# Computational and Theoretical Chemistry 2 (NWI-MOL112)

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# Contents

# Preface

*These lecture notes are not yet finished, I will write them during the course, and of course I will try to stay ahead by at least one week.*

The general approach in this lecture will be: we start solving easy problems the hard way, hoping that later hard problems will become easy. The first actual problem we aim to solve is the computation of the rotation-vibration spectrum of a diatomic molecule, assuming the potential energy curve describing the bonding between the atoms is known. Computing the potential would require solving the electronic Schrödinger equation, which is the topic of another course. Here, we deal with the quantum behavior of nuclei.

We will approach this problem in several steps: we start with a single particle moving in a potential in one dimension, and we will actually start with the classical description of this system. In addition to Newton's equation of motion, we will give Hamilton's classical equations of motion, since this involves a (classical) Hamiltonian, which makes the step to a quantum description a little easier. Although we aim to calculate spectra using the time-independent Schrödinger equation, we will briefly discuss the time-dependent Schrödinger equation too, since it is fundamental to quantum mechanics, and the connection with classical mechanics is clearer.

Solving the Schrödinger equation for this problem is not very difficult, but we will use this simple system to review the basics of quantum mechanics, going through the postulates of quantum mechanics, and by elaborating some of the linear algebra that is used everywhere in quantum mechanics. In particular we will review linear (or vector) spaces, scalar products, and say a few words about Hilbert spaces. The latter is a somewhat advanced topic, but knowing a little bit about it helps to understand infinite dimensional spaces and, more practically, it helps to choose a proper basis set in a calculation.

After we have go through the basics of the quantum mechanics and the necessary math, we start considering two particles moving on straight line, and study the coordinate transformation that separates the center-of-mass motion (which we don't care about in this course) from the relative motion, i.e., the vibrations.

The next step is to go to three-dimensional space. The main topic there is to introduced angular momentum. Much of this is similar to what is needed to study the hydrogen atom, but we'll go a bit further into angular momentum theory, since this is an extremely powerful tool in molecular quantum mechanics.

After this we make the step to an atom-diatom system, for which we will need to couple angular momenta. Mathematically this is closely related to the coupling of angular momentum needed to understand term symbols of atoms.

If we time permits we will discuss electric dipole transitions between different electronic states, which will allow us to compute intensities of ro-vibrational transitions. Finally, we may consider (diatomic) molecules in external electric fields.

*Gerrit C. Groenenboom, Nijmegen, 3-Feb-2020*

# Chapter 1

# A single particle in one dimension

The main goal of this chapter is to review much of the quantum mechanics that we will need later. We will use the one particle system to illustrate the key concepts.

## 1.1 Particle moving in one dimension: classical mechanics

In classical mechanics, a particle moving along a straight line is described by $x(t)$: its *position* $x$ as a functions of *time* $t$. If the particle has mass $m$, then its *kinetic energy* is given by

$$T = \frac{1}{2}mv^2, \tag{1.1}$$

where the velocity $v \equiv \dot{x}(t)$ is the time derivative of the position. If the forces acting on the particle are *conservative* we can assign a *potential energy*, $V(x)$. This potential depends on the position $x$ of the particle only. Also, the total energy $E$, which is the sum of kinetic and potential energy, is *conserved*, i.e., independent of time. If the *initial conditions*, the position $x_0$ and the velocity $v_0$ at time $t_0$ are known, the *classical trajectory* $x(t)$ can be found by solving Newton's equation of motion

$$F = ma, \tag{1.2}$$

where the force $F$ is minus the derivative of the potential,

$$F = -\frac{\partial}{\partial x}V(x), \tag{1.3}$$

and the acceleration $a$ is the time derivative of the velocity, $a \equiv \dot{v}$.

## 1.2 Hamilton's classical equations of motion

Before we make the step to quantum mechanics, we introduce an alternative formulation of Newton's equation. First, we define the *linear momentum* $p$, as the derivative of the kinetic energy with respect to velocity

$$p \equiv \frac{\partial}{\partial v}T = mv \tag{1.4}$$

and we rewrite the kinetic energy in terms of momentum instead of velocity:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{1.5}$$

and we define the *classical Hamiltonian* $H(x,p)$, which gives the total energy of the particle as a function of $x$ and $p$,

$$H(x,p) = T + V(x) = \frac{p^2}{2m} + V(x). \tag{1.6}$$

Hamilton's classical equations of motion

$$\dot{x} = \frac{\partial H(x,p)}{\partial p}, \tag{1.7}$$

$$\dot{p} = -\frac{\partial H(x,p)}{\partial x}. \tag{1.8}$$

It is left as an exercise to show that these equations are equivalent to Newton's equation. The power of Hamilton's approach is that it works in any coordinate system, not only in Cartesian coordinates. This is shown in many textbooks on classical mechanics, see, e.g., Goldstein [1].

## 1.3 Postulates of quantum mechanics

We summarize the postulates of quantum mechanics very briefly. The purpose is not to be exact, but rather to give an overview of what will be discussed in the remaining sections of this chapter.

1. A system is described by a *wave function.* Mathematically, a wave function is an element of *Hilbert space.*
2. Every *observable* is associated with an *Hermitian operator* ($\hat{A}$).
3. Possible outcomes of a measurement are the eigenvalues of $\hat{A}$.
4. The probability of a certain outcome is determined by the square of the absolute values of the scalar product of the wave function of the system and the eigenfunction of $\hat{A}$ corresponding to the eigenvalue.
5. The time-evolution of the wave function is determined by the time-dependent Schrödinger. equation

There is also a postulate about identical particles, but for now we have only one particle, so we'll worry about that later. Since Hermitian operators are central to quantum mechanics, we discuss them in some detail in chapter 2.

## 1.4 Wave functions

The particle is described by a time-dependent *wave function*, $\Psi(x,t)$. We can no longer know exactly where the particle is at a given time, but from the wave function we can calculate the probability $P_{ab}(t)$ of finding the particle in some interval $x \in [a,b]$,

$$P_{ab}(t) = \frac{1}{N^2}\int_a^b |\Psi(x,t)|^2\,dx, \tag{1.9}$$

where $N$ is the *norm* of the wave function and

$$N^2 \equiv \int_{-\infty}^{+\infty} |\Psi(x,t)|^2\,dx. \tag{1.10}$$

Since the particle must be somewhere, $P_{-\infty,+\infty}(t) = 1$. The *probability density* is defined by

$$\rho(x,t) \equiv \frac{1}{N^2}|\Psi(x,t)|^2, \tag{1.11}$$

so the probability is the integral of the probability density

$$P_{ab}(t) = \int_a^b \rho(x,t)\,dx. \tag{1.12}$$

Multiplying the wave function with constant (real or complex), does not change the probability density, so sometimes it is convenient to *normalize* the wave function, i.e.,

$$\widetilde{\Psi}(x,t) = \frac{1}{N}\Psi(x,t) \tag{1.13}$$

so that the probability density in terms of the normalized wave function is a little simpler,

$$\rho(x,t) = |\widetilde{\Psi}(x,t)|^2. \tag{1.14}$$

## 1.5 Hilbert space

As we have just seen, for wave functions it is essential that the norm, i.e., the integral in Eq. (1.10) exists. The set of all possible functions $\phi(x)$ for which the integral exists is called a *Hilbert space*, $\mathscr{H}$. If the function is zero it is still part of the *Hilbert space*, but it is not *normalizable*, so it cannot be used as a wave function. A Hilbert space is a *linear space*, possibly infinite-dimensional, for which a *scalar product* is defined, and it has a *countable orthonormal basis*. Let's go through this list of properties one-by-one.

### 1.5.1 Linear space or vector space

A *linear space* is also called *vector space*, and therefore the elements of the set are sometimes called *vectors*. For the complete definition we refer to the linear algebra course (or `Vector_space` on Wikipedia). We just give three essential properties:

1. If you multiply a vector $\phi \in \mathscr{V}$ from some vector space $\mathscr{V}$ with a number $\lambda$, the result is still an element of the same vector space. A vector space is called *real* of *complex*, depending on whether we only allow real numbers ($\lambda \in \mathbb{R}$), or also complex numbers ($\lambda \in \mathbb{C}$).

2. The sum of two vectors $\phi, \chi \in \mathscr{V}$ is also an element of the same vector space, $\phi + \chi \in V$.

3. A vector space has a unique *null vector*, which we will denote as $\vec{0}$. It has the property that a vector does not change if you add the null vector:

   $$\phi + \vec{0} = \phi \quad \text{for all } \phi \in \mathscr{V}. \tag{1.15}$$

   In our Hilbert space, the null vector is simply a function that is zero everywhere, $f(x) = 0$ for all $x$, so we will also use 0 to denote the null vector in our Hilbert space. We will also use vector spaces $\mathbb{R}^n$ and $\mathbb{C}^n$ with $n > 1$, and in that case we must distinguish the number 0, and the null vector, which has $n$ components that are equal to zero.

It is easy to see that we need the first property, it allows us, e.g., to normalize wave functions. The second property also has direct physical relevance: the sum of two wave functions is also a wave function (also called a *superposition* of wave functions). Combining these two properties allows us to make *linear combinations* of vectors, i.e., with (real or complex) numbers $c_1$ and $c_2$, and vectors $\phi_1, \phi_2 \in \mathscr{V}$ we have

$$\phi_1, \phi_2 \in \mathscr{V} \implies c_1\phi_1 + c_2\phi_2 \in \mathscr{V}. \tag{1.16}$$

### 1.5.2 Linear independence, dimension, and basis sets

If the linear combination in Eq. (1.16) is set to zero

$$c_1\phi_1 + c_2\phi_2 = 0 \tag{1.17}$$

and there is only one solution, namely $c_1 = c_2 = 0$, then the two functions (vectors) $\phi_1$ and $\phi_2$ are called *linearly independent*. Similarly, if

$$\sum_{i=1}^{n} c_i\phi_i = 0 \implies c_i = 0, \quad \text{for } i = 1, 2, \ldots, n, \tag{1.18}$$

then the set of functions $\{\phi_1, \phi_2, \ldots, \phi_n\}$ is called linearly independent. The largest value of $n$ for which such a set of independent functions can be found in $\mathscr{V}$ is called the *dimension* of $\mathscr{V}$. The dimension can be finite or *infinite*, as is the case for our Hilbert space for one particle in one dimension.

If we have a set of functions $B = \{\chi_1, \chi_2, \ldots, \chi_n\}$ and every vector $\phi$ in $\mathscr{V}$ can be *uniquely* written as a linear combination of the elements of $B$,

$$\phi = \sum_{i=1}^{n} c_i\chi_i, \tag{1.19}$$

then the set $B$ is called a *basis* of *basis set* for $\mathscr{V}$. It is easy to show that the elements of $B$ must be linearly independent. The number of vectors in the set $B$ is equal to the dimension of $\mathscr{V}$. For a *finite* dimensional space with dimension $n$ one can also show that *any set of $n$ linearly independent vectors* is a basis and vice versa. If the dimension is infinite, all basis sets must have an infinite number of elements as well, but a set with an infinite number of linearly independent vectors is, unfortunately, not necessarily a basis for that space. This may sound mysterious, but it is actually easy to construct examples (see exercises). Even though our Hilbert space is infinite-dimensional, it has other properties in addition to being a vector space, that actually solve some of the complications that arise from this infinite dimensionality.

### 1.5.3 Scalar products, orthonormal basis sets

Our Hilbert space is not just a vector space, it is also an *inner product space*. That is a vector space, for which a *positive definite scalar product* (also called *inner product*) is defined. A scalar product is a mapping of any two vectors onto a complex number (or on a real number in a real vector space). Several notations are being used to denote scalar products. We will use *bra-ket* notation, which is often used in quantum mechanics. For two functions $\phi, \chi \in \mathscr{H}$ the scalar product is defined by

$$\langle\phi|\chi\rangle = \int_{-\infty}^{+\infty} \phi(x)^*\chi(x)\,dx, \tag{1.20}$$

where the asterisk (*) denotes complex conjugation. Note that in the bra-ket notation we drop the coordinate over which we integrate. Mathematically, one can easily define other mappings of two functions onto a number, but such a mapping is only called a *scalar product*, if it satisfies the following properties:

1. It is *linear* in the *second* vector:

$$\langle\phi|c\chi\rangle = c\langle\phi|\chi\rangle \tag{1.21}$$

$$\langle\phi|\chi_1 + \chi_2\rangle = \langle\phi|\chi_1\rangle + \langle\phi|\chi_2\rangle, \tag{1.22}$$

   where $c \in \mathbb{C}$ and $\phi, \chi, \chi_1, \chi_2 \in \mathscr{H}$.

2. It is *antilinear* in the two vectors
$$\langle\phi|\chi\rangle = \langle\chi|\phi\rangle^*, \tag{1.23}$$
i.e., if we swap the two vectors, we need to take the *complex conjugate* of the scalar product.

3. The scalar product of a vector with itself can only be zero for the null vector
$$\langle\phi|\phi\rangle = 0 \implies \phi = \vec{0}. \tag{1.24}$$

4. From the second property it follows that the scalar product of a vector with itself must be real. For the specific scalar product defined in Eq. (1.20) we see that $\langle\phi|\phi\rangle \geq 0$. Such a scalar product is actually called *positive definite*, and we will only consider such scalar products. Hence, we can define the *norm* of a vector as
$$\|\phi\| \equiv \sqrt{\langle\phi|\phi\rangle}. \tag{1.25}$$

It is left as an exercise is to show that the scalar product defined by the integral in Eq. (1.20) indeed satisfies these defining properties.

From the defining properties it is easy to show that a scalar product is *antilinear* in the first vector

$$\langle c\phi|\chi\rangle = c^*\langle\phi|\chi\rangle \tag{1.26}$$
$$\langle\phi_1 + \phi_2|\chi\rangle = \langle\phi_1|\chi\rangle + \langle\phi_2|\chi\rangle. \tag{1.27}$$

Note that the *anti* only refers to the complex conjugation of the scalar $c$ in Eq. (1.26).

Since we have a norm for our Hilbert space, we also have a *metric*. This simply means that we can define the *distance* between two functions as the norm of this difference

$$d(\phi,\chi) \equiv ||\phi - \chi||. \tag{1.28}$$

If the distance between two functions is zero, they are the same. Having a definition of distance is crucial when working with infinite-dimensional spaces, since we need to be able to discuss convergence if we approximate the infinite-dimensional space with a sequence of finite-dimensional spaces.

One more definition: if the scalar product of two vectors is zero, then the vectors are said to be *orthogonal*. In $\mathscr{R}^n$ this is also called *perpendicular*, so we could write

$$\langle\phi|\chi\rangle = 0 \iff \phi \perp \chi. \tag{1.29}$$

If two vectors are orthogonal, they are automatically linearly independent. The other way around is of course not necessarily true. If all elements of a basis sets are mutually orthogonal, the basis set is called an *orthogonal basis set*. If the basis vectors (the elements of the basis sets) are also normalized, the basis set is called *orthonormal*.

So, for an orthonormal basis set

$$B = \{\phi_1, \phi_2, \ldots, \phi_n\} \tag{1.30}$$

in an $n$-dimensional inner product space we have

$$\langle\phi_i|\phi_j\rangle = \delta_{i,j} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{if } i \neq j. \end{cases} \tag{1.31}$$

Here $\delta_{i,j}$ is called a *Kronecker delta.*

If we expand some vector $\chi$ in the basis $B$,

$$\chi = \sum_{i=1}^{n} c_i \phi_i, \tag{1.32}$$

we will refer to the coefficients $c_i$ as *expansion coefficients.* If the vector $\chi$ and the basis are given, we can compute the expansion coefficients by taking a scalar product,

$$\begin{aligned} \langle \phi_i | \chi \rangle &= \langle \phi_i | \sum_j c_j \phi_j \rangle & (1.33)\\ &= \sum_j \langle \phi_i | \phi_j \rangle c_j & (1.34)\\ &= \sum_j \delta_{ij} c_j = c_i. & (1.35) \end{aligned}$$

### 1.5.4 Finite dimensional Hilbert spaces

Any *finite* dimensional linear space can easily be turned into an *inner product space*, simply by taking any basis set (remember: if the dimension is $n$, there must be a linearly independent set of $n$ functions, and in a finite dimensional space that is automatically a basis), and *defining* that specific basis to be *orthonormal.* Since any vector can be uniquely written as a linear combination of basis vectors, we can define the scalar product of any two vectors by expanding them in the basis, and using the linearity property of the scalar product, i.e., in the orthonormal basis Eq. (1.30) we can uniquely write two arbitrary vectors $\chi, \phi \in \mathscr{V}^{(n)}$ as

$$\begin{aligned} \chi &= \sum_{i=1}^{n} c_i \phi_i, & (1.36)\\ \psi &= \sum_{i=1}^{n} d_i \phi_i & (1.37) \end{aligned}$$

and using the linearity of the scalar product and the orthonormality of the basis functions (1.31), we can compute the scalar product

$$\begin{aligned} \langle \chi | \psi \rangle &= \langle \sum_{i=1}^{n} c_i \phi_i | \sum_{i=1}^{n} d_i \phi_i \rangle & (1.38)\\ &= \sum_{i=1}^{n} \sum_{j=1}^{n} \langle c_i \phi_i | d_j \phi_j \rangle & (1.39)\\ &= \sum_{i=1}^{n} \sum_{j=1}^{n} c_i^* \langle \phi_i | \phi_j \rangle d_j & (1.40)\\ &= \sum_{i=1}^{n} \sum_{j=1}^{n} c_i^* \delta_{i,j} d_j & (1.41)\\ &= \sum_{i=1}^{n} c_i^* d_i. & (1.42) \end{aligned}$$

It is easy to verify that the scalar product defined in this way indeed satisfies all formal properties required for a scalar product.

### 1.5.5 Infinite dimensional Hilbert spaces

For a vector space of infinite dimension, we cannot follow the above procedure to define a scalar product, since an infinite dimensional set of linearly independent vectors is not necessarily a basis set. However, an infinite dimensional *Hilbert space* has, by definition, the property that an orthonormal basis set, $B = \{\phi_1, \phi_2, \ldots\}$ exists. There will be an infinite number of elements in $B$, but they will be *countable* (so we can label them with an integer subscript). With this basis set we can, again by definition of a Hilbert space, approach any vector arbitrarily close in *norm*. That is, for any $\psi \in \mathscr{H}$ we can find expansion coefficients $\{c_1, c_2, \ldots\}$ such that

$$\lim_{n\to\infty} \left\| \psi - \sum_{i=1}^{n} c_i \phi_i \right\| = 0. \tag{1.43}$$

Of course, just *defining* a Hilbert space is just a start. We also need to show that the set of functions, together with the scalar product that we defined (Eq. 1.20), is indeed a Hilbert space, and to actually compute something we to find a basis set. The general solution for these problems we will leave to mathematicians, but we'll encounter recipes below that allow us to solve many problems in quantum mechanics.

Now that we have worked hard to define the mathematical properties of wave functions, we continue with the postulates of quantum mechanics.

## 1.6 Observables and Hermitian operators

For every observable in classical mechanics, there exists a Hermitian operator in quantum mechanics. Before we define what this means, we will first give some examples of the operators corresponding to classical observables momentum, position, potential, and kinetic energy:

The first example is the momentum operator $\hat{p}$ corresponding to the classical momentum $p$. It is defined, for any $\phi \in \mathscr{H}$ by

$$(\hat{p}\phi)(x) \equiv \frac{\hbar}{i} \frac{\partial \phi(x)}{\partial x}, \tag{1.44}$$

or simply

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}. \tag{1.45}$$

The reason to write it as in Eq. (1.44) is that mathematically, an operator is defined as a *mapping* from a set of functions (the Hilbert space in our case, called the *domain*) to another set, called the *range*, which in our case is the same Hilbert space. This may seem a rather formal, but when we want to show that two operators are equal, we often do that by applying them to functions and to show that we get the same. Remember that we carefully defined what “the same” means for functions - the distance being zero.

Also note the parentheses in $(\hat{p}\phi)(x)$: the operator is working on the function giving a new function, and we evaluate that new function in the point $x$. We will not always write the parentheses around the operator and the function, but be aware that $\hat{p}(\phi(x))$ is incorrect: $\phi(x)$ is an element of the *range* of the function $\phi$, i.e., a number, and the operator should be acting on a function, not on a number.

It is important to note that Eq. (1.44) for defining a momentum operator applies to *Cartesian coordinates* and it does not necessarily work in other coordinates, we'll come back to this point when we introduce spherical polar coordinates in three dimensions.

The second example is the position operator $\hat{x}$ corresponding to the classical position of a particle $x$. The operator $\hat{x}$ is defined by its action on any wave function $\phi \in \mathscr{H}$ through

$$(\hat{x}\phi)(x) = x\phi(x). \tag{1.46}$$

This operator is called a *multiplicative operator* for obvious reasons. If we leave out the wave function, as we did for the momentum operator, we actually get $\hat{x} = x$, and not much can actually go wrong if we drop the hat of multiplicative operators. One more example of a multiplicative operator is the potential operator $\hat{V}(x)$, which we will often write as $V(x)$.

The third example is the kinetic energy operator. We can simply find it by replacing the momenta in the classical expression, Eq. (1.5), by momentum operators:

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{1.47}$$

Again, this recipe works for Cartesian coordinates, but is not general.

### 1.6.1 Hermitian operators

First we define *linear operators.* A linear operator $\hat{A}$ acting on a Hilbert space $\mathscr{H}$ is defined by two properties

$$\hat{A}\,(c\phi) = c(\hat{A}\phi) \tag{1.48}$$

$$\hat{A}(\phi + \chi) = \hat{A}\phi + \hat{A}\chi, \tag{1.49}$$

where $c \in \mathbb{C}$ and $\phi, \chi \in \mathscr{H}$. It is not hard to check that the examples above are linear operators.

The *Hermitian conjugate* $\hat{A}^\dagger$ of linear operator $\hat{A}$ is defined by the requirement that for any two functions $\phi, \chi \in \mathscr{H}$ we have

$$\langle \hat{A}^\dagger \phi | \chi \rangle = \langle \phi | \hat{A}\chi \rangle. \tag{1.50}$$

An operator is called *Hermitian* is $\hat{A}^\dagger = \hat{A}$, i.e., if

$$\langle \hat{A}\phi | \chi \rangle = \langle \phi | \hat{A}\chi \rangle \tag{1.51}$$

for any two functions in Hilbert space. It is easy to check that the position operator $\hat{x}$ and the potential operator $\hat{V}$ are Hermitian. For $\hat{p}$ and $\hat{T}$ it is a little more work. The proof requires that we assume that for any wave function $\phi(x,t) \in \mathscr{H}$ we have

$$\lim_{x \to \pm\infty} \phi(x,t) = 0. \tag{1.52}$$

Physically, this is no big deal, we simply assume that the particle we observe is at least somewhere in the lab. Mathematically, showing that this condition is satisfied for all elements in the Hilbert space is not trivial but possible, but the real problem is that we will find perfectly good solutions of the time-independent Schrödinger equation that do not go to zero at infinite, and then extra care will be needed.

Now that we have an Hermitian operator for everything we may want to measure, we can define the third postulate on measurements.

## 1.7 Measurements of observables

Let us assume that the Hermitian operator $\hat{A}$ associated with an observable has a *complete set* of eigenfunction $\Psi_i$ with corresponding eigenvalues $a_i$

$$\hat{A}\Psi_i = a_i\Psi_i. \tag{1.53}$$

With *complete set* we mean that the eigenfunctions $\{\Psi_1, \Psi_2, \ldots\}$ are a basis of the Hilbert space. The possible outcomes of measurement of the observable are the eigenvalues of the operator. The *probability* of measuring $a_i$, when the wave function of the particle is $\phi(x,t)$, is given by

$$p_i(t) = \frac{1}{N^2}|\langle\Psi_i|\phi(t)\rangle|^2, \tag{1.54}$$

where we dropped the $x$ argument in the bra-ket notation. If we repeat the measurement, and the particle is described by the same wave function $\phi(x,t)$ every time, then the average value of the observable corresponding to operator $\hat{A}$ is given by the *expectation value*

$$a(t) = \langle\hat{A}\rangle \equiv \frac{1}{N^2}\langle\phi(t)|\hat{A}\phi(t)\rangle. \tag{1.55}$$

Not all Hermitian operators have a complete and countable set of eigenfunctions, we'll come back to this complication in the next chapter. However, the expression for the expectation value is still valid in that case.

## 1.8 Time-dependent Schrödinger equation

The time-dependent wave function $\phi(x,t)$ is a solution of the *time-dependent* Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = \hat{H}\phi(x,t). \tag{1.56}$$

The initial condition $\phi(x,t_0)$ can be prepared in an experiment in several ways. In particular, if we measure some property $\hat{A}$, and the result is eigenvalue $a_i$, then the wave function of the particle after the measurement is given by the eigenfunction $\Psi_i$ corresponding to the eigenvalue. For now, we ignore the possibility of *degenerate* eigenvalues, i.e., different eigenfunctions with the same eigenvalues. We also ignore the situation where we have incomplete knowledge of the initial state: in that case we would need *density matrices* and methods from quantum statistical mechanics to properly describe the system.

Let's discuss some examples: if we measure the position of a particle, i.e., $\hat{A} = \hat{x}$, we find, on average, at time $t$

$$x(t) = \langle\hat{x}\rangle = \frac{1}{N^2}\langle\phi(t)|\hat{x}\phi(t)\rangle. \tag{1.57}$$

Just as in classical mechanics, we have a position as a function of time, but now this position is only the *average*, and we can only measure the "trajectory" by repeating the experiment for every $t$ that we want to know, since in principle the measurement of $x$ changes the wave function $\phi(t)$, by putting it in an eigenfunction of the $\hat{x}$ operator.

We can also measure the expectation value of the momentum operator $\hat{p}$, again by repeating the experiment many times, and find $p(t)$ which we can compare to the classical momentum. Even though the classical and quantum results may differ, it turns out the time-dependent expectation values $x(t)$ and $p(t)$ satisfy the *classical* Hamilton's equations of motion! The derivation is actually not very difficult, but we will skip it for now.

Instead, we consider one more observable, the energy of the system. The corresponding Hermitian operator is, unsurprisingly, the Hamiltonian operator $\hat{H}$. Thus, a precise measurement of the energy of a system gives one of the eigenvalues $E_i$ of $\hat{H}$,

$$\hat{H}\Psi_i(x) = E_i\Psi_i(x) \tag{1.58}$$

and it will put the system in eigenfunction $\Psi_i(x)$. We can find the time-development of this wave function after the measurement, by making the *ansatz* that is can be written as

$$\Psi(x,t) = \Psi_i(x)f(t). \tag{1.59}$$

Substituting this *ansatz* in the time-dependent Schrödinger equation gives

$$i\hbar\frac{\partial}{\partial t}\Psi_i(x)f(t) = \hat{H}\Psi_i(x)f(t) \tag{1.60}$$

which gives

$$i\hbar\Psi_i(x)\frac{\partial}{\partial t}f(t) = E_i\Psi_i(x)f(t) \tag{1.61}$$

or

$$\Psi_i(x)[i\hbar\frac{\partial}{\partial t} - E_i]f(t) = 0. \tag{1.62}$$

So, since the wave function cannot be the zero everywhere, we must have

$$i\hbar\frac{\partial}{\partial t}f(t) = E_i f(t) \tag{1.63}$$

which has the solution

$$f(t) = f(0)e^{-\frac{i}{\hbar}E_i t}. \tag{1.64}$$

Thus, only the phase of the wave function changes in time, but the probability density is time independent

$$\rho(x,t) = |\Psi(x,t)|^2 = |\Psi_i(x)|^2|e^{-\frac{i}{\hbar}E_i t}|^2 = |\Psi_i(x)|^2, \tag{1.65}$$

where we assumed that the wave function was normalized.

# Chapter 2

# Spectral decomposition of Hermitian operators

Since the Hamiltonian and all other operators associated with observables are Hermitian operators, we need to go a little deeper into their properties.

## 2.1 The expectation value of an Hermitian operator is real

Clearly, if they were complex the measurement postulate would be in trouble. The expectation value of Hermitian operator $\hat{A}$ for any wave function $\phi \in \mathscr{H}$ is given by

$$\langle \hat{A} \rangle = \frac{1}{N^2} \langle \phi | \hat{A} \phi \rangle. \tag{2.1}$$

From the defining equation of an Hermitian operator, we have

$$\langle \hat{A} \phi | \phi \rangle = \langle \phi | \hat{A} \phi \rangle, \tag{2.2}$$

for any $\phi \in \mathscr{H}$ and from the definition of a scalar product, we also have

$$\langle \hat{A} \phi | \phi \rangle = \langle \phi | \hat{A} \phi \rangle^*, \tag{2.3}$$

so clearly $\langle \hat{A} \rangle$ must be real.

## 2.2 The eigenvalues of Hermitian operators are real

Assume we have an Hermitian operator $\hat{A}$, with eigenvector $\phi_i$ and corresponding eigenvalue $a_i$,

$$\hat{A} \phi_i = a_i \phi_i \tag{2.4}$$

then from

$$\langle \hat{A} \phi_i | \phi_i \rangle = \langle \phi_i | \hat{A} \phi_i \rangle, \tag{2.5}$$

and the anti-linearity of the scalar product we have

$$a_i^* \langle \phi_i | \phi_i \rangle = \langle \phi_i | \phi_i \rangle a, \tag{2.6}$$

i.e.,

$$(a_i^* - a_i) \langle \phi_i | \phi_i \rangle = 0 \tag{2.7}$$

so either $\phi_i$ is the null vector, or $a_i^* = a_i$, i.e., $a_i$ is real.

## 2.3 Eigenvectors of Hermitian operators with different eigenvalues are orthogonal

Let us assume two eigenvalues $e_1 \neq e_2$ and corresponding eigenvectors:

$$\hat{H}\psi_1 = e_1\psi_1 \tag{2.8}$$

$$\hat{H}\psi_2 = e_2\psi_1. \tag{2.9}$$

From the hermiticity of $\hat{H}$ we have

$$\langle \hat{H}\psi_1|\psi_2\rangle = \langle \psi_1|\hat{H}\psi_2\rangle \tag{2.10}$$

so

$$\langle e_1\psi_1|\psi_2\rangle = \langle \psi_1|e_2\psi_2\rangle \tag{2.11}$$

For the *real* numbers the scalar product is linear, so

$$(e_1 - e_2)\langle \psi_1|\psi_2\rangle = 0. \tag{2.12}$$

If the eigenvalues are different it follows that $\psi_1$ and $\psi_2$ must be orthogonal.

If the eigenvalues are *degenerate*, $e_1 = e_2 = e$, we find that any linear combination of $\psi_1$ and $\psi_2$ is also an eigenvector of $\hat{H}$:

$$\hat{H}(c_1\psi_1 + c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 \tag{2.13}$$

$$= c_1e\psi_1 + c_2e\psi_2 \tag{2.14}$$

$$= e(c_1\psi_1 + c_2\psi_2). \tag{2.15}$$

Hence, even if $\psi_1$ and $\psi_2$ are not orthogonal, we can find a linear combination

$$\psi_2' = c_1\psi_1 + c_2\psi_2 \tag{2.16}$$

that *is* orthogonal to $\psi_1$ (and nontrivial). The orthogonality condition

$$\langle \psi_1|c_1\psi_1 + c_2\psi_2\rangle = 0 \tag{2.17}$$

gives

$$c_1\langle \psi_1|\psi_1\rangle + c_2\langle \psi_1|\psi_2\rangle = 0 \tag{2.18}$$

so we can take

$$c_1 = N\langle \psi_1|\psi_2\rangle \tag{2.19}$$

$$c_2 = -N\langle \psi_1|\psi_1\rangle, \tag{2.20}$$

where $N$ is a normalization constant and we get $\langle \psi_1|\psi_2'\rangle = 0$. If we have more than two degenerate eigenvectors, we can continue this process, which is known as Gram-Schmidt orthogonalization.

## 2.4 Continuum spectrum

Linear momentum is an observable, and the corresponding Hermitian operator is the momentum operator $\hat{p}$. The eigenvalues $p$ and eigenfunctions $\psi_p(x)$ are solutions of

$$\hat{p}\psi_p(x) = p\psi_p(x), \tag{2.21}$$

i.e., with $\hat{p}$ from Eq. (1.45)

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x) = p\psi(x). \tag{2.22}$$

We try functions of the form

$$\psi_k(x) = e^{ikx} \tag{2.23}$$

and we find that these are eigenfunctions with eigenvalues $p = \hbar k$. There is one problem: these eigenfunctions cannot be normalized, so they are not part of the Hilbert space. Also, we do not get a countable set of eigenvalues since $k$ can be any real number, and we cannot compute scalar products between the eigenfunctions, since they do not vanish at infinite. These momentum eigenfunctions are also eigenfunctions of the kinetic energy operator $\hat{T}$, in which case the eigenvalues are $\frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$. When studying collisions of particles or photodissociation using the time-independent Schrödinger equation we will have to deal with eigenfunctions that are outside Hilbert space. This is the topic of the master course “Quantum Dynamics”. In the present course we focus on bound states, which are always part of the Hilbert space since they go to zero at infinity.

We we must keep in mind, however, that an Hermitian operator may have both a discrete spectrum, for which the eigenfunctions are part of Hilbert space, and a continuum spectrum, for which the eigenfunctions are not in the Hilbert space. If this happens, we may still have a countable, infinite number of orthonormal eigenfunctions, but they would not form a complete basis for the Hilbert space. Perhaps somewhat surprisingly, we could use the continuum functions to represent the “missing part” of Hilbert space. E.g., the momentum eigenfunctions are a Fourier basis, so with an integral over them, we could represent normalizable functions.

In the computation of bound states, often the eigenfunctions of an approximate Hamiltonian are used as a basis set. It is important to keep in mind that if that approximate Hamiltonian supports continuum states–e.g., if it describes a molecule that dissociates above a certain energy–the set of bound states is not a complete basis of the Hilbert space, even if there are an infinite number of bound states.

## 2.5 Commuting Hermitian operators

The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{2.24}$$

If the commutator is zero, the operators are said to *commute*. If $\hat{A}$ and $\hat{B}$ commute, then any eigenvector $\phi$ of $\hat{A}$, with eigenvalue $\lambda$, is also an eigenvector of $\hat{B}$ since

$$\hat{A}(\hat{B}\phi) = \hat{B}\hat{A}\phi = \lambda\hat{B}\phi \tag{2.25}$$

so $\hat{B}\phi$ is also an eigenvector of $\hat{A}$ with eigenvalue $\lambda$. If the eigenvector $\phi$ of $\hat{A}$ with eigenvalue $\lambda$ is nondegenerate, then $\hat{B}\phi$ can only differ from $\phi$ by some factor $\mu$, so

$$\hat{B}\phi = \mu\phi \tag{2.26}$$

so $\phi$ is also an eigenvector of $\hat{B}$, and the corresponding eigenvalue is $\mu$. If the eigenvalue $\lambda$ is $n$-fold degenerate, i.e., there are $n$ linearly independent eigenfunctions of $\hat{A}$ with eigenvalue $\lambda$, then $\hat{B}$ is an Hermitian operator on the degenerate subspace of $\hat{A}$, so it has $n$ eigenvectors which span that space. If $\hat{A}$ and $\hat{B}$ only have a discrete spectrum, then we can construct an orthonormal basis of the Hilbert space consisting of functions $\phi_{\lambda,\mu}$ which are simultaneous eigenfunctions of $\hat{A}$ and $\hat{B}$,

$$\hat{A}\phi_{\lambda,\mu} = \lambda\phi_{\lambda,\mu} \tag{2.27}$$

$$\hat{B}\phi_{\lambda,\mu} = \mu\phi_{\lambda,\mu}. \tag{2.28}$$

## 2.6 Noncommuting operators

An example fundamental to quantum mechanics is the commutator of position and momentum

$$[\hat{x}, \hat{p}] = i\hbar. \tag{2.29}$$

Because of the commutation relation, these operators cannot have a common eigenvector. To show this, suppose they did:

$$\hat{x}\phi = \lambda\phi \tag{2.30}$$

$$\hat{p}\phi = \mu\phi \tag{2.31}$$

then

$$[\hat{x}, \hat{p}]\phi = i\hbar\phi \tag{2.32}$$

so

$$(\lambda\mu - \mu\lambda)\phi = i\hbar\phi \tag{2.33}$$

so $\phi$ must be the null vector.

### 2.6.1 Ladder operators

We now consider an Hermitian operator $\hat{A}$ and another operator $\hat{B}$, which need not be Hermitian, and the following commutation relation:

$$[\hat{A}, \hat{B}] = \mu\hat{B} \tag{2.34}$$

and we assume $\hat{A}$ has an eigenvector $\phi$ with eigenvalues $\lambda$,

$$\hat{A}\phi_1 = \lambda_1\phi_1. \tag{2.35}$$

We can now find a new eigenvector and its eigenvalue using

$$\hat{A}\hat{B}\phi = \{\hat{B}\hat{A} + [\hat{A}, \hat{B}]\}\phi \tag{2.36}$$

$$= \{\hat{B}\lambda \ + \mu\hat{B}\}\phi \tag{2.37}$$

$$= (\lambda + \mu)\hat{B}\phi. \tag{2.38}$$

Thus, we found a new eigenvector of $\hat{A}$,

$$\phi_2 = \hat{B}\phi_1, \tag{2.39}$$

with eigenvalue $\lambda_2 = \lambda_1 + \mu$. The operator $\hat{B}$ is called a *ladder operator*, since you can repeatedly apply it to an eigenvector to create a new one. This process stops if applying $\hat{B}$ gives the null vector. Ladder operators are used, e.g., to find harmonic oscillator eigenfunctions and eigenfunctions of angular momentum operators.

## 2.7 Time development of an observable

Assuming a wave function $\Psi(x,t)$ evolves in time according to the time-dependent Schrödinger equation [Eq. (1.56)], we find for the time development of some observable defined by Hermitian operator $\hat{A}$,

$$\begin{aligned} a(t) = \frac{\partial}{\partial t}\langle\hat{A}\rangle &= \frac{\partial}{\partial t}\langle\Psi(t)|\hat{A}\Psi(t)\rangle && (2.40)\\ &= \langle\dot{\Psi}(t)|\hat{A}\Psi(t)\rangle + \langle\Psi(t)|\hat{A}\dot{\Psi}(t)\rangle && (2.41)\\ &= \langle\frac{-i}{\hbar}\hat{H}\Psi(t)|\hat{A}\Psi(t)\rangle + \langle\Psi(t)|\hat{A}\frac{-i}{\hbar}\hat{H}\Psi(t)\rangle && (2.42)\\ &= \frac{i}{\hbar}\Big\{\langle\Psi(t)|\hat{H}\hat{A}\Psi(t)\rangle - \langle\Psi(t)|\hat{A}\hat{H}\Psi(t)\rangle\Big\} && (2.43)\\ &= \frac{i}{\hbar}\langle\Psi(t)|[\hat{H},\hat{A}]\Psi(t)\rangle. && (2.44)\end{aligned}$$

So we find that if $\hat{A}$ commutes with the Hamiltonian, its expectation value is a constant of the motion.

## 2.8 Commutators and first derivative operators

Consider the first derivative $\frac{\partial}{\partial x}$ acting on the potential energy times the wave function

$$\frac{\partial}{\partial x}V(x)\Psi(x) = V'(x)\Psi(x) + V(x)\frac{\partial}{\partial x}\Psi(x) \tag{2.45}$$

so we find

$$[\frac{\partial}{\partial x}, V(x)]\Psi(x) = V'(x)\Psi(x) \tag{2.46}$$

for any function $\Psi$, so

$$[\frac{\partial}{\partial x}, V(x)] = V'(x). \tag{2.47}$$

In classical mechanics, the force is minus the derivative of the potential, so this equation gives another hint of why commutators are important in quantum mechanics.

## 2.9 Dirac delta functions

We will introduce Dirac-notation in the next section, but to do that properly, we need to introduce Dirac delta functions first.

The delta-function $\delta(x)$ is defined by the relation

$$f(0) = \int_{-\infty}^{\infty}\delta(x)f(x)dx, \tag{2.48}$$

for any function $f$. If we take $f(x) = 1$ we find

$$\int_{-\infty}^{\infty}\delta(x)\,dx = 1. \tag{2.49}$$

By plugging in functions for which $f(0) = 0$ we easily find that $\delta(x) = 0$ for any $x \neq 0$. This seems contradictory, and mathematically, we should not call $\delta(x)$ a function, but rather, a *distribution.*

This means that it only should be used as part of an integrand. We can approximate $\delta(x)$ in many ways, e.g., by

$$g_a(x) = \begin{cases} 1/a, & \text{for } -a/2 < x < a/2 \\ 0, & \text{otherwise.} \end{cases} \tag{2.50}$$

Clearly the integral gives 1, and if we take the limit of $a \to 0$ then $\delta(x) = 0$ for any $x \neq 0$. The problem is also clear: $g_a(0)$ will go to infinity, so strictly speaking, the limit does not exist. The solution is to only take the limit after doing the integral that involves $\delta(x)$, e.g.,

$$\lim_{a\to 0} \int_{-\infty}^{\infty} g_a(x) f(x) dx = f(0). \tag{2.51}$$

If we write

$$\delta(x) = \lim_{a\to 0} g_a(x), \tag{2.52}$$

we really mean Eq. (2.51) for any function $f$. It is easy to verify that $\delta(x-a)$ is an eigenfunction of the position operator $x$ with eigenvalue $a$

$$\hat{x}\delta(x-a) = a\delta(x-a). \tag{2.53}$$

## 2.10 Dirac notation

The simplest way to introduce Dirac notation is to take apart a scalar product $\langle\phi|\chi\rangle$ of two functions $\phi, \chi \in \mathscr{H}$ into a "bra" ($\langle\phi|$) and a "ket" ($|\chi\rangle$). To be a little more precise, we have to make the distinction between the function $\phi \in \mathscr{H}$ and $\phi(x) \in \mathbb{C}$, the value of the function in the point $x \in \mathbb{R}$. The kets in Dirac notation simply denote elements of the Hilbert space, $\mathscr{H}$, i.e., $|\phi\rangle = \phi$. The "bra" is not just the complex conjugate of $\phi$, it also implies taking the scalar product. Multiplying a ket from the left with a bra gives a scalar product:

$$\langle\phi||\chi\rangle \equiv \langle\phi|\chi\rangle. \tag{2.54}$$

Because of this relation, $\langle\phi|$ is called a linear *functional*, because it maps any function $\chi \in \mathscr{H}$ onto a number. The set of all linear functionals on $\mathscr{H}$ is called the *dual space* of $\mathscr{H}$. Note that we can now write a matrix element of an operator in two equivalent ways:

$$\langle\phi|\hat{A}|\chi\rangle = \langle\phi|\hat{A}\chi\rangle. \tag{2.55}$$

Now consider the function $X_a$ defined by

$$X_a(x) = \delta(x-a). \tag{2.56}$$

We have already seen [Eq. (2.53)] that this is an eigenfunction of the position operator, with eigenvalue $a$. In Dirac notation, we denote this function as $|a\rangle = X_a$. We can now easily derive

$$\langle a|\phi\rangle = \int_{-\infty}^{\infty} \delta(x-a)\phi(x)\, dx = \phi(a). \tag{2.57}$$

Note that from the properties of a scalar product we also have

$$\phi(x)^* = \langle\phi|x\rangle. \tag{2.58}$$

### Resolution of identity

To show that two vectors $\phi, \chi \in \mathscr{H}$ are the same,

$$|\psi\rangle = |\chi\rangle \tag{2.59}$$

it is sufficient to show that their scalar products with all elements of the Hilbert space are the same,

$$\langle\phi|\psi\rangle = \langle\phi|\chi\rangle, \quad \text{for all } \phi \in \mathscr{H}. \tag{2.60}$$

If we have a complete basis $B = \phi_1, \phi_2, \ldots$ it is sufficient to show that

$$\langle\phi_i|\psi\rangle = \langle\phi_i|\chi\rangle, \quad \text{for } i = 1, 2, \ldots. \tag{2.61}$$

To show that two *linear operators* $\hat{A}$ and $\hat{B}$ are the same, we have to apply them to all vectors in Hilbert space, and show

$$\hat{A}|\chi\rangle = \hat{B}|\chi\rangle \tag{2.62}$$

and again, if we have a complete basis, we only have to show this for all basis functions.

The *identity operator* $\hat{I}$ is defined by

$$\hat{I}|\phi\rangle = |\phi\rangle, \quad \text{for all } \phi \in \mathscr{H} \tag{2.63}$$

which means that for all $\phi, \chi \in \mathscr{H}$ we must have

$$\langle\phi|\hat{I}|\chi\rangle = \langle\phi|\chi\rangle. \tag{2.64}$$

We now derive a *resolution of the identity operator*. For any two functions $\phi, \chi \in \mathscr{H}$ we have

$$\begin{aligned}
\langle\phi|\chi\rangle &= \int_{-\infty}^{\infty} \phi(x)^* \chi(x)\, dx && (2.65)\\
&= \int_{-\infty}^{\infty} \langle\phi|x\rangle\langle x|\chi\rangle\, dx && (2.66)\\
&= \langle\phi| \underbrace{\left(\int_{-\infty}^{\infty} |x\rangle\langle x| dx\right)}_{\hat{I}} |\chi\rangle && (2.67)
\end{aligned}$$

where we identify the *identity* operator for our Hilbert space:

$$\hat{I} = \int_{-\infty}^{\infty} dx\, |x\rangle\langle x|. \tag{2.68}$$

The matrix elements of the identity operator are

$$\langle x|\hat{I}|x'\rangle = \delta(x - x'). \tag{2.69}$$

The proof is left as an exercise.

Eigenfunctions of the linear momentum operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ can also be used to setup a resolution of identity. In Dirac notation,

$$\hat{p}|p\rangle = p|p\rangle \tag{2.70}$$

and with the position representation of the momentum eigen states

$$\langle x|p\rangle = \frac{1}{2\pi\hbar} e^{\frac{i}{\hbar}px}. \tag{2.71}$$

Be aware that the notation is somewhat cryptic: we cannot use $|5\rangle$ or $|u\rangle$, unless we explicitly mention whether these are position or momentum eigenstates.

The normalization factor $\frac{1}{2\pi\hbar}$ in 2.71 is chosen to give *Dirac normalization*

$$\langle p|p'\rangle = \delta(p-p') \tag{2.72}$$

so that the resolution of identity is given by

$$\hat{p} = \int_{-\infty}^{\infty} dp\,|p\rangle\langle p|. \tag{2.73}$$

We will not prove these results, but the follow directly from the Fourier transform $F(\omega)$ of $f(x)$

$$F(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-i\omega x} f(x)\,dx \tag{2.74}$$

and its inverse

$$f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{i\omega x} F(\omega)\,d\omega. \tag{2.75}$$

Finally, every orthonormal basis set $B = \{\phi_1, \phi_2, \ldots\}$ gives a resolution of identity:

$$\hat{I} = \sum_{i=1}^{\infty} |\phi_i\rangle\langle\phi_i|. \tag{2.76}$$

and its matrix elements in this basis are

$$\langle\phi_i|\hat{I}|\phi_j\rangle = \delta_{ij}. \tag{2.77}$$

The proofs of these last two equations are left as an exercise.

## 2.11 Spectral decomposition of Hermitian operators

Let us first consider an Hermitian operator with only a *discrete* spectrum, i.e., a countable set of eigenfunctions that form a complete basis,

$$\hat{A}|\phi_i\rangle = \lambda_i|\phi_i\rangle, \text{ for } i = 1, 2, \ldots, \tag{2.78}$$

where we assume that the basis functions are orthonormal, $\langle\phi_i|\phi_j\rangle = \delta_{ij}$, for all $i$ and $j$. Then, using the resolution of identity Eq. (2.76) we find

$$\begin{aligned}
\hat{A} &= \hat{I}\hat{A}\hat{I} && (2.79)\\
&= \sum_{ij} |\phi_i\rangle\langle\phi_i|\hat{A}|\phi_j\rangle\langle\phi_i| && (2.80)\\
&= \sum_{ij} |\phi_i\rangle\delta_{ij}\lambda_j\langle\phi_i| && (2.81)\\
&= \sum_{i} |\phi_i\rangle\lambda_j\langle\phi_i|. && (2.82)
\end{aligned}$$

The linear momentum operator $\hat{p}$ has a continuous spectrum. Its expansion is similar to Eq. (2.82), except that we have an integral, rather than a sum, over all eigenvalues

$$\hat{p} = \int_{-\infty}^{\infty} dp\,|p\rangle p\langle p|. \tag{2.83}$$

To prove this expansion, one applies the operator to momentum state $|p\rangle$, and uses $\langle p|p'\rangle = \delta(p-p')$ [Eq. (2.72)].

In general, an Hermitian operator $\hat{H}$ can have both a discrete spectrum, with eigenvectors $\psi_i$ and eigenvalues $\epsilon_i$

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle \tag{2.84}$$

and a continuum part with eigenvalues $\lambda$ and eigenstates $|\lambda\rangle$

$$\hat{H}|\lambda\rangle = \lambda|\lambda\rangle, \tag{2.85}$$

in which case the expansion of the operator requires two terms

$$\hat{H} = \sum_i |\psi_i\rangle\epsilon_i\langle\psi_i| + \int d\lambda\, |\lambda\rangle\lambda\langle\lambda|. \tag{2.86}$$

Finding the proper boundary conditions and normalization of the continuum states is part of the course on quantum dynamics, but here the important thing is to remember that the resolution of identity expressed in the eigenfunctions of $\hat{H}$ has also two terms

$$\hat{I} = \sum_i |\psi_i\rangle\langle\psi_i| + \int d\lambda\, |\lambda\rangle\langle\lambda|. \tag{2.87}$$

For bound state calculations we may use the discrete part as a “basis”, but we must be aware that leaving out the continuum, if there is one, is an approximation. To give one example: if we calculate the polarizability of the hydrogen atom in a basis of its bound states, we only find about half of the experimental value.

## 2.12 Linear variation theory

To solve the time-independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{2.88}$$

if we have a complete orthonormal basis $B = \{\phi_1, \phi_2, \ldots\}$, with the linear variation method, we expand the wave function in the basis

$$|\Psi\rangle = \sum_j |\phi_j\rangle c_j, \tag{2.89}$$

and substitute this into the Schrödinger equation:

$$\hat{H}\sum_j |\phi_j\rangle = E\sum_j |\phi_j\rangle c_j. \tag{2.90}$$

If scalar products with all basis functions $|\phi_i\rangle$ are equal

$$\langle\phi_i|\hat{H}\sum_j |\phi_j\rangle c_j = \langle\phi_i|E\sum_j |\phi_j\rangle c_j, \tag{2.91}$$

then we have an exact solution. Using the linearity of scalar products we can rewrite this as

$$\sum_j \langle\phi_i|\hat{H}|\phi_j\rangle c_j = E\sum_j \langle\phi_i|\phi_j\rangle c_j. \tag{2.92}$$

Using the orthonormality of the basis, $\langle\phi_i|\phi_j\rangle = \delta_{i,j}$ and with Hamiltonian matrix elements defined by

$$H_{ij} \equiv \langle\phi_i|\hat{H}|\phi_j\rangle \tag{2.93}$$

we get

$$\sum_j H_{ij}c_j = Ec_i. \tag{2.94}$$

Here, we still have an infinite number of equations. We can find an approximate solution by truncating the basis, i.e., by keeping only the first $n$ terms in the expansion. We can now rewrite the set of equations in matrix-vector notation as a matrix eigenvalue problem

$$\boldsymbol{Hc} = E\boldsymbol{c} \tag{2.95}$$

where $\boldsymbol{c}$ is a column vector with $n$ elements

$$\boldsymbol{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \tag{2.96}$$

and $\boldsymbol{H}$ is a $n \times n$ matrix

$$\boldsymbol{H} = \begin{pmatrix} H_{1,1} & H_{1,2} & \dots & H_{1,n} \\ \vdots & & & \vdots \\ H_{n,1} & H_{n,2} & \dots & H_{n,n} \end{pmatrix}. \tag{2.97}$$

The matrix-eigenvalue problem has only non-trivial solutions when

$$\det(\boldsymbol{H} - E\boldsymbol{I}) = 0, \tag{2.98}$$

where $\boldsymbol{I}$ is the $n \times n$ identity matrix. The determinant gives a polynomial in $E$ of degree $n$, and there are $n$ zeros $E_i, i = 1, 2, \dots, n$. The eigenvalues $E_i$ are real, because the matrix $\boldsymbol{H}$ is Hermitian. For each eigenvalue we can find a nontrivial eigenvector $\boldsymbol{u}_i$ from

$$(\boldsymbol{H} - E_i\boldsymbol{I})\boldsymbol{u}_i = 0. \tag{2.99}$$

We can normalize the eigenvectors such that $|\boldsymbol{u}_i| = 1$. If eigenvalues $E_i$ and $E_j$ are different, the eigenvectors are orthogonal, $\boldsymbol{u}_i^\dagger\boldsymbol{u}_j = 0$, and for degenerate eigenvalues we can use Gram-Schmidt orthogonalization to make the corresponding eigenvectors orthonormal.

The expectation value of the energy for a wave function given by

$$|\psi\rangle = \sum_{i=1}^{n} |\phi_i\rangle x_i, \tag{2.100}$$

is easily seen to be

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\boldsymbol{x}^\dagger\boldsymbol{Hx}}{\boldsymbol{x}^\dagger\boldsymbol{x}} \equiv R(\boldsymbol{H}, \boldsymbol{x}) \tag{2.101}$$

where $R(\boldsymbol{H}, \boldsymbol{x})$ is called a Rayleigh quotient. Assuming that the eigenvalues of the matrix $\boldsymbol{H}$ are sorted, $E_1 \leq E_2 \leq E_3 \dots$, we can find the lowest eigenvalue, $E_1$ by taking the minimum of the Rayleigh quotient over all possible vectors $\boldsymbol{x} \neq \vec{0}$,

$$E_1 = \min_{\boldsymbol{x}\neq\vec{0}} R(\boldsymbol{H}, \boldsymbol{x}) \tag{2.102}$$

To prove this, we use the fact that for a finite dimensional Hermitian matrix ($\boldsymbol{H}$), we can construct a complete and orthonormal basis from the eigenvectors, $\{\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_n\}$, so we can expand any vector $\boldsymbol{x}$ in this basis

$$\boldsymbol{x} = \sum_{i=1}^{n} \boldsymbol{u}_i a_i \tag{2.103}$$

If we substitute this in the Rayleigh quotient we get

$$R(\boldsymbol{H}, \boldsymbol{x}) = \frac{\sum_{i=1}^{n} E_i |a_i|^2}{\sum_{i=1}^{n} |a_i|^2}. \tag{2.104}$$

We define the weights $w_i$ by

$$w_i = \frac{|a_i|^2}{\sum_{j=1}^{n} |a_j|^2}, \quad \text{for } i = 1, 2, \ldots, n, \tag{2.105}$$

so that $\sum_{i=1}^{n} w_i = 1$, and all $w_i \geq 0$ so we can rewrite the Rayleigh quotient as a weighted average of the energies

$$R(\boldsymbol{H}, \boldsymbol{x}) = \sum_{i=1}^{n} w_i E_i. \tag{2.106}$$

Since all energies $E_i \geq E_1$ we have

$$R(\boldsymbol{H}, \boldsymbol{x}) \geq \sum_{i=1}^{n} w_i E_1 = E_1 \sum_{i=1}^{n} w_i = E_1. \tag{2.107}$$

So the minimum of $R(\boldsymbol{H}, \boldsymbol{x})$ over all $\boldsymbol{x} \neq \vec{0}$ cannot be less than $E_1$, but it can also not be larger than $E_1$ since for $\boldsymbol{x} = \boldsymbol{u}_1$ it is equation to $E_1$.

If we increase the basis, i.e., add $\phi_{n+1}$ to it, the minimum of the Rayleigh quotient cannot go up (since the expansion coefficient of $a_{n+1}$ could be set to zero), so the lowest eigenvalue $E_1^{(n)}$ for the basis with $n$ vectors can only go down with $n$. So $E_1^{(n)}$ is an upper limit of the exact ground state energy for this problem. By increasing the dimension of the basis $n$ we can get as close to the exact solution as we want. Even though any complete basis set will work eventually, convergence can be a lot faster in one basis set than in another. In practice, we can often make the basis set dependent on a set of parameters $\boldsymbol{p}$

$$B_n^{(\boldsymbol{p})} = \{\phi_1^{(\boldsymbol{p})}, \phi_2^{(\boldsymbol{p})}, \ldots, \phi_n^{(\boldsymbol{p})}\}. \tag{2.108}$$

For a fixed dimension $n$, we can now try to minimize the $E_1^{(n)}$ by varying the parameters $\boldsymbol{p}$. This is a nonlinear problem, so it is not easy, but physical insight can help. Also, the parameters don't have to be perfect, since one can always increase $n$ to converge the result. In practice, one often starts with a basis of dimension $n$ that is small, so it is easier to find good parameters $\boldsymbol{p}$, and then $n$ is increased to reach convergence.

# Chapter 3

# Diatomic molecule in one dimension

We consider two particles moving on a straight line, the positions are $x_1$ and $x_2$, and the masses are $m_1$ and $m_2$. We assume that the interaction potential depends only on the distance between the particles

$$V_2(x_1, x_2) = V(x_2 - x_1). \tag{3.1}$$

The classical Hamiltonian for this system is

$$H(x_1, x_2, p_1, p_2) = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(x_2 - x_1). \tag{3.2}$$

We may call this system a "diatomic molecule", but clearly we can only model vibrations in one dimension, and not rotation.

Since the potential depends on both coordinates, Hamilton's equations of motion will consist of four coupled first order differential equations. We can simplify the problem by introducing new coordinates, the distance between the particle $x = x_2 - x_1$, and the center-of-mass coordinate $X$:

$$x = x_2 - x_1 \tag{3.3}$$

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}. \tag{3.4}$$

In these new coordinates, the four equations decouple into two coupled equations for the relative motion (x) and its conjugate momentum (p), and the remaining equations for the center-of-mass motion can be solved easily. Although the transformations are not very difficult, we will try to make the derivation more transparent by introducing matrix-vector notation. We define the vectors

$$\boldsymbol{x} \equiv \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \quad \boldsymbol{v} \equiv \dot{\boldsymbol{x}}, \tag{3.5}$$

where the mass matrix is defined by

$$\boldsymbol{M} = \begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix}. \tag{3.6}$$

Hence, we can write the energy expression in terms of the velocities as

$$T = \frac{1}{2}\boldsymbol{v}^T \boldsymbol{M} \boldsymbol{v} = \frac{1}{2}\sum_i \sum_j v_i M_{ij} v_j. \tag{3.7}$$

The conjugate momenta are defined by

$$p_i = \frac{\partial}{\partial v_i} T, \tag{3.8}$$

and so we find

$$\boldsymbol{p} = \boldsymbol{M}\boldsymbol{v}, \tag{3.9}$$

which would as long as the matrix $\boldsymbol{M}$ is symmetric, $\boldsymbol{M} = \boldsymbol{M}^T$:

$$\begin{aligned} p_k &= \frac{\partial}{\partial v_k} \frac{1}{2} \sum_i \sum_j v_i M_{ij} v_j && (3.10) \\ &= \frac{1}{2} \sum_i \sum_j \left( \frac{\partial v_i}{\partial v_k} M_{ij} v_j + v_i M_{ij} \frac{\partial v_j}{\partial v_k} \right) && (3.11) \\ &= \frac{1}{2} \sum_i \sum_j \left( \delta_{ik} M_{ij} v_j + v_i M_{ij} \delta_{jk} \right) && (3.12) \\ &= \frac{1}{2} \sum_j \left( M_{kj} v_j + v_i M_{ik} \right) = \sum_j M_{kj} v_j. && (3.13) \end{aligned}$$

A linear transformation of the coordinates

$$\tilde{\boldsymbol{x}} = \boldsymbol{A}\boldsymbol{x} \tag{3.14}$$

gives the same linear transformation of the velocities, assuming the transformation is time independent

$$\tilde{\boldsymbol{v}} = \boldsymbol{A}\boldsymbol{v}. \tag{3.15}$$

By inverting this last expression we can write the kinetic energy in terms of the new velocities $\tilde{\boldsymbol{v}}$,

$$T = \frac{1}{2} \tilde{\boldsymbol{v}}^T \widetilde{\boldsymbol{M}} \tilde{\boldsymbol{v}} \tag{3.16}$$

where the new mass matrix is given by

$$\widetilde{\boldsymbol{M}} = \boldsymbol{A}^{-T} \boldsymbol{M} \boldsymbol{A}^{-1} \tag{3.17}$$

and the super script $(-T)$ means invert and transpose. The new momenta are thus

$$\tilde{\boldsymbol{p}} = \widetilde{\boldsymbol{M}} \tilde{\boldsymbol{v}} \tag{3.18}$$

so we have

$$\tilde{\boldsymbol{v}} = \widetilde{\boldsymbol{M}}^{-1} \tilde{\boldsymbol{p}} \tag{3.19}$$

and we find for the Hamiltonian in the new coordinates

$$H(\tilde{\boldsymbol{x}}, \tilde{\boldsymbol{p}}) = \frac{1}{2} \tilde{\boldsymbol{p}}^T \widetilde{\boldsymbol{M}}^{-1} \tilde{\boldsymbol{p}} + V(\tilde{\boldsymbol{x}}). \tag{3.20}$$

The transformation matrix for the center-of-mass coordinates is

$$\boldsymbol{A} = \begin{pmatrix} -1 & 1 \\ \frac{m_1}{M} & \frac{m_2}{M} \end{pmatrix}. \tag{3.21}$$

We actually do not need to invert this matrix, since in Eq. (3.20) we need

$$\widetilde{\boldsymbol{M}}^{-1} = \boldsymbol{A}\boldsymbol{M}^{-1}\boldsymbol{A}^T = \begin{pmatrix} -1 & 1 \\ \frac{m_1}{M} & \frac{m_2}{M} \end{pmatrix} \begin{pmatrix} \frac{1}{m_1} & 0 \\ 0 & \frac{1}{m_2} \end{pmatrix} \begin{pmatrix} -1 & \frac{m_1}{M} \\ 1 & \frac{m_2}{M} \end{pmatrix} = \begin{pmatrix} \frac{1}{m_1} + \frac{1}{m_2} & 0 \\ 0 & \frac{1}{M} \end{pmatrix}, \tag{3.22}$$

so

$$H(x, X, p, P) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(x), \tag{3.23}$$

where $\mu$ is the reduced mass, $1/\mu = 1/m_1 + 1/m_2$. Note that the new momenta are related to the old ones through

$$\tilde{\boldsymbol{p}} = \boldsymbol{A}^{-T}\boldsymbol{p}, \tag{3.24}$$

which we could have used directly transform the old Hamiltonian. From Hamilton's equations of motion we find the the total linear momentum $P$ is conserved

$$\dot{P} = -\frac{\partial H}{\partial X} = 0 \tag{3.25}$$

the center of mass velocity is constant

$$\dot{X} = \frac{\partial H}{\partial P} = \frac{P}{M} \tag{3.26}$$

and we get the one particle result for $(x, p)$, except that we have to use the reduced mass $\mu$.

We found that the total linear momentum is conserved. It is of some interest to see that we could derive that easily without going through the full solution of the problem:

First we use $m_i a_i = m_i \dot{v}_i = \dot{p}_i$, so from Newtons equation of motion we find for the total linear momentum

$$\begin{align} \dot{P} &= \dot{p}_1 + \dot{p}_2 \tag{3.27} \\ &= F_1 + F_2 \tag{3.28} \\ &= \frac{\partial}{\partial x_1} V(x_2 - x_1) + \frac{\partial}{\partial x_2} V(x_2 - x_1) \tag{3.29} \\ &= -V'(x_2 - x_1) + V'(x_2 - x_1) = 0. \tag{3.30} \end{align}$$

## 3.1 Quantum mechanical treatment

The Hamiltonian operator in the coordinates $\boldsymbol{x}$ is

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(x_2 - x_1). \tag{3.31}$$

The coordinate transformation of Eq. (3.14) in components gives

$$\frac{\partial \tilde{x}_i}{\partial x_j} = A_{ij} \tag{3.32}$$

so for the gradient operators we have

$$\frac{\partial}{\partial x_i} = \sum_j \frac{\partial \tilde{x}_j}{\partial x_i} \frac{\partial}{\partial \tilde{x}_j} = \sum_j A_{ji} \frac{\partial}{\partial \tilde{x}_j} \tag{3.33}$$

so for the gradient

$$\boldsymbol{\nabla} = \boldsymbol{A}^T \widetilde{\boldsymbol{\nabla}} \tag{3.34}$$

and with

$$\hat{\boldsymbol{p}} = \frac{\hbar}{i} \boldsymbol{\nabla} \tag{3.35}$$

we can rewrite the momenta as

$$\hat{\boldsymbol{p}} = \frac{\hbar}{i} \boldsymbol{A}^T \widetilde{\boldsymbol{\nabla}}. \tag{3.36}$$

If we define the new momenta as

$$\hat{\tilde{\boldsymbol{p}}} = \frac{\hbar}{i} \widetilde{\boldsymbol{\nabla}} \tag{3.37}$$

we find

$$\hat{\boldsymbol{p}} = \boldsymbol{A}^T \hat{\tilde{\boldsymbol{p}}}, \tag{3.38}$$

completely analogous to the classical expression Eq. (3.24). Before we continue, we should check whether the new momenta are actually conjugate to the new coordinates, i.e., we should check whether the commutation relations are indeed

$$[\hat{\tilde{x}}_i, \hat{\tilde{p}}_j] = i\hbar\delta_{ij}. \tag{3.39}$$

This is left as an exercise to the reader. It should now be obvious that the transformation of the Hamiltonian operator to the new coordinate system is completely analogous to the classical result and we find

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + \hat{V}(x), \tag{3.40}$$

where the total linear momentum operator is

$$\hat{P} = \hat{p}_1 + \hat{p}_2. \tag{3.41}$$

Classically, we found that the total linear momentum is a constant of the motion, and quantum mechanically, we expect the same. To prove it, we need to show that the commutation $[\hat{H}, \hat{P}] = 0$.

Since $\hat{p}_1$ and $\hat{p}_2$ are acting on different coordinates, $[\hat{p}_1, \hat{p}_2] = 0$. Also, $\hat{p}_i$ commutes with $\hat{p}_i^2$ (or, in fact, any function of $\hat{p}_i$). From this it is easy to see that $\hat{P}$ commutes with the kinetic energy operator. For the potential we have

$$[\hat{P}, \hat{V}] = \frac{\hbar}{i}\left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2}\right)V(x_2 - x_1) = \frac{\hbar}{i}\left\{-V'(x_2 - x_1) + V'(x_2 - x_1)\right\} = 0. \tag{3.42}$$

Thus we find that total linear momentum is also a constant of motion in quantum mechanics.

If an operator commutes with $\hat{P}$, it also commutes with $\hat{P}^2$, so we have now written the Hamiltonian as a sum of operators acting on different coordinates

$$\hat{H} = \hat{T}_X + \hat{h}, \tag{3.43}$$

where

$$\hat{T}_X = \frac{\hat{P}^2}{2M} \tag{3.44}$$

$$\hat{h}_x = \frac{\hat{p}^2}{2\mu} + \hat{V}(x). \tag{3.45}$$

Thus we can find eigenfunction by solving Schrödinger equations for the two Hamiltonians separately,

$$\hat{T}_X \chi_P(X) = E_P \chi_P(X) \tag{3.46}$$

$$\hat{h}\psi_i(x) = \epsilon_i \psi_i(x) \tag{3.47}$$

and now the *products* of the eigenfunction are solutions of the full problem

$$\hat{H}\chi_P(X)\psi_i(x) = (E_{\text{com}} + \epsilon_i)\chi_P(X)\psi_i(x). \tag{3.48}$$

Note that we have a continuous spectrum for the center-of-mass motion, with

$$E_P = \frac{P^2}{2M}, \tag{3.49}$$

while we assume a discrete spectrum for the internal motion. This assumption is only valid if to potential goes to infinity for $|x| \to \infty$, since in that case all functions $\psi_i(x)$ must go to zero at infinity as well, and they will be in the Hilbert space.

# Chapter 4

# Diatomic molecule in three dimensions

We consider a diatomic molecule $AB$, where atoms $A$ and $B$ have masses $m_A$ and $m_B$, respectively, and their three-dimensional Cartesian coordinates are $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$. We will assume that the potential $V(r)$ depends only on the distance $r = |\boldsymbol{R}_B - \boldsymbol{R}_A|$.

## 4.1 Classical description

The main goal here is to derive the classical Hamiltonian for the motion of the molecule, and to separate as much as possible the rotation and vibration. The quantum description of $AB$ in the next section will only require a minor modification.

The classical kinetic energy is

$$T = \frac{1}{2} m_A \dot{\boldsymbol{R}}_A \cdot \dot{\boldsymbol{R}}_A + \frac{1}{2} m_B \dot{\boldsymbol{R}}_B \cdot \dot{\boldsymbol{R}}_B. \tag{4.1}$$

As in the one-dimensional case, we introduce center-of-mass coordinates

$$\boldsymbol{X} = \frac{m_A \boldsymbol{R}_A + m_B \boldsymbol{R}_B}{M}, \quad \text{with } M = m_A + m_B \tag{4.2}$$

and

$$\boldsymbol{r} = \boldsymbol{R}_B - \boldsymbol{R}_A = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}, \tag{4.3}$$

where we denoted the $x$, $y$, and $z$ components of $\boldsymbol{r}$ as $\{r_i,\ i = 1, 2, 3\}$. The kinetic energy operator in the center-of-mass coordinates is easily found to be

$$T = \frac{1}{2} M \dot{\boldsymbol{X}} \cdot \dot{\boldsymbol{X}} + \frac{1}{2} \mu \dot{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}}, \tag{4.4}$$

where the reduced mass is defined by

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}. \tag{4.5}$$

Since the potential depends only on $r = |\boldsymbol{r}|$ we can separate the center-of-mass motion and focus on the ro-vibrational motion of the molecule. The classical Hamiltonian is

$$H = \frac{\boldsymbol{p} \cdot \boldsymbol{p}}{2\mu} + V(r) = \frac{p^2}{2\mu} + V(r), \tag{4.6}$$

where the linear momentum is $\boldsymbol{p} = \mu\dot{\boldsymbol{r}}$ and $p = |\boldsymbol{p}|$. Hamilton's equation of motion are

$$\dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{\mu} \tag{4.7}$$

$$\dot{p}_i = \frac{\partial H}{\partial r_i} = -\frac{\partial V(r)}{\partial r_i} = -\frac{\partial r}{\partial r_i}\frac{\partial V(r)}{\partial r} \tag{4.8}$$

The derivatives of $r$ with respect to the components are

$$\frac{\partial r}{\partial r_i} = \frac{\partial}{\partial r_i}\sqrt{r_1^2 + r_2^2 + r_3^2} = \frac{r_i}{r}. \tag{4.9}$$

With the notation $\boldsymbol{r} = r\hat{\boldsymbol{r}}$, where $\hat{\boldsymbol{r}}$ is the unit vector along $\boldsymbol{r}$ we can write the equations of motion more compactly as

$$\dot{\boldsymbol{r}} = \mu^{-1}\boldsymbol{p} \tag{4.10}$$

$$\dot{\boldsymbol{p}} = -\hat{\boldsymbol{r}}\frac{\partial V(r)}{\partial r}. \tag{4.11}$$

The angular momentum of the molecule is defined by

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} \times \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} r_2p_3 - r_3p_2 \\ r_3p_1 - r_1p_3 \\ r_1p_2 - r_2p_1 \end{pmatrix}. \tag{4.12}$$

We can also write down the components of $\boldsymbol{l}$ using the *Levi-Civita tensor* $\epsilon_{ijk}$

$$l_i = \sum_{j=1}^{3}\sum_{k=1}^{3} \epsilon_{ijk} r_j p_k = \epsilon_{ijk} r_j p_k, \tag{4.13}$$

where we introduced Einstein's summation convention: assume a summation over every index in the equation that appears more than once (i.e., $j$ and $k$ in this case). The components of $\epsilon_{ijk}$ follow from the formula of the cross product: $\epsilon_{1,2,3} = 1$, it changes sign if any two indices are permuted, and it is zero when two or more indices are the same. Thus, $\epsilon_{ijk}$ is invariant under cyclic permutations of the indices:

$$\epsilon_{1,2,3} = \epsilon_{2,3,1} = \epsilon_{3,1,2} = 1 \tag{4.14}$$

$$\epsilon_{1,3,2} = \epsilon_{3,2,1} = \epsilon_{2,1,3} = -1 \tag{4.15}$$

and it is zero in all other cases.

From Hamilton's equation of motion we find that the angular momentum is a constant of the motion

$$\dot{\boldsymbol{l}} = \dot{\boldsymbol{r}} \times \boldsymbol{p} \;\; + \;\; \boldsymbol{r} \times \dot{\boldsymbol{p}} \tag{4.16}$$

$$= \mu^{-1}\boldsymbol{p} \times \boldsymbol{p} - r\frac{\partial V(r)}{\partial r}\hat{\boldsymbol{r}} \times \hat{\boldsymbol{r}} = \boldsymbol{0}, \tag{4.17}$$

since cross products of a vector with itself are $\boldsymbol{0}$.

The the square of the length of $\boldsymbol{l}$ is given by

$$l^2 = \boldsymbol{l} \cdot \boldsymbol{l} = (\boldsymbol{r} \times \boldsymbol{p}) \cdot (\boldsymbol{r} \times \boldsymbol{p}) \tag{4.18}$$

$$= (\boldsymbol{r} \cdot \boldsymbol{r})(\boldsymbol{p} \cdot \boldsymbol{p}) - (\boldsymbol{r} \cdot \boldsymbol{p})(\boldsymbol{r} \cdot \boldsymbol{p}) \tag{4.19}$$

$$= r^2p^2 - (\boldsymbol{r} \cdot \boldsymbol{p})^2. \tag{4.20}$$

Here we use the following vector relation, knows als "quadruple product" for vectors in $\mathscr{R}^3$

$$(\boldsymbol{a} \times \boldsymbol{b}) \cdot (\boldsymbol{c} \times \boldsymbol{d}) = (\boldsymbol{a} \cdot \boldsymbol{c})(\boldsymbol{b} \cdot \boldsymbol{d}) - (\boldsymbol{a} \cdot \boldsymbol{d})(\boldsymbol{b} \cdot \boldsymbol{c}). \tag{4.21}$$

We can write this equation in components of the vectors. First, the left hand side, using Einstein summation convention,

$$(\boldsymbol{a} \times \boldsymbol{b})_i (\boldsymbol{c} \times \boldsymbol{d})_i = \epsilon_{ijk}\, \epsilon_{ij'k'}\, a_j b_k\, c_{j'} d_{k'}. \tag{4.22}$$

For the Levi-Civita symbols, we have this relation

$$\epsilon_{ijk}\epsilon_{i,j',k'} = \delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{kj'}, \tag{4.23}$$

where the proof is left as an exercise. The scalar product between two vectors can be written using a Kronecker delta

$$\boldsymbol{a} \cdot \boldsymbol{b} = \delta_{ij} a_i b_j, \tag{4.24}$$

so with Eq. (4.22), together with Eqs. (4.23) and (4.24), we can derive Eq. (4.21). We continue with the expression for $l^2$

$$l^2 = r^2 p^2 - r^2 (\hat{\boldsymbol{r}} \cdot \boldsymbol{p})^2. \tag{4.25}$$

The component of $\boldsymbol{p}$ along $\hat{\boldsymbol{r}}$ is

$$p_r = \hat{\boldsymbol{r}} \cdot \boldsymbol{p}. \tag{4.26}$$

It is left as an exercise to show that $p_r$ is indeed the conjugate momentum of the coordinate $r$. With Eq. (4.25) we can rewrite the kinetic energy operator as

$$T = \frac{p^2}{2\mu} = \frac{l^2}{2\mu r^2} + \frac{p_r^2}{2\mu}. \tag{4.27}$$

The first term is called the centrifugal term, since it depends on the angular momentum $l$ of the molecule, and the second term gives the radial kinetic energy. Since $l$ is conserved, the centrifugal term only depends on $r$, just like the potential energy term. Thus, we can define an *effective potential* $V_l^{\text{eff}}(r)$

$$V_l^{(\text{eff})}(r) = \frac{l^2}{2\mu r^2} + V(r), \tag{4.28}$$

so that for a given value of $l$ we can solve the vibrational motion using the $l$-dependent Hamiltonian

$$H_l = \frac{p_r^2}{2\mu} + V_l^{(\text{eff})}(r). \tag{4.29}$$

From here, we could continue to solve the classical orbit, but our main goal was to show the separation of rotation and vibration, and we now switch to a quantum description of the molecule.

## 4.2 Quantum treatment of rotating and vibrating diatomic molecule

After studying the one-dimensional description of a diatomic molecule classically and quantum mechanically in Chapter 3, and the classical description in three dimensions in the previous section, it should be straightforward to separate the center-of-mass, and to setup the quantum Hamiltonian for rotation vibration problem in Cartesian coordinates,

$$\hat{H} = \frac{\hat{\boldsymbol{p}} \cdot \hat{\boldsymbol{p}}}{2\mu} + V(r), \tag{4.30}$$

where the linear momentum operator is given by

$$\hat{\boldsymbol{p}} = \frac{\hbar}{i}\boldsymbol{\nabla} = \frac{\hbar}{i}\begin{pmatrix}\nabla_1\\ \nabla_2\\ \nabla_3\end{pmatrix} = \frac{\hbar}{i}\begin{pmatrix}\partial/\partial r_1\\ \partial/\partial r_2\\ \partial/\partial r_3\end{pmatrix}. \tag{4.31}$$

Note that we use the hat in $\hat{\boldsymbol{p}}$ because it is an operator, not because it is a unit vector. In analogy to Eq. (4.12), the angular momentum operator is defined by

$$\hat{\boldsymbol{l}} = \boldsymbol{r} \times \hat{\boldsymbol{p}}. \tag{4.32}$$

The main difference with the classical description is that positions and their conjugate momenta do not commute

$$[r_i, \hat{p}_{i'}] = i\hbar\delta_{ii'}. \tag{4.33}$$

As a result, the components of the angular momentum operator also so not commute. Using the Levi-Civita tensor we find

$$[\hat{l}_i, \hat{l}_{i'}] = \epsilon_{ijk}\epsilon_{i'j'k'}[r_j\hat{p}_k, r_{j'}\hat{p}_{k'}]. \tag{4.34}$$

To evaluate the commutator we consider the general case

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \tag{4.35}$$

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}. \tag{4.36}$$

The proof of these two relations is left as an exercise. Applying both rules we find

$$\begin{aligned}[\hat{A}\hat{B}, \hat{C}\hat{D}] &= \hat{A}[\hat{B}, \hat{C}\hat{D}] + [\hat{A}, \hat{C}\hat{D}]\hat{B} &(4.37)\\ &= \hat{A}\hat{C}[\hat{B}, \hat{D}] + \hat{A}[\hat{B}, \hat{C}]\hat{D} + \hat{C}[\hat{A}, \hat{D}]\hat{B} + [\hat{A}, \hat{C}]\hat{D}\hat{B} &(4.38)\end{aligned}$$

so to evaluate the commutator in Eq. (4.34) we need the second and the third term of the last result, i.e.,

$$\begin{aligned}[\hat{l}_i, \hat{l}_{i'}] &= \epsilon_{ijk}\epsilon_{i'j'k'}(r_j[\hat{p}_k, r_{j'}]\hat{p}_{k'} + r_{j'}[r_j, \hat{p}_{k'}]\hat{p}_k) &(4.39)\\ &= i\hbar\epsilon_{ijk}\epsilon_{i'j'k'}(-\delta_{kj'}r_j\hat{p}_{k'} + \delta_{jk'}r_{j'}\hat{p}_k) &(4.40)\\ &\dots &(4.41)\\ &= i\hbar\epsilon_{ii'k}\hat{l}_k. &(4.42)\end{aligned}$$

The missing steps are left as an exercise. So, in components we have

$$[\hat{l}_i, \hat{l}_j] = i\hbar\epsilon_{ijk}\hat{l}_k, \tag{4.43}$$

which we can write a cross product of vector operators

$$\hat{\boldsymbol{l}} \times \hat{\boldsymbol{l}} = i\hbar\hat{\boldsymbol{l}} \tag{4.44}$$

Classically, this cross product would of course give $\mathbf{0}$.

## 4.3 Kinetic energy operator for diatom

Just as for the classical case, we start with the $\hat{l}^2$ operator

$$\hat{l}^2 = \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{l}} = (\boldsymbol{r} \times \boldsymbol{p}) \cdot (\boldsymbol{r} \times \boldsymbol{p}), \tag{4.45}$$

however, we cannot use the "quadruple product" formula, Eq. (4.21), since that applies to vectors in $\mathbb{R}^3$, and all elements commute, and here we have to keep in mind the commutation relation Eq. (4.33). We can, however, write the expression using Levi-Civita tensors, and use Eq. (4.23). Clearly, we will get the same expression as in classical mechanics, plus some term that arise from steps in the derivation where we had to change the order of non-commuting operators. It is left as an exercise to show that we get

$$\hat{l}^2 = r^2 \hat{p}^2 + \hbar^2 (\boldsymbol{r} \cdot \boldsymbol{\nabla})^2 + \hbar^2 \boldsymbol{r} \cdot \boldsymbol{\nabla}. \tag{4.46}$$

Before we rewrite this equation, we show that $\boldsymbol{r} \cdot \boldsymbol{\nabla}$ is an operator that only acts on $r$, and not on the spherical polar angles $\theta$ and $\phi$ defined by

$$\boldsymbol{r} = r\hat{\boldsymbol{r}} = r \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}. \tag{4.47}$$

We have

$$\frac{\partial}{\partial r}\boldsymbol{r} = \frac{\partial}{\partial r} r\hat{\boldsymbol{r}} = \hat{\boldsymbol{r}}, \tag{4.48}$$

or, in components

$$\frac{\partial r_i}{\partial r} = \frac{r_i}{r}, \tag{4.49}$$

as we got already in Eq. (4.9). Using the chain rule, we get (with Einstein summation convention)

$$\frac{\partial}{\partial r} = \frac{\partial r_i}{\partial r}\frac{\partial}{\partial r_i} = \frac{r_i}{r}\frac{\partial}{\partial r_i} = \frac{1}{r} r_i \nabla_i = \frac{1}{r}\boldsymbol{r} \cdot \boldsymbol{\nabla}, \tag{4.50}$$

so

$$\boldsymbol{r} \cdot \boldsymbol{\nabla} = r\frac{\partial}{\partial r}. \tag{4.51}$$

With this result and Eq. (4.46) we can write the kinetic energy operator as

$$\hat{T} = \frac{\hat{p}^2}{2\mu} = -\frac{\hbar^2}{2\mu r^2}\left[\left(r\frac{\partial}{\partial r}\right)^2 + r\frac{\partial}{\partial r}\right] + \frac{\hat{l}^2}{2\mu r^2} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{\hat{l}^2}{2\mu r^2}, \tag{4.52}$$

where we have rewritten the radial kinetic energy term in a more compact form, which will turn out to be particularly convenient shortly. Note that if we would have taken the classical expression, and simply substituted $p_r$ by $-i\hbar\partial/\partial r$, we would have gotten a different result.

By adding the potential energy operator, we get the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{\hat{l}^2}{2\mu r^2} + V(r). \tag{4.53}$$

## 4.4 Solving the Schrödinger equation for a diatom

With the Hamiltonian from Eq. (4.53), the time-independent Schrödinger equation in spherical polar coordinates is

$$\hat{H}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi). \tag{4.54}$$

Before we solve this equation, we have to get a few things out of the way:

### 4.4.1 The angular momentum operator commutes with $r$

The angular momentum operator $\hat{\boldsymbol{l}}$ only acts on the angles $\theta$ and $\phi$, but not on $r$. A straightforward, although somewhat tedious, way to show this is to express the operator in Spherical polar coordinates. Another way is to show that $[\hat{l}_i, r] = 0$ for $i = 1, 2, 3$. First note

$$[\hat{p}_i, r] = \frac{\hbar}{i}\frac{\partial}{\partial r_i} r = \frac{\hbar}{i}\frac{r_i}{r}, \tag{4.55}$$

so

$$[\hat{l}_i, r] = \epsilon_{ijk}[r_j\hat{p}_k, r] = \epsilon_{ijk}(r_j[\hat{p}_k, r] + [r_j, r]\hat{p}_k) = \frac{\hbar}{ir}\epsilon_{ijk}r_j r_k = 0. \tag{4.56}$$

In the last step we used that $(r_j r_k)$ is symmetric under permutation of $j$ and $k$, whereas the Levi-Civita symbol changes sign.

### 4.4.2 Hilbert space and scalar product in three dimensions

The scalar product in Cartesian space is

$$\langle f|g\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\boldsymbol{r})^* g(\boldsymbol{r})\, dr_1\, dr_2\, dr_3. \tag{4.57}$$

In spherical polar coordinates this integral becomes

$$\langle f|g\rangle = \int_0^{\infty} r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi\, f^*(r,\theta,\phi) g(r,\theta,\phi). \tag{4.58}$$

Note that the volume element is $r^2\sin\theta$. It is given by the determinant of the *Jacobian.* With $q_1 \equiv r$, $q_2 \equiv \theta$, $q_1 \equiv \phi$, the elements of the Jacobian matrix are given by

$$J_{ij} = \frac{\partial r_i}{\partial q_j}. \tag{4.59}$$

In vector notation we have

$$\boldsymbol{J} = \left[\frac{\partial \boldsymbol{r}}{\partial r}\ \frac{\partial \boldsymbol{r}}{\partial \theta}\ \frac{\partial \boldsymbol{r}}{\partial \phi}\right] = \left[\hat{\boldsymbol{r}}\ \boldsymbol{r}_\theta\ \boldsymbol{r}_\phi\right]. \tag{4.60}$$

It is left as an exercise to compute the vectors $\boldsymbol{r}_\theta$ and $\boldsymbol{r}_\phi$ [from Eq. (4.47)] and to show that the vectors $\hat{\boldsymbol{r}}$, $\boldsymbol{r}_\theta$, and $\boldsymbol{r}_\phi$ are mutually orthogonal, and that the lengths of these vectors are 1, $r$, and $r\sin\theta$, respectively. To compute the determinant of $\boldsymbol{J}$, we take advantage of the orthogonality of the columns, and the property of determinants that for any two $n \times n$ matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ we have $\det(\boldsymbol{AB}) = \det(\boldsymbol{A})\det(\boldsymbol{B})$ and also $\det(\boldsymbol{A}^T) = \det(\boldsymbol{A})$,

$$|\det(\boldsymbol{J})| = \sqrt{\det(\boldsymbol{J}^T\boldsymbol{J})} = \sqrt{r^2 r^2 \sin^2\theta} = r^2\sin\theta. \tag{4.61}$$

### 4.4.3 Angular part of the problem

The total angular momentum operator $\hat{l}^2$ commutes with all three components of $\hat{\boldsymbol{l}}$,

$$[\hat{l}^2, \hat{l}_i] = 0, \quad \text{for } i = 1, 2, 3. \tag{4.62}$$

The Hamiltonian [Eq. (4.53)] also commutes with $\hat{\boldsymbol{l}}$, so we can make simultaneous eigenfunctions of $\hat{H}$, $\hat{l}^2$, and $\hat{l}_3$. We could have taken the $\hat{l}_1$ or $\hat{l}_2$ components too, but only one of the three $\hat{l}_i$, since they do not commute amongst each other. In the next chapter we will start from the commutation relations to derive the angular momentum eigenfunctions, but here we give the solutions, so we can go on to solve the Schrödinger equation for the diatomic molecule. The solutions are the spherical harmonic functions, $Y_{lm}(\theta, \phi)$:

$$\hat{l}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi), \qquad \text{for } l = 0, 1, 2, \ldots \tag{4.63}$$

$$\hat{l}_3 Y_{lm}(\theta, \phi) = \hbar m Y_{lm}(\theta, \phi), \qquad \text{with } m = -l, -l+1, \ldots, l. \tag{4.64}$$

These functions are orthonormal,

$$\langle lm|l'm'\rangle = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \; Y^*_{lm}(\theta, \phi) Y_{l',m'}(\theta, \phi) = \delta_{ll'}\delta_{mm'}. \tag{4.65}$$

### 4.4.4 Rovibrational wave function for diatomic molecule

It is now left as an exercise to show that the wave functions

$$\Psi_{vlm}(r, \theta, \phi) = \frac{\chi_{vl}(r)}{r} Y_{lm}(\theta, \phi) \tag{4.66}$$

are solutions of Schrödinger equation Eq. (4.54), where the vibrational wave functions are solutions of the *radial* Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right] \chi_{vl}(r) = \epsilon_{vl} \chi_{vl}(r). \tag{4.67}$$

We note a few things:

- Just as in classical mechanics, we have an effective potential that depends on the angular momentum of the system, but of course in quantum mechanics, the angular momentum $l\hbar$ is quantized.

- By including the factor $1/r$ in the definition of $\Psi_{vlm}$, we simplified the kinetic energy operator for $\chi_{vl}(r)$: it looks line the operator for one Cartesian coordinate, except that the range or the coordinate is different, $r > 0$.

- The wave function $\Psi_{vlm}(r, \theta, \phi)$ must be finite, so we have the boundary condition $\chi_{vl}(0) = 0$.

- When calculating matrix elements the $1/r$ in the definition of the wave functions $\Psi_{vlm}$ cancels against the $r^2$ factor in the volume element for spherical polar coordinates.

# Chapter 5

# Angular momentum theory

In the last chapter we derived the Schrödinger to describe the rotation and vibration of a diatomic molecule. We saw that the rotational wave functions are given by spherical harmonics, $Y_{lm}(\theta, \phi)$. In this chapter we will derive the expressions for these eigenfunctions of the $\hat{l}^2$ and $\hat{l}_z$ operators. Although expressions for spherical harmonics can be found in A&S and many textbooks, understanding the derivation has many benefits. A seemingly minor issue is particularly important in practical calculations involving rotational wave functions: the sign or the complex phase of an eigenfunction can be chosen arbitrarily.

## 5.1 Angular momentum states

We assume that the Hermitian operators $\hat{\boldsymbol{l}}$ act on a Hilbert space and satisfy commutation relations Eq. (4.43). Hence, $[\hat{l}^2, \hat{l}_z] = 0$ and common eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$ exists. We call these eigenfunctions *angular momentum states* and denote them by $|ab\rangle$. At this point we only know that the eigenvalues must be real numbers,

$$\hat{l}^2|ab\rangle = a\hbar^2|ab\rangle \tag{5.1}$$

$$\hat{l}_z|ab\rangle = b\hbar|ab\rangle \tag{5.2}$$

and we will assume that the eigenstates are orthonormal,

$$\langle a'b'|ab\rangle = \delta_{a'a}\delta_{b'b}. \tag{5.3}$$

We included $\hbar^2$ and $\hbar$, so that $a$ and $b$ are dimensionless. For the square of any Hermitian operator $\hat{A}$ we have

$$\langle ab|\hat{A}^2|ab\rangle = \langle ab|\hat{A}^\dagger \hat{A}|ab\rangle = \left\| \hat{A}|ab\rangle \right\|^2 \geq 0, \tag{5.4}$$

and since $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$, the eigenvalues $a$ cannot be negative. Also, we must have $b^2 \leq a$ (why?).

## 5.2 Angular momentum ladder operators

The angular momentum ladder operators are defined by

$$\hat{l}_\pm \equiv \hat{l}_x \pm i\hat{l}_y. \tag{5.5}$$

These operators are not Hermitian, but instead, $\hat{l}_\pm^\dagger = \hat{l}_\mp$. They satisfy the following commutation relations

$$[\hat{l}^2, \hat{l}_\pm] = 0 \tag{5.6}$$

$$[\hat{l}_z, \hat{l}_\pm] = \hat{l}_\pm. \tag{5.7}$$

From this last relation we find

$$\hat{l}_\pm |ab\rangle = N_\pm(a,b)|a, b \pm 1\rangle, \tag{5.8}$$

where $N_\pm(a,b)$ is a normalization constants. We can compute these constants from

$$|N_\pm(a,b)|^2 = \langle ab|\hat{l}_\pm^\dagger \hat{l}_\pm|a,b\rangle = \langle ab|\hat{l}_\mp \hat{l}_\pm|a,b\rangle. \tag{5.9}$$

It is left as an exercise to show that

$$\hat{l}_-\hat{l}_+ = \hat{l}^2 - \hat{l}_z^2 - \hbar\hat{l}_z \tag{5.10}$$

$$\hat{l}_+\hat{l}_- = \hat{l}^2 - \hat{l}_z^2 + \hbar\hat{l}_z. \tag{5.11}$$

Thus, we find

$$|N_+(a,b)|^2 = \hbar^2[a - b(b+1)] \tag{5.12}$$

$$|N_-(a,b)|^2 = \hbar^2[a - b(b-1)]. \tag{5.13}$$

By repeatedly applying the $\hat{l}_+$ operator, we can make $b$ larger in steps of one, but this must end at some maximum value $b = l$, since $b^2$ cannot be larger then $a$, so $N_+(a,l) = 0$, i.e.,

$$a = l(l+1). \tag{5.14}$$

For now, we only know that $l$ is some real number. Starting from the state with the highest $b$, $|l(l+1), l\rangle$, we apply the $\hat{l}_-$ operator $k$ times, so $b$ becomes $l-k$, for which we have

$$|N_-[l(l+1), l-k]|^2 = l(l+1) - (l-k)(l-k-1). \tag{5.15}$$

For some large $k$ this would become negative, so it must end at some point with $N_-[l(l+1), l-k] = 0$, which gives

$$l(l+1) - (l-k)(l-k-1) = (2l-k)(k+1) = 0, \tag{5.16}$$

so $l = k/2$, i.e., $l$ can be either integer of half-integer. By a slight change of notation, where we replace $b$ by $m$, and write $|lm\rangle$, instead of $|l(l+1), m\rangle$, and use $C_\pm(l,m) = N_\pm([l(l+1), m]$, we get

$$\hat{l}^2|lm\rangle = l(l+1)\hbar^2|lm\rangle \tag{5.17}$$

$$\hat{l}_z|lm\rangle = m\hbar|lm\rangle \tag{5.18}$$

$$\hat{l}_\pm|lm\rangle = \hbar C_\pm(l,m)|l, m \pm 1\rangle, \tag{5.19}$$

where $m = -l, -l+1, \ldots, +l$ and

$$C_\pm(lm) = \sqrt{l(l+1) - m(m \pm 1)}. \tag{5.20}$$

We could have included any complex phase factor in the definition of $C_\pm(l,m)$ and the present choice is part of the Condon and Shortley convention. Sometimes a factor $i$ is included, which is known as the Racah convention. It simplifies the *time-reversal* operation, as we will see later. We can now also find the action of the $\hat{l}_x$ and $\hat{l}_y$ operators, since

$$\hat{l}_x = \frac{\hat{l}_+ + \hat{l}_-}{2} \tag{5.21}$$

$$\hat{l}_y = \frac{\hat{l}_+ - \hat{l}_-}{2i}. \tag{5.22}$$

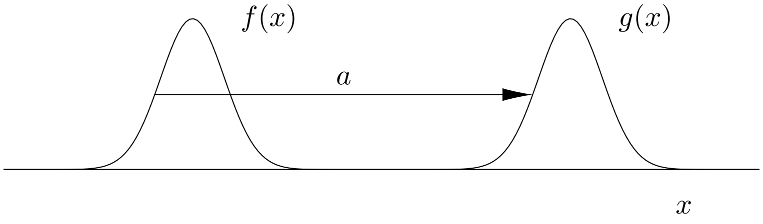

Figure 5.1: Translation of a function: $g(x) = f(x - a)$.

## 5.3 Matrix representation of angular momentum operators

From this result, we can represent the angular momentum operators acting on angular momentum states with a given value of $l$, as a $2l + 1$ dimensional matrices. Clearly, $\hat{l}^2$ and $\hat{l}_z$ become diagonal matrices, with elements

$$\langle l'm'|\hat{l}^2|lm\rangle = \hbar^2 l(l+1)\ \delta_{l'l}\delta_{m'm} \tag{5.23}$$

$$\langle l'm'|\hat{l}_z|lm\rangle = \hbar m\ \delta_{l'l}\delta_{m'm}. \tag{5.24}$$

$$\langle l'm'|\hat{l}_\pm|lm\rangle = \hbar C_\pm(l,m)\ \delta_{l'l}\delta_{m',m\pm 1}. \tag{5.25}$$

The orthonormality relation Eq. (5.3 becomes

$$\langle l'm'|lm\rangle = \delta_{l'l}\delta m'm. \tag{5.26}$$

## 5.4 Functions of operators

Below, we will need functions of operators, so here we define what that means. As a first example, consider the exponential function, which has the Taylor expansion

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n. \tag{5.27}$$

We define $e$ to the power of some operator $\hat{A}$ by replacing $x$ by $\hat{A}$ in this expansion

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n. \tag{5.28}$$

In general, if some (complex) function $f : \mathbb{C} \to \mathbb{C}$ has a Taylor expansion at $x = 0$,

$$f(x) = f(0) + f'(0)x + \frac{1}{2} f''(0)x^2 + \ldots = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} x^n, \tag{5.29}$$

then for the operator $\hat{A}$ we define

$$f(\hat{A}) = f(0)\hat{I} + f'(0)\hat{A} + \frac{1}{2} f''(0)\hat{A}^2 + \ldots = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} \hat{A}^n. \tag{5.30}$$

For an *analytic* function, this Taylor series converges for every value of $x$, and we will only encounter analytic functions of operators.

## 5.5 Functions of Hermitian matrices

A function of a matrix is defined through the Taylor series of the function, just as for operators, e.g., for a $n \times n$ matrix $\boldsymbol{A}$,

$$e^{\boldsymbol{A}} = \sum_{k=0}^{\infty} \frac{1}{k!} \boldsymbol{A}^k. \tag{5.31}$$

When $\boldsymbol{A}$ is Hermitian this sum can be calculated easily if the eigenvalue problem is solved,

$$\boldsymbol{A}\boldsymbol{u}_i = \lambda_i \boldsymbol{u}_i, \text{ for } i = 1, 2, \ldots, n. \tag{5.32}$$

We can write all eigenvectors next to each other,

$$[\boldsymbol{A}\boldsymbol{u}_1 \, \boldsymbol{A}\boldsymbol{u}_2 \, \ldots \boldsymbol{A}\boldsymbol{u}_n] = [\lambda_1 \boldsymbol{u}_1 \, \lambda_2 \boldsymbol{u}_2 \ldots \lambda_n \boldsymbol{u}_n] \tag{5.33}$$

and turn the set of equations into matrix form

$$\boldsymbol{A} \underbrace{[\boldsymbol{u}_1 \, \boldsymbol{u}_2 \, \ldots \boldsymbol{u}_n]}_{\equiv \boldsymbol{U}} = [\boldsymbol{u}_1 \, \boldsymbol{u}_2 \, \ldots \boldsymbol{u}_n] \underbrace{\begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_n \end{pmatrix}}_{\equiv \boldsymbol{\Lambda}}. \tag{5.34}$$

so

$$\boldsymbol{A}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{\Lambda}. \tag{5.35}$$

So the columns of the matrix $\boldsymbol{U}$ are the eigenvectors of $\boldsymbol{A}$, and since $\boldsymbol{A}$ is Hermitian we can take them to be orthonormal, so

$$\boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{I}, \tag{5.36}$$

where $\boldsymbol{I}$ is the $n \times n$ identity matrix, so that the Hermitian conjugate of $\boldsymbol{U}$ is its inverse

$$\boldsymbol{U}^\dagger = \boldsymbol{U}^{-1} \tag{5.37}$$

so we also have

$$\boldsymbol{U}\boldsymbol{U}^\dagger = \boldsymbol{I}. \tag{5.38}$$

If we multiply Eq. (5.35) with $\boldsymbol{U}^\dagger$ on the right we get the matrix equivalent of the spectral decomposition of an Hermitian operator

$$\boldsymbol{A} = \boldsymbol{U}\boldsymbol{\Lambda}\boldsymbol{U}^\dagger \tag{5.39}$$

We can now compute the square of the matrix by

$$\boldsymbol{A}^2 = \boldsymbol{U}\boldsymbol{\Lambda} \underbrace{\boldsymbol{U}^\dagger \boldsymbol{U}}_{\boldsymbol{I}} \boldsymbol{\Lambda}\boldsymbol{U}^\dagger = \boldsymbol{U}\Lambda^2 \boldsymbol{U}^\dagger. \tag{5.40}$$

For any power of $\boldsymbol{A}$ we can use the same trick to get

$$\boldsymbol{A}^k = \boldsymbol{U}\boldsymbol{\Lambda}^k \boldsymbol{U}^\dagger \tag{5.41}$$

Since $\boldsymbol{\Lambda}$ is a diagonal matrix (with the eigenvalues of $\boldsymbol{A}$ on the diagonal), we can simply take powers of the diagonal elements,

$$\boldsymbol{\Lambda}^k = \begin{pmatrix} \lambda_1^k & & & \\ & \lambda_2^k & & \\ & & \ddots & \\ & & & \lambda_n^k \end{pmatrix}. \tag{5.42}$$

Also, any linear combination of powers of $\boldsymbol{A}$ gives the same linear combination of powers of $\boldsymbol{\Lambda}$,

$$c_1\boldsymbol{A}^{k_1} + c_2\boldsymbol{A}^{k_2} = \boldsymbol{U}(c_1\boldsymbol{\Lambda}^{k_1} + c_2\boldsymbol{\Lambda}^{k_2})\boldsymbol{U}^\dagger. \tag{5.43}$$

So for the exponential we find

$$e^{\boldsymbol{A}} = \sum_{k=0}^{\infty} \frac{1}{k!}\boldsymbol{A}^k = \boldsymbol{U}\left(\sum_{k=0}^{\infty}\frac{1}{k!}\boldsymbol{\Lambda}^k\right)\boldsymbol{U}^\dagger \tag{5.44}$$

The Taylor series in $\boldsymbol{\Lambda}$ becomes the same Taylor series for the eigenvalues of $\boldsymbol{A}$ on the diagonal, and for diagonal element on row $j = 1, \ldots, n$ we get

$$\sum_{k=0}^{\infty}\frac{1}{k!}\lambda_j^k = e^{\lambda_j}. \tag{5.45}$$

Putting everything together

$$e^{\boldsymbol{A}} = \boldsymbol{U}\begin{pmatrix} e^{\lambda_1} & & & \\ & e^{\lambda_2} & & \\ & & \ddots & \\ & & & e^{\lambda_n}\end{pmatrix}\boldsymbol{U}^\dagger. \tag{5.46}$$

For any function $f(x)$ for which we have a Taylor series we can show in the same way that

$$f(\boldsymbol{A}) = \boldsymbol{U}f(\boldsymbol{\Lambda})\boldsymbol{U}^\dagger = \boldsymbol{U}\begin{pmatrix} f(\lambda_1) & & & \\ & f(\lambda_2) & & \\ & & \ddots & \\ & & & f(\lambda_n)\end{pmatrix}\boldsymbol{U}^\dagger. \tag{5.47}$$

## 5.6 Translation as a unitary operator

Angular momentum and rotation are closely connected. To better understand this relation, it is instructive to first have a look at a simpler problem: translation of functions in one dimension. We start by defining a function that translates a point on the real axis over a distance $a$,

$$t_a(x) = x + a. \tag{5.48}$$

If $a$ is positive (negative), we call this a translation to the right (left). For the inverse we have $t_a^{-1} = t_{-a}$.

Figure 5.1 shows a *function* $f(x)$ translated to the right over a distance $a$ to give function $g(x)$,

$$g(x) \equiv (\hat{T}_a f)(x) = f(x-a). \tag{5.49}$$

Note that translating the function to the right corresponds applying the inverse operation to the argument

$$\hat{T}_a f(x) = f[t_{-a}(x)]. \tag{5.50}$$

This is called the *Wigner convention.* We can derive an explicit expression for the translation operator $\hat{T}_a$ from the Taylor expansion

$$f(x-a) = f(x) - af'(x) + \frac{1}{2}a^2 f''(x) + \dots \tag{5.51}$$

$$= \sum_{n=0}^{\infty} \frac{(-a)^n}{n!} \frac{\partial^n}{\partial x^n} f(x) \tag{5.52}$$

$$= e^{-a\frac{\partial}{\partial x}} f(x) \tag{5.53}$$

so we may define

$$\hat{T}_a \equiv e^{-a\frac{\partial}{\partial x}}. \tag{5.54}$$

Note that the first derivative operator $\frac{\partial}{\partial x}$ is *anti-Hermitian*

$$\langle \frac{\partial}{\partial x} f | g \rangle = -\langle f | \frac{\partial}{\partial x} g \rangle. \tag{5.55}$$

and that a translation of a function leaves its norm invariant, i.e., it is a unitary transformation. We can rewrite the translation operator in terms of the *Hermitian* momentum operator

$$\hat{p}_x \equiv \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{5.56}$$

as

$$\hat{T}_a = e^{-a\frac{\partial}{\partial x}} = e^{-\frac{i}{\hbar} a \hat{p}_x}. \tag{5.57}$$

Next, we consider translation in three Cartesian dimensions. We can translate a function over a vector

$$\boldsymbol{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \lambda \hat{\boldsymbol{n}}, \tag{5.58}$$

where $\hat{\boldsymbol{n}}$ is a unit vector, $|\hat{\boldsymbol{n}}| = 1$, and $\lambda$ is the length of the vector $\boldsymbol{a}$. The translation operator can now be written using the momentum vector operator $\hat{\boldsymbol{p}}$,

$$\hat{T}(\boldsymbol{a}) = e^{-\frac{i}{\hbar} a_x \hat{p}_x}\, e^{-\frac{i}{\hbar} a_y \hat{p}_y}\, e^{-\frac{i}{\hbar} a_z \hat{p}_z} \tag{5.59}$$

$$= e^{-\frac{i}{\hbar} \hat{\boldsymbol{a}} \cdot \hat{\boldsymbol{p}}}. \tag{5.60}$$

The last step is only allowed because the linear momentum operators commute.

$$[\hat{p}_x, \hat{p}_y] = [\hat{p}_x, \hat{p}_z] = [\hat{p}_y, \hat{p}_z] = 0. \tag{5.61}$$

Finally, we redefine the translation operator as depending on some direction $\hat{\boldsymbol{n}}$ and a distance $\lambda$,

$$\hat{T}(\hat{\boldsymbol{n}}, \lambda) = e^{-\frac{i}{\hbar} \lambda \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{p}}}. \tag{5.62}$$

We are now ready to introduce rotation operators in 3D.

## 5.7 Rotation operator

If we have a function defined in spherical polar coordinates $r$, $\theta$, and $\phi$ [Eq. 4.47], a rotation around the $z$-axis using the Wigner convention is defined by

$$\hat{R}_z(\alpha)\Psi(r,\theta,\phi) = \Psi(r,\theta,\phi-\alpha). \tag{5.63}$$

So, mathematically, this is simply a translation of the $\phi$ angle. We can follow the derivation for translation in 1D, but replace $\partial/\partial x$ by $\partial/\partial\phi$, and we find

$$\hat{R}_z(\alpha) = e^{-\alpha\frac{\partial}{\partial\phi}}. \tag{5.64}$$

The $\frac{\partial}{\partial\phi}$ operator is related to the angular momentum operator $\hat{l}_z$, rather than the linear momentum $\hat{p}_z$. In Cartesian coordinates we have

$$\hat{l}_z = x\hat{p}_y - y\hat{p}_x \tag{5.65}$$

and it is left as an exercise to rewrite the operator in spherical polar coordinates:

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}, \tag{5.66}$$

so we may write a rotation around the $z$-axis as

$$\hat{R}_z(\alpha) = e^{-\frac{i}{\hbar}\alpha\hat{l}_z}. \tag{5.67}$$

The operator $\hat{l}_z$ can be written as $\boldsymbol{e}_z\cdot\hat{\boldsymbol{l}}$, where $\boldsymbol{e}_z$ is the unit vector along the $z$-axis, so we may rewrite the last equation as

$$\hat{R}(\boldsymbol{e}_z,\alpha) = e^{-\frac{i}{\hbar}\alpha\boldsymbol{e}_z\cdot\hat{\boldsymbol{l}}}. \tag{5.68}$$

If we want to rotate around some arbitrary (unit) vector $\hat{\boldsymbol{n}}$, rather then the $z$-axis, the rotation operator is given by

$$\hat{R}(\boldsymbol{n},\alpha) = e^{-\frac{i}{\hbar}\alpha\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{l}}}. \tag{5.69}$$

To derive this last relation, we first consider rotations in $\mathbb{R}^3$ in some detail.

## 5.8 Rotations in $\mathbb{R}^3$

A rotating a vector $\boldsymbol{x}$ around a normalized vector $\hat{\boldsymbol{n}}$ over an infinitesimal angle $\epsilon$ gives

$$\boldsymbol{R}(\hat{\boldsymbol{n}},\epsilon)\boldsymbol{x} = \boldsymbol{x} + \epsilon\hat{\boldsymbol{n}}\times\boldsymbol{x}. \tag{5.70}$$

The cross product is given by

$$\begin{aligned}
\hat{\boldsymbol{n}}\times\boldsymbol{x} &= \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \times \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} n_2x_3 - n_3x_2 \\ n_3x_1 - n_1x_3 \\ n_1x_2 - n_2x_1 \end{pmatrix} && (5.71) \\
&= \begin{pmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} && (5.72) \\
&\equiv \boldsymbol{N}\boldsymbol{x} && (5.73)
\end{aligned}$$

so we may write

$$\boldsymbol{R}(\hat{\boldsymbol{n}},\epsilon) = (\mathbf{1}_{3\times 3} + \epsilon\boldsymbol{N})\boldsymbol{x}, \tag{5.74}$$

where $\mathbf{1}_{3\times 3}$ is the $3\times 3$ identity matrix. The rotation operator is unitary

$$\begin{align}
\boldsymbol{R}^T\boldsymbol{R} &= (\mathbf{1}+\epsilon\boldsymbol{N})^T(\mathbf{1}+\epsilon\boldsymbol{N}) \tag{5.75}\\
&= \mathbf{1} + \epsilon(\boldsymbol{N}^T+\boldsymbol{N}) + \epsilon^2\boldsymbol{N}^T\boldsymbol{N} \tag{5.76}\\
&= \mathbf{1} + O(\epsilon^2). \tag{5.77}
\end{align}$$

The term linear in $\epsilon$ is zero, because the matrix $\boldsymbol{N}$ is anti-Hermitian

$$\boldsymbol{N}^T = -\boldsymbol{N}. \tag{5.78}$$

We can find the expression for the rotation over a finite angle $\phi$ by applying $n$ rotations over an angle $\phi/n$, and taking the limit of $n \to \infty$,

$$\boldsymbol{R}(\hat{\boldsymbol{n}},\phi) = \lim_{n\to\infty}\boldsymbol{R}(\hat{\boldsymbol{n}},\frac{\phi}{n})^n = \lim_{n\to\infty}(\mathbf{1}+\frac{\phi}{n}\boldsymbol{N})^n = e^{\phi\boldsymbol{N}}. \tag{5.79}$$

The matrix $\boldsymbol{N}$ can be written as a linear combination of anti-Hermitian matrices,

$$\begin{align}
\boldsymbol{N} &= n_1\begin{pmatrix}0&0&0\\0&0&-1\\0&1&0\end{pmatrix} + n_2\begin{pmatrix}0&0&1\\0&0&0\\-1&0&0\end{pmatrix} + n_3\begin{pmatrix}0&-1&0\\1&0&0\\0&0&0\end{pmatrix} \tag{5.80}\\
&= n_1\boldsymbol{N}_1 + n_2\boldsymbol{N}_2 + n_3\boldsymbol{N}_3 \tag{5.81}\\
&= \boldsymbol{n}\cdot\underline{\boldsymbol{N}}, \tag{5.82}
\end{align}$$

where $\underline{\boldsymbol{N}}$ is a "vector" of the matrices $\boldsymbol{N}_1$, $\boldsymbol{N}_2$, and $\boldsymbol{N}_3$. These matrices satisfy the commutation relation

$$[\boldsymbol{N}_1,\boldsymbol{N}_2] = \boldsymbol{N}_3, \tag{5.83}$$

and two other commutation relations that are found by cyclic permutation of the indices. These commutation relations can also be written in a single expression using the Levi-Civita tensor $\epsilon_{i,j,k}$,

$$[\boldsymbol{N}_i,\boldsymbol{N}_j] = \sum_{k=1}^{3}\epsilon_{i,j,k}\boldsymbol{N}_k. \tag{5.84}$$

The Levi-Civita tensor is defined by $\epsilon_{1,2,3} = 1$, and the requirement that it changes sign whenever you permute two indices. The matrices are anti-Hermitian and so we obtain Hermitian matrices if we multiply them by the imaginary number $i$

$$\underline{\boldsymbol{L}} \equiv i\hbar\underline{\boldsymbol{N}} \tag{5.85}$$

for which the components satisfy the commutation relations

$$[\boldsymbol{L}_i,\boldsymbol{L}_j] = i\hbar\sum_{k=1}^{3}\epsilon_{i,j,k}\boldsymbol{L}_k. \tag{5.86}$$

We can now express the rotation matrix in terms of the Hermitian matrices as

$$\boldsymbol{R}(\hat{\boldsymbol{n}},\phi) = e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\underline{\boldsymbol{L}}}. \tag{5.87}$$

The relation between rotations in 3D and in the Hilbert space is given by

$$\hat{R}(\hat{\boldsymbol{n}},\phi)\Psi(\boldsymbol{r}) \equiv \Psi[\boldsymbol{R}(\hat{\boldsymbol{n}},-\phi)\,\boldsymbol{r}]. \tag{5.88}$$

To derive the rotation operator $\hat{R}(\hat{\boldsymbol{n}},\phi)$, we again first consider an infinitesimally small rotation $\phi = \epsilon$. Starting from the right-hand-side we find

$$\Psi\left(e^{\frac{i}{\hbar}\epsilon\,\hat{\boldsymbol{n}}\cdot\underline{\boldsymbol{L}}}\,\boldsymbol{r}\right) = \Psi(\boldsymbol{r} - \epsilon\,\boldsymbol{n}\times\boldsymbol{r}) + \dots \tag{5.89}$$

The dots refer to higher orders in $\epsilon$. The first order expansion of a function with three variables ($r_1$, $r_2$, and $r_3$) in this case, can be written as:

$$\begin{aligned}
\Psi(\boldsymbol{r}+\boldsymbol{a}) &= \Psi(\boldsymbol{r}) + a_1\frac{\partial}{\partial r_1}\Psi(\boldsymbol{r}) + a_2\frac{\partial}{\partial r_2}\Psi(\boldsymbol{r}) + a_3\frac{\partial}{\partial r_3}\Psi(\boldsymbol{r}) + \dots && (5.90)\\
&= \Psi(\boldsymbol{r}) + \boldsymbol{a}\cdot\boldsymbol{\nabla}\Psi(\boldsymbol{r}) && (5.91)\\
&= (1+\boldsymbol{a}\cdot\boldsymbol{\nabla})\Psi(\boldsymbol{r}). && (5.92)
\end{aligned}$$

So with $\boldsymbol{a} = -\epsilon\boldsymbol{n}\times\boldsymbol{r}$ we find

$$\begin{aligned}
\Psi(\boldsymbol{r}-\epsilon\boldsymbol{n}\times\boldsymbol{r}) &= [1-\epsilon(\boldsymbol{n}\times\boldsymbol{r})\cdot\boldsymbol{\nabla}]\Psi(\boldsymbol{r}) && (5.93)\\
&= [1-\epsilon\boldsymbol{n}\cdot(\boldsymbol{r}\times\boldsymbol{\nabla})]\Psi(\boldsymbol{r}) && (5.94)\\
&= [1-\frac{i}{\hbar}\epsilon\,\boldsymbol{n}\cdot(\boldsymbol{r}\times\hat{\boldsymbol{p}})]\Psi(\boldsymbol{r}) && (5.95)\\
&= (1-\frac{i}{\hbar}\epsilon\,\boldsymbol{n}\cdot\hat{\boldsymbol{l}})\Psi(\boldsymbol{r}), && (5.96)
\end{aligned}$$

so for small rotations

$$\hat{R}(\hat{\boldsymbol{n}},\epsilon) = 1 - \frac{i}{\hbar}\epsilon\,\boldsymbol{n}\cdot\hat{\boldsymbol{l}}. \tag{5.97}$$

From this, we find the expression for rotation over a finite angle $\phi$ just as we did above for finite rotations in $\mathbb{R}^3$,

$$\hat{R}(\hat{\boldsymbol{n}},\phi) = \lim_{n\to\infty}\hat{R}(\boldsymbol{n},\frac{\phi}{n})^n = e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{l}}}. \tag{5.98}$$

## 5.9 Wigner rotation matrices

We will now evaluate the action of a rotation operator on an angular momentum state

$$\hat{R}(\boldsymbol{n},\phi)|lm\rangle = e^{-\frac{i}{\hbar}\phi\boldsymbol{n}\cdot\hat{\boldsymbol{l}}}|lm\rangle. \tag{5.99}$$

Formally, the exponential operator is defined by it Taylor series, so in principle it can be written as a polynomial in $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$. Since these operators do not change the $l$ quantum number, the result must be some linear combination of angular momentum states with the same $l$, but potentially contributions from all $2l+1$ values of $m'$,

$$\hat{R}(\boldsymbol{n},\phi)|lm\rangle = \sum_{m'=-l}^{l}|lm'\rangle D^{(l)}_{m'm}(\boldsymbol{n},\phi), \tag{5.100}$$

where the coefficients $D^{l}_{m'm}(\boldsymbol{n},\phi)$ are matrix elements of the so-called Wigner $D$-matrix. For compactness, we will also write this relation as

$$\hat{R}|lm\rangle = \sum_{m'=-l}^{l}|lm'\rangle D^{(l)}_{m'm}(\hat{R}). \tag{5.101}$$

By projecting the equation from the left with $\langle lm'|$ and using the orthonormality of the angular momentum states [Eq. (5.26)] we find an explicit expression for the $D$-matrix elements

$$D^{l}_{m',m}(\hat{R}) = \langle lm'|\hat{R}|lm\rangle. \tag{5.102}$$

For rotations around the $z$-axis, these matrix elements can be found easily,

$$D^{l}_{m',m}(\boldsymbol{e}_z, \phi) = \delta_{m'm} e^{-im\phi}. \tag{5.103}$$

For other rotation angles, one way to compute Wigner $D$-matrices uses matrix exponentiation. For example, to compute the matrix $\boldsymbol{D}^{(l)}(\boldsymbol{e}_y, \beta)$,

$$D^{(l)}_{m',m}(\boldsymbol{e}_y, \beta) = \langle lm'|e^{-\frac{i}{\hbar}\beta\hat{l}_y}|lm\rangle, \tag{5.104}$$

one first computes the $(2l+1)\times(2l+1)$ matrix $\boldsymbol{L}_y$ with matrix elements

$$\boldsymbol{L}_y(m, m') = \langle lm|\hat{l}_y|lm'\rangle \tag{5.105}$$

and then the $(2l+1)\times(2l+1)$ rotation matrix is given by

$$\boldsymbol{D}^{(l)}(\boldsymbol{e}_y, \beta) = e^{-\frac{i}{\hbar}\beta\boldsymbol{L}_y}. \tag{5.106}$$

The matrix $\boldsymbol{D}^{(l)}(\hat{R})$ is said to be a $(2l+1)$ dimensional *matrix representation* of the operator $\hat{R}$, since for any two rotation operators $\hat{R}_1$ and $\hat{R}_2$ the matrix representing the product $\hat{R}_1\hat{R}_2$ is the product of the matrix representations of $\hat{R}_1$ and $\hat{R}_2$

$$\boldsymbol{D}^{(l)}(\hat{R}_1\hat{R}_2) = \boldsymbol{D}^{(l)}(\hat{R}_1)\boldsymbol{D}^{(l)}(\hat{R}_2). \tag{5.107}$$

It is left as an exercise to derive this from the definition of the Wigner $D$-matrices in Eq. (5.101). From the definition one also finds the the representation of the identity operator $\hat{1}$ (a rotation over zero degrees) is the identity matrix,

$$\boldsymbol{D}^{(l)}(\hat{1}) = \mathbf{1}_{(2l+1)\times(2l+1)}. \tag{5.108}$$

From the representation property Eq. (5.107) one can derive many useful relations, e.g., where $\hat{1}$ is the identity operator, i.e., some rotation over 0 degrees. Rotations are unitary operators

$$\hat{R}\hat{R}^\dagger = \hat{1} \tag{5.109}$$

or

$$\hat{R}^{-1} = \hat{R}^\dagger \tag{5.110}$$

and their representations have the same properties,

$$\boldsymbol{D}^{(l)}(\hat{R}^{-1}) = [\boldsymbol{D}^{l}(\hat{R})]^{-1} = [\boldsymbol{D}^{l}(\hat{R})]^\dagger. \tag{5.111}$$

## 5.10 Wigner *D*-matrix elements as wave functions

We define the action of a rotation operator on a Wigner $\boldsymbol{D}$-matrix following the Wigner convention

$$\begin{align}\hat{R}_1\boldsymbol{D}^{(l)}(\hat{R}_2) &\equiv \boldsymbol{D}^{(l)}(\hat{R}_1^{-1}\hat{R}_2) \tag{5.112}\\ &= \boldsymbol{D}^{(l)}(\hat{R}_1)^\dagger\boldsymbol{D}^{(l)}(\hat{R}_2). \tag{5.113}\end{align}$$

From this result one finds the action of a rotation operators $\hat{R}_1$ on the complex conjugate of a Wigner $\boldsymbol{D}$-matrix element

$$\hat{R}_1 \underbrace{D^{(l),*}_{mk}(\hat{R}_2)}_{|(k)lm\rangle} = \sum_{m'=-l}^{l} \underbrace{D^{(l),*}_{m'k}(\hat{R}_2)}_{|(k)lm'\rangle} D^{(l)}_{m'm}(\hat{R}_1). \tag{5.114}$$

By comparing this equation to Eq. (5.101) we find the complex conjugates of $\boldsymbol{D}$-matrix elements transform exactly as angular momentum states

$$\hat{R}|(k)lm\rangle = \sum_{m'=-l}^{l} |(k)lm'\rangle D^{(l)}_{m'm}(\hat{R}), \tag{5.115}$$

where we use Dirac notation $|(k)lm\rangle$ to represent $D^{(l),*}_{mk}(\hat{R}_2)$.

## 5.11 Euler angles

So far, we used the so-called $(\hat{\boldsymbol{n}}, \phi)$ parameterization of rotations. Another parameterization that is particularly convenient in quantum mechanics is the $zyz$-Euler angles parameterization. The two are related by

$$\hat{R}(\hat{\boldsymbol{n}}, \phi) = \hat{R}(\boldsymbol{e}_z, \alpha)\hat{R}(\boldsymbol{e}_y, \beta)\hat{R}(\boldsymbol{e}_z, \gamma) \equiv \hat{R}(\alpha, \beta, \gamma). \tag{5.116}$$

This relation uniquely defines the Euler angles $\alpha$, $\beta$, and $\gamma$. The ranges for $\alpha$ and $\gamma$ are $[0, 2\pi]$, and $\beta \in [0, \pi]$, when $\hat{\boldsymbol{n}}$ can take all directions on a sphere, and $\phi \in [0, 2\pi]$. Although there is a one-to-one mapping $(\hat{\boldsymbol{n}}, \phi) \leftrightarrow (\alpha, \beta, \gamma)$, it is a little bit of work to find the Euler angles corresponding to some vector $\hat{\boldsymbol{n}}$ and angle $\phi$ and vice versa, except when $\hat{\boldsymbol{n}} = \boldsymbol{e}_z$, in which case we can easily find that $\beta = 0$ and $\alpha + \gamma = \phi$. Since $\hat{l}_y$ and $\hat{l}_z$ do not commute, the rotation matrices $\hat{R}_y(\beta) \equiv \hat{R}(\boldsymbol{e}_y, \beta)$ and $\hat{R}_z(\gamma) \equiv \hat{R}(\boldsymbol{e}_z, \gamma)$ do not commute in general. The Wigner $\boldsymbol{D}$-matrix representation in $zyz$-Euler representation is denoted by

$$\boldsymbol{D}^{(l)}(\alpha, \beta, \gamma) \equiv \boldsymbol{D}^{(l)}[\hat{R}(\alpha, \beta, \gamma)]. \tag{5.117}$$

The reason $zyz$ Euler angles are particularly convenient is that the $\boldsymbol{D}$-matrix corresponding to rotation around the $z$-axis is diagonal and very simple, so

$$D^{(l)}_{mk}(\alpha, \beta, \gamma) = e^{-im\alpha} d^{(l)}_{mk}(\beta) e^{-ik\gamma}, \tag{5.118}$$

where the "little-d matrix" $\boldsymbol{d}^{(l)}(\beta)$ is the representation of the rotation around the $y$-axis,

$$d^{(l)}_{mk}(\beta) \equiv \langle lm| e^{-\frac{i}{\hbar}\beta \hat{l}_y} |lk\rangle. \tag{5.119}$$

It is left as an exercise to show that this matrix is real [*hint: use Eqs. (5.106), (5.105), (5.22), and (5.5)*].

The Wigner $\boldsymbol{D}$-matrix elements satisfy the orthogonality relation

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma\, D^{(l),*}_{mk}(\alpha, \beta, \gamma) D^{(l')}_{m'k'}(\alpha, \beta, \gamma) = \frac{8\pi^2}{2l+1} \delta_{mm'} \delta_{kk'} \delta_{ll'}. \tag{5.120}$$

When we set $k = 0$, the $\boldsymbol{D}$-matrix becomes independent of the third Euler angle. The so-called Racah-normalized spherical harmonics are defined by the relation

$$C_{lm}(\theta, \phi) \equiv D^{(l)*}_{m,0}(\phi, \theta, 0) = e^{im\phi} d^{(l)}_{m,0}(\theta) \tag{5.121}$$

Note that the order of $\theta$ and $\phi$ in the arguments of $C_{lm}$ is chosen to match the order of the arguments in spherical harmonics.

When we also set $m$ to zero we find functions that depend only on $\theta$ which turn out be related to Legendre polynomials through

$$P_l(\cos\theta) = C_{l,0}(\theta, 0). \tag{5.122}$$

Since $C_{lm}(\theta, \phi)$ Racah normalized spherical harmonics only differ from the spherical harmonics that we used before by a normalization factor:

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta, \phi). \tag{5.123}$$

It is eay to show that

$$C_{lm}(0, 0) = \delta_{m,0}, \tag{5.124}$$

whereas the $Y_{lm}$'s are normalized by condition Eq. (4.65).

# Chapter 6

# Numerical solution of one-dimensional Schrödinger equation

## 6.1 Finite difference method

In a *numerical approach* a wave function is represented by its values on a grid, rather than by an expansion in a basis, as is done in a variational calculation. The simplest scheme is to use an equally spaced grid,

$$r_i = r_0 + i\Delta, \quad \text{with } i = 1, 2, \ldots, n, \tag{6.1}$$

where $\Delta$ is the grid spacing. The wave function is represented by column vector $\boldsymbol{c}$, with components

$$c_i = \chi(r_i). \tag{6.2}$$

To find a representation of the Hamiltonian we first consider the potential energy. We may represent $V(r)\chi(r)$ by a vector with components

$$V(r_i)\chi(r_i) = V(r_i)c_i, \tag{6.3}$$

which corresponds to representing the potential energy operator by a diagonal matrix $\boldsymbol{V}$ with elements

$$V_{i,j} = V(r_i)\delta_{i,j}, \tag{6.4}$$

i.e.,

$$\boldsymbol{V} = \begin{pmatrix} V_1 & & & \\ & V_2 & & \\ & & \ddots & \\ & & & V_3 \end{pmatrix}, \tag{6.5}$$

where $V_i \equiv V(r_i)$.

A representation of the kinetic energy operator may be found by approximating the second derivative operator by a finite-difference formula,

$$\frac{\partial^2}{\partial r^2}\chi(r)|_{r=r_i} \approx \frac{\chi(r_{i-1}) - 2\chi(r_i) + \chi(r_{i+1})}{\Delta^2} = \frac{c_{i-1} - 2c_i + c_{i+1}}{\Delta^2}. \tag{6.6}$$

Hence, the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} \tag{6.7}$$

is represented by the matrix

$$\boldsymbol{T} = -\frac{\hbar^2}{2\mu\Delta^2}\begin{pmatrix} -2 & 1 & & \\ 1 & -2 & 1 & \\ & 1 & -2 & 1 \\ & & 1 & \ddots \end{pmatrix}, \tag{6.8}$$

or, in components

$$T_{i,j} = -\frac{\hbar^2}{2\mu\Delta^2}(\delta_{i+1,j} - 2\delta_{i,j} + \delta_{i,j+1}). \tag{6.9}$$

The Hamiltonian matrix is the sum of kinetic and potential energy matrices,

$$\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V} \tag{6.10}$$

and the eigenvectors and eigenvalues can be found by solving the matrix eigenvalue equation

$$\boldsymbol{H}\boldsymbol{c} = E\boldsymbol{c}. \tag{6.11}$$

This numerical method is not variational, i.e., the energies that are found are not necessarily upper limits. To converge to the exact result two conditions have to be met: the grid spacing $\Delta$ must be sufficiently small and the *range*, $[r_1, r_n]$ must be sufficiently large.

In practice, to set up a grid we first decide on the maximum energy $E_{\max}$ for which we want converged results. The highest kinetic energy that we have to represent is then $T_{\max} = E_{\max} - V_e$, here $V_e$ is the minimum of the potential. A plane wave with this kinetic energy would be

$$\psi(r) = \sin(k_{\max} r - \varphi) \tag{6.12}$$

with

$$\frac{\hbar^2 k_{\max}^2}{2\mu} = T_{\max}. \tag{6.13}$$

The corresponding de Broglie wavelength $\lambda_{\min}$ is found by solving

$$k_{\max}\lambda_{\min} = 2\pi. \tag{6.14}$$

As a minimum, about four points per de Broglie wavelength are required to represent the oscillations in the wave function on a grid, so

$$\Delta_{\min} \approx \frac{\lambda_{\min}}{4}. \tag{6.15}$$

As a rule of thumb, about 10 points per de Broglie wavelength are required for accurate results.

By choosing a grid ranging from $r_1$ to $r_n$, we implicitly assume that the wave functions are zero for $r < r_1$ and for $r > r_n$. Clearly, the grid must at least include the part of the potential that is classically allowed, i.e., $V(r) < E_{\max}$. In particular when the reduced mass $\mu$ is small, wave functions will tunnel into the classically forbidden region, so the grid must be extended accordingly.

Higher order finite-difference approximations of the second derivative operator give more accurate results for the same grid spacing [2]. In particular, the infinite order finite difference formula is often used. This method is known as the Colbert-Miller DVR (discrete variable representation)[3] or sinc-function DVR [4, 5].

## Chapter 7

# Atom-diatom system

So far we considered diatomic molecules, where the only source of angular momentum is the rotation of the molecule, and we solved the rotational wave functions, the spherical harmonics, with analytic techniques. In more complex systems, there can be more sources of angular momentum. For now, we will not consider molecules with more than two atoms, but rather a "van der Waals complex" of a diatomic molecule and an atom, e.g., the complex of the CO molecule with a helium atom. Here, the CO molecule can rotate, but the atom and the molecule can also rotate around their common center of mass. In the next section we will first define so called *Jacobi coordinates*, which are particularly convenient to describe such a complex and we will give the Hamiltonian for the complex.

### 7.1 Collinear AB+C, Jacobi coordinates

First, we consider three atoms that can only move along a straight line. The atoms A, B, and C, have masses $m_{\mathrm{A}}$, $m_{\mathrm{B}}$, and $m_{\mathrm{C}}$, and Cartesian coordinates $x_{\mathrm{A}}$, $x_{\mathrm{B}}$, and $x_{\mathrm{C}}$, respectively. We define three new coordinates, $X$, the center-of-mass of the three atoms, $r$, the AB bond length, and $R$, the distance between the center-of-mass of molecule AB and atom C

$$X = \frac{m_{\mathrm{A}} x_A + m_{\mathrm{B}} x_B + m_{\mathrm{C}} x_C}{m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}} \tag{7.1}$$

$$r = x_{\mathrm{B}} - x_{\mathrm{A}} \tag{7.2}$$

$$R = x_C - \frac{m_{\mathrm{A}} x_A + m_{\mathrm{B}} x_B}{m_{\mathrm{A}} + m_{\mathrm{B}}} \tag{7.3}$$

vector notation,

$$\boldsymbol{q} = \begin{pmatrix} X \\ r \\ R \end{pmatrix}, \quad \text{and} \quad \boldsymbol{x} = \begin{pmatrix} x_{\mathrm{A}} \\ x_{\mathrm{B}} \\ x_{\mathrm{C}} \end{pmatrix}, \tag{7.4}$$

and the transformation

$$\boldsymbol{q} = \boldsymbol{Q}\boldsymbol{x}, \quad \text{with} \quad \boldsymbol{Q} = \begin{pmatrix} \frac{m_A}{M} & \frac{m_B}{M} & \frac{m_C}{M} \\ -1 & 1 & 0 \\ -\frac{m_A}{m_{\mathrm{AB}}} & -\frac{m_B}{m_{\mathrm{AB}}} & 1 \end{pmatrix}, \tag{7.5}$$

where $M_{\mathrm{AB}} = m_{\mathrm{A}} + m_{\mathrm{B}}$ and $M = m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}$. The classical kinetic energy of this system in Cartesian coordinates is given by

$$T = \frac{1}{2}\boldsymbol{v}^T \boldsymbol{M} \boldsymbol{v}, \quad \text{where the mass matrix,} \quad \boldsymbol{M} = \begin{pmatrix} m_{\mathrm{A}} & 0 & 0 \\ 0 & m_{\mathrm{B}} & 0 \\ 0 & 0 & m_{\mathrm{C}} \end{pmatrix}. \tag{7.6}$$

and $\boldsymbol{v} \equiv \dot{\boldsymbol{x}}$ is the velocity vector. With the velocities in the Jacobi coordinates, $\dot{\boldsymbol{q}} = \boldsymbol{Q}\boldsymbol{v}$, we can express the kinetic energy as

$$T = \frac{1}{2}\dot{\boldsymbol{q}}^T \boldsymbol{Q}^{-T} \boldsymbol{M} \boldsymbol{Q}^{-1} \dot{\boldsymbol{q}} \equiv \frac{1}{2}\dot{\boldsymbol{q}}^T \widetilde{\boldsymbol{M}} \dot{\boldsymbol{q}}, \tag{7.7}$$

where $\boldsymbol{Q}^{-T}$ is the transpose of the inverse of the matrix $\boldsymbol{Q}$ and the mass matrix in Jacobi coordinates

$$\widetilde{\boldsymbol{M}} = \boldsymbol{Q}^{-T} \boldsymbol{M} \boldsymbol{Q}^{-1}. \tag{7.8}$$

Although it is not very difficult to invert the matrix $\boldsymbol{Q}$, i.e., to express the Cartesian coordinates in terms of the Jacobi coordinates, it is a little easier to first compute the inverse of $\widetilde{\boldsymbol{M}}$,

$$\widetilde{\boldsymbol{M}}^{-1} = \boldsymbol{Q} \boldsymbol{M}^{-1} \boldsymbol{Q}^T. \tag{7.9}$$

It is left as an exercise to do the matrix multiplications to find

$$\widetilde{\boldsymbol{M}}^{-1} = \begin{pmatrix} \frac{1}{M} & 0 & 0 \\ 0 & \frac{1}{m_{\mathrm{A}}} + \frac{1}{m_{\mathrm{B}}} & 0 \\ 0 & 0 & \frac{1}{M_{\mathrm{AB}}} + \frac{1}{m_C} \end{pmatrix}. \tag{7.10}$$

A big advantage of Jacobi coordinates is that this mass matrix is diagonal, such that, with reduced masses

$$\frac{1}{\mu_{\mathrm{AB}}} \equiv \frac{1}{m_{\mathrm{A}}} + \frac{1}{m_{\mathrm{B}}} \tag{7.11}$$

$$\frac{1}{\mu} \equiv \frac{1}{M_{\mathrm{AB}}} + \frac{1}{m_C}, \tag{7.12}$$

the kinetic energy has three terms

$$T = \frac{1}{2}M\dot{X}^2 + \frac{1}{2}\mu_{\mathrm{AB}}\dot{r}^2 + \frac{1}{2}\mu\dot{R}^2. \tag{7.13}$$

We introduce the conjugate momenta

$$P = \frac{\partial T}{\partial \dot{X}} = M\dot{X} \tag{7.14}$$

$$p_r = \frac{\partial T}{\partial \dot{r}} = \mu_{\mathrm{AB}}\dot{r} \tag{7.15}$$

$$P_R = \frac{\partial T}{\partial \dot{R}} = \mu\dot{R} \tag{7.16}$$

to find the kinetic energy part of the classical Hamiltonian

$$T = \frac{P^2}{2M} + \frac{p_r^2}{2\mu_{\mathrm{AB}}} + \frac{p_R^2}{2\mu}. \tag{7.17}$$

## 7.2 AB+C, Jacobi coordinates

It is rather straightforward to introduce Jacobi coordinates of the AB+C system in three-dimensions. With Cartesian coordinates $\boldsymbol{r}_\mathrm{A}$, $\boldsymbol{r}_\mathrm{B}$, and $\boldsymbol{r}_\mathrm{C}$ we have

$$\boldsymbol{X} \equiv \frac{m_\mathrm{A}}{M}\boldsymbol{r}_A + \frac{m_\mathrm{B}}{M}\boldsymbol{r}_B + \frac{m_\mathrm{C}}{M}\boldsymbol{r}_C \tag{7.18}$$

$$\boldsymbol{r} \equiv \boldsymbol{r}_\mathrm{B} - \boldsymbol{r}_\mathrm{A} \tag{7.19}$$

$$\boldsymbol{R} \equiv \boldsymbol{r}_\mathrm{C} - \frac{m_\mathrm{A}\boldsymbol{r}_\mathrm{A} + m_\mathrm{B}\boldsymbol{r}_\mathrm{B}}{M_\mathrm{AB}}. \tag{7.20}$$

With the momenta $\boldsymbol{P}$, $\boldsymbol{p}_r$, and $\boldsymbol{p}_R$ conjugate to the coordinates $\boldsymbol{X}$, $\boldsymbol{r}$, and $\boldsymbol{R}$, respectively, the Hamiltonian becomes

$$T = \frac{\boldsymbol{P}\cdot\boldsymbol{P}}{2M} + \frac{\boldsymbol{p}_r\cdot\boldsymbol{p}_r}{2\mu_\mathrm{AB}} + \frac{\boldsymbol{p}_R\cdot\boldsymbol{p}_R}{2\mu}. \tag{7.21}$$

The first term is the center-of-mass kinetic energy, and if the potential does not depend on $\boldsymbol{X}$, then it can be separated from the other coordinates. The second term is exactly what we found before for the rotation/vibration of diatomic molecule AB. The last term, describing the motion of the atom, is mathematically equivalent to the kinetic energy of a diatomic molecule, where one "atom" has mass $m_\mathrm{A} + m_\mathrm{B}$, and the other atom has mass $m_\mathrm{C}$.

In general, for a system of $N$ atoms we can define Jacobi coordinates by separating the $N$-atom molecule in two fragments, and take the vector that connects the centers of mass of the fragments a Jacobi vector, and we can easily write down the contribution to the kinetic energy by computing the reduced mass for the two fragments. Within each fragment we can repeat this process.

## 7.3 Hamiltonian operator for AB+C

We assume that their are no external fields, so the potential is independent of the center-of-mass coordinates $\boldsymbol{X}$. The potential would also be independent of the orientation of the complex, so that it does not depend on all six Jacobi coordinates $\boldsymbol{R}$ and $\boldsymbol{r}$, but only on the lengths, $R \equiv |\boldsymbol{R}|$, and $r \equiv |\boldsymbol{r}|$, and on the angle between the vectors $\boldsymbol{R}$ and $\boldsymbol{r}$, $\theta = \angle(\boldsymbol{R}, \boldsymbol{r})$. In a center-of-mass frame the Hamiltonian operator is given by

$$\hat{H} = \frac{\hat{\boldsymbol{p}}_R\cdot\hat{\boldsymbol{p}}_R}{2\mu} + \frac{\hat{\boldsymbol{p}}_r\cdot\hat{\boldsymbol{p}}_r}{2\mu_\mathrm{AB}} + V(R, r, \theta), \tag{7.22}$$

where the momenta operators are given by

$$\hat{\boldsymbol{p}}_R = \frac{\hbar}{i}\boldsymbol{\nabla}_R \tag{7.23}$$

$$\hat{\boldsymbol{p}}_r = \frac{\hbar}{i}\boldsymbol{\nabla}_r. \tag{7.24}$$

Each kinetic energy term can be written as a radial kinetic energy and a centrifugal term, just as we had for a single diatomic molecule. We will use $\hat{\boldsymbol{j}}$ for the angular momentum operators of the diatomic molecule AB

$$\hat{\boldsymbol{j}} \equiv \boldsymbol{r} \times \hat{\boldsymbol{p}}_r \tag{7.25}$$

and $\boldsymbol{l}$ for the "end-over-end" rotation

$$\hat{\boldsymbol{l}} \equiv \boldsymbol{R} \times \hat{\boldsymbol{p}}_R. \tag{7.26}$$

Thus, we can write the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{l}^2}{2\mu R^2} - \frac{\hbar^2}{2\mu_{\mathrm{AB}}}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{j}^2}{2\mu_{\mathrm{AB}} r^2} + V(R,r,\theta). \tag{7.27}$$

The volume element, when using spherical polar coordinates $(R, \theta_R, \phi_R)$ and $(r, \theta_r, \phi_r)$ for Jacobi vectors $\boldsymbol{R}$ and $\boldsymbol{r}$, respectively, is

$$d\tau = R^2 dR\, \sin\theta_R d\theta_R\, d\phi_R\, r^2 dr\, \sin\theta_r d\theta_r\, d\phi_r. \tag{7.28}$$

## 7.4 AB+C, uncoupled basis set

As it stands, we have a six-dimensional problem. In principle we could find bound states using variational calculation, with basis functions:

$$\Psi_{v_{\mathrm{AB}},n,j,m_j,l,m_l}(r,R,\theta_r,\phi_r,\theta_R,\phi_R) = \frac{\phi_{v_{\mathrm{AB}}}(r)}{r}\frac{\chi_n(R)}{R}Y_{jm_j}(\theta_r,\phi_r)Y_{lm_l}(\theta_R,\phi_R), \tag{7.29}$$

or, in Dirac notation

$$|v_{\mathrm{AB}}, n, j, m_j, l, m_l\rangle = |v_{\mathrm{AB}}\rangle|n\rangle|jm_j\rangle|lm_l\rangle. \tag{7.30}$$

For the radial basis functions $|v_{\mathrm{AB}}\rangle$ and $|n\rangle$ could use, e.g., harmonic oscillator functions. Calculating the matrix elements of the kinetic energy terms is relatively easy, since it is essentially the same as for a diatomic calculation. For instance, for the radial kinetic energy we have

$$\langle v'_{\mathrm{AB}}n'j'm'_jl'm'_l| - \frac{\hbar^2}{2\mu_{\mathrm{AB}}}\frac{1}{r}\frac{\partial^2}{\partial r^2}r|v_{\mathrm{AB}}njm_jlm_l\rangle = -\frac{\hbar^2}{2\mu_{\mathrm{AB}}}\langle v'_{\mathrm{AB}}|\frac{1}{r}\frac{\partial^2}{\partial r^2}r|v_{\mathrm{AB}}\rangle\delta_{n'n}\delta_{j'j}\delta_{m'_jm_j}\delta_{m'_lm_l}, \tag{7.31}$$

where

$$\langle v'_{\mathrm{AB}}|\frac{1}{r}\frac{\partial^2}{\partial r^2}r|v_{\mathrm{AB}}\rangle = \int_0^\infty \phi^*_{v_{\mathrm{AB}}}(r)\frac{\partial^2}{\partial r^2}\phi_{v_{\mathrm{AB}}}\,dr. \tag{7.32}$$

Note that we assumed that the radial basis functions are orthonormal. Strictly speaking, this would not be correct for harmonic oscillator functions, since they are orthonormal when the integral is from $-\infty$ to $+\infty$. When the basis functions are negligible for $r < 0$ the may be an acceptable approximation. If not, another basis set, or a numerical representation of the radial wave function must be chosen.

Matrix elements of the potential energy term, however, would be complicated, since it would involve six-dimensional integrals. Another problem is that the number of basis functions needed to converge the results may be large, so a huge number of matrix elements would have to be computed; for $N$ basis functions, we need $N(N+1)/2$ Hamiltonian matrix elements, since the Hamiltonian is Hermitian, and finally, the computer time needed for the numerical diagonalization of the matrix typically scales with $N^3$.

It turns out that we can substantially simplify the problem by introducing an new angular basis. In the next section we introduce this new basis, and we will come back to the problem of computing potential energy matrix elements after that.

## 7.5 Total angular momentum representation

The Hamiltonian for a diatomic molecule [Eq. (4.53)] is invariant under rotation of the coordinates since it commutes with all three components of the angular momentum operator $\hat{\boldsymbol{l}}$. As a result, $l$

and $m_l$ are good quantum numbers, and we can do a separate variational calculation for each value of $l$ separately. The solutions have a degeneracy of $(2l+1)$, and all calculations are independent of $m_l$. For the atom-diatom system, however, the potential depends not only on $r$ and $R$, but also on the angle between the Jacobi vectors $\boldsymbol{r}$ and $\boldsymbol{R}$. As a result, the Hamiltonian is only invariant under *simultaneous* rotation of $\boldsymbol{r}$ and $\boldsymbol{R}$. The corresponding rotation operator is

$$\hat{R}(\hat{\boldsymbol{n}}, \phi) = e^{-\frac{i}{\hbar}\phi \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{l}}} e^{-\frac{i}{\hbar}\phi \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{j}}}. \tag{7.33}$$

For two operators $\hat{A}$ and $\hat{B}$ that commute, $[\hat{A}, \hat{B}] = 0$, we have

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}}. \tag{7.34}$$

The angular momentum operators $\hat{\boldsymbol{l}}$ and $\hat{\boldsymbol{j}}$ act on different coordinates, so their components commute, $[\hat{l}_i, \hat{j}_k] = \delta_{ik}$, so the rotation operator can be written as

$$\hat{R}(\hat{\boldsymbol{n}}, \phi) = e^{-\frac{\hbar}{i}\phi \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}, \tag{7.35}$$

where $\hat{\boldsymbol{J}}$ is the *total angular momentum* operator

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{j}} + \hat{\boldsymbol{l}}. \tag{7.36}$$

The rotation operator commutes with the Hamiltonian, since all three components of $\hat{\boldsymbol{J}}$ commute with $\hat{H}$,

$$[\hat{H}, \hat{J}_i] = 0. \tag{7.37}$$

It is not hard to verify that $\hat{J}$ satisfies all the angular momentum commutation relations,

$$[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k \tag{7.38}$$

and with

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \tag{7.39}$$

we also have

$$[\hat{J}^2, \hat{J}_i] = 0. \tag{7.40}$$

The set of commuting operators $\hat{H}$, $\hat{J}^2$, and $\hat{J}_z$, have common eigenfunctions, and we can simplify the solution of the Schrödinger equation by first finding the angular momentum states $|JM\rangle$, which are eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$. From the general angular momentum theory we know that we must have

$$\hat{J}^2|JM\rangle = \hbar^2 J(J+1)|JM\rangle \tag{7.41}$$

$$\hat{J}_z|JM\rangle = \hbar M|JM\rangle. \tag{7.42}$$

We can find such total angular momentum eigen states in the $(2j+1) \times (2l+1)$ Hilbert space spanned by the *uncoupled* angular momentum states

$$\{|jm_j\rangle|lm_l\rangle,\ \ m_j = -j, -j+1, \ldots, j \text{ and } m_l = -l, -l+1, \ldots, l\}. \tag{7.43}$$

These uncoupled angular momentum states are eigenfunctions of the $\hat{J}_z$ operator,

$$\hat{J}_z|jm_j\rangle|lm_l\rangle = (\hat{j}_z + \hat{l}_z)|jm_j\rangle|lm_l\rangle = \hbar(m_j + m_l)|jm_j\rangle|lm_l\rangle \tag{7.44}$$

and the more difficult problem is to find linear combinations of the uncoupled states that are eigenfunctions of $\hat{J}^2$. One eigenfunction of $\hat{J}$ is actually easy to find: the uncoupled state with $m_j = j$ and $m_l = l$ has eigenvalue $M = m_j + m_l = j + l$ with respect to $\hat{J}_z$. This state also must be an eigenstate of $\hat{J}^2$ with total angular momentum quantum number $J = j + l$, since from the general theory we know that $|M| \leq J$. Note that if $J$ were larger than $j + l$, there also would have to be a state with $M = J$, but this is not possible since $m_j + m_l$ is at most $j + l$. To explicitly show that $|jj\rangle|ll\rangle$ is an eigenfunction of $\hat{J}^2$ one rewrites $\hat{J}^2$ using ladder operators

$$\begin{aligned}\hat{J}_\pm &\equiv \hat{J}_x \pm i\hat{J}_y &(7.45)\\ &= \hat{j}_x + \hat{l}_x \pm i(\hat{j}_y + \hat{l}_y) &(7.46)\\ &= \hat{j}_x \pm i\hat{l}_y + \hat{l}_x \pm i\hat{l}_y &(7.47)\\ &= \hat{j}_\pm + \hat{l}_\pm. &(7.48)\end{aligned}$$

From

$$\begin{aligned}\hat{J}_-\hat{J}_+ &= (\hat{J}_x - i\hat{J}_y)(\hat{J}_x + i\hat{J}_y) &(7.49)\\ &= \hat{J}_x^2 + \hat{J}_y^2 + i[\hat{J}_x, \hat{J}_y] &(7.50)\\ &= \hat{J}_x^2 + \hat{J}_y^2 - \hbar\hat{J}_z &(7.51)\end{aligned}$$

we get

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{J}_z^2 + \hbar\hat{J}_z + \hat{J}_-\hat{J}_+. \tag{7.52}$$

It is left as an exercise to show that

$$\hat{J}^2|jj\rangle|ll\rangle = \hbar^2 J(J+1)|jj\rangle|ll\rangle, \quad \text{with } J = j + l. \tag{7.53}$$

We will denote the total angular momentum eigenstates as $|(jl)JM\rangle$, where the $(lj)$ indicates that they are linear combinations of the uncoupled function $|jm_j\rangle|lm_l\rangle$. Thus, so far we have found the state $|(jl)J_{\max}, J_{\max}\rangle$, with $J_{\max} = j + l$. We can now apply the $\hat{J}_-$ ladder operator to find other states $|(jl)J_{\max}M\rangle$, since

$$\hat{J}_-|(jl)J_{\max}M\rangle = \hbar C_-(JM)|(jl)J_{\max}, M-1\rangle. \tag{7.54}$$

Remember that $C_\pm(JM)$ is given by [Eq. (5.20)]

$$C_\pm(JM) = \sqrt{J(J+1) - M(M\pm 1)}. \tag{7.55}$$

We do not have a ladder operator that changes the $J$ quantum number, but we can still find the state with $J = J_{\max} - 1 = j + l - 1$ with the following trick:

There are only two uncoupled states with $M = j + l - 1$, namely, $|jj\rangle|l, l-1\rangle$ and $|j, j-1\rangle|ll\rangle$. Thus, the coupled state we are looking for must be some linear combination of these two uncoupled states

$$|(jl)J_{\max} - 1, J_{\max} - 1\rangle = |jj\rangle|l, l-1\rangle c_1 + |j, j-1\rangle|ll\rangle c_2. \tag{7.56}$$

From the normalization condition we know that $|c_1|^2 + |c_2|^2 = 1$, so we need one other equation to be able to solve for $c_1$ and $c_2$. From the general theory we know that all angular momentum states must be orthogonal. We already have the state $|(jl)J_{\max}, J_{\max} - 1\rangle$, which is also a linear combination of the uncoupled states with $M = J_{\max} - 1$, so the required equation is

$$\langle(jl)J_{\max}, J_{\max} - 1|(jl)J_{\max} - 1, J_{\max} - 1\rangle = 0. \tag{7.57}$$

We can continue this procedure: for the state with $J = M = J_{\max} - 2$ three different uncoupled states contribute, but we can use the orthogonality with respect to $|(jl)J_{\max}, M\rangle$ and $|(jl)J_{\max} - 1, M\rangle$, etc.

## 7.6 Recursion relations for Clebsch-Gordan coefficients

The procedure described above shows how the coupled states can be found in principle. Here, we describe a convenient implementation of the idea. First, we introduce a notation for the expansion coefficients. First, we introduce a slightly more compact notation for the uncoupled states

$$|jm_jlm_l\rangle \equiv |jm_j\rangle|lm_l\rangle. \tag{7.58}$$

The resolution of identity in the uncoupled basis can now be written as

$$\hat{\boldsymbol{I}} = \sum_{m_j=-j}^{j}\sum_{m_l=-l}^{l} |jm_jlm_l\rangle\langle jm_jlm_l|. \tag{7.59}$$

The coupled states can now be expanded as follows

$$|(jl)JM\rangle = \hat{\boldsymbol{I}}|(jl)JM\rangle = \sum_{m_j=-j}^{j}\sum_{m_l=-l}^{l} |jm_jlm_l\rangle\langle jm_jlm_l|\,|(jl)JM\rangle. \tag{7.60}$$

The scalar product is written more compactly as

$$\langle jm_jlm_l|JM\rangle \equiv \langle jm_jlm_l|(jl)JM\rangle. \tag{7.61}$$

The expansion coefficients $\langle jm_jlm_l|JM\rangle$ are known as Clebsch-Gordan coefficients (CG-coefs). Since both the coupled and the uncoupled basis are orthonormal, the CG-coefs are element of a unitary matrix, and since the coefficients are real, we can define

$$\langle JM|jm_jlm_l\rangle = \langle jm_jlm_l|JM\rangle \tag{7.62}$$

and we have the orthonormality relations

$$\sum_{m_j=-j}^{j}\sum_{m_l=-l}^{l} \langle J'M'|jm_jlm_l\rangle\langle jm_jlm_l|JM\rangle = \delta_{J'J}\delta_{M'M} \tag{7.63}$$

$$\sum_{J=|j-l|}^{j+l}\sum_{M=-J}^{J} \langle jm_j'lm_l'|JM\rangle\langle JM|jm_jlm_l\rangle = \delta_{m_j'm_j}\delta_{m_l'm_l}. \tag{7.64}$$

We derive recursion relations for the CG-coefs by applying the ladder operators to the coupled states

$$\hat{J}_\pm|(jl)JM\rangle = (\hat{j}_\pm + \hat{l}_\pm)\sum_{m_jm_l} |jm_j\rangle|lm_l\rangle\langle jm_jlm_l|JM\rangle \tag{7.65}$$

$$|(jl)J, M\pm 1\rangle C^\pm_{JM} = \sum_{m_jm_l}\left[|j, m_j \pm 1\rangle|lm_l\rangle C^\pm_{jm_j} + |jm_j\rangle|l, m_l \pm 1\rangle C^\pm_{lm_l}\right]\langle jm_jlm_l|JM\rangle. \tag{7.66}$$

The last equation can be rewritten by replacing $m_j$ by $m_j \mp 1$ and $m_l$ by $m_l \pm 1$ everywhere, and adapting the ranges of the summations accordingly,

$$|(jl)J, M\pm 1\rangle C^\pm_{JM} = \sum_{m_jm_l} |jm_jlm_l\rangle\left[C^\pm_{j,m_j\mp 1}\langle j, m_j \mp 1, l, m_l|JM\rangle + C^\pm_{l,m_l\mp 1}\langle j, m_j, l, m_l \mp 1|JM\rangle\right]. \tag{7.67}$$

Projecting from the left with $|jm_jlm_l\rangle$ gives (with semicolumns for readability)

$$\langle jm_jlm_l|J, M \pm 1\rangle C^{\pm}_{JM} = C^{\pm}_{j,m_j\mp1}\langle j, m_j \mp 1; lm_l|JM\rangle + C^{\pm}_{l,m_l\mp1}\langle jm_j; l, m_l \mp 1|JM\rangle. \tag{7.68}$$

If we take the upper sign and set $M = J$ we find

$$0 = C^{+}_{j,m_j-1}\langle j, m_j - 1; lm_l|JJ\rangle + C^{+}_{l,m_l-1}\langle jm_j; l, m_l - 1|JJ\rangle. \tag{7.69}$$

This equation contains two CG-coefs needed to expand the coupled state with $M = J$. The CG-coefs are only nonzero when $m_j + m_l = J + 1$ (the $+1$ is here because we redefined $m_j$ and $m_l$ after equation 7.67). We can now start the recursion by taking $m_j = j$, and assuming that $\langle j, j; l, J - j|JJ\rangle$ is a positive real number (say, $G_{JJ}$). The CG-coefs with $m_j = j - 1$ is then

$$\langle j, j - 1; l, m_l|JJ\rangle = -\frac{C^{+}_{l,m_l-1}}{C^{+}_{j,j-1}} G_{JJ}, \quad \text{where } m_l = J - j + 1. \tag{7.70}$$

We can continue this by taking $m_j = j - 2, j - 3, \ldots$ until we find all CG-coefs needed for the coupled state with $M = J$. All elements will still depend on $G_{JJ}$, but we can get that value from the normalization condition. Taking $G_{JJ}$ to be positive is not necessary, but this is known as the Condon-Shortley phase convention.

Once we have found the coupled state $|(jl)JJ\rangle$, we can find CG-coefs for all lower values of $M$ by applying the ladder operator $\hat{J}_{-}$, i.e., from the lower sign in Eq. (7.68).

*Remaining problem: computation of matrix elements of the potential energy. This problem is addressed in the next chapter.*

# Chapter 8

# Atom-diatom: potential energy matrix elements

The atom-diatom potential $V(R, r, \theta)$ depends on the angle $\theta$ between the Jacobi vectors $\boldsymbol{r}$ and $\boldsymbol{R}$ (see Figure 8.1). The angular part of the basis functions, however, depends on the polar angles of the vectors $\boldsymbol{r}$ and $\boldsymbol{R}$:

$$\langle \theta_r, \phi_r, \theta_R, \phi_r | j m_j l m_l \rangle = Y_{j m_j}(\theta_r, \phi_r) Y_{l m_l}(\theta_R, \phi_R). \tag{8.1}$$

Two approaches are possible: we can try to set up a basis that depends on $\theta$, or we re-express the potential in terms of spherical polar angles $\hat{\boldsymbol{r}} = (\theta_r, \phi_r)$ and $\hat{\boldsymbol{R}} = (\theta_R, \phi_R)$. These angles are sometimes called *space-fixed* coordinates and the angle $\theta$ may be referred to as a *body-fixed* angle, since it is independent on overall rotation of the complex. Below, we will drop the $r$ and $R$ dependence of the potential and solve the angular part of this problem in four steps:

1. First we expand the angular potential in Legendre polynomials

$$V(\theta) = \sum_L c_L P_L(\cos\theta). \tag{8.2}$$

   We can use the *orthogonality* of Legendre polynomials to express the expansion coefficients as an integral:

$$c_L = \frac{2L+1}{2} \int_0^\pi P_L(\cos\theta) V(\theta) \sin\theta \, d\theta \tag{8.3}$$

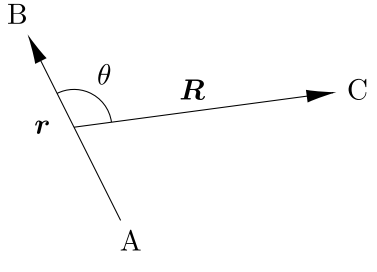

Figure 8.1: Jacobi coordinates for AB+C system.

and we will do this integral numerically using a *Gauss-Legendre quadrature approximation*

$$\int_0^\pi P_L(\cos\theta)V(\theta)\sin\theta\,d\theta \approx \sum_{i=1}^n w_i P_L(\cos\theta_i)V(\theta_i), \tag{8.4}$$

where $\theta_i$ and $w_i$ (with $i = 1, \ldots, n$) are Gauss Legendre *quadrature points* and *weights*, respectively.

2. We transform the potential from the body-fixed coordinate $\theta$ to the space-fixed coordinates $\theta_r, \phi_r$ and $\theta_R, \phi_R$ using the *spherical harmonics addition theorem*

$$P_L(\cos\theta) = \sum_{K=-L}^{L} (-1)^K C_{L,-K}(\theta_r, \phi_r) C_{LK}(\theta_R, \phi_R). \tag{8.5}$$

3. We will use the orthogonality relation for Wigner D-matrices [Eq. 5.120] and the *Clebsch-Gordan* series for the product of Wigner D-matrix elements to derive the expression for the matrix elements of (Racah normalized) spherical harmonics in terms of Clebsch-Gordan coefficients

$$\begin{aligned}\langle jm_j|C_{LM_L}|lm_l\rangle &= \int_0^{2\pi}\int_0^\pi Y^*_{jm_j}(\theta,\phi)C_{LM_L}(\theta,\phi)Y_{lm_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi &(8.6)\\ &= \sqrt{\frac{2l+1}{2j+1}}\langle LM_L lm_l|jm_j\rangle\langle L,0,l,0|j,0\rangle. &(8.7)\end{aligned}$$

## 8.1 Expansion of potential in Legendre polynomials

Legendre polynomials are *orthogonal polynomials.* Just like Hermite polynomials, they are defined in Chapter 22 of the *Handbook of Mathematical Functions* by Abramowitz and Stegun [6]. Legendre polynomials $P_l(z)$ are orthogonal with respect to the scalar product defined by

$$\langle f|g\rangle = \int_{-1}^1 f(z)g(z)\,dz. \tag{8.8}$$

They are defined by the recurrence relations

$$\begin{aligned}P_0(z) &= 1 &(8.9)\\ P_1(z) &= z &(8.10)\\ P_{l+1}(z) &= \frac{z(2l+1)P_l(z) - lP_{l-1}(z)}{l+1}. &(8.11)\end{aligned}$$

The "standardization" of Legendre polynomials is such that $P_l(1) = 1$, and the orthogonality relation is

$$\int_{-1}^1 P_{l'}(z)P_l(z)\,dz = \frac{2}{2l+1}\delta_{l'l}. \tag{8.12}$$

The recursion relations show that $P_l(z)$ is a polynomial in $z$ of degree $l$. If $f(z)$ is a polynomial of degree $n$, it can be expanded in Legendre polynomial

$$f(z) = \sum_{l=0}^n c_l P_l(z). \tag{8.13}$$

To find and expression for the expansion coefficients we use the orthogonality of the Legendre polynomials

$$\langle P_l|f\rangle = \langle P_l|\sum_{l'=0}^{n} c_{l'}P_{l'}\rangle = \sum_{l'=0}^{n} c_{l'}\frac{2}{2l'+1}\delta_{l'l} = c_l\frac{2}{2l+1} \tag{8.14}$$

so

$$c_l = \frac{2l+1}{2}\int_{-1}^{1} P_l(z)f(z)\,dz. \tag{8.15}$$

If we define $z \equiv \cos\theta$ and $V(\theta) \equiv f(\cos\theta)$ and use

$$dz = -\sin\theta\,d\theta, \tag{8.16}$$

we can rewrite the result as an integral over $\theta$

$$\int_{-1}^{1} P_l(z)f(z)dz = -\int_{\pi}^{0} P_l(\cos\theta)V(\theta)\,\sin(\theta)d\theta = \int_{0}^{\pi} P_l(\cos\theta)V(\theta)\,\sin(\theta)d\theta \tag{8.17}$$

to derive Eq. (8.3).

## 8.2 Gauss-Legendre quadrature

In principle, the potential $V(\theta)$ can be found by solving the electronic Schrödinger equation for fixed geometries of the complex, i.e., using the Born-Oppenheimer approximation. To minimize the number of points needed, we use the most suitable *Gaussian quadrature* to evaluate the integral in Eq. (8.3).

An $n-point$ quadrature is defined by a set of quadrature points ($x_i$) (called *abscissae*) and weights ($w_i$), and the integral is approximated as a weighted sum

$$\int_{-1}^{1} f(x)dx \approx \sum_{i=1}^{n} w_i f(x_i). \tag{8.18}$$

The perhaps simplest quadrature is the midpoint rule, where the integration range (here $[-1,1]$) is divided into $n$ equal intervals of width $2/n$, and the abscissae $x_i$ are taken to be the midpoints of these intervals, and the weights $w_i = 2/n$ are all equal to the width of the intervals. In Gaussian quadratures, the $n$ points and weights are chosen such the quadrature is exact for polynomials up to and including degree $2n-1$. Since there are $2n$ polynomials with degree $2n-1$ or less, it is perhaps not surprising that this is possible, since there are $2n$ parameters in an $n$-point Gaussian quadrature.

The abscissae of an $n$-point Gaussian qaudrature are the zeros of $P_n(z)$. The weights can be found from the requirement that the orthogonality relation

$$\langle P_0|P_l\rangle = 2\delta_{0,l} \tag{8.19}$$

is reproduced by the quadrature approximation for $l = 0,1,\ldots,n-1$. This results in a set of $n$ linear equations:

$$\sum_{i=1}^{n} P_l(x_i)w_i = 2\delta_{0,l}, \quad l = 0,1,\ldots,n-1. \tag{8.20}$$

The zeros of a polynomial can be found in various ways. One insightful, or at least intriguing, way is the following: setup the matrix representation of the $\hat{z}$ operator in the basis of normalized Legendre polynomials, $\{\widetilde{P}_0, \widetilde{P}_1, \ldots, \widetilde{P}_{n-1}\}$, i.e., compute the matrix elements

$$(\boldsymbol{Z})_{l'l} = \langle \widetilde{P}_{l'} | z | \widetilde{P}_l \rangle, \tag{8.21}$$

where

$$\widetilde{P}_l(z) = \sqrt{\frac{2l+1}{2}} P_l(z) \tag{8.22}$$

and compute the eigenvalues of the matrix $\boldsymbol{Z}$. It turns out that these eigenvalues are the zeros of $P_n(z)$.

A rigorous derivation of the above results can be found in the book “Introduction to Numerical Analysis” by Stoer and Bulirsch [7].

Finally, we recall that Legendre polynomials are a special case of a Wigner rotation matrix, with $z = \cos\theta$,

$$P_l(\cos\theta) = D^{(l)}_{0,0}(0, \theta, 0). \tag{8.23}$$

Note that for $\theta = 0$, we have $\cos\theta = 1$, and $P_l(1) = 1$, but also, for $\theta = 0$, the representation of the rotation is the identify matrix. We use this connection between Legendre polynomials and rotation matrices in the next section.

## 8.3 Spherical harmonics addition theorem

To derive the spherical harmonic addition theorem, we first define the directions $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{R}}$ by rotating the $\boldsymbol{e}_z$ unit vector.

$$\hat{\boldsymbol{r}} = \boldsymbol{R}_1 \boldsymbol{e}_z \tag{8.24}$$

$$\hat{\boldsymbol{R}} = \boldsymbol{R}_2 \boldsymbol{e}_z, \tag{8.25}$$

where $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ are $3 \times 3$ orthormal matrices (with determinant $+1$). We may now write the cosine of the angle between these two vectors as

$$\begin{aligned} \cos\theta &= \hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{R}} && (8.26)\\ &= \boldsymbol{R}_1 \boldsymbol{e}_z \cdot \boldsymbol{R}_2 \boldsymbol{e}_z && (8.27)\\ &= \boldsymbol{e}_z \cdot \boldsymbol{R}_1^\dagger \boldsymbol{R}_2 \boldsymbol{e}_z. && (8.28) \end{aligned}$$

We now define the Euler angles $\alpha$, $\beta$, and $\gamma$ by expressing $\boldsymbol{R}_1^\dagger \boldsymbol{R}_2$ in $zyz$-Euler angles

$$\boldsymbol{R}_1^\dagger \boldsymbol{R}_2 = \boldsymbol{R}_z(\alpha) \boldsymbol{R}_y(\beta) \boldsymbol{R}_z(\gamma). \tag{8.29}$$

We may now rewrite $\cos\theta$ as (Figure 8.1)

$$\begin{aligned} \cos\theta &= \boldsymbol{e}_z \cdot \boldsymbol{R}_z(\alpha) \boldsymbol{R}_y(\beta) \boldsymbol{R}_z(\gamma) \boldsymbol{e}_z && (8.30)\\ &= \boldsymbol{e}_z \cdot \boldsymbol{R}_y(\beta) \boldsymbol{e}_z && (8.31)\\ &= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \sin\beta \\ 0 \\ \cos\beta \end{pmatrix} && (8.32)\\ &= \cos\beta, && (8.33) \end{aligned}$$

so $\theta = \beta$. Without having to find the angles $\alpha$ and $\gamma$, we can already evaluate Wigner $D$-matrix elements with $m = k = 0$,

$$D^{(l)}_{0,0}(\boldsymbol{R}_1^\dagger \boldsymbol{R}_2) = D^{(l)}_{0,0}[\boldsymbol{R}_z(\alpha)\boldsymbol{R}_y(\beta)\boldsymbol{R}_z(\gamma)] = D^{(l)}_{0,0}(\alpha,\theta,\gamma) = P_l(\cos\theta). \tag{8.34}$$

The representation property of $D$-matrices gives

$$\begin{aligned} D^{(l)}_{0,0}(\boldsymbol{R}_1^\dagger \boldsymbol{R}_2) &= \sum_m D^{(l)}_{0,m}(\boldsymbol{R}_1^\dagger) D^{(l)}_{m,0}(\boldsymbol{R}_2) && (8.35)\\ &= \sum_m D^{(l),*}_{m,0}(\boldsymbol{R}_1) D^{(l)}_{m,0}(\boldsymbol{R}_2) && (8.36)\\ &= \sum_m C_{lm}(\hat{\boldsymbol{r}}) C^*_{lm}(\hat{\boldsymbol{R}}). && (8.37) \end{aligned}$$

[Exercise: show that $D^{(l),*}_{m,0}(\boldsymbol{R}) = C_{lm}(\hat{\boldsymbol{r}})$ when $\hat{\boldsymbol{r}} = \boldsymbol{R}\boldsymbol{e}_z$]. For the complex conjugate of a spherical harmonic we have this relation:

$$C^*_{lm}(\theta,\phi) = (-1)^m C_{l,-m}(\theta,\phi) \tag{8.38}$$

so we may also write the spherical harmonic addition theorem as

$$P_l(\cos\theta) = \sum_{m=-l}^{l} (-1)^m C_{l,-m}(\hat{\boldsymbol{r}}) C_{lm}(\hat{\boldsymbol{R}}). \tag{8.39}$$

## 8.4 Clebsch-Gordan series

We recall Eq. (5.120), the orthogonality relation for Wigner D-matrices:

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma\, D^{(l),*}_{mk}(\alpha,\beta,\gamma) D^{(l')}_{m'k'}(\alpha,\beta,\gamma) = \frac{8\pi^2}{2l+1}\delta_{mm'}\delta_{kk'}\delta_{ll'}, \tag{8.40}$$

the definition of Racah normalized spherical harmonics

$$C_{lm}(\theta,\phi) = D^{(l),*}_{m,0}(\phi,\theta,0), \tag{8.41}$$

and their relation to spherical harmonics

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta,\phi). \tag{8.42}$$

Clearly, the orthogonality relations for spherical harmonics are a special case of the orthogonality relations for Wigner D-matrices. We will derive the expression for matrix elements of spherical harmonics, Eq. (8.6), as a special case of an integral involving three Wigner D-matrices.

Consider the rotation of a coupled angular momentum state

$$\hat{R}|(jl)JM\rangle = \hat{R} \sum_{m_j,m_l} |jm_j\rangle |lm_l\rangle \langle jm_j lm_l|JM\rangle. \tag{8.43}$$

The rotation operator $\hat{R} = \hat{R}(\hat{\boldsymbol{n}},\phi)$ is given by

$$\hat{R}(\hat{\boldsymbol{n}},\phi) = e^{-\frac{i}{\hbar}\phi \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}, \tag{8.44}$$

where $\hat{\boldsymbol{J}}$ is the total angular momentum operator

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{j}} + \hat{\boldsymbol{l}}. \tag{8.45}$$

Since the operators $\hat{\boldsymbol{j}}$ and $\hat{\boldsymbol{l}}$ are acting on different spaces they commute, and we can factorize the rotation operator

$$e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}} = e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{j}}}e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{l}}} \tag{8.46}$$

so we have

$$\hat{R}|(jl)JM\rangle = \sum_{m_j,m_l}(\hat{R}|jm_j\rangle)\,(\hat{R}|lm_l\rangle)\langle jm_jlm_l|JM\rangle. \tag{8.47}$$

Using the defining equation of Wigner rotation matrices we get

$$\sum_{K'}|(jl)JK'\rangle D^{(J)}_{K'M}(\hat{R}) = \sum_{m_j,m_l}\sum_{k_jk_l}|jk_j\rangle D^{(j)}_{k_j,m_j}(\hat{R})\;|lk_l\rangle D^{(l)}_{k_l,m_l}(\hat{R})\langle jm_jlm_l|JM\rangle \tag{8.48}$$

Projecting from the left with the coupled state $\langle(jl)JK|$ and using the orthonormality relation

$$\langle(jl)JK|(jl)JK'\rangle = \delta_{KK'} \tag{8.49}$$

gives

$$D^{(J)}_{KM}(\hat{R}) = \sum_{m_jm_lk_jk_l} D^{(j)}_{k_j,m_j}(\hat{R})\;D^{(l)}_{k_l,m_l}(\hat{R})\;\langle jk_jlk_l|JK\rangle\langle jm_jlm_l|JM\rangle. \tag{8.50}$$

It is left as an exercise to derive this equation:

$$D^{(j)}_{k_j,m_j}(\hat{R})\;D^{(l)}_{k_l,m_l}(\hat{R})\; = \sum_{JKM}\langle jk_jlk_l|JK\rangle\langle jm_jlm_l|JM\rangle D^{(J)}_{KM}(\hat{R}). \tag{8.51}$$

*Hint: start from Eq. (8.48), project with the uncoupled basis from the left, and use the orthonormality relation of Clebsch-Gordan coefficients Eq. (7.64).*

Expressing the rotation in terms of Euler angles, and using the orthogonality relation Eq. (5.120) we now derive

$$\int_0^{2\pi}d\alpha\int_0^{\pi}\sin\beta d\beta\int_0^{2\pi}d\gamma D^{(J),*}_{KM}(\alpha,\beta,\gamma)D^{(j)}_{k_jm_j}(\alpha,\beta,\gamma)D^{(l)}_{k_lm_l}(\alpha,\beta,\gamma) = \frac{8\pi^2}{2J+1}\langle jk_jlk_l|JK\rangle\langle jm_jlm_l|JM\rangle. \tag{8.52}$$

It is left as an exercise to show that Eq. (8.6) follows from this relation.

# Chapter 9

# Two-fold symmetries

Symmetry is important in quantum mechanics for several reasons. First of all, if a system contains two identical particles, the square of the wave function must remain the same if we interchange the coordinates of these particles - if not, we would not call the particles identical, since the square of the wave function gives the density, which is an observable. If the identical particles are *bosons*, also the wave function must be invariant under the permutation of the particles, whereas for *fermions* the wave function must change sign. Mathematically, we can describe symmetry by introducing symmetry operators. The permutation operator, $\hat{P}_{1,2}$, e.g., is defined by

$$\hat{P}_{1,2}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=\Psi(\boldsymbol{r}_2,\boldsymbol{r}_1), \tag{9.1}$$

so if particles 1 and 2 are bosons we must have

$$\hat{P}_{1,2}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) \tag{9.2}$$

and for fermions we must have

$$\hat{P}_{1,2}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2). \tag{9.3}$$

Particles that have an half integer spin, such as, e.g., electrons, or protons, which have spin quantum number $S = 1/2$ (electrons), or $I = 1/2$ (protons), are fermions, whereas particles with integer spin, such as, e.g., oxygen nuclei (with nuclear spin $I = 0$), are bosons. The Hamiltonian that describes a system with contains identical particles (whether bosons or fermions) must not change if the coordinates of two identical particles are interchanged. Mathematically, this means that the Hamiltonian commutes with the corresponding permutation operator, e.g., for the above example,

$$[\hat{H},\hat{P}_{1,2}]=0. \tag{9.4}$$

When we talk about the permutation or the interchange of two particles, we not only refer to the *positions* of the particles (the coordinates $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in the above example), but also to their *spin functions.* The spin part of a two-electron wave function can be symmetric or anti-symmetric under permutation of the electrons. In particular, singlet wave functions are anti-symmetric:

$$\begin{aligned}\hat{P}_{1,2}\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}} &\equiv \frac{\alpha(2)\beta(1)-\beta(2)\alpha(1)}{\sqrt{2}} && (9.5)\\ &= -\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}. && (9.6)\end{aligned}$$

while triplet spin functions are symmetric:

$$\hat{P}_{1,2}\alpha(1)\alpha(2) = \alpha(1)\alpha(2) \tag{9.7}$$

$$\hat{P}_{1,2}\beta(1)\beta(2) = \beta(1)\beta(2) \tag{9.8}$$

$$\hat{P}_{1,2}\frac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}} = \frac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}}. \tag{9.9}$$

The total electron wave function, however, must be antisymmetric, so for a singlet wave function the orbital part must be symmetric, while for a triplet wave function the orbital part must be antisymmetric.

Another example would be the permutation of the nuclei in the $H_2$ molecule. The protons have nuclear spin of a half, just like electrons, and so the nuclear spin wave function can also be singlet (antisymmetric) or triplet (symmetric). If we permute that nuclei, the Jacobi vector $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ will change sign. For the polar coordinates $\theta$ and $\phi$ this means

$$\theta \to \pi - \theta \tag{9.10}$$

$$\phi \to \phi + \pi \tag{9.11}$$

[Check this with Eq. (4.47)]. Spherical harmonics [$Y_{lm}$], the rotational wave functions for $H_2$ are either symmetric or antisymmetric under this transformation, depending on the $l$ quantum number:

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \tag{9.12}$$

Thus, the lowest rotational state, with $l = 0$, has a symmetric rotational wave function, so it must have a singlet nuclear spin function, whereas the first excited rotational state, with $l = 1$, must have a triplet nuclear wave function. Since the nuclear spin wave function does not easily change, there are two forms of molecular hydrogen: *ortho*-hydrogen, with triplet nuclear spin and odd $l$ and *para* hydrogen, with singlet nuclear spin and even $l$.

## 9.1 Symmetry operators

So far, we only considered the permutation operator $\hat{P}_{1,2}$. This is a two-fold symmetry operator, if we apply it twice we are back where we started: $\hat{P}_{1,2}^2 = 1$. Another example of a two-fold symmetry is inversion, $\hat{\imath}$, it is defined on Cartesian coordinates vectors in 3D by

$$\hat{\imath}\boldsymbol{r} = -\boldsymbol{r}. \tag{9.13}$$

We saw that for $H_2$, the permutation of the nuclei results in inversion of the Jacobi vector $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$. If we have a heteronuclear diatomic molecule, e.g., HF, the rotational wave functions are still spherical harmonics, which are symmetric or anti-symmetric with respect to inversion:

$$\hat{\imath}Y_{lm}(\hat{\boldsymbol{r}}) = Y_{lm}(-\hat{\boldsymbol{r}}) = (-1)^l Y_{lm}(\hat{\boldsymbol{r}}). \tag{9.14}$$

Since the nuclei are not identical, both even and odd $l$ are allowed: The rotational wave functions are said to have even or odd *parity*. Hamiltonians that describe molecules (without the presence of external electric fields) commute with the inversion operator, so molecular eigen states have a well defined parity.

The permutation operators and the inversion operator are *unitary* operators. This is no coincidence: the general definition of a symmetry operator is *a unitary operator that commutes with the Hamiltonian.*

Two-fold symmetry operators have additional properties. Assume $\hat{A}$ is a two-fold symmetry operator, then we have:

$$\hat{A}^2 = \hat{I}, \tag{9.15}$$

where $\hat{I}$ is the identify operator. Since $\hat{A}$ is a unitary operator it has an inverse, so we can multiply both sides of this equation with $\hat{A}^{-1}$:

$$\hat{A} = \hat{A}^{-1}. \tag{9.16}$$

Furthermore, unitarity means that for any vector vectors $f$ and $g$ from the Hilbert space for which $\hat{A}$ is defined we have:

$$\langle \hat{A}f|\hat{A}g\rangle = \langle f|g\rangle \tag{9.17}$$

so also

$$\langle f|\hat{A}^\dagger\hat{A}g\rangle = \langle f|g\rangle \tag{9.18}$$

and we must have

$$\hat{A}^\dagger\hat{A} = 1. \tag{9.19}$$

If we multiply this equation from the right with $\hat{A}^{-1}$ we find

$$\hat{A}^\dagger = \hat{A}^{-1}. \tag{9.20}$$

Taken together we find $\hat{A} = \hat{A}^\dagger$, so $\hat{A}$ must also be Hermitian. Thus, $\hat{A}$ must have real eigenvalues $\lambda$ and a complete set of eigenfunctions

$$\hat{A}|f\rangle = \lambda|f\rangle \tag{9.21}$$

and from $\hat{A}^2 = \hat{I}$ we find $\lambda^2 = 1$, so the eigenvalues can only be plus or minus one, $\lambda = \pm 1$. The corresponding eigenvectors are called *symmetric* and *antisymmetric*, respectively, but also *even* and *odd*, or *gerade* and *ungerade* (mostly for electronic wave functions).

## 9.2 Matrix-elements for functions with well defined symmetries

Let us consider two function $\chi_+$ and $\chi_-$ which have even and odd parity

$$\hat{\imath}|\chi_\pm\rangle = \pm|\chi_\pm\rangle. \tag{9.22}$$

We immediately know that these functions must be orthogonal, since they are eigenfunctions of an Hermitian operator and they have different eigenvalues,

$$\langle \chi_+|\chi_-\rangle = 0. \tag{9.23}$$

By definition, the Hamiltonian commutes with its symmetry operators, so we know that

$$\hat{\imath}\hat{H}|\chi_\pm\rangle = \hat{H}\hat{\imath}|\chi_\pm\rangle = \pm\hat{H}|\chi_\pm\rangle, \tag{9.24}$$

i.e., $\hat{H}|\chi_\pm\rangle$ has the same parity as $|\chi_\pm\rangle$, so

$$\langle \chi_+|\hat{H}\chi_-\rangle = 0 \tag{9.25}$$

and, of course also

$$\langle \chi_-|\hat{H}\chi_+\rangle = 0. \tag{9.26}$$

Another way to derive this same result is using $\hat{I} = \hat{\imath}^\dagger \hat{\imath}$, so

$$\begin{aligned}
\langle \chi_- | \hat{H} \chi_+ \rangle &= \langle \chi_- | \hat{I} \hat{H} \chi_+ \rangle && (9.27)\\
&= \langle \chi_- | \hat{\imath}^\dagger \hat{\imath} \hat{H} \chi_+ \rangle && (9.28)\\
&= \langle \hat{\imath} \chi_- | \hat{H} \hat{\imath} \chi_+ \rangle && (9.29)\\
&= -\langle \chi_- | \hat{H} \chi_+ \rangle && (9.30)
\end{aligned}$$

so

$$2\langle \chi_- | \hat{H} \chi_+ \rangle = 0. \qquad (9.31)$$

This result has an immediate application in variational calculations: we can use a basis set of only functions with even parity to compute eigenfunctions of the Hamiltonian with even parity and the eigenfunctions with odd parity can be found in a *separate* calculation, in which we would only use odd parity basis functions. Since, in general, matrix diagonalisation scales with the third power of the dimension of the basis, this gives substantial savings in computer time: if we only need functions of one parity we save a factor of $2^3 = 8$, and if we need both parities, we still save a factor of four. Also, we will need less memory to store the Hamiltonian matrix and the eigenvectors.

## 9.3 Symmetry adaptation

In some cases, we may have a basis set of functions which are not symmetry adapted, i.e., which are not eigenfunctions of a symmetry operator. We take inversion symmetry as an example, and we assume

$$\hat{\imath} | f \rangle = | g \rangle, \qquad (9.32)$$

where $|g\rangle$ is linearly independent of $|f\rangle$. We can construct parity-adapted functions $\chi_\pm$ in the following way:

$$|\chi_\pm\rangle = (\hat{I} \pm \hat{\imath}) | f \rangle \qquad (9.33)$$

We can readily verify that the functions $|\chi_\pm\rangle$ are eigenfunctions of $\hat{\imath}$:

$$\begin{aligned}
\hat{\imath} | \chi_\pm \rangle &= \hat{\imath} (\hat{I} \pm \hat{\imath}) | f \rangle && (9.34)\\
&= (\hat{\imath} \pm \hat{\imath}^2) | f \rangle && (9.35)\\
&= (\hat{\imath} \pm \hat{I}) | f \rangle && (9.36)\\
&= \pm (\hat{I} \pm \hat{\imath}) | f \rangle && (9.37)\\
&= \pm | \chi_\pm \rangle. && (9.38)
\end{aligned}$$

One must be aware that if $|f\rangle$ already has symmetry, e.g., if it has even parity, then $\chi_-$ will actually be the null vector. If the symmetry adapted function is nonzero, we may still have to normalize it, even if the function $f$ was already normalized.

## 9.4 Selection rules

In spectroscopy, the intensity of a one-photon transition is proportional to the square of a matrix element of the dipole operator. If the polarization of the photon is along the $z$-axis, we need to compute matrix elements

$$A_{i,f} = \langle \phi_i | \hat{\mu}_z | \phi_f \rangle, \qquad (9.39)$$

where $\phi_i$ is the initial state, $\hat{\mu}_z$ is the $z$ component of the dipole operator, and $\phi_f$ is the final state. For a system of $n$ particles, with Cartesian $z$-coordinates $z_i$ and charges $q_i$, the dipole operator is given by

$$\hat{\mu}_z = \sum_{i=1}^{n} q_i z_i. \tag{9.40}$$

The dipole operator has odd parity, since $\hat{i} z_i = -z_i$. For an operator it is convenient to define symmetry with the following relation

$$\hat{i}\hat{\mu}_z\hat{i}^\dagger = -\hat{\mu}_z. \tag{9.41}$$

At first you may wonder why we introduced the $\hat{i}^\dagger$ in this equation, but it makes sense if you apply the operator to some function, e.g., with $\chi_+$ an even parity function, we may compute

$$\begin{aligned}
\hat{i}\hat{\mu}_z|\chi_+\rangle &= \hat{i}\hat{\mu}_z \underbrace{\hat{i}^\dagger\hat{i}}_{\text{identity}} |\chi_+\rangle & (9.42)\\
&= \underbrace{\hat{i}\hat{\mu}_z\hat{i}^\dagger}_{-\hat{\mu}_z} \hat{i}|\chi_+\rangle & (9.43)\\
&= -\hat{\mu}_z|\chi_+\rangle. & (9.44)
\end{aligned}$$

We can also write Eq. (9.41) as

$$\hat{i}\hat{\mu}_z = -\hat{\mu}_z\hat{i} \tag{9.45}$$

which simply shows that if we apply the inversion operator it must act on the dipole operator, but also on any other function or operator to the right of it.

It is now left as an exercise to show that matrix elements of the dipole operator between states of the same parity must be zero

$$\langle\chi_\pm|\hat{\mu}_z\chi_\pm\rangle = 0. \tag{9.46}$$

# Chapter 10

# Rigid rotor

## 10.1 Classical Hamiltonian for rigid rotor

We consider a nonlinear, rigid molecule, consisting of $n$ atoms with time-dependent Cartesian coordinates $\boldsymbol{r}_i(t), i = 1, 2, \ldots, n$. We take the center of mass of the molecule as the origin of the coordinate system. Since we assume the molecule to be rigid, all atoms at any given time must be rotating around the same vector, $\hat{\boldsymbol{n}}$ (we take $|\hat{\boldsymbol{n}}| = 1$), with the same angular velocity $\dot{\phi}$ (in radian per unit of time). The velocities of the particles are

$$\dot{\boldsymbol{r}}_i = \dot{\phi}\, \hat{\boldsymbol{n}} \times \boldsymbol{r}_i. \tag{10.1}$$

The distance $r_\perp(i)$ of $\boldsymbol{r}_i$ to the rotation axis is equal to

$$r_\perp(i) = |\hat{\boldsymbol{n}} \times \boldsymbol{r}_i| \tag{10.2}$$

and the velocity of particle $i$ is

$$v_i = |\dot{\boldsymbol{r}}_i| = \dot{\phi}\, r_\perp(i). \tag{10.3}$$

With

$$\boldsymbol{\omega} \equiv \dot{\phi}\, \hat{\boldsymbol{n}} \tag{10.4}$$

we have

$$\dot{\boldsymbol{r}}_i = \boldsymbol{\omega} \times \boldsymbol{r}_i. \tag{10.5}$$

The rotational kinetic energy is

$$\begin{aligned} T &= \frac{1}{2} \sum_{i=1}^{n} m_i |\dot{\boldsymbol{r}}_i|^2 && (10.6) \\ &= \frac{1}{2} \sum_{i=1}^{n} m_i (\boldsymbol{\omega} \times \boldsymbol{r}_i) \cdot (\boldsymbol{\omega} \times \boldsymbol{r}_i) && (10.7) \end{aligned}$$

From Eq. (4.21), with $\omega \equiv |\boldsymbol{\omega}|$ and $r_i \equiv |\boldsymbol{r}_i|$, we have

$$\begin{aligned} (\boldsymbol{\omega} \times \boldsymbol{r}) \cdot (\boldsymbol{\omega} \times \boldsymbol{r}) &= \omega^2 r_i^2 - (\boldsymbol{\omega} \cdot \boldsymbol{r}_i)\,(\boldsymbol{r}_i \cdot \boldsymbol{\omega}) && (10.8) \\ &= \boldsymbol{\omega}^T \boldsymbol{\omega}\, r_i^2 - \boldsymbol{\omega}^T \boldsymbol{r}_i\, \boldsymbol{r}_i^T \boldsymbol{\omega} && (10.9) \\ &= \boldsymbol{\omega}^T (r_i^2 \mathbf{1}_{3\times 3} - \boldsymbol{r}_i \boldsymbol{r}_i^T) \boldsymbol{\omega}, && (10.10) \end{aligned}$$

where $\mathbf{1}_{3\times 3}$ is the 3 × 3 identity matrix. Thus, for the kinetic energy we find

$$T = \frac{1}{2}\boldsymbol{\omega}^T \boldsymbol{I}\boldsymbol{\omega}, \tag{10.11}$$

where the 3 × 3 inertia tensor is given by

$$\boldsymbol{I} = \sum_{i=1}^{n} m_i \left( r_i^2 \mathbf{1}_{3\times 3} - \boldsymbol{r}_i \boldsymbol{r}_i^T \right). \tag{10.12}$$

If we denote the components of the vector $\boldsymbol{r}_i$ by $x_i$, $y_i$, and $z_i$ we have in components

$$\boldsymbol{I} = \sum_{i=1}^{n} m_i \begin{pmatrix} y_i^2 + z_i^2 & -x_i y_i & -x_i z_i \\ -y_i x_i & x_i^2 + z_i^2 & -y_i z_i \\ -z_i x_i & -z_i y_i & x_i^2 + y_i^2 \end{pmatrix}. \tag{10.13}$$

The linear momenta of the atoms are

$$\boldsymbol{p}_i = m_i \dot{\boldsymbol{r}}_i \tag{10.14}$$

and the total angular momentum of the molecule is

$$\boldsymbol{L} = \sum_{i=1}^{n} \boldsymbol{r}_i \times \boldsymbol{p}_i = \sum_{i=1}^{m} m_i \boldsymbol{r}_i \times \dot{\boldsymbol{r}}_i = \sum_{i=1}^{m} m_i \boldsymbol{r}_i \times (\boldsymbol{\omega} \times \boldsymbol{r}_i). \tag{10.15}$$

For a general vector triple product we have

$$\boldsymbol{a} \times (\boldsymbol{b} \times \boldsymbol{c}) = (\boldsymbol{a} \cdot \boldsymbol{c})\boldsymbol{b} - (\boldsymbol{a} \cdot \boldsymbol{b})\boldsymbol{c}. \tag{10.16}$$

It is left as an exercise to derive this equation from the contraction of two Levi-Civita symbols [Eq. (4.23)] and to use it to derive that the total angular momentum is related to the angular velocity as

$$\boldsymbol{L} = \boldsymbol{I}\boldsymbol{\omega}. \tag{10.17}$$

Assuming that the inversion of the inertia tensor exists, we have

$$\boldsymbol{\omega} = \boldsymbol{I}^{-1}\boldsymbol{L} \tag{10.18}$$

so for the kinetic energy we have

$$T = \frac{1}{2}\boldsymbol{L}^T \boldsymbol{I}^{-1} \boldsymbol{L}. \tag{10.19}$$

## 10.2 Body-fixed frame

In the previous section we started by assuming that in a rigid molecule all atoms must be rotating around the same axis with the same angular velocity, which results in Eq. (10.5). We can derive this result by assuming that the atoms have fixed coordinates $\boldsymbol{r}_i^{(0)}$ with respect to a time-dependent frame $\boldsymbol{Q}(t)$,

$$\boldsymbol{r}_i(t) = \boldsymbol{Q}(t)\boldsymbol{r}_i^{(0)}, \tag{10.20}$$

where

$$\boldsymbol{Q} = [\boldsymbol{q}_1 \; \boldsymbol{q}_2 \; \boldsymbol{q}_3]. \tag{10.21}$$

We assume that this frame is orthonormal

$$\boldsymbol{Q}^T\boldsymbol{Q} = \boldsymbol{Q}\boldsymbol{Q}^T = \mathbf{1}_{3\times 3} \tag{10.22}$$

and right-handed, i.e., its determinant is one

$$\det(\boldsymbol{Q}) = 1. \tag{10.23}$$

The orthonormality means that for the columns of $\boldsymbol{Q}$ we have

$$\boldsymbol{q}_i \cdot \boldsymbol{q}_j = \delta_{ij} \tag{10.24}$$

and because it is right-handed we have

$$\boldsymbol{q}_1 \times \boldsymbol{q}_2 = \boldsymbol{q}_3 \tag{10.25}$$

or, more general

$$\boldsymbol{q}_i = \epsilon_{ijk}\boldsymbol{q}_j\boldsymbol{q}_k. \tag{10.26}$$

In components,

$$(\boldsymbol{q}_i)_j = Q_{ji} \tag{10.27}$$

this gives a relation we will use below:

$$Q_{i'i} = \epsilon_{ijk}(\boldsymbol{q}_j \times \boldsymbol{q}_k)_{i'} = \epsilon_{ijk}\epsilon_{i'j'k'}Q_{j'j}Q_{k'k}. \tag{10.28}$$

We assume that the coordinates $\boldsymbol{r}_i^{(0)}$ are time-independent, so the velocities are determined by the time-dependence of the frame

$$\dot{\boldsymbol{r}}_i = \dot{\boldsymbol{Q}}\boldsymbol{r}_i^{(0)} \tag{10.29}$$

From inverting Eq. (10.20) we have

$$\boldsymbol{r}_i^{(0)} = \boldsymbol{Q}^T\boldsymbol{r}_i \tag{10.30}$$

so we can relate the velocities $\dot{\boldsymbol{r}}_i$ to the positions $\boldsymbol{r}_i$ by

$$\dot{\boldsymbol{r}}_i = \dot{\boldsymbol{Q}}\boldsymbol{Q}^T\boldsymbol{r}_i = \boldsymbol{\Omega}(t)\boldsymbol{r}_i \tag{10.31}$$

where

$$\boldsymbol{\Omega}(t) = \dot{\boldsymbol{Q}}\boldsymbol{Q}^T. \tag{10.32}$$

We can easily show that this matrix must be anti-symmetric:

$$\frac{\partial}{\partial t}(\boldsymbol{Q}\boldsymbol{Q}^T) = \dot{\boldsymbol{Q}}\boldsymbol{Q}^T + \boldsymbol{Q}\dot{\boldsymbol{Q}}^T = \mathbf{0}_{3\times 3}, \tag{10.33}$$

where the $3 \times 3$ matrix with zeros is the time-derivative of the identity matrix. Thus,

$$\boldsymbol{\Omega}(t) = -\boldsymbol{Q}\dot{\boldsymbol{Q}}^T = -\boldsymbol{\Omega}(t)^T. \tag{10.34}$$

A $3 \times 3$ antisymmetric matrix must have zeros on the diagonal, and it depends on three parameters. By defining them as

$$\boldsymbol{\Omega}(t) = \begin{pmatrix} 0 & -\omega_3(t) & \omega_2(t) \\ \omega_3(t) & 0 & -\omega_1(t) \\ -\omega_2(t) & \omega_1 & 0 \end{pmatrix}, \tag{10.35}$$

we have

$$\dot{\boldsymbol{r}}_i = \boldsymbol{\Omega}(t)\boldsymbol{r}_i = \boldsymbol{\omega} \times \boldsymbol{r}_i, \tag{10.36}$$

which agrees with Eq. (10.5).

## 10.3 Principle axis frame

The rotation of a rigid molecule is given by the time dependence of the frame, $\boldsymbol{Q}(t)$, but we have complete freedom in choosing the frame at some initial time, say $t = 0$. This choice determines the "body-fixed coordinates" $\boldsymbol{r}_i^{(0)}$,

$$\boldsymbol{r}_i^{(0)} = \boldsymbol{Q}^T(0)\boldsymbol{r}_i(0). \tag{10.37}$$

To describe the motion of a rigid molecule, a particular convenient choice is the principle axis frame: we take the columns of $\boldsymbol{Q}(0)$ to be be eigenvectors of the inertia tensor. This is possible since the inertia tensor is real and symmetric. With the eigenvalues $I_a$, $I_b$, and $I_c$, called *principle moments of inertia*, we have

$$\boldsymbol{Q}(0)^T\boldsymbol{I}(0)\boldsymbol{Q}(0) = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix} = \boldsymbol{I}_0. \tag{10.38}$$

It is left as an exercise to derive from Eqs. (10.20) and (10.12) that at any time $t$ we have

$$\boldsymbol{Q}(t)^T\boldsymbol{I}(t)\boldsymbol{Q}(t) = \boldsymbol{I}_0. \tag{10.39}$$

Note that without loss of generality, we can assume that at $t = 0$ the molecule is oriented along the principle axes, so $\boldsymbol{Q}(0) = \mathbf{1}_{3\times3}$ and $\boldsymbol{I}(0) = \boldsymbol{I}_0$.

In rotational spectroscopy, the convention is to sort the principle moments of inertia such that

$$I_a \le I_b \le I_c. \tag{10.40}$$

For a linear molecule we have $I_a = 0$ and $I_b = I_c$.

For a nonlinear molecule all inertia moments are positive, so we can invert the inertia tensor

$$\boldsymbol{I}^{-1} = (\boldsymbol{Q}\boldsymbol{I}_0\boldsymbol{Q}^T)^{-1} = \boldsymbol{Q}\boldsymbol{I}_0^{-1}\boldsymbol{Q}^T \tag{10.41}$$

and the kinetic energy [Eq. (10.19)] can be written as

$$T = \frac{1}{2}\boldsymbol{L}^T\boldsymbol{Q}\boldsymbol{I}_0^{-1}\boldsymbol{Q}^T\boldsymbol{L}. \tag{10.42}$$

By defining body-fixed angular momenta

$$\boldsymbol{P} \equiv \boldsymbol{Q}^T\boldsymbol{L} \tag{10.43}$$

the kinetic energy simplifies to

$$\begin{aligned} T &= \frac{1}{2}\boldsymbol{P}^T\boldsymbol{I}_0^{-1}\boldsymbol{P} && (10.44) \\ &= \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c} && (10.45) \\ &= AP_a^2 + BP_b^2 + CP_c^2 && (10.46) \end{aligned}$$

with rotational constants defined by

$$A \equiv \frac{1}{2I_a}, \quad B \equiv \frac{1}{2I_b}, \quad C \equiv \frac{1}{2I_c}. \tag{10.47}$$

For the rotational constants we have, by convention,

$$A \ge B \ge C. \tag{10.48}$$

When two moments of inertial are equal, the molecule is called a *symmetric top*. Table 10.1 gives all the names of different types of rotors, determined by which moments of inertia are equal. A symmetric top molecule must have a three-fold symmetry axis (see exercises).

Table 10.1: Classification of rigid rotors by their principle moments of inertia.

| | name | examples |
|---|---|---|
| $I_a = 0$ and $I_b = I_c$ | Linear molecules | $H_2$, CO, $CO_2$ |
| $I_a = I_b = I_c$ | Spherical tops | $CH_4$, $SF_6$, $C_{60}$ |
| $I_a = I_b < I_c$ | Oblate symmetric top | $NH_3$, $SO_3$, $C_6H_6$ |
| $I_a < I_b = I_c$ | Prolate symmetric top | $CH_3Cl$, $H_3CCN$ |
| $I_a < I_b < I_c$ | Asymmetric top | $H_2O$, $H_2CO$ |

## 10.4 Quantum description of rigid rotor

The orientation of a rigid molecule can be specified by *zyz* Euler angles $(\alpha, \beta, \gamma)$, so its wave function can be written as $\Psi(\alpha, \beta, \gamma)$. For symmetric top molecules, the rotational wave functions are Wigner D-matrix elements

$$\Psi_{JMK}(\alpha, \beta, \gamma) = \sqrt{\frac{2j+1}{8\pi^2}}\, D^{(J)*}_{MK}(\alpha, \beta, \gamma). \tag{10.49}$$

Compared to linear molecules, we have one new quantum number $K$, which is associated with the angular momentum around the symmetry axis. The corresponding angular momentum operator is a *body-fixed* operator, $\hat{P}_a$, which we will define below, for prolate symmetric top molecules, and $\hat{P}_c$ for oblate symmetric tops. For asymmetric top molecules the $K$ quantum number is no longer a good quantum number, and the wave function is a linear combination of Wigner $D$-functions with different values of $K$.

Since the wave function depends on Euler angles, it seems logical to start by expressing space-fixed and body-fixed angular momentum operators in terms of these coordinates. This is done in most books, and this also done in the original literature. Unfortunately, the expressions are quite complex. In our derivation, we will use Cartesian coordinates as much as possible.

## 10.5 Space-fixed angular momentum operators

We first recall the most important results for space-fixed angular momentum operators from Chapter 4. For an atom with Cartesian coordinates $\boldsymbol{r}_i$ we have the linear momentum operator

$$\hat{\boldsymbol{p}}_i = \frac{\hbar}{i}\boldsymbol{\nabla}_i. \tag{10.50}$$

and the angular momentum operator

$$\hat{\boldsymbol{l}}_i = \boldsymbol{r}_i \times \hat{\boldsymbol{p}}_i \tag{10.51}$$

The total angular momentum is the sum

$$\hat{\boldsymbol{L}} = \sum_{i=1}^{n} \hat{\boldsymbol{l}}_i. \tag{10.52}$$

The angular momentum operators are generators of rotation. For angular momenta $\hat{\boldsymbol{j}}$ a rotation operator is defined

$$\hat{R}(\hat{\boldsymbol{n}}, \phi; \hat{\boldsymbol{j}}) \equiv e^{-\frac{i}{\hbar}\phi \boldsymbol{n}\cdot\hat{\boldsymbol{j}}}. \tag{10.53}$$

The corresponding rotation matrix in three-dimensional space is denoted by $\boldsymbol{R}(\hat{\boldsymbol{n}},\phi)$. Thus, for the $n$-atom wave function $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)$ we have

$$\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{l}}_i)\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_i,\ldots,\boldsymbol{r}_n)=\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{R}(\hat{\boldsymbol{n}},-\phi)\boldsymbol{r}_i,\ldots,\boldsymbol{r}_n). \tag{10.54}$$

For a rigid molecule, we cannot rotate just one of the atoms, but a rotation of all atoms is allowed. Since the angular momentum operators for different atoms commute, we have

$$\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{L}})=\Pi_{i=1}^{n}\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{l}}_i) \tag{10.55}$$

and

$$\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{L}})\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)=\Psi[\boldsymbol{R}(\hat{\boldsymbol{n}},-\phi)\boldsymbol{r}_1,\boldsymbol{R}(\hat{\boldsymbol{n}},-\phi)\boldsymbol{r}_2,\ldots,\boldsymbol{R}(\hat{\boldsymbol{n}},-\phi)\boldsymbol{r}_n]. \tag{10.56}$$

By defining a body-fixed frame $\boldsymbol{Q}=[\boldsymbol{q}_1\,\boldsymbol{q}_2\,\boldsymbol{q}_3]$ [see Sec. 10.2] we can simplify things by defining an angular momentum operator $\hat{\boldsymbol{\mathcal{L}}}$ that just acts on the columns of the frame,

$$\hat{\boldsymbol{\mathcal{L}}}=\frac{\hbar}{i}\sum_{j=1}^{3}\boldsymbol{q}_j\times\boldsymbol{\nabla}_j, \tag{10.57}$$

where

$$(\boldsymbol{\nabla}_j)_i=\frac{\partial}{\partial Q_{i,j}} \tag{10.58}$$

so

$$(\boldsymbol{\nabla}_j)_i(\boldsymbol{q}_{j'})_{i'}=\frac{\partial Q_{i'j'}}{\partial Q_{ij}}=\delta_{jj'}\delta_{ii'}. \tag{10.59}$$

Since the coordinates of the atoms in the body-fixed frame are constants, the wave function will be a function of $\boldsymbol{Q}$ and we have

$$\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{L}})\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)=\hat{R}(\hat{\boldsymbol{n}},\phi;\hat{\boldsymbol{\mathcal{L}}})\Psi(\boldsymbol{Q}). \tag{10.60}$$

By taking the derivative with respect to $\phi$, and multiplying with $\hbar/i$ we find

$$\hat{L}\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)=\hat{\boldsymbol{\mathcal{L}}}\Psi(\boldsymbol{Q}). \tag{10.61}$$

For rigid rotors, both $\hat{L}$ and $\hat{\boldsymbol{\mathcal{L}}}$ are the total angular momentum operators and their difference is only formal. Body-fixed frames, however, are also useful in the description of semi-rigid and floppy molecules. In that case the operator $\hat{\boldsymbol{L}}$ describes the total angular momentum, including vibrational angular momentum, whereas $\hat{\boldsymbol{\mathcal{L}}}$ does not include vibrational angular momentum. We can express the frame using three Euler angles, and give explicit expressions for $\hat{\boldsymbol{\mathcal{L}}}$ in terms of these angles. However, most of the derivation below is easier if we define $\hat{\boldsymbol{\mathcal{L}}}$ by its action on the (nine) elements of $\boldsymbol{Q}$. Note that $\hat{\boldsymbol{\mathcal{L}}}$ has all the usual (space-fixed) properties of angular momenta. In particular, the commutation relations are

$$[\hat{\mathcal{L}}_i,\hat{\mathcal{L}}_j]=i\hbar\epsilon_{ijk}\hat{\mathcal{L}}_k, \tag{10.62}$$

and all components components commute with the total angular momentum

$$\hat{\mathcal{L}}^2=\hat{\mathcal{L}}_1^2+\hat{\mathcal{L}}_2^2+\hat{\mathcal{L}}_3^2. \tag{10.63}$$

In the next section we will define body-fixed angular momentum operators $\hat{\boldsymbol{\mathcal{P}}}$ and we show that their commutation relations are *anomalous*.

## 10.6 Body-fixed angular momentum operators

In analogy to the classical treatment, we define

$$\hat{\boldsymbol{\mathcal{P}}} \equiv \boldsymbol{Q}^T \hat{\boldsymbol{\mathcal{L}}} \tag{10.64}$$

or, in components, with the Einstein summation convention

$$\hat{\mathcal{P}}_j = Q_{ij} \hat{\mathcal{L}}_i. \tag{10.65}$$

For a unitary matrix $\boldsymbol{U}$ that commutes with $\hat{\boldsymbol{\mathcal{L}}}$ we have

$$\boldsymbol{U}^T \hat{\boldsymbol{\mathcal{L}}} \cdot \boldsymbol{U}^T \hat{\boldsymbol{\mathcal{L}}} = \hat{\mathcal{L}}^2. \tag{10.66}$$

However, since $\hat{\boldsymbol{\mathcal{L}}}$ acts on the matrix elements of $\boldsymbol{Q}$ we need a little work to evaluate $\hat{\mathcal{P}}^2$.

First, we evaluate the action of $\hat{\boldsymbol{\mathcal{L}}}$ on any column $\boldsymbol{q}$ of the matrix $\boldsymbol{Q}$, in components,

$$[\hat{\mathcal{L}}_i, q_j] = [\frac{\hbar}{i} \epsilon_{ikl} q_k \nabla_l, q_j] = -i\hbar \epsilon_{ikl} q_k [\nabla_l, q_j] = i\hbar \epsilon_{ijk} q_k. \tag{10.67}$$

Since $\hat{\mathcal{L}}_i$ acts the same on each column of $\boldsymbol{Q}$ we have

$$[\hat{\mathcal{L}}_i, Q_{kl}] = -i\hbar \epsilon_{ijk} Q_{jl}. \tag{10.68}$$

With this result can show that $\hat{\mathcal{P}}_i$ is Hermitian:

$$(\hat{\mathcal{P}}_i)^\dagger = (Q_{ji} \hat{\mathcal{L}}_j)^\dagger = \hat{\mathcal{L}}_j Q_{ji} = [\hat{\mathcal{L}}_j, Q_{ji}] + Q_{ji} \hat{\mathcal{L}}_j = \hat{\mathcal{P}}_i, \tag{10.69}$$

where we used that $\hat{\mathcal{L}}_j$ is Hermitian and $Q_{ji}$ is real. Next, we evaluate the commutation relation between space-fixed and body-fixed operators,

$$[\hat{\mathcal{L}}_i, \hat{\mathcal{P}}_j] = [\hat{\mathcal{L}}_i, Q_{kj} \hat{\mathcal{L}}_k] \tag{10.70}$$

$$= Q_{kj} [\hat{\mathcal{L}}_i, \hat{\mathcal{L}}_k] + [\hat{\mathcal{L}}_i, Q_{kj}] \hat{\mathcal{L}}_k \tag{10.71}$$

$$= i\hbar \epsilon_{ikl} Q_{kj} \hat{\mathcal{L}}_l - i\hbar \epsilon_{ilk} Q_{lj} \hat{\mathcal{L}}_k = 0. \tag{10.72}$$

In the last step we used that by the Einstein summation convention there is a sum over $k$ and over $l$, so we rename these indices to $l$ and $k$ in the second term. For the total body-fixed angular momentum we find

$$\hat{\mathcal{P}}^2 = \hat{\mathcal{P}}_i \hat{\mathcal{P}}_i = Q_{ji} \hat{\mathcal{L}}_j Q_{ki} \hat{\mathcal{L}}_k \tag{10.73}$$

$$= Q_{ji} [\hat{\mathcal{L}}_j, Q_{ki}] \hat{\mathcal{L}}_k + Q_{ji} Q_{ki} \hat{\mathcal{L}}_j \hat{\mathcal{L}}_k \tag{10.74}$$

$$= -i\hbar \epsilon_{jlk} Q_{ji} Q_{li} \hat{\mathcal{L}}_k + \delta_{jk} \hat{\mathcal{L}}_j \hat{\mathcal{L}}_k \tag{10.75}$$

$$= -i\hbar \epsilon_{jlk} \delta_{jl} \hat{\mathcal{L}}_k + \hat{\mathcal{L}}^2 = \hat{\mathcal{L}}^2. \tag{10.76}$$

Thus, the total body-fixed angular momentum is equal to the total space-fixed angular momentum. We will also need

$$[\hat{\mathcal{P}}_i, Q_{kj}] = [Q_{li} \hat{\mathcal{L}}_l, Q_{kj}] = Q_{li} [\hat{\mathcal{L}}_l, Q_{kj}] = -i\hbar \epsilon_{lj'k} Q_{li} Q_{j'j} \tag{10.77}$$

$$= -i\hbar (\boldsymbol{q}_i \times \boldsymbol{q}_j)_k = -i\hbar \epsilon_{ijl} (\boldsymbol{q}_l)_k \tag{10.78}$$

$$= -i\hbar \epsilon_{ijl} Q_{kl}. \tag{10.79}$$

If we compare this to the action of the space-fixed operators on the frame we see that whereas $\hat{\mathcal{L}}_i$ is acting on columns of $\boldsymbol{Q}$, the body-fixed operators $\hat{\mathcal{P}}_i$ are acting on rows of $\boldsymbol{Q}$. Finally, we compute the commutation relation between two body-fixed angular momentum operators,

$$\begin{aligned}
[\hat{\mathcal{P}}_i, \hat{\mathcal{P}}_j] &= [\hat{\mathcal{P}}_i, Q_{kj}\hat{\mathcal{L}}_k] = [\hat{\mathcal{P}}_i, Q_{kj}]\hat{\mathcal{L}}_k = -i\hbar\epsilon_{ijl}Q_{kl}\hat{\mathcal{L}}_k = -i\hbar\epsilon_{ijl}\hat{\mathcal{P}}_l && (10.80)\\
&= -i\hbar\epsilon_{ijk}\hat{\mathcal{P}}_k. && (10.81)
\end{aligned}$$

Compared to the commutator of space-fixed angular momentum operators there is an extra minus sign, so these commutation relations are called *anomalous.*

## 10.7 Angular momentum operators applied to Wigner D-functions

A Wigner $D$-matrix is a matrix representation of a rotation operator acting on the abstract angular momentum space $\{|jm\rangle, m = -j, \ldots, j\}$, parameterized by a rotation matrix in $\mathbb{R}^3$.

$$\hat{R}[\boldsymbol{R}(\hat{\boldsymbol{n}}, \phi); \hat{\boldsymbol{J}}] \equiv e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}. \tag{10.82}$$

We will also use the more compact notation, $\hat{R}(\boldsymbol{Q})$, with $\boldsymbol{Q} = \boldsymbol{R}(\hat{\boldsymbol{n}}, \phi)$, where we drop the $(\boldsymbol{n}, \phi)$ parameterization as well as the $\hat{\boldsymbol{J}}$ argument. We use Wigner's convention to define the action of a rotation in $\mathbb{R}^3$ onto this operator

$$\hat{R}(\hat{\boldsymbol{n}}, \phi; \hat{\boldsymbol{\mathcal{L}}})\hat{R}(\boldsymbol{Q}) = \hat{R}[\boldsymbol{R}(\hat{\boldsymbol{n}}, -\phi)\boldsymbol{Q}], \tag{10.83}$$

which gives,

$$e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{\mathcal{L}}}}\hat{R}(\boldsymbol{Q}) = \hat{R}(\hat{\boldsymbol{n}}, -\phi)\hat{R}(\boldsymbol{Q}) = e^{\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}\hat{R}(\boldsymbol{Q}). \tag{10.84}$$

Taking the derivative with respect to $\phi$ and then setting $\phi = 0$, and taking $\hat{\boldsymbol{n}}$ as the unit vector $\boldsymbol{e}_i$ of the standard basis gives

$$\hat{\mathcal{L}}_i\hat{R}(\boldsymbol{Q}) = -\hat{J}_i\hat{R}(\boldsymbol{Q}). \tag{10.85}$$

If we take matrix elements in the angular momentum basis, we find, e.g., for $\hat{\mathcal{L}}_z$

$$\begin{aligned}
\hat{\mathcal{L}}_z D^{(J)}_{MK}(\boldsymbol{Q}) &= \hat{\mathcal{L}}_z\langle JM|\hat{R}(\boldsymbol{Q})|JM\rangle = -\langle JM|\hat{J}_z\hat{R}(\boldsymbol{Q})|JK\rangle && (10.86)\\
&= -M\langle JM|\hat{R}(\boldsymbol{Q})|JK\rangle = -MD^{(J)}_{MK}(\boldsymbol{Q}). && (10.87)
\end{aligned}$$

The minus sign here shows that the $D$-matrices will not be suitable as wave functions. We saw already in Eq. (5.113), however, that the *complex conjugates* of Wigner $D$-matrices rotate as angular momentum states. So we try the last three steps again, but starting with the inverse, $\hat{R}^\dagger$

$$\begin{aligned}
e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{\mathcal{L}}}}\hat{R}^\dagger(\boldsymbol{Q}) &= \hat{R}^\dagger[\boldsymbol{R}(\hat{\boldsymbol{n}}, -\phi)\boldsymbol{Q}] && (10.88)\\
&= \hat{R}[\boldsymbol{Q}^T\boldsymbol{R}(\hat{\boldsymbol{n}}, \phi)] && (10.89)\\
&= \hat{R}^\dagger(\boldsymbol{Q})e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}. && (10.90)
\end{aligned}$$

Again, taking the derivative with respect to $\phi$ with $\hat{\boldsymbol{n}} = \boldsymbol{e}_i$ and then setting $\phi$ to zero gives

$$\hat{\mathcal{L}}_i\hat{R}^\dagger(\boldsymbol{Q}) = \hat{R}^\dagger(\boldsymbol{Q})\hat{J}_i. \tag{10.91}$$

We can now take matrix elements in the angular momentum basis, keeping in mind that $\hat{L}_i$ is acting on the coordinates $\boldsymbol{Q}$ only,

$$\hat{\mathcal{L}}_i\langle JK|\hat{R}^\dagger(\boldsymbol{Q})|JM\rangle = \langle JK|\hat{R}^\dagger(\boldsymbol{Q})\hat{J}_z|JM\rangle = M\langle JK|\hat{R}^\dagger(\boldsymbol{Q})|JM\rangle. \tag{10.92}$$

From this, we find again that the complex conjugate of the $D$-matrix acts as an angular momentum state

$$\hat{\mathcal{L}}_i D^{(J)*}_{MK}(\boldsymbol{Q}) = M D^{(J)*}_{MK}(\boldsymbol{Q}). \tag{10.93}$$

It is left as an exercise to show that for the ladder operators

$$\hat{\mathcal{L}}_\pm = \hat{\mathcal{L}}_x \pm i\hat{\mathcal{L}}_y \tag{10.94}$$

we get

$$\hat{\mathcal{L}}_\pm D^{(J)*}_{MK}(\boldsymbol{Q}) = \sqrt{J(J+1) - M(M\pm 1)}\, D^{(J)*}_{M\pm 1,K}(\boldsymbol{Q}). \tag{10.95}$$

To find the action of the body-fixed operators we use Eq. (10.91),

$$\hat{\mathcal{P}}_i \hat{R}^\dagger(\boldsymbol{Q}) = Q_{ji}\hat{\mathcal{L}}_j \hat{R}^\dagger(\boldsymbol{Q}) = \hat{R}^\dagger(\boldsymbol{Q}) Q_{ji}\hat{J}_j. \tag{10.96}$$

Next, we can use the following relation, which holds for any set of angular momentum operators $\hat{\boldsymbol{J}}$ that satisfy the usual (space-fixed) commutation relations

$$e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}\hat{J}_i e^{\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}} = \sum_j R_{ji}(\hat{\boldsymbol{n}},\phi)\hat{J}_j. \tag{10.97}$$

Thus, if we take $(\hat{\boldsymbol{n}},\phi)$ to be the parameters of the rotation matrix $\boldsymbol{Q} = \boldsymbol{R}(\hat{\boldsymbol{n}},\phi)$ we have

$$\hat{\mathcal{P}}_i \hat{R}^\dagger(\boldsymbol{Q}) = \hat{R}^\dagger(\boldsymbol{Q}) Q_{ji}\hat{J}_j = e^{\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}\; e^{-\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}}\hat{J}_i e^{\frac{i}{\hbar}\phi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}}} = \hat{J}_i \hat{R}^\dagger(\boldsymbol{Q}). \tag{10.98}$$

It is left as an exercise to show that action of body-fixed angular momentum operators $\hat{\boldsymbol{\mathcal{P}}}$ on complex conjugeted Wigner $D$-matrices is *anomalous*, i.e.,

$$\hat{\mathcal{P}}_z D^{(J)*}_{MK}(\boldsymbol{Q}) = K D^{(J)*}_{MK}(\boldsymbol{Q}) \tag{10.99}$$

$$\hat{\mathcal{P}}_\pm D^{(J)*}_{MK}(\boldsymbol{Q}) = C_\mp(J,K) D^{(J)*}_{M,K\mp 1}(\boldsymbol{Q}), \tag{10.100}$$

where we defined the body-fixed ladder operators as

$$\hat{\mathcal{P}}_\pm = \hat{\mathcal{P}}_x \pm i\hat{\mathcal{P}}_y. \tag{10.101}$$

## 10.8 Quantum Hamiltonian for rigid rotor

The quantum Hamiltonian for the rigid rotor can be found by replacing the body-fixed angular momenta in the classical expression [Eq. (10.46)] by body-fixed angular momenta operators

$$\hat{T} = A\hat{P}_a^2 + B\hat{P}_b^2 + C\hat{P}_c^2. \tag{10.102}$$

Note that this method to quantize is not general: in the classical Hamiltonian the order of angular momenta and coordinate-dependent factors is arbitrary, but if the corresponding quantum mechanical operators do not commute the order matters in the Hamiltonian operator. In the expression for the rigid rotor the rotational constants commute with the operators, so it may seem that nothing can go wrong. Still, in the first attempt to properly derive the Hamiltonian for rotation-vibration of polyatomic molecules, Carl Eckart did not get it right [8], and he explained and resolved the problem in a subsequent paper [9].

As before, it will be convenient to use ladder operators. For their squares we have

$$\hat{\mathcal{P}}_\pm^2 = (\hat{\mathcal{P}}_x \pm i\hat{\mathcal{P}}_y)(\hat{\mathcal{P}}_x \pm i\hat{\mathcal{P}}_y) = \hat{\mathcal{P}}_x^2 - \hat{\mathcal{P}}_y^2 \pm i[\hat{\mathcal{P}}_x\hat{\mathcal{P}}_y + \hat{\mathcal{P}}_y\hat{\mathcal{P}}_x] \tag{10.103}$$

so that we can use

$$\hat{\mathcal{P}}_x^2 - \hat{\mathcal{P}}_y^2 = \frac{1}{2}\left(\hat{\mathcal{P}}_+^2 + \hat{\mathcal{P}}_-^2\right). \tag{10.104}$$

We also have

$$\hat{\mathcal{P}}^2 = \hat{\mathcal{P}}_x^2 + \hat{\mathcal{P}}_y^2 + \hat{\mathcal{P}}_z^2. \tag{10.105}$$

We can now find Hamiltonians and rigid rotor eigenfunctions for all cases in table 10.1

### 10.8.1 Spherical top

For the spherical top we have $A = B = C$, so

$$\hat{T}_{\text{sr}} = B\hat{P}^2 \tag{10.106}$$

and the eigenfunctions are

$$\hat{T}_{\text{sr}} D_{MK}^{(J)*}(\alpha,\beta,\gamma) = BJ(J+1)\hbar^2 D_{MK}^{(J)*}(\alpha,\beta,\gamma). \tag{10.107}$$

### 10.8.2 Prolate symmetric top

For a prolate symmetric top, $A > B = C$ we have

$$\hat{T}_{\text{prol}} = B\hat{\mathcal{P}}^2 + (A-B)\hat{\mathcal{P}}_a^2 \tag{10.108}$$

Thus, by taking principle axis $c$ as the $z$-axis we have

$$\hat{T}_{\text{prol}} D_{MK}^{(J)*}(\alpha,\beta,\gamma) = [B\,J(J+1) + (A-B)K^2]\hbar^2\, D_{MK}^{(J)*}(\alpha,\beta,\gamma). \tag{10.109}$$

Note that since $A > B$ the energy increases with $K^2$.

### 10.8.3 Oblate symmetric top

Here we have $A = B > C$, so

$$\hat{T}_{\text{prol}} = B\hat{\mathcal{P}}^2 + (C-B)\hat{\mathcal{P}}_a^2. \tag{10.110}$$

and with principle axis $a$ as the $z$-axis we have

$$\hat{T}_{\text{obl}} D_{MK}^{(J)*}(\alpha,\beta,\gamma) = [B\,J(J+1) - (B-C)K^2]\hbar^2\, D_{MK}^{(J)*}(\alpha,\beta,\gamma). \tag{10.111}$$

Now, since $B > C$, the energy decreases with $K^2$.

### 10.8.4 Asymmetric top

We can write the Hamiltonian in different ways. If $B - C < A - B$ the rotor looks more like a prolate-symmetric top, and it is conventional to use

$$\hat{T}_{\text{asym}} = \frac{1}{2}(B+C)\hat{\mathcal{P}}^2 + [A - \frac{1}{2}(B+C)]\hat{\mathcal{P}}_a^2 + \frac{1}{4}(B-C)(\hat{\mathcal{P}}_+^2 + \hat{\mathcal{P}}_-^2). \tag{10.112}$$

To find the eigenvalues we need to digonalize the matrix representation of the kinetic energy operator in a basis of Wigner $D$-functions with $K = -J, -J+1, \ldots, J$.

When $A - B < B - C$, the oblate-like case, we write the Hamiltonian as

$$\hat{T}_{\text{asym}} = \frac{1}{2}(A+B)\hat{\mathcal{P}}^2 + [C - \frac{1}{2}(A+B)]\hat{\mathcal{P}}_a^2 + \frac{1}{4}(A-B)(\hat{\mathcal{P}}_+^2 + \hat{\mathcal{P}}_-^2). \tag{10.113}$$

## 10.9 Rotation-vibration Hamiltonian for semi-rigid molecules

A semi-rigid molecule has an equilibrium structure and vibrations can be described by oscillations around the equilibrium. In first approximation rotations and vibrations can be treated separately.

To take into account the coupling between rotations and vibrations the Watson Hamiltonian can be used. There are actually two papers published by James Watson, one for nonlinear molecules [10] in 1968 and one for linear molecules [11], in 1970. The time between these papers gives a hint that the difference between linear and nonlinear molecules is nontrivial. Also, note that already in 1934, Eckart wrote one of the first papers on the "The kinetic energy of polyatomic molecules" [8].

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