12.1 INTRODUCTION

In 1995 several groups succeeded in producing Bose-Einstein condensation in dilute gases of alkali atoms. 796-798 As will be discussed in detail in Section 12.5, Bose-Einstein condensation is a phenomenon that occurs when collections of bosons (particles of integer spin) macroscopically condense into their lowest quantum state. In 2003 molecular Bose-Einstein condensates of alkali dimers were reported. 799-801 The temperatures of these atomic and molecular condensates are on the order of nK-μK. Theoretical studies show that even at these ultracold temperatures, chemical reactions may occur, and may even be very fast. 802-803

In this chapter we start our journey with Arrhenius' 19th century description of reactions at ambient temperatures and then work our way down to lower and lower temperatures. In the Arrhenius equation, the temperature (T) dependent reaction rate is given by

$$k(T) = A e^{-E_a/k_B T}.$$ (12.1)

where \(k_B\) is the Boltzmann constant and \(A\) is a proportionality constant, usually referred to simply as the pre-exponential factor, or \(A\)-factor. The activation energy \(E_a\) is the energy required to pass the transition state. Eq. (12.1) can be derived using classical statistical mechanics. It predicts that the reaction rate drops to zero quickly when \(k_B T < E_a\).

Some reactions, however, are barrierless \((E_a \sim 0)\), and their rate may increase at lower temperatures. This is particularly true for ion-molecule reactions. As early as 1905, Langevin derived an expression for the reaction rate of ion-molecule reactions. As discussed in Section 12.2, this expression only depends on the long range part of the intermolecular potential, and the model is called a 'capture model'. 804 Later, it was found that neutral radical-radical reactions and even some radical-molecule reactions may also be fast at low temperatures. These barrierless reactions are very important in the lower parts of the stratosphere, where temperatures may be around 200 K.

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*At this point the reader may wish to review the material covered in Section 3.2.3.*

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Cold and Ultracold Collisions

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The air around us contains on the order of \(10^{19}\) molecules per cm\(^3\). In interstellar space, areas where the density is on the order of 10\(^6\) cm\(^{-3}\) appear as clouds when observed through telescopes, against a background of even lower density in most of the interstellar medium. Interstellar clouds have temperatures in the range of 10-100 K. Still, chemical reactions occur and play a crucial role in, e.g., the formation of stars. 805

As discussed in previous chapters, the calculation of a reaction rate (or a cross section) requires knowledge of the potential energy surface. Depending on the chemical system under consideration, it may be sufficient to know only the potential around the transition state or only the long range part. Computation of the potential surface always requires quantum mechanics, since it involves the motion of the electrons in the system. However, to compute the nuclear dynamics on the surface, classical mechanics is generally a good starting point. At lower temperatures, one has to consider quantum effects, such as tunnelling, resonances, zero-point energy, quantization of the angular momenta of the reactants and products, and quantization of the angular momentum of the colliding complex as a whole.

Such quantum effects become dominant at around 1 K. The cosmic background radiation has a temperature of 2.76 K, and the coldest known place in the universe – outside the laboratory – is about 1 K. However, in laboratory experiments even lower temperatures can be reached. At temperatures around 1 K, molecules have a kinetic energy that is comparable to their interaction energy with electric and magnetic fields of the strengths achievable in laboratory-based experiments. This provides many opportunities to study and manipulate cold gases, and such studies have become an active area of research.806,807

The focus of this tutorial chapter is primarily theoretical. Collisions at low temperatures, or low collision energies, present a unique set of challenges and opportunities for theory, and we outline the main approaches that are currently available to study cold collisions from a theoretical point of view. Experimental aspects concerning the production of cold molecules and the study of cold collisions are covered in Study Boxes 12.1 and 12.5. The chapter starts with sections describing classical and quantum capture theory. Section 12.4 discusses the Wigner threshold laws, particular solutions of the Schrödinger equation that are valid at low energies. Finally, Section 12.5 outlines what happens to matter at ultra-low temperatures, and in particular describes the phenomenon of Bose-Einstein condensation.

12.2 CLASSICAL CAPTURE THEORY

The term 'capture model' reflects the fact that the reaction rate (or cross section) is approximated as the rate at which the reactants come together and reach the barrier or transition state. As already discussed, at low temperatures, or under low collision energy conditions, reactions that possess a potential energy barrier along the reaction coordinate tend to become very slow, and therefore only exothermic reactions taking place on attractive potential energy surfaces have significant reaction rates. For such processes, the only barrier to be traversed is the centrifugal barrier, 822 and once past this barrier, the reaction probability can often be assumed to be near unity. So called 'recrossing' of the barrier back to reactants is not usually accommodated in the capture models to be described. It is for this reason that capture theories tend to be most applicable to reactions on attractive potential energy surfaces, for which the capture process (crossing the barrier) is usually rate determining.

12.2.1 Classical Central Force Problem

To introduce the key concepts* of low energy scattering theory we review the problem of two point particles A and B interacting through a potential \(V(r)\) that only depends on the distance \(r\) between

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STUDY BOX 12.1: MAKING COLD MOLECULES

Cooling of molecules into the ‘cold’ (10 K to 1 mK) and ‘ultracold’ (sub 1 mK) regimes is currently an area of intense research interest, and a number of techniques have been developed to achieve these low temperatures in molecular gases. The aim of the following is to highlight a few of these techniques, rather than to provide an exhaustive review. For more detailed information the reader is referred to ref. [811].

Techniques for cooling molecules may be separated into ‘first-stage’ and ‘second-stage’ methods. First-stage methods are used to slow molecules down to temperatures of a few Kelvin or less, at which point they can be captured into an electromagnetic trap. Once the atoms or molecules have been trapped, second-stage techniques allow further cooling into the ‘ultracold’ regime.

First-stage Cooling Techniques

A number of first-stage cooling techniques for molecules are based on deceleration of molecules produced in a supersonic expansion. Supersonic jet expansions produce internally cold molecules with a narrow velocity distribution simply by expanding gas from a high pressure region to a low pressure region through a small orifice. Cooling of a molecule’s internal degrees of freedom is achieved virtually ‘for free’, and beam temperatures in the region of 1–2 K are readily achievable. The key difference between molecules in a molecular beam and the cold molecules of interest is that in a molecular beam the narrow velocity distribution is centred around a velocity that is not zero. From the point of view of cold molecule production, the problem therefore lies in finding a suitable means to decelerate the beam.

There have been numerous approaches to this problem. The simplest method uses a rotating assembly that moves the beam source backwards as the gas expands in order to cancel out the beam velocity. The idea was in fact first used in reverse by Moon et al., as a means of beam acceleration, but has more recently been adopted for cold molecule production by Gupta and Herschbach. The technique has been demonstrated successfully for beams of O₂, SF₆, and CH₃F, with lowest speeds of 67, 55, and 91 m s⁻¹, respectively. However, while it is a completely general technique, there are considerable technical difficulties associated with the mechanical assembly, and it is also unlikely that the technique will prove capable of producing molecules in the ‘ultracold’ regime.

More sophisticated methods use electric or magnetic fields either to select the low-velocity tail of a molecular beam, or to slow a narrow ‘slice’ of the beam velocity distribution to much lower velocities. If the beam gas has a large enough dipole, velocity selection with a bent electrostatic quadrupole may be used to select slow molecules from the beam, as shown in Figure 12.1. A quadrupole may be used to select low-field-seeking states of strongly dipolar molecules in much the same way as a hexapole is used to perform a similar action on symmetric top molecules (see Section 9.3.2.2). When a bend is introduced into the quadrupole, only molecules moving slowly enough to interact strongly with the guiding field are transported around the bend, with the remainder of molecules being lost from the quadrupole. The fraction of the beam that is velocity-selected in this way depends on the potential applied to the quadrupole rods (with lower potentials yielding a lower-velocity fraction), the radius of the bend (with tighter bends yielding a lower-velocity fraction), and on the magnitude of the ratio between the Stark shift in the quadrupole field and the mass of the beam molecules (molecules with larger Stark shifts and smaller masses are more easily guided round the bend in the quadrupole).

An increasingly popular approach to molecular beam deceleration is the Stark deceleration technique pioneered by Gerard Meijer and coworkers. A Stark decelerator uses time-varying electric fields to decelerate a ‘velocity slice’ from a molecular beam to zero velocity in the lab frame. Such a decelerator is shown schematically in Figure 12.2. Pairs of electrodes are placed along the beam axis, with every second electrode set to high voltage and the interleaving electrodes grounded. When travelling between a grounded electrode and one at high potential, a molecule in a low-field-seeking Stark state will be climbing a potential gradient and will be slowed down. If the potential applied to the rods were static, once the molecule had passed the high-field electrode it would then accelerate down the potential gradient on the other side and convert the potential energy it had gained back to kinetic energy. However, if as the molecule nears the high-potential electrode, the electrode potentials are switched (so that those at high potential are now grounded, and vice versa), the molecule again finds itself climbing a potential gradient, and is slowed further. Repeating this switching process as the molecule travels through the decelerator allows molecules to be slowed to velocities low enough that they may be captured into an electrostatic trap. Only a certain fraction of beam molecules are decelerated, whose initial velocity, position, and quantum state place them in phase with the switching frequency of the decelerator.

![Figure 12.1](image1.png)

**Figure 12.1** Selection of a low-velocity fraction from a molecular beam using a bent quadrupole.

![Figure 12.2](image2.png)

**Figure 12.2** (a) A section of a Stark decelerator; (b) Inside the decelerator, low-field-seeking Stark states climb a potential gradient and are slowed. On switching the decelerator field, the molecules are returned to the 'bottom of the hill', and must climb the potential gradient again. This process is repeated along the length of the decelerator.

An alternative technique, known as Zeeman deceleration, uses a similar principle but employs a pulsed magnetic field.
Another approach to first-stage deceleration relies on molecular beam scattering processes. Crossed molecular beam experiments or molecular photodissociation experiments often produce some fraction of products that are stationary in the laboratory frame. This occurs when the product recoil velocity exactly cancels the velocity of the centre of mass of the reaction system. As an example, Chandler and coworkers have shown that in crossed beam inelastic scattering of NO with Argon, rovibrationally quantum-state selected NO molecules with velocities of less than 15 m s⁻¹ may be produced with densities of up to 10¹⁰ molecules cm⁻³.

Not all first-stage cooling techniques employ molecular beams. A popular approach to first-stage cooling is a method known as buffer gas cooling, in which the molecules of interest are cooled by collisions with a few hundred milliKelvin buffer gas, such as cryogenic helium gas stored in a cryostat. This is an entirely general and very promising technique, applicable to any molecule that can survive a large number of collisions with atomic helium. A disadvantage of the technique is the challenge of separating the cold molecules from the buffer gas after cooling has taken place.

**Second Stage Cooling**

Second-stage cooling techniques nearly all have their origins in laser-based methods for cooling and trapping of atoms. Steve Chu, Claude Cohen-Tannoudji, and William Phillips were the first to produce ultracold atoms in this way, and won the 1997 Nobel Prize in Physics for their efforts.

Laser cooling is based on momentum transfer from the photons in a laser beam to the atoms to be cooled in order to slow the atoms down. Each time an atom absorbs a photon, a small amount of momentum is transferred to the atom, slightly changing its velocity. Many absorption-emission cycles are required to slow an atom down appreciably, and so an atomic transition is required that forms a **closed optical loop**. This means that after absorption, spontaneous emission returns the atom back to its original state. Atoms with suitable two-level closed systems include alkali metals, metastable rare gas atoms, or singly charged alkalii-earth ions. Atoms that emit to other states can also be laser cooled, but an additional laser is required to excite a suitable transition to return the 'lost' atoms to the optical loop.

The most common laser cooling technique is called Doppler cooling, and usually involves an experimental setup consisting of six intersecting laser beams, as shown in Figure 12.3. This is usually achieved using three orthogonally propagating beams, each reflected back along its own beam path by a mirror. The frequency of each laser beam is tuned slightly to the red of an atomic transition. Due to the Doppler effect, atoms moving towards the light source absorb more photons than those moving away, and are slowed. The excited state will of course receive a second momentum 'kick' when it emits a photon to return to the ground state, but the direction of this second kick is random, so that the net force after many transitions is along the laser beam direction. The three-axis laser beam configuration means that atoms are slowed down no matter which direction they are moving in. Temperatures as low as 150 μK may be achieved for using this technique.

To prevent cooled atoms from falling out of the laser interaction region under the force of gravity, Doppler cooling is often combined with a magnetic trapping force to give a **magneto-optical trap** (MOT). Zeeman splitting of the energy levels in the magnetic field increases as atoms move away from the centre of the trap, shifting the atomic resonance closer to the laser frequency, and increasing the chance of the atom receiving a photon 'kick' towards the centre of the trap when the appropriate (circular) polarization of light is employed.

Other laser cooling methods are available to reduce the temperature of the atom cloud still further. Of these, 'Sisyphus cooling', also known as 'polarization gradient cooling', also earned a share of the 1997 Nobel Prize.

Figure 12.3 Laser beam geometry for Doppler cooling of an atomic gas.

While laser cooling has been highly successful for a number of atomic species, the absence of suitable closed optical cycle transitions within the much more complicated energy level structure of a molecule means that the technique cannot be extended into the molecular realm. A number of techniques have been developed to overcome this limitation.

**Sympathetic cooling**

Sympathetic cooling is an attractive approach in which an ensemble of laser-cooled and trapped ultracold atoms translationally cools an ensemble of co-trapped ions or molecules via elastic (thermalizing) collisions. One of the first molecular species to be cooled in this way was a 43-atom molecular ion of a dye called Alexa Fluor 350. The method has since been applied to ions with masses of up to several tens of thousands of atomic mass units. The lowest achievable temperature for the molecular species is determined by the temperature of the trapped atoms.

**Evaporative cooling**

Evaporative cooling relies on elastic (thermalizing) collisions between trapped molecules, without the presence of a co-trapped laser-cooled atomic species. As the trap depth is reduced, the warmest molecules escape, and so long as thermal equilibrium is maintained through collisions within the trap, the Boltzmann distribution gradually shifts to lower and lower temperatures. In principle evaporative cooling could be an effective second-stage cooling technique for molecules, but in practice the number densities of trapped molecules required to maintain thermal equilibrium through collisions have not yet been achieved.

**Other methods**

Other methods of forming cold molecules using laser-cooled atoms include photoassociation and Feshbach resonance magnetic tuning. Methods of this type, which form cold molecules from cold atoms, are referred to as indirect cooling methods, to distinguish them from direct cooling of 'warm' molecules into the ultracold regime. Both of the indirect methods referred to above produce highly internally excited diatomic species (though it is possible to use shaped femtosecond laser pulses to coax the system into the ground state and reduce the vibrational excitation). These techniques have been used successfully to produce ultracold molecules, but they are limited to a few species, with little scope for generalization to larger systems.

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the two particles (often referred to as a central force or central potential problem). Let the positions of the particles, with masses \( m_A \) and \( m_B \), be given by the Cartesian coordinates \( r_A \) and \( r_B \) with respect to a space-fixed frame. The first step in finding the classical equations of motion of the particles is the introduction of Jacobi coordinates (shown previously in Figure 3.1), i.e. the coordinates of the centre-of-mass (CM) of the system,

\[
R_{CM} = \frac{m_A r_A + m_B r_B}{m_A + m_B},
\]

and the relative coordinates

\[
r = r_B - r_A.
\]

The classical kinetic energy of the system is given by

\[
T = \frac{1}{2} m_A \dot{r}_A \cdot \dot{r}_A + \frac{1}{2} m_B \dot{r}_B \cdot \dot{r}_B = \frac{1}{2} M \dot{R}_{CM} \cdot \dot{R}_{CM} + \frac{1}{2} \mu \dot{r} \cdot \dot{r},
\]

where \( M = m_A + m_B \) is the total mass of the system, \( \mu = (1/m_A + 1/m_B)^{-1} \) is the reduced mass, and the dot over a symbol indicates its time-derivative. In the absence of external forces, the CM of the system moves with a constant velocity throughout the collision. The relative motion is decoupled from that of the CM, and the equations of motion for \( r \) are equivalent to the equations of motion for a single particle with mass \( \mu \) moving in a potential \( V(r) \). The components of the conjugate momentum \( p \) are defined by

\[
\mu \dot{r}_i = \frac{\partial T}{\partial \dot{r}_i} = \mu \dot{r}_i,
\]

where \( i = 1, 2, 3 \) labels the Cartesian components of the vector. The classical Hamiltonian of the system can then be expressed as a function of coordinates and their conjugate momenta as (see Chapter 3)

\[
H = \frac{p^2}{2 \mu} + V(r),
\]

where \( p \) is the magnitude of \( \dot{r} \). The classical equations of motion in Jacobi coordinates, known as the Hamilton-Jacobi equations of motion, are given by

\[
\dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{\mu},
\]

\[
\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\frac{\partial V(r)}{\partial r_i} = \frac{\partial (\partial V(r)/\partial r)}{\partial r} = -\frac{\partial V(r)}{\partial r}.
\]

With \( r = \hat{r} r \), where \( \hat{r} \) is a unit vector pointing along \( r \), these equations may be written in vector notation as

\[
\dot{r} = \mu^{-1} \hat{r} p
\]

\[
\dot{p} = -m \hat{r} \frac{\partial V(r)}{\partial r}.
\]

For readers not familiar with the Hamilton-Jacobi equations, we note that from the last two equations one readily recovers Newton's equations of motion \( \dot{F} = \mu \dot{r} \), where the force \( F \) is seen to be equal to \( \dot{p} \).

**Cold and Ultracold Collisions**

The angular momentum of the system,

\[
\ell = r \times p,
\]

is conserved, i.e. independent of time, since

\[
\dot{\ell} = r \times \dot{p} + p \times \dot{r} = \mu^{-1} \dot{p} \times p - r \frac{\partial V(r)}{\partial r} \times \dot{r} = 0.
\]

Hence, the vectors \( r, p, \) and \( \dot{r} \) are always in a plane perpendicular to \( \ell \). The square of the length of \( \ell \) is given by

\[
|\ell|^2 = (r \times p) \cdot (r \times p) = (r \cdot r)(p \cdot p) - (r \cdot p)(r \cdot p) = r^2 p^2 - (r \cdot p)^2.
\]

Defining the momentum along the vector \( r \) as \( p_r \equiv \ell \cdot p \), we may rewrite the equation as

\[
r^2 p^2 = |\ell|^2 + r^2 p_r^2,
\]

which we may use to write the Hamiltonian of the system as

\[
H = \frac{p^2}{2 \mu} + V(r) = \frac{|\ell|^2}{2 \mu r^2} + \frac{p_r^2}{2 \mu} + V(r).
\]

Hence, the problem of finding \( \eta(t) \) is equivalent to solving a one-dimensional problem with an effective potential

\[
V_{eff}(r) = \frac{|\ell|^2}{2 \mu r^2} + V(r),
\]

where the first term is called the centrifugal term, and accounts for the rotational kinetic energy of the reactant pair (see Chapter 1, Section 1.4.3). The equation of motion for \( r \) is

\[
\mu \ddot{r} = - \frac{dV_{eff}(r)}{dr}.
\]

To find the complete solution \( \eta(t) = r(t) \hat{r}(t) \) we expand \( \hat{r} \) as

\[
\hat{r} = e_x \cos \varphi + e_y \sin \varphi,
\]

where \( e_x \) and \( e_y \) are two orthonormal vectors in the plane perpendicular to \( \ell \) and \( \varphi \) is a time-dependent polar angle. For the time derivative of the direction \( \hat{r} \) we have

\[
\dot{\hat{r}} = \dot{\varphi}(e_x \sin \varphi + e_y \cos \varphi) = \dot{\varphi} \hat{\varphi} \times \hat{r}_\perp,
\]

where \( \hat{r}_\perp \) is the unit vector perpendicular to both \( \ell \) and \( \hat{r} \). From Eqs. (12.11) and (12.9) we have

\[
\ell = \mu \dot{r} \times \hat{r} = \mu \dot{r}^2 \hat{\varphi} \times \hat{r}_\perp,
\]

and so, since \( |\hat{r} \times \hat{r}_\perp| = 1 \), we find that
Cold and Ultracold Collisions

When \( |\ell| \) is known, the effective potential given in Eq. (12.16) is known, and Eq. (12.17) can be solved to find \( r(t) \). The result may be substituted into Eq. (12.22) to determine the full trajectory.

### 12.2.2 Cross Sections

Collisions may be elastic, inelastic, or reactive. In an elastic collision, the direction of relative motion of the particles changes. In the CM-frame, the speeds of the particles are conserved. However, in the laboratory-fixed frame speeds may change as a result of collisions. It is through these elastic collisions that thermal equilibrium is reached after a hot gas is expanded into a cold gas. This principle is used in the buffer gas cooling technique, where, e.g., laser-ablated CaH is cooled to 0.4 K by collisions with a cryogenically cooled helium buffer gas. For this reason, in the context of cold chemistry, elastic collisions are sometimes called good collisions.

In an inelastic collision, the internal state of at least one of the colliding particles changes, e.g., it is rotationally or vibrationally excited or relaxed. Experiments on molecules with non-zero spin, and thus with a non-zero magnetic moment, are often carried out by trapping them in a magnetic field. In a collision, the orientation of the spin may change into a state that is expelled from the trap, and therefore this kind of inelastic collision is sometimes called a bad collision.

In a reactive collision, the composition of the particles changes, e.g., \( A + BC \rightarrow AB + C \). Whether or not a collision leads to a reaction depends on the impact parameter. As discussed in Chapters 1 and 3, and illustrated in Figure 12.4, if a reaction only occurs when the impact parameter \( b \) is less than some value \( b_{\text{max}} \) and then occurs with unit probability, the cross section, \( \sigma \), for that process is:

\[
\sigma = n b_{\text{max}}^2. \tag{12.27}\]

The cross section has the dimensions of area, and in general depends on the kinetic energy of the particles, \( E = \frac{1}{2} \mu v^2 \). It is also possible that the reaction occurs with some probability that depends both on the impact parameter and on the collision energy, \( 0 \leq P(b, E) \leq 1 \). In this case the cross section is given by:

\[
\sigma(E) = 2\pi \int_0^{b_{\text{max}}} P(b, E) b \, db. \tag{12.28}\]

As noted in Chapter 1, the function \( P(b, E) \) is called the opacity function. Cross sections for elastic and inelastic processes are defined in a similar way.

### 12.2.3 Canonical Reaction Rates

For a binary process

\[
A + B \rightarrow C
\]

the evolution in time of the concentrations \([A]\), \([B]\), and \([C]\) (in units of molecules cm\(^{-3}\)) is given by

\[
\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k(T)[A][B], \tag{12.29}\]

*Note that in this chapter we drop the 'rel' notation for relative velocity, \( v_{\text{rel}} \).*
where $k(T)$ is the temperature dependent reaction rate in units of cm$^3$ s$^{-1}$ molecule$^{-1}$. It may be computed as the Boltzmann average of the cross section ($\sigma(E)$),

$$\begin{align*}
k(T) = \int_0^\infty \sigma(E) f(v) \, dv,
\end{align*}$$
\hspace{1cm} (12.30)

where $f(v)$ is the Maxwell-Boltzmann speed distribution. At ultralow temperatures this expression completely breaks down, not only because the rate will depend on whether the particles are bosons or fermions, but also because Eq. (12.29) will no longer apply, as we shall see in Section 12.5.6. The Maxwell-Boltzmann speed distribution for particles with mass $m$ is given by

$$f(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_BT},$$
\hspace{1cm} (12.31)

The distribution is normalized such that

$$\int_0^\infty f(v) \, dv = 1.$$  \hspace{1cm} (12.32)

For the average kinetic energy, we have

$$\int_0^\infty \frac{1}{2} mv^2 f(v) \, dv = \frac{3}{2} k_BT,$$  \hspace{1cm} (12.33)

and the average speed of the particles is

$$\bar{v} = \frac{1}{\int_0^\infty v f(v) \, dv} = \sqrt{\frac{8k_BT}{\pi m}}.$$  \hspace{1cm} (12.34)

It is possible to have a mixture of gases for which the speed distributions are characterized by different temperatures $T_1$ and $T_2$. If the masses of the different particles are $m_1$ and $m_2$, the relative speed distribution is found by replacing the temperature $T$ by the mass-weighted average

$$\bar{T} = \frac{m_2 T_1 + m_1 T_2}{m_1 + m_2},$$
\hspace{2cm} (12.35)

and $m$ by the reduced mass $\mu$. If the two gases are in thermal equilibrium, we have $T_1 = T_2 = \bar{T} = T$. If, however, one gas is much colder than the other, e.g., $T_2 \ll T_1$, then Eq. (12.35) simplifies to

$$\bar{T} \approx \frac{m_2}{m_1 + m_2} T_1 = \frac{\mu}{m_1} T_1.$$  \hspace{1cm} (12.36)

*Apart from the change in notation for $r_{coh}$ this is the same as Eq. (1.12).*

### Cold and Ultracold Collisions

The rate constant in Eq. (12.30) may alternatively be written as an integral over the relative kinetic energy $E = \frac{1}{2} \mu v^2$, using $dE = \mu \, dv$,

$$k(T) = \int_0^\infty \sigma(E) e^{-E/k_BT} \, dE.$$  \hspace{1cm} (12.37)

Substituting $x = \frac{E}{k_BT}$ and $\bar{v} = \sqrt{8k_BT/\mu}$ gives

$$k(T) = \bar{v} \int_0^\infty \sigma(xk_BT) e^{-x} \, dx = \bar{v} \sigma.$$  \hspace{1cm} (12.38)

This shows that if $\sigma(E)$ is constant, then $k(T) \propto \bar{v} \propto \sqrt{T}$. Eq. (12.30) shows that if $\sigma(E) \propto v^{-1} \propto E^{-\frac{1}{2}}$ then $k(T)$ is a constant. Below we will see that these two cases apply to elastic and inelastic collisions at low temperatures, respectively.

#### 12.2.4 Isotropic Interactions

In capture theory we assume that cross sections are completely determined by long range attractive interactions between particles.* Collisions with zero impact parameter $b = 0$ are assumed to be reactive, with unit reaction probability. For non-zero impact parameters, $b > 0$, the system has non-zero angular momentum $|\ell| = \mu b$ and the effective potential given by Eq. (12.16) contains a repulsive centrifugal term, which may give rise to a centrifugal barrier. It is assumed that trajectories contribute to the cross section if, and only if, they pass over this centrifugal barrier. In many cases the long range interaction is well described by the leading term of the potential when expanded in powers of $1/r$ (see Study Box 12.2). By assuming a long range interaction of the form

$$V_a(r) = -\frac{C_a}{r^a},$$
\hspace{1cm} (12.39)

where $C_a > 0$ is called the long range coefficient, we derive analytic formulas for cross sections and reaction rates in the capture model. We give the derivation only for $n > 2$. For $n = 2$ it is actually easier, and we leave this as an exercise for the reader. We do not consider $n = 1$, i.e., ion-ion collisions. First, we find the maximum in the effective potential by solving

$$\frac{d}{dr} V_{eff}(r) = -|\ell|^2 \mu b + nC_a \mu b^2 = 0.$$  \hspace{1cm} (12.40)

The solution $r = r_0$ is

$$r_0 = \left( \frac{nC_a \mu b^2}{|\ell|^2} \right)^{1/(n-2)}.$$  \hspace{1cm} (12.41)

*It might be helpful to reread Section 1.4.3 at this point. See also ref. [823], particularly Chapter 4, page 175, for a recent general reference to much of the material covered in this section.*
STUDY BOX 12.2: LONG RANGE INTERACTION POTENTIALS

As we will see, in order to apply capture models it is necessary to know the form of the long range interaction potential. Generally, one can write the radial dependence of the long range potential between two particles as a sum of dipole, quadrupole, octapole, etc. terms of the form

\[ V(r) = - \sum_{n} c_n r^n, \]  

(B12.2.1)

where \( c_n \) is a constant depending on the charges \( q_1 \) and \( q_2 \), dipole moments \( \mu_1 \) and \( \mu_2 \), polarizabilities \( \alpha_1 \) and \( \alpha_2 \), and ionization potentials \( I_1 \) and \( I_2 \) of the two interacting species, and \( n \) depends on the type of interaction. The terms discussed here arise from first- and second-order perturbation theory, with a multipole expansion for the Coulomb interaction operator (and without inclusion of relativistic effects). Specifically, for two multipoles, a 2\( l \)-pole and a 2\( l \)-pole, the electrostatic interaction varies with the power \( n = i + j + 1 \). In some cases, particular terms in the expansion will dominate over others at certain separations, and the expansion can be approximated by a single term.

Examples of interaction potentials between two particles are given in the following table, in which the polarizability volume \( \alpha' \) is defined as \( \alpha' = \alpha/4\pi a_0^3 \).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>( n )</th>
<th>( c_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ion-ion</td>
<td>1</td>
<td>( \frac{\mu_1 \mu_2}{4\pi a_0^3} )</td>
</tr>
<tr>
<td>ion-dipole</td>
<td>2</td>
<td>( \frac{\mu_1 \mu_2}{2\pi a_0} )</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>3</td>
<td>( \frac{\mu_1 \mu_2}{2\pi a_0} )</td>
</tr>
<tr>
<td>ion-induced dipole</td>
<td>4</td>
<td>( \frac{1}{32\pi a_0^3} )</td>
</tr>
<tr>
<td>dipole-induced dipole</td>
<td>6</td>
<td>( \frac{\mu_1 \mu_2}{4\pi a_0} )</td>
</tr>
<tr>
<td>induced dipole-dipole</td>
<td>6</td>
<td>( \frac{3\pi a_0^3}{16\pi a_0^3} )</td>
</tr>
</tbody>
</table>

Note that the dipole-dipole interaction is in general a function of the relative orientation of the two dipoles, as given in Section 12.2.5. If the dipoles are aligned parallel to each other the interaction reduces to the following

\[ V(r) = -\frac{\mu_1 \mu_2}{2\pi a_0^3} P_2(\cos \theta), \]  

(B12.2.2)

where \( \theta \) defines the direction of the dipoles with respect to the vector \( r \) joining the two dipoles, and the second Legendre polynomial is defined as \( P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1) \). The dipole-dipole interaction given in the table is that for two dipoles fixed parallel to one another, in a linear configuration (\( \theta = 0 \)), such that \( P_2(\cos \theta) = 1 \). The various induced-dipole interactions listed in the table represent averages over orientation angle. The induced dipole-induced dipole interaction is more commonly known as the dispersion or London interaction, and unlike the other interactions is purely quantum mechanical in origin, arising from the interactions between instantaneous or induced dipoles on the two particles. The dispersion interaction is only approximately given by the expressions given in the above table.

A realistic intermolecular potential has a long range attractive component, encompassing the above interactions, and a short range component arising from the overlap and subsequent bonding antibonding interactions between partially or completely filled atomic and molecular orbitals. To obtain the precise form of this shorter range region of the potential requires detailed calculation using the techniques discussed in Chapter 2.

For the centrifugal barrier \( V_{\text{eff}}(r_0) \) we find, after factorization,

\[ V_{\text{eff}}(r_0) = \frac{|\ell|^2}{2\mu r_0^2} - \frac{\alpha_0}{r_0^2} \left( \frac{|\ell|^2}{\mu} \right)^{n/2} \frac{n-2}{2n} \left( \frac{\alpha_0}{r_0^2} \right)^{-n/2}, \]  

(12.42)

Trajectories are reactive when \( V_{\text{eff}}(r_0) \leq E \). This results in a maximum value for \( |\ell| \):

\[ |\ell_{\text{max}}|^2 = \mu n (\alpha_0)^{2/n} \left( \frac{2E}{n-2} \right)^{2/n}, \]  

(12.43)

a corresponding maximum impact parameter

\[ b_{\text{max}} = \frac{|\ell_{\text{max}}|}{\mu}, \]  

(12.44)

a cross section (assuming \( F(b,E) = 1 \))

\[ \sigma(E) = \pi b_{\text{max}}^2 = \frac{2\pi}{2} \left( \frac{n-2}{n} \right)^{2/n} \left( \frac{\alpha_0}{E} \right)^{2/n}, \]  

(12.45)

and a rate

\[ k(T) = \sqrt{\frac{2\pi}{\mu n}} \left( \frac{2}{n-2} \right)^{(n-2)/2n} \left( \alpha_0 \right)^{2/n} (k_B T)^{n/2} \Gamma(2 - \frac{n}{2}), \]  

(12.46)

where the Gamma function is defined by

\[ \Gamma(n) = \int_0^\infty x^{n-1} e^{-x} \, dx. \]  

(12.47)

The Gamma function has the special value \( \Gamma(1/2) = \sqrt{\pi} \), and it satisfies the recurrence relation \( \Gamma(n+1) = n \Gamma(n) \), so we also have \( \Gamma(3/2) = \sqrt{\pi} \). For integer values \( \Gamma(n+1) = n! \).

The position of the centrifugal barrier at collision energy \( E \) is found by substituting Eq. (12.43) into Eq. (12.41),

\[ r_0 = \left( \frac{n-2}{n} \right)^{1/n} \frac{\alpha_0}{2E}. \]  

(12.48)

For this to be valid, the potential for \( r > r_0 \) must be given to a good approximation by the leading long range term \( V_{\text{eff}}(r) \). The classical capture theory cross sections and rate constants for different values of \( n \) are given in Table 12.1.
Table 12.1 Classical capture theory energy dependent cross sections $\sigma_c(E)$ and temperature dependent reaction rates $k_r(T)$ for $-c_4/r^2$ long range potentials.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\sigma_c(E)$</th>
<th>$k_r(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\pi c_4/E$</td>
<td>$2\sqrt{2}c_4/(k_BT)^{1/2}$</td>
</tr>
<tr>
<td>3</td>
<td>$3\pi(5/2E)^{1/3}$</td>
<td>$4\sqrt{2}(1/3)(5/2)(k_BT)^{-1/6}$</td>
</tr>
<tr>
<td>4</td>
<td>$2\pi \sqrt{c_4/E}$</td>
<td>$2\pi \sqrt{2\pi}$</td>
</tr>
<tr>
<td>5</td>
<td>$3\pi(5/2)^{1/3}(c_4/E)^{1/3}$</td>
<td>$3\sqrt{2}(3/5)(5/2)^{1/5}(c_4/E)^{1/3}(k_BT)^{-1/6}$</td>
</tr>
<tr>
<td>6</td>
<td>$3\pi(1/2)^{1/3}(c_4/E)^{1/3}$</td>
<td>$3\sqrt{2}(1/2)^{1/3}(c_4/E)^{1/3}(k_BT)^{1/6}$</td>
</tr>
</tbody>
</table>

Capture theory was first developed in 1905 by Langevin, who used it to study reactions between ions and polarizable atoms. In that case the interaction is proportional to $r^{-5}$ and the long range coefficient is given by (see Study Box 12.2)

$$c_4 = \frac{1}{4\pi n_0^2}$$ (12.49)

where $q$ is the charge of the ion, and $a$ is the polarizability of the atom. Substituting $c_4$ into the capture rate coefficient (see table 12.1) gives

$$k_{\text{Langevin}}(T) = \frac{2nq}{4\pi n_0^2} \frac{\sqrt{a}}{\mu}$$ (12.50)

Note that this Langevin rate is independent of the temperature.

The expression for the rate for $n = 6$ was first given by E. Gorin in 1939. This is relevant to the case when there are no electrostatic interactions between the two atoms or molecules (i.e. when there are no permanent charges or dipoles on the particles involved). As shown in Study Box 12.2, the leading long range term is then proportional to $r^{-6}$.

12.2.5 Anisotropic Interactions

The first order electrostatic interaction between two neutral molecules with a non-zero dipole moment is proportional to $r^{-3}$ (see Study Box 12.2). However, we cannot use the $k_c(T)$ capture rate formula directly in this case, because the interaction depends on the orientation of the molecules. For some orientations the interaction will be attractive, but for other orientations the interaction will be repulsive. To be precise, the interaction potential is given by

$$V(r, \theta_1, \phi_1, \theta_2, \phi_2) = -\frac{\mu_1 \mu_2}{4\pi \epsilon_0 r^2} [2\cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)]$$ (12.51)

where $r$ is the distance between the centers of mass of the molecules, $\mu_1$ and $\mu_2$ are the magnitudes of the dipole moments of the molecules, and $(\theta_1, \phi_1)$ and $(\theta_2, \phi_2)$ are the spherical polar angles defining the orientations of the dipole vectors of the molecules in a dimer fixed frame, i.e. a frame in which the

*Note that for parallel dipoles, $\phi_1 - \phi_2 = 0$ and $\theta_1 = \theta_2$, and Eq. (12.51) reduces to Eq. (B12.2.2) of Study Box 12.2.

*Note that, as elsewhere in this text, we reserve the symbol $\ell$ for the orbital angular momentum quantum number.

12.3 QUANTUM CAPTURE THEORY

So far, our treatment has been completely classical. Quantum mechanics requires several modifications of the model. First of all, in quantum mechanics angular momenta are quantized, and, in particular, the magnitude of the orbital angular momentum becomes $|\ell| = h\sqrt{\ell(\ell + 1)}$, where $\ell$ is a non-negative integer. The wave functions corresponding to different values of the quantum number $\ell$ are referred to as partial waves. The classical expression $|\ell| = \mu \nu b$ [Eq. (12.20)] shows that for a fixed value of $|\ell|$, the impact parameter $b$ goes to infinity when the velocity $v$ goes to zero. This suggests that when the temperature approaches zero, only the $\ell = 0$ partial wave can contribute to cross sections, and that, in general, at lower temperatures fewer partial waves contribute than at higher temperatures.

When the interaction potential is anisotropic, which is usually the case in collisions involving molecules, we must also treat rotation of the colliding fragments. Since the rotational constants of the colliding molecules may be much larger than the rotational constant of the resulting collision complex, quantization of the rotation of the molecules may be important at higher temperatures where many partial waves still contribute to the cross sections. This is particularly true in molecular scattering experiments, in which the colliding molecules are cooled to the lowest rotational states, while the CM collision energy may still be high.

In the classical capture theory outlined above, trajectories are assumed reactive when the energy is above the centrifugal barrier, and nonreactive otherwise. In quantum mechanics, tunnelling may lead to reaction at energies below the barrier, while reflection may occur even if the energy is above the barrier.

To derive quantum capture theory, we start with the exact quantum mechanical expression for the energy dependent state-to-state differential cross section. This gives the most detailed information about a collision event.
12.3.1 Quantum Scattering Theory

If there is no interaction between the two particles, the wave function may be written as a plane wave. We denote the quantum numbers describing the states of the particles collectively by $|n\rangle$. As an example, for a system consisting of two diatomic molecules in a certain vibrational state we have $|n\rangle = |v_n, m_n, v_b, m_b\rangle$, where $v_n$ and $v_b$ are the vibrational quantum numbers, and $m_n$ and $m_b$ are the projections of the angular momenta onto a space fixed axis. A flux normalized plane wave with wave vector $k = h_{\mathcal{F}}\hat{k}$ is given by

$$\Psi_{\mathcal{F}}^{\text{in}} = |n\rangle v_n^{-\frac{1}{2}} e^{i k_{\mathcal{F}} \cdot r} = |n\rangle v_n^{-\frac{1}{2}} \sum_{\ell} (2\ell + 1) j_{\ell}(k_{\mathcal{F}} r) P_{\ell}(\hat{k} \cdot \hat{r}),$$

(12.53)

where $P_{\ell}$ is a Legendre polynomial and $j_{\ell}$ a spherical Bessel function of the first kind, and the velocities $v_n$ are given by $v_n = \hbar k_n/\mu$, with $\mu$ the reduced mass. Using the spherical harmonic addition theorem [239],

$$P_{\ell}(\hat{k} \cdot \hat{r}) = \frac{4\pi}{2\ell + 1} \sum_{m_- = -\ell}^{\ell} Y_{\ell m_-}(\hat{r}) Y_{\ell m_+}(\hat{k}),$$

(12.54)

and the asymptotic form of the spherical Bessel function

$$j_{\ell}(z) \approx \sin(z - \ell\pi/2)/z = e^{i (\ell\pi/2) - e^{-i (\ell\pi/2)/2}},$$

(12.55)

the plane wave may be written, for large $r$, as

$$\Psi_{\mathcal{F}}^{\text{in}} \approx \frac{2\pi}{i k_{\mathcal{F}}^n} \sum_{\ell m_\ell} |n\rangle v_n^{-\frac{1}{2}} Y_{\ell m_-}(\hat{r}) \left[ e^{i (\ell\pi/2) - e^{-i (\ell\pi/2)/2}} \right] f_{\ell} Y_{\ell m_+}(\hat{k}).$$

(12.56)

The effect of switching on the interaction is to modify the outgoing wave form, so asymptotically the scattering wave function can be written as

$$\Psi_{\mathcal{F}}^{\text{out}} \approx \frac{2\pi}{i k_{\mathcal{F}}^n} \sum_{\ell m_\ell} \sum_{\ell' m_\ell'} |n\rangle v_n^{-\frac{1}{2}} Y_{\ell m_-}(\hat{r}) \left[ e^{i (\ell\pi/2) - e^{-i (\ell\pi/2)/2}} \right] f_{\ell} Y_{\ell m_+}(\hat{k}) + \sum_{n'} |n'\rangle v_{n'}^{-\frac{1}{2}} f_{n'} T_{\ell m_\ell m_\ell'} Y_{\ell m_+}(\hat{k}),$$

(12.57)

where $T_{\ell m_\ell m_\ell'}$ are the scattering matrix (or $S$-matrix) elements, introduced in Chapter 3 and discussed further below. Solving the time-independent scattering problem amounts to finding solutions of the Schrödinger equation that satisfy the so-called $S$-matrix boundary conditions for large $r$,

$$\Psi_{\mathcal{F}}^{\text{out}} = \frac{1}{r} \sum_{\ell m_\ell} |n\rangle v_n^{-\frac{1}{2}} Y_{\ell m_-}(\hat{r}) \left[ e^{-i (\ell\pi/2) - e^{i (\ell\pi/2)/2}} \right] S_{\ell m_\ell m_\ell'} Y_{\ell m_+}(\hat{k}).$$

(12.58)

As noted above, it is these individual solutions that are referred to as partial waves. The $S$-matrix is a complex symmetric unitary matrix. When the potential is zero, the $S$-matrix is a unit matrix, $S_{\ell' m_\ell' m_\ell m_\ell} = \delta_{\ell' \ell} \delta_{m_\ell' m_\ell} \delta_{m_\ell' m_\ell}$, and the partial waves add up to a plane wave again. The $S$-matrix is related to the $T$-matrix through $S = I - T$, where $I$ is a unit matrix.

As discussed in Chapter 3, the scattering wave function of Eq. (12.57) may be reorganized into an incoming plane wave plus an outgoing spherical wave, as illustrated in Figure 12.5,

$$\Psi_{\mathcal{F}}^{\text{in}} \approx |n\rangle v_n^{-\frac{1}{2}} e^{i k_{\mathcal{F}} \cdot r} + \sum_{n'} |n'\rangle v_{n'}^{-\frac{1}{2}} f_{n' \rightarrow n} T_{\ell m_\ell m_\ell'} Y_{\ell m_+}(\hat{k}),$$

(12.59)

where the so-called scattering amplitude, introduced in Chapter 3, is given by

$$f_{\ell' \rightarrow \ell}(r, \hat{k}) = \frac{2\pi}{i k_{\mathcal{F}}^n} \sum_{m_- m_+} f_{\ell' m_- \ell m_+} T_{\ell m_\ell m_\ell'} Y_{\ell m_+}(\hat{k}).$$

(12.60)

The notation with the arrow is used because initial and final quantum numbers should not be interchanged, i.e. $f_{\ell' \rightarrow \ell} \neq f_{\ell \rightarrow \ell'}$. The state-to-state differential cross section for a particular incident direction $\hat{k}$ is given by

$$\sigma_{\ell' \rightarrow \ell}(r, \hat{k}) = |f_{\ell' \rightarrow \ell}(r, \hat{k})|^2.$$  

(12.61)

The state-to-state integral cross section for a particular incident direction is given by

$$\sigma_{\ell' \rightarrow \ell}(\hat{k}) = \int \sigma_{\ell' \rightarrow \ell}(r, \hat{k}) dr.$$  

(12.62)

*Note that Eq. (12.61) is essentially the same as that given in Eq. (3.45), apart from notation.
Assuming that the incident directions are isotropically distributed, such as they would be in a bulk gaseous sample, the state-to-state integral cross section is obtained by taking an average over all incoming directions $\hat{k}$
\[
\sigma_{\ell'=n} = \frac{1}{4\pi} \int \sigma_{\ell'-n}(\hat{k}) \, d\hat{k} = \frac{\pi}{k_n^2} \sum_{m'c} |T_{\ell'\ell m'c} e^{-i\theta_{\ell'\ell m'c}}|^2 = \frac{\pi}{k_n^2} P_{\ell'\ell n'}
\]
(12.63)
where we have introduced the reaction probability matrix $P$ in the last step. So far, the formalism applies to inelastic scattering. To extend it to reactive scattering we only have to include an arrangement label $\gamma$ to the quantum numbers $n$ that describe the molecules. This modification is sufficient as long as three-body breakup cannot occur.

### 12.3.2 Connection with Classical Capture Theory

The diagonal elements of the $T$-matrix determine the elastic scattering cross sections and the off-diagonal elements determine the inelastic and reactive cross sections. The off-diagonal elements of the $T$-matrix are equal to the off-diagonal elements of the $S$-matrix. The $S$-matrix is unitary, so the sum of the squares of the absolute values of all elements of a given column is equal to one. Hence, the sum over $\ell'$, $m'_c$ in Eq. (12.63), excluding the diagonal element, gives at most one for each column. This is still true if we sum over all possible reaction products $n'$. Thus, the maximum contribution of the partial wave with a given $\ell$ to the inelastic or reactive cross section for some initial state $|n\rangle$ is given by
\[
\sigma_{\ell'\ell n}^{\text{max}} = \frac{\pi}{k_n^2} (2\ell + 1),
\]
(12.64)
where $k_n$ is the wavenumber for channel $n$, and the factor $(2\ell + 1)$ arises from the summation over $m'$. Assuming that all partial waves up to some maximum value $\ell_{\text{max}}$ are fully reactive and higher partial waves are nonreactive, we obtain an initial state selected cross section
\[
\sigma_{\ell} = \sum_{\ell' n} \sigma_{\ell'\ell n}^{\text{max}} = \frac{\pi}{k_n^2} (\ell_{\text{max}} + 1)^2,
\]
(12.65)
where we have used the fact that $\Sigma_{\ell=0}^{\ell_{\text{max}}} = n(n+1)/2$. To compare this result to the classical expression $\mu b_{\ell_{\text{max}}}^2$, given in Eq. (12.27), we associate the classical angular momentum squared $(\ell^2 \ell_{\text{max}} + 1)$ with $h^2 \ell_{\text{max}} (\ell_{\text{max}} + 1)$. Using Eq. (12.26) this gives
\[
b_{\ell_{\text{max}}}^2 = \frac{h^2 \ell_{\text{max}} (\ell_{\text{max}} + 1)}{\mu v^2},
\]
(12.66)
and with $\mu v = p = \hbar k_n$ we obtain
\[
\sigma = \pi b_{\ell_{\text{max}}}^2 = \frac{\pi}{k_n^2} (\ell_{\text{max}} + 1).
\]
(12.67)
One expects the classical theory only to work when a sufficient number of partial waves contribute, in which case $\ell_{\text{max}} (\ell_{\text{max}} + 1) \gg (\ell_{\text{max}} + 1)^2$.

### 12.3.3 Coupled Channels Capture Theory

In quantum capture theory it is assumed that the capture cross sections can be found by solving the Schrödinger equation in a restricted region of the potential energy surface that is located entirely in the reactant arrangement. The computation then becomes very similar to a coupled channels calculation for inelastic scattering, discussed in Chapter 3. The only difference lies in the boundary conditions at small internuclear separations $r$. The wave function is not assumed to be finite, but the flux is assumed to be inwards (towards small $r$) at some point $r = r_c$. Here we will not derive the coupled channels equation, but only summarize the main results and give the capture theory boundary conditions.

In the coupled channels approach (see also Chapter 3, Section 3.3.4.2, the Hamiltonian is written as the sum of the radial kinetic energy operator and the remainder $(\Delta \hat{H})$,
\[
\hat{H} = \frac{\hbar^2}{2\mu} r^{-1} \frac{d^2}{dr^2} r + \Delta \hat{H}
\]
(12.68)
and the Schrödinger equation in the reactant arrangement is written as
\[
\frac{\hbar^2}{2\mu} r^{-1} \frac{d^2}{dr^2} r \Psi = (\Delta \hat{H} - E) \Psi.
\]
(12.69)
The wave function is expanded in channel functions $|n\rangle$,
\[
\Psi = r^{-1} \sum_{n'} |n'\rangle U_{n'n}(r),
\]
(12.70)
where each column of the coefficient matrix $U(r)$ defines a wave function. To simplify the notation, we assume that the partial wave quantum numbers $\ell$ and $m_c$ are included in $n$. By substituting the expansion into the Schrödinger equation and projecting onto the channel eigenfunctions, a set of coupled second order differential equations for the expansion coefficients is found:
\[
U''(r) = W'(r)U(r),
\]
(12.71)
where the primes denote derivatives with respect to $r$. The coupling matrix is given by
\[
W_{n'n}(r) = \frac{2\mu}{\hbar^2} \langle n'|\Delta \hat{H} - E|n\rangle.
\]
(12.72)
In an inelastic scattering problem the condition that the wave function is finite gives the boundary condition that $U(r = 0) = 0$. As we have seen in Chapter 3, Section 3.3.4.3, this boundary condition, together with the coupled channels equation (12.71), defines a linear relation between the expansion coefficients and their derivatives with respect to $r$,
\[
U'(r) = Y(r)U(r),
\]
(12.73)
where $Y(r)$ is called the log-derivative matrix. In the capture problem, the boundary condition is that at some small value of $r$, inside the centrifugal barrier, the flux can only be inwards. For a one-dimensional single channel problem with $\Delta H = V(r)$, this means that around some point $r = r_c$ the

*Note that apart from notation this equation is the same as Eq. (3.56) of Chapter 3.
wave function has the simple travelling wave form $e^{ikr}$, where \( k \) is the wave number at \( r = r_a \), i.e.

\[
\frac{\hbar^2 k^2}{2\mu} = E - V(r_a),
\]

and the boundary condition for the \((1 \times 1)\) log-derivative matrix is \( Y(r_a) = U(r_a)/U(r_a) = -ik \). To define the boundary conditions in the multichannel case, the coupling matrix \( W(r_a) \) is diagonalized to obtain a set of uncoupled one-dimensional problems,

\[
W(r_a) Q(r_a) = \mathcal{A}(r_a) Q(r_a),
\]

where \( \mathcal{A}(r_a) \) is a diagonal matrix of eigenvalues, and the columns of the matrix \( Q(r_a) \) are the eigenvectors of the matrix \( W(r_a) \). The negative eigenvalues correspond to open channel eigenfunctions, with \( \lambda_{-\infty} = -\hbar^2 k^2 \) and the positive eigenvalues correspond to closed channel eigenfunctions with \( \lambda_{+\infty} = \hbar^2 k^2 \). Transforming the coupled channels problem to the channel eigenfunction basis with

\[
U(r) = Q(r_a) U(r),
\]

gives

\[
\tilde{U}'(r) = \mathcal{Q}'(r_a) W(r) \mathcal{Q}(r_a) \tilde{U}(r) \approx \mathcal{A}(r_a) \tilde{U}(r).
\]

The approximation of assuming that the \( W(r) \) matrix is constant around \( r_a \) results in a set of one-dimensional problems, and the matrix \( \tilde{U}(r) \) becomes diagonal. The inward flux boundary conditions for open channel eigenfunctions are now given by

\[
\tilde{U}_{-\infty}(r) = e^{-ikr},
\]

and the boundary conditions for closed channels are

\[
\tilde{U}_{+\infty}(r) = e^{ikr}.
\]

The log-derivative matrix in the channel eigenfunction basis is also diagonal at \( r = r_a \), and the boundary conditions are given by

\[
\mathcal{Y}_{-\infty}(r_a) = \mathcal{Q}'(r_a) \mathcal{Y}(r_a) \mathcal{Q}(r_a) \approx \left\{ \begin{array}{ll} -ik_r & \text{for open channels,} \\ k_r & \text{for closed channels.} \end{array} \right.
\]

Since the matrix \( \mathcal{Q} \) with eigenvectors is unitary, the boundary conditions for the log-derivative matrix in the original basis are given by

\[
Y(r_a) = Q(r_a) \mathcal{Y}(r_a) Q(r_a) = \mathcal{Q}'(r_a) Y'(r_a) Q(r_a).
\]

The boundary conditions of Eqs. (12.78) and (12.79) apply if the channel eigenvalues \( \mathcal{A}(r) \) are approximately constant around \( r = r_a \). Sometimes it is better to approximate the channel eigenvalues by a linear function of \( r \). For that case the boundary conditions can be found in ref. [828].

The general technique for propagating the log-derivative matrix to some point \( r = r_a \) far outside the centrifugal barrier relies on dividing \([r_a, r_b]\) into a set of small sectors \([r_a, r_{a+1}]\).

In each sector one determines a so-called embedding type propagator defined by

\[
\begin{bmatrix}
U_r' \\
U_{r+1}'
\end{bmatrix} =
\begin{bmatrix}
\mathcal{Y}_r^{(0)} & \mathcal{Y}_r^{(0)}
\end{bmatrix}
\begin{bmatrix}
-iU_r \\
U_{r+1}
\end{bmatrix},
\]

where \( U_r = U(r_r) \). The minus sign in the definition is not essential, but with this choice one can show that \( \mathcal{Y}_r^{(1)} = \mathcal{Y}_r^{(0)} \). To find the propagator one can diagonalize the \( W(r) \) matrix in the middle of the sector and assume it to be constant, which results in a set of uncoupled one-dimensional problems, as above. For the one-dimensional problems the propagator can be found analytically, and the result can be transformed back to the original basis. More accurate propagators have been developed, which, e.g., assume the eigenvalues of the \( W(r) \) matrix to change linearly over the interval, and correct for non-zero coupling with a Green's function technique. Once the sector propagator is found it can be used to propagate the log-derivative matrix at \( r = r_a \) defined by

\[
U_r' = Y(r_r) U_r,
\]

to \( r_{a+1} \):

\[
Y(r_{a+1}) = \mathcal{Y}_r^{(0)} - \mathcal{Y}_r^{(0)} \left[ Y(r_r) + \mathcal{Y}_r^{(0)^{-1}} Y_r^{(0)} \right] Y_r^{(0)}.
\]

In this way, the log-derivative matrix can be propagated to \( r = r_b \). For sufficiently large \( r \) the \( S \)-matrix boundary conditions for \( U(r) \) are given by [cf. Eq. (12.69)]

\[
U(r) = -I(r) + O(r)S,
\]

where \( I(r) \) is a diagonal matrix with flux normalized incoming waves

\[
I_{\text{in}}(r) = \begin{bmatrix} v_{\text{in}} e^{-ikr_{\text{in}} - \frac{\phi}{2}} \end{bmatrix},
\]

and \( O(r) = I(r)^* \) are the outgoing waves. By substituting the asymptotic form of the wave function into the defining relation of the log-derivative matrix [Eq. (12.73)] we can relate the \( S \)-matrix to the log-derivative matrix

\[
S(E) = [Y(r_b)O(r_b) - O'(r_b)]^{-1} Y(r_b) I(r_b) - I'(r_b).
\]

Because of the complex boundary conditions at \( r = r_a \), the \( S \)-matrix is not unitary and the capture probability for a given incoming channel can be found by

\[
P_{\text{out}}(E) = 1 - \sum_{n \neq \text{out}} |S_{n \text{out}}(E)|^2,
\]

where we have written the partial wave quantum numbers explicitly again for clarity. The capture cross section for incoming channel \( n \) is found as

\[
\sigma_n(E) = \frac{\pi}{k_n^2} \sum_{\text{out}} P_{\text{out}}(E).
\]

Note that this capture approximation provides initial state selected cross sections only and information about the product state distribution is lost. A model exists for complex-forming reactions in
which capture theory ideas are used in reactant as well as product arrangements. Together with a statistical model to describe the complex, this provides partial information about the product state distribution.\(^{328}\)

12.3.4 Quantum Adiabatic Capture Theory

At low temperatures the collision time is long compared with the characteristic vibrational and rotational timescales of the colliding molecules. This allows us to introduce an approximation analogous to the Born-Oppenheimer approximation, which exploits the difference in time scales of electronic and nuclear motion, and simplifies the dynamical calculation. Solving the Schrödinger equation for the fast motion amounts to diagonalizing the \(W(r)\) matrix on a grid of \(r\) points, as in Eq. (12.75), and treating the eigenvalues \(\lambda_n(r)\) as uncoupled one-dimensional potentials (multiplied by a factor of \(2\mu/k_B^2\)). These potentials will asymptotically correlate with molecular states. For each molecular state asymptotically allowed at an energy \(E\), the capture probability is computed by solving the one-dimensional quantum capture problem. This calculation is done exactly as the coupled channels equation, except that all matrices become scalars, and the propagators and log-derivative matrices in the eigenfunction basis are never transformed back to the original basis. The result is again a capture probability for each initial state \(n\), and the capture cross section is obtained as in Eq. (12.89).

Often, the result of this approximation is in good agreement with full coupled channels capture theory.\(^{304,329,330}\) When the coupling between different rotational states is strong, the initial state selected capture rates may not be very good. However, often one is only interested in the Maxwell-Boltzmann average of the capture rates over all initial states, in the case of thermal equilibrium. These thermally averaged rates will still be good, even for strong rotational coupling.

In the next section we show that the thermal capture rate only depends on the cumulative capture rate at a given total energy. We derive an expression for the thermal rate coefficient in terms of the cumulative reaction probability, \(N(E)\), introduced in Section 7.5.1.*

12.3.5 Thermal Capture Rates

For an initial state \(|n\) with channel energy (i.e. internal energy) \(e_n\) and kinetic energy \(E_{\text{kin}}\) the total energy is

\[
E = e_n + E_{\text{kin}} = e_n + \frac{\hbar^2 k_n^2}{2\mu}.
\]  

(12.90)

In time-independent scattering theory one computes the state-to-state cross section as a function of the total energy [Eq. (12.63)],

\[
\sigma_{s'\rightarrow s}(E) = \frac{\pi}{k_n^2} P_{s'n}(E).
\]  

(12.91)

The state-to-state temperature dependent reaction rate is given by [Eq. (12.37)]

\[
k_{s'\rightarrow s}(T) = \sqrt{\frac{8\pi k_B}{\mu}} \frac{1}{k_B T} \int_0^\infty \sigma_{s'\rightarrow s}(E)e^{-E_{\text{kin}}/k_B T} e^\frac{-e_n}{k_B T} E_{\text{kin}} dE_{\text{kin}}.
\]  

(12.92)

*An alternative derivation of the expression given here for \(k(T)\), and an introductory discussion about \(N(E)\), can be found in ref. [10].

Sometimes, only the Boltzmann averaged reaction rate is required,

\[
k(T) = Q^{-1}(T) \sum_{n' n} k_{n'\rightarrow n}(T)e^{-e_n/\beta k_B T},
\]  

(12.93)

where the internal partition function is given by

\[
Q_{\text{int}}(T) = \sum_n e^{-e_n/\beta k_B T}.
\]  

(12.94)

By substituting Eq. (12.92) into Eq. (12.93) and changing the order of integration and summation, one obtains a much simplified expression

\[
k(T) = \frac{1}{2\pi \hbar Q_{\text{int}}} \int_{-\infty}^\infty N(E) e^{-E_{\text{kin}}/\beta k_B T} dE,
\]  

(12.95)

where the translational partition function per volume is given by

\[
Q_{\text{trans}} = \frac{1}{\hbar^2} \left( \frac{\mu k_B T}{2\pi} \right)^{3/2},
\]  

(12.96)

and the cumulative reaction probability \(N(E)\) is defined as the sum of the reaction probabilities over all open reactant and product states

\[
N(E) = \sum_{n' n} P_{s'n}(E).
\]  

(12.97)

When there are no open channels at a given total energy, \(N(E)\) is set to zero, so the range of integration can be taken from \(-\infty\) to \(+\infty\) in Eq. (12.95). Since \(N(E)\) depends on the unweighted sum over initial states, one sees that an approximation that does not properly describe the mixing of initial states may still produce an accurate thermal rate. In particular, this explains why adiabatic capture theory may be much more accurate for the thermal capture rate than for initial state selected rates.

12.3.6 Total Angular Momentum Representation

When no external fields are present, both the collision complex and its Hamiltonian are invariant under overall rotation. This invariance gives rise to total angular momentum conservation. This symmetry can be exploited by using the total angular momentum representation for the wave function. In Section 12.3.1 we employed an uncoupled angular momentum basis for two colliding molecules. For an atom-diatom system the uncoupled rotational basis is \(|jm_j \ell m_\ell\rangle\), where \(|jm_j\rangle\) is the rotational wave function of the molecule and \(|\ell m_\ell\rangle\) is the orbital angular momentum of the collision partners. The coupled angular momentum basis is defined by

\[
|jm_j \ell m_\ell \rangle = \sum_{j' \ell' m'_{\ell'}} |jm_{j'} \ell m_{\ell'} \rangle |jm_{j'}, \ell m_{\ell'} \rangle, \quad (12.98)
\]

where \(|jm_{j'}, \ell m_{\ell'} \rangle\) is a Clebsch-Gordan coefficient.\(^{329}\) The coupled states are eigenfunctions of the square of the total angular momentum operator for the system (\(\hat{J}\)) and of its space-fixed
z-component $J_z$. The total angular momentum quantum number $J$ can take the values $|J-J_z|$, $|J-J_z|+1$, ..., $J+J_z$, and the projection quantum number $M_J$ can take the values $-J$, ..., $-J+1$, ..., $J$. For a given $j$ and $\ell$ there are as many coupled basis functions as uncoupled ones

$$\sum_{j=|J-J_z|}^{J+J_z} (2j+1) = (2j+1)(2\ell+1),$$

(12.99)

and the coupled basis functions are orthonormal, i.e. the Clebsch-Gordan coefficients are elements of a unitary transformation. When a scattering wave function is written in the coupled basis, the $S$-matrix is related to the $S$-matrix in the uncoupled basis through

$$S_{ef'\ell'\ell''j'}^{M_{f'}M_{e'j}} = \sum_{M_{f},M_{e}} \langle f M_{f'}|m_{f}\ell_{f}m_{f}\rangle S_{ef\ell\ell j}^{M_fM_e} \langle m_{e}\ell_{e}m_{e}|j\rangle \langle jM_J|\ell'\ell'\ell''j'\rangle.$$  

(12.100)

When the system has cylindrical symmetry, i.e. when there is no external field, or when an external field is applied parallel to the space-fixed z-axis, the projection of the total angular momentum on the z-axis is conserved, i.e. $M_{f'} = m_{f} + m_{f'} = M_{f'}$, and the $S$-matrix elements are zero when $M_{f'} \neq M_{f}$. When the system has spherical symmetry, i.e. there are no external fields, then $J$ is also a good quantum number, and the $S$-matrix is independent of $M_{f}$,

$$S_{ef'\ell'\ell''j'}^{M_{f'}M_{e'j}} = \delta_{M_{f}M_{f'}} \delta_{\ell_{f}\ell_{f'}} \delta_{\ell_{e}\ell_{e'}} \delta_{j'j},$$

(12.101)

and Eq. (12.100) may be inverted to give

$$S_{ef\ell\ell j}^{M_{f}M_{e}} = \sum_{M_{f'}} \langle f M_{f'}|m_{f}\ell_{f}m_{f}\rangle S_{ef'\ell'\ell''j'}^{M_{f'}M_{e'j}} \langle m_{e}\ell_{e}m_{e}|j\rangle \langle jM_J|\ell'\ell'\ell''j'\rangle.$$  

(12.102)

The $T$-matrix satisfies an analogous relation, and hence, using the orthogonality relations of the Clebsch-Gordan coefficients, we may derive an expression for the sum of the reaction probabilities over all projection quantum numbers

$$\sum_{M_{f},M_{f'}} P_{ef\ell\ell j}^{M_{f}M_{e}} = \sum_{f} (2J+1) P_{ef'\ell'\ell''j'},$$

(12.103)

where the factor $(2J+1)$ is the result of summing over $M_{f'}$.

To construct a total angular momentum basis for two colliding molecules one must first couple the rotational wave functions of the molecules, $|j_{m_{f}}\rangle$ and $|j_{m_{e}}\rangle$ to give a coupled basis $|j_{m_{f}}j_{m_{e}}\rangle$, which in turn can be coupled with the end-over-end rotational function $|\ell m_{e}\rangle$ to obtain the total angular momentum basis functions $|\ell j_{m_{f}}j_{m_{e}}\rangle$.

For cold collisions in electrostatic or magnetic traps it may be important to include the external field in the calculation. In such cases it is advantageous to use the uncoupled representation; otherwise the coupled representation is more efficient.

12.4 WIGNER THRESHOLD LAWS

Even in the early days of quantum mechanics, solutions of the Schrödinger equation in the limit of low collision energies were analyzed and expressions were found for the energy-dependence of the collision cross section. For example, it was found that for potentials of finite range, i.e. potentials that are vanishingly small when the distance between collision partners is larger than some value $r_0$, the elastic cross section at low energy is dominated by s-wave scattering, i.e. by the contribution of the $\ell = 0$ partial wave, and the cross section is energy independent. The inelastic cross section is also dominated by the s-wave, but it increases as $E^{-1/3}$ when the collision energy $E \equiv E_{c}$ is sufficiently low. Here we will derive the general results obtained by Wigner in 1948. These results are known as the Wigner threshold laws.

12.4.1 Bouncing Off a Cliff

To demonstrate the difference between quantum mechanics and classical mechanics in the limit of low energies we consider the one-dimensional problem shown in Figure 12.6. The potential takes the values $V(x) = 0$ for $x < 0$ and $V(x) = V_0 < 0$ for $x \geq 0$. A classical particle with mass $\mu$ moving in the positive x-direction will have zero probability of reflection at $x = 0$ and unit probability of transmission.

In the quantum mechanical description, for $x < 0$ the wave function contains contributions from a unit flux incoming part and a reflected part,

$$\Psi_{I}(x) = v^{-1/2}(e^{ix} - Re^{-ikx}), \quad x < 0$$

(12.104)

and a contribution solely from a transmitted part for $x \geq 0$ from,

$$\Psi_{R}(x) = v^{-1/2}Te^{ikx}, \quad x \geq 0.$$  

(12.105)

![Figure 12.6](image-url)
The total energy is
\[ E = \frac{\hbar^2 k^2}{2\mu} = V_0 + \frac{\hbar^2 k_0^2}{2\mu}, \]  
(12.106)

with velocities to the left and right of the cliff \( v = \hbar k/\mu \) and \( v_0 = \hbar k_0/\mu \). Matching the wave functions \( \Psi_L(x) \) and \( \Psi_R(x) \) and their first derivatives at \( x = 0 \) gives
\[ T = \frac{2a}{a^2 + 1} \]  
(12.107)
\[ R = \frac{1 - \frac{a^2}{a^2 + 1}}{1}, \]  
(12.108)

where \( a = \sqrt{k/k_0} \) and \(|T|^2 + |R|^2 = 1\). Hence, in this one-dimensional problem, if \( k/k_0 \ll 1 \) the probability of transmission is proportional to \(|T|^2 \propto k \propto \sqrt{E}\) and the probability of reflection, \(|R|^2\), approaches unity when the energy \( E \) approaches zero. This quantum result is very different from the classical result, in which the probability of reflection is always zero. The quantum effect is sometimes referred to as quantum suppression, because unlike for a classical particle the transmission probability is not unit. The classical result is recovered in the high energy limit \( E \gg V_0, k \approx k_0, \) and \( a \approx 1\).

### 12.4.2 s-wave Elastic Scattering

Solutions of the quantum central force problem may be expanded in partial waves
\[ \Psi_{\ell m}(r) = r^{-1}u_\ell(r)Y_{\ell m}(\hat{r}), \]  
(12.109)

where \( u_\ell(r) \) describes the radial dependence of the wavefunction, and the spherical harmonic, \( Y_{\ell m}(\hat{r}) \), its angular dependence. For \( u_\ell(r) \), the so-called s-wave, the Schrödinger equation for the radial motion is
\[ \left[ \frac{\hbar^2}{2\mu} \frac{\alpha^2}{r^2} + V(r) - E \right] u_\ell(r) = 0, \]  
(12.110)

and the boundary condition at \( r = 0 \) is \( u_\ell(0) = 0 \). As before, we assume that the potential is negligible for \( r > r_0 \). The log-derivative matrix at \( r_0 \), defined by
\[ u'_\ell(r_0) = Y(r_0)u_\ell(r_0), \]  
(12.111)
is found by propagation from \( r = 0 \) to \( r = r_0 \). In this region, the kinetic energy
\[ E = \frac{\hbar^2 k_0^2}{2\mu}, \]  
(12.112)
is assumed to be so small compared to the potential \( V(r) \) that it may be neglected and \( Y(r_0) \) becomes energy independent. To find the energy dependence of the \( T \)-matrix we first determine the radial wave function with \( K \)-matrix boundary conditions, which is convenient because it uses real functions,
\[ u_\ell(r) = \sin(\ell r) - K \cos(\ell r), \text{ for } r > r_0. \]  
(12.113)

Consider this equation in conjunction with Eq. (12.109). Note that the term \( r^{-1} \sin(\ell r) \) is usually called the regular solution, since \( r^{-1} \sin(\ell r) \) is finite for \( r = 0 \), while \( r^{-1} \cos(\ell r) \) is called the irregular solution. We now assume that \( kr_0 \ll 1 \) so that we can replace \( \sin(\ell r) \) and \( \cos(\ell r) \) by the leading term in their Taylor expansion for \( r = r_0 \),
\[ u_\ell(r) \approx kr - K \]  
(12.114)
and
\[ u'_\ell(r) \approx k. \]  
(12.115)

Since we assume the log-derivative matrix at \( r = r_0 \) to be energy-independent, we find that the \( K \)-matrix must be proportional to \( k \),
\[ K \propto k \propto \sqrt{E}. \]  
(12.116)

The \( S \)-matrix is related to the \( K \)-matrix through (see Problem 2)
\[ S = (1 - ik)(1 + ik)^{-1}. \]  
(12.117)

For small \( K \) we have, to first order in \( K \)
\[ (1 + ik)^{-1} \approx 1 - iK + \ldots, \]  
(12.118)

so
\[ T = 1 - S \approx 1 - (1 - iK)^2 \approx 2iK. \]  
(12.119)

Hence, the \( T \)-matrix is also proportional to \( k \), and the elastic s-wave scattering cross section,
\[ \sigma(E) = \frac{\pi}{K^2} |T|^2, \]  
(12.120)
is energy independent for small \( E \).

### 12.4.3 Scattering Length

The boundary condition for scattering off a hard sphere with radius \( r_h \) is \( u_\ell(r_h) = 0 \), i.e. the particle cannot penetrate the sphere so the wavefunction is zero at its boundary. The wave function \( u_\ell(r) \) in Eq. (12.114) looks like the wave function corresponding to a hard-sphere problem, with radius \( r_h = K/k \). This motivates the definition of the scattering length \( a \) as
\[ a = \lim_{K \to 0} \frac{K}{k}. \]  
(12.121)

The scattering length may also be defined in terms of a quantity known as the phase shift, \( \delta \), which is related to the \( S \)-matrix by \( S = e^{i\delta} \), and represents the shift in phase of the wavefunction on scattering. For small phase shifts we have \( S \approx 1 + 2i\delta \) and \( K \approx -\delta \). With Eq. (12.120) and \( T \approx 2iK \), the elastic s-wave cross section in the limit of low energy is related to the scattering
length through

\[ \sigma = 4na^2. \]  
(12.122)

In the Born approximation, the total elastic cross section, in the case of an isotropic potential, is given by

\[ \sigma = \frac{\mu^2}{4\pi \hbar^2} \left| \int \int \int V(r)dr \right|^2. \]  
(12.123)

As we will see shortly, it is helpful to consider a \( \delta \)-function potential of the form

\[ V(r) = \frac{4na\hbar^2}{\mu} \delta(r), \]  
(12.124)

for which we have

\[ \sigma = \frac{\mu^2}{4\pi \hbar^2} \left| \frac{4na\hbar^2}{\mu} \right|^2 = 4na^2. \]  
(12.125)

The fact that this expression is the same as that given in Eq. (12.122) suggests that, to simplify the calculation of the properties of ultracold gases, one can often replace the actual potential by a \( \delta \)-function potential that gives the same scattering length and hence the same elastic cross section. Notice that a positive scattering length corresponds to an effectively repulsive interaction, and a negative scattering length to an effectively attractive interaction.

### 12.4.4 Inelastic Scattering at Low Energy

We will now consider the energy dependence of the cross section for an inelastic or reactive process when the kinetic energy in the incoming channel approaches zero. As above, we assume that the potential is negligible for \( r > r_0 \). Furthermore, we will consider all partial waves, and not limit ourselves to s-wave scattering. This is important since we may be interested in a process that changes the angular momentum of the colliding molecules. In the absence of external fields, the total angular momentum is conserved, so the incoming and outgoing partial waves cannot both be s-waves if the angular momentum of one of the species changes.

As in the one-channel elastic case, we will use \( K \)-matrix boundary conditions, which give real wave functions. The expansion of the wave function,

\[ \Psi_{el} = r^{-1} \sum_{n\ell} \chi_{\ell}(r) U_{n\ell} e_{el}(r), \]  
(12.126)

is similar to the expansion of the wave function with \( S \)-matrix boundary conditions, but instead of incoming and outgoing waves there are regular and irregular waves for large \( r \),

\[ U_{n\ell} e_{el}(r) \approx f_{el}(r) \delta_{n\ell}\delta_{n\ell} + g_{el}(r) K_{n\ell} e_{el}. \]  
(12.127)

The regular waves are defined by

\[ f_{el}(r) = \frac{1}{\nu_a} k_n j_{\ell}(k_n r), \]  
(12.128)

and the irregular waves by

\[ g_{el}(r) = \nu_a^{-\frac{1}{2}} k_n j_{\ell+1}(k_n r), \]  
(12.129)

where \( j_{\ell} \) is a spherical Bessel function of the second kind. For \( \ell = 0 \) we have the s-wave functions, \( z\phi(z) = \sin z \) and \( y\phi(z) = -\cos z \). The total energy is conserved,

\[ E = E_n + \frac{\hbar^2 k_n^2}{2\mu} = E_n + \frac{\hbar^2 k_n^2}{2\mu}. \]  
(12.130)

We will analyze the wave function for small kinetic energy in the incoming channel, \( k_n \to 0 \). This means that all inelastic processes must be exothermic, and the kinetic energy in the outgoing channel \( |e'\rangle \), namely \( \hbar^2 k_{n'}^2/2\mu \), is determined by \( E_{n'} - E_n > \hbar^2 k_{n'}^2/2\mu \). Since this implies that \( k_{n'} \) is approximately constant under these assumptions, we may assume that \( f_{el}(r) \) and \( g_{el}(r) \) are energy independent. As in the derivation for s-wave scattering, we assume that the kinetic energy of the incoming channel may also be neglected when propagating the log-derivative matrix \( Y(r_0) \) from \( r = 0 \) to \( r = r_0 \). When matching the wave function at \( r = r_0 \) to the \( K \)-matrix boundary conditions, we assume that for the incoming channel \( k_{n} r_0 \ll 1 \) and the regular and irregular functions are replaced by the leading term in the Taylor expansion. For the Bessel functions we have

\[ j_{\ell}(k_n r_0) \approx (k_n r_0)^{\ell}, \]  
(12.131)

\( y_{\ell}(k_n r_0) \approx (k_n r_0)^{-\ell+1}\)  
(12.132)

and hence for the regular and irregular waves around \( r = r_0 \)

\[ f_{el}(r) \propto k_n^{\ell+1/2}, \]  
(12.133)

\[ g_{el}(r) \propto k_n^{-\ell+1/2}. \]  
(12.134)

The defining equation for the log-derivative matrix, Eq. (12.73), shows that \( Y(r_0) \) is energy independent only if each column of the matrix \( U(r_0) \) has the same dependence on \( k_n \) since the log-derivative matrix is independent of scaling of the columns of \( U \). The \( k_n \) dependence of the matrix elements \( K_{n'\ell} e_{el} \) therefore follows from Eq. (12.127) and from the \( k_n \) dependence of the regular and irregular waves for the elastic and inelastic channels. For the elastic \( K \)-matrix elements for the incoming channel with small kinetic energy we obtain

\[ k_n^{\ell+1/2} \propto k_{n'}^{-\ell+1/2} K_{n'\ell} e_{el}. \]  
(12.135)

or

\[ K_{n'\ell} e_{el} \propto k_n^{\ell+1}. \]  
(12.136)

Since we assumed the irregular waves for exothermic channels to be energy independent, we find for inelastic matrix elements

\[ K_{n'\ell} e_{el} \propto k_n^{\ell+1}. \]  
(12.137)
In the $K$-matrix there are also elements that relate two exothermic channels, and these must of course be independent of $k_s$. Hence, the $K$-matrix, which is real and symmetric, has a block structure

$$K = \begin{pmatrix} K_{s,p} & K_{s,p}^T \\ K_{s','p} & K_{s','p}^T \end{pmatrix}.$$  \hfill (12.138)

Because of the energy independent $(p', p)$ block we cannot directly use the analogue of Eq. (12.118), but we use instead

$$T = I - S = I - \frac{I - iK}{I + iK} = 2i(I + iK)^{-1}K,$$  \hfill (12.139)

and, together with the general expression for the inverse of a block matrix

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & -A^{-1}B(D - CA^{-1}B)^{-1} \\ -(D^{-1}C(A - BD^{-1}C)^{-1}) & (D - CA^{-1}B)^{-1} \end{pmatrix},$$  \hfill (12.140)

one may derive for the $T$-matrix elements for low energy elastic scattering

$$|T_{s,p,s'|p'}|^2 \propto k_n^{2m+2l^2+2},$$  \hfill (12.141)

and for low energy inelastic scattering

$$|T_{s,p,s'|p'}|^2 \propto k_n^{2m+1}.$$  \hfill (12.142)

Hence, for elastic cross sections we find

$$\sigma_{s'\rightarrow s} \propto k_n^{2m+2l^2},$$  \hfill (12.143)

and for the inelastic cross sections

$$\sigma_{s'\rightarrow s''} \propto k_n^{2m - l^2 - 1}.$$  \hfill (12.144)

We find again that for low energy $s$-wave scattering, $l = l' = 0$, the elastic cross sections are energy-independent. The $s$-wave inelastic cross sections depend on the kinetic energy as $E^{-1/2}$, which, as discussed in Section 12.2, results in a temperature independent rate constant. A temperature independent rate constant was also found for the classical Langevin ion-molecule capture rate, but that was the result of classical motion on the long range $1/r^2$ potential. The effect of the long range potential in the quantum regime is discussed in ref. [832]. It is concluded that the expression for low energy inelastic $T$-matrix elements, Eq. (12.142), is valid if the potential falls off in the long range more rapidly than $1/r^2$. The expression for single channel elastic scattering, Eq. (12.141), is valid if $T > (n-3)/2$ for a long range potential $-c_0/r^n$. Otherwise $T_{s,s'} \propto k_n^{-2-2l^2}$. For processes that result in a change of $\Delta m$ in the angular momentum projection quantum number, but which do not change the internal energy, the threshold law for the cross section is

$$\sigma_{\Delta m} \propto k_n^{2(\Delta m+1)} \quad \text{for} \quad \Delta m \quad \text{even},$$  \hfill (12.145)

By way of an illustration, we discuss the case of the scattering of OH by $^3\text{He}$ in a weak magnetic field. To start with, it is helpful to consider the energy level structure of OH($^{2}\Pi_{1/2}$) in the presence of such a field, as illustrated in Figure 12.7. The figure shows the energies of the two lowest $j = 3/2$ states of OH($^{2}\Pi_{1/2}$) with odd and even parity, labeled $e$ and $f$ respectively. These levels are $2j + 1 = 4$ fold degenerate. In a magnetic field the degeneracy of the $m_j = 3/2, 1/2, -1/2, -3/2$ levels is lifted, as shown in the figure. The $m_j = 3/2, 1/2$ levels is a 'low-field seeking' state, and it can be trapped in a magnetic trap with minimum field strength in the centre. Such a trap can be created with two magnetic coils in the anti-Helmholtz configuration. The trap can be loaded with OH radicals using the buffer gas loading technique, in which the radicals are cooled by collisions with cryogenically cooled $^3\text{He}$ buffer gas of approximately 0.5 K. More details of buffer-gas cooling are given in Study Box 12.1. Collisions of OH with helium atoms can produce $m_j < 0$, 'high field seeking' states, which are expelled from the trap. Elastic collisions between helium and OH are necessary to cool the OH and bring it into thermal equilibrium with the helium buffer gas. Note that elastic collisions do not exchange energy in the CM-frame, where each collision is referenced to the velocity of the centre of mass of the collision partners, but in the LAB-frame they are responsible for producing thermal equilibrium (see Section 5.2.2.)

![Figure 12.7 Illustration of the Zeeman effect for the lowest few rotational levels of the OH radical. The OH radical has a $^{2}\Pi_{1/2}$ ground state. The total electron spin $S$ is $1/2$, and the total angular momentum $j = 3/2$ has projections $\Omega = \pm 3/2$ on the diatomic axis. The two $(\Omega = 3/2)$ levels combine to give states of odd and even parity, labeled $e$ and $f$, respectively, in the figure. (The spectroscopic parity of the states varies as $(-1)^j$, as is discussed further in Chapter 5.) See text for further details. Adapted from refs. [833,834].](attachment:figure12.7.png)
Cross sections for elastic and inelastic $^3\text{He} + \text{OH}(^2\Pi_{1/2}, m_J = 3/2, \ell)$ collisions, at several magnetic field strengths, are shown in Figure 12.8. In the inelastic collisions the $m_J$ quantum number can change. The parity of the OH radical can change if the collision energy and/or the magnetic field is sufficiently strong (see Figure 12.7). For collision energies above approximately $0.1 \text{ cm}^{-1}$ many resonances are found in the inelastic cross sections. The ratio between elastic and inelastic cross sections approaches unity, which is very unfavorable for a buffer gas cooling experiment. At lower energies a resonance is seen at an energy of around $0.01 - 0.1 \text{ cm}^{-1}$. For a magnetic field strength, $B$, of $B = 0.5 \text{ T}$, for $B > 0$ the $m_J$ changing collisions are inelastic and $\sigma \propto E_\ell^{-1/2}$. For $B = 0$ the $m_J$ levels are degenerate and the "reorientation threshold laws" apply, as given in Eqs. (12.145) and (12.146). For $\Delta m = 1, 2$ these equations give $\sigma \propto E_\ell^2$, as can be seen in the figure.

Finally, for exothermic reactive processes, the threshold law is the same as for exothermic inelastic processes. This quantum result does not rely on a capture model, and so it also applies when there is a reaction barrier.

It should also be noted that here we have only considered processes in which there are at most two reactants or two products. More complicated processes including, e.g., three-body breakup are discussed in ref. [836].

### 12.5 ULTRACOLD PHENOMENA

To explore the world of ultracold phenomena, we will consider ultracold gases that are confined in space, e.g., in a three-dimensional box. Experimentally, gases have been confined in magnetic traps, which can be modelled as three-dimensional harmonic oscillators. In a $T = 0$ K ideal Bose gas, i.e., a gas of non-interacting bosons, the translational motion of each particle is described by the same ground state wave function of the trap. This is not true for fermions, since two fermions cannot be simultaneously in the exact same quantum state.

So far in this chapter we have assumed that the rate of a reaction is determined by the collision rate and the two-particle collision cross section. When considering reactions in a $T = 0$ K Bose gas, this is no longer appropriate; since the bosons occupy the same state, the "collisions" occur simultaneously throughout the trap, and a full quantum description of the system is required.

For a macroscopic system, e.g., a cubic box with a volume of 1 cm$^3$, the excitation energy to the first excited quantum state is extremely small. For example, for a sodium atom in such a box it would be on the order of $10^{-12} \text{ cm}^{-1}$ (1 cm$^{-1}$ corresponds to 1.44 K). However, as a result of a quantum statistical effect described in detail in Section 12.5.2, the ground state of the trap will acquire a macroscopic population at much higher temperatures if the density of the gas is sufficiently high. This effect is called Bose-Einstein condensation. Bose-Einstein condensates, or BECs, were first predicted by Bose for photons in 1924, and the ideas were rapidly developed by Einstein to yield a complete theory of condensate formation for particles. However, it was not until a full 70 years later that a group of scientists led by Eric Cornell and Carl Wieman at JILA provided the first experimental proof, forming a BEC in a vapour of rubidium-87 atoms at a temperature of less than 170 nK.

Figure 12.9 shows data from the first experiments on Bose-Einstein condensation in a dilute gas of Rb atoms. The atoms were optically pre-cooled, loaded into a magnetic trap, and then further cooled by evaporation. Below the critical temperature, the onset of BEC formation is clearly observed in the experimentally measured velocity distributions as the growth of a peak at extremely low velocity, corresponding to atoms in the lowest energy state within the trap. The peak has a finite width due to the Heisenberg uncertainty principle, with the width of the velocity distribution being determined by the confinement of the atoms in space within the trap.
Chapter 12

Study Box 12.3 provides a brief introduction to this theory of Bose-Einstein condensation, which is discussed in more detail in the next few sections. In the next section we will derive the condensation phenomenon for an ideal Bose gas. Section 12.5.4, on the Gross-Pitaevskii equation, shows how the condensate wave function changes when interactions between the bosons are taken into account. In the last section we will show how the quantum statistics of bosons and fermions affects the rates of reactions.

12.5.1 Particle in a Box

The energy levels of a one-dimensional particle in a box with size $a$ are given by

$$\varepsilon_n = \frac{n^2\pi^2}{2ma^2}A^2, \quad n = 1, 2, 3, \ldots,$$

(12.147)

where $m$ is the mass of the particle. The corresponding wave functions are

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right).$$

(12.148)

The canonical partition function for $N$ non-interacting distinguishable particles at a temperature $T$ is

$$\Omega(T) = \left(\sum_{n=1}^{\infty} e^{-\beta\varepsilon_n}\right)^N,$$

(12.149)

where $\beta = \frac{1}{k_B T}$. For a large cubic box the energy spacings are small, so the sum may be replaced by the integral

$$\Omega(T) = \left(\int_0^{\infty} e^{-\beta\varepsilon_n x^2} \, dx\right)^N = \left(\frac{a^N}{\beta}\right),$$

(12.150)

provided that the box is sufficiently large, or that the temperature is sufficiently high (and $\beta$ small). In Eq. (12.150), $\Lambda$ is the thermal de Broglie wavelength, defined as

$$\Lambda = \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{1/2}.$$  

(12.151)

For a three-dimensional box the energy levels are

$$\varepsilon_n = \varepsilon_{n_x} + \varepsilon_{n_y} + \varepsilon_{n_z},$$

(12.152)

where $\varepsilon_n$ are the energies associated with motion along the $x$, $y$, and $z$ directions, as given in Eq. (12.147), and the wave functions are

$$\phi_n(x) = \phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z),$$

(12.153)

where $\phi_{n_x}$ are the one-dimensional wavefunctions as given in Eq. (12.148).

Cold and Ultracold Collisions

STUDY BOX 12.3: AN INTRODUCTION TO THE THEORY OF BOSE-EINSTEIN CONDENSATION

Explaining the phase transition that leads to formation of a BEC in a gas of identical bosons below a critical temperature $T_c$, requires a little statistical mechanics. You will already be familiar with the Boltzmann distribution, which describes the thermal distribution of atomic or molecular quantum states at a given temperature. The Boltzmann distribution becomes inaccurate at low temperatures, and we must use instead the Fermi-Dirac distribution (for fermions, with half integer spin), or the Bose-Einstein distribution (for bosons, with integer spin). According to Bose-Einstein statistics, the number of bosons $n_i$ in a given state with energy $\varepsilon_i$ is

$$n_i = \frac{1}{\exp\left(\frac{\varepsilon_i}{k_B T}\right) - 1},$$

(12.123.1)

where $\mu$ is the chemical potential. The total number of particles is $N = \sum n_i$. Since $n_i$ cannot take negative values, it is clear from inspection of Eq. (12.123.1) that this distribution only makes sense if $\mu$ is smaller than the lowest possible value of $\varepsilon_i$. Also, at sufficiently low temperature, this condition on $\mu$ is not compatible with conservation of the total number of particles, since as $T \to 0$, $n_i$ becomes vanishingly small. The chemical potential reduces as the temperature is lowered (recall that $\mu$ is essentially the molar Gibbs free energy, that $dG/dT = -S$, and that $S$ is always positive), and will eventually reach zero if $\varepsilon_i = 0$. For $N$ particles in a volume $V$, there is therefore a critical temperature $T_c$ defined by the condition

$$N = \sum_i \frac{1}{\exp\left(\frac{\varepsilon_i}{k_B T_c}\right) - 1}.$$  

(12.123.2)

Because for a free particle the translational energy levels are so closely spaced as to form essentially a continuum, we can replace the sum in the above expression by an integral, and it then becomes possible to solve the resulting integral equation to find $T_c$. The solution is

$$T_c = \frac{\hbar^2}{mk_B} n^{1/3},$$

(12.123.3)

where $m$ is the boson mass, $n = N/V$ is the number density, and the constant $\alpha$ is given by

$$\alpha = \frac{2\pi}{[\zeta(3/2)]^{1/3}} \approx 3.3,$$

(12.123.4)

where $\zeta(x)$ is the Riemann zeta function.

Below the critical temperature, summing the state populations given by the Bose-Einstein distribution (Eq. (12.123.1)) yields a number less than the total number of atoms $N$. Einstein postulated that the 'excess' atoms must be scattered into the ground state, corresponding to the lowest value of $\varepsilon_i$. At $T = T_c$, the fraction of atoms in this state is zero, rising to 1 at $T = 0$; quantitatively, we have for the fraction in the ground state $f = 1 - (T/T_c)^{1/2}$. This is the phenomenon known as Bose-Einstein condensation.
The condition for Bose-Einstein condensation may be reformulated in terms of the thermal de Broglie wavelength, \( \lambda = \sqrt{2\pi\hbar^2/(mk_BT)} \), giving

\[
\Lambda_c = 1.377 \left( \frac{V}{N} \right)^{1/3}
\]  
(B12.3.5)

BEC therefore occurs when the thermal wavelength associated with each particle becomes larger than the interparticle separation. The particles then 'overlap' in space and condense into a single quantum mechanical entity.

Claire Vallance

12.5.2 Bose-Einstein Condensation

To describe Bose-Einstein condensation we will use the grand canonical partition function

\[
Z(V, T, \mu) = \sum_{N=0}^{\infty} e^{\beta_0 N} Q(N, V, T),
\]  
(12.154)

where \( V \) is the volume of the container, \( \mu \) is the chemical potential, \( N \) is the number of bosons in the sample, and \( Q \) is the canonical partition function. For an ideal Bose gas, this expression becomes

\[
Z(V, T, \mu) = \prod_k \frac{1}{1 - e^{-\beta_0 k}},
\]  
(12.155)

where \( k \) runs over all single particle energy levels and \( \lambda \) is the fugacity

\[
\lambda = e^{\beta_0} = e^{\mu/k_BT}.
\]  
(12.156)

The equation of state of the ensemble is

\[
pV = k_BT \ln Z,
\]  
(12.157)

where \( p \) is the pressure. The connection with thermodynamics is made through the relation

\[
d(pV) = S \, dT + N \, d\mu + p \, dV,
\]  
(12.158)

where \( S \) is the entropy. For the total number of particles in the system \( N \) we find,

\[
N = \left. \frac{d(pV)}{d\mu} \right|_{V,T} = k_BT \left( \frac{\partial \ln Z}{\partial \mu} \right)_{V,T} = \sum_k \frac{\lambda e^{-\beta_0 k}}{1 - e^{-\beta_0 k}} = \sum_k \bar{n}_k.
\]  
(12.159)

Cold and Ultracold Collisions

Here \( \bar{n}_k \) represents the average population of state \( k \), with energy \( \epsilon_k \), and is defined as

\[
\bar{n}_k = \frac{\lambda e^{-\beta_0 k}}{1 - \lambda e^{-\beta_0 k}}.
\]  
(12.160)

The fugacity \( \lambda \) and the related chemical potential \( \mu \) are simply parameters that, together with the temperature and the energy levels \( \epsilon_k \), determine the populations \( \bar{n}_k \), and thus the total number of particles \( N \), through Eqs. (12.159) and (12.160). The possible values of \( \lambda \) and \( \mu \) are determined by the requirement that populations cannot be negative. This condition is

\[
0 \leq \lambda e^{-\beta_0 k} = e^{\mu(k-\mu)} < 1.
\]  
(12.161)

With \( \epsilon_0 \) defined as the lowest energy, the condition is \( \mu < \epsilon_0 \). In the expressions only \( \epsilon_k - \mu \) appears, so we can take the zero of energy as \( \epsilon_0 = 0 \), and thus \( \mu < 0 \) and \( 0 < \lambda < 1 \). When \( \lambda \) is small, the populations of the states are proportional to \( e^{-\beta_0 k} \), which corresponds to the classical Maxwell-Boltzmann distribution. Notice that in this case the chemical potential \( \mu = 0 \), even though the interaction between the particles is zero for our ideal Bose gas. Next, consider the population of the ground state with \( \epsilon_0 = 0 \),

\[
\bar{n}_0 = \frac{\lambda}{1 - \lambda}.
\]  
(12.162)

When \( \lambda \) approaches 1 (\( \mu \) approaches 0), the population of the ground state \( \bar{n}_0 \) can become arbitrarily large. The total number of particles \( N \) is the sum of \( \bar{n}_0 \) and the total population of the excited states \( N - \bar{n}_0 \). We will now determine \( N - \bar{n}_0 \) as a function of \( \lambda \) in the statistical limit. This means that for a given temperature \( T \), or a given \( \beta \), we assume the box to be so large that the energy spacings between the levels \( \epsilon_k \) are small compared to \( k_BT \). Thus, for the lowest excited state, which is three fold degenerate, we assume that \( \epsilon_4 \ll 1 \), such that \( e^{-\beta_0 \epsilon_4} \approx 1 - \epsilon_4 \). We note that the population of the ground state can only become considerably larger than that of \( k = 1 \) and higher states if \( \lambda \) is very close to 1. If we write \( \lambda = 1 - \delta \), where \( \delta \approx 0 \), we find that the ground state population is

\[
\bar{n}_0 = \frac{\lambda}{1 - \lambda} \approx \frac{1}{\delta},
\]  
(12.163)

and the population of the first excited state is (from Eq. (12.160))

\[
\bar{n}_1 \approx \frac{(1 - \delta)(1 - \beta_4)}{1 - (1 - \delta)(1 - \beta_4)} \approx \frac{1}{\delta} + \beta_4.
\]  
(12.164)

Hence, \( \bar{n}_0 \) can only be considerably larger than \( \bar{n}_1 \) if \( \delta \) is small compared to \( \beta_4 \). When \( \lambda \) increases, the population \( \bar{n}_0 \) of each level increases, since the numerator in Eq. (12.160) increases with \( \lambda \) and the denominator decreases with \( \lambda \). We may therefore compute an upper limit to the population of all excited states by setting \( \lambda = 1 \),

\[
N - \bar{n}_0 = \sum_{k>0} e^{-\beta_0 k}.
\]  
(12.165)

For bosons in a three-dimensional box, the energy levels \( \epsilon_k \) are given by \( \epsilon_n \) of Eq. (12.152) and the summation over \( k \) must be replaced by

\[
\sum_{n=1}^{\infty} \sqrt{\frac{\pi}{2}} \left( \frac{n^2 + 1/4}{\pi} \right)^{1/4} \epsilon_n.
\]  
(12.166)
The energies \(\varepsilon_n\) can be written as \(bn^2\), with \(n^2 = n_x^2 + n_y^2 + n_z^2\) and

\[
b = \frac{\hbar^2 \pi^2}{2ma^2}.
\]

(12.167)

The summation can be approximated by an integral over one octant of a sphere,

\[
\sum_{n_x > 0, n_y > 0, n_z > 0} f(n) \approx \frac{\pi}{2} \int_0^\infty n^2 f(n) dn,
\]

(12.168)

or, with \(\varepsilon = bn^2\) and \(n^2 \varepsilon = (1/2)b^{-3/2}\sqrt{\varepsilon} ds\),

\[
N - \bar{n}_0 = \frac{\pi}{4} b^{-3/2} \int_0^\infty \sqrt{\varepsilon} e^{-\varepsilon \bar{n}_0} ds.
\]

(12.169)

To evaluate the integral we use the series expansion

\[
(1 - x)^{-1} = \sum_{n=0}^{\infty} x^n, \quad \text{for} \ |x| < 1,
\]

(12.170)

for \(x = e^{-\bar{n}_0}\), which gives

\[
N - \bar{n}_0 = \frac{\pi}{4} b^{-3/2} \sum_{l=1}^{\infty} \frac{\Gamma(3/2)}{l \Gamma(l)}.
\]

(12.171)

With \(\Gamma(3/2) = \sqrt{\pi}/2\), \(a^3 = V\), the Riemann-zeta function defined by

\[
\zeta(n) = \sum_{n=1}^{\infty} \frac{1}{n^n}
\]

and the de Broglie wavelength defined in Eq. (12.151), the contribution of the excited states to the density is at most

\[
\rho_{ex} = \frac{N - \bar{n}_0}{V} = \frac{(m\hbar)^{3/2}}{2\pi b^3} \zeta(3/2) = \Lambda^{-1/2} \zeta(3/2),
\]

(12.173)

where \(\zeta(3/2) \approx 2.612\). This equation shows that if the temperature is lowered, the excited states are less occupied. When \(\rho_{ex}\) drops significantly below the total density \(\rho\), the ground state must accommodate the difference, i.e., \(\rho = \rho_0 - \rho_{ex}\), and a Bose-Einstein condensate is formed. This happens at the critical temperature \(T_c\). The corresponding density is called the critical density \(\rho_c\). Below the critical temperature the total density is given by

\[
\rho = \rho_0 + \rho_{ex} = \frac{1}{V} \frac{\lambda}{1 - \lambda} + \Lambda^{-3} \zeta(3/2).
\]

(12.174)

The excited state density is related to the density \(\rho_c\) at the critical temperature through

\[
\frac{\rho_{ex}}{\rho_c} = \left( \frac{\Lambda}{\lambda} \right)^3 \left( \frac{T}{T_c} \right)^{3/2}.
\]

(12.175)

where \(\Lambda\) is the de Broglie wavelength at temperature \(T_c\). Hence, the condensate fraction is

\[
\frac{\rho_0 - \rho_{ex}}{\rho_c} = 1 - \left( \frac{T}{T_c} \right)^{3/2}.
\]

(12.176)

In this limit of a large volume there is a discontinuity in the derivative of the condensate fraction at \(T = T_c\), which marks the phase transition. The process of Bose-Einstein condensation is explored in more detail in Study Box 12.4.

12.5.3 A Bose-Einstein Condensate in a Harmonic Trap

In contrast to the ‘particle in a box’ description of the previous sections, Bose-Einstein condensates of dilute gases created in experiments such as that shown in Figure 12.9 are not in practice confined by walls, but by magneto-optical traps. The confining field in such a trap may be modelled by a three-dimensional harmonic oscillator potential

\[
V_{trap}(r) = \frac{1}{2}(K_x x^2 + K_y y^2 + K_z z^2).
\]

(12.177)

We will only consider isotropic potentials, for which the three force constants \(K_x = K_y = K_z\) are equal to the same constant \(K\). In this case, the one-particle energy levels are given by

\[
\varepsilon_n = (n_x + n_y + n_z + 1)\hbar\omega,
\]

(12.178)

where \(\omega = \sqrt{K/m}\) is 2\(n\) times the trap frequency, and the quantum numbers \(n_x, n_y,\) and \(n_z\) are non-negative integers. The ground state one-particle wave function is given by

\[
\phi(r) = \frac{(m\hbar\omega)^{1/4}}{2\pi R} \exp \left( -\frac{1}{2} \frac{m\hbar\omega}{R^2} r^2 \right).
\]

(12.179)

The relation between the number of particles and the critical temperature is

\[
k_B T_c = \hbar \omega \left( \frac{N}{V} \right)^{1/3} \approx 0.94 \hbar \omega N^{1/3},
\]

(12.180)

and the formula for the condensate fraction is

\[
\frac{N_0}{N} = 1 - \left( \frac{T}{T_c} \right)^{1/3}.
\]

(12.181)

The derivation of this relation is similar to that of Eq. (12.176) in the previous section, and may be found in, e.g., ref. [840].

12.5.4 The Gross-Pitaevskii Equation

In this section we develop the Schrödinger equation for the condensate, known as the Gross-Pitaevskii equation, the solution of which provides the condensate wave function. For \(N\)
STUDY BOX 12.4: A SIMULATION OF BOSE-EINSTEIN CONDENSATION

Here we describe a simple numerical simulation of Bose-Einstein condensation in a three-dimensional cubic box. Readers with some programming experience may like to try writing a code to carry out this simulation themselves. The results of the simulation are shown in Figure 12.10. In the calculations, the mass, $m$, is set to the mass of a sodium atom, and the temperature, $T$, is fixed at a value corresponding to a thermal de Broglie wavelength of $\lambda = 100 a_0$. The solid lines in the figure correspond to a large box of volume $V = a^3 = 1000 \lambda^3$ and the dashed lines correspond to a small box of volume $20 \lambda^3$. The dimensionless parameter $\chi$ is defined by

$$\chi = \frac{N^{1/3} a}{\lambda^2} = \rho^{1/3} \lambda,$$

so at $\chi = 1$ there is one particle per $\lambda^3$. In the simulation, all states with energies less than $15 \hbar \omega$ are included. To make the plot, a set of $\lambda$ values is chosen and the populations $\rho_k$ follow from Eq. (12.160), after which $N = \Sigma_k \rho_k$ and $\chi$ can be computed. (For those interested in trying this for themselves it will be necessary to find a good grid of $\lambda$ (or $\rho$) values, which will require careful study of Section 12.5.2.)

The plot in Figure 12.10 shows that at this fixed temperature $T$ the fractional population of the ground state $\rho_0/N$ approaches unity as the density (or $\chi$) increases. The plot shows that the fractional population of the first excited state $\rho_1/N$ remains small at all densities. Note that $\rho_1 < \rho_0$ for all $\chi$. Also, for the larger box the maximum population of the first excited state is less than for the smaller box (dashed line). At infinite box size the fractional populations of all excited states are infinitesimal.

Gerrit Groenenboom

Figure 12.10 Numerical simulation of Bose-Einstein condensation in a three-dimensional cubic box. $\rho_k/N$ represents the fractional population in level $k$, while $\chi$ is a dimensionless parameter which is inversely proportional to the size of the box. The solid lines correspond to a box of volume $V = a^3 = 1000 \lambda^3$, while the dashed lines correspond to a box of volume $20 \lambda^3$. See the text of this study box for details.

STUDY BOX 12.5: COLD AND ULTRACOLD CHEMISTRY

Chemists tend to be very familiar with chemistry occurring at or near room temperature or higher, a regime in which reaction rates are described by the Arrhenius equation, and kinetics and dynamics may be understood in terms of passage over energetic barriers along the reaction coordinate of the appropriate potential energy surface. When considering chemistry at very low temperatures, we enter an entirely different regime. Molecules simply do not have enough energy to surmount energetic barriers, and only barrierless reactions, such as ion-molecule or radical-radical reactions, are able to proceed through a classical mechanism. When a small barrier is present, reaction may still sometimes proceed, but only via a mechanism involving quantum-mechanical tunnelling through the barrier, leading to novel kinetic and dynamical behaviour. At still lower temperatures, the thermal wavelengths of the reacting molecules become larger than the molecules themselves, and the outcome of reaction occurring as a result of a classical collision is decided entirely by how far apart they are. For example, at temperatures in the milliKelvin range, thermal wavelengths are often several nanometres or even tens of nanometres. Reactions can no longer be viewed in terms of a collision between two ‘hard spheres’, but must be considered in terms of interference between two waves.

The lowest known temperatures found in nature are in interstellar space. As noted in the Introduction to this chapter, the cosmic background radiation corresponds to a temperature of around 2.7 K, which sets an approximate lower limit to the temperature a molecule might experience in space. Temperatures in interstellar gas clouds, in which most of the molecules known to exist in space have been observed, range from around 100 K near the edges of a cloud down to around 10 K in the ‘dense’ core. Temperatures down to a few Kelvin are the regime of ‘cold chemistry’, and the desire to understand the formation of molecular species in interstellar space has sparked a great deal of interest in chemistry at these temperatures.

Many reactions of interstellar significance have been studied using the CRESU technique. The acronym stands for the French ‘Cinétique de Réaction en Ecoulement Supersonique Uniforme’, or (in English) Reaction Kinetics in Uniform Supersonic Flow. The technique is based on expanding a high-pressure gas through a specially shaped nozzle called a de Laval nozzle. The nozzle is designed to collimate the gas into a uniform, collision-free, supersonic beam at a characteristic temperature, and by adjusting the nozzle design, gas flows with temperatures from room temperature down to around 10 K may be achieved. The gas density in the expansion is relatively high (in the range from $10^{16}$ to $10^{18}$ cm$^{-3}$), so that thermal equilibrium is maintained at all times, and the flow is uniform with respect to temperature, density, and velocity. This is in marked contrast to a pulsed molecular beam, in which no thermal equilibrium, and therefore no well-defined temperature, is established. Chemical kinetics measurements within the gas flow are generally performed using laser-pump-probe techniques (see Chapter 1 and Study Box 5.2). The pump laser typically generates a reactive species through photolysis of a precursor molecule, and product detection in the probe step is often through laser-induced fluorescence (see Study Box 5.2). The CRESU technique is typically used to study reactions with essentially no activation barrier, in which the long-range part of the intermolecular potential provides the energetic driving force. These types of reactions are often well-described by the capture theories treated in detail in this chapter, and include radical reactions and ion-molecule reactions. A wide range of astrophysically relevant reactions have been studied using the CRESU technique.

Ion-molecule reactions have also been widely studied using the Selected-Ion Flow Tube (SIFT) technique, in which mass-selected ions are flowed down a drift tube in an inert carrier gas and react with molecular species injected downstream of the ion inlet. Reaction products are then detected by a mass spectrometer.

Temperatures below 1 K take us into the regime of ‘ultracold chemistry’, and have only been achieved on earth in the laboratory. Study Box 12.1 outlined some of the ways in which molecular species may be cooled to such temperatures. In principle, any of these techniques...
could be used to create cold reactants for a scattering experiment. However, in practice studying the chemistry of these molecules presents huge challenges. Ultracold molecules can generally only be produced at extremely low number densities, orders of magnitude lower than those typically used in a crossed molecular beam experiment, so that exclusively sensitive detection techniques are required in order to monitor the very small number of products formed through collisions. For this reason there have been very few successful experimental studies of ultracold chemistry. We will look at two examples.

Our first example involves a general technique for studying ultracold ion-molecule reactions in an electromagnetic trap. When ions are laser-cooled and trapped, they form a crystalline array in which the positions of the ions are approximately fixed (with some small degree of motion caused by the oscillating trap potentials). The relative positions of the ions are determined by the balance between the confining forces of the trap and the Coulomb repulsion of the ions, with typical spacings on the order of 10–20 μm. During the laser cooling process, the ions are continuously absorbing and emitting photons, and by detecting the emitted fluorescence, an image of the crystal may be obtained. Such an image is shown in Figure 12.11. Coulomb crystals may be stored for several hours in a suitable vacuum, and provide an ideal and general method for studying ultracold collisions between ions and other chemical species. When an individual ion reacts to form another chemical species, it is no longer resonant with the cooling laser, and its fluorescence is extinguished. For example, Softey et al. have combined Coulomb crystals with a velocity-selected molecular beam to study the kinetics of the reaction Ca⁺ + CH₃F → CaF⁺ + CH₄ at relative translational temperatures down to 1 K.

\[ \Psi(r_1, r_2, \ldots, r_N) = \prod_{i=1}^{N} \phi(r_i), \]  
(12.182)

where the single particle wave function \( \phi(r) \) is normalized,

\( \int |\phi(r)|^2 \, dr = 1. \)
(12.183)

For particles in a cubic box, \( \phi(r) \) is the ground state wave function \( \phi_{0,0,0} \) from Eq. (12.153), and for an isotropic three-dimensional harmonic trap it is given by Eq. (12.179). To find an approximate wave function for the condensate in the presence of interactions between the particles, we will use the Hartree product (i.e. the non-interacting wave function) as an ansatz (starting function) for the wave function and variationally optimize the single particle wave function \( \phi(r) \). This is a mean-field approach, and it is analogous to the Hartree-Fock approach for fermions. We consider a pairwise additive interaction between the particles, with the effective pair potential of Eq. (12.124)

\[ \hat{U} = U_0 \sum_{i<j} \delta(r_i - r_j), \]
(12.184)

where \( U_0 \) is determined by the scattering length, \( U_0 = 4\pi a s \hbar^2/\mu \). The total Hamiltonian of the gas also contains the kinetic energy of the particles and the trap potential \( V_{\text{trap}}(r) \),

\[ \hat{H} = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + V_{\text{trap}}(r_i) \right] + \hat{U}, \]
(12.185)

where \( \mu = \sqrt{\lambda} \). For the trap potential the expectation value is given by

\[ \langle \Psi | \sum_{i=1}^{N} V_{\text{trap}}(r_i) | \Psi \rangle = N \langle \phi | V_{\text{trap}}(r) | \phi \rangle = N \int V_{\text{trap}}(r) |\phi|^2 \, dr, \]
(12.186)
and for the kinetic energy it is
\[
\langle \Psi | \sum_{i=1}^{N} \frac{p_i^2}{2m} | \Psi \rangle = \frac{N}{2m} \langle \phi | \hat{p}^2 | \phi \rangle = \frac{N \hbar^2}{2m} \int |\hat{\nabla} \phi(r)|^2 \, dr.
\] (12.187)

Finally, to evaluate the expectation value of the two-particle interaction operator for a single interaction between the particles \(i\) and \(j\) we use
\[
\int \int \phi(r_i)^* \phi(r_j)^* \delta(r_i - r_j) \phi(r_i) \phi(r_j) \, dr_i \, dr_j = \int |\phi(r_i)|^4 \, dr_i,
\] (12.188)
and note that the sum over all \(i\neq j\) gives \(N(N-1)/2\) identical contributions,
\[
\langle \Psi | \hat{U} | \Psi \rangle = U_0 \frac{N(N-1)}{2} \int |\phi(r)|^4 \, dr.
\] (12.189)
We assume \(N\) to be large, so we set \(N(N-1)/2 \approx N^2/2\), and find for the total energy
\[
E = N \int \left[ \frac{\hbar^2}{2m} |\hat{\nabla} \phi(r)|^2 + V_{\text{imp}}(r) |\phi(r)|^2 + \frac{1}{2} N U_0 |\phi(r)|^4 \right] \, dr.
\] (12.190)

Before we variationally minimize this energy expression, we consider the particles in a box problem, for which \(V_{\text{imp}}(r) = 0\). If we take the ground state particle in a box wave function \([\text{Eq. (12.153)}]\) for \(\phi(r)\) we find
\[
E = \frac{3 \pi^2 \hbar^2}{2m} \alpha^3 + \frac{27}{16} \hbar^2 V U_0.
\] (12.191)
where \(V = a^3\) is the volume of the box, \(\rho = N/V\) is the particle density, and we have used the integral
\[
\int_0^\alpha \sin^4 \left( \frac{\pi x}{a} \right) \, dx = \frac{3a}{8}.
\] (12.192)

We note that the second term in Eq. (12.191) scales with the volume of the box and the square of the density. Hence, if either the volume or the density is sufficiently high, this term will dominate. We may also compute the expectation value of the energy for the wave function for a homogeneous gas: \(\phi(r) = V^{-3/2}\). Strictly, this wave function does not satisfy the particle in a box boundary conditions, but if we assume that the volume is large, we may neglect the effects at the boundary and we find
\[
E = \frac{1}{2} \rho^3 V U_0.
\] (12.193)

Thus, when the interaction is repulsive (\(U_0 > 0\)) and the volume and density are sufficiently high, we find that (invoking the variational principle) the homogeneous gas wave function describes the condensate better than the particle in a box wave function, since \(\frac{3 \pi^2 \hbar^2}{2m} \alpha^3 < \frac{1}{2} \rho^3 V U_0\). For attractive interactions (\(U_0 < 0\)) we observe that the nonlinear \(|\phi(r)|^4\) term favours the least homogeneous solution, which in practice may result in collapse of the condensate.

### Cold and Ultracold Collisions

We will now derive the Gross-Pitaevskii equation, which minimizes the energy of Eq. (12.190) variationally. It is convenient to introduce the function
\[
\psi(r) = N^{1/2} \phi(r).
\] (12.194)
The normalization of \(\psi\) is such that the particle density is given by
\[
\rho(r) = |\psi(r)|^2.
\] (12.195)
The integral over the density is the total number of particles \(N\). Thus, within the present ansatz, \(\psi(r)\) contains all information about the condensate wave function and it is sometimes referred to as "the condensate wave function." The energy expression as a functional of \(\psi\) is
\[
E[\psi] = \int \left[ \frac{\hbar^2}{2m} |\hat{\nabla} \psi(r)|^2 + V(r) |\psi(r)|^2 + \frac{1}{2} \rho_0 |\psi(r)|^4 \right] \, dr.
\] (12.196)

According to the variational principle, we must vary \(\psi\) to minimize the energy \(E\), but we must satisfy the constraint that the number of particles
\[
\int |\psi(r)|^2 \, dr = N |\psi| = N
\] (12.197)
is conserved. For this constraint minimization the Lagrange multiplier method is used. This amounts to introducing a new parameter, \(\mu\), and performing the unconstrained minimization of \(E[\psi] - \mu N |\psi|\), such that for first order variations \(\delta \psi\),
\[
E[\psi + \delta \psi] - \mu N |\psi + \delta \psi| = E[\psi] - \mu N |\psi|.
\] (12.198)

In principle the wave function may be complex, but instead of varying the real and imaginary part it is more convenient (and mathematically equivalent) to vary \(\psi\) and \(\psi^*\) separately. Therefore, we rewrite the energy expression as
\[
E[\psi] = \int \left[ \frac{\hbar^2}{2m} \hat{\psi}^*(r) \hat{\nabla}^2 \hat{\psi}(r) + V(r) \hat{\psi}^*(r) \hat{\psi}(r) + \frac{1}{2} U_0 \hat{\psi}^*(r) \hat{\psi}(r)^2 \right] \, dr,
\] (12.199)
substitute \(\hat{\psi} \rightarrow \psi + \delta \psi^*\), and set terms linear in \(\delta \psi\) equal to zero. The result
\[
\left[ \frac{\hbar^2}{2m} \hat{\nabla}^2 + V(r) + U_0 |\psi(r)|^2 \right] \psi(r) = \mu \psi(r)
\] (12.200)
is known as the time-independent Gross-Pitaevskii equation. The variation \(\psi \rightarrow \psi + \delta \psi\) can be used to show that \(\mu\) must be real. If one finds a \(\psi(r)\) that satisfies the Gross-Pitaevskii equation, one cannot normalize the result to obtain a condensate wave function for a given number of particles \(N\), because the equation is nonlinear in \(\psi\). Instead, one must choose a value for \(\mu\), find a solution \(\psi(r)\), and determine the number of particles to which it corresponds.

*The choice of the symbol \(\mu\) for this parameter will become obvious in the following discussion.*
The parameter $\mu$ is the chemical potential, $\mu = \delta E/\delta N$. This follows from rewriting Eq. (12.198) as

$$\mu = \frac{E[\psi + \delta \psi] - E[\psi]}{N[\psi + \delta \psi] - N[\psi]} = \frac{\Delta E}{\Delta N}. \tag{12.201}$$

12.5.5 Thomas-Fermi Approximation

We saw above that when the volume is large and the interaction $V_0$ is repulsive, the kinetic energy term in the Gross-Pitaevskii equation may be neglected. This is known as the Thomas-Fermi approximation. The solution is

$$|\psi(r)|^2 = \rho(r) = \frac{\mu - V_{\text{trap}}(r)}{U_0} \tag{12.202}$$

in regions where the right hand side is positive, and $\psi(r)=0$ otherwise. The discontinuity in the derivative of the wave function at the edge of the cloud defined by $V_{\text{trap}}(r)=\mu$ is the result of neglecting the kinetic energy term. As before, we find that the density is constant when $V_{\text{trap}}(r)=0$.

In that case we also find $\mu = NV^{-1}U_0$ and $E = N^{3/2}V^{-1}U_0/2$, which agrees with the definition of the chemical potential $\mu = \delta E/\delta N$.

The density profile of a Bose-Einstein condensate is very characteristic. The classical thermal Boltzmann distribution is proportional to $e^{-\frac{V}{k_B T}}$. If the temperature is lowered and a condensate fraction is formed, it is easily recognized in the experiment as a separate phase with a localized density distribution near the minimum of the trap.

12.5.6 Bose-enhancement and Pauli-blocking

For a reaction occurring in a trap, the available product states are fully quantized. Not only the internal states of the atoms or molecules that are formed are quantized, but also their translational motion. When the products are fermions, they must satisfy Pauli’s exclusion principle: the occupation of a given product state can be at most 1. This is called Pauli-blocking. It can only affect the rate of a process at ultralow temperatures, because at normal temperatures the number of available product states is enormous and the average population of product states will be much smaller than unity. For bosons, there is no restriction on the occupation of a given state. In fact, the rate of a process producing a product in an already occupied state is enhanced. This effect is called Bose enhancement or Bose stimulation.

To show the origin of this enhancement, we consider a model two level system of $N_1+N_2=N$ identical bosons. For instance, a Bose-Einstein condensate of $N_2$ ground state atoms in which $N_1$ atoms in some excited state are introduced. We also consider a perturbation that induces transitions between the two levels. For concreteness we take the component of the dipole operator that connects the two levels. Matrix elements of this operator determine the rate of spontaneous emission.

To define the wave functions we introduce the shorthand notation $a(i) = \phi_i(r)$ and $b(i) = \phi_2(r)$, where $\phi_1$ and $\phi_2$ are the one-particle wave functions corresponding to the two levels and $i$ labels the particles. We will assume those functions to be normalized and orthogonal to each other. The wave function that describes a system with $N_1$ particles in level 1 and $N_2$ particles in level 2 may be written as

$$|N_1N_2\rangle = n(N_1N_2)\hat{S}a(1)a(2)\cdots a(N_1)b(N_1+1)b(N_1+2)\cdots b(N_1+N_2)|0\rangle, \tag{12.203}$$

where $\hat{S}$ is the symmetrizer, which is the sum of all $N!$ permutations $\hat{P}_k$ of the $N = N_1 + N_2$ particle labels,

$$\hat{S} = \sum_{k=1}^{N!} \hat{P}_k \tag{12.204}$$

and $n(N_1, N_2)$ is the normalization constant. To compute it we note that

$$\hat{P}_k \hat{S} = \sum_{i=1}^{N!} \hat{P}_i \hat{P}_k = \hat{S} \tag{12.205}$$

because $\hat{P}_k \hat{P}_k$ runs over all permutations, although in a different order. We can use this result to show that

$$\hat{S}\hat{S} = \sum_{i=1}^{N!} \hat{P}_i \hat{S} = N! \hat{S}. \tag{12.206}$$

Since $\hat{S}$ is Hermitian, we may derive

$$\langle N_1N_2\rangle = n(N_1N_2)\langle \hat{S}a(1)\cdots b(N_1)|\hat{S}a(1)\cdots b(N_1)\rangle = n(N_1N_2)|\langle a(1)\cdots b(N_1)|a(1)\cdots b(N_1)\rangle|^2 \tag{12.207}$$

Out of the $N!$ terms, there will be $N_1N_2$ terms that yield 1, and all the others will be zero, so the normalization constant is

$$n(N_1N_2) = (N_1N_2)!^{-\frac{1}{2}}. \tag{12.208}$$

Let $\hat{d}$ be the component of the dipole operator that couples the levels $a$ and $b$. It is written as the sum of one-particle operators

$$\hat{d} = \sum_{i=1}^{N_1} \hat{d}_i \tag{12.209}$$

with matrix elements

$$\langle a(i)|\hat{d}|b(i)\rangle = d_{ab}. \tag{12.210}$$

The rate of spontaneous emission, a process in which the population of the upper level is decreased by one, and the population of the lower level is increased by one, is proportional to

$$\kappa = \langle N_1N_2\rangle |\hat{d}|N_1 - 1, N_2 + 1|^2. \tag{12.211}$$

A derivation similar to the one used to derive the normalization of the wave function shows that the wave function

$$\kappa = N_1(N_2 + 1)|d_{ab}|^2. \tag{12.212}$$

What is remarkable about this result is that the rate not only depends on the number of particles $N_1$ in the upper level, but also on the number of particles in the lower level, $N_2$. This effect is called
Bose enhancement of the dipole matrix element. It should be noted that the above treatment of spontaneous emission is still lacking some essential ingredients. For example, photons carry momentum, and total momentum must be conserved. A more rigorous theoretical treatment predicts that enhancement of spontaneous emission can occur in an interacting Bose-Einstein condensate.

The analogous relation for fermions contains a factor \( N_f(1 - N_f) \) which shows that the process can only proceed if the initial state has an occupation of 1, and the final state is empty.

At ultralow temperatures there is no energy available for endothermic reactions, and one would expect that the energy released by an exothermic reaction would destroy the condensate. However, Bose enhancement may occur in resonance reactions, where the energy of the reactants is equal to the energy of the products. For example, two alkali atoms may form a diatomic molecule in its highest vibrational state. The molecular level can be tuned into resonance with the atomic level with a magnetic field, since the magnetic moment of the diatom will in general not be exactly twice the magnetic moment of the atom. Such a resonance is called a Feshbach resonance (see Chapter 6). This technique has been used to produce both ultracold molecules, and molecular Bose-Einstein condensates. Other methods to achieve resonance are the use of Raman transitions or photo-dissociation of Bose-Einstein condensates.

Most theoretical papers on ultracold chemistry use the second quantization formalism to denote wave functions of the form Eq. (12.182) and the operators acting on them. A short introduction to this formalism, with applications to Bose-Einstein condensates can be found in ref. [844].

### 12.6 OUTLOOK

Producing and manipulating cold and ultracold atoms and molecules is a very active and rapidly expanding field. In this chapter we only covered some of the basics of cold and ultracold collisions. Review papers and books describing the state of the art appear regularly, and major steps forward are reported frequently. To give just a few examples of recent progress, we mention the creation of a gas of ultracold polar molecules, the creation of a Bose-Einstein condensate of strontium atoms, the observation of an ultracold atom-exchange reaction (further details of this work may be found at the end of Study Box 12.5), and the trapping of molecules on a chip.

### 12.7 PROBLEMS

1. (a) A simple classical one-dimensional model for the collision energy dependence of the cross section of a chemical reaction uses the following expression

   \[ E_t = K R^2 + V_{eff}(R), \]

   where \( E_t \) is the initial collision energy, and \( V_{eff}(R) \) is the radial dependence of the effective potential. Explain the origins of this expression, and present arguments to show that the effective potential may be written

   \[ V_{eff}(R) = V(R) + E_t \frac{b^2}{R^2}, \]

   where \( V(R) \) is the radial dependence of the potential energy, and \( b \) is the impact parameter for the collision. Recall that the kinetic energy associated with orbital motion can be written \( E_{kin} = b^2 / 2 \mu R^2 \).

(c) Hence show that, for the radial kinetic energy at the barrier to be greater than zero, the impact parameter for the ion-molecule reaction is limited by the equation

   \[ b^2 \leq \left( \frac{4C_4}{E_t} \right)^{1/2}. \]

(b) For a reaction between an ion and a molecule, the long range ion-induced dipole interaction potential has the form

   \[ V(R) = -\frac{C_4}{R^4}, \]

   where the coefficient is defined \( C_4 = \alpha' \alpha^2 \langle 8\pi \alpha \rangle \), and the constant \( \alpha' \) is the polarizability volume of the molecule. Use this expression, together with equation (12.213) above, to show that the location of the maximum in the centrifugal barrier on the effective potential is given by the expression

   \[ R_0 = \left( \frac{2C_4}{E_t b^2} \right)^{1/2}. \]

Use this expression to estimate the cross section for the reaction (known as the capture cross section), stating any additional assumptions made, and sketch the dependence of the cross section on collision energy (i.e., the excitation function).

(d) The polarizability volume, \( \alpha' \), of O\(_2\) is \( 1.4 \times 10^{-30} \) m\(^3\). Estimate the ion-induced dipole contribution to the capture cross section for the Ca\(^+\) + O\(_2\) reaction. Employ a mean collision energy corresponding to a temperature of 10 K.

2. The K-matrix boundary conditions for an s-wave are given in Eq. (12.113),

   \[ \psi_{K}(r) = \sin kr - K \cos kr. \]

The S-matrix boundary conditions for this wave function are

   \[ \psi_{S}(r) = -e^{-i\theta} \psi_{K}(r). \]

The difference between these boundary conditions is only the normalization of the wave function, i.e.,

   \[ \psi_{S}(r) = A \psi_{K}(r). \]

where \( A \) is a constant. Derive the relation between the S- and the K-matrix [Eq. (12.117)].

Hint: take the derivative with respect to \( r \) of the last equation:

   \[ \frac{d}{dr} \psi_{S}(r) = A \frac{d}{dr} \psi_{K}(r). \]

Assume \( K \) be known. For some fixed value of \( r \) Eqs. (12.216) and (12.217) are now two equations in \( A \) and \( S \), so they can be solved to find \( S \).
Further Reading

CHAPTER 1


CHAPTER 2


Tutorials in Molecular Reaction Dynamics
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Further Reading


CHAPTER 3

5. J. J. Sakurai, Modern Quantum Mechanics, (Benjamin/Cummings, Menlo Park CA, USA, 1985).
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CHAPTER 4


CHAPTER 5


CHAPTER 6


CHAPTER 7


CHAPTER 8


CHAPTER 9


CHAPTER 10


CHAPTER 11


CHAPTER 12

Glossary of Acronyms

BEC  Bose-Einstein condensate
BO  Born-Oppenheimer
CASSCF  complete active space self-consistent field
CC  coupled channel
CC  coupled cluster
CCD  charge-coupled device
CCSD  coupled cluster with single and double excitations
CCSD(T)  coupled cluster with fully calculated single and double excitations and
triple excitations calculated using perturbation theory
CCSDTQ  coupled cluster with single, double, triple and quadruple excitations
CDCS  (pair) correlated differential cross section
CG  Clebsch Gordan (coefficient)
CI  configuration interaction
CIC  conical intersection
CID  configuration interaction with double excitations
CIS  configuration interaction with single excitations
CISD  configuration interaction with single and double excitations
CM  centre of mass
CMB  crossed molecular beams
CNP  complete nuclear permutation
CS  coupled states
CW  continuous wave
DAF  distributed approximating function
DC  direct current
DCS  differential cross section
DFFFD  dispersion fitted finite difference
DFG  difference frequency generation
DFT  density functional theory
DI  direct inelastic (scattering)
DVR  discrete variable representation
EI  electron impact
FBR  finite basis representation
FD  finite difference
Glossary of Acronyms

- FFT: fast Fourier transform
- FHG: fourth harmonic generation
- FT: Fourier transform
- FWHM: full width at half maximum
- GDD: group delay dispersion
- GP: geometric phase
- GVD: group velocity dispersion
- GWP: Gaussian wavepacket
- HF: Hartree-Fock
- HHG: high-order harmonic generation
- HOMO: highest occupied molecular orbital
- ICS: integral cross section
- IMLS: interpolating moving least squares (interpolation method)
- IOSA: infinite-order sudden approximation
- IR: infra-red
- IRP: intrinsic reaction path
- ISC: intersystem crossing
- IVR: intramolecular vibrational redistribution
- KE: kinetic energy
- KER: kinetic energy release
- LAB: laboratory (frame)
- LIF: laser-induced fluorescence
- LUMO: lowest unoccupied molecular orbital
- MCP: microchannel plate
- MCSCF: multiconfigurational self-consistent field
- MCTDH: multiconfigurational time-dependent Hartree
- MEP: minimum energy path
- MOT: magneto-optical trap
- MPn: nth order Møller Plesset perturbation theory
- MS: modified Shepard (interpolation method)
- NGP: neglect of geometric phase
- NMR: nuclear magnetic resonance
- OPA: optical parametric amplifier
- PC: personal computer
- PDDCS: polarization-dependent differential cross section
- PDF: probability density function
- PE: potential energy
- PES: potential energy surface
- PHOTOC: Photoinduced reaction analyzed by the law of cosines
- PI: photoionization
- PP: polarization parameter
- PRB: laser beam probe frame
- QBS: quantum bottleneck state
- QCT: quasi-classical trajectory
- QM: quantum mechanics or quantum mechanical
- QQT: quasi quantum treatment
- RAS: restricted active space
- REMPI: resonance-enhanced multiphoton ionization
- RKHS: reproducing kernel Hilbert space (interpolation method)
- RP: reaction path
- RRKM: Rice Rampsberger Kassel Marcus (theory)
- SA: steric asymmetry
- SCF: self-consistent field
- SFG: sum frequency generation
- SHG: second harmonic generation
- SI: symplectic integrator
- SLM: spatial light modulator
- SOP: split operator
- SSH: Schwartz Slawsky Herzfeld (theory)
- TD: time-dependent
- TD: trapping-desorbing
- TDSE: time-dependent Schrödinger equation
- TDWP: time-dependent wavepacket
- THG: third harmonic generation
- TI: time-independent
- TISE: time-independent Schrödinger equation
- TOF: time of flight
- TRPEI: time-resolved photoelectron imaging
- TRPES: time-resolved photoelectron spectroscopy
- UMP2: spin unrestricted MP2 (see MPn)
- UV: ultraviolet
- VAP: vibrationally adiabatic potential
- VDW: van der Waals (interaction)
- VMI: velocity-mapped imaging
- VUV: vacuum ultraviolet
- XUV: extreme ultraviolet
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