

Cold collisions: chemistry at ultra-low temperatures; in: *Tutorials in molecular reaction dynamics*, edited by M. Brouard and C. Vallance, *in preparation* (RSC, Cambridge, 2009)

Gerrit C. Groenenboom and Liesbeth M. C. Janssen
Theoretical Chemistry, Institute for Molecules and Materials,
Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ, Nijmegen, The Netherlands
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I. INTRODUCTION

In 1995 several groups succeeded in producing Bose-Einstein condensation in dilute gases of alkali atoms[1–3]. In 2003 molecular Bose-Einstein condensates of alkali dimers were reported[4–6]. The temperatures of these atomic and molecular condensates is in the order of $nK - \mu K$. Theoretical studies show that at these ultracold temperatures, chemical reactions may occur and even may be very fast[7, 8].

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

$$k(T) = Ae^{-E_a/k_B T}, \quad (1)$$

where k_B is the Boltzmann constant and A is a proportionality constant. The activation energy E_A is the energy required to pass the transition state. The expression can be derived using classical statistical mechanics. It predicts that the reaction rate drops to zero quickly when $k_B T \ll E_a$.

Some reactions, however, are barrierless and their rate may increase at lower temperatures. This is particularly true for ion-molecule reactions. Already in 1905, Langevin derived an expression for the reaction rate of ion-molecule reactions. This expression only depends on the long range part of the potential and the model is called a 'capture model' [9]. Later, it was found that also neutral radical - neutral radical reactions and even some radical - molecule reactions may 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.

The air around us contains in the order of 10^{19} molecules per cm^3 . In the interstellar space, areas where the density is in the order of 10^6 cm^{-3} look like clouds when observed with telescopes, because densities are even lower in most of the interstellar space. 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[10].

The calculation of a reaction rate requires a potential energy surface. Depending on the system it may be sufficient to only know the potential around the transition state or only the long range part. The computation of the potential always requires quantum mechanics, since it involves the motion of the electrons. To compute the nuclear dynamics, classical mechanics is generally a good starting point. At lower temperatures, one has to consider quantum effects, such as tunneling, 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 around 1 K. The cosmic background radiation has a temperature of 2.76 K, and presumably no parts of the universe are colder than that. However, in lab experiments such low temperatures can be reached. At temperatures around 1 K molecules have a kinetic energy that is comparable to the interaction energy of the molecules with electric and magnetic fields that are achievable in experiments. This provides many opportunities to study and manipulate cold gases and this has become an active area of research[11].

II. CLASSICAL CAPTURE THEORY

A. Classical central force problem

To introduce the key concepts of low energy scattering theory we review the problem of two point particles interacting through a potential $V(r)$ that only depends on the distance r between the two particles. Let the positions of the particles A and B , with masses m_A and m_B , be given by the Cartesian coordinates \mathbf{r}_A and \mathbf{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, i.e., the coordinates of the center of mass of the system,

$$\mathbf{R}_{CM} = \frac{m_A \mathbf{r}_A + m_B \mathbf{r}_B}{m_A + m_B} \quad (2)$$

and the relative coordinates

$$\mathbf{r} = \mathbf{r}_B - \mathbf{r}_A. \quad (3)$$

The classical kinetic energy of the system is given by

$$T = \frac{1}{2} m_A \dot{\mathbf{r}}_A \cdot \dot{\mathbf{r}}_A + \frac{1}{2} m_B \dot{\mathbf{r}}_B \cdot \dot{\mathbf{r}}_B = \frac{1}{2} M \dot{\mathbf{R}} \cdot \dot{\mathbf{R}} + \frac{1}{2} \mu \dot{\mathbf{r}} \cdot \dot{\mathbf{r}}, \quad (4)$$

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. The center of mass of the system moves with a constant velocity. The relative motion is decoupled from the center of mass and the equations of motion for \mathbf{r} correspond to the equations of motion of a single particle with mass μ moving in a potential $V(r)$. The conjugate momentum \mathbf{p} is defined by

$$p_i = \frac{\partial T}{\partial \dot{r}_i} = \mu \dot{r}_i, \quad (5)$$

where $i = 1, 2, 3$ labels the Cartesian components of the vectors. The classical Hamiltonian of the system can be expressed as a function of coordinates and their conjugate momenta as

$$H = \frac{p^2}{2\mu} + V(r). \quad (6)$$

The Hamilton-Jacobi equations of motion are given by

$$\dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{\mu} \quad (7)$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\frac{\partial V(r)}{\partial r_i} = -\frac{\partial r}{\partial r_i} \frac{\partial V(r)}{\partial r} = -\frac{r_i}{r} \frac{\partial V(r)}{\partial r}. \quad (8)$$

With $\mathbf{r} = r\hat{\mathbf{r}}$, these equations may be written in vector notation as

$$\dot{\mathbf{r}} = \mu^{-1}\mathbf{p} \quad (9)$$

$$\dot{\mathbf{p}} = -\hat{\mathbf{r}} \frac{\partial V(r)}{\partial r}. \quad (10)$$

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 $\mathbf{F} = \mu\ddot{\mathbf{r}}$, where the force \mathbf{F} is seen to be equal to $\dot{\mathbf{p}}$.

The angular momentum of the system,

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} \quad (11)$$

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

$$\dot{\mathbf{l}} = \dot{\mathbf{r}} \times \mathbf{p} + \mathbf{r} \times \dot{\mathbf{p}} = \mu^{-1}\mathbf{p} \times \mathbf{p} - r \frac{\partial V(r)}{\partial r} \hat{\mathbf{r}} \times \hat{\mathbf{r}} = \mathbf{0}. \quad (12)$$

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

$$l^2 = \mathbf{l} \cdot \mathbf{l} = (\mathbf{r} \times \mathbf{p}) \cdot (\mathbf{r} \times \mathbf{p}) = (\mathbf{r} \cdot \mathbf{r})(\mathbf{p} \cdot \mathbf{p}) - (\mathbf{r} \cdot \mathbf{p})(\mathbf{r} \cdot \mathbf{p}) = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2. \quad (13)$$

Defining the momentum along the vector \mathbf{r} as $p_r \equiv \hat{\mathbf{r}} \cdot \mathbf{p}$, we may rewrite the equation as

$$r^2 p^2 = l^2 + r^2 p_r^2, \quad (14)$$

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

$$H = \frac{p^2}{2\mu} + V(r) = \frac{l^2}{2\mu r^2} + \frac{p_r^2}{2\mu} + V(r) \quad (15)$$

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

$$V_{\text{eff}}(r) = \frac{l^2}{2\mu r^2} + V(r), \quad (16)$$

where the first term is called the centrifugal term. The equation of motion for r is

$$\mu\ddot{r} = -\frac{dV_{\text{eff}}(r)}{dr}. \quad (17)$$

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

$$\hat{\mathbf{r}} = \mathbf{e}_x \cos \varphi + \mathbf{e}_y \sin \varphi, \quad (18)$$

where \mathbf{e}_x and \mathbf{e}_y are two orthonormal vectors in the plane perpendicular to \mathbf{l} and φ is a time dependent polar angle. For the time derivative of the direction $\hat{\mathbf{r}}$ we have

$$\dot{\hat{\mathbf{r}}} = \dot{\varphi}(-\mathbf{e}_x \sin \varphi + \mathbf{e}_y \cos \varphi) = \dot{\varphi} \hat{\mathbf{r}}_{\perp} \quad (19)$$

From Eqs. (11) and (9) we have

$$\mathbf{l} = \mu r^2 \hat{\mathbf{r}} \times \dot{\hat{\mathbf{r}}} = \mu r^2 \dot{\varphi} \hat{\mathbf{r}} \times \hat{\mathbf{r}}_{\perp} \quad (20)$$

and so

$$l = \mu r^2 \dot{\varphi}. \quad (21)$$

Since l is a constant and $r(t)$ can be found from Eq. (17) the angle φ is given by the integral

$$\varphi(t) = \varphi(0) + \int_0^t \frac{l}{\mu r(t)^2} dt. \quad (22)$$

As initial conditions ($t = 0$) we assume the particle is in the xy -plane with a large positive value of the x coordinate, moving in the negative \mathbf{e}_x direction

$$\dot{\mathbf{r}}(0) = -v\mathbf{e}_x \quad (23)$$

and the position at ($t = 0$) is

$$\mathbf{r}(0) = a\mathbf{e}_x + b\mathbf{e}_y. \quad (24)$$

The coefficient b , which is taken positive, is called the *impact parameter*. If the potential $V(r)$ would be zero then $\mathbf{r}(t)$ would move parallel to the x -axis and pass the origin at a distance b , i.e., the impact parameter would correspond to the nearest approach of the two particles. By substituting Eqs. (23) and (24) into (11) we get

$$\mathbf{l} = -v(a\mathbf{e}_x + b\mathbf{e}_y) \times \mathbf{e}_x = \mu v b \mathbf{e}_z \quad (25)$$

and we find how the impact parameter, the initial velocity, and the reduced mass determine the angular momentum of the system

$$l = \mu v b. \quad (26)$$

When l is known the effective potential Eq. (16) is known and Eq. (17) can be solved to find $r(t)$. The result may be substituted into Eq. (22) to find the full trajectory.

B. Cross sections

Collisions may be *elastic*, *inelastic*, or *reactive*. In an elastic collision the direction of relative motion of the particles changes. In the center of mass frame, the speeds of the particles are conserved. However, in the laboratory-fixed frame speeds may change as a result of collisions. By this mechanism, 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[12]. For this reason 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. Molecules with nonzero spin, and hence with a magnetic moment, can be trapped in a magnetic field. In a collision the orientation of the spin may change into a state that is expelled from the trap, and hence 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. If a reaction only occurs when the impact parameter b of the trajectory is less than b_{\max} , then the cross section for that process is

$$\sigma = \pi b_{\max}^2. \quad (27)$$

The cross section has the dimension 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 on the impact parameter and on the energy, $0 \leq P(b, E) \leq 1$. In this case the cross section is given by

$$\sigma(E) = 2\pi \int_0^{\infty} P(b, E) b db. \quad (28)$$

The function $P(b, E)$ is called the *opacity* function. Cross sections for elastic and inelastic processes are defined in a similar way.

C. Canonical reaction rates

For a binary process



the time development of the concentrations $[A]$, $[B]$, and $[C]$ (in *molecules cm⁻³*) is given by

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k(T)[A][B], \quad (29)$$

where $k(T)$ is the temperature dependent reaction rate in *cm³s⁻¹/molecule*. It may be computed as the Boltzmann average of the cross section $\langle v\sigma(E) \rangle$,

$$k(T) = \int_0^\infty v\sigma(E)f(v)dv, \quad (30)$$

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. (29) will no longer apply, as we shall see in Section xxx. The Maxwell-Boltzmann speed distribution for particles with mass m is given by

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}, \quad (31)$$

where k is Boltzmann's constant. The distribution is normalized such that

$$\int_0^\infty f(v)dv = 1. \quad (32)$$

For the average kinetic energy we have

$$\int_0^\infty \frac{1}{2}mv^2 f(v)dv = \frac{3}{2}k_B T \quad (33)$$

and the average speed of the particles is

$$\bar{v} = \int_0^\infty v f(v)dv = \sqrt{\frac{8k_B T}{m\pi}}. \quad (34)$$

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

$$\bar{T} = \frac{m_2 T_1 + m_1 T_2}{m_1 + m_2} \quad (35)$$

and m by the reduced mass μ . 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., $T_2 \ll T_1$, we must use

$$\bar{T} = \frac{m_2}{m_1 + m_2} T_1 = \frac{\mu}{m_1} T_1. \quad (36)$$

The rate constant may also be written as an integral over the relative kinetic energy $E = \frac{1}{2}\mu v^2$, using $dE = \mu v dv$,

$$k(T) = \sqrt{\frac{8k_B T}{\pi\mu}} \frac{1}{(k_B T)^2} \int_0^\infty \sigma(E) e^{-E/k_B T} E dE. \quad (37)$$

Substituting $x = \frac{E}{k_B T}$ and $\bar{v} = \sqrt{\frac{8k_B T}{\mu\pi}}$ gives

$$k(T) = \bar{v} \int_0^\infty \sigma(xk_B T) e^{-x} x dx = \bar{v} \bar{\sigma}. \quad (38)$$

This shows that if $\sigma(E)$ is constant, then $k(T) \propto \bar{v} \propto \sqrt{E}$. Equation (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.

D. 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. For nonzero impact parameter $b > 0$ the system has nonzero angular momentum $l = \mu v b$ and the effective potential contains a repulsive centrifugal term [Eq. (16)], which may give rise to a centrifugal barrier. It is assumed that trajectories contribute to the cross section if, and only if they pass 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 $1/r$. By assuming a long range interaction of the form

$$V_n(r) = -\frac{c_n}{r^n}, \quad (39)$$

where $c_n > 0$ 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. We do not consider $n = 1$, i.e., ion-ion collisions. First, we find the maximum in the effective potential by solving

$$\frac{d}{dr} V_{\text{eff}}(r) = -\frac{l^2}{\mu r^3} + \frac{nc_n}{r^{n+1}} = 0. \quad (40)$$

The solution $r = r_0$ is

$$r_0 = \left(\frac{n\mu c_n}{l^2} \right)^{\frac{1}{n-2}}. \quad (41)$$

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

$$V_{\text{eff}}(r_0) = \frac{l^2}{2\mu r_0^2} - \frac{c_n}{r_0^n} = \left(\frac{l^2}{\mu} \right)^{\frac{n-2}{n-2}} \frac{n-2}{2n} (nc_n)^{-\frac{2}{n-2}}. \quad (42)$$

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

$$l_{\text{max}}^2 = \mu n (c_n)^{\frac{2}{n}} \left(\frac{2E}{n-2} \right)^{\frac{n-2}{n}}, \quad (43)$$

a corresponding maximum impact parameter

$$b_{\text{max}} = \frac{l_{\text{max}}}{\mu v}, \quad (44)$$

a cross section

$$\sigma(E) = \pi b_{\text{max}}^2 = \frac{\pi}{2} n \left(\frac{2}{n-2} \right)^{\frac{n-2}{n}} \left(\frac{c_n}{E} \right)^{2/n}, \quad (45)$$

and a rate

$$k(T) = \sqrt{\frac{2\pi}{\mu}} n \left(\frac{2}{n-2} \right)^{\frac{n-2}{n}} (c_n)^{2/n} (k_B T)^{\frac{n-4}{2n}} \Gamma\left(2 - \frac{2}{n}\right), \quad (46)$$

where the Gamma function is defined by

$$\Gamma(n) = \int_0^\infty x^{n-1} e^{-x} dx. \quad (47)$$

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 $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$. For integer values $\Gamma(n+1) = n!$.

The position of the centrifugal barrier with height E is found by substituting Eq. (43) into Eq. (41),

$$r_0 = \left(\frac{(n-2)c_n}{2E} \right)^{1/n}. \quad (48)$$

TABLE I: Classical capture theory energy dependent cross sections $\sigma_n(E)$ and temperature dependent reaction rates $k_n(T)$ for $-c_n/r^n$ long range potentials.

n	$\sigma_n(E)$	$k_n(T)$
2	$\pi c_2/E$	$2\sqrt{\frac{2\pi}{\mu}} c_2 (k_B T)^{-1/2}$
3	$\frac{3\pi}{\sqrt{2}} (c_3/E)^{2/3}$	$4\sqrt{\frac{\pi}{3\mu}} \Gamma(1/3) (c_3)^{2/3} (k_B T)^{-1/6}$
4	$2\pi\sqrt{c_4/E}$	$2\pi\sqrt{\frac{2c_4}{\mu}}$
5	$5\pi\sqrt{2} 3^{-3/2} (c_5/E)^{2/5}$	$5\sqrt{\frac{2\pi}{\mu}} \left(\frac{2}{3}\right)^{3/2} (c_5)^{2/5} (k_B T)^{1/10} \Gamma(3/5)$
6	$\frac{3\pi}{4} (c_6/E)^{1/3}$	$2^{11/6} \Gamma(2/3) \sqrt{\frac{\pi}{\mu}} (c_6)^{1/3} (k_B T)^{1/6}$

For the model to be valid, the potential for $r \geq r_0$ must be given to a good approximation by the leading long range term $V_n(r)$.

Capture theory was first developed by Langevin in 1905, who studied reactions between ions and polarizable atoms. In that case the interaction is proportional to r^{-4} and the long range coefficient is given by

$$c_4 = \frac{1}{2} \alpha q^2, \quad (49)$$

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

$$k_{\text{Langevin}}(T) = 2\pi q \sqrt{\frac{\alpha}{\mu}}. \quad (50)$$

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. When there are no electrostatic interactions between two atoms or molecules, the leading long range term is proportional to r^{-6} . This interaction term is called the dispersion interaction.

E. Anisotropic interactions

The first order electrostatic interaction between two neutral molecules with a nonzero dipole moment is proportional to r^{-3} . However, we cannot use the $k_3(T)$ 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

$$V(r, \theta_1, \phi_1, \theta_2, \phi_2) = -\frac{\mu_1 \mu_2}{r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)], \quad (51)$$

where r is the distance between the centers of mass of the molecules, μ_1 and μ_2 are the magnitudes of the dipole moments of the molecules, and (θ_1, ϕ_1) and (θ_2, ϕ_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 z -axis is the parallel to the vector pointing from the center of mass of molecule 1 to the center of mass of molecule 2. In principle, the classical capture rate can be found by computing a large number of classical trajectories and by determining for each trajectory whether or not it crosses the centrifugal barrier. One strategy is to determine the opacity function as the fraction of “reactive trajectories” for a given impact parameter b , and use Eq. (28), where the integral over b is also done numerically.

An approximate analytical result can be found with the Infinite Order Sudden Approximation. In this approximation the expression for $k_3(T)$ is found as the average over all orientations of both dipole vectors, setting the rate equal to zero whenever the interaction for a certain orientation is repulsive. When the interaction is attractive an orientation dependent c_3 coefficient is determined from Eq. (51) and the formula from table I is used. Reorientation of the molecules during the collision is not taken into account. The result of the procedure is

$$k_3^{\text{dip-dip}}(T) = 1.765 (\mu_1 \mu_2)^{2/3} \sqrt{\frac{\pi}{\mu}} (k_B T)^{-1/6}. \quad (52)$$

More cases can be found in Ref. [9].

III. QUANTUM CAPTURE THEORY

So far, our treatment was completely classical. Quantum mechanics requires several modifications of the model. First of all, in quantum mechanics angular momenta are quantized. For clarity, we will, from now on, use l_c^2 for the classical angular momentum squared, and $l(l+1)\hbar^2$ as the quantum expression, where l is a nonnegative integer and \hbar is Planck's constant divided by 2π . The wave functions corresponding to different values of the quantum number l are referred to as *partial waves*. The classical expression $l_c = \mu v b$ [Eq. (26)] shows that for a fixed value of l_c , the impact parameter b goes to infinity when the velocity v goes to zero. This suggests that when the temperature approaches zero, only the $l = 0$ partial wave can contribute to cross sections, and in general, that at lower temperatures fewer partial waves contribute than at higher temperatures.

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

In the classical capture theory, trajectories are assumed reactive when the energy is above the centrifugal barrier, and nonreactive otherwise. In quantum mechanics tunneling 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 of a collision event.

A. 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 $|\mathbf{n}\rangle$. For example, for a system consisting of two diatomic molecules in a certain rovibrational state we have $|\mathbf{n}\rangle = |v_a j_a m_a, v_b j_b m_b\rangle$, where v_a, v_b are the vibrational quantum number, j_a and j_b are the diatom angular momentum quantum numbers and m_a and m_b are the projections of the angular momenta on a space fixed axis. A flux normalized plane wave with wave vector $\mathbf{k}_n = k_n \hat{\mathbf{k}}$ is given by

$$\Psi_{\mathbf{n}}^{\text{pw}} = |\mathbf{n}\rangle v_n^{-\frac{1}{2}} e^{i\mathbf{k}_n \cdot \mathbf{r}} = |\mathbf{n}\rangle v_n^{-\frac{1}{2}} \sum_l i^l (2l+1) j_l(k_n r) P_l(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}), \quad (53)$$

where P_l is a Legendre polynomial and j_l a spherical Bessel function of the first kind. Using the spherical harmonic addition theorem

$$P_l(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}) = \frac{4\pi}{2l+1} \sum_{m_l=-l}^l Y_{lm_l}(\hat{\mathbf{r}}) Y_{lm_l}(\hat{\mathbf{k}})^* \quad (54)$$

and the asymptotic form of the spherical Bessel function

$$j_l(z) \approx \frac{\sin(z - l\pi/2)}{z} = \frac{e^{i(z-l\pi/2)} - e^{-i(z-l\pi/2)}}{2iz} \quad (55)$$

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

$$\Psi_{\mathbf{n}}^{\text{pw}} \approx \frac{2\pi}{ik_n r} \sum_{lm_l} |\mathbf{n}\rangle v_n^{-\frac{1}{2}} Y_{lm_l}(\hat{\mathbf{r}}) [e^{i(k_n r - l\pi/2)} - e^{-i(k_n r - l\pi/2)}] i^l Y_{lm_l}(\hat{\mathbf{k}})^*. \quad (56)$$

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

$$\begin{aligned} \Psi_{\mathbf{n}}^{\text{sc}} \approx & \frac{2\pi}{ik_n r} \sum_{lm_l} \sum_{\mathbf{n}'} \sum_{l'm_l'} |\mathbf{n}'\rangle v_{n'}^{-\frac{1}{2}} Y_{l'm_l'}(\hat{\mathbf{r}}) \\ & \times [-e^{-i(k_n r - l\pi/2)} \delta_{\mathbf{n}'\mathbf{n}} \delta_{l'l} \delta_{m_l'm_l} + e^{i(k_n r - l\pi/2)} S_{\mathbf{n}'l'm_l';nlm_l}] i^l Y_{lm_l}(\hat{\mathbf{k}})^*. \end{aligned} \quad (57)$$

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 ,

$$\Psi_{\mathbf{n},l,m_l} = \frac{1}{r} \sum_{\mathbf{n}'} \sum_{l'm'_l} |\mathbf{n}'\rangle v_{\mathbf{n}'}^{-\frac{1}{2}} Y_{l'm'_l}(\hat{\mathbf{r}}) [-e^{-i(k_{\mathbf{n}'}r - l\pi/2)} \delta_{\mathbf{n}'\mathbf{n}} \delta_{l'l} \delta_{m'_l m_l} + e^{i(k_{\mathbf{n}'}r - l\pi/2)} S_{\mathbf{n}'l'm'_l; \mathbf{n}lm_l}]. \quad (58)$$

These individual solutions are called *partial waves*. The matrix with elements $S_{\mathbf{n}'l'm'_l; \mathbf{n}lm_l}$ is called the S -matrix. It is a complex symmetric unitary matrix. When the potential is zero the S -matrix is a unit-matrix, $S_{\mathbf{n}'l'm'_l; \mathbf{n}lm_l} = \delta_{\mathbf{n}'\mathbf{n}} \delta_{l'l} \delta_{m'_l m_l}$, and the partial waves add up to a plane wave again. The S -matrix is related to the T -matrix through $\mathbf{S} = \mathbf{1} - \mathbf{T}$, where $\mathbf{1}$ is a unit matrix. The scattering wave function of Eq. (57) may be reorganized into an incoming plane wave plus an outgoing spherical wave

$$\Psi_{\mathbf{n}}^{\text{sc}} \approx |\mathbf{n}\rangle v_{\mathbf{n}}^{-\frac{1}{2}} e^{i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}} + \sum_{\mathbf{n}'} |\mathbf{n}'\rangle v_{\mathbf{n}'}^{-\frac{1}{2}} \frac{e^{ik_{\mathbf{n}'}r}}{r} f_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{r}}; \hat{\mathbf{k}}), \quad (59)$$

where the so called *scattering amplitude* is given by

$$f_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{r}}, \hat{\mathbf{k}}) = \frac{2\pi}{ik_{\mathbf{n}}} \sum_{l m_l l' m'_l} i^{l-l'} Y_{l'm'_l}(\hat{\mathbf{r}}) T_{\mathbf{n}'l'm'_l; \mathbf{n}lm_l} Y_{lm_l}(\hat{\mathbf{k}})^*. \quad (60)$$

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

$$\sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{r}}, \hat{\mathbf{k}}) = |f_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{r}}, \hat{\mathbf{k}})|^2. \quad (61)$$

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

$$\sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{k}}) = \iint \sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{r}}, \hat{\mathbf{k}}) d\hat{\mathbf{r}}. \quad (62)$$

Assuming that the incident directions are isotropically distributed, the state-to-state integral cross section is obtained by taking an average over all incoming directions $\hat{\mathbf{k}}$

$$\sigma_{\mathbf{n}' \leftarrow \mathbf{n}} = \frac{1}{4\pi} \iint \sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(\hat{\mathbf{k}}) d\hat{\mathbf{k}} = \frac{\pi}{k_{\mathbf{n}}^2} \sum_{l m_l l' m'_l} |T_{\mathbf{n}'l'm'_l; \mathbf{n}lm_l}|^2 = \frac{\pi}{k_{\mathbf{n}}^2} P_{\mathbf{n}'\mathbf{n}}, \quad (63)$$

where we introduced the reaction probability matrix \mathbf{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* γ to the quantum numbers \mathbf{n} that describe the molecules. This modification is sufficient as long as three-body breakup cannot occur.

B. 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 l', m'_l in Eq. (63), excluding the diagonal element, gives at most one for each column. This is still true if we sum over all possible reaction products \mathbf{n}' . Thus, the maximum contribution of the partial wave with a given l to the inelastic or reactive cross section for some initial state $|\mathbf{n}\rangle$ is given by

$$\sigma_{\mathbf{n},l}^{\text{max}} = \frac{\pi}{k_{\mathbf{n}}^2} (2l + 1), \quad (64)$$

where the factor $(2l + 1)$ arises from the summation over m_l . Assuming that all partial waves up to some maximum value l_{max} are fully reactive and higher partial waves are nonreactive, gives an initial state selected cross section

$$\sigma_{\mathbf{n}} = \sum_{l=0}^{l_{\text{max}}} \sigma_{\mathbf{n},l}^{\text{max}} = \frac{\pi}{k_{\mathbf{n}}^2} (l_{\text{max}} + 1)^2. \quad (65)$$

To compare this result to the classical expression Eq. (27) we associate an angular momentum squared l_c^2 with $\hbar^2 l_{\max}(l_{\max} + 1)$. Using Eq. (26) this gives

$$b_{\max}^2 = \frac{\hbar^2 l_{\max}(l_{\max} + 1)}{\mu^2 v^2} \quad (66)$$

and with $\mu v = p = \hbar k_{\mathbf{n}}$ this gives

$$\sigma = \pi b_{\max}^2 = \frac{\pi}{k_{\mathbf{n}}^2} l_{\max}(l_{\max} + 1). \quad (67)$$

One expects the classical theory only to work when a sufficient number of partial waves contribute, in which case $l_{\max}(l_{\max} + 1) \approx (l_{\max} + 1)^2$.

C. 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 that is located entirely in the reactant arrangement. The computation then becomes very similar to a coupled channels calculation for inelastic scattering. The only difference is that the boundary conditions at small r are different. The wave function is not assumed to be finite, but the flux is assumed to be inwards at some point $r = r_a$. 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 the Hamiltonian is written as the sum of the radial kinetic energy operator and the remainder ($\Delta\hat{H}$),

$$\hat{H} = -\frac{\hbar^2}{2\mu} r^{-1} \frac{d^2}{dr^2} r + \Delta\hat{H} \quad (68)$$

and the Schrödinger equation in the reactant arrangement is written as

$$\frac{\hbar^2}{2\mu} r^{-1} \frac{d^2}{dr^2} r \Psi = (\Delta\hat{H} - E) \Psi. \quad (69)$$

The wave function is expanded in channel functions $|\mathbf{n}'\rangle$,

$$\Psi_{\mathbf{n}} = r^{-1} \sum_{\mathbf{n}'} |\mathbf{n}'\rangle U_{\mathbf{n}'\mathbf{n}}(r), \quad (70)$$

where each column of the matrix $\mathbf{U}(r)$ defines a wave function. To keep the notation short we assume that the partial wave quantum numbers l and m_l are included in \mathbf{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

$$\mathbf{U}''(r) = \mathbf{W}(r)\mathbf{U}(r), \quad (71)$$

where the primes denote derivatives with respect to r and the coupling matrix is given by

$$\mathbf{W}_{\mathbf{n}'\mathbf{n}}(r) = \frac{2\mu}{\hbar^2} \langle \mathbf{n}' | \Delta\hat{H} - E | \mathbf{n} \rangle. \quad (72)$$

In an inelastic scattering problem the condition that the wave function is finite gives the boundary condition that $\mathbf{U}(r=0) = \mathbf{0}$. This boundary condition, together with the coupled channels equation (71), defines a linear relation between the expansion coefficients and their derivatives with respect to r ,

$$\mathbf{U}'(r) = \mathbf{Y}(r)\mathbf{U}(r), \quad (73)$$

where $\mathbf{Y}(r)$ 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 $\Delta\hat{H} = V(r)$, this means that around some point $r = r_a$ the wave function has the form e^{-ikr} , where k is the wave number at $r = r_a$, i.e.,

$$\frac{\hbar^2 k^2}{2\mu} = E - V(r_a) \quad (74)$$

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

$$\mathbf{W}(r_a)\mathbf{Q}(r_a) = \mathbf{Q}(r_a)\mathbf{\Lambda}(r_a), \quad (75)$$

where $\mathbf{\Lambda}(r_a)$ is a diagonal matrix with eigenvalues and the columns of the matrix $\mathbf{Q}(r_a)$ are the eigenvectors of the matrix $\mathbf{W}(r_a)$. The negative eigenvalues correspond to open channel eigenfunctions, with $\mathbf{\Lambda}_{oo} = -k_o^2$, and the positive eigenvalues correspond to closed channel eigenfunctions with $\mathbf{\Lambda}_{cc} = k_c^2$. Transforming the coupled channels problem to the channel eigenfunction basis with

$$\tilde{\mathbf{U}}(r) = \mathbf{Q}^\dagger(r_a)\mathbf{U}(r) \quad (76)$$

gives

$$\tilde{\mathbf{U}}''(r) = \mathbf{Q}^\dagger(r_a)\mathbf{W}(r)\mathbf{Q}(r_a)\tilde{\mathbf{U}}(r) \approx \mathbf{\Lambda}(r_a)\tilde{\mathbf{U}}(r). \quad (77)$$

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

$$\tilde{\mathbf{U}}_{oo}(r) = e^{-ik_o r} \quad (78)$$

and the boundary conditions for closed channels are

$$\tilde{\mathbf{U}}_{cc}(r) = e^{k_c r}. \quad (79)$$

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

$$\tilde{\mathbf{Y}}_{ii}(r_a) = [\mathbf{Q}^\dagger\mathbf{Y}(r_a)\mathbf{Q}]_{ii} = \begin{cases} -ik_i, & \text{for open channels,} \\ k_i, & \text{for closed channels.} \end{cases} \quad (80)$$

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

$$\mathbf{Y}(r_a) = \mathbf{Q}(r_a)\tilde{\mathbf{Y}}(r_a)\mathbf{Q}^\dagger(r_a). \quad (81)$$

The boundary conditions Eqs. (78) and (79) apply if the channel eigenvalues $\mathbf{\Lambda}(r)$ 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. [13].

The general technique to propagate the log-derivative matrix to some point $r = r_b$ sufficiently far outside the centrifugal barrier relies on dividing $[r_a, r_b]$ in a set of small sectors $[r_n, r_{n+1}]$. In each sector one determines a so called imbedding type propagator defined by

$$\begin{bmatrix} \mathbf{U}'_n \\ \mathbf{U}'_{n+1} \end{bmatrix} = \begin{bmatrix} \mathcal{Y}_1^{(n)} & \mathcal{Y}_2^{(n)} \\ \mathcal{Y}_3^{(n)} & \mathcal{Y}_4^{(n)} \end{bmatrix} \begin{bmatrix} -\mathbf{U}_n \\ \mathbf{U}_{n+1} \end{bmatrix}, \quad (82)$$

where $\mathbf{U}_n = \mathbf{U}(r_n)$. The minus sign in the definition is not essential, but with this choice one can show that $\mathcal{Y}_2^{(n)} = \mathcal{Y}_3^{(n)}$. To find the propagator one can diagonalise the \mathbf{W} 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 $\mathbf{W}(r)$ matrix to change linearly over the interval, and correct for nonzero coupling with a Green's function technique. Once the sector propagator is found it can be used to propagate the log-derivative matrix at $r = r_n$, defined by

$$\mathbf{U}'_n = \mathbf{Y}(r_n)\mathbf{U}_n \quad (83)$$

to r_{n+1} :

$$\mathbf{Y}(r_{n+1}) = \mathcal{Y}_4^{(n)} - \mathcal{Y}_3^{(n)}[\mathbf{Y}(r_n) + \mathcal{Y}_1^{(n)}]^{-1}\mathcal{Y}_2^{(n)}. \quad (84)$$

In this way, the log-derivative matrix can be propagated to $r = r_b$. For sufficiently large r the S -matrix boundary conditions for $\mathbf{U}(r)$ are given by

$$\mathbf{U}(r) = -\mathbf{I}(r) + \mathbf{O}(r)\mathbf{S}, \quad (85)$$

where $\mathbf{I}(r)$ is a diagonal matrix with flux normalized incoming waves

$$\mathbf{I}_{\mathbf{n},\mathbf{n}}(r) = v_{\mathbf{n}}^{-\frac{1}{2}} e^{-i(k_{\mathbf{n}}r - l\pi/2)} \quad (86)$$

and $\mathbf{O}(r) = \mathbf{I}(r)^*$ are the outgoing waves. By substituting the asymptotic form of the wave function in the defining relation of the log-derivative matrix [Eq. (73)] we can relate the \mathbf{S} matrix to the log-derivative matrix

$$\mathbf{S}(E) = [\mathbf{Y}(r_b)\mathbf{O}(r_b) - \mathbf{O}'(r_b)]^{-1}[\mathbf{Y}(r_b)\mathbf{I}(r_b) - \mathbf{I}'(r_b)]. \quad (87)$$

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

$$P_{nlm_l}(E) = 1 - \sum_{\mathbf{n}'l'm'_l} |S_{\mathbf{n}'l'm'_l;nlm_l}(E)|^2 \quad (88)$$

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

$$\sigma_{\mathbf{n}}(E) = \frac{\pi}{k_{\mathbf{n}}^2} \sum_{lm_l} P_{nlm_l}(E). \quad (89)$$

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 product arrangements which, together with a statistical model to describe the complex, provides partial information about the product state distribution[13].

D. Quantum adiabatic capture theory

At low temperatures the collision time is long compared to characteristic vibrational and rotational timescales in 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. Solving the Schrödinger equation for the fast motion amounts to diagonalising the $\mathbf{W}(r)$ matrix on a grid of r points, as in Eq. (75) and treating the eigenvalues $\Lambda_{nn}(r_a)$ as uncoupled one-dimensional potentials (multiplied by a factor $2\mu/\hbar^2$). 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 channel eigenfunction basis are never transformed back to the original basis. The result is again a capture probability for each initial state \mathbf{n} , and the capture cross section is obtained as in Eq. (89).

Often, the result of this approximation is in good agreement with full coupled channels capture theory. [9, 14, 15] 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 possible initial states, in the case of thermal equilibrium. These thermally averaged rates may 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.

E. Thermal capture rates

For an initial state $|\mathbf{n}\rangle$ with channel energy $\epsilon_{\mathbf{n}}$ and kinetic energy $E_{\mathbf{n}}^{(\text{kin})}$ the total energy is

$$E = \epsilon_{\mathbf{n}} + E_{\mathbf{n}}^{(\text{kin})} = \epsilon_{\mathbf{n}} + \frac{\hbar^2 k_{\mathbf{n}}^2}{2\mu}. \quad (90)$$

In time-independent scattering theory one computes the state-to-state cross section as a function of the total energy [Eq. (63)],

$$\sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(E) = \frac{\pi}{k_{\mathbf{n}}^2} P_{\mathbf{n}' \mathbf{n}}(E). \quad (91)$$

The state-to-state temperature dependent reaction rate is given by [Eq. (37)]

$$k_{\mathbf{n}' \leftarrow \mathbf{n}}(T) = \sqrt{\frac{8k_B T}{\pi \mu}} \frac{1}{(k_B T)^2} \int_0^\infty \sigma_{\mathbf{n}' \leftarrow \mathbf{n}}(E) e^{-E_{\mathbf{n}}^{(\text{kin})}/k_B T} E_{\mathbf{n}}^{(\text{kin})} dE_{\mathbf{n}}^{(\text{kin})}. \quad (92)$$

Sometimes, only the Boltzmann averaged reaction rate is required,

$$k(T) = Q_{\text{int}}^{-1}(T) \sum_{\mathbf{n}' \mathbf{n}} k_{\mathbf{n}' \leftarrow \mathbf{n}}(T) e^{-\epsilon_{\mathbf{n}}/k_B T}, \quad (93)$$

where the internal partition function is given by

$$Q_{\text{int}}(T) = \sum_{\mathbf{n}} e^{-\epsilon_{\mathbf{n}}/k_B T}. \quad (94)$$

By substituting Eq. (92) into Eq. (93) and changing the order of integration and summation, one obtains a much simplified expression

$$k(T) = \frac{1}{2\pi \hbar Q_t Q_{\text{int}}} \int_{-\infty}^{\infty} N(E) e^{-\frac{E}{k_B T}} dE, \quad (95)$$

where the translational partition function per volume is given by

$$Q_t = \frac{1}{\hbar^3} \left(\frac{\mu k_B T}{2\pi} \right)^{3/2} \quad (96)$$

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

$$N(E) = \sum_{\mathbf{n}' \mathbf{n}} P_{\mathbf{n}' \mathbf{n}}(E). \quad (97)$$

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. (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.

F. Total angular momentum representation

In Section III A we employed an uncoupled angular basis for two colliding molecules. For an atom-diatom system the uncoupled rotational bases is $|jm_j\rangle|lm_l\rangle$, where $|jm_j\rangle$ is the rotational wave function of the molecule and $|lm_l\rangle$ is the orbital angular momentum of the collision partners. The coupled angular momentum basis is defined by

$$|(jl)JM_J\rangle = \sum_{m_j=-j}^j \sum_{m_l=-l}^l |jm_j\rangle|lm_l\rangle \langle jm_j lm_l | JM_J \rangle, \quad (98)$$

where $\langle jm_j lm_l | JM_J \rangle$ is a Clebsch-Gordan coefficient. The coupled states are eigenfunctions of the total angular momentum operator squared of the system (\hat{J}^2) and of its space-fixed z -component \hat{J}_z . The total angular momentum quantum number J can take the values $|j-l|, |j-l|+1, \dots, j+l$, and the projection quantum number M_J can take the values $-J, -J+1, \dots, J$. For a given j and l there are as many coupled basis functions as uncoupled ones

$$\sum_{J=|l-j|}^{l+j} (2J+1) = (2j+1)(2l+1), \quad (99)$$

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

$$S_{\mathbf{n}'j'l',\mathbf{n}jl}^{J',M'_J;JM_J} = \sum_{m'_j m'_l m_j m_l} \langle J'M'_J | j'm'_j l'm'_l \rangle S_{\mathbf{n}'j'm'_j l'm'_l; \mathbf{n}j m_j m_l} \langle j m_j l m_l | JM_J \rangle. \quad (100)$$

When the system has cylindrical symmetry, i.e., when there is no external field or an external field parallel to the space-fixed z -axis, the projection of the total angular momentum on the z -axis is conserved, i.e., $M'_J = m'_j + m'_l = m_j + m_l = M_J$, and the S -matrix elements are zero when $M'_J \neq M_J$. 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_J ,

$$S_{\mathbf{n}'j'l',\mathbf{n}jl}^{J',M'_J;JM_J} = \delta_{J'J} \delta_{M'_J M_J} S_{\mathbf{n}'j'l',\mathbf{n}jl}^J \quad (101)$$

and the equation 100 may be inverted to give

$$S_{\mathbf{n}'j'm'_j l'm'_l; \mathbf{n}j m_j m_l} = \sum_{JM_J} \langle j'm'_j l'm'_l | J'M_J \rangle S_{\mathbf{n}'j'l',\mathbf{n}jl}^J \langle JM_J | j m_j l m_l \rangle. \quad (102)$$

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

$$\sum_{m'_j m'_l m_j m_l} P_{\mathbf{n}'j'm'_j l'm'_l; \mathbf{n}j m_j m_l} = \sum_J (2J+1) P_{\mathbf{n}'j'l',\mathbf{n}jl}^J \quad (103)$$

where the factor $(2J+1)$ is the result of summing over M_J .

To construct a total angular momentum basis for two colliding molecules one must first couple the rotational wave functions of the molecules, $|j_a m_a\rangle$ and $|j_b m_b\rangle$ to a coupled basis $|j_a j_b j m_j\rangle$, which in turn can be coupled with the end-over-end rotational function $|l m_l\rangle$ to obtain the total angular momentum basis functions $| \{j_a j_b j l\} JM_J \rangle$.

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.

IV. WIGNER THRESHOLD LAWS

Already in the early days of quantum mechanics, solutions of the Schrödinger equation in the limit of low collision energies were analysed and expressions were found for the energy-dependence of cross sections. 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 $l=0$ partial wave, and the cross section is energy independent. The inelastic cross section is also dominated by the s -wave, but it increases as $E^{-\frac{1}{2}}$ when the collision energy E is sufficiently low. Here we will derive the general results obtained by Wigner in 1948. These results are known as the Wigner threshold laws.

A. 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 Fig. 1. The potential $V(x) = 0$ for $x < 0$ and $V(x) = V_0 < 0$ for $x > 0$. A classical particle with mass μ 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 the wave function consists of a unit flux incoming part and a reflected part for $x < 0$,

$$\Psi_L(x) = v^{-\frac{1}{2}} (e^{ikx} - R e^{-ikx}) \quad (104)$$

and a transmitted part for $x > 0$,

$$\Psi_R(x) = v_0^{-\frac{1}{2}} T e^{ik_0 x}. \quad (105)$$

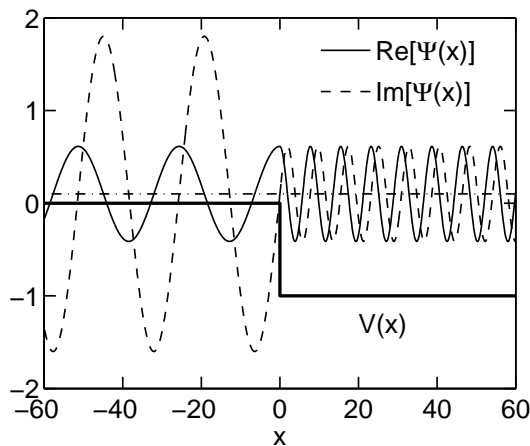


FIG. 1: Real and imaginary part of the scattering wave function for a one-dimensional step-function potential $V(x)$.

The total energy is

$$E = \frac{\hbar^2 k^2}{2\mu} = V_0 + \frac{\hbar^2 k_0^2}{2\mu} \quad (106)$$

with $v = \hbar k/\mu$ 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

$$T = \frac{2\alpha}{\alpha^2 + 1} \quad (107)$$

$$R = \frac{1 - \alpha^2}{\alpha^2 + 1} \quad (108)$$

where $\alpha = \sqrt{k/k_0}$ and $|T|^2 + |R|^2 = 1$. Hence, in this one-dimensional problem, 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, where the probability of reflection is always zero. The quantum effect is sometimes referred to as quantum *suppression*. The classical result is recovered in the high energy limit ($E \gg V_0$, $k \approx k_0$, and $\alpha \approx 1$).

B. *s*-wave elastic scattering

Solutions of the quantum central force problem may be expanded in partial waves

$$\Psi_{lm}(\mathbf{r}) = r^{-1} u_l(r) Y_{lm}(\hat{r}). \quad (109)$$

For $u_0(r)$, the so-called *s*-wave, the radial Schrödinger equation is

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) - E \right] u_0(r) = 0 \quad (110)$$

and the boundary condition at $r = 0$ is $u_0(0) = 0$. As before, we assume that the potential is negligible for $r > r_0$. The log-derivative matrix at r_0 , defined by

$$u'_0(r_0) = Y(r_0) u_0(r_0), \quad (111)$$

is found by propagation from $r = 0$ to $r = r_0$. In this region, the energy

$$E = \frac{\hbar^2 k^2}{2\mu} \quad (112)$$

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,

$$u_0(r) = \sin kr - K \cos kr, \quad \text{for } r > r_0. \quad (113)$$

Here $r^{-1} \sin kr$ is called the regular solution, since $r^{-1} \sin kr$ is finite for $r = 0$, and $r^{-1} \cos kr$ is called the irregular solution. We now assume that $kr_0 \ll 1$ so that we can replace $\sin(kr)$ and $\cos(kr)$ by the leading term in their Taylor expansion for $r = r_0$,

$$u_0(r) \approx kr - K \quad (114)$$

and

$$u'_0(r) \approx k. \quad (115)$$

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 ,

$$K \propto k \propto \sqrt{E}. \quad (116)$$

The S -matrix is related to the K -matrix through

$$S = (1 - iK)(1 + iK)^{-1}. \quad (117)$$

For small K we have to first order in K

$$(1 + iK)^{-1} \approx 1 - iK + \dots \quad (118)$$

so

$$T = 1 - S \approx 1 - (1 - iK)^2 \approx 2iK \quad (119)$$

Hence, the T -matrix is also proportional to k and the elastic s -wave scattering cross section

$$\sigma(E) = \frac{\pi}{k^2} |T|^2 \quad (120)$$

is energy independent for small E .

C. Scattering length

The boundary condition for scattering off a hard sphere with radius r_h is $u_0(r_h) = 0$. The wave function $u_0(r)$ in Eq. (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

$$a = \lim_{k \rightarrow 0} \frac{K}{k}. \quad (121)$$

The scattering length may also be defined in terms of the phase shift δ , which is related to the S -matrix by $S = e^{2i\delta}$, so for small phase shifts we have $S \approx 1 + 2i\delta$ and $K \approx -\delta$. With Eq. (120) and $T \approx 2iK$, the elastic s -wave cross section in the limit of low energy is related to the scattering length through

$$\sigma = 4\pi a^2. \quad (122)$$

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

$$\sigma = \frac{\mu^2}{4\pi\hbar^4} \left| \int \int \int V(\mathbf{r}) d\mathbf{r} \right|^2. \quad (123)$$

Thus, for a δ -function potential

$$V(\mathbf{r}) = \frac{4\pi a \hbar^2}{\mu} \delta(\mathbf{r}), \quad (124)$$

we have

$$\sigma = \frac{\mu^2}{4\pi\hbar^4} \left| \frac{4\pi a\hbar^2}{\mu} \right|^2 = 4\pi a^2. \quad (125)$$

To compute the properties of ultracold gases one often replaces the actual potential by a δ -function potential that gives the same scattering length and hence the same elastic cross section, to simplify the calculations. Notice that a positive scattering length corresponds to a repulsive interaction, and a negative scattering length to an attractive interaction.

D. 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 one may be interested in a process that changes the angular momentum of the molecules. In the absence of external fields the total angular momentum is conserved, so the ingoing and outgoing partial waves cannot both be s -waves.

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

$$\Psi_{nl} = r^{-1} \sum_{\mathbf{n}'l'} |\mathbf{n}'l'\rangle U_{\mathbf{n}'l';nl}(r), \quad (126)$$

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 ,

$$U_{\mathbf{n}'l';nl}(r) \approx f_{nl}(r)\delta_{\mathbf{n}'\mathbf{n}}\delta_{l'l} + g_{\mathbf{n}'l'}(r)K_{\mathbf{n}'l';nl}. \quad (127)$$

The regular waves are defined by

$$f_{nl}(r) = v_{\mathbf{n}}^{-\frac{1}{2}} k_{\mathbf{n}} r j_l(k_{\mathbf{n}} r) \quad (128)$$

and the irregular waves by

$$g_{nl}(r) = v_{\mathbf{n}}^{-\frac{1}{2}} k_{\mathbf{n}} r y_l(k_{\mathbf{n}} r) \quad (129)$$

where y_l is a spherical Bessel functions of the second kind[16]. For $l = 0$ we have the s -wave functions, $zj_0(z) = \sin z$ and $zy_0(z) = -\cos z$. The total energy is conserved,

$$E = \epsilon_{\mathbf{n}} + \frac{\hbar^2 k_{\mathbf{n}}^2}{2\mu} = \epsilon_{\mathbf{n}'} + \frac{\hbar^2 k_{\mathbf{n}'}^2}{2\mu}. \quad (130)$$

We will analyse the wave function for small kinetic energy in the incoming channel $k_{\mathbf{n}} \rightarrow 0$. This means that all inelastic processes must be exothermic, and the kinetic energy in the outgoing channel $|\mathbf{n}'l'\rangle$, $\hbar^2 k_{\mathbf{n}'}^2/2\mu$, is determined by $\epsilon_{\mathbf{n}} - \epsilon_{\mathbf{n}'} \gg \hbar^2 k_{\mathbf{n}}^2/2\mu$. Hence, we will assume $f_{\mathbf{n}'l'}(r)$ and $g_{\mathbf{n}'l'}(r)$ to be 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 $\mathbf{Y}(r_0)$ 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 $k_{\mathbf{n}} r_0 \ll 1$ and the regular and irregular functions are replaced by the leading term in the Taylor expansion. For the Bessel functions we have

$$j_l(k_{\mathbf{n}} r) \approx (k_{\mathbf{n}} r)^l, \quad (131)$$

$$y_l(k_{\mathbf{n}} r) \approx (k_{\mathbf{n}} r)^{-(l+1)}, \quad (132)$$

and hence for the regular and irregular waves around $r = r_0$,

$$f_{nl}(r) \propto k_{\mathbf{n}}^{l+\frac{1}{2}}, \quad (133)$$

$$g_{nl}(r) \propto k_{\mathbf{n}}^{-(l+\frac{1}{2})}. \quad (134)$$

The defining equation for the log-derivative matrix Eq. (73) shows that $\mathbf{Y}(r_0)$ is energy independent only if each column of the matrix $\mathbf{U}(r_0)$ has the same dependence on k_n , since the log-derivative matrix is independent of scaling of the columns of \mathbf{U} . Hence the k_n dependence of the matrix elements $K_{n'l';nl}$ follows from Eq. (127) and the k_n dependence of the regular and irregular waves for the elastic and inelastic channels. Hence, for the elastic K -matrix elements for the incoming channel with small kinetic energy we must have

$$k_n^{l+\frac{1}{2}} \propto k_n^{-(l'+\frac{1}{2})} K_{n'l';nl} \quad (135)$$

or

$$K_{n'l';nl} \propto k_n^{l'+l+1}. \quad (136)$$

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

$$K_{n'l';nl} \propto k_n^{l+\frac{1}{2}}. \quad (137)$$

In the K -matrix there are also elements that relate two exothermic channels, and these must of course be independent of k_n . Hence, the K -matrix, which is real and symmetric, has a block structure

$$\mathbf{K} = \begin{pmatrix} \mathbf{K}_{n,n} & \mathbf{K}_{n',n}^T \\ \mathbf{K}_{n',n} & \mathbf{K}_{n',n'} \end{pmatrix}, \quad (138)$$

Because of the energy independent (n', n') block we cannot directly use the analogue of Eq. (118), but we use instead

$$\mathbf{T} = \mathbf{1} - \mathbf{S} = \mathbf{1} - \frac{\mathbf{1} - i\mathbf{K}}{\mathbf{1} + i\mathbf{K}} = -2i(\mathbf{1} + i\mathbf{K})^{-1}\mathbf{K} \quad (139)$$

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

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix}^{-1} = \begin{pmatrix} (\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1} & -\mathbf{A}^{-1}\mathbf{B}(\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B})^{-1} \\ -\mathbf{D}^{-1}\mathbf{C}(\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1} & (\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B})^{-1} \end{pmatrix} \quad (140)$$

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

$$|T_{n'l';nl}|^2 \propto k_n^{2l+2l'+2} \quad (141)$$

and for low energy inelastic scattering

$$|T_{n'l';nl}|^2 \propto k_n^{2l+1}. \quad (142)$$

Hence, for elastic cross sections we find

$$\sigma_{n'l' \leftarrow nl} \propto k_n^{2l+2l'} \quad (143)$$

and for the inelastic cross sections

$$\sigma_{n'l' \leftarrow nl} \propto k_n^{2l-1}. \quad (144)$$

We find again that for low energy s -wave scattering, $l = l' = 0$, the cross sections are energy-independent. The s -wave inelastic cross sections depend on the kinetic energy as $E_{\text{kin}}^{-\frac{1}{2}}$, which 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 $1/r^4$ potential. The effect of the long-range potential in the quantum regime is discussed in Ref. [17]. It is concluded that the formula for low energy inelastic T -matrix elements is valid if the potential falls off in the long range more rapidly than $1/r^2$. The formula for single channel elastic scattering is valid if $l > (n-3)/2$ for a long range potential $-c_n/r^n$, while $T_{l,l} \propto k_n^{n-2}$ otherwise.

For processes that result in a change of the angular momentum projection quantum number by Δm , but which do not change the internal energy, the threshold law for the cross section is $k_n^{\Delta m}$ when Δm is even and $k_n^{\Delta m+1}$ for m is odd[18].

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.

Here we 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. [19].

V. ULTRACOLD CHEMISTRY

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 modeled as three-dimensional harmonic oscillators. In a $T = 0$ 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 in the exact same quantum state.

So far, we assumed that the rate of a reaction is determined by the collision rate and the cross section for two-particle collisions. When considering reactions in a $T = 0$ Bose gas, this is no longer appropriate, since the bosons occupy the same wave function, the “collisions” occur simultaneously throughout the trap, and 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^{-15} cm^{-1} (1 cm^{-1} corresponds to 1.44 K). As a result of a quantum statistical effect, however, 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. It happens when the density is on the order of one particle per Λ^3 , where Λ is the thermal de Broglie wavelength. For a particle of mass m , Λ is given by

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (145)$$

In the next section we will derive this result for an ideal Bose gas. Section VD, 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.

A. Particle in a box

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

$$\epsilon_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2, \quad n = 1, 2, 3, \dots \quad (146)$$

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

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin n \frac{\pi x}{a}. \quad (147)$$

The canonical partition function for *distinguishable particles* at a temperature T is

$$q_t(T) = \sum_{n=1}^{\infty} e^{-\beta \epsilon_n}, \quad (148)$$

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

$$q_t(T) = \int_0^{\infty} e^{-\beta \frac{\hbar^2 \pi^2}{2ma^2} n^2} dn = \frac{a}{\Lambda}, \quad (149)$$

when the box is sufficiently large, or when the temperature is sufficiently high (and β small). For a three-dimensional box the energy levels are

$$\epsilon_{\mathbf{n}} = \epsilon_{n_x} + \epsilon_{n_y} + \epsilon_{n_z} \quad (150)$$

and the wave functions are

$$\phi_{\mathbf{n}}(\mathbf{r}) = \phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z). \quad (151)$$

B. Bose-Einstein condensation

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

$$Z(V, T, \mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q(N, V, T), \quad (152)$$

where V is the volume, μ is the chemical potential, N is the number of bosons, and Q is the canonical partition function. For an ideal Bose gas, this expression becomes[20]

$$Z(V, T, \mu) = \prod_k \frac{1}{1 - \lambda e^{-\beta\epsilon_k}}, \quad (153)$$

where k runs over all single particle energy levels and λ is the fugacity

$$\lambda = e^{\beta\mu} = e^{\frac{\mu}{k_B T}}. \quad (154)$$

The equation of state of the ensemble is

$$pV = k_B T \ln Z, \quad (155)$$

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

$$d(pV) = SdT + Nd\mu + pdV, \quad (156)$$

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

$$N = \left. \frac{d(pV)}{d\mu} \right|_{V,T} = k_B T \left(\frac{\partial \ln Z}{\partial \mu} \right)_{V,T} = \sum_k \frac{\lambda e^{-\beta\epsilon_k}}{1 - \lambda e^{-\beta\epsilon_k}} = \sum_k \bar{n}_k. \quad (157)$$

The average population of state k , with energy ϵ_k , is

$$\bar{n}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1 - \lambda e^{-\beta\epsilon_k}}. \quad (158)$$

The fugacity λ and the related chemical potential μ are simply parameters that, together with the temperature and the energy levels ϵ_k , determine the populations \bar{n}_k through Eq. (158) and hence the total number of particles N . The possible values of λ and μ are determined by the requirement that populations cannot be negative. This condition is

$$0 \leq \lambda e^{-\beta\epsilon_k} = e^{-\beta(\epsilon_k - \mu)} < 1. \quad (159)$$

With ϵ_0 defined as the lowest energy, the condition is $\mu < \epsilon_0$. In the expressions only $\epsilon_k - \mu$ appears, so we take the zero of energy as $\epsilon_0 = 0$, and hence $\mu < 0$ and $0 \leq \lambda < 1$. When λ is small the populations of the states are proportional to $e^{-\beta\epsilon_k}$, which corresponds to the classical Maxwell-Boltzmann distribution. Notice that in this case the chemical potential $\mu \ll 0$, even though the interaction between the particles is zero for our ideal Bose gas. Next, consider the population of the ground state with $\epsilon_0 = 0$,

$$\bar{n}_0 = \frac{\lambda}{1 - \lambda}. \quad (160)$$

When λ approaches 1 (μ 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 λ in the statistical limit. This means that for a given temperature T , or a given β , we assume the box to be so large that the energy spacings between the levels ϵ_k are small compared to $k_B T$. Hence, for the lowest excited state, which is three fold degenerate, we assume that $\beta\epsilon_1 \ll 1$ such that $e^{-\beta\epsilon_1} \approx 1 - \beta\epsilon_1$. We note that the population of the ground state can only be considerably larger than that of $k = 1$ and higher states if λ is very close to 1. If we write $\lambda = 1 - \delta$, where $\delta \approx 0$, we find that the ground state population is

$$\bar{n}_0 = \frac{\lambda}{1 - \lambda} \approx \frac{1}{\delta} \quad (161)$$

and the population of the first excited state is

$$\bar{n}_1 \approx \frac{(1-\delta)(1-\beta\epsilon_1)}{1-(1-\delta)(1-\beta\epsilon_1)} \approx \frac{1}{\delta + \beta\epsilon_1}. \quad (162)$$

Hence, \bar{n}_0 can only be considerably larger than \bar{n}_1 if δ is small compared to $\beta\epsilon_1$. When λ increases, the population \bar{n}_k of each level increases, since the numerator in Eq. (158) increases with λ and the denominator decreases with λ . Hence, we may compute an upper limit to the population of all excited states by setting $\lambda = 1$,

$$N - \bar{n}_0 = \sum_{k>0} \frac{e^{-\beta\epsilon_k}}{1 - e^{-\beta\epsilon_k}}. \quad (163)$$

For bosons in a three-dimensional box, the energy levels ϵ_k are given by $\epsilon_{\mathbf{n}}$ of Eq. (150) and the summation over k must be replaced by

$$\sum_k = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty}. \quad (164)$$

The energies $\epsilon_{\mathbf{n}}$ can be written as bn^2 , with $n^2 = n_x^2 + n_y^2 + n_z^2$ and

$$b = \frac{\hbar^2 \pi^2}{2ma^2}. \quad (165)$$

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

$$\sum_{n_x>0} \sum_{n_y>0} \sum_{n_z>0} f(n) = \frac{\pi}{2} \int_0^{\infty} n^2 f(n) dn \quad (166)$$

or, with $\epsilon = bn^2$ and $n^2 dn = (1/2)b^{-3/2}\sqrt{\epsilon}d\epsilon$,

$$N - \bar{n}_0 = \frac{\pi}{4} b^{-3/2} \int_0^{\infty} \frac{\sqrt{\epsilon} e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} d\epsilon. \quad (167)$$

To evaluate the integral we use the series expansion

$$(1-x)^{-1} = \sum_{l=0}^{\infty} x^l, \quad \text{for } |x| < 1, \quad (168)$$

for $x = e^{-\beta\epsilon}$ which gives

$$N - \bar{n}_0 = \frac{\pi}{4} b^{-3/2} \sum_{l=1}^{\infty} \int_0^{\infty} \sqrt{\epsilon} e^{-\beta l \epsilon} d\epsilon = \frac{\pi}{4} b^{-3/2} \sum_{l=1}^{\infty} \frac{\Gamma(3/2)}{(\beta l)^{3/2}}. \quad (169)$$

With $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$, $a^3 = V$, the Riemann-zeta function defined by

$$\zeta(n) = \sum_{l=1}^{\infty} \frac{1}{l^n}, \quad (170)$$

and the de Broglie wavelength defined in Eq. (145) the contribution of the excited states to the density is at most

$$\rho_{\text{ex}} = \frac{N - \bar{n}_0}{V} = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \zeta(3/2) = \Lambda^{-3} \zeta(3/2), \quad (171)$$

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

$$\rho = \rho_0 + \rho_{\text{ex}} = \frac{1}{V} \frac{\lambda}{1-\lambda} + \Lambda^{-3} \zeta(3/2). \quad (172)$$

The excited states density is related to the density ρ_c at the critical temperature through

$$\frac{\rho_{\text{ex}}}{\rho_c} = \left(\frac{\Lambda_c}{\Lambda}\right)^{3/2} = \left(\frac{T}{T_c}\right)^{3/2}, \quad (173)$$

where Λ_c is the de Broglie wavelength at temperature T_c . Hence, the condensate fraction is

$$\frac{\rho_0}{\rho_c} = \frac{\rho_c - \rho_{\text{ex}}}{\rho_c} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \quad (174)$$

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.

C. Condensate in a harmonic trap

Bose-Einstein condensates of dilute gases that have been created in experiments, were not confined by walls, but by magnetic traps. The confining field in such a trap may be modeled by a three-dimensional harmonic oscillator potential

$$V_{\text{trap}}(\mathbf{r}) = \frac{1}{2}(K_x x^2 + K_y y^2 + K_z z^2). \quad (175)$$

We will only consider isotropic potentials for which the three force constants $K_x = K_y = K_z$ are equal to K . In that case the one-particle energy levels are given by

$$\epsilon_{\mathbf{n}} = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega, \quad (176)$$

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

$$\phi(\mathbf{r}) = \left(\frac{m\omega}{\pi\hbar}\right)^{3/4} e^{-\frac{1}{2}\frac{m\omega}{\hbar}r^2}. \quad (177)$$

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

$$k_B T_c = \left(\frac{\hbar\omega N^{1/3}}{\zeta(3)}\right)^{1/3} \approx 0.94\hbar\omega N^{1/3} \quad (178)$$

and the formula for the condensate fraction is

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^3. \quad (179)$$

The derivation of this relation is similar to the derivation in the previous section and can be found, e.g., in Ref. [21].

D. The Gross-Pitaevskii equation

The wave function for a condensate of N non-interacting bosons is the Hartree product,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi(\mathbf{r}_i), \quad (180)$$

where the single particle wave function $\phi(\mathbf{r})$ is normalized,

$$\langle \phi | \phi \rangle = \int |\phi(\mathbf{r})|^2 d\mathbf{r} = 1. \quad (181)$$

For particles in a cubic box $\phi(\mathbf{r})$ is $\phi_{0,0,0}$ in Eq. (151) and for an isotropic three-dimensional harmonic trap it is given by Eq. (177). To find an approximate wave function for the condensate in the presence of interactions between the particles, we will use the Hartree product as an *Ansatz* for the wave function and variationally optimize the single particle wave function $\phi(\mathbf{r})$. This is a mean-field approach and it is analogous to the Hartree-Fock approach for fermions. We consider a pairwise additive interaction with the effective pair potential of Eq. (124)

$$\hat{U} = U_0 \sum_{i < j} \delta(\mathbf{r}_i - \mathbf{r}_j), \quad (182)$$

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

$$\hat{H} = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} + V_{\text{trap}}(\mathbf{r}_i) \right] + \hat{U}, \quad (183)$$

where $\mathbf{p} = \frac{\hbar}{i} \nabla$. For the trap potential the expectation value is given by

$$\langle \Psi | \sum_{i=1}^N V_{\text{trap}}(\mathbf{r}_i) | \Psi \rangle = N \langle \phi | V_{\text{trap}}(\mathbf{r}) | \phi \rangle = N \int V_{\text{trap}}(\mathbf{r}) |\phi(\mathbf{r})|^2 d\mathbf{r} \quad (184)$$

and for the kinetic energy it is

$$\langle \Psi | \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} | \Psi \rangle = \frac{N}{2m} \langle \phi | \mathbf{p}^2 | \phi \rangle = \frac{N}{2m} \langle \mathbf{p} \phi | \mathbf{p} \phi \rangle = \frac{N \hbar^2}{2m} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r}. \quad (185)$$

Finally, to evaluate the expectation value of the two-particle interaction operator we use

$$\int \int \phi(\mathbf{r}_i)^* \phi(\mathbf{r}_j)^* \delta(\mathbf{r}_i - \mathbf{r}_j) \phi(\mathbf{r}_i) \phi(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j = \int |\phi(\mathbf{r}_i)|^4 d\mathbf{r}_i. \quad (186)$$

and we note that the sum over all $i < j$ gives $N(N-1)/2$ identical contributions,

$$\langle \Psi | \hat{U} | \Psi \rangle = U_0 \frac{N(N-1)}{2} \int |\phi(\mathbf{r})|^4 d\mathbf{r}. \quad (187)$$

We assume N to be large, so we set $N(N-1)/2 \approx N^2/2$, and find the total energy

$$E = N \int \left[\frac{\hbar^2}{2m} |\nabla \phi(\mathbf{r})|^2 + V_{\text{trap}}(\mathbf{r}) |\phi(\mathbf{r})|^2 + \frac{1}{2} N U_0 |\phi(\mathbf{r})|^4 \right] d\mathbf{r}. \quad (188)$$

Before we variationally minimize this energy expression we, consider the particles in a box problem, for which $V_{\text{trap}}(\mathbf{r}) = 0$. If we take the ground state particle in a box wave function [Eq. (151)] for $\phi(\mathbf{r})$ we find

$$E = \frac{\pi^2 \hbar^2}{2m} \rho + \frac{27}{16} \rho^2 V U_0, \quad (189)$$

where $V = a^3$ is the volume of the box, $\rho = N/V$ is the particle density, and we used the integral

$$\int_0^a \sin^4\left(\frac{\pi x}{a}\right) dx = \frac{3a}{8}. \quad (190)$$

We note that the second term in Eq. (189) 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: $\phi(\mathbf{r}) = V^{-\frac{1}{2}}$. 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

$$E = \frac{1}{2} \rho^2 V U_0. \quad (191)$$

Thus, when the interaction is repulsive ($U_0 > 0$) and the volume and density are sufficiently high, we find that the homogeneous gas wave function describes the condensate better than the particle in a box wave function, since $\frac{1}{2}\rho^2 V U_0 < \frac{27}{16}\rho^2 V U_0$. For attractive interactions ($U_0 < 0$) we observe that the nonlinear $|\phi(\mathbf{r})|^4$ term favors the least homogeneous solution which in practice may result in collapse of the condensate.

We will now derive the Gross-Pitaevskii equation, which minimizes the energy of Eq. (188) variationally. It is convenient to introduce the function

$$\psi(\mathbf{r}) = N^{1/2}\phi(\mathbf{r}). \quad (192)$$

The normalization of ψ is such that the particle density is given by

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2. \quad (193)$$

The integral over the density is the total number of particles N . Thus, within the present *Ansatz*, $\psi(\mathbf{r})$ 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 ψ is

$$E[\psi] = \int \left[\frac{\hbar^2}{2m} |\nabla\psi(\mathbf{r})|^2 + V(\mathbf{r})|\psi(\mathbf{r})|^2 + \frac{1}{2}U_0|\psi(\mathbf{r})|^4 \right] d\mathbf{r}. \quad (194)$$

According to the variational principle, we must vary ψ to minimize the energy E , but we must satisfy the constraint that the number of particles

$$\int |\psi(\mathbf{r})|^2 d\mathbf{r} = N[\psi] = N \quad (195)$$

is conserved. For this constraint minimization the Lagrange multiplier method is used. This amounts to introducing a new parameter, μ , and performing the unconstrained minimization of $E[\psi] - \mu N[\psi]$, such that for first order variations $\delta\psi$,

$$E[\psi + \delta\psi] - \mu N[\psi + \delta\psi] = E[\psi] - \mu N[\psi]. \quad (196)$$

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 ψ and ψ^* separately. Therefore, we rewrite the energy expression as

$$E[\psi] = \int \left[-\frac{\hbar^2}{2m} \psi^*(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r}) \psi^*(\mathbf{r}) \psi(\mathbf{r}) + \frac{1}{2} U_0 \psi^*(\mathbf{r})^2 \psi(\mathbf{r})^2 \right] d\mathbf{r}, \quad (197)$$

substitute $\psi^* \rightarrow \psi^* + \delta\psi^*$, and set terms linear in $\delta\psi^*$ equal to zero. The result

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + U_0 |\psi(\mathbf{r})|^2 \right] \psi(\mathbf{r}) = \mu \psi(\mathbf{r}) \quad (198)$$

is known as the time-independent Gross-Pitaevskii equation. The variation $\psi \rightarrow \psi + \delta\psi$ can be used to show that μ must be real. If one finds a $\psi(\mathbf{r})$ 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 ψ . Instead, one must choose a value for μ , find a solution $\psi(\mathbf{r})$, and determine the number of particles to which it corresponds.

The parameter μ is the chemical potential, $\mu = \partial E / \partial N$. This follows from rewriting Eq. (197) as

$$\mu = \frac{E[\psi + \delta\psi] - E[\psi]}{N[\psi + \delta\psi] - N[\psi]} = \frac{\Delta E}{\Delta N}. \quad (199)$$

E. Thomas-Fermi approximation

We saw above that when the volume is large and the interaction U_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

$$|\psi(\mathbf{r})|^2 = \rho(\mathbf{r}) = \frac{\mu - V_{\text{trap}}(\mathbf{r})}{U_0} \quad (200)$$

in regions where the right hand side is positive, and $\psi(\mathbf{r}) = 0$ otherwise. The discontinuity in the derivative of the wave function at the edge of the cloud defined by $V_{\text{trap}}(\mathbf{r}) = \mu$ is the result of neglecting the kinetic energy term. As before, we find that the density is constant when $V_{\text{trap}}(\mathbf{r}) = 0$. In that case we also find $\mu = NV^{-1}U_0$ and $E = N^2V^{-1}U_0/2$, which agrees with the definition of the chemical potential $\mu = \partial E/\partial N$.

The density profile of a Bose-Einstein condensate is very characteristic. The classical thermal Boltzmann distribution is proportional to $e^{-V(\mathbf{r})/k_B T}$. 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.

F. 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 the 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 1. 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 $a(i) = \phi_1(\mathbf{r}_i)$ and $b(i) = \phi_2(\mathbf{r}_i)$, where ϕ_1 and ϕ_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

$$|N_1 N_2\rangle = n(N_1, N_2) \hat{S}[a(1)a(2)\dots a(N_1)b(N_1+1)b(N_1+2)\dots b(N_1+N_2)], \quad (201)$$

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,

$$\hat{S} = \sum_{k=1}^{N!} \hat{P}_k \quad (202)$$

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

$$\hat{P}_l \hat{S} = \sum_k \hat{P}_l \hat{P}_k = \hat{S}, \quad (203)$$

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

$$\hat{S}^2 = \left(\sum_l \hat{P}_l\right) \hat{S} = N! \hat{S}. \quad (204)$$

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

$$\begin{aligned} \langle N_1 N_2 | N_1 N_2 \rangle &= |n(N_1, N_2)|^2 \langle \hat{S} a(1) \dots b(N) | \hat{S} | a(1) \dots b(N) \rangle \\ &= |n(N_1, N_2)|^2 \langle a(1) \dots b(N) | \hat{S}^2 | a(1) \dots b(N) \rangle \\ &= |n(N_1, N_2)|^2 N! \sum_k \langle a(1) \dots b(N) | \hat{P}_k | a(1) \dots b(N) \rangle. \end{aligned} \quad (205)$$

Out of the $N!$ terms, there will be $N_1! N_2!$ terms that yield 1, and all the others will be zero, so the normalization constant is

$$n(N_1, N_2) = (N! N_1! N_2!)^{-\frac{1}{2}}. \quad (206)$$

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

$$\hat{\mu} = \sum_{i=1}^N \hat{\mu}_i, \quad (207)$$

with matrix elements

$$\langle a(i) | \hat{\mu}_i | b(i) \rangle = \mu_{ab}. \quad (208)$$

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

$$\tilde{k} = |\langle N_1 N_2 | \hat{\mu} | N_1 - 1, N_2 + 1 \rangle|^2. \quad (209)$$

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

$$\tilde{k} = N_1(N_2 + 1) |\mu_{ab}|^2. \quad (210)$$

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. The above treatment of spontaneous emission is still lacking some essential ingredients. E.g., photons carry momentum, and total momentum must be conserved. A more rigorous theoretical treatment [22] predicts that enhancement of spontaneous emission can occur in an interacting Bose Einstein condensate.

The analogous relation for fermions contains a factor $N_1(1 - N_2)$, 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 molecule and the magnetic moment of the diatom will in general not be exactly two times the magnetic moment of the atom. Such a resonance is called a Feshbach resonance and this technique has been used to produce ultracold molecules and molecular Bose-Einstein condensates[23]. Other methods to achieve resonance are the use of Raman transitions [24] or photodissociation of Bose-Einstein condensates [25].

Most theoretical papers on ultracold chemistry use second quantization formalism to denote wave functions of the form 180 and the operators acting on[17]. A short introduction to this formalism, with applications to Bose-Einstein condensates can be found in Ref. [26].

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