only contains the torsional angular momentum operator \(\hat{I}\), but also the total angular momentum \(\hat{J}\). By absorbing the second term of equation (1) into equation (2), the remaining rotational Zeeman Hamiltonian obtains the usual form it has for a rigid molecule, and we obtain an effective \(\hat{H}_{\text{Zeeman}}\), with \(b(\gamma)\) replaced by

\[
b'(\gamma) = b(\gamma) - g(\gamma) \hat{\rho}.
\]

(3)

Finally, the intrinsic magnetic moments of the protons \(K = 1, 2, 3\) in the CH\(_3\) group and proton \(K = 4\) in the OH group interact with the magnetic field as

\[
\hat{H}_{\text{hf}} = -\mu_n \mathbf{k} \cdot \sum_k B \cdot \hat{I}_k.
\]

(4)

where \(g_\text{p}\) is the proton \(g\) factor. The total Zeeman Hamiltonian is a sum of the rotational, torsional and nuclear spin Zeeman terms

\[
\hat{H}_{\text{Zeeman}} = \hat{H}_{\text{Zeeman}} + \hat{H}_{\text{Zeeman}} + \hat{H}_{\text{Zeeman}}.
\]

(5)

Coulpling tensors. The response of methanol to magnetic fields is theoretically modelled by including the coupling of the relevant angular momenta—the rotational angular momentum, the torsional momentum and the nuclear spin angular momentum—to the magnetic field vector. The couplings between these angular momentum operators and the magnetic field involve a rank-2 coupling tensor and a \(g\) vector. This coupling tensor and vector are given by \(\hat{H}_{\text{Zeeman}}\) and \(\mathbf{g}(\gamma)\). The derivation of the hyperfine coupling tensors is in the Supplementary Information. In the following, we describe the methods used to evaluate all coupling parameters.

Rotational \(g\) tensor. Rotational Zeeman effects are represented by the molecule-specific \(g\) tensor, which for rigid non-paramagnetic molecules has been extensively studied experimentally for its valuable information on the electronic structure\(^\text{34–37}\). Nowadays, quantum chemical calculations\(^\text{38–40}\) are able to reproduce these experiments with high accuracy. The rotational \(g\) tensor \(g(\gamma)\) can be obtained from ab initio electronic structure calculations with the program package CFOUR\(^4\). We carried out calculations with CFOUR at the coupled-cluster level of theory including single and double excitations with perturbative addition of the triplets contribution (CCSD(T)), in an augmented triple-zeta correlation-consistent (aug-cc-pVTZ) basis set\(^5\). The geometry of methanol was optimized at this level, which yields OH, CO and CH bond lengths of 0.958 Å, 1.427 Å and 1.096 Å, respectively. COH and OCH bond angles of 108.8° and 109.9°, respectively, and an HOCH torsional angle of 180°. The electronic contributions to \(g(\gamma)\) were calculated at the same level of theory for 13 equidistant values of \(\gamma\) by fixing the HOC fragment and rotating the CH\(_3\) group over these angles about the OC bond axis. The nuclear contribution to \(g(\gamma)\) was also given by CFOUR, but was also calculated directly from the nuclear coordinates. Because of methanol’s symmetry, we could fit our ab initio calculated values for the rotational \(g(\gamma)\)-tensor elements to either \(\Sigma_i a_i \cos(3\xi_i)\) or \(\Sigma_i a_i \sin(3\xi_i)\) functions of the internal rotation angle. The expansion coefficients, \(a_i\) are listed in Supplementary Table 1.

Torsional \(b\)-vector. Torsional Zeeman interactions are represented by the molecule-specific \(b\)-vector (Supplementary equations (16) and (21)). The calculation of the electronic contribution to the \(b\)-vector has not been implemented in the available quantum chemical program packages. To estimate the torsional Zeeman effects in methanol, we compare its internally rotating CH\(_3\) group with the CH\(_3\) groups of nitromethane and methyl-boron-difluoride, of which the torsional Zeeman effect has been investigated experimentally\(^\text{41}\). The torsional Zeeman coupling vectors of nitromethane and methyl-boron-difluoride were determined to be \(b = g \hat{\lambda}\), with \(g = 0.347\) and 0.3415, respectively. In these molecules, the unit vector \(\hat{\lambda}\) that defines the direction of the internal rotation axis lies along the main principal axis. The small difference in the \(g\) values of these two molecules is explained by the electron drainage from the CH\(_3\) groups by the attached functional group (see Supplementary Information). This electron drainage can be estimated from the partial atomic charges given by a Mulliken population analysis\(^4\). We calculated Mulliken populations, \(P\), of the CH\(_3\) groups of nitromethane and methyl-boron-difluoride at the CCSD(T) level in an augmented double-zeta correlation consistent (aug-cc-pVDZ) basis, at their ab initio optimized geometries, and found these to be \(P(\text{CH}_3-\text{CH}_3) = 8.714\) and \(P(\text{CH}_3-\text{CH}) = 9.232\), respectively. We computed the Mulliken population of the OH group in methanol at the same level and found this to be \(P(\text{CH}_3-\text{CH}_3) = 8.737\). Then, we obtained the \(b\)-vector of methanol by interpolation as \(b = g \hat{\lambda}\), with \(g = 0.3468\) (see Supplementary Table 1). In this estimate of \(b\), we have assumed that it is independent of the torsional angle \(\gamma\) and is parallel to \(\hat{\lambda}\). The latter assumption holds only when \(\hat{\lambda}\) is directed along one of the principal axes, which is almost the case for methanol\(^\text{41}\).
The expression in curly brackets is a 6j-symbol. Substitution of this result into equation (6) yields the hyperfine-state-specific collisional cross-sections

$$
\sigma_{\text{coll}}(K, J) = \sum_{K', J', F} p^{(2)}(K, J) \sum_{K, J, F} p^{(2)}(K, J', F) \left| F \right| F' \left| F \right| F' \left| K \right| K' \left| J \right| J' $$

(9)

The triangular condition imposes the constraint \(|J - \frac{1}{2}| \leq \frac{5}{2}, \frac{7}{2} \). Each of these values of \( L \) contributes to the total hyperfine-state-specific collisional rates. Except for very low collision energies where resonances may occur, which are not important under the methanol maser conditions, the largest contribution comes from \( L = \left| \Delta J \right| \). Considering this contribution only would directly relate the hyperfine-state-specific rate with the rotational rate (6).

To analyse which final hyperfine levels, \( F \), are mostly populated by (de-) excitation, we must sum equation (9) over all initial hyperfine states \( F \). Then, we find, for example, for the collisional de-excitation \( J = 6 \rightarrow 5 \) that the \( F = \frac{1}{2} + 2 \) state has a 14% higher propensity to be populated than the \( F = \frac{1}{2} + 2 \) state. The other hyperfine states with \( F = \frac{1}{2} \) and \( F = 2 \) are linear combinations of two nuclear spin states, and have population propensities lower than the \( F = \frac{1}{2} + 2 \) state and higher than the \( F = \frac{1}{2} \) state.

Actually, one can also analyse the ratio between hyperfine rates including all \( L \) channels with equation (6), and find that hyperfine-state-specific collisional propensities for the \( F = \frac{1}{2} + 2 \) state are even higher for the other \( L \) channels. We can therefore say that the hyperfine collisional de-excitation propensity is over 14% higher for the \( F = \frac{1}{2} + 2 \) state than for the \( F = \frac{1}{2} - 2 \) state. Hyperfine-state-specific collisional rate propensities of intermediate \( F \) states are somewhere between the two extremes. More generally, we find consistently that in collisional (de-)excitation, for \( \Delta J < 0 \) transitions, high \( F \) states have a higher propensity for every \( \Delta L \) channel. In \( \Delta J = 0 \) transitions, there is no hyperfine preference, and in \( \Delta J > 0 \) transitions, low \( F \) hyperfine states have the highest probability to be populated.

Hyperfine-state resolved radiative rates. To investigate which hyperfine transitions are favoured by radiative de-excitation, we recouple the line strength of a torsion–rotation transition to a hyperfine basis. From the line strength, one can easily compute the Einstein coefficient.

The line strength of a transition between torsion–rotation states \((K, \sigma, \nu)\) and \((K', \sigma', \nu')\) is

$$
S_{(K, \sigma, \nu) \rightarrow (K', \sigma', \nu')} = \int \left| F \right| F' \left| K \right| K' \left| J \right| J'$$

(10)

where \( d \) stands for the total dipole moment vector of all charged particles, electrons and nuclei. In recoupling the rotational line strength to hyperfine–state–specific line strengths, we recognize that the line strength transforms as a rank-1 tensor operator, and we use equation (7) to obtain

$$
S_{(K, \sigma, \nu) \rightarrow (K', \sigma', \nu')} = \int \left| F \right| F' \left| K \right| K' \left| J \right| J'$$

(11)

The Einstein A coefficient is related to the line strength by

$$
A_{(K, \sigma, \nu) \rightarrow (K', \sigma', \nu')} = \frac{2 \omega^6}{3 \pi \hbar c} \int \left| F \right| F' \left| K \right| K' \left| J \right| J'$$

(12)

where \( \epsilon_0, \hbar, c \) and \( \omega \) are the vacuum permittivity, Planck’s constant and the speed of light, respectively; \( \omega \) is the transition frequency, which to a very good approximation does not depend on the hyperfine splittings of the rotational states.

To analyse which final hyperfine levels \( F \) are mostly populated by (de-) excitation, we must sum equation (9) over all initial hyperfine states \( F \).

$$
A_{(K, \sigma, \nu) \rightarrow (K', \sigma', \nu')} = \frac{2 \omega^6}{3 \pi \hbar c} \int \left| F \right| F' \left| K \right| K' \left| J \right| J'$$

(13)
The intermediate hyperfine states with $F = J$ and $J = 2$ are linear combinations of two nuclear spin states, and have population propensities lower than the $F = J = 2$ state and higher than the $F = J = 2$ state. The ratio calculated in equation (1) increases exponentially for lower $J$. For rotational states with higher $J$, it decreases to 1.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Author contributions


Competing interests

The authors declare no competing financial interests.

Additional information

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Paper II

*Characterizing maser polarization: effects of saturation, anisotropic pumping, and hyperfine structure*

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Characterizing maser polarization: effects of saturation, anisotropic pumping and hyperfine structure

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ABSTRACT

Context. The polarization of masers contains information on the magnetic field strength and direction of the regions they occur in. Many maser polarization observations have been performed over the last 30 years. However, versatile maser polarization models that can aide in the interpretation of these observations are not available.

Aims. We aim to develop a program suite that can compute the polarization by a magnetic field of any non-paramagnetic maser species at arbitrarily high maser saturation. Furthermore, we aim to investigate the polarization of masers by non-Zeeman polarizing effects. We aim to present a general interpretive structure for maser polarization observations.

Methods. We expand existing maser polarization theories of non-paramagnetic molecules and incorporate these in a numerical modeling program suite.

Results. We present a modeling program that CHAracterizes Maser Polarization (CHAMP) that can examine the polarization of masers of arbitrarily high maser saturation and high angular momentum. Also, hyperfine multiplicity of the maser-transition can be incorporated. The user is able to investigate non-Zeeman polarizing mechanisms such as anisotropic pumping and polarized incident seed radiation. We present an analysis of the polarization of $\nu = 1$ SiO masers and the 22 GHz water maser. We comment on the underlying polarization mechanisms, and also investigate non-Zeeman effects.

Conclusions. We identify the regimes where different polarizing mechanisms will be dominant and present the polarization characteristics of the SiO and water masers. From the results of our calculations, we identify markers to recognize alternative polarization mechanisms. We show that comparing randomly generated linear vs. circular polarization ($p_L - p_V$) scatter can be a promising method to ascertain the average magnetic field strength of a large number of masers.

Key words. methods: numerical – masers – polarization – stars: magnetic fields

1. Introduction

Observation of the polarized emission from masers is an established method to obtain information on the magnetic field in the maser region. Linear polarization reveals the (projected) magnetic field direction and circular polarization reveals information on the magnetic field strength. Maser polarization observations have been performed for OH (e.g. Baudry & Diamond 1998; Fish & Reid 2006), H$_2$O (e.g. Vlemmings et al. 2006b), SiO (e.g. Kemball & Diamond 1997; Kemball et al. 2009; Herpin et al. 2006) and methanol (e.g. Vlemmings 2008; Vlemmings et al. 2011b; Lankhaar et al. 2018). Such observations have indicated, among other things, an ordered magnetic field around asymptotic giant branch (AGB) stars, such as TX Cam (Kemball & Diamond 1997), a magnetically collimated jet from an evolved star (Vlemmings et al. 2006a), the first extragalactic Zeeman-effect detection in (ultra)luminous infrared galaxies (Robishaw et al. 2008) and the magnetically regulated infall of mass on a massive protostellar disk (Vlemmings et al. 2010).

The analysis of maser-polarization observations is often based on the theories of Goldreich et al. (1973) (GKK73), that are derived analytically for masers under the limiting conditions of (i) strong saturation, where the rate of stimulated emission, $R$, is significantly higher than the isotropic decay rate, $\Gamma (R \gg \Gamma)$, (ii) (very) strong magnetic fields, where the magnetic precession rate $g\Omega$ is significantly higher than $R (g\Omega \gg R)$ and (iii) high thermal widths, where the thermal broadening, $\Delta \omega$ in frequency units, is significantly higher than $g\Omega (\Delta \omega \gg g\Omega)$. In fact, these requirements are seldom fulfilled and one needs to invoke numerical approaches to ascertain the maser polarization characteristics at intermediary conditions. Well known numerical approaches to characterizing maser-polarization have been presented by Deguchi & Watson (1990) (D&W90) and Gray & Field (1995) (G&F95). The latter models are aimed at the polarization of masers arising from paramagnetic molecules like OH, but can be generalized to masers from a non-paramagnetic species (Gray 2012). Even though the G&F95 and the D&W90 models have been shown to be isomorphic (Gray 2003), they have made different assumptions in their formulation. For instance, the direct time-dependence of the population ($p_{aa}$ and $p_{ab}$), coupling elements ($p_{ab}$) and the electric field elements have been integrated out in the D&W90 models. This was shown by Trung (2009) to have no impact on the simulation results. However, reversely, the G&F95 models do not take into account the off-diagonal elements of the state-populations ($p_{aa}$, $a \neq a'$). Especially in the regions where magnetic field interactions become comparable to the rates of stimulated emission ($g\Omega \sim R$), or when accounting for non-Zeeman effects as anisotropic pumping of the maser or partially polarized incident radiation, this approximation is not valid.
The D&W90 models have been applied in a number of incarnations:

i) In Nedoluha & Watson (1990) (N&W90), the maser polarization model of D&W90 is applied for one frequency. Circular polarization can not be computed. Linear polarization can be computed in both the Stokes-\(U\) and \(-Q\) parameters. It is possible to introduce anisotropic pumping. Only one hyperfine sub-transition can be accounted for. N&W90 report that simulations can be made at up to \(J = 3 - 2\) transitions. Convergence issues arise for higher angular momentum transitions.

ii) In Nedoluha & Watson (1992) (N&W92), the maser polarization model of D&W90 is applied under the limiting condition of \(g\Omega > R\). Therefore, the Stokes-\(U\) component of the radiation can be ignored, and only diagonal elements of the density-population matrices need to be regarded. It is in this respect, that this variant of the D&W90 models is similar to the G&F95 models. Circular polarization can be computed, as well as linear polarization, but the polarization angle can only be \(\chi = 0^\circ\) or \(\chi = 90^\circ\). Multiple hyperfine sub-transition can be included.

iii) In Nedoluha & Watson (1994) (N&W94), we find the most extensive variant of the D&W90 models. In the N&W94 models, one accounts for off-diagonal elements in the population-densities, the Stokes-\(U\) component of the radiation field, and multiple frequency bins along the maser-line. Anisotropic pumping can be introduced, but multiple hyperfine sub-transitions cannot be included. Because of the computational costs of this approach, N&W94 give only results for the \(J = 1 - 0\) transition.

However, only the qualitative results of these approaches are available.

In this paper, we present a program that we call CHAMP (CHAracterizing Maser Polarization) that simulates the propagation of maser radiation through a medium permeated by a magnetic field. The user is able to use the three approaches of N&W90, N&W92 and N&W94. We have reproduced these models, and made two significant improvements: (i) the transition of arbitrary angular momentum can be simulated, and (ii) we have expanded the N&W94 formalism to include multiple (and high \(F\)) hyperfine transitions. These improvements are vital when analyzing the polarization of high-frequency masers that have become more relevant in the era of ALMA and its full capabilities (see, e.g. Pérez-Sánchez & Vlemmings 2013). The source code of CHAMP and a number of standard input files are available on GitHub at https://github.com/blankhaar/CHAMP.

As a way of outlining the capabilities of CHAMP, we will perform a range of simulations of the non-paramagnetic maser species SiO and \(\text{H}_2\text{O}\), and comment on their relation to simplified methods of analysis performed in the past. We will focus on a range of SiO \(v = 1, J - (J - 1)\) maser transitions, and the 22 GHz water maser transition. We will present simulations of non-Zeeman polarizing effects, like anisotropy in the maser pumping and polarized seed radiation. We leave maser polarization simulations and analysis of methanol masers, including its complex hyperfine structure (Lankhaar et al. 2016), for a later publication. It is possible to investigate the polarization of any non-paramagnetic maser (e.g. formaldehyde) with CHAMP. The paramagnetic OH masers can also be investigated with these models, but this would be an unnecessary complication of the maser polarization theory, because simplifications from the complete spectral decoupling of the magnetic sub-transitions are not utilized.

This paper is built-up as follows. In § 2, we will recall the theory of maser-radiation put forth by GKK73 and D&W90, and expand their work by considering multiple hyperfine-transitions within a certain rotational maser line. In § 3, we will present the three numerical approaches, based on N&W90, N&W92 and N&W94, to solve the polarized maser-propagation simulations. We will dedicate extra attention in this section to the improvements made that dealt with previous convergence issues. In § 4 we will apply our models to simulate the polarization of SiO and water masers. In § 5, the results will be evaluated by outlining distinguishable polarizing mechanisms, along with an evaluation of some of the existing maser polarization literature. We will conclude with a summary of the results in § 6.

2. Theory

2.1. Maser polarization by a magnetic field

The theory presented here is based on GKK73, and the extension for numerical modeling by (Western & Watson 1984; Deguchi & Watson 1990; Nedoluha & Watson 1994). We extend these formalisms by considering multiple hyperfine-transitions that lie close to each other in frequency. Often, it is a rotational transition that is masing, and we consider only the states relevant—the hyperfine manifold and magnetic substates—to this transition. Interactions of these states with other molecular states (collisionally or radiatively) are absorbed into the phenomenological pumping and decay term. Because the maser-molecules are permeated by a magnetic field, the degeneracy of the magnetic substates is lifted. The consequential spectral decoupling of the photon-transitions with different helicity will cause a polarization of the radiation. This means that we have to consider all the magnetic substates of the maser-transitions, as well as all the modes of polarization in the radiation.

Up to this point, we have not mentioned the analytical maser polarization theory by Elitzur (see Elitzur 1991, 1993, 1995, 1998). In this elegant formalism, the no-divergence requirement of the electric component of the radiation field is shown to put constraints on the phases of the propagated electric field polarizations. These phase-relations yield the polarization solutions of GKK73, but general to any degree of saturation. This result is very different from the other theories of maser polarization, including the one we present here. The idealized presuppositions of the Elitzur models, such as the equal populations of magnetic substates throughout propagation, are however not reproduced by the D&W90 (and the CHAMP) models—while the radiation field is always subject to the constraint of no-divergence. We work within the D&W90 formalism, because of mutual confirmation between G&F95 and D&W90 on multiple levels of analysis: the isomorphism of the theories of D&W90 and the G&F95 models (Gray 2003; Trung 2009), their reproduction of the earlier derived theories of GKK73 and their strong resemblance to the non-maser radiative transfer models of Degl’Innocenti & Landolfi (2006).

Setting up the theory of maser radiation propagation can be divided in two parts. On the one hand, we will present a model on the occupation of the molecular state-populations under the influence of a (polarized) radiation field, and on the other hand, we will present a model on the propagation of the radiation field that is dependent on the state-populations.
2.1.1. Evolution of the density operator

Let us consider a maser transition between two (torsion-)rotational states. The maser medium is permeated by a magnetic field and the two states are coupled by the radiation field. Before considering the interaction of the radiation field and the two (torsion-)rotational states, we will dedicate special attention to hyperfine splitting of the line. When the molecules total nuclear spin, \( I \), is nonzero, both (torsion-)rotational levels participating in the maser-transition are split up further by hyperfine interactions in an ensemble of \( n_F = 2I + 1 \) hyperfine states,

\[
F_i^{(1)}, F_i^{(2)}, \ldots, F_{n_F}^{(1)}, \quad F_i^{(2)}, F_i^{(2)}, \ldots, F_{n_F}^{(2)},
\]

for the upper and the lower level. As a consequence, the single maser transition splits up in a manifold of hyperfine transitions, where any transition \( F_i^{(1)} \rightarrow F_i^{(2)} \) is allowed as long as the selection rule \( \Delta F = 0, \pm 1 \) is fulfilled. The hyperfine splitting thus results in a manifold of hyperfine states, of which each upper state is radiatively coupled to multiple lower states.

However, it turns out that each upper hyperfine level is radiatively coupled strongest to only one lower hyperfine level; dominating other transitions by an order of magnitude. By virtue of this, we can simplify our problem by decomposing the maser transition into their strongest transitions: \( F_i^{(1)} \rightarrow F_i^{(2)} \) and neglect all other couplings. In this way, we are left with \( n_F \) systems, all independently interacting with the same radiation field.

The Hamiltonian of the \( i \)'th transition is

\[
\hat{H}_i = \left( \frac{\hbar}{V_i} \right)_{11} \left( \hat{v}^{(12)}_i \right)_{11},
\]

(1)

where the elements of the diagonal matrix elements are defined in the frame where the magnetic field is along the \( z \)-axis, and are

\[
\langle F_i^{(1)}m_F|\hat{H}_i^{(1)}|F_i^{(1)}m_F\rangle = E_i^{(1)} + g\Omega_i^{(1)}m_F,
\]

\[
\langle F_i^{(2)}m_F|\hat{H}_i^{(2)}|F_i^{(2)}m_F\rangle = E_i^{(2)} + g\Omega_i^{(2)}m_F,
\]

(2)

where \( E_i^{(1,2)} \) are the hyperfine energies of the upper and lower level, and \( g\Omega_i^{(1,2)} \) their respective Zeeman splittings. The coupling elements are

\[
\hat{v}^{(12)}_i = -\hat{d} \cdot \vec{E},
\]

(3)

where \( \hat{d} \) is the dipole operator, and \( \vec{E} \) is the electric field. With this decomposition, we can formulate the evolution equation for the states for the \( n_F \) independent systems, following the Liouville-von Neumann equation

\[
\dot{\rho}_i = -\frac{i}{\hbar} [\hat{H}_i, \rho_i] + \hat{\Lambda}_i - \hat{\Gamma}_i \rho_i,
\]

(4)

where we take into account the excitation of both levels, by including a phenomenological term for the pumping of the maser: \( \hat{\Lambda}_i \), and the decay of the states by \( \hat{\Gamma}_i \). Just as the Hamiltonian of Eq. (1), we can express the density-operator in its parts

\[
\rho_i = \begin{pmatrix} \rho_i^{(1)} & \rho_i^{(12)} \\ \rho_i^{(21)} & \rho_i^{(2)} \end{pmatrix},
\]

(5)

so that the evolution of the decomposed density operators is

\[
\dot{\rho}_i^{(1)} = -\frac{i}{\hbar} \left( [\hat{H}_i^{(1)} , \rho_i^{(1)}] + \hat{\Gamma}_i^{(1)} \rho_i^{(1)} - \rho_i^{(1)} \hat{\Gamma}_i^{(1)} \right) - \frac{1}{\hbar} \left( [\hat{H}_i^{(1)} , \rho_i^{(2)}] + \hat{\Lambda}_i^{(1)} \rho_i^{(2)} - \rho_i^{(2)} \hat{\Lambda}_i^{(1)} \right)
\]

(6a)

\[
\dot{\rho}_i^{(2)} = -\frac{i}{\hbar} \left( [\hat{H}_i^{(2)} , \rho_i^{(2)}] + \hat{\Gamma}_i^{(2)} \rho_i^{(2)} - \rho_i^{(2)} \hat{\Gamma}_i^{(2)} \right) - \frac{1}{\hbar} \left( [\hat{H}_i^{(2)} , \rho_i^{(1)}] + \hat{\Lambda}_i^{(2)} \rho_i^{(1)} - \rho_i^{(1)} \hat{\Lambda}_i^{(2)} \right)
\]

(6b)

\[
\dot{\rho}_i^{(12)} = -\frac{i}{\hbar} \left( [\hat{H}_i^{(12)} , \rho_i^{(12)}] + \hat{\Gamma}_i^{(12)} \rho_i^{(12)} - \rho_i^{(12)} \hat{\Gamma}_i^{(12)} \right) - \frac{1}{\hbar} \left( [\hat{H}_i^{(12)} , \rho_i^{(1)}] + \hat{\Lambda}_i^{(12)} \rho_i^{(1)} - \rho_i^{(1)} \hat{\Lambda}_i^{(12)} \right).
\]

(6c)

In D&W90, it is shown how to integrate out the time-dependence of the off-diagonal elements of Eq. (6c). The solutions of these integrations, are subsequently inserted into the population-equations of Eqs. (6a) and (6b). We assume a steady state: \( \dot{\rho}_i^{(1)} = \dot{\rho}_i^{(2)} = 0 \). After somewhat involved rearrangements that are analogous to D&W90, we find the expressions for the upper state-populations

\[
0 = -(\Gamma_i + i\omega_{a_i})\rho_{a_i\phi}(v) + \phi(v)\lambda_{a_i\phi}
\]

\[
+ \frac{\pi}{\hbar^2} \sum_{b_i} \rho_{b_i\phi}(v) \left( \gamma_{a_i\phi}^{(b_i)} \gamma_{b_i\phi}^{(a_i\phi)} \right)_{\omega_a} + \left( \gamma_{a_i\phi}^{(b_i)} \gamma_{b_i\phi}^{(a_i\phi)} \right)_{\omega_b}
\]

\[
- \sum_{b_i} \rho_{a_i\phi}(v) \left( \gamma_{a_i\phi}^{(b_i)} \gamma_{b_i\phi}^{(a_i\phi)} \right)_{\omega} - \sum_{a_i} \rho_{a_i\phi}(v) \left( \gamma_{a_i\phi}^{(b_i)} \gamma_{b_i\phi}^{(a_i\phi)} \right)_{\omega},
\]

(7)

where \( a_i \) and \( b_i \) are the indices for the magnetic substates of the upper and lower levels, energy difference between magnetic substates are represented by \( \hbar\omega_{a_i\phi} = \omega_a - \omega_{a_i\phi} \). Elements of the pumping operator have been represented as \( \lambda_{a_i\phi} = \phi(v)\lambda_{a_i\phi} \), where \( \phi(v) \) stands for the Maxwell-Boltzmann distribution. Furthermore, we have used the simplified notations

\[
\gamma_{ij}^{(kl)} = I(\omega)\delta_{i}^{(kl)} - Q(\omega)\delta_{Q}^{(kl)} - iU(\omega)\delta_{U}^{(kl)} + V(\omega)\delta_{V}^{(kl)}
\]

(8)

and \( I, Q, U, V \) are the Stokes-parameters as defined in D&W90. The delta-operators are related to the dipole-elements by

\[
\delta_{R}^{(kl)} = (d_{i}^{(k)} d_{i}^{(l)}, (d_{i}^{(l)} d_{i}^{(k)})^{*})
\]

(9a)

\[
\delta_{I}^{(kl)} = (d_{i}^{(k)} d_{i}^{(l)} d_{i}^{(l)} d_{i}^{(k)})^{*}
\]

(9b)

\[
\delta_{U}^{(kl)} = (d_{i}^{(k)} d_{i}^{(l)} d_{i}^{(l)} d_{i}^{(k)})^{*}
\]

(9c)

\[
\delta_{V}^{(kl)} = (d_{i}^{(k)} d_{i}^{(l)} d_{i}^{(l)} d_{i}^{(k)})^{*}
\]

(9d)

with explicit elements (D&W90)

\[
d_{x}^{ab} = \pm d_{x}^{M=1} \frac{1 + \cos \theta}{2} + i d_{x}^{M=0} \frac{\sin \theta}{\sqrt{2}} \pm d_{x}^{M=-1} \frac{1 - \cos \theta}{2}
\]

(10)

where \( \theta \) is the angle between the magnetic field and propagation directions. We have also used a simplified notation for the integral

\[
\langle \gamma_{ij}^{(kl)} \rangle_{\omega} = \int d\omega \gamma_{ij}^{(l)}(\omega, v)\gamma^{(kl)(n\omega)}(\omega)
\]

(11)

with

\[
\gamma_{ij}^{(kl)} = \frac{1}{\Gamma_i} \left[ \omega_{a_i\phi} - \omega(1 - \frac{\gamma_i}{\hbar}) \right]
\]

(12)

The lower state-populations follow from a similar derivation. The population equations for the upper- and lower-level of the
The expressions for the propagation coefficients are

\begin{align}
A(\omega) &= \frac{-\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} + \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14a) \\
B(\omega) &= \frac{\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} + \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14b) \\
C(\omega) &= \frac{-\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} + \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14c) \\
D(\omega) &= \frac{-i\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} - \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14d) \\
E(\omega) &= \frac{i\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} - \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14e) \\
F(\omega) &= \frac{i\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} - \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14f) \\
G(\omega) &= \frac{-\pi \omega}{c} \sum_i \sum_{a,b_i} \int \! dv \left[ \sum_{b_i'} \langle p_{b_i' | b} (\gamma_+^{a_{b_i'} + a_{b_i}} + \gamma_-^{a_{b_i'}}) \delta_{a_{b_i'} a_{b_i}} \rangle \right], \quad (14g) \\

\end{align}

where the sum \(i\) runs over all hyperfine transitions and \(a_i\) and \(b_i\) are the magnetic sublevels of the upper, respectively lower level of the \(i\)'th hyperfine transition. The tight relation between the molecular states and the feed to the radiation field is reflected also in these equations, as again, the radiative coupling between the two states is represented by the \(\delta\)-operators. In the method section, we will outline the three approaches to numerically solve Eqs. (7) and (14).

### 2.2. Anisotropic pumping

We have so far left the expression for the matrix-elements of the pumping-operator general. The pumping-operator is a phenomenological term that, together with the decay-operator, ab-

\[
\frac{d}{d\tau} \begin{pmatrix} I(\omega) \\ Q(\omega) \\ U(\omega) \\ V(\omega) \end{pmatrix} = \begin{pmatrix} A(\omega) & B(\omega) & F(\omega) & C(\omega) \\ B(\omega) & A(\omega) & E(\omega) & G(\omega) \\ F(\omega) & -E(\omega) & A(\omega) & D(\omega) \\ C(\omega) & -G(\omega) & -D(\omega) & A(\omega) \end{pmatrix} \begin{pmatrix} I(\omega) \\ Q(\omega) \\ U(\omega) \\ V(\omega) \end{pmatrix}.
\]
sorbs all the interactions with molecular states that are not participating in the maser-transition. The decay-operator is concerned with the decay of the maser-levels to other states. The pumping-operator encapsulates the collisional and radiative (de-)excitation that will eventually populate our two maser-levels. A certain directional alignment may have already crept in the molecular states that will later destine to populate our maser levels. After all, the magnetic field tends to direct all molecular states. Alignment will also manifest itself in a molecular state when a (de-)excitation to it has a preferred direction. An example of a directional excitation would be the directional pumping radiation, like the radiation from central stellar object that leads to the SiO maser (Gray 2012). The introduced alignment in the directionally excited molecular state will be transferred (with some depolarization) from state to state in the cascade to our maser levels. The reflection of this partial anisotropy in the pumping operator was already formulated by Nedoluha & Watson (1990) and Western & Watson (1983, 1984), who defined the elements of a the partial anisotropic pumping operator as

$$\Lambda_{m''m'} = \alpha \left[ 1 + \epsilon \left( \frac{F^2 + F - 1 + m'^2}{(2F - 1)(2F + 3)} - 1 \right) \right] \delta_{m'm'},$$

(15)

where $\alpha$ is the overall pumping, $F$ is the total angular momentum of the associated state, $m$ is the magnetic quantum number, $\delta_{m'm'}$ is the Kronecker-delta and $\epsilon$ is the degree of anisotropy in the pumping. In Eq. (15) we have assumed the direction of the isotropic pumping to be along the magnetic field direction. If the pumping-direction has a different orientation with respect to the magnetic field, the pumping-matrix can be obtained by the simple rotation

$$\Lambda' = D'((\alpha'\beta'\gamma')^TAD((\alpha'\beta'\gamma')^T,$$

(16)

over the Euler-angles $(\alpha'\beta'\gamma')$ that describe the rotation from the pumping-direction to the magnetic field direction.

The partial alignment of the directionally pumped maser will result in the emittance of partially polarized radiation. The polarization will depend not only on the degree of anisotropy in the pumping, $\epsilon$, but will also be dependent on the pumping-efficiency,

$$\eta = \frac{\epsilon}{\delta},$$

(17)

where we let $\eta$ be the anisotropy-parameter, and

$$\delta = 2\frac{\lambda_u - \lambda_l}{\lambda_u + \lambda_l}$$

(18)

is the pumping-efficiency, with the overall-pumping of the upper and lower level given by $\lambda_{u,l}$. The pumping-efficiency has been investigated for water masers. Estimation of the mean population inversion $\Delta n$ from high-resolution observations of water masers around AGB-stars revealed for most masers $\Delta n \lesssim 0.01$. The most luminous masers had higher degrees of population inversion up to $\delta \sim 0.1$ (Richards et al. 2011). It is to be expected that for the more saturated masers that the population inversion will decrease. Richards et al. (2011) estimated that most masers in the sample, though, were unsaturated. For unsaturated masers, their mean population inversion reflects the pumping-efficiency $2\Delta n \sim \delta$, thus we estimate $\delta \sim 0.02$. The anisotropy degree $\epsilon$ of anisotropically pumped masers is estimated to be of the same order of magnitude (Nedoluha & Watson 1990).

3. Methods

3.1. Three numerical approaches

In this work, we have reproduced and extended the the numerical approximations reported in N&W90, N&W92 and N&W94. The difference between approaches can be traced back to different approximations to the integrals in Eqs. (7) and (14):

i) In N&W90, integrals are approximated to peak sharply around the maximum of $\gamma_j^{jj'}$,

$$\int d\omega \gamma_j^{jj'}(\omega, v) \xi_{l_{mm'}}^{\delta_{mm'}}(\omega, \omega_j),$$

(19)

where $\omega_j$ is the transition frequency between levels $i$ and $j$. Similarly, the integration over density-matrix elements is

$$\int dv \rho_{ij}(v) \xi_{l_{mm'}}^{\delta_{mm'}}(\omega, v) = \frac{\pi c}{\omega_i} \rho_{ij}(v_0).$$

(20)

We only account for one frequency and velocity bin in the Stokes-parameters and density-matrix elements. A consequence of this approximation is that only one hyperfine-transition can be included and that circular polarization is not computed. Within this approximation we are left with the following simplified density equations ($\rho_{ij} = \rho_{ij}(v_0)$ and $\xi^{ijkl} = \xi^{ijkl}(\omega_0)$)

$$0 = -(\Gamma + i\omega_\text{unr}) \rho_{\text{unr}} + A_\text{unr} + \frac{2\omega_\text{unr}^2}{c^2} \sum_{ba} \rho_{bb} \xi_{b_{\text{unr}},b_{\text{unr}}} + \sum_{ba} \rho_{ba} \xi_{b_{\text{unr}},b_{\text{unr}}},$$

(21)

where we have dropped the $i$-indices because we cannot treat a hyperfine manifold in this method. Similarly, the propagation coefficients are

$$A(\omega) = -\frac{2\pi^2 \omega}{c} \sum_{ab} \left[ \sum_{ba} \rho_{ba} \delta_{ab} - \sum_{ab} \rho_{ba} \delta_{ab} \right],$$

(22a)

$$B(\omega) = \frac{2\pi^2 \omega}{c} \sum_{ab} \left[ \sum_{ba} \rho_{ba} \delta_{ab} - \sum_{ab} \rho_{ba} \delta_{ab} \right],$$

(22b)

$$C(\omega) = -\frac{2\pi^2 \omega}{c} \sum_{ab} \left[ \sum_{ba} \rho_{ba} \delta_{ab} - \sum_{ab} \rho_{ba} \delta_{ab} \right],$$

(22c)

$$G(\omega) = -\frac{2\pi^2 \omega}{c} \sum_{ab} \left[ \sum_{ba} \rho_{ba} \delta_{ab} - \sum_{ab} \rho_{ba} \delta_{ab} \right],$$

(22d)

and $D(\omega) = E(\omega) = F(\omega) = 0$.

ii) N&W92 assume a strong magnetic field. Thus, from Eq. (7), under the limiting condition $g_2 \gg R$, it follows that diagonal elements will dominate the density-populations and that we can neglect off-diagonal elements. Through this simplification, we can assume the Stokes- $U$ component of the radiation absent. Integrals are simplified in the following way

$$\int d\omega \gamma_j^{ab}(\omega, v) \xi_{l_{mm'}}^{\delta_{mm'}}(\omega, \omega_j) \approx \pi \xi_{l_{mm'}}^{\delta_{mm'}}(\omega_{ab}/(1 - v/c))$$

(23a)

$$\int dv \gamma_j^{ab}(\omega, v) \rho_{kh}(v) \approx \frac{\pi c}{\omega_h} \rho_{kh}(\epsilon(\omega - \omega_{ab})/\omega).$$

(23b)
The populations and $\zeta$-parameters are evaluated for $2N + 1$ channels

$$\omega = \{\omega_N, \omega_{N+1}, \ldots, \omega_0, \ldots, \omega_N\}$$

where $\omega_j = \omega_0 + j\Delta\omega$, and $\Delta\omega$ is the width of the frequency channel. The frequency channels are related to the velocity channels, as $v = \frac{\omega}{c}\omega_0$, so that $v_j = j\Delta v = j\frac{\Delta\omega}{\omega_0}\omega_0$. For each channel, the population and $\zeta$-parameters are

\[
\rho_{ab}(c(\omega_j - \omega_0)/\omega_0) \approx \rho_{ab}(v_j)
\]

\[
-\frac{c}{\omega_0} \frac{\partial \rho_{ab}}{\partial v_j} \left( m_{abg}\Omega_1/2 - m_{bg}\Omega_2/2 \right)
\]

\[
\frac{\partial \zeta^{ab'}_{a''b''}}{\partial \omega} \bigg|_{v_j} \approx \frac{\partial \zeta^{ab'}_{a''b''}(\omega_j)}{\partial \omega}
\]

Leading to simplified density equations as well as simplified propagation coefficients. To solve the individual integrals, we assume that the function $\omega/\Delta\omega$ can be approximated as a Taylor expansion around $\omega_0$, truncated at first-order

\[
\zeta^{ab'}_{a''b''} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left( \frac{d^n \zeta^{ab'}_{a''b''}}{d\omega^n} \right)_{\omega_0} (\omega_j - \omega_0)^n
\]

This leads to the approximate expression of the integrals

\[
\int_{-\Delta\omega/2}^{\Delta\omega/2} d\omega' \frac{\gamma_{ab}^{\omega}(\omega, \omega')}{\zeta^{ab'}_{a''b''}(\omega_j) + \omega'}
\]

The remaining integrals can be solved analytically. From the definition of the $\gamma_{ab}^{\omega}(\omega, \omega')$ function of Eq. (12), we have the following analytical solutions

\[
\int_{-\Delta\omega/2}^{\Delta\omega/2} d\omega' \frac{\gamma_{ab}^{\omega}(\omega, \omega')}{\zeta^{ab'}_{a''b''}(\omega_j) + \omega'}
\]

where $q_{up} = \omega_0 - \frac{\Delta\omega}{2} + \frac{\Delta\omega}{2} (1 - j\Delta v)$ and $q_{down} = \omega_0 + \frac{\Delta\omega}{2} + \frac{\Delta\omega}{2} (1 - j\Delta v)$.
where the derivatives \( \frac{d\rho}{d\nu_e} \), again, can be evaluated via the finite-difference method. We have evaluated the accuracy of the truncated Taylor expansion, and found that adding higher-order terms had minimal effect. Using the numerical expressions of Eqs. (27) and (28) for the integrals, the density-equations and propagation-matrix can be set up. The latter will contain all 7 propagation-coefficients. Solving the density-equations will be the subject of the next subsection.

Note that above, we have assumed that different frequency-components of the radiation field are uncorrelated, which is a standard assumption in maser theory (Gray 2012). The same goes for the different velocity-components of the molecular states. Numerical simulation of maser polarization propagation can be made using these formalisms, by (i) computing the state-populations for a given radiation-field (see next paragraph) with the use of Eq. (7) and (ii) computing the propagation coefficients using Eq. (14) and the newly found state-populations. Subsequently, the radiation field is propagated using Eq. (13), where, for small enough \( \Delta s \), the propagated vector of Stokes-parameters can be approximated by \( I(s + \Delta s, \omega) = e^{\Delta s K(s, \omega)} I(s, \omega) \), where \( K(s, \omega) \) stands for the matrix of propagation-coefficients (see Eq. 13). The initial radiation field may be black-body radiation, and the initial guess for the state-populations \( \sim \Lambda / \Gamma \). In the following paragraph, we will put extra emphasis on the computation of the state-populations.

3.2. Solving the density-equations

Because convergence issues have been known to arise for the density-equations of N&W90 and N&W94 at high maser saturation, we will explicitly comment on our used method of solving the density-equations. In the following, we will consider the density-equations for N&W90, but similar methodology was used for the other approaches. From Eq. (21), we have \( n_2^2 + n_2^2 \) coupled equations for the density-matrix (for N&W92, the dimensionality is reduced to \( n_F + n_F \)). To ensure hermiticity of the solutions, it is convenient to separate the density-matrix elements in their real and imaginary parts,

\[
\rho_{\alpha \beta} = \text{Re}(\rho_{\alpha \beta}) + i \text{Im}(\rho_{\alpha \beta}),
\]

and we require \( \text{Re}(\rho_{\alpha \beta}) = \text{Re}(\rho_{\beta \alpha}) \) as well as \( \text{Im}(\rho_{\alpha \beta}) = -\text{Im}(\rho_{\beta \alpha}) \). We will bundle the unique elements in the vector \( \rho = [\rho_{a}, \rho_{b}]^{\text{T}} \), where

\[
\rho_{a} = [\rho_{a}^{(a)}, \rho_{b}^{(a)}, \ldots, \rho_{a}^{(n_F, n_F)}, \text{Re}(\rho_{a}^{(a)}), \text{Im}(\rho_{a}^{(a)}), \ldots, \text{Im}(\rho_{b}^{(n_F, n_F)})]
\]

and \( \rho_{b} \) is the analogous population-vector for the lower-state. We take the real and imaginary parts from Eq. (21) and find

\[
\text{Re}(A_{\alpha \beta}) = -i \text{Re}(\rho_{\alpha \beta}) + \text{Im}(\rho_{\alpha \beta})\frac{2\omega \gamma^2}{\hbar^2} + \sum_{b \alpha} \left[ \left( \text{Re}(\rho_{b \alpha}) \text{Re}(\zeta^{b \alpha \beta}) - \text{Im}(\rho_{b \alpha}) \text{Im}(\zeta^{b \alpha \beta}) \right) \right]
\]

\[
\times \left\{ \sum_{b \alpha} \left( \text{Re}(\rho_{b \alpha}) \text{Re}(\zeta^{b \alpha \beta}) - \text{Im}(\rho_{b \alpha}) \text{Im}(\zeta^{b \alpha \beta}) \right) \right\},
\]

\[
\text{Im}(A_{\alpha \beta}) = -i \text{Im}(\rho_{\alpha \beta}) - \text{Re}(\rho_{\alpha \beta})\frac{2\omega \gamma^2}{\hbar^2} - \sum_{b \alpha} \left[ \left( \text{Re}(\rho_{b \alpha}) \text{Im}(\zeta^{b \alpha \beta}) + \text{Im}(\rho_{b \alpha}) \text{Re}(\zeta^{b \alpha \beta}) \right) \right]
\]

\[
\times \left\{ \sum_{b \alpha} \left( \text{Re}(\rho_{b \alpha}) \text{Im}(\zeta^{b \alpha \beta}) + \text{Im}(\rho_{b \alpha}) \text{Re}(\zeta^{b \alpha \beta}) \right) \right\},
\]

\[
= a^{\alpha \beta} \rho, \quad (31)
\]

The collection of density-equations can thus be formulated in the following matrix-equation

\[
\lambda = M \rho, \quad (33)
\]

where all matrices and vectors are real, and we have the elements of the matrix

\[
M = [a_{11}, a_{22}, \ldots, a_{n_F, n_F}, b_{12}, \ldots, b_{n_F, n_F - 1}, \ldots]^{\text{T}}, \quad (34)
\]

where the last part is omitted, but is comprised of the analogous density-equations of the lower level. We can solve for all densities by

\[
\rho = \text{inv}(M) \lambda. \quad (35)
\]

The matrix-inversion is performed using an LQ-decomposition, taken from the standard LAPACK-libraries (Anderson et al. 1999). This method is very robust, as exemplified by the fact that these density-equations are soluble for arbitrary angular momentum transitions (matrix-dimensionality) and maser saturation. This is in contrast to N&W90 and N&W94, where convergence problems were reported for transitions of \( J > 3 \) (Nedoluha & Watson 1990).

3.3. Experiments

We present the developed methods by using them to analyze masers with a non-paramagnetic Zeeman effect that have shown polarization in their emission. In the following, we only present results from the most rigorous N&W94 method. We consider all Stokes parameters, high rates of stimulated emission and non-Zeeman polarizing mechanisms.

We report our calculations mainly through contour maps of the linear polarization degree, \( p_L = \sqrt{Q^2 + U^2}/I_0 \), polarization angle, \( p_a = \text{atan}(U/Q)/2 \) and circular polarization degree, \( p_V = (V_{\text{max}} - V_{\text{min}})/I_0 \). The circular polarization degree is
taken to be negative if \( V_{\text{max}} \) occurs at a frequency \( \omega < \omega_0 \). The Stokes-parameters \( I_0 \), \( Q_0 \), and \( U_0 \) are taken at the peak of \( I(\omega) \). The polarization angle is relative to the rejection of the magnetic field direction from the propagation direction, i.e. the magnetic field direction projected onto the plane of the sky.

3.3.2. Water masers

We present the polarization of water masers in the parameter \( v \), \( g \), \( \Omega \), and that magnetic field strength, angular momentum transitions, and propagation angles \( \theta \). The molecular parameters that are used in the simulation are given in Table 3. We perform calculations for the SiO masers in the vibrational state \( v = 1 \). SiO masers also occur in higher vibrational states. The results we present can roughly be taken to be similar to higher vibrational states. Only the different isotropic decay rates, that scale roughly as \( \Gamma \sim 50 \, \text{s}^{-1} \) (Elitzur 1992), will lead to a different ratio \( g \Omega / T \) which will have a small impact on the presented results.

Maser polarization properties converge for \( \omega D \gg g \Omega \). To ensure \( \omega D \gg g \Omega \), we use a thermal maser width of \( \Delta \omega_{\text{th}} \approx 1000 \times g \Omega \times I \), where \( I \) is the angular momentum of the upper level. This thermal maser width corresponds to \( v_{\text{th}} \approx \frac{0.83 \times c^2 \pi}{3 \hbar} \, \text{km/s} \). We perform studies with

- isotropic pumping, where the pumping matrix is \( \Lambda = \lambda I \)
- polarized incident seed radiation, with isotropic pumping, but with seed radiation of \( U/I = 0.1 \) and \( U/I = 0.5 \).
- anisotropic pumping, where the pumping matrix characterized by Eq. (16). We run simulations for with moderate, \( \eta = 0.1 \) and high \( \eta = 0.5 \) degrees of anisotropy. We run simulations for three anisotropy-directions, namely (i) parallel to the magnetic field, (ii) perpendicular to the magnetic field and propagation direction, (iii) at \( 45^\circ \) from the magnetic field in the plane perpendicular to the propagation direction.

3.3.2. Water masers

We present the polarization of water masers in the parameter space relevant to observations. From maser observations, we know that the strongest water masers do not exceed \( T_{\text{maser}} \Delta \Omega = 10^{13} \, \text{Ksr} \) (Garay et al. 1989; Sobolev et al. 2018), and that magnetic field estimates range from \( B \approx 1 \, \text{mG} \) to \( 1 \, \text{G} \). As was shown in N&W92, the thermal width of the maser-molecules affects the maser polarization, so we will analyze the water masers excited at different temperatures. Preferred hyperfine pumping is a possibility for this maser specie, so we will analyze a range of relevant cases. Also, we will explore the effect of alternative polarization mechanisms on the polarization of water masers.

4. Results

We report here the results of representative numerical simulations to several \( v = 1 \) SiO masers and the 22 GHz water maser. Results are only reported for the most rigorous N&W94 approach. We divide up this section into experiments on SiO and water masers, and will further compartmentalize experiments of: isotropically pumped masers, masers with polarized seed radiation, and anisotropically pumped masers. The results are graphically summarized as polarization landscapes, dependent on maser luminosity and propagation-magnetic field angle. A large part of the results are placed in the Appendix. In this section, we lay out observable patterns in the reported polarization landscapes. Then, in the following section, we discuss the physical processes that give rise to these patterns.

4.1. SiO masers

4.1.1. Isotropic pumping

Simulations of a \( J = 1 \) – 0 SiO maser in a 1 G magnetic field with varying luminosity and magnetic field angle are given in Fig. 1. Simulations of higher angular momentum and at different magnetic fields are given in Figs. A.1-3. The only polarizing entity in these simulations is the magnetic field and its interaction with the directional maser radiation. We observe, regardless of the magnetic field strength or angular momentum of the transition, a peak in the linear polarization fraction around \( \log(R/g \Omega) \approx 0 \) that is, in the region where the rate of magnetic precession \( g \Omega \) and stimulated emission rate \( R \) become comparable in size. The peak of the linear polarization fraction is in the order of the GKK73-estimate of linear polarization fraction, but can exceed it by 10%. This excess of polarization is associated with significant polarization in the Stokes-\( U \) spectrum, and is most pronounced for strong magnetic fields and around \( \theta = 20^\circ \). The linear polarization fraction increases with the magnetic field strength, and decreases with the angular momentum \( J \) of the transition. A large region, around \( \log(R/g \Omega) \approx 0 \), \( 0 - 0.5 \), and \( 0 - 2.5 \), for \( B = 100 \, \text{mG} \). 1 G and 10 G has a stable polarization fraction of about \( p_{\text{ll}} = 1/3 \) (for the \( J = 1 \) – 0 transition) for a large range of angles. The stability of the polarization fraction over \( R/g \Omega \) correlates with the propagation angle and magnetic field strength. For \( \theta \) close to 90\(^\circ\), and strong magnetic fields, the polarization fraction is stable for a large range of \( R/g \Omega \). Significant polarization occurs for a much greater region of \( R \) and \( \theta \) when the magnetic field strength is increased.

We note that the polarization fraction function fulfills the symmetry relation: \( p_{\text{ll}}(\theta) = p_{\text{ll}}(180^\circ - \theta) \). The polarization angle \( \theta \) for different transitions. At \( \theta = \theta_0 \), the polarization flip will get less sharp. These features are particularly clear in Fig. 2. In the intermediate region around \( \log(R/g \Omega) \), the region of highest linear polarization, arbitrary polarization angles can be produced. Overall, apart from the sharper 90\(^\circ\)-flip at \( \theta_0 \), the polarization angle as a function of \( \log(R/g \Omega) \) and \( \theta \) is very consistent for the different magnetic field strengths and different transitions. At \( \log(R/g \Omega) \approx 1 \), the polarization vectors will be aligned (\( \theta = 0 \)) with the (projected) magnetic field direction at any propagation angle \( \theta \).

We continue by analyzing the landscape of circular polarization. We observe that the highest circular polarization fractions occur around \( \theta = 20^\circ \), and is associated with the region of maximal linear polarization fractions. However, for circular polarization maximal polarization occurs at slightly higher \( R \). Circular polarization is most significant between \( \log(R/g \Omega) \approx -1 \) and \( \log(R/g \Omega) < 2.5 \), and quickly drops to zero for \( \theta \to 90^\circ \). Circular polarization contours for other magnetic field strengths
Table 1: Molecular parameters for $v = 1$ SiO masers

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu_0$ (GHz)</th>
<th>$g\Omega_{\text{up}}/B$ (s$^{-1}$/mG)</th>
<th>$g\Omega_{\text{down}}/B$ (s$^{-1}$/mG)</th>
<th>$A_{ij}$ (s$^{-1}$)</th>
<th>$\Gamma$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1−0</td>
<td>43.122</td>
<td>0.75</td>
<td>0.75</td>
<td>3.024 $\times$ 10$^{-6}$</td>
<td>5</td>
</tr>
<tr>
<td>2−1</td>
<td>86.243</td>
<td>0.75</td>
<td>0.75</td>
<td>2.903 $\times$ 10$^{-5}$</td>
<td>5</td>
</tr>
<tr>
<td>3−2</td>
<td>129.363</td>
<td>0.75</td>
<td>0.75</td>
<td>1.050 $\times$ 10$^{-4}$</td>
<td>5</td>
</tr>
<tr>
<td>4−3</td>
<td>172.481</td>
<td>0.75</td>
<td>0.75</td>
<td>2.580 $\times$ 10$^{-4}$</td>
<td>5</td>
</tr>
<tr>
<td>5−4</td>
<td>215.595</td>
<td>0.75</td>
<td>0.75</td>
<td>5.134 $\times$ 10$^{-4}$</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2: Molecular parameters for the 22.235 GHz water maser

<table>
<thead>
<tr>
<th>$F$</th>
<th>$\Delta\nu_{\text{hyp}}$ (kHz)</th>
<th>$g\Omega_{\text{up}}/B$ (s$^{-1}$/mG)</th>
<th>$g\Omega_{\text{down}}/B$ (s$^{-1}$/mG)</th>
<th>$A_{ij}$ (s$^{-1}$)</th>
<th>$\Gamma$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5−4</td>
<td>−33.38</td>
<td>−0.79</td>
<td>−1.34</td>
<td>1.789 $\times$ 10$^{-9}$</td>
<td>1</td>
</tr>
<tr>
<td>6−5</td>
<td>0</td>
<td>3.71</td>
<td>4.12</td>
<td>1.806 $\times$ 10$^{-9}$</td>
<td>1</td>
</tr>
<tr>
<td>7−6</td>
<td>43.018</td>
<td>6.51</td>
<td>7.24</td>
<td>1.860 $\times$ 10$^{-9}$</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 1: Contour polarization plots of $v = 1$ SiO masers. The linear polarization fraction (a), angle (b) and circular polarization fraction (c) are plotted as a function of the propagation angle $\theta$ and the rate of stimulated emission. Magnetic field strength and transition angular momentum are denoted inside the figure. For simulations with $J_{\text{up}} > 1$ and other magnetic field strengths, see Figs. A.1-3.

(Appendix) show similar circular polarization landscapes. The maximum circular polarization fraction does not change much for stronger magnetic field strengths, although the region of significant polarization becomes larger. We saw an analogue effect for the linear polarization. Reversely, lower magnetic field strength does decrease the maximum circular polarization fraction, and also decreases region of significant circular polarization. For these simulations, we have chosen a thermal width,
$\Delta \omega$, so that $\Delta \omega = 1000g\Omega$ ($v_{\text{th}}^{\text{SiO}} J=1-0 = 0.033 \, \text{km/s}$), and found that variations in the thermal width did not yield significantly different circular polarization as long as the requirement $\Delta \omega \gg g\Omega$ was fulfilled\(^1\).

Simulations of the $J = 2 - 1$ SiO maser-transition reveal a sharp drop in both linear and circular polarization fractions with respect to the $J = 1 - 0$ transitions. The maxima of the polarization fractions are $p_{Q\text{max}} = 0.20$ and $p_{V\text{max}} = 0.10$ for $B = 1$ G, constituting a 60% loss in polarization with respect to the $J = 1 - 0$ transition. The general shapes of the contour maps are retained, although the weaker polarization does entail that the area of polarization is smaller. The 90°-flip, caused by increase in $R$, characteristic for the $\theta < \theta_m$ masers, is observed to be a less sharp, and occurs at higher $\log(R/g\Omega)$. Going to higher angular momentum transitions, the changes become less pronounced with respect to the $J = 2 - 1$ transition, although we do observe a minor but steady loss in polarizing strength of the maser with increasing $J$.

We also investigate the spectral properties of the SiO maser polarization. In Fig. 3, we report three spectra of $J = 1 - 0$, $B = 100$ mG, isotropically pumped SiO masers at $\log(R/g\Omega) = -1, 0$ and 1. In the figure, all Stokes parameters are plotted, as well as the polarization angle across the spectrum. We note that the spectrum is broadening with $R$. Because we have already passed the saturation level at $\log(R/g\Omega) = -1$. With the broadening, though, the Stokes-V fraction does not decrease as would be expected from an LTE analysis. The linear polarization follows roughly the same spectral form as the Stokes-I spectrum and the polarization angle can change with up to $\sim 30^\circ$ across the spectrum. We note also the perfect anti-symmetrical nature of the Stokes-V spectrum, as is expected from an LTE analysis, which is retained for all $R$.

### 4.1.2. Polarized incident radiation

Simulations of the polarization of a $J = 1 - 0$ SiO maser at $B = 1$ G with partially polarized seed radiation are reported in Figs. 4 and 5. Simulations of higher angular momentum and at different magnetic fields are given in Figs. A.4-9. In analyzing these types of masers, we should make the distinction between the regime of weak maser emission, where the rate of stimulated emission is significantly weaker than the magnetic field ($\log(R/g\Omega) < -2$), and the regime of strong maser emission, where the two quantities are comparable in size. In the weak maser-regime, the incident polarized radiation is simply amplified and the fractional polarization from the incident radiation is retained, along with the polarization angle of the incident radiation. In the strong maser-regime, we notice distinct differences in the polarization landscapes, between the strongly ($U/I = 0.5$) and the weakly ($U/I = 0.1$) polarized incident radiation. The linear and circular polarization landscapes of the weakly polarized incident radiation, above $\log(R/g\Omega) > 0$ look very similar to the landscapes generated from isotropic seed radiation. In contrast, the linear polarization landscape of the strongly polarized incident seed radiation looks completely different, and only converges to the landscape of isotropic seed radiation for $\log(R/g\Omega) \geq 2$. Interestingly, the effects on the circular polarization landscapes are rather small, even for the strongly polarized incident seed radiation. Although the effects are small, we observe an increase in circular polarization fraction with the polarized incident seed radiation.

Figure 2: Plots of the linear polarization fraction (a) and angle (b) of isotropically pumped $v = 1$ SiO masers as a function of the propagation angle $\theta$ for different saturation rates. Note the sharp 90°-flip of the polarization at the magic angle (denoted with the black-dotted line) that blunts and disappears with increasing levels of saturation. Magnetic field strength and transition angular momentum are denoted inside the figure.

\(^1\) We should note that these remarks are concerned with the polarizing mechanism around $-2 < \log(R/g\Omega) < 2$. As will be discussed later, circular polarization can be introduced via pure spectral decoupling of the $\Delta m = \pm 1$ transitions. Circular polarization via such a mechanism is dependent on the line-width and thus maser thermal width.
Fig. 3: SiO $J = 1 \rightarrow 0$ maser spectra for different levels of saturation. We plot all Stokes parameters (left y-axis) as well as the polarization angle (right y-axis). The polarization angle is defined with respect to the magnetic field direction projected on the plane of the sky. Simulations were carried out at $B = 100$ mG, with a magnetic field propagation angle of $\theta = 45^\circ$.

4.1.3. Anisotropic pumping

When anisotropic pumping is in play, one should make the distinction between strong masers, where the radiation significantly influences the direction of the molecule ($R \gtrsim g\Omega$), and weak masers, where this is not the case. Weak masers propagating through an anisotropically pumped medium, will accrue polarization monotonically. The polarization will rise until the point where the radiative interaction becomes stronger than the degree of anisotropic pumping. After this point, the polarization degree will drop, and the standard magnetic field-polarization mechanism will take over as the main source of polarization. Fig. 6 shows the polarization of anisotropically pumped SiO masers with varying intensity of seed radiation as a function of the rate of stimulated emission.

The polarization of weak masers is independent of the magnetic field strength, but will be highly dependent on the intensity of the seed radiation, as well as the anisotropy of the pumping, $\eta$. Strong masers have as their main polarization mechanism the magnetic-field interaction, but are still minorly influenced by the anisotropic pumping, especially in the transitory period between the weak and strong maser. The polarization of the strongest masers is independent of the intensity of the incoming radiation.

The polarization landscape of an anisotropically pumped SiO maser at $B = 1$ G is plotted in Fig. 7. Simulations of higher angular momentum and at different magnetic fields are given in Figs. A.10-18. If we examine the weak-maser region, we notice directly a strong decline of polarization for $\theta \rightarrow 0$. For higher rates of stimulated emission, at $\log(R/g\Omega) > 1$, we notice that the polarization is largely similar to polarization generated by an isotropically pumped maser (Fig. 1), although we observe additional polarization in the regions around $\theta = 90^\circ$ and $R \sim g\Omega$. Also, we actually observe a decrease in polarization in the region around $\theta = 20^\circ$ and $R \sim g\Omega$ with respect to the isotropically pumped maser. However, if the anisotropy-parameter is in-

...
A & A proofs: manuscript no. pol_lands_aa_5

increased the resemblance to the isotropically pumped maser will vanish rapidly and arbitrarily high polarization can be achieved.

We observe that for increasing the angular momentum of the transition, the same anisotropy parameter, $\eta$, will yield a weaker polarization build-up in the weak maser-regime. Still, though, large fractional linear polarization can be achieved for the higher angular momentum transitions as a result of the anisotropic pumping. A sufficiently large anisotropy-parameter can yield polarization as high as 100%.

The orientation of the anisotropy in Fig. 7, is perpendicular to both the magnetic field direction, $\mathbf{b}$, and propagation direction, $\mathbf{s}$. In this orientation, the polarization maps are symmetric so that $p_L(\theta) = p_L(180^\circ - \theta)$, $p_a(\theta) = -p_a(180^\circ - \theta)$ and $p_V(\theta) = -p_V(180^\circ - \theta)$. This symmetry will however be broken when the direction of the anisotropy orients itself in the plane that $\mathbf{b}$ spans with $\mathbf{s}$ (see Appendix).

We direct our attention to the circular polarization of the anisotropically pumped SiO maser. We can discern some influence of the anisotropic pumping on the circular polarization, but the structure is mostly similar to the one obtained from isotropic pumping, and the enhancement of polarization is not as strong as it was for the linear polarization analogues. Comparing two orientations of the anisotropy directions, $a_1 \perp \mathbf{b}, \mathbf{s}$ and $a_2 \parallel \mathbf{b}$, we find that the anisotropic pumping in the $a_1$ direction actually lowers the circular polarization, while pumping in the $a_2$ direction enhances it. In the weak-maser regime, there is no large circular polarization fraction, nor does the fraction depend on the brightness of the seed radiation.

4.2. H$_2$O masers

4.2.1. Isotropic pumping

We examined the regime of magnetic fields from $B = 20$ mG to $B = 100$ mG, at $v_\parallel = 0.6$ km/s ($T = 260$ K) to $v_\parallel = 3.0$ km/s ($T = 6500$ K). We summarize the results of these simulations in Fig. 8, and further results can be found in Figs. A.19-20. The linear polarization fraction for these water masers is only appreciable from about $T_\parallel \Delta \Omega = 10^{10}$ Ksr, or $\log (R/g\Omega) > -1.5$, where the strongest masers display the strongest polarization. The magnetic field interaction term is not strong enough to facilitate the large overshoot in polarization around $\theta = 20^\circ$ that we have seen earlier. Rather, the maximum linear polarization is found around $\theta \rightarrow 90^\circ$. In the range of $B = 20$ mG to $B = 100$ mG...
mG, the linear polarization of the water masers does not change significantly, although there is a slight general increase in linear polarization fraction. For simulations at higher thermal widths, \( v_{\text{th}} > 1 \text{ km/s} \), there is no significant effect on the linear polarization fraction. For \( v_{\text{th}} < 1 \text{ km/s} \), we observe minor effects, as lines are not completely blended anymore. For these simulations, polarization will start at higher maser intensity, but will soon converge to the landscape of the other \( v_{\text{th}} \) solutions, as broadening of the maser blends the individual lines. Analysis of the polarization angle maps reveal no significant differences between different magnetic field strengths, as well as different thermal widths. The most striking feature of the polarization angle maps are the sharp 90°-flips, associated with crossing the magic angle that are general for any \( T_{\text{b}} \Delta \Omega \). We observe another sharp angle-flip, around \( \log(\frac{R}{\Omega}) \sim 0.75 \) for \( \theta < \theta_m \), but this concerns a 180°-flip.

The circular polarization maps present a rather complicated landscape of circular polarization, never quite reaching high degrees of circular polarization. Weaker masers with \( T_{\text{b}} \Delta \Omega \ll 10^{11} \text{ Ksr} \), follow roughly the LTE estimate of the circular polarization

\[
p_V \propto 2 A F_p B_{\text{Gauss}} \cos \theta/\Delta v_F (\text{km/s}) \quad \text{(Fiebig & Güsten 1989)}.
\]

Indeed, for these masers, we observe the strongest circular polarization for \( \theta \to 0^\circ \) and low \( v_{\text{th}} \), which gradually diminishes for higher \( v_{\text{th}} \) and angles \( \theta \to 90^\circ \). When \( T_{\text{b}} \Delta \Omega > 10^9 \text{ Ksr} \), the simulation results for circular polarization depart from the LTE estimates. For the strongest masers, around \( T_{\text{b}} \Delta \Omega \sim 10^{13} \text{ Ksr} \), we find (for \( B = 20 \text{ mG} \)) highest circular polarization, that can get up to 0.55% around \( \theta \sim 60^\circ \). Circular polarization in this region has only a minor dependence on the magnetic field strength and maser thermal width.

We have already touched upon the complicating multi-transitional nature of the water-maser. It is very well possible that asymmetries occur in the pumping of the different hyperfine transitions (see Walker 1984; Lankhaar et al. 2018). To further investigate this, we plot for a number of preferred hyperfine pumping ratios \( \lambda = \lambda_{F = 7/6}/\lambda_{\text{other}} \), the fractional circular and linear polarizations of a water maser at \( \theta = 45^\circ \) as a function of the maser luminosity. The \( F = 7 \rightarrow 6 \) transition is the strongest hyperfine transition and, incidentally, also the transition with the

\[
\text{Circular polarization maps}
\]

\[
\text{Linear polarization maps}
\]
highest Zeeman-coefficient. From Fig. 10, quite surprisingly, we observe a negative correlation between the generated linear polarization and the favoring of the $F = 7 \rightarrow 6$ transition. However, the circular polarization does increase as a result of the preferred pumping of the $F = 7 \rightarrow 6$ transition. Another interesting feature that was not apparent from the contour maps, are the discontinuities in both the linear and circular polarization fractions. Discontinuities in these functions arise because of the complex nature of the multi-transitional lines—and indeed do not occur for the most preferably pumped masers.

In Fig. 9, we present the 22 GHz water maser spectra for different levels of saturation. It is immediately obvious that for all levels of saturation, the Stokes-$I$ spectra are slightly asymmetric because of the multiple hyperfine components of this maser. This asymmetry is also seen in the linear polarization, that follows roughly the total intensity spectrum. We should note that circular polarization profiles are not the anti-symmetric S-shaped signals we observed for the single-transition SiO-masers. Through the contributions from multiple hyperfine components an asymmetric circular polarization spectrum arises (Nedoluha & Watson 1992; Vlemmings et al. 2001). A preferably pumped water maser will however show the characteristic S-shaped circular polarization signal.

### 4.2.2. Polarized incident radiation

We already observed in the SiO masers that for the higher-angular momentum contours, the general structure of polarization contours is strongly influenced by the incoming polarized radiation. This is thus also the case for water masers, who generally also show weaker magnetic field interactions. The simulations with strongly polarized incoming radiation, have nearly no general dependence on $\theta$, as the incoming (linear) polarization fraction smoothly deteriorates from $T_b \Delta \Omega > 10^{12}$ Ksr. The weakly polarized incident radiation has a less pronounced effect on the polarization landscape, although it strongly dominates the landscape for $T_b \Delta \Omega < 10^{10}$ Ksr.

These effects are also reflected in the landscape of circular polarization, which is strongly affected for the highly polarized incoming radiation, in contrast to the weak effects incident polar-
ized seed radiation had on the SiO maser. Incident polarized seed radiation can cause relatively high fractions of circular polarization, especially in the region around $\theta = 90^\circ$—interestingly the region where isotropic incoming radiation leads to no circular polarization—, where for the highly polarized incoming radiation, the circular polarization can get up to 5% (1% for weakly polarized incoming radiation).

4.2.3. Anisotropic pumping

As a consequence of the shocked material that water masers occur in, photons that are associated with the radiative relaxation from the collisionally excited water molecules, may have a preferred escape direction. This can lead to a small anisotropy in the maser pumping. Analyzing our simulations of the anisotropically pumped water maser, we notice that the linear accrual of polarization with the maser brightness is also characteristic of these masers. We notice for the perpendicularly pumped water masers from Fig. 12 that masers of $\theta \to 90^\circ$ gather the most linear polarization from the propagation. In fact, for the water masers it seems that the standard magnetic-field polarization mechanism has barely any effect on the polarization maps of both weak and strong anisotropy, as signified by the symmetry of the linear polarization landscapes. The polarization of these masers are almost independent of the magnetic field strength, but will be highly dependent on the intensity of the seed radiation, as well as the anisotropy of the pumping, $\eta$. Anisotropic pumping can generate arbitrary linear polarization fractions for the water masers.

High circular polarization fractions are only weakly associated with the drastically higher linear polarization from anisotropic pumping. Only the brightest of the strongly anisotropically pumped masers show significantly higher circular polarization, but not exceeding 5%.

5. Discussion

We will divide the discussion up in two parts. First, we will discuss the results we have presented in the previous section, and lay out the physical mechanisms behind the phenomena we have observed from the simulations. In the second part of the discussion, we will discuss these results in the context of previous SiO and water maser polarization observations.
5.1. SiO masers

5.1.1. Simulations

80\(^\circ\) flip of the polarization angle. We have observed two processes that can give rise to a 90\(^\circ\)-flip in the polarization angle: an increase in rate of stimulated emission over two orders of magnitude, or the crossing of the magic angle, \(\theta_m\). When \(g\Omega \gtrsim 100R\), the magnetic field determines the symmetry axis of the molecule. When this condition is fulfilled, and for the propagation radiation at an angle with the magnetic field smaller than \(\theta_m\), the polarization will be oriented perpendicular to the magnetic field. For angles greater than \(\theta_m\), polarization will be oriented parallel to the magnetic field. Thus, when we cross the magic angle and the condition \(g\Omega \gtrsim 100R\) is fulfilled, we see a sharp 90\(^\circ\)-flip in the polarization angle across \(\theta_m\). For stronger masers, where \(100 \gtrsim g\Omega/R \gtrsim 0\), we also observed a flip in the polarization angle, but this flip is rather gradual (over \(\sim 10^\circ\)), and does not predict zero polarization at the magic angle. The 90\(^\circ\)-flip feature of \(J = 1 - 0\) SiO masers has recently be investigated by Tobin et al. (2019). Tobin et al. (2019) analyze the changing polarization fraction and angle of SiO maser spots across a clump. They assume a gradually changing propagation angle with the projected angular distance. From an analysis based on GKK73, they fit the observed polarization fraction and angle. Indeed, a 90\(^\circ\)-flip is observed around the magic angle, but the 90\(^\circ\)-flip is rather gradual. According to their analysis, this is due to the free \(K\)-parameter that arises in the GKK73 models. Usually, this parameter is as-

Fig. 9: Water 22 GHz maser spectra for different levels of saturation. We plot all Stokes parameters (left y-axis) as well as the polarization angle (right y-axis). The polarization angle is defined with respect to the magnetic field direction projected on the plane of the sky. Simulations were carried out at \(B = 100\) mG, \(v_b = 1\) km/s and with a magnetic field propagation angle of \(\theta = 45^\circ\).

Fig. 10: Plots of the (a) linear and (b) circular polarization fraction of water masers as a function of the maser luminosity. Different degrees of preferred pumping are plotted. Magnetic field strength, angle \(\theta\) and thermal width denoted inside the figure.
Fig. 11: Contour plots of the (a,c) linear and (b,d) circular polarization fraction of a water maser as a function of the propagation angle $\theta$ and the rate of maser luminosity. Maser simulations performed with incident polarized radiation of (a,b) $U/I = 0.1$ and (c,d) $U/I = 0.5$. Magnetic field strength and thermal width are denoted inside the figure. For simulations with other $v_{th}$ and other magnetic field strengths, see Figs. A.21-22 in the Appendix.

sumed zero on the grounds of symmetry. According to our analysis, one need not invoke such a free parameter. Because as we have seen in our simulations (Fig. 2), a blunt $90^\circ$-flip around the magic angle is characteristic of masers where the rate of stimulated emission is in the same order as the magnetic precession rate. Indeed, Tobin et al. (2019) estimate $\log(R/g\Omega) \sim -1$, and our simulations of a magic angle flip at these conditions (Fig. 2, $\log(R/g\Omega) = -1$) show a similar blunted magic angle flip in the polarization angle. We should note that our analysis underestimates the polarization fraction with respect to the observations, and one needs to invoke non-Zeeman polarizing mechanisms to reach the observed polarization fractions.

Sometimes, it is stated in the literature that in the limit $R \gg g\Omega$, maser polarization will be randomly oriented (Plambeck et al. 2003). This is not the case. Even though the radiation field determines the alignment of the molecules, its interaction with the magnetic field through the maser medium is still the polarizing mechanism. It is therefore that the magnetic field determines the polarization direction. A $90^\circ$-flip across $\theta_m$, however, will not occur in the case of $R \gg g\Omega$ as the orientation of the polarization is invariably parallel to the magnetic field. This is also associated with the alternative mechanism that leads to a $90^\circ$-polarization angle flip. When $R \ll g\Omega$ and the propagation angle is smaller than $\theta_m$, maser polarization will be oriented perpendicular to the magnetic field direction. However, if the rate of stimulated emission would increase, or the magnetic field strength would decrease, and the condition $g\Omega \gg R$ would not be fulfilled anymore, the polarization would gradually align itself parallel to the magnetic field. A change in two orders of magnitude of $R$ or $g\Omega$ can cause a $90^\circ$-flip in the polarization angle.

A peak in polarization at $g\Omega \sim R$. Invariably, the highest linear and circular polarization fractions are observed for the case that the magnetic field strength is of the same order of magnitude as the rate of stimulated emission. This effect seems to be most pronounced for angles smaller than the magic angle, specifically around the propagation angle $\theta = 20^\circ$. The extra polarization is coming from a strongly enhanced Stokes-$U$ component in the radiation, and significant off-diagonal state density elements. The effect is absent for $90^\circ$-propagation, because off-diagonal elements need not be invoked in these masers.

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Absence of polarization below $R = 1 \text{s}^{-1}$ ($T_b \Delta \Omega = 9 \times 10^6 \text{Ksr}$). Considering an isotropically pumped maser, and when $R$ is so small that $R \ll g\Omega$, we recognize from Eq. (7) that the radiation field has only a small influence on the populations of the magnetic substates of SiO, and will be minimally polarized because of this. Also, because the (isotropic) decay of the states, described by the term $\Gamma$, is larger than $R$, the polarization of the states will be drastically lowered through the depolarizing decay.

The circular polarization of SiO masers. Just as for linear polarization, the highest circular polarization fraction was found in the region $R \sim g\Omega$. The polarization fraction in this region is not dependent on the maser thermal width. The high degree of circular polarization found here, is due to an effect that was earlier described as “intensity-dependent circular polarization” (Nedoluha & Watson 1994). Circular polarization is associated with the changing of the molecular symmetry axis that in the transition from $R < g\Omega$ to $R > g\Omega$, changes from parallel to the magnetic field, to parallel to the propagation direction.

A version of the above described effect is also responsible for the circular polarization that will be generated by a randomly oriented magnetic field that is strong enough to align the molecule. Wiebe & Watson (1998) investigated the propagation of polarized radiation through a medium with a randomly oriented magnetic field along $(128 \times 128)$ maser propagation paths. Along the path, linear polarization builds up. However, this linear polarization would not be aligned with the orientation of the molecules along the changing magnetic field. Locally, the linearly polarized radiation is rotated towards the (local) molecular alignment axis, with the associated production of circular polarization. In this way, relatively high degrees (< 3%) of circular polarization could be generated already from magnetic fields of (~ 30 mG) (Wiebe & Watson 1998). Because circular polarization is generated from the linear polarization, the circular polarization should not exceed a certain linear polarization-dependent limit. Through analyzing this relation, Cotton et al. (2011) found that the polarizing effects described by Wiebe & Watson (1998) could not explain the high degrees of circular polarization found in their observations of SiO $J = 1 - 0$ masers. The circular polarization effects we have included in our models alone can also not fully explain the observations of Cotton et al. (2011) (see also our discussion of the maser line-profiles that follows).
Slow convergence to the GKK73 solutions. With a magnetic precession rate of \( g \Omega = 1500 \times B(G) \) s\(^{-1}\) and an isotropic decay rate of \( \Gamma = 5 \) s\(^{-1}\), the SiO maser generally fulfills the condition \( g \Omega \gg \Gamma \). For the GKK73 solutions to maser linear polarization to apply, we furthermore have a constraint on the rate of stimulated emission so that \( g \Omega \gg R \gg \Gamma \). For an \( R \) in the range from \( \Gamma \) to \( g \Omega \), this requirement cannot be fulfilled for magnetic field strengths expected around SiO masers. This is confirmed from our calculations, where we do not find the GKK73 solutions in the relevant parameter space. Convergence to the GKK73 solutions only occurs for unphysically strong magnetic fields and unphysically luminous masers.

Dependence of polarization on the angular momentum, \( J \), of the transition. The difference in polarization fraction between the \( J = 1 \) and \( J = 2 \) transitions is very large. For higher \( J \)-transitions, the polarization decrease with \( J \) is less drastic. This phenomenon has already been observed by D&W90 and N&W90, and can be explained by the inability for the \( J = 0 \)-state to get polarized. The radiation field couples directly to the (in irreducible tensor terms) rank-0, 1 and 2 elements. Coupling to higher rank elements is mediated by higher order effects and is therefore orders of magnitude weaker. The maximum rank of the elements of a certain state is \( 2J + 1 \). Therefore, all the polarization modes of the radiation field can couple directly to states of \( J \geq 1 \). Direct coupling of the polarization thus exists for all transitions but \( J = 1 \), leading to this transition to be highly polarized. The further consistent polarization decrease with \( J \) can be explained by the introduction of more higher rank irreducible population terms, to which some of the polarization leaks away to, and which do not couple directly to the radiation field.

Incident polarized seed radiation as a polarization mechanism. One principal result of the simulations with polarized seed radiation was contained in the distinction between a weak-maser regime and a strong-maser regime. We observed that the in the weak-maser regime, the incident polarization was retained, and in the strong-maser regime the polarization would converge to the polarization obtained with isotropic seed radiation. In the weak-maser regime, the magnetic field is defining the symmetry axis. Because the radiation field is so weak, there is no appreciable influence of it on the molecular states. In fact, we can consider the states to be unpolarized. That means that amplification is characterized by a dominant \( A_{\omega} \)-term (see Eqs. 14). Thus, radiation is amplified and not altered in terms of polarization until it becomes a significant entity that can align and polarize the molecular states. After the weak-maser regime, at about \( \log(R/|g\Omega|) = -1 \), a transition regime can be recognized, where both the initial polarization, as well as the overall radiation have an appreciable influence on the molecular states. The feedback of the polarized molecular states in the propagation of the polarized radiation causes the radiation to converge to a polarization that is general for the system (in terms of \( R, g\Omega \) and \( \delta \)), invariable of its initial conditions, which is what we call the strong-maser regime. Convergence is attained later for strongly polarized seed radiation, and lower magnetic fields. High degrees of polarization can be obtained in the transition regime. Later in this discussion, we will comment on the effect these high degrees of linear polarization have on the circular polarization.

Anisotropic pumping as a polarization mechanism. For the anisotropically pumped maser, we have a weak-maser regime and a strong-maser regime as well. We should however note that these regimes carry a different meaning with respect to the regimes of the masers with polarized seed radiation of the same name. The weak-maser regime of the anisotropically pumped maser is characterized by a linear growth of the polarization with maser luminosity. This growth can continue to arbitrary degrees of (linear) polarization until the radiation becomes strong enough to align the molecular states. In the weak-maser regime, because the pumping is anisotropic—where the anisotropic part can be represented by a second-rank irreducible tensor—polarization is pumped into the molecular states; causing a feed to the radiation field via the propagation coefficients \( B_{\omega} \) and \( F_{\omega} \) (see Eqs. 14). The build-up of polarization is thus dependent on the relative anisotropy in the pumping, \( \epsilon \), but also on the relative size of \( A_{\omega} \), given by \( \delta \) (Eq. 18), leading to the anisotropy-parameter \( \eta = \epsilon/\delta \). The build-up of polarization in the weak-maser regime is independent of the magnetic field and is not associated with circular polarization. But it is dependent on the brightness of the seed radiation.

When radiative interactions become strong enough to influence the alignment of the molecule, a transition regime begins and, generally, the strongly polarized radiation begins to lose most of its polarization. The alignment of the molecular states is countering the large overshoot in polarization left from the weak-maser regime and converges in the strong-maser regime to a polarization that is a function of the anisotropy of the pumping (including direction), \( R \) and \( \theta \) that is independent of the incoming radiation.

Maser line-profiles. Maser line-profiles are often much narrower than their LTE counterparts because of the stimulated emission mechanism. This is most manifest when the rate of stimulated emission is near the isotropic decay rate \( R \sim \Gamma \). After that point, broadening of the line starts and increases with \( R \). From analyzing the polarized spectra, we observe that linear polarization spectra roughly follow the Stokes-\( I \) spectrum, which is expected because the molecular states get polarized by the directional intensity field. The difference in polarizing intensity also leads to a variable polarization angle across the spectrum. This is particularly present for rates of stimulated emission \( R \sim g\Omega \). The degree of change of the polarization angle across the maser-line can therefore be taken as a proxy for the saturation level.

We observe that the polarizing mechanism under investigation in our simulations produce perfect anti-symmetrical S-shaped spectra for the Stokes-\( V \) component of the radiation field. Such anti-symmetrical spectra are often seen in astrophysical maser spectra (Amiri et al. 2012). However, asymmetric Stokes-\( V \) spectra are observed regularly as well. Cotton et al. (2011) report the observation of many strongly asymmetrically circularly polarized SiO masers. Our models do not produce such asymmetrical spectra in the absence of hyperfine multiplicity, but would need to include alternative effects. A velocity gradient across the maser column or the presence of strong anisotropic resonant scattering in either a foreground cloud or as a part of the maser action itself, are known to be able to produce asymmetric Stokes-\( V \) spectra (Houde 2014). Kinematic effects coming from other polarized background maser sources could also explain the asymmetric signals.

Interesting evidence for kinematic effects can be found by analyzing some individual maser line-spectra (Cotton et al. 2011). The polarization spectra of the maser spot of figure 5, row 1, from Cotton et al. (2011), show for the polarization angle similar variation across the spectrum as our Fig. 3 of the
spectral polarization of SiO masers. Indeed, this maser shows an S-shaped antisymmetric Stokes-V spectrum. Analyzing then rows 3 and 4 of the same figure in Cotton et al. (2011), we see a variation in the polarization angle across the maser line that is more reminiscent of the 22 GHz water maser spectra of Fig. 9. Indeed, also the circular polarization of these signals is similar to our spectral models of the water masers (Fig. 9). The different hyperfine components in water masers can reasonably be considered to emulate kinematic effects as they would occur for an SiO maser. A deeper analysis of such effects is beyond the scope of this paper, but we can suggest that asymmetric circular polarization signals can be the product of kinematic effects.

Alternative polarizing mechanisms and circular polarization. An interesting result of our investigations to the effects of anisotropic pumping and polarized incident radiation is the rather marginal effects these polarizing mechanisms have on the circular polarization fraction of the maser. This can be best explained in a tensorial picture of the matter-radiation interactions. In a tensorial picture of the polarized radiation, Stokes-\(Q\) and -\(U\) (and -\(I\)) are expressed as second-rank components of the irreducible radiation tensor, while Stokes-V is a first rank component of this tensor (Degl’Innocenti & Landolfi 2006). Direct polarization of the molecular states by linearly polarized radiation will thus only affect the second-rank populations. It is also the second-rank populations that are pumped by the anisotropic pumping. Thus, for incident polarized radiation and anisotropic pumping, there exist no direct coupling to the first rank populations, and thus no direct coupling to the Stokes-V radiation. Indeed, the Stokes-V will only be slightly enhanced by higher-order effects, such as anisotropic resonant scattering (Houde et al. 2013) that will be more pronounced with high linear polarization of the radiation.

Observational heuristics. Generally, we can recognize different regimes that are connected to the maser luminosity that show particular behavior regarding maser polarization. We therefore define characteristic maser luminosities that will simplify the analysis. The maser luminosity at which the rate of stimulated emission is equal to the rate of magnetic precession is defined as

\[
(T_\Omega \Delta \Omega)_{\text{mag sat}} = \frac{4\pi \omega_b g(\Omega)}{A_{jj}k_B},
\]

(36)

where \(\omega_b\) is the masers natural frequency, \(k_B\) is the Boltzmann constant and \(A_{jj}\) is the Einstein coefficient. Furthermore, we define the luminosity after which the maser will start broadening because of saturation

\[
(T_\Omega \Delta \Omega)_{\text{sat}} = \frac{4\pi \omega_b \Gamma}{A_{jj}k_B}.
\]

(37)

Table 3 gives these luminosities for the different SiO masers. Already at weak magnetic fields of \(B > 10\) mG, \((T_\Omega \Delta \Omega)_{\text{mag sat}} > (T_\Omega \Delta \Omega)_{\text{mag sat}}\). For the weakest masers, where \(T_\Omega \Delta \Omega < (T_\Omega \Delta \Omega)_{\text{sat}}\), linear polarization is mostly absent in the emission, because of the depolarizing effect of the isotropic decay. Circular polarization is generated through the Zeeman effect. Because of the Zeeman effect, the \(\sigma^+ (\Delta m = \pm 1)\) transitions will have a slight spectral disposition, that, if subtracted from each other, will yield the S-shaped Stokes-V spectrum. It can be shown via an LTE analysis that the circular polarization will follow (Fiebig & Güsten 1989; Watson & Wyld 2001)

\[
\rho_V = \frac{2A_{jj} B_{\text{Gauss}} \cos \theta}{\Delta V_L (\text{km/s})}.
\]

(38)

Table 3: Characteristic maser luminosities temperatures for \(v = 1\) SiO masers

<table>
<thead>
<tr>
<th>Transition</th>
<th>((T_\Omega \Delta \Omega)_{\text{mag sat}}) (Ksr)</th>
<th>((T_\Omega \Delta \Omega)_{\text{mag sat}}/B) (Ksr/mG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J = 1 - 0)</td>
<td>(4.35 \times 10^7)</td>
<td>(6.52 \times 10^6)</td>
</tr>
<tr>
<td>(J = 2 - 1)</td>
<td>(9.00 \times 10^6)</td>
<td>(1.35 \times 10^6)</td>
</tr>
<tr>
<td>(J = 3 - 2)</td>
<td>(3.73 \times 10^6)</td>
<td>(5.60 \times 10^5)</td>
</tr>
<tr>
<td>(J = 4 - 3)</td>
<td>(2.03 \times 10^6)</td>
<td>(3.04 \times 10^5)</td>
</tr>
<tr>
<td>(J = 5 - 4)</td>
<td>(1.27 \times 10^6)</td>
<td>(1.90 \times 10^5)</td>
</tr>
</tbody>
</table>

where \(A_{jj}\) is a transition-dependent constant and \(\Delta V_L\) is the FHWM of the maser profile. The LTE estimates for the constant \(A_{jj}\) of SiO transitions are

\[
A_{jj} = \frac{1.1807 \times 10^{-3}}{J},
\]

where \(J\) is the rotational quantum number of the upper-state. It is usual to employ an LTE analysis of the circular polarization of weak masers, since the maser circular polarization mechanism for these masers is similar to the LTE mechanism. To check the validity of this analysis, we plot the results of our simulations for the \(A_{jj}\)-constants for three transitions at \(B = 1\) G in Fig. 13. For \(T_\Omega \Delta \Omega \leq (T_\Omega \Delta \Omega)_{\text{mag sat}}/1000\), the \(A_{jj}\)-coefficient obtained from our simulations is similar to the LTE estimate. However, already for \(T_\Omega \Delta \Omega \sim (T_\Omega \Delta \Omega)_{\text{mag sat}}/100\), we find that the \(A_{jj}\)-constants from our simulations are twice that of the LTE estimate, meaning that an LTE analysis of the magnetic field strength would lead to an overestimation by a factor of 2.

For masers \(T_\Omega \Delta \Omega \ll (T_\Omega \Delta \Omega)_{\text{mag sat}}\), the highest circular polarization will be found for the masers that haven’t started broadening yet \((T_\Omega \Delta \Omega \sim (T_\Omega \Delta \Omega)_{\text{sat}})\). After \(T_\Omega \Delta \Omega > (T_\Omega \Delta \Omega)_{\text{sat}}\), the maser starts saturating with the associated broadening. So long as the magnetic precession rate remains far greater than the rate of stimulated emission, \(T_\Omega \Delta \Omega \ll (T_\Omega \Delta \Omega)_{\text{mag sat}}\), the circular polarization will decrease because of this broadening. Linear polarization starts to build up, either oriented parallel \((\theta > \theta_m)\) or perpendicular \((\theta < \theta_m)\) to the projected magnetic field direction. Linear polarization will rise steadily with the maser luminosity, until it reaches the GKK73 solution for the specific propagation angle. However, (long) before the GKK73 solution is reached, when the maser luminosity approaches \((T_\Omega \Delta \Omega)_{\text{mag sat}}\), alternative polarization effects will take over.

In the regime of \(T_\Omega \Delta \Omega \sim (T_\Omega \Delta \Omega)_{\text{mag sat}}\), polarization associated with the change in molecular alignment will manifest itself in the emission spectrum. Linear polarization in this regime can therefore exceed the GKK73 solutions by ~ 10%. For \(\theta < \theta_m\), the polarization vector will change from perpendicular to parallel between \(T_\Omega \Delta \Omega \sim (T_\Omega \Delta \Omega)_{\text{mag sat}}/10\) and \(T_\Omega \Delta \Omega \sim 10(T_\Omega \Delta \Omega)_{\text{mag sat}}\), and will have intermediate polarization angles within this range. With the gradual changing of the polarization angle a lot of circular polarization is associated. This is reflected in the high \(A_{jj}\)-constants for the circular polarization (see Fig. 13). Constancy of \(A_{jj}\) over \(\theta\) is also lost. For the lower angular momentum transitions, there is a large overshoot of the Zeeman circular polarization. Already for weak magnetic fields, high degrees of circular polarization can be generated and the Zeeman analysis cannot be applied directly. Extraction of the magnetic field strength from masers in the regime \(T_\Omega \Delta \Omega \sim (T_\Omega \Delta \Omega)_{\text{mag sat}}\) can be achieved by a simultaneous analysis of both the linear and circular polarization of the radiation, which will be demonstrated later on.

Alternative polarizing mechanisms such as anisotropic pumping can enhance the polarization of masers to arbitrar-
Fig. 13: The $A_{J'J}$ coefficients of an isotropically pumped SiO maser at $B = 1$ G as a function of the magnetic field-propagation direction angle $\cos \theta$. The different subfigures give the (a) $J = 1 - 0$, (b) $J = 2 - 1$ and (c) $J = 3 - 2$ transitions. Plots are given for different $\log(R/g \Omega)$. The LTE solutions (constant over $\cos \theta$) are denoted with a dotted line.

The presence of anisotropic pumping could be discerned by analyzing the weaker masers ($T_b \Delta \Omega \ll (T_b \Delta \Omega)_{mag \ sat.}$) for their polarization. The (linear) polarization degree of these masers should be proportional to their luminosity. When the anisotropically pumped maser approaches the luminosity ($T_b \Delta \Omega$)_{mag \ sat.}, linear polarization will drop as the standard polarizing mechanisms take over. Indeed, Richter et al. (2016) find in their VLBA observations of VY CMa the strongest polarization for the weaker masers, and observe a drop in polarization after a certain maser luminosity threshold. Turning to polarized seed radiation, in the regime ($T_b \Delta \Omega \ll (T_b \Delta \Omega)_{mag \ sat.}$), the polarization is simply that of the seed radiation, and has no dependence on the maser luminosity. Circular polarization is only slightly enhanced for alternatively polarized masers.

Finally, we should make a note that the polarization properties are a function of the maser luminosity $T_b \Delta \Omega (\propto R)$, which cannot be measured directly. To estimate the maser luminosity from observations, one requires knowledge about the maser beaming solid angle $\Delta \Omega$. Direct observations of $\Delta \Omega$ have proven difficult to date, but have been performed with VLBA measurements to SiO around AGB stars (Assaf et al. 2013). In these observations, Assaf et al. (2013) measure, with a sizable error margin due to (relatively) low resolution, $\Delta \Omega \sim 5 \times 10^{-2}$ sr. This maser beaming solid angle is independent of its brightness when the amplification is matter bounded (most easily approximated by the cylindrical maser) (Elitzur et al. 1992). When the maser is amplification bounded (most easily approximated by the spherical maser) the beaming solid angle drops with increasing maser brightness. To the best of our knowledge, no investigations have been done to the geometrical nature of the maser amplification of SiO masers.

5.1.2. SiO maser polarization observations

Many SiO maser polarization observations have been performed. VLBI observations have shown that SiO masers orient themselves in a ring-like structure around the central stellar object. The polarization of these SiO masers, irrespective of their angular momentum transition, show well-ordered polarization vectors with respect to this structure (Kemball & Diamond 1997; Cotton et al. 2004; Plambeck et al. 2003; Vlemmings et al. 2011a, 2017). This is taken to be an indicator of an ordered magnetic field. The linear polarization fraction of individual masers can be arbitrarily high, but median values are much lower. The $J = 1 - 0$-transition has median linear polarization fractions of $\sim 25\%$ (Kemball & Diamond 1997). Analyzing the angu-
lar momentum dependence of the linear polarization fraction, we note the general trend of lower degrees of polarization for the higher-angular momentum transitions. This is not to say that high (> 50%) fractions of linear polarization do not occur for high J SiO maser-transitions. It is almost certain that the most strongly polarized masers are the product of anisotropically pumped maser action, as incident polarized radiation at these fractions is unlikely; and should lead to the same effect for the high-J masers. The hypothesis of anisotropic pumping could be further supported by correlating maser-brightness for the weaker masers (R < gΩ) to linear polarization.

The relationship between maser-brightness and polarization fraction is unfortunately not well-documented. However, Barvainis et al. (1987) meticulously tabulated their observations, from which we could construct a scatter plot that indicated lowest fractions of polarization for the strongest masers. This is in line with the simulations we have delineated above, where we have seen that above R ~ gΩ, polarization fractions start to drop.

Herpin et al. (2006) have been able to derive an interesting relation between the circular polarization and linear polarization of SiO J = 2 − 1 masers. In a large survey of a number of evolved stars, they analyzed, among other things, the correlation between linear and circular polarization fractions of the SiO masers. Even though the correlation was highly scattered, a clear linear relation was observed between linear and circular polarization (figure 4, Herpin et al. (2006)). Also, invariably, high circular polarization was associated with high linear polarization. To simulate their observations, we have used CHAMP to compute the linear and circular polarization fractions of 200 isotropically pumped SiO masers, at randomly selected luminosities between $T_B \Delta \Omega = 10^6 - 10^{11}$ Ksr and randomly selected propagation angles $\theta$. We plot the results for SiO J = 2 − 1 masers pumped at $T = 1000$ K, and magnetic field of $B = 1$ G in Fig. 14. Herpin et al. (2006) found a rough linear relation between the linear and circular polarization, $p_v = 0.25 p_L + 0.015$, which we plot in the figure.

Only for lower degrees of linear polarization we find a reasonable agreement between our simulations and the observations of Herpin et al. (2006). Our simulations seems to underestimate the circular polarization with respect to the observations of Herpin et al. (2006). This is especially true for the strongly linearly polarized masers. One factor that could play a role here is the enhancement of circular polarization by the presence of a velocity gradient along the propagation path of the SiO-maser. N&W94 have shown that this can enhance the circular polarization. Another explanation of the high circular polarization might be the anisotropic resonant scattering of maser radiation by a foreground cloud of non-masing SiO (Houde et al. 2013; Houde 2014). Via anisotropic resonant scattering, linearly polarized radiation can be converted to circularly polarized radiation. Anisotropic resonant scattering will not necessarily produce the anti-symmetric S-shaped Stokes-V spectrum profile, characteristic for circular polarization generated by the Zeeman effect, but it can arise from scattering of a cloud outside the velocity-range of the maser. Indeed, non anti-symmetric Stokes-V spectra were observed by Herpin et al. (2006), but these can also be explained by a velocity gradient along the propagation path of the maser, or the lack of spatial resolution from the single-dish observations.

\[
\begin{align*}
R_p &= 0.25 p_L + 0.015 \\
B &= 1 \text{ G} \\
T &= 1000 \text{ K} \\
\end{align*}
\]

Fig. 14: Scatter plot for the linear to circular polarization fraction relation $p_L = p_v$. In red, the observations of (a) Herpin et al. (2006) and (b) Surcis et al. (2011) are reported. In subfigure (a), the blue points come from our simulations of the $J = 2 − 1$ transition at $B = 1$ G, with the kinetic temperature of the maser $T = 1000$ K. Subfigure (b), the blue points come from our simulations of the isotropically pumped water maser at $v_B = 1.0 \text{ km/s}$ and $B = 200 \text{ mG}$. To generate these scatters, we have computed the polarization fractions from (a) 200 (b: 30) isotropically pumped masers with a randomly selected luminosity between (a) $T_B \Delta \Omega = 10^6 - 10^{11}$ (b: $T_B \Delta \Omega = 10^{8.5} - 10^{11}$) and a randomly selected propagation angle $\theta$. In the scatter plot, we do not include masers that show polarization < 0.5% (b: < 0.1%). Inside the figure (a), we also report the linear regression analysis result from Herpin et al. (2006).

5.2. H$_2$O masers

5.2.1. Simulations

The relevant characteristic maser luminosities are tabulated in Table 4. We tabulate the relevant luminosities for individual hyperfine transitions as well as the blended line. Compared to the SiO maser, radiative interactions remain relatively weak with respect to magnetic interactions up to high maser luminosities. This is due to the much smaller line strength of this maser-transition. Because of this, the Zeeman effect will be the dominating polarizing mechanism up to high maser luminosities, and
will thus follow Eq. (38) up to high maser brightness. Linear polarization will also remain rather low because the isotropic decay will thus follow Eq. (38) up to high maser brightness. Linear polarization can be described by Eq. (38). An LTE analysis of a completely blended water-maser line gives $A_{\text{blend}} = 8.2$. Fig. 15 shows the results of our full radiative transfer analysis of the circular polarization constants. Apart from the standard maser line-profile, water masers are further broadened by their hyperfine structure. This will lead to an overestimation of $\Delta v_L$. The dominant Zeeman effect though, will come from a single hyperfine transition. This produces higher Zeeman $A_{\text{ff}}$ coefficients with respect to an LTE analysis. We observe that this effect is most pronounced for masers pumped at $v_{th} = 0.6 \text{ km/s}$, where the hyperfine transitions are minimally mixed. At $v_{th} = 2.0 \text{ km/s}$, the hyperfine broadening is negligible and the LTE value for the $A_{\text{ff}}$ coefficient of the $F = 7 - 6$ hyperfine transition is returned for the weakest masers. Paradoxically, the preferred pumping of the hyperfine component with the strongest Zeeman effect precession rate effectively increases, and the $(T_b \Delta \Omega)_{\text{mag sat}}$ is out of reach. Thus, the change in molecular symmetry-axis that is associated with the production of linear polarization, occurs only for the strongest masers. It is therefore, that transitions with weaker Zeeman interactions are associated with higher degrees of linear-polarization in the relevant brightness regime for the water maser. We should note that this effect is not as pronounced for the high-temperature masers, where the broadening of the lines causes the other transitions to blend in more. The maser circular polarization is proportional to the strength of the Zeeman effect as expected from Eq. (38).

### Table 4: Characteristic maser luminosities for the 22 GHz water maser

<table>
<thead>
<tr>
<th>Transition</th>
<th>$(T_b \Delta \Omega)_{\text{sat}}$ (Ksr)</th>
<th>$(T_b \Delta \Omega)_{\text{mag sat}} / B$ (Ksr/mG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F = 7 - 6$</td>
<td>$7.2 \times 10^9$</td>
<td>$3.1 \times 10^{10}$</td>
</tr>
<tr>
<td>$F = 6 - 5$</td>
<td>$7.4 \times 10^9$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>$F = 5 - 4$</td>
<td>$7.5 \times 10^9$</td>
<td>$2.3 \times 10^9$</td>
</tr>
<tr>
<td>blend</td>
<td>$7.4 \times 10^9$</td>
<td>$6.0 \times 10^9$</td>
</tr>
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</table>

5.2.2. Water maser polarization observations

We start this subsection with a note on the water maser beaming solid angle. Richards et al. (2011) performed water maser observations around AGB stars with e-MERLIN. For the brightest masers, a beaming solid angle in the order of $\Delta \Omega \sim 1.5 \times 10^{-3}$ sr was found. For some AGB stars, the geometrical masing mechanism seemed to be amplification bounded, but also hints of matter-bounded amplification were found for some sources. Line-profile analysis by Vlemmings & van Langevelde (2005) revealed a $\Delta \Omega \sim 10^{-2} - 10^{-3}$ sr for water masers around AGB stars. A line-profile analysis of the extremely strong water masers around Orion-KL, yielded beaming solid angles as low as $\Delta \Omega \sim 10^{-3}$ sr (Nedoluha & Watson 1991).

Water masers have been observed for their polarization on many occasions, both around evolved stars (Vlemmings et al. 2006b) and around star forming regions (Garay et al. 1989). The most striking observations were the early observations of the flaring, very strong "super" water maser (Garay et al. 1989; Fiebig & Güsten 1989). Garay et al. (1989) report the 7-year monitoring of the polarization characteristics of the most powerful water maser feature of Orion-KL. Brightness temperatures over $T_b = 10^{15}$ K were observed with associated maser fluxes of $T_b \Delta \Omega \leq 10^{10}$ (Nedoluha & Watson 1991). High degrees of linear polarization up to 75% were observed. Analysis of the relation between the polarization fraction and the maser brightness for the highly polarized strongest feature, shows a decline of polarization with the maser-intensity. This is in line with an anisotropically pumped maser at high brightness beyond $(T_b \Delta \Omega)_{\text{mag sat}}$.

Circular polarization up to $\sim 2\%$ for these strong maser flares was also detected (Fiebig & Güsten 1989). Fiebig & Güsten (1989) also included the masers of a number of other star-forming regions in their sample. Stokes-V spectra show the characteristic S-shaped spectra, which is an anomaly for water masers that we found only to occur for preferably pumped water masers, where one hyperfine transition dominates the others. The spread in circular polarization fractions can be explained by the variable projection of the magnetic field ($10 - 100 \text{ mG}$) onto the propagation axis, and variable magnetic fields in the sources. Vlemmings et al. (2001, 2002) investigated the circular polarization of masers occurring in the circumstellar envelopes of late type stars. Magnetic fields around these masers are expected to be strong ($\sim \text{G}$), and circular polarization should thus be detectable in the stronger maser features. Circular polarization up to 13% is found, but this concerns a single outlier. The weaker masers show circular polarization up to 6%, which can be generated by a magnetic field of $\sim 400 \text{ mG}$. Generally, circular polarization seems to decline with increasing maser-brightness, but this might an effect of the of the detection limit.

A large sample of polarization observations of water masers comes from VLBI measurements around the high-mass star forming region W75N (Surcis et al. 2011). Here, for 17 maser features, significant linear and circular polarization is found. Linear polarization tends to be small $< 10\%$, but relatively high circular polarization ($< 3\%$) is found. In part, the large fraction of highly circularly polarized masers is due to observational bias against weakly polarized masers. A similar scatter analysis as performed for the SiO maser sample of Herpin et al. (2006), assuming that the water maser is pumped isotropically with no hyperfine-preference, at a thermal width of $\Delta v_{th} = 1 \text{ km/s}$, and the magnetic field is randomly oriented per maser, shows that a magnetic field of $\sim 200 \text{ mG}$ best reproduces the obtained linear-to-circular polarization distribution (see Fig. 14).

6. Conclusions

In this paper, we present CHAMP, a program that performs one-dimensional numerical maser polarization simulations of non-paramagnetic molecules. Simulations are possible for masers with arbitrary high angular momentum transitions. Also, multiple close-lying hyperfine transitions that contribute to the same maser can be included in our modeling. Simulation of the polarization of complex and highly excited masers will become more relevant in the era of ALMA and its full polarization capabilities.

Illustrative calculations of the SiO and water masers reveal the following general observations about the polarization of masers

- Linear polarization is mostly absent when the rate of stimulated emission is smaller than the isotropic decay $(T_b \Delta \Omega < < Article number, page 23 of 48
Fig. 15: The $A_{FF'}$ coefficients of an isotropically pumped water maser at $B = 20$ G as a function of the magnetic field-propagation direction angle $\cos \theta$. Subfigures denote different thermal widths $v_{th} = (a) 0.6 \text{ km/s}$, (b) 1.0 km/s and (c) 2.0 km/s. Plots are given for different $\log(R/g\Omega)$. The LTE solutions (constant over $\cos \theta$) of the different hyperfine sub-transitions are denoted with a dotted line.

$T_{b} \Delta \Omega_{sat}$). If polarization occurs for such weak masers, alternative polarizing mechanisms are in play. Circular polarization however, is present for such weak masers and comes from the Zeeman effect. An LTE analysis of the Zeeman effect will give a reasonable estimate of the polarizing effects, but this approximation worsens with the maser brightness. The 90° polarization angle flip at the magic angle, $\theta_{m}$, predicted by GKK73, is sharp only in the limit, $g\Omega \gg R$, when the magnetic precession rate is far greater than the rate of stimulated emission. However, for $g\Omega/R < 100$, the 90°-flip blunts and significant polarization is found also at propagation at the magic angle, $\theta_{m}$.

Anisotropic pumping of a maser can lead to arbitrarily high linear polarization fractions, but will only be weakly associated with circular polarization. Characteristic for an anisotropically pumped weak maser, is a linear growth in linear polarization fraction as a function of the maser-brightness.

Incident polarized seed radiation will maintain its polarization degree up until the rate of stimulated emission becomes comparable to the magnetic precession rate. From here, it will slowly converge to the standard isotropic polarization solution.

Circular polarization fractions are highest in the region where the rate of stimulated emission is in the same order as the magnetic precession rate. Circular polarization in this regime is associated with high linear polarization. Weak masers are weakly polarized, with a polarizing effect akin to thermal polarization.

Overall polarization will drop strongly between the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions. The polarization of transitions with increasing angular momentum will gradually deteriorate.

A cursory overview of existing maser polarization observations leads to a reinforcement of the idea that highly-polarized SiO masers are the product of anisotropic pumping. A similar mechanism probably underlies the highly polarized water “super” maser at Orion that also showed a drop in polarization with maser-brightness, as predicted by our theories. We show that comparing randomly ($\theta$ and $T_{b} \Delta$) generated (at fixed $B$) $p_{L} - p_{V}$ scatter-plots to the observationally obtained $p_{L} - p_{V}$ scatter, can be a promising method to ascertain the overall magnetic field strength of a region with a large number of masers. Finally, we have found the variation of the polarization angle across a maser spectrum can be used as a proxy for the rate of stimulated emission. This would be an important additional measure to deter-
mine the maser saturation level and beaming angle, which are
difficult to observe directly.

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Appendix A: Appended figures
Fig. A.1: Simulations of an isotropically pumped SiO maser. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.2: Simulations of an isotropically pumped SiO maser. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.3: Simulations of an isotropically pumped SiO maser. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.4: Simulations of a SiO maser with 10% polarized seed radiation. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.5: Simulations of a SiO maser with 10% polarized seed radiation. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.6: Simulations of a SiO maser with 10% polarized seed radiation. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.7: Simulations of a SiO maser with 50% polarized seed radiation. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.8: Simulations of a SiO maser with 50% polarized seed radiation. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.9: Simulations of a SiO maser with 50% polarized seed radiation. Linear polarization fraction (a,d,g) and angle (b,e,h) and circular polarization fraction (c,f,i). Magnetic field strength and transition angular momentum are denoted inside the figure.
Fig. A.10: Simulations of $J = 1\rightarrow 0$ SiO masers with anisotropic pumping direction parallel to the magnetic field. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 10$ G for (d,e,f).
Fig. A.11: Simulations of $J = 2 - 1$ SiO masers with anisotropic pumping direction parallel to the magnetic field. Linear polarization fraction (a,d,f) and angle (b,e,h) and circular polarization fraction (c,f,g). Magnetic field strengths are $B = 100 \, \text{mG}$ for (a,b,c), $B = 1 \, G$ for (d,e,f) and $B = 10 \, G$ for (g,h,i).
Fig. A.12: Simulations of $J = 3 - 2$ SiO masers with anisotropic pumping direction parallel to the magnetic field. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.13: Simulations of $J = 1 - 0$ SiO masers with anisotropic pumping direction perpendicular to the magnetic field and propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 10$ G for (d,e,f).
Fig. A.14: Simulations of $J = 2 - 1$ SiO masers with anisotropic pumping direction perpendicular to the magnetic field and propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.15: Simulations of $J = 3 - 2$ SiO masers with anisotropic pumping direction perpendicular to the magnetic field and propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.16: Simulations of $J = 1 - 0$ SiO masers with anisotropic pumping direction at 45° from the magnetic field in the plane perpendicular to the propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.17: Simulations of $J = 2 - 1$ SiO masers with anisotropic pumping direction at 45° from the magnetic field in the plane perpendicular to the propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.18: Simulations of $J = 3 - 2$ SiO masers with anisotropic pumping direction at 45° from the magnetic field in the plane perpendicular to the propagation direction. Linear polarization fraction (a,d) and angle (b,e) and circular polarization fraction (c,f). Magnetic field strengths are $B = 100$ mG for (a,b,c) and $B = 1$ G for (d,e,f).
Fig. A.19: Polarization of a water maser isotropically pumped at $B = 20$ mG. Linear polarization fraction (a,d,g), angle (b,e,h) and circular polarization fraction (c,f,i). Thermal width used $v_{th} = 0.6$ km/s (a,b,c), 1 km/s (d,e,f) and 2 km/s (g,h,i).
Fig. A.20: Polarization of a water maser isotropically pumped at $B = 100$ mG. Linear polarization fraction (a,d,g), angle (b,e,h) and circular polarization fraction (c,f,i). Thermal width used $v_{th} = 0.6$ km/s (a,b,c), 1 km/s (d,e,f) and 2 km/s (g,h,i).
Fig. A.21: Polarization of a water maser with 10% polarized seed radiation at $B = 20 \text{ mG}$. Linear polarization fraction (a,d,g), angle (b,e,h) and circular polarization fraction (c,f,i). Thermal width used $v_{th} = 0.6 \text{ km/s} \ (a,b,c)$, $1 \text{ km/s} \ (d,e,f)$ and $2 \text{ km/s} \ (g,h,i)$. 
Fig. A.22: Polarization of a water maser with 50\% polarized seed radiation at $B = 20$ mG. Linear polarization fraction (a,d,g), angle (b,e,h) and circular polarization fraction (c,f,i). Thermal width used $v_{th} = 0.6 \text{ km/s} (a,b,c), 1 \text{ km/s} (d,e,f) \text{ and } 2 \text{ km/s} (g,h,i)$. 
Paper III

PORTAL: Three-dimensional polarized (sub)millimeter line radiative transfer

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PORTAL: Three-dimensional polarized (sub)millimeter line radiative transfer

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ABSTRACT

Context. Magnetic fields are important to the dynamics of many astrophysical processes and can typically be studied through polarization observations. Polarimetric interferometry capabilities of modern (sub)millimeter telescope facilities have made it possible to obtain detailed velocity resolved maps of molecular line polarization. To properly analyze these for the information they carry regarding the magnetic field, the development of adaptive three-dimensional polarized line radiative transfer models is necessary.

Aims. We aim to develop an easy-to-use program to simulate the polarization maps of molecular and atomic (sub)millimeter lines in magnetized astrophysical regions, such as protostellar disks, circumstellar envelopes, or molecular clouds.

Methods. By considering the local anisotropy of the radiation field as the only alignment mechanism, we can model the alignment of molecular or atomic species inside a regular line radiative transfer simulation by only making use of the converged output of this simulation. Calculations of the aligned molecular or atomic states can subsequently be used to ray trace the polarized maps of the three-dimensional simulation.

Results. We present a three-dimensional radiative transfer code, POlarized Radiative Transfer Adapted to Lines (PORTAL), that can simulate the emergence of polarization in line emission through a magnetic field of arbitrary morphology. Our model can be used in stand-alone mode, assuming LTE excitation, but it is best used when processing the output of regular three-dimensional (nonpolarized) line radiative transfer modeling codes. We present the spectral polarization map of test cases of a collapsing sphere and protoplanetary disk for multiple three-dimensional magnetic field morphologies.

Key words. radiative transfer – polarization – line: formation – magnetic fields – methods: numerical – ISM: magnetic fields

1. Introduction

Magnetic fields permeate the Universe and often play an important role in the dynamics of astrophysical processes (Crutcher 2012; Vlemmings 2013; Crutcher & Kemball 2019). It is difficult to directly observe magnetic fields; one typically has to use the polarization properties of the observed light (e.g., Han 2017). For (sub)millimeter interferometers, such as ALMA, magnetic field detection is done mostly through dust (e.g., Hull et al. 2017) and line polarization observations (e.g., Vlemmings et al. 2017). However, it has recently become increasingly clear that dust polarization does not always faithfully trace the magnetic field morphology, but instead it can be affected by processes such as self-scattering (Kataoka et al. 2015, 2017). Line polarization observations are not affected by such processes, and therefore they likely trace the magnetic field structure of the observed region. However, to interpret line polarization observations, modelers have to defer to the theory of Goldreich & Kylafis (1981), which relies on the large velocity gradient (LVG) approximation, and therefore they cannot treat three-dimensional (3D, magnetic field) structures.

In this paper, we present Polarized Radiative Transfer Adapted to Lines (PORTAL)\(^1\), which is a 3D polarized radiative transfer code that simulates the emergence of polarization in the emission of atomic or molecular (sub)millimeter lines. PORTAL can be used in stand-alone mode or process the output of regular 3D radiative transfer codes. We are able to model the emergence of linear polarization in (sub)millimeter lines through two main approximations: (i) the strong magnetic field approximation and (ii) the anisotropic intensity approximation. We show that both of them are valid in the majority of astrophysical regions.

Regular radiative transfer models of astrophysical environments only take the total radiation intensity and its effect on the local isotropic populations into account (van der Tak et al. 2007; Brinch & Hogerheijde 2010). The local populations are determined by the balance of collisional and radiative events that both excite and de-excite the populations of the molecular and atomic species. Collisional events are isotropic and a function of the density and temperature of the environment. At the outset, for unaligned quantum states, spontaneous emission events are also isotropic, that is, the direction of the next spontaneously emitted photon of a certain molecule is random. The probability of absorption of those randomly directed photons, however, need not be isotropic (Goldreich & Kylafis 1981). Anisotropy in the local absorption of photons aligns the quantum states that are associated with the line-transition, which in turn leads to polarization in the emission (Morris et al. 1985; Degl’Innocenti & Landolfi 2006). By considering the directional dependance of the photon-escape probability in a medium with an anisotropic velocity gradient, Goldreich & Kylafis (1981) showed that radiation emitted from such a system is partially polarized. This effect is known in the literature as the Goldreich-Kylafis (GK) effect. It is strongest for lines with optical depth

\(^1\) The source code of PORTAL is available on Github at https://github.com/blankhaar/PORTAL.
Numerical modeling of the GK effect has been based on the theory presented in Goldreich & Kylafis (1982). In such models, the perpendicular and parallel components (with respect to the projected magnetic field direction) of the radiation field are propagated through a medium with an anisotropic velocity gradient. The velocity-gradient is so strong that the LVG approximation can be applied. The LVG escape probability is a function of the velocity-gradient and is therefore anisotropic. This leads to alignment in the molecular or atomic states associated with the transition under investigation. Because of this, the emitted radiation is partially polarized. Deguchi & Watson (1984) later showed that in order to accurately model the GK effect, it is vital to perform comprehensive (polarized) excitation modeling of the molecular or atomic quantum states and also of the ones that are not associated with the transition under investigation. Cortes et al. (2005) showed that an external anisotropic radiation source, such as a nearby stellar object, can enhance the polarized emission significantly. These numerical models only considered the one-dimensional propagation of polarized radiation, and the representation of the radiation field in perpendicular and parallel components is only valid when the magnetic field direction is constant over the investigated path. Furthermore, because of its heavy reliance on the LVG approximation, numerical modeling based on Goldreich & Kylafis (1982) cannot only consider the introduction of anisotropy in the escape probability through an anisotropic velocity gradient. In light of recently developed polarimetric capabilities of interferometers, such as ALMA, these types of approximations cannot be afforded anymore. Rather, one needs comprehensive modeling of the 3D radiative transfer and its anisotropy, taking both the spatial and velocity structure into account for the astrophysical region under investigation as well as the 3D structure of the magnetic field.

In this paper, we demonstrate how such modeling can be attained. By using two (main) approximations, we show that regular (nonpolarized) radiative transfer codes can be extended with polarization capabilities. In Sect. 2, we introduce these approximations and show their simplifying impact on the theory of line polarization. In Sect. 3, we show how our PORTAL code provides the option of computing the emerging polarization using the output from a regular 3D radiative transfer code, in particular LIME (Brinch & Hogerheijde 2010). In Sect. 4, we present the capabilities of PORTAL through the simulation of the emergence of polarization in a protoplanetary disk and a collapsing sphere. We discuss our results in Sect. 5 and conclude in Sect. 6.

### 2. Theory

We describe the introduction of anisotropy in the molecular or atomic populations through an anisotropic radiation field using the formalism of Degl’Innocenti & Landolfi (2006). We make the following approximations:

First, we assume the magnetic field precession rate is way higher than collisional and radiative rates. We call this the strong magnetic field approximation. The magnetic precession rate is in the order of \( \frac{\text{s}^{-1}}{\text{MG}} \) for dymagnetic (i.e., weakly magnetizable) molecules. Typical collisional rates are on the order of \( 10^{-5} \, \text{cm}^{-3} \) s\(^{-1} \) and radiative rates are on the order of \( 10^{-4} \, \text{s}^{-1} \) for a transition at 100 GHz with a dipole moment of 0.1 Debye, which is shone upon isotropically by 400 Kelvin black-body radiation. Therefore, for almost all molecules, magnetic field interactions already dominate at very weak magnetic fields (\( \mu \text{G} \)). Under the assumption of a strong magnetic field, many terms in the polarized density-equations can be dropped (Degl’Innocenti & Landolfi 2006). The strong magnetic field approximation is also invoked by Goldreich & Kylafis (1981). In Sect. 5.2 we discuss special cases where a dominant magnetic field cannot be assumed.

Second, we assume that only the total intensity of the radiation has an influence on the (polarized) populations of the molecular or atomic states. This is a reasonable assumption if the polarization fraction is low, which is corroborated by polarization observations of molecular emission lines. We refer to this approximation as the anisotropic intensity approximation. We discuss the validity of the anisotropic intensity approximation in more detail in Sect. 5.1, where we also compare our modeling with that of Goldreich & Kylafis (1981), who take the influence of both the Stokes-\( I \) and -\( Q \) parameters on the alignment of the molecular states into account.

These assumptions lead to significant simplifications in the theory behind the alignment of molecular and atomic quantum states and the radiation with which they interact. They allow for the implementation of such a model as an extension to a regular line radiative transfer code. In the following, we introduce the formalism that we used to model the alignment to molecular or atomic quantum states. After this, we outline how aligned quantum states influence the propagation of polarized radiation.

#### 2.1. Polarized statistical equilibrium equations

The polarizing mechanism we focus on is the anisotropic radiation field. Mathematically, anisotropy in the radiation field that affects the quantum state alignment is most easily described in terms of an irreducible tensor-element expansion. The irreducible tensor components of the radiation field, which are in direction \( \Omega \) and at the position \( r \), are obtained as (Landi Degl’Innocenti 1984)

\[
J^K_Q(r, \nu, \Omega) = \sum_j T^K_\Omega(j, \Omega) S_j(r, \nu, \Omega),
\]

where \( K \) represents the irreducible tensor rank and \( Q \) is its projection, \( S_j(\nu, \Omega) \) are the Stokes-parameters at frequency \( \nu \), and \( j \) runs over all four Stokes parameters. We define the Stokes parameters in relation to the complex electric field vector components as

\[
I = |E_x|^2 + |E_y|^2, \quad Q = \Re \{E_x E_y^\ast\}, \quad U = -2 \Im \{E_x E_y^\ast\}, \quad V = 2 \Re \{E_x E_y^\ast\},
\]

where \( x \) and \( y \) refer to the axes that are perpendicular to the propagation direction, \( z \), and each other. In this work, we consistently chose the axis of \( x \) along the rejection of the (local) magnetic field direction from the propagation direction. The transformation coefficients \( T^K_\Omega(j, \Omega) \) are defined in Eq. (A6) from Landi Degl’Innocenti (1984). If we only consider alignment by Stokes-\( I \) radiation and if we furthermore assume a dominant magnetic field, only the \( K = 0, 2 \) and \( Q = 0 \) components are of interest (Degl’Innocenti & Landolfi 2006). Under these
conditions, the irreducible tensor components of the radiation field reduce to

\[ J^0_v(r, v, \Omega) = I(r, v, \Omega), \]

\[ J^2_v(r, v, \Omega) = \frac{1}{2} J^0_v(r, v, \Omega), \]

where \( \Omega = (\theta, \phi) \) is expressed in terms of the inclination and azimuth angles that are gauged with respect to the magnetic field direction. The quantity \( P_2(\mu) \) is the second-order Legendre polynomial and \( \mu = \cos \theta \). The solid-angle integrated tensors at position \( r \) are readily obtained as

\[ P_0^0(r, \nu) = \frac{1}{4\pi} \int_{-1}^{1} d\mu \int_{0}^{2\pi} d\phi \ I(r, \nu, \cos(\mu), \phi), \]

\[ P_2^0(r, \nu) = \frac{1}{4\pi \sqrt{2}} \int_{-1}^{1} d\mu \int_{0}^{2\pi} d\phi \ I(r, \nu, \cos(\mu), \phi). \]

In the following, we refer to the ratio \( P_2^0(r, \nu)/P_0^0(r, \nu) \) as the relative alignment of the radiation field. For an isotropic radiation field \( (I(r, v, \Omega) = I(r, v)) \), it should be noted that only the (isotropic) \( P_0^0(r, \nu) \)-term survives.

Just as for the radiation field, we represent the molecular or atomic quantum states as irreducible tensor elements in order to most optimally utilize their symmetry properties. Quantum states are denoted as \( \rho^K(J) \), where \( K \) is the rank of the irreducible tensor element and \( Q \) is its projection. The total angular momentum of the associated quantum state is \( J \) and all other quantum numbers characterizing the quantum state are collected in \( \alpha \). The rank \( K \) is positive and restricted to values of \( \leq 2J \). The elements \( \rho^K(J) \) of the population tensor relate to the alignment of the quantum state and the \( K = 0 \) element relates to the population of the quantum state. Under the assumption of a strong magnetic field, we can neglect all but the \( Q = 0 \) projection elements. Because of the symmetry of the radiation field, we only have to take elements into account where \( K \) is even. Degl’Innocenti & Landolfi (2006) presented the statistical equilibrium equations for the polarized quantum state \( \rho^K(J) \) under the following conditions:

\[ \rho^K_J(\alpha J) = \sum_{\alpha J l, k l} \rho^K_{\alpha J l, k l} \left[ I_{l, k l}^{\alpha l, k l} C_{l, k l}^{(C_0)} \delta_{l, k l} + \frac{1}{J} \delta_{k l} \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \right] + \sum_{\alpha J l, k l} \rho^K_{\alpha J l, k l} \left[ I_{l, k l}^{\alpha l, k l} \delta_{l, k l} \delta_{l, k l} + \frac{1}{J} \delta_{l, k l} \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \right] + \frac{1}{J} \delta_{l, k l} \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \delta_{k l} \delta_{l, k l} + \rho^K_0(\alpha J) \left[ I_{l, k l}^{\alpha l, k l} \delta_{l, k l} + r_{l, k l} \delta_{k l} \delta_{l, k l} + \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \right] \delta_{k l} \delta_{l, k l} + \rho^K_0(\alpha J) \left[ I_{l, k l}^{\alpha l, k l} \delta_{l, k l} + \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \right] \delta_{k l} \delta_{l, k l} \delta_{k l} \delta_{l, k l} \right]. \]

In Eq. (5), the rate of radiative absorption events toward the \( \rho^K_0(\alpha J) \) from lower level \( \rho^K_{\alpha J l, k l} \) is given by \( I_{l, k l}^{\alpha l, k l} \) and the collisional contribution is \( \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \). The rate of stimulated and spontaneous emission events toward the \( \rho^K_0(\alpha J) \) from upper level \( \rho^K_{\alpha J l, k l} \) is given by \( I_{l, k l}^{\alpha l, k l} \) and \( \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \), and the collisional contribution is \( \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \). The rates of absorption, stimulated emission, and spontaneous emission from the level \( \rho^K_0(\alpha J) \) to all other levels is given by \( I_{l, k l}^{\alpha l, k l} \) and \( \left( C_{l, k l}^{(C_0)} \right)^0_{l, k l} \). Finally, the collisional depolarization rates are \( D^K(\alpha J) \). More detailed expressions for the radiative rates from Eq. (5) can be found in equations 7.20 from Degl’Innocenti & Landolfi (2006). By assuming a steady-state, \( \rho^K_0(\alpha J) = 0 \), the statistical equilibrium equations can be solved as a linear set of equations. The solution yields the quantum state populations, including their relative alignment.

We should note that the statistical equilibrium equations of Eq. (5) are isomorphic to those presented in Deguchi & Watson (1984). While Deguchi & Watson (1984) set up the statistical equilibrium equations in the standard angular momentum basis \( |jm\rangle \), where \( j \) is the total angular momentum of the eigenstate and \( m \) is its projection, we worked in a spherical tensor representation. We refer to Degl’Innocenti & Landolfi (2006) for a detailed discussion on the relation between the two representations. We chose to work in a spherical tensor representation because of its symmetry properties. The properties of the spherical tensor expansion of both the molecular (or atomic) states and the radiation are such that truncation of higher-order \( K \)-terms in the \( \rho^K_0(\alpha J) \)-expansion can be done with minimal loss of accuracy in the description of the statistical equilibrium equations for our system. Such truncation is not possible in the representation that Deguchi & Watson (1984) used, and it results in a rapid and unmitigable increase in computational effort when high angular momentum states are considered.

### 2.2. Polarized radiative transfer

After having obtained the (aligned) quantum state populations, we can evaluate their impact on the radiation propagation. Because of the strong magnetic field, (locally) only Stokes-\( Q \) radiation is produced. The propagation of radiation around frequency, \( \nu_{\alpha'J'\alpha J} \), associated with a transition \( \alpha'J' \rightarrow \alpha J \), can be described by

\[
\frac{d}{ds} I_{\nu} = -\kappa_{\nu}^{\alpha'J'\alpha J} I_{\nu} + \epsilon_{\nu}^{\alpha'J'\alpha J},
\]

where \( I_{\nu} = [I_{\nu Q}, I_{\nu V}] \) is the Stokes vector and the propagation matrix

\[
\kappa_{\nu}^{\alpha'J'\alpha J} = \begin{bmatrix}
\eta_{\nu}^{\alpha'J'\alpha J}(\nu) & \eta_{\nu}^{\alpha'J'\alpha J}(\nu) & 0 & \eta_{\nu}^{\alpha'J'\alpha J}(\nu) \\
\eta_{\nu}^{\alpha'J'\alpha J}(\nu) & \eta_{\nu}^{\alpha'J'\alpha J}(\nu) & 0 & 0 \\
0 & 0 & \eta_{\nu}^{\alpha'J'\alpha J}(\nu) & 0 \\
0 & 0 & 0 & \eta_{\nu}^{\alpha'J'\alpha J}(\nu)
\end{bmatrix}
\]

is significantly simplified if one assumes a dominant magnetic field. Because we only consider diamagnetic molecules with Zeeman splitting that are far weaker than the thermal broadening, the production of Stokes-\( V \) radiation through the Zeeman effect is negligible and we set \( \eta_{\nu}^{\alpha'J'\alpha J}(\nu) \rightarrow 0 \). Thus, in PORTAL, we only consider the propagation of linearly polarized radiation. The expressions for the \( \eta \)-elements of Eq. (7) are (Landi Degl’Innocenti 1984)

\[
\eta_{\nu}^{\alpha'J'\alpha J}(\nu) = \frac{\hbar \nu_{\alpha'J'\alpha J}}{4\pi} B_{\alpha'J'\alpha J} \varphi_{\nu}^{\alpha'J'\alpha J}(\nu) \left\{ \left( N_{\alpha'J'} - N_{\alpha J} \right) \frac{|J'|}{|J|} + \left( \frac{J'2}{J} \right) N_{\alpha'J'} \frac{2}{2} \sigma_{\nu}^{\alpha'J'\alpha J}(\nu) \right\} \times \frac{3 \cos^2 \theta - 1}{2 \sqrt{2}}.
\]
where $N_{aJ} = N(J) \, \rho_0(\alpha J)$ is the number density of the quantum state $aJ$, and $\phi_{\nu \alpha, v',r',aJ}$ denotes the normalized line-profile centered at $v_{\nu \alpha, v',r',aJ}$ in frequency-space. The symbols

$$w_{\nu \alpha}^{(2)} = (-1)^{J_1 + J_2} \frac{3 \sin^2 \theta}{2 \sqrt{2}},$$

were introduced by Landi Degl’Innocenti (1984). The quantity between curly brackets is a Wigner-6j symbol (Biedenharn et al. 1981). We use the short-hand notation $\sigma_{\nu \alpha}^2(aJ) = \rho_0^2(\alpha J)/\rho_0^2(\alpha J)$ for the relative alignment of the quantum state $aJ$. The spontaneous emission events in the Monte Carlo radiative transfer equations of Eq. (6) are represented in the $\epsilon$-vector. The spontaneous emission contribution to the Stokes-$I$ is zero in the strong magnetic field limit we consider. The Zeeman effect for diamagnetic molecules is way smaller than the thermal broadening, so we can set $\sigma_{\nu \alpha}^2(aJ) \rightarrow 0$. The contributions to the Stokes-$I$ and $Q$ parameters are (Landi Degl’Innocenti 1984)

$$\eta_{\nu \alpha}^{F, \phi_{\nu \alpha}}(v) = - \frac{h v_{\nu \alpha}}{4 \pi} \frac{N_{aJ}}{\sigma_{\nu \alpha}^2(aJ) \rho_{\nu \alpha, v',r',aJ}(v)}$$

and

$$\eta_{\nu \alpha}^{F, \phi_{\nu \alpha}}(v) = \frac{h v_{\nu \alpha}}{4 \pi} \frac{N_{aJ}}{\sqrt{3[J + 1]} \frac{1}{J} \frac{1}{J'} \frac{1}{J'}}.$$  

$$w_{\nu \alpha}^{(2)} = (-1)^{J_1 + J_2} \frac{3 \sin^2 \theta}{2 \sqrt{2}},$$

In the following, we outline in more detail how we implemented PORTAL. In the first paragraph, we discuss setting up the polarized statistical equilibrium equations using the output of a line radiative transfer code. In order to do this, we dedicated most of our attention to the mapping of the local anisotropy of the radiation fields. In the second paragraph, we detail the polarized radiative transfer that was performed in the polarized ray-tracing. Especially for simulations with nonuniform magnetic fields, it is crucial to pay extra attention to the frame of reference of the polarized radiation and the proper way to relate different frames of reference.

In PORTAL, we used the anisotropic intensity approximation and formulated the polarized statistical equilibrium equations in terms of irreducible tensor elements. This approach differs from other efforts such as LinePol (Kuiper et al. 2020), which builds on LIME, is optimized for CO, and uses the formalism of Goldreich & Kylafis (1982) to describe the propagation of polarized radiation and its interaction with the molecular medium. LinePol takes a polarization modes of the radiation into account and uses a polarized accelerated lambda iteration scheme to obtain the state-populations in the simulation. At minimal cost to the accuracy of our results (see Secs. 3.1 and 5.1), the approximations in PORTAL speed up the simulation tremendously and lead to the possibility to treat more complex systems. PORTAL allows for complex geometries, magnetic field structures, and the treatment of molecules with extensive energy structures.

### 3.1. Polarized statistical equilibrium equations

The quantum state alignment is dependent on the local anisotropy of the radiation field, so it is important to obtain a good angular sampling of the radiation field at the location of the simulation nodes. Different angular integrations of Eq. (4) for the case of an internal source of radiation (e.g., a central stellar object) and the case of no internal radiation source were used. For the latter, the local angular integration was performed as

$$f_{\alpha}^0(r, v) = \frac{1}{4\pi} \sum_{i=1}^{N_r} w^d_\mu \sum_{j=1}^{N_{\phi_\mu}(\mu)} w^d_\phi f(r, v, \mu, \phi_\mu),$$  

$$f_{\alpha}^0(r, v) = \frac{1}{4\pi} \sum_{i=1}^{N_r} w^d_\mu \sum_{j=1}^{N_{\phi_\mu}(\mu)} w^d_\phi f(r, v, \mu, \phi_\mu)$$

where $\mu_i$ and $w^d_\mu$ are the coordinates and the weights, which were taken from the $N_\mu$-point Gaussian quadrature rule. The integration over $\phi$ was performed over $N_\phi(\mu) \approx \sqrt{1 - \mu^2}$ equidistant points all with weight $2\pi/N_\phi$.

In the case of an internal radiation source, it should be appreciated that the solid angle associated with the radiation coming from this internal source is well-defined. Therefore, the solid angle integration was divided up into rays coming from the internal radiation source; the number of rays is proportional to the solid-angle of the internal source $\Delta \Omega = \pi(|r|/R)^2$ and all of the other rays were distributed equally over the remaining sphere surface.

The local radiation field parameters of a node at the position $r$, summarized in $f_{\alpha}^0(r, v)$ and $f_{\alpha}^0(r, v)$, were obtained by ray tracing $N$ rays with directions $k_{\theta, \phi}$ to that node. The parameters $\mu$ were chosen with respect to the magnetic field direction \(\mathbf{b} \cdot k_{\theta, \phi} = \mu\). The angles $\phi$ were gauged with respect to a canonical direction not parallel to the magnetic field. The choice of the canonical direction is free as the angle $\phi$ is integrated out.
The quantum state populations and alignment were obtained from the statistical equilibrium equations (SEE) given in Eq. (5). The SEE are a balance of the radiative and collisional transition events. The radiative transition events are dependent on local parameters for the (an)isotopic radiation field at frequencies of all of the allowed transitions and their associated Einstein coefficients. Collisional rates are dependent on the temperature-dependent collisional cross-sections and (local) number densities of the relevant collisional partners. The relevant Wigner coupling symbols were calculated using the WIGXJPF package (Johansson & Forssen 2016). The SEE were formulated in terms of a set of linearly dependent equations and were subsequently solved via an LQ decomposition (using the LAPACK libraries, Anderson et al. 1999) under the following physical constraint: \(\sum_{ij} \gamma_{ij} n_i n_j = 1\). The solutions also included the isotropic populations that were compared to the LIME-output. We found that neglecting the quantum state alignment terms, \(n_i\) and \(n_q\) as well as \(\epsilon_1\) and \(\epsilon_0\) are constant. It is then straightforward to evaluate the integrals inside the evolution operator as well as the integral over the evolution operator: \(\int \mathrm{d}s' \mathcal{O}(s, s')\). Having done so, the propagation of the Stokes-\(I\) and -\(Q\) within a single cell is given by

\[I(s) = o_I \epsilon_I + o_Q \epsilon_Q + [\cosh(n_Q s)I(0) - \sinh(n_Q s)Q(0)] e^{-\eta_Q s},\]  
\[Q(s) = o_Q \epsilon_I + o_I \epsilon_Q + [\cosh(n_I s)Q(0) - \sinh(n_I s)I(0)] e^{-\eta_I s},\]

where

\[o_I = \frac{n_I}{n_I} - \frac{n_Q}{n_Q} \left(1 - \frac{\cosh(n_I s) + \frac{n_Q}{n_I} \sinh(n_I s)}{\cosh(n_Q s) + \frac{n_I}{n_Q} \sinh(n_Q s)} e^{-\eta_I s}\right),\]

\[o_Q = -\frac{n_Q}{n_I} \frac{n_Q}{n_Q} \left(1 - \frac{\cosh(n_Q s) + \frac{n_I}{n_Q} \sinh(n_Q s)}{\cosh(n_I s) + \frac{n_Q}{n_I} \sinh(n_Q s)} e^{-\eta_Q s}\right),\]

are the factors that were obtained from integrating the elements of the evolution operator.

### 4. Simulations

We applied PORTAL to known astrophysical problems. We consider the standard problem of a spherically symmetric collapsing molecular cloud, and we investigate the emergence of polarization in molecular lines through an anisotropic radiation field in a standard protoplanetary disk system. It should be noted that neither of these problems illustrate the full 3D capabilities of PORTAL. We focus, however, on these models because of their more straightforward interpretation and we leave more complex modeling for further work.

#### 4.1. Collapsing spherical cloud

A benchmark problem in radiative transfer modeling, which furthermore allows for local anisotropy to establish itself in the radiation field, is the problem of a collapsing spherical cloud. We consider the emergence of polarization in HCO\(^+\) lines. The density, velocity, and temperature distribution are taken from the Shu (1977) collapse model, using the same parameters as van Zadelhoff et al. (2002). Only the ground vibrational state of HCO\(^+\) is considered. We assume a uniform HCO\(^+\) abundance of \(10^{-9}\) and assume constant turbulent broadening of 200 m s\(^{-1}\). We assume that a strong radial magnetic field (origin: center of mass) permeates the cloud.

First of all, an overview of the relevant isotropic and anisotropic interactions is instrumental to an eventual discussion of the quantum state alignment and radiation polarization characteristics. We report the cumulative radiative and collisional rates of the \(J=2\) and \(J=3\) level of HCO\(^+\) in Fig. 1. Of the different interactions, only stimulated emission and absorption are anisotropic interactions. Using the spherical symmetry of the collapsing sphere-problem, we only plotted the rates as a function of the distance to the center. We observe that for the

---

\(\mathcal{O}(s, s') = e^{U(s, s')} \mathcal{O}(s, 0) e^{U(s, 0)}\)

\(\mathcal{O}(s, 0)\) is the evolution operator (see Chap. 8 of Landi Degl’Innocenti 1984). The propagation for each crossed cell was considered, and within such a propagation, the coefficients \(n_i\) and \(n_q\) as well as \(\epsilon_1\) and \(\epsilon_0\) are constant. It is then straightforward to evaluate the integrals inside the evolution operator as well as the integral over the evolution operator: \(\int \mathrm{d}s' \mathcal{O}(s, s')\). Having done so, the propagation of the Stokes-\(I\) and -\(Q\) within a single cell is given by

\(I(s) = o_I \epsilon_I + o_Q \epsilon_Q + [\cosh(n_Q s)I(0) - \sinh(n_Q s)Q(0)] e^{-\eta_Q s},\)

\(Q(s) = o_Q \epsilon_I + o_I \epsilon_Q + [\cosh(n_I s)Q(0) - \sinh(n_I s)I(0)] e^{-\eta_I s},\)

where

\(o_I = \frac{n_I}{n_I} - \frac{n_Q}{n_Q} \left(1 - \frac{\cosh(n_I s) + \frac{n_Q}{n_I} \sinh(n_I s)}{\cosh(n_Q s) + \frac{n_I}{n_Q} \sinh(n_Q s)} e^{-\eta_I s}\right),\)

\(o_Q = -\frac{n_Q}{n_I} \frac{n_Q}{n_Q} \left(1 - \frac{\cosh(n_Q s) + \frac{n_I}{n_Q} \sinh(n_Q s)}{\cosh(n_I s) + \frac{n_Q}{n_I} \sinh(n_Q s)} e^{-\eta_Q s}\right),\)

are the factors that were obtained from integrating the elements of the evolution operator.

#### 3.2. Polarized radiative transfer

The quantum state populations and alignment obtained from the SEE were used to compute the (polarized) absorption and emission factors for each node in the simulation. The angle \(\theta\) in Eqs. (8)–(9) was obtained from the local magnetic field direction and the ray-trace direction. The ray-trace direction was chosen by defining an inclination angle and azimuth angle. The polarized radiation was gauged with respect to a canonical axis, \(\mathbf{x}_{\text{global}}\), perpendicular to the ray-tracing direction. The local and global Stokes parameters are related as (Degl’Innocenti & Landolfi 2006)

\[\begin{pmatrix} Q_{\text{local}} \\ U_{\text{local}} \end{pmatrix} = \begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ -\sin 2\alpha & \cos 2\alpha \end{pmatrix} \begin{pmatrix} Q_{\text{global}} \\ U_{\text{global}} \end{pmatrix},\]

and \(I_{\text{local}} = I_{\text{global}}\). In Eq. (11), \(\alpha\) is the angle between \(\mathbf{x}_{\text{global}}\) and \(\mathbf{x}_{\text{local}}\) and the local reference axis is the unit vector along the rejection of the local magnetic field direction from the ray-tracing direction.

The local Stokes-parameters were propagated using the polarized radiative transfer equations. Equations (6)–(7) show that only the Stokes-\(Q\) and -\(I\) coefficients are coupled in the polarized radiative transfer. That means that the propagation of the Stokes-\(U\) radiation is simply \(U(s) = U(0)e^{-\eta_U s}\). To evaluate the propagation of the other Stokes parameters, \(i = [U, Q]\), the evolution operator formalism of Degl’Innocenti & Landolfi (2006) was used, where the propagation is described by

\[i(s) = \int_0^s \mathrm{d}s' \mathcal{O}(s, s')e^{(s') + \mathcal{O}(s, 0) i(0)},\]

for example, the dimensionality of the polarized SEE for the first 41 rotational levels of CO reduced from 861 to 151 by setting \(k_{\text{max}} = 6\).
inner regions of the collapsing sphere, collisions become dominant as the density of this regions increases. Even though there is appreciable alignment of the radiation field, the quantum states do not align themselves because of the dominant isotropizing collisions. From about 400 AU, radiative interactions take over as the dominant interaction and the quantum states align themselves. We also give the magnetic precession rate for a magnetic field of 1 mG and 1 µG and note that for a HCO\(^+\) molecule in the collapsing sphere, the magnetic field can be taken to define the symmetry axis when it is \(\sim 10^{-100}\times\) stronger than other interactions. From Fig. 1, we estimate this to be the case at magnetic field strengths of \(\sim 10^{-100}\) µG.

In the same Fig. 1, we plotted the relative anisotropy of the radiation field and the relative alignment of the quantum states \(J = 2\) and \(J = 3\). We note that the radiation anisotropy increases, thus moving away from the collapsing-sphere center. The radiation anisotropy in the collapsing sphere is partly a result of the density structure and partly the result of the velocity structure. Both structures are spherically symmetric, but this spherical symmetry is only manifest when the center is taken as the origin. For any cell that is not located at the center of the collapsing sphere, the radiation field is therefore anisotropic. Higher

anisotropy in the radiation is associated with a stronger alignment of the quantum states.

We report the azimuthally averaged total intensity and polarization fraction of the HCO\(^+\) \(J = 3 - 2\) and \(J = 2 - 1\) transitions in Fig. 2. Indeed, we note that close to the center of the collapsing sphere, the polarization fraction is the lowest and gradually increases when moving outward. Polarization fractions are above 1% for a radial distance greater than 600 AU for the \(J = 3 - 2\) transition and 900 AU for the \(J = 2 - 1\) transition. We report the associated spectra at \(R = 1400\) AU in Fig. 3. We observe that the linear polarization spectra roughly follow the spectral shape of the total intensity.

The polarization angles are oriented in a radial fashion along the magnetic field lines. One should be aware that for a radial magnetic field, the angle between the magnetic field lines and the propagation direction toward the observer is a function of the propagation position. Accordingly, at the magic angle of \(\theta_{\text{magic}} \approx 54.7\) or \(z/R = \frac{1}{\sqrt{3}}\), the propagation elements \(n_\theta\) flip sign and some of the earlier produced polarization is negated.

### 4.2. Protoplanetary disk

The protoplanetary disk is a prime example of an anisotropic astrophysical structure. Both the anisotropy in the density and velocity structure produce a locally anisotropic radiation field. Magnetic fields in the protoplanetary disk have been conjectured through dust-polarization observations (Stephens et al. 2017), and recently, stringent limits have been put on the magnetic field strength through ALMA line circular polarization observations (Vlemmings et al. 2019).

We consider the polarization of \(^{12}\)CO in a general toy model of a protoplanetary disk having a number-density distribution of

\[
n_{\text{H}_2}(r_c, h) = 4 \times 10^{14}\left(\frac{h}{\text{AU}}\right)^{-2.25} e^{-50(h/\text{AU})^2} \text{ m}^{-3},\tag{14}
\]

where \(r_c\) is the radial distance and \(h\) is the height. The disk is assumed to be rotating, resulting in a model velocity-field of

\[
\mathbf{v}(r) = v(\cos \phi \hat{x} - \sin \phi \hat{y}),\tag{15}
\]

where

\[
v = 2.11 \times 10^4\left(\frac{r_c}{\text{AU}}\right)^{-1} \text{ m s}^{-1},
\]
Fig. 3. Spectra of the (polarized) intensity (in Kelvin) of the (a) \( J = 2 - 1 \) and (b) \( J = 3 - 2 \) transitions from a collapsing sphere. The spectra are azimuthally averaged at 1400 AU.

\[ \tan \phi = \frac{y}{x} \]

The temperature is given by

\[ T(r_c) = 400 \left( \frac{r_c}{\text{AU}} \right)^{-1} \text{ K}. \] (16)

Furthermore, we assume a constant CO abundance of \( 10^{-3} \) and a constant turbulent doppler broadening of \( b_{\text{turb}} = 200 \text{ m s}^{-1} \). We only take the vibrational ground-state of \(^{12}\text{CO}\) into account. We neglect any line-overlap with transitions from other species. We explore the emergence of polarization in a protoplanetary disk for three types of (strong) magnetic fields: radial, toroidal, and poloidal.

We note that perhaps this toy model of the protoplanetary disk does not capture all features of the protoplanetary disk that are important in considering the polarization of thermal lines. For instance, we neglect to represent the inner midplane region by optically thick dust, so that the anisotropic radiation field resulting therefrom is not accounted for. Also, by not taking vibrationally excited levels and the transitions between different vibrational levels into account, we fail to include their significant aligning interactions (see Sect. 5.2). We explore more detailed and thorough modeling of protoplanetary disk regions in future work. These results should be taken as a simplified, but generally indicative, model of the mechanisms involved in the polarization of thermal line radiation of radiation by a magnetic field in protoplanetary disk regions.

It is important to map out the rates of isotropic and anisotropic interactions in order to understand the relative alignment of the molecules or atoms. Because of the cylindrical symmetry of the protoplanetary disk, we are able to analyze the interaction rates as a function of the radial distance and the height. In Fig. 4, we report the cumulative radiative and collisional rates for the \( J = 3 \) level of CO. The rates are plotted as a function of \( r_c \) for different height-cross-sections. We also report the magnetic precession rate of a 1 \( \mu \text{G} \) and a 1 mG magnetic field. It is apparent that magnetic interactions dominate other interactions and that we are justified in choosing the projection-axis along the magnetic field direction. Further, we observe a dominance of collisions over other interactions in a large region of the inner parts of the protoplanetary disk. In the disk mid-plane, isotropic collisions dominate the radiative interactions in the disk, but this dominance becomes weaker with the radial distance. In the outer parts of the disk, where the density drops, collisions become weaker and radiative events dominate.

In Fig. 4 we also plotted the relative anisotropy of the radiation field resonant with the \( J = 3 - 2 \)-transition and the relative alignment of the \( J = 3 \) state. Both of these parameters are defined with respect to a toroidal magnetic field configuration.
Fig. 5. Contour plots of (the logarithm of) the total intensity (in Kelvin) of a protoplanetary disk. The disk is viewed face on (panels a and b) and at an inclination of 45° (panels c and d). We overlaid the intensity plot with polarization vectors from PORTAL simulations that come from a radial magnetic field (a,c) and a toroidal magnetic field (b,d). Polarization vector lengths scale with the polarization fraction.

The radiation anisotropy is strongest in the outer parts of the disk and weakest in the bulk of the disk. The same dependence is seen for the relative alignment of the quantum states. The relative anisotropy of the radiation is almost constant as a function of the radial distance at a height of 1 AU. This is because the disk is optically thick in the midplane. The local angular radiation profile is not isotropic because of the temperature gradient. Due to dominant collisions, the quantum state alignment in the midplane is not large enough to significantly polarize radiation that is coming through.

We analyzed the emergence of polarization through two different magnetic field configurations: toroidal and radial. In Fig. 5a we report the contour map of the $J = 3 - 2$ CO-transition at 345.8 GHz of the total intensity (in Kelvins) overlayed with polarization vectors resulting from the polarized emission of CO aligned with a radial magnetic field. The polarization vectors are scaled with respect to the polarization fraction and are parallel to the radial configuration of the magnetic field. Figure 5b gives the polarization map coming from a toroidal magnetic field. We note that the polarization fraction for the face-on view of the protoplanetary disk is cylindrically symmetric.

It is striking that the polarization vector maps viewed face on, for both the toroidal and radial magnetic field, have the same configurations. This similarity can be traced back to the anisotropy introduced in the molecular states via the anisotropic radiation field, $J_0^2(r)$ (Eq. (4)). When performing the integration to acquire $J_0^2(r)$, the $\mu$-angle is gauged with respect to the magnetic field direction. The different gauges with respect to the toroidal and radial magnetic field configurations lead to the $J_0^2(r)$, which is associated with the toroidal magnetic field, to be negative, while the $J_0^2(r)$ of the radial magnetic field is positive. Thus, in the region where polarization is produced, and further more the angle between propagation and the magnetic field $\theta_{\text{prop}} > \theta_{\text{magic}}$ for both magnetic field configurations, this gives rise to perpendicular and parallel orientations of the polarization vectors with respect to the toroidal and radial magnetic fields, that is, polarization vectors that are identically oriented. Only when we view the disk at a significant inclination are we able to discern the orientation of the magnetic field from its polarization vectors, which can be seen in Figs. 5c and 5d.

The polarization maps of a protoplanetary disk viewed at a 45° inclination show large polarization fractions for the poloidal and toroidal magnetic field configurations. Lower but still significant polarization fractions are seen to emerge from the radial magnetic field configuration. The highest polarization fractions occur at the edges of the protoplanetary disk. In the disk midplane, almost no polarization arises. This effect can be ascribed to the high optical depth from this region; it should, however, also be noted that our method underestimates
the polarization fraction coming from optically thick regions (see Sect. 5.1).

For the face-on view of a protoplanetary disk that is permeated by a poloidal magnetic field, no significant polarization emerges even though the quantum states are aligned. This is because for a large part of the disk, the magnetic field is almost aligned along the propagation direction. When this is the case, the propagation coefficients are \( \gamma_Q \rightarrow 0 \), and no polarization is produced. When the disk is viewed at a significant inclination, the poloidal magnetic field produces a large polarization fraction.

Figure 6 is a plot of the azimuthally averaged polarization fraction as a function of the radial distance. Near the center of the protoplanetary disk, the polarization fraction is low and increases as one moves outward. The maximum polarization fraction of the protoplanetary disk viewed face on is \(~0.5\%\), but polarization fractions up to \(~9\%\) are observed when the disk is viewed at an inclination of \(45^\circ\). We analyze the azimuthally averaged (\(r_c = 50\) AU) spectrum of the total (polarized) intensity in Fig. 7. The polarization roughly follows the spectral shape of the total intensity.

It is a general trend that high-frequency transitions have a larger tendency to emit polarized radiation. This is because the radiative rates scale with the frequency. Radiative interactions of high-frequency transitions therefore tend to dominate over collisional interactions. At the same time, the transition optical depth falls (generally) with the transition frequency; for transitions that are too optically thin, radiation intensity is too low to align the quantum states.

5. Discussion

The anisotropic intensity approximation and the strong magnetic field approximation are central to the quality of the method we employed in PORTAL. We discuss these two approximations in the following two subsections. We discuss general remarks about the simulations of astrophysical regions using PORTAL in Sect. 5.3.

5.1. The anisotropic intensity approximation

Our method heavily relies on the approximation that it is only the anisotropy in the total intensity that contributes to the alignment of the molecular or atomic states under investigation. We call this approximation the anisotropic intensity approximation. We were able to directly compare the anisotropic intensity approximation to the LVG problem of Goldreich & Kylafis (1981). Goldreich & Kylafis (1981) accounted for the influence of the anisotropy of both the Stokes \(I\) and Stokes \(Q\) on the quantum state alignment. In the GK approach, the Stokes \(U\) component of the radiation field is neglected because the LVG method can only treat a constant magnetic field. The comparison is summarized in Fig. 8.

We note that below polarization fractions of \(2\%\), our method agrees with the GK effect for any optical depth. Furthermore, for low optical depth, \(\tau < 0.3\), our method reproduces the GK effect very well regardless of the polarization fraction. It is only for very high degrees of polarization and large optical depths that the polarization fraction obtained through the anisotropic intensity approximation starts to deviate from the GK polarization fraction. For strongly polarized lines (\(p \gg 6\%\)), the polarization fraction can be underestimated by up to a factor 1.5 for \(\tau > 1\) and this underestimation is sustained with increasing \(\tau\). We note that the polarization angle is identical for both methods.

The anisotropic intensity approximation loses its quality through the following: (i) the fact that a significant part of the radiation is polarized, which has an impact on the irreducible tensor representation of the radiation field (see Eq. (1)), and (ii) that this simplification subsequently impacts the source function, resulting in a magnification of the error. The latter error is particularly manifest at high optical depths, and it is also a consequence of the local approximation of an LVG-like problem. We expect this error to be ameliorated when the local approximation is abandoned as in PORTAL.

The polarization of (sub)millimeter lines through the GK effect has been observed in a number of sources. For most line observations, the observed polarization fraction is lower than \(2\%\) (Lai et al. 2003). This can be taken as a direct indicator of the quality of the anisotropic intensity approximation. There is a fraction of emission lines for which high polarization fractions are observed; the most strongly polarized emission lines go up to \(13\%\) (Vlemmings et al. 2012; Cortes et al. 2005). The large polarization fractions are most probably due to large sources of external radiation in the vicinity.
One avenue to remedy the anisotropic intensity approximation is to iteratively perform the inward ray-tracing steps (see Sect. 3.1) for all radiative polarization modes and perform the irreducible tensor integration as Eq. (1). After each iteration, the alignment of the quantum states for each cell is recomputed until convergence is attained. We plan to implement such a scheme in a later version of PORTAL, although this will significantly increase the calculation time.

5.2. The strong magnetic field approximation

The symmetry axis of the molecular and atomic states determines the (projected) direction of polarization. In our models, it is assumed that the symmetry axis is along the local magnetic field direction. This requires the magnetic precession rate to be 10–100 times stronger than other directional interaction rates. If an alternative directional interaction is about as strong or stronger than the magnetic precession rate, then the symmetry axis of the quantum states is rotated.

The magnetic precession rate for a nonparamagnetic molecule is given by

\[ g\Omega = 4.8g_{\text{mol}} \left( \frac{B}{\text{mG}} \right) \text{s}^{-1}, \]  

(17)

where \( g_{\text{mol}} \) is the molecular g-factor. A dimensionless factor that determines the coupling of the molecule to the magnetic field. For linear molecules, \( g_{\text{mol}} \) is the same for all rotational levels. The molecular g-factors of CO and HCO\(^+\) that we consider in this work are \( g_{\text{CO}} = -0.269 \) (Flygare & Benson 1971) and \( g_{\text{HCO}^+} = 0.0063 \).

We compare the magnetic precession rate (1 mG and 1 \( \mu \)G) to the cumulative rate of stimulated emission in Figs. 1 and 4. For the problems we considered, the magnetic precession rate is dominant over all other interactions and it is justified to assume that the quantum state symmetry axis is along the magnetic field direction.

Earlier, we saw that HCO\(^+\) had an exceptionally low magnetic moment. Conversely, the dipole moment of HCO\(^+\) is very large. Thus radiative interactions for such a molecule are very strong, and therefore also a strong magnetic field is required to justify the dominant magnetic field approximation. Indeed, for a large region of the collapsing sphere, a 1 \( \mu \)G magnetic field would not determine the HCO\(^+\) symmetry axis. We stress that for molecules that have strong radiative interactions, one should be extra vigilant and check the relevant interaction rates to verify that the magnetic field truly defines the symmetry axis of the quantum states and thus if the polarization vectors do indeed trace the magnetic field structure.

It is conceivable that a strong external radiation field that has a large angular size, such as a large stellar object, determines the quantum state symmetry axis. The directional rate of interaction of a general lower quantum state, 1, by an external black-body radiation source at the solid angle \( \Delta\Omega \), and with the temperature \( T \), is (Nedoluha & Watson 1992; Morris et al. 1985)

\[ R_{12} = \frac{g_1}{g_2} A_{21} \left[ e^{h\nu_{21}/kT} - 1 \right]^{-1} \Delta\Omega, \]

where \( g_i \) is the degeneracy of level \( i \) and \( A_{21} \) and \( \nu_{21} \) are the Einstein coefficient and frequency of the transition from upper level 2 to lower level 1. It is apparent from this expression that (sub)millimeter lines have relatively low interaction rates. Rather, vibrational transitions in the IR region have associated directional interaction rates that are far greater and are more likely to compete with magnetic interactions to determine the symmetry axis of the quantum states. For instance, the interaction rate of the \((\nu, J), (0, 0) \rightarrow (1, 1)\) transition of CO is \( \sim 7.8 \text{ s}^{-1} \) when it is excited by a 2000 Kelvin black-body radiation source at \( \Delta\Omega = 1 \text{ sr} \). The rate drops quadratically with the distance to the external radiation source and it is not corrected for absorption. We implemented a module in PORTAL that can incorporate the interactions resulting from a bright external source of radiation through vibrational transitions. This is particularly important when investigating the circumstellar envelopes of evolved stars (Morris et al. 1985; Ramos et al. 2005).

The strong magnetic field approximation should be abandoned when multiple directional interactions have similar interaction rates. In that case, one must comprehensively model all anisotropies affecting the quantum state alignment. This can be done at the expense of a computational effort as it increases the dimensionality of the problem greatly. For example, in treating the first 41 rotational levels of a linear rotor and by setting \( k_{\text{max}} = 6 \), the dimensionality of the SEE would increase from 151 to 1086, provided that we neglect orientation elements of uneven \( k \). The general theory of setting up the complete SEE can be found in Chap. 7 of Degl’Innocenti & Landolfi (2006).

Fig. 8. Comparison of the polarization fraction computed through the GK method (solid line) and the radiation anisotropy method we employ in this paper (dotted line). For more details on the simulation parameters, see Goldreich & Kylafis (1981). We consider a \( J = 1 - 0 \) transition at 100 GHz, with a strong magnetic field along the \( \hat{x} \)-axis and a velocity gradient of \( 10^{-3} \text{s}^{-1} \) in the \( xy \)-plane. We consider a temperature \( T = 10 \text{K} \). Three ratios for the collision-radiative rates are considered and denoted inside the figure. The polarization fraction was computed for a ray traveling along the \( \hat{x} \)-axis.
5.3. General remarks

5.3.1. (Sub)millimeter line polarization in astrophysical regions

It is clear from our calculations that the only requirement for the emergence of polarized emission is a source that has some form of anisotropy. This anisotropy may come from the velocity field, which has already been explored by Goldreich & Kylafis (1981), but it is not necessarily limited to this. To present the capabilities of PORTAL, we computed the emergence of polarized radiation in a protoplanetary disk and a collapsing sphere. In the protoplanetary disk, anisotropy mostly comes from the density structure. For the collapsing sphere, anisotropy comes from both the velocity-field and the density structure.

Furthermore, we confirm the earlier observation of Goldreich & Kylafis (1981), which is that namely around optical depths of unity, the polarization of line emission is the strongest. The physical reason behind this is that for sources with some sort of anisotropy, around $\tau \sim 1$, this anisotropy is most manifest in the local radiation field. Subsequently leading to the highest polarization degrees.

5.3.2. Sampling

The sampling of the space that we used is identical to the sampling used by LIME in which a random sampling, weighed by the density-structure, of the space is performed and neighboring cells are found through a Voronoi tessellation. We found that the extensive angular sampling that we performed to compute the local anisotropic radiation field generally requires a higher sampling of the space than would be necessary if one is generating a nonpolarized image. We found that for insufficient sampling of the space, strong local variation in the polarization fractions manifest themselves even though similar variations would not be visible in the total intensity. Also, local 90° flips of the polarization vectors can be a product of sampling of the surrounding space that is too sparse. For a source with symmetry in both the magnetic field and the radiative transfer structure, it can be prudent to use symmetrical averages in the case of a sampling that is too sparse.

5.3.3. Collisions

In order for appreciable polarization in the emission from astrophysical regions to be produced, one requires the rate of isotropic collisions to be relatively low. When collisions occur more than 100 times as frequent as the aligning absorption and stimulated emission events, no observable polarization is produced. Polarization is therefore not produced in regions of high number density and temperature. In general, regions that are in LTE show no appreciable polarization in their emission.

In the astrophysical problems that we analyzed, we represented collisions only by their rank-0 elements, that is, we assumed all magnetic substates to be equally pumped. At the same time, we assumed no depolarization through elastic collisions. The systematic errors of both assumptions are opposite. Such an approximation for the alignment characteristics of collisional rates is a common assumption in the modeling of alignment of quantum states (Degl’Innocenti & Landolfi 2006). Indeed, collisional rates resolved at the level of magnetic substates are not readily available, even though it is possible to compute these using modern quantum-dynamical methods (Alexander 1979; Faure & Lique 2012; Degl’Innocenti & Landolfi 2006).

5.3.4. External radiation

We found that an external source of directional radiation enhances the polarization appreciably. Similar conclusions have also been drawn in maser polarization theory (Lankhaar & Vlemmings 2019) and also for the GK effect (Deguchi & Watson 1984; Cortes et al. 2005). In particular, Cortes et al. (2005) found that they could explain the 90°-flip in polarization angle between the CO $J = 1 - 0$ and the $J = 2 - 1$ transitions through the anisotropic radiation coming from an external source. We confirm that this is one possible explanation, but we stress that there are other avenues to attain such a polarization effect. According to our theory, this 90°-flip is most generally explained by the $Q^0_0$ and the $Q^2_1$ elements being of opposite signs. This does not necessarily require an external radiation source.

It should be emphasized that polarization enhancement through external radiation is most manifest when hot objects irradiate high-frequency transitions, such as vibrational lines. It is also the case for such transitions that are most likely to compromise the strong magnetic field approximation (see Sect. 5.2).

In this work, we have abstained from including higher vibrational states when computing the polarization maps, but we will further explore this when we use PORTAL in conjunction with more detailed models of astrophysical regions and the involved radiative processes.

5.3.5. Alternative routes to polarization

Dust emission is often observed to be partially polarized. This has been seen in protoplanetary disks (Hull et al. 2017), in circumstellar envelopes of evolved stars (Vlemmings et al. 2017), and molecular clouds (Soler et al. 2013). Polarized emission from dust follows from its alignment. Dust can get aligned to the magnetic field through the process of radiative torque alignment (Draine & Weingartner 1997), but alignment to a strong external source of radiation (Lazarian & Hoang 2007) or through self-scattering (Kataoka et al. 2015) is also possible.

The dust polarization is indicative of the alignment and therefore does not always trace the (projected) magnetic field direction. Polarization fractions are observed to be up to a few percent. In PORTAL, we neglected the contribution of the dust polarization to the molecular state alignment because we used the anisotropic intensity approximation. In the ray-tracing step, we implemented the dust polarization module outlined in Padovani et al. (2012) and added it to the regular line polarization ray-tracing. We have found in the simulations we present here that the contribution of the dust polarization around the line-frequency is negligible because the line-opacity is some orders of magnitude greater than the dust opacity. This means that for strong enough magnetic fields (see Sect. 5.2), line polarization faithfully traces the (projected) magnetic field direction with 90° ambiguity.

Recently, it has been proposed that through forward scattering of radiation by a collective of molecules, a phase difference can be induced to the parallel and perpendicularly polarized components of the radiation field (Houde et al. 2013). The phase difference subsequently leads to a conversion of Stokes-$U$ to Stokes-$V$ radiation. This process, called anisotropic resonant scattering, would lead to the production of circular polarization at the cost of linear polarization, and it also changes the polarization angle. Observational evidence for this phenomenon is accruing (Hezareh et al. 2013; Chamma et al. 2018). Anisotropic resonant scattering is typically thought to occur in a foreground cloud, between the observer and the source of...
polarized line emission (Houde et al. 2013), but it could also be a feature of the radiative transfer inside the source. A better estimate of the relative strength of anisotropic resonant scattering has to be developed before we can evaluate the importance of this effect on the emergence of linear polarization in thermal line emission.

5.3.6. Ground state alignment

Yan & Lazarian (2006) showed that polarization can emerge in atomic (hyper)line-structure lines through (i) a strong magnetic field that defines the symmetry axis and (ii) an external UV radiation field that induces directional transitions, aligning the quantum states. If the pumping rate is much lower than the spontaneous decay rates of the excited states, only the ground state of the atomic system is aligned. Collisions and stimulated emission events are neglected in the formalism of ground state alignment (GSA). Through neglecting collisions and stimulated emission events and adapting an idealized geometry, Yan & Lazarian (2006) are able to formulate semianalytical expressions for the polarization fractions emerging from atomic lines. GSA has been proposed as a polarizing mechanism for atomic lines in the ISM (Zhang & Yan 2018).

PORTAL builds on the same theory as GSA, but it explicitly incorporates the effect of collisions and stimulated emission events. Furthermore, instead of assuming that a radiation field only comes from an external source, PORTAL maps out the full 3D radiation field structure of the medium in which the investigated species is embedded. In this work, we focus on the polarized radiative transfer of (sub)millimeter molecular and atomic lines because its radiative transfer does not involve any scattering (Brinch & Hogerheijde 2010). We plan to extend our model to also incorporate the emergence of polarization in atomic fine-structure lines, where we will pay special attention to scattering in the radiative transfer of these systems.

6. Conclusions

We present PORTAL, a 3D polarized radiative transfer program that is adapted to lines. The program uses the strong magnetic field approximation and the anisotropic intensity approximation, both of which we show to hold for the majority of relevant astrophysical problems. PORTAL can be used in stand-alone mode using an LTE estimate of the molecular or atomic excitation. Alternatively, the output of existing 3D radiative transfer programs can be input in PORTAL.

To outline PORTAL's capabilities, we computed the polarization maps of a collapsing sphere and a simple protoplanetary disk model. The polarization spectrum of a collapsing sphere shows polarization in its spectral lines up to 2% with the associated polarization vectors aligned with the projected magnetic field direction. The protoplanetary disk when viewed face on shows polarization fractions up to ~0.5%, but the polarization fraction rises to ~9% at significant inclinations. The polarization vectors resulting from a radial and toroidal magnetic field configuration are identical for a face-on view of the protoplanetary disk, and they can only be distinguished when viewed at a significant inclination. In forthcoming papers, we plan to use PORTAL to analyze the emergence of polarization in spectral lines in more detailed models of protoplanetary disks, to a molecular outflow, and to the circumstellar envelopes of AGB stars.

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Paper IV

Collisional polarization of molecular ions: a signpost of ambipolar diffusion

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Collisional polarization of molecular ions: a signpost of ambipolar diffusion

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ABSTRACT

Magnetic fields play a role in the dynamics of many astrophysical processes, but they are hard to detect. In a partially ionized plasma, a magnetic field works directly on the ionized medium but not on the neutral medium, which gives rise to a velocity drift between them: ambipolar diffusion. In this process, it is suggested to be important in the process of star formation, but has never been directly observed. We introduce a method that could be used to detect ambipolar diffusion and the magnetic field that gives rise to it, where we exploit the velocity drift between the charged and neutral medium. By using a representative classical model of the collision dynamics, we show that molecular ions partially align themselves when a velocity drift is present between the molecular ion and its main collision partner $H_2$. We demonstrate that ambipolar diffusion potently aligns molecular ions in regions denser than their critical density. We include a model for HCO$^+$ and show that collisional polarization could be detectable for the ambipolar drifts predicted by numerical simulations of the inner protostellar disk regions. The polarization vectors are aligned perpendicular to the magnetic field direction projected on the plane of the sky.

Key words. magnetic fields – stars: pre-main sequence – stars: magnetic field – polarization

1. Introduction

Ambipolar diffusion arises in a partially ionized and magnetized plasma, where the neutral and ionized medium are collisionally coupled (Mestel & Spitzer 1956; Lizano & Shu 1989; Fiedler & Mouschovias 1993). The magnetic field that works on the charged medium causes the ions and electrons to drift with respect to the neutral components of the plasma. The velocity drift is determined by the balance of the magnetic force and the friction between the charged and neutral medium. Through this friction, the magnetic field thus couples indirectly to the neutral medium. Ambipolar diffusion is generally thought to be a prime regulatory agent in the process of star formation (Mouschovias & Ciolek 1999). However, ambipolar diffusion has yet to be confirmed through direct observations (Yen et al. 2018).

The primary characteristic of ambipolar diffusion is a velocity drift between the neutral and charged medium of an astrophysical plasma. The magnitude of this drift velocity determines the dynamical influence of ambipolar diffusion. At large scales, an order-of-magnitude estimate of the drift velocity between the ionized and neutral medium is $0.85 \left( n/10^6 \text{ cm}^{-3} \right)^{0.61} \text{ km s}^{-1}$ (Draine 2010). Closer to the protostar, the velocity slip is expected to be higher, but estimates of the drift velocity on smaller scales vary greatly. Numerical magnetohydrodynamic (MHD) simulations predict the ambipolar drift to be $\sim 0.1 - 1 \text{ km s}^{-1}$ at hundreds of au from the central protostar (Ciolek & Königl 1998; Li et al. 2011; Zhao et al. 2018). ALMA observations by Yen et al. (2018) were unable to show such a velocity drift between $^{13}\text{CO}$ and $^{18}\text{CO}$ in their line profiles toward B335. Instead, Yen et al. (2018) constrained the ambipolar drift to be smaller than $0.3 \text{ km s}^{-1}$ at scales of 100 au.

Because it is on the order of the thermal velocity of the molecular components that make up the gas in a star-forming region, a velocity drift below $0.3 \text{ km s}^{-1}$ is hard to detect, even with the spectral resolution of ALMA. In this Letter, we show that when ambipolar drift velocities are on the order of thermal velocities, a significant alignment manifests itself in a linear molecular ion, such as HCO$^+$, through preferentially directed collisions with the neutral medium. The molecular alignment subsequently leads to a partial linear polarization of the emitted radiation, which will be a signpost of both ambipolar diffusion and the magnetic field direction.

It has long been known that atoms tend to collisionally align themselves in beam expansion experiments, and emit polarized radiation as a result (Ellett et al. 1926). Investigating collisions between partially aligned atoms through the polarized emission that they emit after the scattering event has very successfully elevated our understanding of atomic collisions (Andersen et al. 2001). Molecules also align themselves in molecular beam experiments (Friedrich et al. 1991). Molecular alignment can be attained through the interaction with a modest electric field (Friedrich & Herschbach 1991), but even without an electric field, partial alignment in the population of linear molecules arises naturally as the result of a velocity difference between the expansion carrier gas and the molecule of interest (Sinha et al. 1974; Friedrich et al. 1991).

Although it is analogous to mechanical alignment, one of the possible dust alignment mechanisms (Gold 1952; Lazarian 1997), the alignment of molecules through collisions has, as far as
as we have been able to find, not been the subject of any astrophysical investigations. Rather, the emergence of polarization in thermal molecular lines is commonly thought to be quenched by collisions (Goldreich & Kylafis 1981; Lankhaar & Vlemmings 2020). Alignment will not manifest itself when collisions are randomly oriented, which is the case for the majority of molecular collisions in astrophysical regions. However, through the process of ambipolar diffusion, a velocity drift arises between the ionized and the neutral medium that leads to a preferred direction of collisions. In this Letter, we show that these (partially) directional collisions lead to detectable polarization.

2. Collisional polarization

**Molecular alignment.** We considered the collisional interaction between a linear molecular ion and an H₂ molecule in the (spherically symmetric) j = 0 state. It is usual to treat ion-neutral collisions using the Langevin model, where the collisional dynamics are described by the charge-dipole interaction (Draine 2010). The Langevin cross section captures mainly elastic collisions, which transfer linear momentum between the collision partners. We did not follow this approach because the assumption of steady state, Eq. (3) can be solved under the physical constraint, \( \frac{1}{2} \int \cos \theta \, n_0 \, d \cos \theta = n \). The relative alignment of the molecular states is \( \sigma_\theta \), where we described the 90° rotation between the drift-frame and the magnetic field-frame with the Wigner D-matrix element, in Fig. 1.

We focused on “hard collisions”, which transfer a relatively large amount of angular momentum (Sinha et al. 1974). In a hard collision, the collisional process has no memory of its original angular momentum direction and randomizes the product angular momentum orientation. In this picture, the rate at which the molecular ion, oriented with respect to the ambipolar diffusion direction, \( \mathbf{z} \), by angle \( \cos \theta = \mathbf{k} \cdot \mathbf{z} \), is scattered to a new angle \( \theta' \), is

\[
k_{\theta \rightarrow \theta'} = \frac{1}{2} n \frac{B}{2} f_h \sigma_\theta + \frac{1}{2} \left( n \frac{B}{2} \sigma_\theta \right) \frac{1}{2} \left( \int \sigma_\theta \, v_{\text{drift}} \, |v_{\text{thermal}}| \right) + 1 \right],
\]

where the factor 2 is a normalization factor. We let \( n \frac{B}{2} \) be the molecular hydrogen number density, and \( k_0 = \left( n \frac{B}{2} \sigma_\theta \right) \) is the thermal collision rate. The thermal collision rate is dependent on the angularly averaged collision rate \( \sigma_0 = \frac{1}{2} \int \cos \theta \, \sigma_\theta \) because of the random orientation of the thermal velocities.

**Fig. 1.** Relative alignment of the molecular states as a function of the ratio, \( v_{\text{drift}}/v_{\text{th}} \), of the ambipolar drift velocity to the thermal velocity for different anisotropy-parameters \( b/a \). On the right-hand axis we note the associated predicted optically thin polarization fraction of a \( J = 3 \rightarrow 2 \) transition (see Eq. (7)). For the HCO⁰⁻H₂ complex, we assume \( b/a = 0.4 \).

When we consider the time-dependence of the population of molecular ions at the orientation \( \theta_0 \), we have

\[
h_0 = -n_0 \int d \cos \theta' \, k_{\theta \rightarrow \theta} + \int d \cos \theta' \, n_0 \mu k_{\theta \rightarrow \theta}.
\]

Because the collisional timescale is significantly shorter than the dynamical timescale, we can assume steady state: \( n_0 = 0 \). Under the assumption of steady state, Eq. (3) can be solved under the physical constraint, \( \frac{1}{2} \int \cos \theta \, n_0 \, d \cos \theta = n \). The relative alignment of the molecular states is \( \sigma_\theta = \sqrt{5} (P_2(\cos \theta) n_0/n) \) (Blum 1981). The square brackets denote that alignment is defined with respect to the velocity drift direction. The magnetic precession rate is higher than the rate of collisions, \( \frac{d \Omega}{dt} \sim 10^4 \mu \text{mg}^{-1} \text{cm}^{-1} \), so the alignment will reorient to the magnetic field after each collision event. The relation between the alignment with respect to the magnetic field and the drift velocity is \( \sigma_\theta B_\text{field} = -\frac{1}{2} \int \sigma_\theta \, \frac{d \cos \theta}{d \cos \theta} \), where we described the 90° rotation between the drift-frame and the magnetic field-frame with the Wigner D-matrix element \( D_{00}^{(2)}(\pi/2) = -\frac{1}{2} \). We have thus obtained the molecular alignment relevant to the production of polarized emission: \( \sigma_\theta B_\text{field} = \sigma_\theta \).

The molecular alignment is marginally dependent on the angular momentum state. We plot the relative alignment of the molecular states, \( \sigma_\theta^2 \), as a function of \( v_{\text{drift}}/v_{\text{thermal}} \) and for different anisotropy coefficients, \( b/a \), in Fig. 1.

**Emergent polarization.** The emergence of polarization from the partially aligned molecular ions can be computed from the polarized radiative transfer equation (Landi Degl’Innocenti et al. 2008). We consider a transition \( J' \rightarrow J \) at frequency \( v_0 \) and local thermal equilibrium. We formulate the polarized radiative transfer equations in terms of the optical depth

\[
\tau_\nu = \frac{\mu}{4\pi} B_{1J} N_j \left( 1 - e^{-h v_0/k T} \right) \phi_\nu,
\]

where

\[
\phi_\nu = \frac{1}{4\pi} B_{1J} N_j \left( 1 - e^{-h v_0/k T} \right) \phi_\nu,
\]

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where \( B_{JF} \) is the Einstein \( B \)-coefficient, \( \phi \) is the line profile as a function of the frequency \( \nu \), and \( N_J \) is the column density for lower level \( J \). The polarized radiative transfer coefficients under the assumption of local thermal equilibrium are (Degl’Innocenti & Landolfi 2006; Lankhaar & Vlemmings 2020)

\[
\begin{align*}
I_\parallel &= \frac{q_1}{\nu_\tau} = 1 + \sigma_0 \left[ w_{2J}^{(2)} - w_{2J}^{(0)} e^{-\hbar\nu_0/RT} \right] \frac{3 \cos^2 \chi - 1}{2 \sqrt{2}}, \\
I_\perp &= \frac{q_2}{\nu_\tau} = -\sigma_0 \left[ w_{2J}^{(2)} - w_{2J}^{(0)} e^{-\hbar\nu_0/RT} \right] \frac{3 \sin^2 \chi}{2 \sqrt{2}}, \\
q_1 &= \frac{e_{q1}}{\tau_\nu} = B_q(T) \left[ 1 + \sigma_0^2 w_{2J}^{(2)} \right] \frac{3 \cos^2 \chi - 1}{2 \sqrt{2}} \right], \\
q_2 &= \frac{e_{q1}}{\tau_\nu} = -B_q(T) \sigma_0^2 w_{2J}^{(2)} \frac{3 \sin^2 \chi}{2 \sqrt{2}},
\end{align*}
\]

where \( B_q(T) \) is the Planck function, \( w_{2J}^{(2)} \) are functions dependent on the angular momentum state of the upper and lower level (see, e.g., Degl’Innocenti & Landolfi 2006), and \( \chi \) is the angle between the radiative propagation and the magnetic field. It is convenient to express the radiative transfer equation in terms of the parallel and perpendicular polarization components of the radiation field: \( I_{\parallel \perp} = \frac{1}{2}(I \pm Q) \). The polarization direction is with respect to the magnetic field direction projected on the plane of the sky. We define the propagation coefficients in these terms as \( t_{\parallel \perp} = t_1 \pm t_2 \) and \( e_{\parallel \perp} = (e_\parallel \pm e_\perp)/2 \). We thus note the radiative transfer equation for the polarized components of the radiation field

\[
\frac{d}{dr}I_{\parallel \perp} = n_{\parallel \perp} q_{\parallel \perp} + e_{\parallel \perp} B_q(T).
\]

The polarization fraction is defined as Eq. (10) of Goldreich & Kylafis (1981) and can be readily evaluated assuming a background radiation field, which we took as the cosmic microwave background radiation field. We plot the predicted polarization fraction of the \( J = 3 \rightarrow 2 \) transition of HCO\(^+\) as a function of the optical depth for a number ambipolar drift-thermal ratio ratios in Fig. A.1. We report the polarization fractions assuming a propagation angle of \( \chi = 90^\circ \); for other angles, it is a good approximation to multiply the estimates by \( \sin^2 \chi \). The polarization coming from ambipolar drift collisions is directed perpendicular to the projected magnetic field direction.

In Fig. A.1 we plot the polarization fraction of HCO\(^+\) for different drift velocities as a function of the optical depth. We assumed an anisotropy parameter of \( b/a = 0.4 \) for HCO\(^+\)–H\(_2\) collisions in this figure (see the paragraph on model assumptions below for the discussion of this parameter). A large fraction of polarization emerges in the radiation when the drift velocity is greater than the thermal velocity (\( \nu_{\text{drift}}/\nu_{\text{thermal}} > 10 \)). At low optical depths our method estimates a polarization fraction of 7\%, which increases to 9\% for high optical depths. At drift velocities on the order of the thermal velocity (\( \nu_{\text{drift}}/\nu_{\text{thermal}} \approx 1 \)), polarization fractions on the order of 4–5\% are expected. When drift velocities are ten times lower than the thermal velocity, the polarization fraction is estimated to be 0.7–1\%. Polarization fractions of \( \sim 0.5\% \) arise for \( \nu_{\text{drift}}/\nu_{\text{thermal}} = 0.05 \).

**Model assumptions.** A number of simplifications were made in order to derive the above results. First, we represent the cross section of the H\(_2\)-molecular ion collision-complex as a classical sphere-prolate ellipsoid collision. We stress that this is a rather simplified modeling of the collision dynamics between a molecular ion and a hydrogen molecule. However, because we have assumed dominant collisions, we only need to capture the relative anisotropy of the inelastic collisions. We estimate the anisotropy factor \( b/a = 0.4 \) for H\(_2\)–HCO\(^+\), which we base on the geometry of the collision complex. It is possible that this anisotropy factor is an overestimation because we did not include elastic collisions. Even though elastic collisions do not change the magnitude of the angular momentum vector, a fraction of them might change its orientation. On the other hand, the orientation of the scattered angular momentum vector is not likely to be random because the collisions have a preferred direction. A more thorough analysis requires quantum-dynamical calculations of the state-to-state differential cross sections. Such cross sections are quantum-state transition specific and might vary in directional character between each other. It is expected that the ortho-to-para ratio of H\(_2\) affects the state-to-state differential cross-sections and also that the gas temperature has influence on the cross-section anisotropy. Having state-to-state and angularly resolved cross-sections allows for a more precise treatment of the quantum angular momentum dynamics of the system, which we assume to behave classically in our current approach. Even though we do not capture the complex collision dynamics, we nevertheless expect that our classical model captures the order of the anisotropy of the collision complex, and thus it provides realistic predictions of the emergent polarization fraction through collisionally induced polarization.

Second, we assume that the ratio of directional to random collisions is determined by the ratio of the drift velocity to the thermal velocity of the collisional complex. This approach has been successfully employed in molecular beam experiments (Friedrich et al. 1991), but it is only an approximation to the proper incorporation of thermal motions and a drift velocity (Alexander et al. 1977). Additionally, it has been shown that the presence of a magnetic field perpendicular to a flow leads to changes in the velocity distribution of both the molecular ions and neutrals (Pinto et al. 2012). These are second-order effects to our problem, but likely influence the polarization estimates. A more detailed treatment of the velocity distribution of the collisional particles is necessary for accurate modeling of the effect we present.

Third, in our approach we assumed collisions to be dominant in determining the alignment and population of the molecular quantum states. This can safely assumed to be the case in dense gases, above the critical density. This can be contrasted to other pathways to polarization, like the Goldreich–Kylafis (GK) effect (Goldreich & Kylafis 1981), where collisions are generally thought to be unfavorable to the emergence of polarization in thermal line emission (Goldreich & Kylafis 1981; Lankhaar & Vlemmings 2020). In the absence of a velocity drift between two collisionless species, collisions are isotropic and work actively against the alignment of the quantum states. Rather, the alignment of quantum states must be introduced through directional radiation (Lankhaar & Vlemmings 2020). By comparing their interaction rates, we can estimate the ratio between collisional-to-radiative alignment to be on the order of \( \sim \nu_{\text{drift}}/\nu_{\text{thermal}}/\pi \) for optically thin lines, and \( \sim (n_{\text{opt}}/n_{\text{bulk}}) \) for optically thick lines. Estimating the density of the region from where polarization radiation appears, as well as the optical depth of the probed transition, thus provides a natural means to distinguish between the mechanism by which the polarization has emerged.

Last, ambipolar diffusion presupposes movement in the (charged) medium that together with the magnetic field gives rise to a Lorentz force. A definite direction in the ambipolar diffusion requires a directional flow of the gas. Turbulence on smaller

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scales than this flow injects an element of randomness to these motions, and thus also to the ambipolar drift. If the magnetic field is unaffected by the turbulent motions, it is conceivably that the ambipolar drift is not always perpendicular to the magnetic field. We note that therefore the perpendicular relation between the drift velocity and magnetic field is idealized. The magnetic field alignment is expected to be slightly tapered by turbulent motions.

3. Observation of ambipolar diffusion

We can formulate a simple relation for the polarization fraction due to collisional polarization by ambipolar diffusion by solving Eq. (6) for low optical depth,

\[ p_l \approx e_{l}/e_{i} \approx - \frac{3}{4} \sqrt{\frac{(J + 1)(2J + 3)}{J(2J - 1)}} \sigma_{\text{col}}^{(2)} \sin^{2} \chi, \tag{7} \]

where we use an analytical expression for the \( w_{R}^{(2)} \) symbol for a \( J \rightarrow J-1 \) transition (Morris et al. 1985). The polarization fraction decreases with \( J \), the square-root factor tends to 1 for high \( J \). We note that at high optical depths, the predicted polarization fraction is consistently higher than the low optical depth estimate (see Fig. A.1). However, optically thin tracers are less affected by the GK effect (Goldreich & Kylafis 1981).

As a specific example, we considered the nearby star-forming region B335 and estimated the viability of collisional polarization detection in the signal of HCO\(^+\). Yen et al. (2018) recently constrained the ambipolar diffusion drift in this source to be <0.3 km s\(^{-1}\) at scales of 100 au. They furthermore estimated the gas kinetic temperature around the protostar to vary as \( T \sim 38 (\text{r}/100 \text{ au})^{-0.4} \) K (see also Evans et al. 2015) and the hydrogen number density as \( n_{\text{H}} \sim 9 \times 10^{6} (\text{r}/100 \text{ au})^{-2.1} \) cm\(^{-3}\). As shown in Yen et al. (2018), optically thin H\(^{13}\)CO\(^+\) transitions probe the midplane of the infalling envelope. Here we expect the magnetic field and ambipolar drift to be strongest.

We focused on the H\(^{13}\)CO\(^+\) \( J = 3 \rightarrow 2 \) transition. The collisional-to-radiative alignment ratio scales as \( \langle n_{\text{H}}/n_{\text{H}^0} \rangle/\tau \) for this optically thin species. Considering the critical density of HCO\(^+\) as \( 10^{5} \text{ cm}^{-3} \), and using the temperature profile to roughly estimate the thermal velocity as a function of the \( r, v_{\text{thermal}} = \sqrt{8kT/\pi m_{\text{H}}} \sim 0.66 (\text{r}/100 \text{ au})^{-0.2} \) km s\(^{-1}\), we can rule out contamination of the collisional polarization signal by GK polarization within some 100 au of the protostar.

Figure 1 reports the optically thin linear polarization fraction of the H\(^{13}\)CO\(^+\) \( J = 3 \rightarrow 2 \) transition on the right-hand axis. We estimated the anisotropy parameter \( b/\alpha = 0.4 \) for a HCO\(^+\)–H\(_2\) collision. With this parameter, the drift velocity that gives rise to a 1% polarization fraction through collisional polarization at 100 au is \( v_{\text{drift}} \sim 0.1 \) km s\(^{-1}\). In the case of very modest anisotropy in the collisions, \( b/\alpha = 0.8 \), \( v_{\text{drift}} \sim 0.1 \) km s\(^{-1}\) gives 0.2% polarization, which is just within the current ALMA detection limit. Closer to the protostar, MHD modeling predicts that the drift velocity increases more strongly than does the thermal velocity (Li et al. 2011; Yen et al. 2018), therefore larger polarization fractions are expected. These regions are of particular interest to the outflow-launching mechanism (Shu et al. 1994; Blandford & Payne 1982; Bjerkeli et al. 2019). However, the dynamics and magnetic field morphology become increasingly complex toward the near protostellar regions (Machida et al. 2008). Our simple radiative transfer model breaks down for complex magnetic fields and flows, which means that this likely affects the polarization estimates. To model complex regions, three-dimensional polarized radiation transfer modeling using codes such as PORTAL (Lankhaar & Vlemmings 2020) might be used.

4. Conclusions

We proposed a new method for detecting ambipolar diffusion. We showed that the velocity drift between the charged and neutral medium that characterizes ambipolar diffusion leads to a partial alignment of linear molecular ions. The molecular alignment subsequently results in partially polarized radiation emitted from these species: collisional polarization. The polarization fraction is indicative of the ambipolar drift velocity, while the polarization vectors are aligned perpendicular to the magnetic field direction. Through using optically thin species in dense regions, we can distinguish collisional polarization from polarization through the GK effect. Collisional polarization is expected in star-forming regions on scales 1–100 au, where ambipolar diffusion is likely present, but hard to detect by other means.

We used a simple classical model for our estimates of the molecular alignment and assumed an idealized geometry for the radiative transfer of polarized radiation. More rigorous predictions can be made through employing quantum-dynamically obtained state-to-state (tensorial) cross sections of directional collisions. These cross sections can be used in conjunction with three-dimensional polarized radiation transfer (Lankhaar & Vlemmings 2020); such modeling would constrain the effects of ambipolar diffusion on the emergence of polarization in molecular ions more quantitatively.

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References

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\(^{1}\) Glenn et al. (1997) set a 0.4% upper limit on the polarization fractions of \( J = 1 \rightarrow 0 \) HCO\(^+\) transitions toward the outflow lobes associated with different young protostellar systems. The polarization of such lines is expected to be the result of the GK effect because densities in these regions are too low for collisional polarization to be of importance.

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Appendix A: Additional figure

Fig. A.1. Polarization fraction of the $J = 3 - 2$ transition of HCO$^+$ as a function of the optical depth. The polarization fractions resulting from different ratios of ambipolar drift velocity to thermal velocity are plotted.
Paper V

Spectral line polarization in protoplanetary disks

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Spectral line polarization in protoplanetary disks

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ABSTRACT

Context. Magnetic fields are fundamental to the accretion dynamics of protoplanetary disks and they likely affect planet formation. Typical methods to study the magnetic field morphology are by observing the polarization of dust or spectral lines. However, it has recently become clear that dust-polarization in ALMA’s spectral regime not always faithfully traces the magnetic field structure of protoplanetary disks, which leaves spectral line polarization as a promising method of mapping the magnetic field morphologies of such sources.

Aims. We aim to model the emergent polarization of different molecular lines in the ALMA wavelength regime that are excited in protoplanetary disks. We intend to explore the variety of disk models and molecules to identify those properties that are conducive to the emergence of polarization in spectral lines and may therefore be viably used for magnetic field measurements in protoplanetary disks.

Methods. Recently, we developed PORTAL (POlarized Radiative Transfer Adapted to Lines), that simulates the emergence of polarization in line emission through a magnetic field. Here, we use PORTAL in conjunction with LIME (Line Emission Modeling Engine). Together, they allow us to treat the polarized line radiative transfer of complex three-dimensional physical and magnetic field structures.

Results. We present simulations of the emergence of spectral line polarization of different molecules and molecular transitions in the ALMA wavelength regime. We find that molecules that thermalize at high densities, such as HCN, are also most susceptible to polarization. We find that such molecules are expected to be significantly polarized in protoplanetary disks, while molecules that thermalize at low densities, such as CO, are only significantly polarized in the outer disk regions. We present the simulated polarization maps at a range of inclinations and magnetic field morphologies, and we comment on the observational feasibility of ALMA linear polarization observations of protoplanetary disks.

Conclusions.

Key words. Magnetic fields; Stars: pre-main sequence; stars: magnetic fields; polarization

1. Introduction

The formation of solar type stars is in its advanced stages accompanied by a protoplanetary disk. The protoplanetary disk is a thin rotating disk structure composed of dense gas and dust that surrounds the forming (proto)star. Protoplanetary disks are believed to be sites of ongoing planet formation, and they are vital to the accretion of mass onto the central forming (proto)star (Armitage & Kley 2019). The dynamics of a protoplanetary disk are strongly impacted by a magnetic field (Li et al. 2014). Magnetic fields are important to many aspects of disk accretion, since they can provide the transport of angular momentum through magnetic tension, or through the launching of an outflow (Blandford & Payne 1982; Bjerkeli et al. 2016). Magnetic fields are a key part in the magneto rotational instability (MRI) (Balbus & Hawley 1991), which is believed to be one of the major sources of turbulence in the disk (Flock et al. 2017), and also key to amplifying the viscosity to allow for efficient accretion (Pringle 1981).

To properly gauge the importance of these disk-dynamical processes, we require direct measurements of the strength of a magnetic field, as well as the magnetic field morphology. Donati et al. (2005) detected a strong magnetic field of 1 kG in the inner parts of the accretion disk of FU Orionis, but up to now, there have been no direct detections of the global magnetic field in protoplanetary disks (Vlemmings et al. 2019). Magnetic fields have been shown to be present and important to the dynamics of the earlier stages of star-formation on larger scales (Crutcher et al. 2010; Hull & Zhang 2019), as well as on the surface of accreting protostars (Donati et al. 2011; Sokal et al. 2018).

The magnetic field morphology is typically determined through the observation of polarized radiation from dust or molecules (Crutcher & Kemball 2019). The polarization direction is indicative of the alignment of the emitting species. Typically, dust aligns itself with respect to the magnetic field direction via the radiative torque (RAT) mechanism (Lazarian & Hoang 2007), while molecules align themselves with respect to the magnetic field through the Goldreich-Kylafis (GK) effect (Goldreich & Kylafis 1981). It has recently become clear that in protoplanetary disks, the RAT alignment mechanism competes with alternative alignment mechanisms such as self-scattering or radiative alignment, and that therefore, the polarized emission of dust does not faithfully trace the magnetic field direction (Kataoka et al. 2015, 2017; Stephens et al. 2017). On the other hand, the line-emission polarization angle due to the GK effect has a 90° ambiguity with respect to the projected magnetic field direction, and polarization of spectral lines will only manifest in regions where radiative interactions are strong and anisotropic (Goldreich & Kylafis 1981; Lankhaar & Vlemmings 2020b).

The GK effect is a consequence of the different absorption (or stimulated emission) probabilities of \( \Delta m = \pm 1 (\sigma^+ ) \) and \( \Delta m = 0 (\pi) \) transitions when resonant radiation is anisotropic...
When either $\sigma^+$- or $\pi$-transitions are favored, this will cause an overpopulation of some magnetic sublevels with respect to others. Generally, collisions do not favor the population of any magnetic sublevel, and they therefore tend to isotropize the magnetic sublevels (see Goldreich & Kylafis 1981) and Degl’Innocenti & Landolfi (2006). For an exception to this, see Lankhaar & Vlemmings (2020b). The differential population of certain magnetic sublevels within a rotational energy level is most conveniently thought of as that level being aligned (Blum 1981; Degl’Innocenti & Landolfi 2006; Lankhaar & Vlemmings 2020b). When the magnetic precession rate (on the order of $s^{-1}$) is higher than collisional or radiative interaction rates (typically $\lesssim 10^{-4} s^{-1}$), the alignment is either parallel or perpendicular to the magnetic field direction (Degl’Innocenti & Landolfi 2006).

The alignment of an energy level causes transitions that involve the energy level to partially polarize in the direction of the alignment of the participating energy levels. This process, the GK effect, has been detected in star-forming regions (Cortes et al. 2005, 2006), outflows (Glenn et al. 1997b; Girart et al. 1999) and in the circumstellar envelope around evolved stars (Glenn et al. 1997a; Girart et al. 2012; Vlemmings et al. 2012, 2017; Huang et al. 2020), and has provided observers with information on the magnetic field morphology of the investigated sources. But the GK-effect has yet to be detected in protoplanetary disks (Stephens et al. 2020).

Numerical modeling of GK effects has traditionally been done using the large velocity gradient (LVG) approximation (Goldreich & Kylafis 1981; Deguchi & Watson 1984; Cortes et al. 2005). LVG modeling finds that polarization is maximal for optical depths around unity and for strong (compared to collisional) radiative interactions. However, the LVG approximation is not particularly suited to model three-dimensional and direction dependent properties of a protoplanetary disk, due to its complex geometry. Instead, in order to properly interpret and predict polarization signals due to the GK effect in a complicated physical structure such as a protoplanetary disk, we have to perform three-dimensional (3D) polarized line-radiative transfer simulations.

Recently, we developed a 3D polarized radiative transfer code adapted to line polarization (PORTAL), which we presented in Lankhaar & Vlemmings (2020b). With PORTAL, the emergence of polarized line emission in geometrically complex astrophysical structures and magnetic fields can be investigated. PORTAL can treat the extensive energy-level structure of a number of molecules, including also interactions with vibrationally excited states. In this paper, we explore the polarization properties of different molecules in protoplanetary disks with a range of magnetic field configurations. We investigate the influence of disk characteristics such as the disk mass and velocity profile on the polarization characteristics of molecular lines. We focus particularly on CO, that is the most abundant molecule (after H$_2$) in protoplanetary disks, and HCN, which has a particularly strong dipole moment, thought to be conducive to the emergence of polarization in its spectral lines. In the method section, we briefly summarize the characteristics of PORTAL and LIME, which we have used in our simulations, and we outline the relevant characteristics of the disk model we have used, as well as the molecular excitation modeling. After that, we present and comment on the simulations of a fiducial disk model. We present the polarization characteristics of the spectral lines of CO and HCN for different inclinations. In the discussion section, we comment on the effect of variations on the fiducial disk model on the polarization characteristics of spectral lines excited in protoplanetary disks. We end the discussion section by commenting on the observational feasibility of linear polarization observations in protoplanetary disks. We summarize our findings in the conclusion section.

### 2. Methods

We simulated the emergence of polarization in molecular spectral lines in protoplanetary disks using PORTAL. PORTAL is a parallelized non-LTE three-dimensional polarized radiative transfer code that is adapted to spectral lines. PORTAL uses the anisotropic intensity and strong magnetic field approximations, which are explained in Lankhaar & Vlemmings (2020b). PORTAL requires as its input a physical structure, including gas-density, temperature and other parameters relevant to the molecular excitation. PORTAL can be used in a stand-alone mode, assuming LTE excitation, but in this work, we used the molecular excitation solutions of LIME in conjunction with PORTAL.

LIME is a parallelized non-LTE three-dimensional line radiative transfer code that uses a random (density weighed) grid (Brinch & Hogerheijde 2010). Arbitrary physical structures and geometries may be input. The grid cells are connected by a Delaunay triangulation. With the input of a physical structure, LIME computes the radiative transfer and molecular excitation using a Monte-Carlo scheme, which is sped-up by an accelerated lambda iteration (Rybicki & Hummer 1991).

In the following, we briefly introduce the protoplanetary disk physical model that we use. We performed simulations on a range of molecules and before presenting the results of the simulations, we discuss some general characteristics of these molecules that are relevant to their polarization.

#### 2.1. Proto-planetary disk model

We assumed an axisymmetric tapered disk as our protoplanetary disk model (Andrews et al. 2009; Lynden-Bell & Pringle 1974; Hartmann et al. 1998). The tapered disk model of the density structure, $\rho(r,z)$, is dependent on the parameters $\gamma$, the characteristic radius $R$, and a scale-height profile defined by the scale height at 100 AU, $H_{100}$ and $\psi$:

$$\rho(r,z) = \frac{\Sigma(r_c)}{\sqrt{2\pi H}} e^{-\left(\frac{r^2}{2}\right)},$$

$$\Sigma(r_c) = \int_{r_c}^{\infty} r^{-\gamma} e^{-\left(\frac{r}{R_c}\right)^{\gamma}},$$

$$H = H_{100} \frac{R}{100 \text{ AU}}^{\psi},$$

where $r_c = \sqrt{x^2 + y^2}$ is the cylindrical radius and $z$ is the height. The total disk-mass can be related to the characteristic column density when $\gamma \neq 2$, via $\Sigma_c = \frac{2\gamma M_{\text{disk}}}{\sqrt{2\pi H} \pi^2 R^2}$. We represented the gas-temperature of the disk by a power law, where we distinguished between the atmosphere temperature, $T_{\text{atm}}$, and the midplane temperature, $T_{\text{mid}}$, that smoothly go over in each other (Huang et al. 2018). For $z < 4H$, we used the temperature

$$T(r_c, z) = T_{\text{atm}} \left(\frac{r_c}{10 \text{ AU}}\right)^q (1 - \cos z [\pi z/8H])$$

$$+ T_{\text{mid}} \left(\frac{r_c}{10 \text{ AU}}\right)^q \cos z [\pi z/8H],$$

while for $z \geq 4H$, we used $T(r_c) = T_{\text{atm}} \left(\frac{r_c}{10 \text{ AU}}\right)^q$. The velocity structure of the gas was assumed to be Keplerian motion around the central protostar.
the poloidal magnetic field direction was chosen to be along the Keplerian rotation velocity, while the toroidal magnetic field direction was chosen to be parallel to the toroidal magnetic field configuration. The toroidal magnetic field direction was chosen to be along the influence of a radial, toroidal and poloidal magnetic field. We investigated the emergence of polarization in the spectral lines of a range of molecules. We investigated the band 7 transitions of CO, CS, HCN, HCO\(^+\) and N\(_2\)H\(^+\), of which some relevant properties are summarized in table 1. We dedicate most of our attention to CO and HCN: CO is the second most abundant molecule, after H\(_2\), and emits strongly, while HCN is a prototypical molecule that is excited under non-LTE conditions.

Since our analysis crucially depends on the lines being excited under non-LTE conditions, we comprehensively modeled radiative and collisional interactions in the (local) excitation. We used collisional and radiative rate coefficients from the LAMDA database (Schöier et al. 2005). The collisional rate coefficients for CO come from Yang et al. (2010), for HCN they come from Dumouchel et al. (2010), for HCO\(^+\) they come from Flower (1999), and for CS they come from Lique et al. (2006). We use the collisional rate coefficients of HCO\(^+\) for N\(_2\)H\(^+\), as is standard in the LAMDA database, and is warranted because of their similar collision dynamics.

We focused on CO and HCN as the main molecules of investigation. It should be noted from table 1, that CO transitions have comparatively low \(A/\tilde{C}\)-factors, meaning that their critical density is rather low. Indeed, when analyzing spectral radiation emitted from protoplanetary disk-CO, it is often assumed that the energy levels are Boltzmann distributed. It should however also be stressed, that we expect CO emission to trace regions that are relatively high up in the atmosphere of the disk, where the gas is more diffuse (Zhang et al. 2017). In addition to CO, we focused on the polarization properties of HCN. The strong dipole moment of HCN leads to comparatively strong radiative interactions, and makes it that its transitions are susceptible to polarize, provided the radiation morphology is anisotropic.

Chemical modeling of protoplanetary disks shows that the molecular abundance profile throughout the disk varies tremendously, through freeze-out processes, UV dissociation and other chemical reactions (Walsh et al. 2010, 2012). We did not include spatial variation of the molecular abundance in our modeling, but we do discuss possible effects of it on the polarization signal later on.

### Table 1: Properties of the molecular transitions that we investigate in this work.

We report the radiative rates by way of the Einstein coefficients, \(A_{ij}\), are evaluated at 100 K and at number density \(n_{H_2} = 10^7\) cm\(^{-3}\). We also report the molecular abundance, \(x_{mol}\).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>(v_0) (GHz)</th>
<th>(x_{mol})</th>
<th>(A_{ij}) ((10^{-3} \text{ s}^{-1}))</th>
<th>(\tilde{C}_{ij}) ((10^{-3} \text{ s}^{-1}))</th>
<th>(A_{ij}/\tilde{C}_{ij})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>(J = 3 \rightarrow 2)</td>
<td>345.796</td>
<td>10(^{-4})</td>
<td>0.2497</td>
<td>7.6</td>
<td>0.0328</td>
</tr>
<tr>
<td>CS</td>
<td>(J = 8 \rightarrow 7)</td>
<td>342.883</td>
<td>10(^{-9})</td>
<td>83.95</td>
<td>5.72</td>
<td>14.7</td>
</tr>
<tr>
<td>HCN</td>
<td>(J = 4 \rightarrow 3)</td>
<td>354.505</td>
<td>10(^{-8})</td>
<td>205.4</td>
<td>1.15</td>
<td>178</td>
</tr>
<tr>
<td>HCO(^+)</td>
<td>(J = 4 \rightarrow 3)</td>
<td>356.734</td>
<td>10(^{-9})</td>
<td>362.7</td>
<td>42</td>
<td>8.64</td>
</tr>
<tr>
<td>N2H(^+)</td>
<td>(J = 3 \rightarrow 2)</td>
<td>372.673</td>
<td>10(^{-10})</td>
<td>309.3</td>
<td>42</td>
<td>7.36</td>
</tr>
</tbody>
</table>

We explore the polarization properties of spectral lines under the influence of a radial, toroidal and poloidal magnetic field. The toroidal magnetic field direction, \(b_\text{tor}\), we chose to be parallel to the Keplerian rotation velocity, while the poloidal magnetic field direction was chosen to be along \(b_\text{pol} \times b_\text{rad}\).

We performed simulations on a disk with \(M_\text{disk} = 10 M_\odot\), \(\gamma = 0.5\), \(R_\odot = 50\) AU, \(H_{100\text{AU}} = 20\) AU, \(\psi = 0.28\), \(q = 0.5\), \(T_{\text{atm}} = 126.5\) K and \(T_{\text{mid}} = 31.6\) K. The central protostellar mass we chose 0.5 \(M_\odot\). In the discussion section, we discuss the effects of changing these disk parameters on spectral polarization signals.

#### 2.2. Molecules

We investigated the emergence of polarization in the spectral lines of a range of molecules. We investigated the band 7 transitions of CO, CS, HCN, HCO\(^+\) and N\(_2\)H\(^+\), of which some relevant properties are summarized in table 1. We dedicate most of our attention to CO and HCN: CO is the second most abundant molecule, after H\(_2\), and emits strongly, while HCN is a prototypical molecule that is excited under non-LTE conditions.

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### 3. Simulations

We present our PORTAL simulation results by first discussing the results for our fiducial protoplanetary disk system. We present the characteristics of the alignment for CO and HCN, and show polarization maps of their \(J = 3 \rightarrow 2\) and \(J = 4 \rightarrow 3\) transitions at different inclinations. After that, in the discussion section, we discuss the influence of some of the disk-parameters on the alignment and polarization properties.

We begin our discussion of the PORTAL simulations by analyzing the relative alignment of the molecular states, which are represented by the parameter \(\sigma_{ij}^\alpha(\psi)\) (Lankhaar & Vlemmings 2020b). In Fig. 1, we plot the relative alignment of the \(J = 3\) states of CO and HCN, for an axisymmetric disk as a function of the cylindrical radius and the height. We find that significant alignment manifests itself in the molecular states in the outer atmosphere of the disk, but that near the midplane, alignment is significantly quenched. The same trend can be seen for the relative anisotropy of the radiation. Indeed, we expect that both the density and optical depth increase towards the midplane. Collisions are more prominent in the denser regions of the disk, while a high optical depth tends to isotropize the radiation field. Both these factors result in no significant alignment of the quantum states, and accordingly, no polarization in the associated transitions. In the disk atmosphere and outer regions of the disk, optical depths and densities become lower, so that alignment and anisotropy can manifest itself in the molecular states and radiation field.

Comparing the alignment properties of different disk molecules, we observe that CO only gets significantly aligned farther out in the atmosphere and the disk, when compared to HCN. This is to be expected due to the low critical density of CO. HCN thermalizes at densities of about 2 orders of magnitude higher than CO. Collisional interactions thus dominate and quench alignment in CO already at far lower densities. The other molecules that we investigated, HCO\(^+\), CS and N\(_2\)H\(^+\), have alignment properties somewhere between the extremes of CO and HCN. Particularly, the molecular ions have a similar dipole moment to HCN, but relatively strong collisional interactions. We assumed the collisional interactions of molecular ions to be isotropic, but they might be anisotropic, due to an ambipolar velocity drift (Lankhaar & Vlemmings 2020a), which would provide additional alignment.

We move on to estimates of the polarization fraction for different molecules from a face-on \((i = 0^\circ)\) image of the protoplanetary disk. We plot polarization fraction estimates for the band 7 transitions of CO, HCO\(^+\), HCN, CS and N\(_2\)H\(^+\), coming from a face-on \((i = 0^\circ)\) oriented protoplanetary disk, in Fig. 2.
Because images of a face-on disk are axisymmetric (and we explore only axisymmetric magnetic fields), we may average them azimuthally and plot the brightness temperature and polarization fraction as a function of the offset to the central star. We consider the emergent polarization fraction for three different magnetic field configurations: a toroidal, poloidal and radial magnetic field.

As could be expected, brightness temperatures are high close to the central protostar and decrease towards the outer parts of the disk. Significant CO emission is sustained up to 275 AU, while the other molecules, that are significantly less abundant, have negligible emission already 200 AU away from the central protostar. For all species, and magnetic field morphologies, we find significant polarization in the outer parts of the disk in a rather small spatial window where the emission dies out. In addition, HCN emission is significantly polarized throughout the disk, with a sharp increase in the polarization fraction in the outer parts of the disk.

We explore the polarization of molecular spectral lines in an edge-on disk in Figs. 3 and 4. In Fig. 3 we report the integrated intensity maps of CO and HCN for an edge-on disk with the associated polarization fractions at the velocity-channel of maximum intensity. We used a poloidal magnetic field for the edge-on disk polarization maps. The maps of CO are more extended and the contour plots we report cover a larger range in both height and radius. The CO polarization fraction is significant for a towards the periphery of the edge-on observed protoplanetary disk. However, in the brightest regions, emission tends to be unpolarized due to the high densities the CO emission is tracing here. Polarized emission is seen mainly at high vertical offset (z > 100 AU), or rc > 225 AU. In these regions, the diffuse disk atmosphere is traced, which is reflected in the rather low integrated intensity of these regions \( \lesssim 5 \text{ K km s}^{-1} \). We find similar polarization morphologies for HCN, but the HCN emission is significantly polarized in the inner regions of the disk. At a vertical offset z > 40 AU, or rc > 150 AU, significant polarization may emerge from the line emission of HCN. In these regions, integrated brightness temperatures of \( \sim 20 \text{ K km s}^{-1} \) may be expected.

In Fig. 4, we present position-velocity (PV) diagrams of the HCN emission and polarization fraction from a poloidal magnetic field at z = 40 AU and z = 60 AU. In the position-velocity diagrams, we find that polarization fractions can be very high (> 1.5\%) in particular regions. However, particularly regions of low emission are polarized most strongly. The weakest polarization fractions may be expected at the smallest position-offset. At the wings of the emission, at high velocity and position offset, strong polarization fractions are found.

In Fig. 5a we report the total integrated intensity and the polarization fraction at maximal emission of HCN emission of a 45° inclined protoplanetary disk with a poloidal magnetic field configuration. We note that the expected polarization is significantly weaker for this configuration in comparison to the edge-on oriented disk. Partially, this may be explained through the orientation of the magnetic field, which at a 45° inclined angle with respect to the line-of-sight, causes \( \sin(45°) = 1/2 \) times smaller polarization (see equation (8) of Lankhaar & Vlemmings (2020b)). Significant polarization fractions are expected only in regions of weak emission. This behavior is also reflected in Fig. 5b, where we report the position-velocity diagram at height z = 60 AU. Only in regions of weaker emission do we see significant polarization for a 45° inclined disk.

4. Discussion

In the previous section, we focused on a fiducial disk model, and estimates of the polarization fractions for CO and HCN. In this section, we explore the effects of variations of the fiducial disk model on the polarization estimates. We put our work in context by first discussing the relation of our 3D polarized radiative transfer calculations to LVG GK modeling.

4.1. GK effect

The emergence of linear polarization in the line emission of non-paramagnetic molecules is a consequence of the partial align-
ment of the molecules. Molecules align themselves under the influence of an anisotropic radiation field, because directional radiation has differential interaction probabilities for \( \Delta m = \pm 1, 0 \) transitions. In order for significant alignment to manifest, we require that the rate of radiative interactions is comparable to, or larger than collisional interactions, while we also require that the relative anisotropy of the radiation field (Lankhaar & Vlemmings 2020b)

\[
\delta_0^2 = \frac{\int d\Omega P_\nu(\cos \theta) I_\nu(\Omega)/\sqrt{2}}{\int d\Omega I_\nu(\Omega)},
\]

is significant (\( \delta_0^2 > 1\% \)) at the frequencies resonant with transitions associated with the molecule under investigation.

From the protoplanetary disk model we used for our studies, it is straightforward to estimate the ratio between radiative and collisional interactions for a given transition, by dividing the Einstein-A coefficient of that transition by the local collision rate. In Table 1 we tabulate these values for certain transitions of a range of molecules. In Fig. 6 we plot the surface contours of the radiative to collisional interaction rates for a given transition, by dividing the vertical direction. This behavior is not captured by the LVG model.

It is more difficult to estimate the anisotropy of the radiation field. The classic result of Goldreich & Kylafis (1981) emphasized that maximal polarization emerges at optical depths \( \sim 1 \). In systems with \( \tau \ll 1 \), the anisotropy parameter \( \delta_0^2 \) of the radiation field is high, but radiative interactions are relatively weak, while at \( \tau \gg 1 \), radiative interactions are strong, but the relative anisotropy of the radiation field goes to zero. In addition, in non-local simulations such as those with PORTAL, radiative anisotropy can also manifest when variations of the physical conditions, such as the temperature, over the optical depth are significant.

In order to evaluate the applicability of the LVG GK formalism to a protoplanetary disk, we evaluate the general polarization characteristics by representing the excitation of molecular lines in the atmosphere of a protoplanetary disk as a plane-parallel slab problem. Along the \( z \)-axis of the disk, we assume no velocity gradient, but in the \( \hat{r} \times \hat{z} \) direction perpendicular to the cylindrical radius and the height, we have Keplerian rotation introducing a velocity gradient of \( \frac{dv}{dr} = \Omega c_{K}. \) Thus, we can get a measure for the optical depth in the disk atmosphere using the Sobolev approximation (Goldreich & Kylafis 1981)

\[
\tau_{\text{LVG}} = \frac{c(\kappa_\nu/\phi_\nu)}{v_0(dv/dr)},
\]

where \( \kappa_\nu \) and \( \phi_\nu \) are the line-opacity and profile. We evaluate the \( \tau_{\text{LVG}} \) at 1 scale height as a function of the cylindrical radius. We compute that \( \tau_{\text{LVG}} = 1 \) at \( r_c \sim 150 \) AU for CO, while the other lines have \( \tau_{\text{LVG}} = 1 \leq 100 \) AU. Comparing these results to the relative alignment of the molecular states, as presented in Fig. 1 and our results on the emergence of polarization in the emission, we note that in particular, regions with low LVG optical depth are significantly aligned and emit polarized emission. This is not expected from the theory of GK, and points to a more complex polarization mechanism due to the complex (radiation) morphology of the protoplanetary disk.

The complex radiation morphology of the protoplanetary disk arises because the gas properties change over a unit optical depth in large parts of the disks. The local approximation that is central to LVG prohibits one to take account of this. Additionally, in large parts of the disk atmosphere, the optical depth is \( \lesssim 1 \) in the vertical direction. This behavior is not captured by the LVG approximation, which assumes the optical depth perpendicular to the velocity-gradient to go to infinity.

The vertical optical depth can provide us with an additional measure to estimate the polarization characteristics of molecular lines. In Fig. 6, we plot the optical depth in our protoplanetary disk model. Observing a disk face-on, radiation that has come from lower in the disk is almost completely reprocessed above the optical depth \( \tau_{\text{vert}} = 1 \) surface. Thus, it is the molecular alignment properties around the \( \tau_{\text{vert}} = 1 \) surface that determine the polarization characteristics of the emergent line-radiation.

It is striking to observe from Fig. 6, that the \( \tau_{\text{vert}} = 1 \) surface of both CO and HCN is located at densities low enough for significant radiative interactions to manifest. For CO, the \( \tau_{\text{vert}} = 1 \) surface is \( A/C \approx 0.1 \) for the \( J = 3 \rightarrow 2 \) transition, while for HCN, the \( \tau_{\text{vert}} = 1 \) surface is in a region of significant radiative interactions: \( A/C \gg 1 \) for the \( J = 4 \rightarrow 3 \) transition. This points to that the limiting factor of the alignment is the limited amount of radiation anisotropy in the region around the \( \tau_{\text{vert}} = 1 \) surface.

4.2. Polarization and disk characteristics

4.2.1. Disk Mass

In Fig. 7, we plot polarization fraction estimates for the CO \( J = 3 \rightarrow 2 \) and the HCN \( J = 4 \rightarrow 3 \) lines for disk masses of 1, 10 and 100 M_\odot. The general trend of the polarization fraction is similar for all disk masses: we find the highest polarization fractions in the outskirts of the disk, where the density falls

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Fig. 2: Plots of the azimuthally averaged total emission and polarization fraction of transitions of a range of molecules from a face-on axisymmetric disk. The relevant parameters for the molecular transitions are given in Table 1. The polarization fraction is omitted for \( T_b < 0.1 \) K.
Fig. 3: Integrated intensity maps of an edge-on protoplanetary disk (left side) and the associated polarization fraction at the maximum intensity at that position (right side). We plot results for the CO $J = 3 \rightarrow 2$ transition (a) and the $J = 4 \rightarrow 3$ transition of HCO$^+$ (b) and HCO$^+$ (c). The magnetic field has a poloidal morphology.

4.2.2. Characteristic length

In Fig. 8, we present the polarization fraction of CO $J = 3 \rightarrow 2$ and the HCN $J = 4 \rightarrow 3$ transitions for a face-on disk with characteristic lengths of $R_c = 50$ and 100 AU. We note that at small offset, the polarization fractions and total emission of both disks are rather similar, with the polarization estimates slightly higher for larger characteristic length. At higher characteristic lengths, the tapering of the disk sets in farther away from the central (proto)star. The disk-mass is therefore more smeared out for larger characteristic lengths, leading to slightly lower densities close to the protostar. At larger offsets, we note that the emission is sustained farther out for the $R_c = 100$ AU simulations, as well as that the polarization is consistently weaker in the disk with larger characteristic length. We may ascribe this
Fig. 4: Position-velocity diagrams of the HCN $J = 4 - 3$ transition for $z = 15$ AU (a), $z = 40$ AU (b) and $z = 60$ AU (c). For each height-slice, we give the total brightness temperature (left) and the polarization fraction (right). The magnetic field has a poloidal morphology.

4.2.3. Vertical profile

We have represented the vertical profile of a disk by assuming a Gaussian distribution across the midplane $\rho(z) \propto \exp\left(-\left(z/H\right)^2\right)$, where the scale height, $H$, is a function of the cylindrical radius as in Eqs. (1). However, such a profile corresponds to an isothermal (in the $z$-direction) disk, and does not include a realistic magnetic pressure. At larger $z/h$, such a profile underestimates the density, while it is precisely in these regions where we expect our molecular species to be excited. Therefore, for our purposes of simulating the emergence of polarization, it is important that we accurately model the gas-density in these regions. A vertical profile that includes the contribution of the magnetic pressure can be approximated by (Armitage & Kley...
Fig. 5: Integrated intensity maps (a) and position-velocity diagrams (b) of the HCN $J = 4 \rightarrow 3$ transition. The PV-diagram is taken at $z = 60$ AU. On the left-hand side, we plot the total intensity, and on the right hand side, the associated polarization fraction is shown. The magnetic field has a poloidal morphology.

\[
\rho (r_c,z) = \frac{\Sigma (r_c) }{\sqrt{2\pi h(1 + \epsilon)}} \left[ e^{-z^2/(2\sqrt{2}h)} + \frac{\sqrt{4\pi \epsilon}}{3} e^{-2z^2/3h} \right]
\]

and has additional non-Gaussian profile that dominates for larger $z/h$. We performed simulations with such an extended profile and indeed observed slightly larger (~10%) polarization fractions for all molecules tested. This can be directly ascribed to the lower density in the molecular emission regions.

4.2.4. Substructures

Recent observations reveal pronounced substructures in a variety of protoplanetary disks in both the dust and molecular spectral emission Andrews et al. (2018); Huang et al. (2018). These substructures may be concentric or local, and can be associated with intensity depressions or elevation; linked to pressure, density and temperature gradients. In this work, we have not investigated the possible influence of sub-structures to the polarization profile of protoplanetary disks. However, considering the enhancement of the radiation anisotropy in the vicinity of a substructure, it may be hypothesized that the polarization characteristics of line emission are affected by substructures. Polarization observations would thus provide an interesting opportunity to investigate the nature of these substructures; particularly their connection to the magnetic field (Suriano et al. 2018). We leave such investigations for future work.
4.3. Polarization and line characteristics

4.3.1. Molecular transition

In the simulations we presented up to now, we used molecular lines that are in ALMA’s band 7. In Fig. 9, we report the polarization properties of other transitions of HCN and CO. The general trend that we observed earlier, where lines are polarized most strongly in the outer part of the disk, while polarization fractions drop towards the protostar, is seen in all transitions of both HCN and CO. In fact, the polarization properties of the different lines of CO are very similar, and we observe no significant variation of the polarization fraction predictions between the $J = 1 \to 0$, $J = 2 \to 1$ and $J = 3 \to 2$ transitions. We may explain this behavior through a combination of circumstances that affect the polarization of these lines. On the one hand, lower levels of alignment produce higher polarization fractions for lines with low angular momentum (Lankhaar & Vlemmings 2020a), but at the same time, collisional interactions become increasingly important for lower levels. Also, we expect that the emission from the $J = 1 \to 0$ line emerges from higher up in the disk compared to the higher frequency lines (check this).

The polarization behavior of different HCN lines shows more complicated behavior. In the inner parts of the disk, for $r_c < 100$ AU, the $J = 2 \to 1$, $J = 3 \to 2$ and the $J = 4 \to 3$ transitions show very similar polarization behavior, but we expect significantly lower polarization for the $J = 1 \to 0$ line. At larger offsets, the expected polarization fraction of the $J = 1 \to 0$ transitions rises quickly, and significant polarization is predicted from $r_c > 150$ AU. We observe that the steep rise in polarization fraction occurs at larger offsets for the higher frequency transitions. Later on in this section, we will discuss the feasibility of detecting polarization in these lines.

4.3.2. Isotopologues of CO

The radiative and collisional rates between the CO isotopologues are comparable at any point in the disk. But, the emission emerges from closer towards the midplane for the less abundant $^{13}$CO and C$^{18}$O, compared to the main isotopologue of CO (see also, Zhang & Yan 2018). In other words, the $\tau_{\text{vert}} = 1$ surface of $^{13}$CO and C$^{18}$O is closer to the midplane compared to the $\tau_{\text{vert}} = 1$ surface of $^{12}$CO. Thus, $^{12}$CO traces more diffuse gas
than its isotopologues. Especially in the dense environments that characterize the protoplanetary disk, this will mean that $^{12}$CO will be consistently more polarized than its isotopologues in the optically thick parts of the disk, as may be seen in Fig. 10. Also, in optically thin parts of the line emission, $^{12}$CO is more polarized because its significant emission extends farther out than $^{13}$CO and C$^{18}$O, and thus traces more diffuse gas.

A similar effect can be observed when one analyzes the spectrum of the polarization of $^{12}$CO emission lines. For a face-on disk, maximum polarization is found at the line-center, where the emission originates farthest from the midplane, whereas off-resonance, radiation comes from closer to the disk midplane.

4.3.3. Effects of vibration

In this work, we considered molecules that have close-lying states that may be radiatively excited through FIR radiation. As an example, if we focus on the triatomics, HCN, HCO$^+$, N$_2$H$^+$, and C$_2$H, they have bending-modes with associated wave-numbers of $\tilde{\nu} = 760$ cm$^{-1}$, 829 cm$^{-1}$, 687 cm$^{-1}$ and 372 cm$^{-1}$, respectively, while the Einstein coefficients of vibrational transitions are in the order of $\sim s^{-1}$. Consequently, thermal radiation of $\sim 150$ K interacts with levels of these molecules in similar rates as collisions would around $n_{H_2} \sim 10^8$ cm$^{-1}$. In practice, this means that at the denser and warmer inner regions, we hypothesize that alignment may manifest through these vibrational transitions.

In addition to an enhancement of the polarization fraction, strong radiative interactions with higher vibrational states may alter the symmetry-axis of the molecule. In PORTAL, we assume that the symmetry-axis of the molecules is along the magnetic field direction. This is the case when the magnetic precession rate ($\alpha \tilde{\Omega} \sim s^{-1}$/mG) is $10$–$100$ times higher than any other aligning interaction. Interactions with a low-lying vibrational state via a strong radiation field may occur at similar rates as the magnetic precession rate. This gives rise to the Hanle-effect, and generally is associated with an increase in polarization fraction and the rotation of the molecular alignment direction; thus also leading to a rotation in the polarization angle of the emission.

We performed simulations including the low-lying bending modes (760 cm$^{-1}$) of HCN. We assumed vibration level-changing collisional transitions to be negligible with respect to radiative vibrational transitions (Ziurys & Turner 1986). The vibrational transition Einstein coefficients we computed using equation (13) of Ramos et al. (2005) with $A_0 = 3.7$ s$^{-1}$ (Ziurys & Turner 1986). We find that the estimated polarization fractions of transitions in the ground state are unaffected by including radiative interactions with the vibrational bending mode. The radiation field around 760 cm$^{-1}$ is too weak to interact with ground state levels of HCN at a high rate. We found that a small fraction of the HCN may be found in the vibrationally excited bending mode, and there it is significantly aligned: much more so than in the vibrational ground state. These result thus lead to the conclusion that vibrational interactions may be ignored when analyzing the alignment of molecules in protoplanetary disks. Still, at other stages of star-formation, these effects might be of importance and may enhance polarization fractions significantly.

Other molecules that are sensitive to FIR radiation are rotors with relatively light constituents such as NH$_3$ or H$_2$O. Radiative
interactions of these molecules happen at rather high rates because of the large rotational energy these molecules possess per quantum. Critical densities of these molecules are accordingly anomalously high (Elitzur 1992). Alignment can manifest itself already at high densities for these types of molecules and they might be of interest for future polarization studies.

4.4. Observational feasibility of spectral line polarization

The GK effect has yet to be detected in protoplanetary disks. Recently, Stephens et al. (2020) report upper limits of 3% on the CO (and isotopologues) polarization fraction in the inclined protoplanetary disk HD 142527 and IM Lupus. Indeed, our simulations find lower polarization fractions for CO in the inner regions of the disk. Only in the outer regions can polarization fractions rise to higher levels. Stephens et al. (2020) speculate that the isotopologues of CO are better candidates for polarization observations, because their optical depths are around unity in disk regions of interest, but we find the opposite to be the case. It is the case that CO isotopologues optical depths are lower, and closer to unity in the inner parts of the disk, but this has as a consequence that the emission comes from deeper in the disk, where densities are higher and tend to thermalize the energy levels. Thus the alignment necessary for the production of polarization for these species is effectively quenched. $^{12}$CO emission comes from higher in the disk atmosphere, but, indeed, its high optical depth tends to isotropize the radiation close to the protostar, thus also suppressing the polarization fraction.

For disks $\geq 10 M_J$, CO is only marginally aligned in the regions where they emit strongly. Only in the diffuse outer parts of the protoplanetary disk do they emit radiation that is significantly polarized. Instead of CO observations, observers might be advised to use molecules with higher dipole moments, such as HCN. In our simulations, we have found that HCN is aligned in a larger part of the disk, both through its lower optical depth, and because of its higher critical density. Higher polarization fraction estimates are therefore expected for this species for any inclination, and also closer to the central protostar. We have not found a strong dependence of the polarization fraction on the transition, only the tendency that low $J$ transitions are less polarized in the inner parts, but higher in the outer parts. Also, low mass disks tend to lead to high polarization fractions. However, the polarization quenching effect that one might expect for higher mass disks is not so pronounced, because the emission from more massive disks comes from higher up in the disk atmosphere.

Other molecules that have high dipole moments are the molecular ions HCO$^+$ and N$_2$H$^+$. Estimated polarization fractions of these species are lower than HCN, because the collisional cross sections between ions and H$_2$ are relatively large. However, in these PORTAL simulations, we have not included the possible alignment-enhancing directional collision interactions, that could be instantiated through ambipolar diffusion (Lankhaar & Vlemmings 2020a). Particularly towards the midplane of the disk, ionization fractions are low, and thus would predict high ambipolar drift velocities (Cleeves et al. 2015; Mousschovias & Ciolek 1999).

We presented polarization fraction estimates for a face-on, edge-on and 45°-inclined disks. In the appendix, we present polarization maps overlaying the polarization vectors over total intensity maps. A face-on disk presents us with the simplest geometry and the interpretation of the polarization results is the most straightforward. Face-on disk polarization observations are not sensitive to a poloidal magnetic field configuration. From the polarization vector maps (Appendix), we note that for any inclination, the polarization vectors from toroidal or poloidal magnetic field geometries are perpendicularly oriented. For a face-on disk, polarization vectors from both magnetic field configurations are oriented perpendicular to the magnetic field direction. But for an edge on disk, polarization vectors from both magnetic field configurations are oriented parallel to the magnetic field direction.

The polarization fractions we report might be underestimated due to the anisotropic intensity approximation (Lankhaar & Vlemmings 2020b). In PORTAL, we only consider the total intensity in formulating the aligning part of the radiation interaction. In Lankhaar & Vlemmings (2020b), it is shown that this leads to an underestimation of alignment in regions of high optical depth and strongly polarized radiation.

We estimate the observational viability of HCN and CO polarization measurements of the well-known protoplanetary disk around TW Hya. TW Hya is almost face-on, with an inclination of $i = 5^\circ$. It is at a distance of 60 pc and has a disk mass of about 10 $M_J$ (Huang et al. 2018). In Fig. 11, we plot estimates of the polarization emission of the $J = 3 \rightarrow 2$ and $J = 2 \rightarrow 1$ transitions of CO and the $J = 4 \rightarrow 3$ and $J = 3 \rightarrow 2$ transitions of HCN, while using a beam size (FWH) of 0.3″ × 0.3″ for the band 7 transitions and 0.5″ × 0.5″ for the band 6 transitions. We note that the current ALMA detection limit 0.2% for linear polarization. It is apparent that CO emission has its significant polarization in the outer parts of the disk, while HCN has its most strongly polarized emission around 1″ (60 AU). Note here, that higher frequency transitions have their peak polarized emission slightly closer to the disk-center. The polarized emission is much stronger for HCN than for CO, and it is doubtful that polarized emission from CO is detectable for a 10 $M_J$ disk. According to our predictions, HCN emission should have a detectable polarization between 1″ and 3″.

5. Conclusions

We present spectral polarization estimates of molecular lines that are excited in protoplanetary disk regions. We explored the polarization characteristics of different molecules, of which those with strong dipole moments and relatively low collision rates are the most useful for polarization measurements. We took HCN to...
Fig. 11: Plots of the azimuthally averaged polarized emission of transitions of HCN and CO from a face-on axisymmetric disk of mass 10 $M_\odot$. We plot the $J = 3 \rightarrow 2$ and $J = 2 \rightarrow 1$ transitions of CO and the $J = 4 \rightarrow 3$ and $J = 3 \rightarrow 2$ transitions of HCN. We assume a source of distance 60 pc and a beam size (FWHM) of 0.3'' × 0.3'' (band 7 transitions) and 0.5'' × 0.5'' (band 6 transitions). The polarized emission is computed for a toroidal magnetic field configuration. We also plot the total emission divided by 500 associated with each transition in a dotted line of the same color; to represent the (current) ALMA sensitivity limit of the detectability of linear polarization.

be typical of such a species, and found its spectral lines to be significantly polarized in large regions of the protoplanetary disk. CO, which has been traditionally been observed as a molecule exhibiting polarization in its line emission, is less suitable for polarization observations in disks. Even though the abundance of CO is high, and its visible emission comes from high up in the disk, where the gas is diffuse, its high optical depth isotropizes the radiation, thus leading to marginal polarization in its line emission. CO isotopologues, that exhibit lower optical depth are excited in the lower regions of the disk, where collisions dominate the excitation and thus no alignment can manifest itself, leading to still lower polarization estimates for these species compared to regular $^{12}$CO.

The disk characteristic that impacts polarization characteristics of molecular lines most strongly is the disk mass. Still, for lines that are optically thick, the influence of the disk mass is mitigated through these lines emerging from higher up in the disk, where the gas is more diffuse. Low mass disks predict higher line polarization fractions observations targets, but significant polarization in the line emission of high mass disks is also present.

Our simulations indicate that molecules with strong dipole moments and relatively weak collisional rate coefficients, such as HCN, should be targeted for polarization observations. Such species reveal the magnetic field configuration of the inner parts of the disk; and may yield important information on the accretion dynamics of protoplanetary disks.

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References

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Appendix A: Appended figures
Fig. A.1: Contour plots of the total intensity (in Kelvin) of a protoplanetary disk overlayed with polarization obtained from PORTAL simulations using a toroidal magnetic field. We truncate the polarization vector lengths above 1%. Subfigures (a), (b), (c), (d) and (e) are of the $v = 0$ km/s channel at inclination 0, 30, 45, 60 and 90 degrees inclination. Subfigures (f), (g) and (h) are of the velocity channels $v = 0.62$, $v = 1.25$ and $v = 1.88$ km/s at inclination of 45 degrees.
Fig. A.2: Contour plots of the total intensity (in Kelvin) of a protoplanetary disk overlayed with polarization obtained from PORTAL simulations using a poloidal magnetic field. We truncate the polarization vector lengths above 1%. Subfigures (a), (b), (c), (d) and (e) are of the $v = 0$ km/s channel at inclination 0, 30, 45, 60 and 90 degrees inclination. Subfigures (f), (g) and (h) are of the velocity channels $v = 0.62$, $v = 1.25$ and $v = 1.88$ km/s at inclination of 45 degrees.
Fig. A.3: Contour plots of the total intensity (in Kelvin) of a protoplanetary disk overlayed with polarization obtained from PORTAL simulations using a radial magnetic field. We truncate the polarization vector lengths above 1%. Subfigures (a), (b), (c), and (d) are of the $v = 0 \text{ km/s}$ channel at inclination 0, 30, 45, 60 and 90 degrees inclination. Subfigures (f), (g) and (h) are of the velocity channels $v = 0.62$, $v = 1.25$ and $v = 1.88 \text{ km/s}$ at inclination of 45 degrees.