Quantum dynamics (NWI-SM295)

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June 14, 2024

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Chapter 1

Born-Oppenheimer approximation

1.1 Molecular Hamiltonian

We consider a molecular system consisting of n electrons and N nuclei. The notation of the Cartesian coordinates, linear momenta, masses, and charges are shown in Table 1.1. The Hamiltonian is given by

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e,e} + \hat{V}_{e,N} + \hat{V}_{N,N}, \tag{1.1}$$

with the kinetic energy of the electrons

$$\hat{T}_e = \sum_{i=1}^{n} \frac{\hat{p}_i^2}{2m_e} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2, \tag{1.2}$$

the kinetic energy of the nuclei

$$\hat{T}_N = \sum_{\alpha=1}^{N} \frac{\hat{P}_\alpha^2}{2m_\alpha} = -\sum_{\alpha=1}^{N} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2, \tag{1.3}$$

the Coulomb repulsion between the electrons

$$\hat{V}_{e,e} = \sum_{i<j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \tag{1.4}$$

the Coulomb attraction between the electrons and nuclei

$$\hat{V}_{e,N} = \sum_{i=1}^{n} \sum_{\alpha=1}^{N} \frac{e^2}{4\pi\epsilon_0} \frac{-Z_\alpha}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|}, \tag{1.5}$$

Particles	coordinates	momenta	masses	charges
Electrons $(i = 1, \ldots, n)$	$\boldsymbol{r}_i$	$\hat{p}_i = \frac{\hbar}{i}\boldsymbol{\nabla}_i$	m_e	$-e$
Nuclei $(\alpha = 1, \ldots, N)$	$\boldsymbol{R}_\alpha$	$\hat{P}_\alpha = \frac{\hbar}{i}\boldsymbol{\nabla}_\alpha$	M_α	$Z_\alpha e$

Table 1.1: Notation of coordinates, linear momenta, masses, and charges.

and the Coulomb repulsion between the nuclei

$$\hat{V}_{N,N} = \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0} \frac{Z_\alpha Z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}. \tag{1.6}$$

1.2 Mass weighted coordinates

Before we proceed, we introduce mass weighted coordinates. This is not essential, but it simplifies the equations. Coordinate transformations are frequently used in quantum dynamics to simplify a problem. For N nuclei, we define $3N$ mass weighted coordinates by

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \sqrt{M_1}\boldsymbol{R}_1; \quad \begin{pmatrix} Q_4 \\ Q_5 \\ Q_6 \end{pmatrix} = \sqrt{M_2}\boldsymbol{R}_2; \ \dots \ ; \quad \begin{pmatrix} Q_{3N-2} \\ Q_{3N-1} \\ Q_{3N} \end{pmatrix} = \sqrt{M_N}\boldsymbol{R}_N. \tag{1.7}$$

We will use the column vector $\boldsymbol{Q}$ to denote all $3N$ nuclear mass weighted coordinates. The nuclear kinetic energy operator (Eq. 1.3) now takes the form

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_{i=1}^{3N} \frac{\partial^2}{\partial Q_i^2} = -\frac{\hbar^2}{2}\nabla_Q^2. \tag{1.8}$$

The $3n$ electronic coordinates are denoted by the column vector $\boldsymbol{q}$, and the total Coulomb interaction will be denoted by

$$\hat{V}(\boldsymbol{q};\boldsymbol{Q}) \equiv \hat{V}_{e,e} + \hat{V}_{e,N} + \hat{V}_{N,N}. \tag{1.9}$$

1.3 The Born-Oppenheimer approximation

The Born-Oppenheimer approximation relies on the nuclei being much heavier than the electrons, $M_\alpha \gg m_e$. Already the hydrogen nucleus has 1836.15 times the mass of an electron. This allows a two-step approach to solving the Schrödinger equation. In the first step the kinetic energy of the nuclei is neglected and the electronic Hamiltonian is defined,

$$\hat{H}^{(\mathrm{el})} \equiv \hat{T}_e + \hat{V}(\boldsymbol{q};\boldsymbol{Q}). \tag{1.10}$$

For a given choice of the positions of the nuclei ($\boldsymbol{Q}$), the electronic wave functions $\Phi_i^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q})$ ($i = 0, 1, \dots$) are the solutions of the electronic Schrödinger equation,

$$\hat{H}^{(\mathrm{el})}\Phi_i^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q}) = E_i^{(\mathrm{el})}(\boldsymbol{Q})\Phi_i^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q}). \tag{1.11}$$

The electronic energies $E_i^{(\mathrm{el})}(\boldsymbol{Q})$ depend on the positions of the nuclei, and they are usually referred to as *adiabatic* or *Born-Oppenheimer* potential energy surfaces. We assume that the electronic wave functions are orthonormal

$$\langle\Phi_i^{(\mathrm{el})}|\Phi_j^{(\mathrm{el})}\rangle_{\boldsymbol{q}} \equiv \int\cdots\int \Phi_i^{(\mathrm{el}),*}(\boldsymbol{q};\boldsymbol{Q})\,\Phi_j^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q})dq_1 dq_2\cdots dq_{3n} = \delta_{i,j}. \tag{1.12}$$

In the second step of the Born-Oppenheimer approximation we use the electronic wave functions as a basis to expand the total wave function

$$\Psi(\boldsymbol{q}, \boldsymbol{Q}) = \sum_i \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_i(\boldsymbol{Q}). \tag{1.13}$$

To find an equation for the nuclear wave functions $\chi_i(\boldsymbol{Q})$ we first substitute the expansion into the time-independent Schrödinger equation

$$[\hat{T}_N + \hat{H}^{(\text{el})} - E] \sum_j \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_j(\boldsymbol{Q}) = 0. \tag{1.14}$$

Next, we project from the left with electronic wave functions, integrating over the electronic coordinates

$$\langle \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})|\hat{T}_N + \hat{H}^{(\text{el})} - E| \sum_j \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_j(\boldsymbol{Q})\rangle_{\boldsymbol{q}} = 0. \tag{1.15}$$

When evaluating the matrix elements, one has to remember that the nuclear kinetic energy operator acts on the nuclear as well as the electronic wave function since

$$\nabla_Q^2 \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_j(\boldsymbol{Q}) = \tag{1.16}$$
$$[\nabla_Q^2 \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})]\chi_j(\boldsymbol{Q}) + 2[\boldsymbol{\nabla}_Q \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})] \cdot \boldsymbol{\nabla}_Q \chi_j(\boldsymbol{Q}) + \Phi_j^{(\text{el})}(\boldsymbol{Q})\nabla_Q^2 \chi_j(\boldsymbol{Q}).$$

In this equation the gradient $\boldsymbol{\nabla}_Q$ is the vector operator

$$\boldsymbol{\nabla}_Q = \begin{pmatrix} \frac{\partial}{\partial Q_1} \\ \vdots \\ \frac{\partial}{\partial Q_{3N}} \end{pmatrix}. \tag{1.17}$$

To evaluate the matrix elements of the electronic Hamiltonian we use Eqs. (1.11) and (1.12) and find

$$\langle \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})|\hat{H}^{(\text{el})} - E| \sum_j \Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_j(\boldsymbol{Q})\rangle_{\boldsymbol{q}} = [E_i^{(\text{el})}(\boldsymbol{Q}) - E]\chi_i(\boldsymbol{Q}). \tag{1.18}$$

Combining the last four equations we arrive at a set of coupled equations

$$[\hat{T}_N + E_i(\boldsymbol{Q}) - E]\chi_i(\boldsymbol{Q}) = \hbar^2 \sum_j \left[\frac{1}{2}G_{i,j}(\boldsymbol{Q}) + \boldsymbol{F}_{i,j}(\boldsymbol{Q}) \cdot \boldsymbol{\nabla}_Q\right] \chi_j(\boldsymbol{Q}), \tag{1.19}$$

where the *non-adiabatic coupling matrix elements* are given by

$$G_{i,j}(\boldsymbol{Q}) \equiv \langle \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})|\nabla_Q^2|\Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\rangle_{\boldsymbol{q}} \tag{1.20}$$

$$\boldsymbol{F}_{i,j}(\boldsymbol{Q}) \equiv \langle \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})|\boldsymbol{\nabla}_Q|\Phi_j^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\rangle_{\boldsymbol{q}}. \tag{1.21}$$

In the *Born-Oppenheimer approximation* all non-adiabatic coupling matrix elements are neglected and Eq. (1.19) can be solved separately for each electronic state (i)

$$[\hat{T}_N + E_i(\boldsymbol{Q})]\chi_{i,v}(\boldsymbol{Q}) = E_{i,v}\chi_{i,v}(\boldsymbol{Q}). \tag{1.22}$$

The total wave function is then a product of an electronic and a nuclear wave function

$$\Psi_{i,v}(\boldsymbol{q}; \boldsymbol{Q}) = \Phi_i^{(\text{el})}(\boldsymbol{q}; \boldsymbol{Q})\chi_{i,v}(\boldsymbol{Q}). \tag{1.23}$$

1.4   Validity of the Born-Oppenheimer approximation

In general, the Born-Oppenheimer approximation is accurate when the separation of the electronic energies is large compared to the nuclear kinetic energy. To show this, we first observe that

$$\boldsymbol{F}_{i,j}(\boldsymbol{Q}) = -\boldsymbol{F}_{j,i}^{*}(\boldsymbol{Q}), \tag{1.24}$$

which follows from taking the first derivative of Eq. (1.12). Dropping the subscript $\boldsymbol{q}$ for the scalar products we have

$$\frac{\partial}{\partial Q_\alpha}\langle\Phi_i^{(\mathrm{el})}|\Phi_j^{(\mathrm{el})}\rangle = \langle\frac{\partial\Phi_i^{(\mathrm{el})}}{\partial Q_\alpha}|\Phi_j^{(\mathrm{el})}\rangle + \langle\Phi_i^{(\mathrm{el})}|\frac{\partial\Phi_j^{(\mathrm{el})}}{\partial Q_\alpha}\rangle = \frac{\partial}{\partial Q_\alpha}\delta_{i,j} = 0, \tag{1.25}$$

which shows that

$$\langle\Phi_i^{(\mathrm{el})}|\frac{\partial\Phi_j^{(\mathrm{el})}}{\partial Q_\alpha}\rangle = -\langle\frac{\partial\Phi_i^{(\mathrm{el})}}{\partial Q_\alpha}|\Phi_j^{(\mathrm{el})}\rangle = -\langle\Phi_j^{(\mathrm{el})}|\frac{\partial\Phi_i^{(\mathrm{el}),*}}{\partial Q_\alpha}\rangle. \tag{1.26}$$

For *non-degenerate real electronic wave functions* we have

$$\boldsymbol{F}_{i,j}(\boldsymbol{Q}) = -\boldsymbol{F}_{j,i}(\boldsymbol{Q}) \tag{1.27}$$

and hence $\boldsymbol{F}_{i,i}(\boldsymbol{Q}) = \boldsymbol{0}$. To derive an expression for $i \neq j$ we taking the first derivative with respect to nuclear coordinate Q_α of

$$\langle\Phi_i^{(\mathrm{el})}|\hat{H}^{(\mathrm{el})}|\Phi_j^{(\mathrm{el})}\rangle = 0, \tag{1.28}$$

which gives

$$\langle\frac{\partial}{\partial Q_\alpha}\Phi_i^{(\mathrm{el})}|\hat{H}^{(\mathrm{el})}|\Phi_j^{(\mathrm{el})}\rangle + \langle\Phi_i^{(\mathrm{el})}|\frac{\partial\hat{H}^{(\mathrm{el})}}{\partial Q_\alpha}|\Phi_j^{(\mathrm{el})}\rangle + \langle\Phi_i^{(\mathrm{el})}|\hat{H}^{(\mathrm{el})}|\frac{\partial}{\partial Q_\alpha}\Phi_j^{(\mathrm{el})}\rangle = 0, \quad (\text{for } i \neq j). \tag{1.29}$$

Again restricting ourselves to the real, non-degenerate case we derive, using Eqs. (1.11), (1.27), and (1.29)

$$\boldsymbol{F}_{i,j}(\boldsymbol{Q}) = \frac{\langle\Phi_i^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q})|\left[\boldsymbol{\nabla}_Q, \hat{H}^{(\mathrm{el})}\right]|\Phi_j^{(\mathrm{el})}(\boldsymbol{q};\boldsymbol{Q})\rangle}{E_j^{(\mathrm{el})}(\boldsymbol{Q}) - E_i^{(\mathrm{el})}(\boldsymbol{Q})}. \tag{1.30}$$

This result shows that the first derivative couplings $\boldsymbol{F}_{i,j}(\boldsymbol{Q})$ are small when the electronic energies are well separated, i.e., when $|E_j^{(\mathrm{el})}(\boldsymbol{Q}) - E_i^{(\mathrm{el})}(\boldsymbol{Q})|$ is large. Conversely, when two electronic states are close in energy, the nonadiabatic coupling can become large.

When the electronic wave function Φ is complex in a non-trivial way, i.e., when Φ and Φ^* are linearly independent this derivation breaks down. However, since the electronic Hamiltonian is real, the functions Φ and Φ^* are degenerate, and breakdown of the Born-Oppenheimer approximation is expected.

In the next section we consider the second derivative couplings.

1.5   Second derivative nonadiabatic coupling

The second derivative couplings $G_{i,j}(\boldsymbol{Q})$ are related to the first derivative couplings $\boldsymbol{F}_{i,j}(\boldsymbol{Q})$. For the divergence of the latter, we have, from Eq. (1.21),

$$\boldsymbol{\nabla}_Q \cdot \boldsymbol{F}_{i,j}(\boldsymbol{Q}) = \langle \boldsymbol{\nabla}_Q \Phi_i^{(\text{el})} | \boldsymbol{\nabla}_Q \Phi_j^{(\text{el})} \rangle + \langle \Phi_i^{(\text{el})} | \nabla_Q^2 \Phi_j^{(\text{el})} \rangle. \tag{1.31}$$

The first term on the right-hand side can be rewritten by inserting a resolution of identity over the electronic states

$$\langle \boldsymbol{\nabla}_Q \Phi_i^{(\text{el})} | \boldsymbol{\nabla}_Q \Phi_j^{(\text{el})} \rangle = \sum_k \langle \boldsymbol{\nabla}_Q \Phi_i^{(\text{el})} | \Phi_k^{(\text{el})} \rangle \cdot \langle \Phi_k^{(\text{el})} | \boldsymbol{\nabla}_Q \Phi_j^{(\text{el})} \rangle. \tag{1.32}$$

Using the definitions of the non-adiabatic couplings and Eq. (1.24) we find

$$G_{i,j}(\boldsymbol{Q}) = \boldsymbol{\nabla}_Q \cdot \boldsymbol{F}_{i,j}(\boldsymbol{Q}) - \sum_k \boldsymbol{F}_{k,i}^*(\boldsymbol{Q}) \boldsymbol{F}_{k,j}(\boldsymbol{Q}). \tag{1.33}$$

For real wave functions $k = i$ and $k = j$ do not contribute to the last term. Hence, if two electronic states i and j are close in energy, and all other electronic states are far away in energy, the second derivative couplings may be computed as the divergence of the first-derivative couplings.

Chapter 2

Diatomic molecules

We will discuss a diatomic molecule in the Born-Oppenheimer approximation. The Schrödinger equation for the nuclear motion, vibration and rotation, is mathematically very similar to the electronic Schrödinger equation of the hydrogen atom. The main difference is that the Coulomb interaction between the proton and the electron is replaced by the Born-Oppenheimer potential $V(r)$, where r is the distance between the atoms. Therefore, we will only summarize the key results here, without a full derivation.

We denote the Cartesian coordinates of the atoms A and B, with masses M_A and M_B by $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$. The nuclear kinetic energy operator in Cartesian coordinates is given by

$$\hat{T} = -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2. \tag{2.1}$$

Since the motion of the center of mass is not coupled to the rotation and vibration of the molecule, it is advantageous to introduce new coordinates. The center of mass is given by

$$\boldsymbol{X} = \frac{M_A\boldsymbol{R}_A + M_B\boldsymbol{R}_B}{M_A + M_B}. \tag{2.2}$$

Furthermore, we define

$$\boldsymbol{r} \equiv \boldsymbol{R}_B - \boldsymbol{R}_A. \tag{2.3}$$

In these coordinates the kinetic energy operator becomes

$$\hat{T} = -\frac{\hbar^2}{2M_{\text{tot}}}\nabla_X^2 - \frac{\hbar^2}{2\mu}\nabla_r^2, \tag{2.4}$$

with total mass

$$M_{\text{tot}} = M_A + M_B, \tag{2.5}$$

and reduced mass μ, defined by

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}. \tag{2.6}$$

Since we do not consider external electric or magnetic fields, the potential only depends on the distance $r = |\boldsymbol{r}|$, and it is convenient to use spherical polar coordinates (r, θ, ϕ), defined by

$$\boldsymbol{r} = r \begin{pmatrix} \cos\phi\sin\theta \\ \sin\phi\sin\theta \\ \cos\theta \end{pmatrix}. \tag{2.7}$$

In principle, the kinetic energy operator for the relative motion can be written in these new coordinates by applying the chain rule to ∇_r^2. That approach is tedious and the result gives little insight in how to proceed and solve the resulting Schrödinger equation. An indirect but more effective approach starts with identifying Hermitian operators that commute with the Hamiltonian.

Let us consider the *angular momentum operator* $\hat{\boldsymbol{l}}$ defined by a cross product

$$\hat{\boldsymbol{l}} \equiv \boldsymbol{r} \times \hat{\boldsymbol{p}}, \tag{2.8}$$

where $\boldsymbol{p} = \frac{\hbar}{i}\boldsymbol{\nabla}$ is the linear momentum operator, and the total angular momentum operator $\hat{l}^2$,

$$\hat{l}^2 \equiv \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{l}}. \tag{2.9}$$

By substituting Eq. (2.8) into Eq. (2.9) one can derive

$$\hat{l}^2 = -\hbar^2 r^2 \nabla_r^2 + \hbar^2 r \frac{\partial^2}{\partial r^2} r. \tag{2.10}$$

The Schrödinger equation for the rotational and vibrational motion, which is decoupled from the center-of-mass motion, can be written as

$$[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2} + V(r) - E]\psi(r,\theta,\phi) = 0. \tag{2.11}$$

The first term of the Hamiltonian operator represents the radial kinetic energy and the second term the rotational energy. The solutions can be factorized,

$$\psi_{vlm_l}(r,\theta,\phi) = \frac{1}{r}\chi_{vl}(r)Y_{lm_l}(\theta,\phi), \tag{2.12}$$

where $v = 0, 1, \ldots$ is the vibrational quantum number. The angular part is a spherical harmonic, it is an eigenfunction of the total angular momentum operator and of $\hat{l}_z$,

$$\hat{l}^2 Y_{l,m_l}(\theta,\phi) = \hbar^2 l(l+1)Y_{l,m_l}(\theta,\phi), \quad \text{with } l = 0, 1, 2, \ldots \tag{2.13}$$

$$\hat{l}_z Y_{l,m_l}(\theta,\phi) = \hbar m_l Y_{l,m_l}(\theta,\phi), \quad \text{and } m_l = -l, -l+1, \ldots, l. \tag{2.14}$$

The spherical harmonics are orthonormal,

$$\langle l'm_l'|lm_l\rangle \equiv \int_0^{2\pi}\int_{-1}^1 Y_{l'm_l'}^*(\theta,\phi)\,Y_{lm_l'}(\theta,\phi)\,d\cos\theta\,d\phi = \delta_{l'l}\delta_{m_l'm_l}. \tag{2.15}$$

An equation for the radial wave functions $\chi_{vl}(r)$ is found by substituting Eq. (2.12) into Eq. (2.11), using Eq. (2.13), projecting the equation with a spherical harmonic, using the orthonormality of spherical harmonics [Eq. (2.15)], and multiplying the equation with r. The result is

$$[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)]\chi_{vl}(r) = E_{vl}\chi_{vl}(r). \tag{2.16}$$

The solutions can be made orthonormal,

$$\int_0^\infty \chi_{v'l'}^*(r)\,\chi_{vl}(r)\,dr = \delta_{v'v}\delta_{l'l}. \tag{2.17}$$

With this normalization, the functions $\psi_{vl,m_l}(r,\theta,\phi)$ are also orthonormal, since the volume element for spherical polar coordinates is

$$d\tau = r^2 dr \, d\cos\theta \, d\phi \tag{2.18}$$

and the r^2 in the volume element cancels against the factors $1/r$ introduced in Eq. (2.12).

The radial Schrödinger equation for $\chi_{vl}(r)$ looks like a one-dimensional Schrödinger equation in Cartesian coordinates, except that $r \geq 0$, and the rotation modifies the potential $V(r)$ by adding the so called *centrifugal term* $\hbar^2 l(l+1)/2\mu r^2$.

The energies E_{vl} depend on the vibration quantum number v, and the rotational quantum number l, but not on m_l, so for each v and l, there are $2l+1$ degenerate eigenfunctions.

2.1   Harmonic oscillator approximation

The Born-Oppenheimer potential for a diatomic molecule can be expanded around its minimum at $r = r_e$ in a Taylor series,

$$V(r) = V(r_e) + \frac{1}{2}k(r - r_e)^2 + \dots, \tag{2.19}$$

where k is a force constant. Truncating the expansion after the quadratic term results in the harmonic oscillator approximation, which can be solved analytically.

First we consider a non-rotating molecule, i.e., $l = 0$, and introduce a mass-weighted coordinate

$$q \equiv \sqrt{\mu}(r - r_e). \tag{2.20}$$

By taking $V(r_e)$ as the zero of energy the Hamiltonian becomes

$$\hat{H}_0 = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial q^2} + \frac{\hbar^2}{2}\omega^2 q^2, \tag{2.21}$$

where

$$\omega = \sqrt{\frac{k}{\mu}}. \tag{2.22}$$

The solutions of the quantum harmonic oscillator problem

$$\hat{H}_0 \phi_v(q) = \epsilon_v \phi_v(q) \tag{2.23}$$

are given by

$$\phi_v(q) = H_n(\sqrt{\omega}q)e^{-\frac{1}{2}\omega q^2}\left(\frac{\omega}{\pi}\right)^{\frac{1}{4}}(2^n n!)^{-\frac{1}{2}}, \tag{2.24}$$

where H_n are Hermite polynomials

$$
\begin{aligned}
H_0(q) &= 1 &\qquad (2.25)\\
H_1(q) &= 2q &\qquad (2.26)\\
H_{v+1}(q) &= 2qH_v(q) - 2vH_{v-1}(q), \quad \text{for } v = 1, 2, \dots &\qquad (2.27)
\end{aligned}
$$

and the energies are given by

$$\epsilon_v = (v + \frac{1}{2})\hbar\omega. \tag{2.28}$$

2.2   Anharmonic oscillator, variational approach

In general, analytic solutions are not available for real potentials. There are several ways to compute rovibrational wave functions and energies in that case. In the linear variational method the wave function is expanded in a basis

$$\chi(q) = \sum_i \phi_i(q) c_i. \tag{2.29}$$

The basis functions $\phi_i(q)$ may be chosen as the analytic solution corresponding to an approximation of the potential. For example, we may write $V(q)$ as

$$V(q) = V_0(q) + \Delta V(q), \tag{2.30}$$

where $V_0(q)$ is a harmonic approximation of the potential. The Hamiltonian then becomes

$$\hat{H} = \hat{H}_0 + \Delta V(q), \tag{2.31}$$

where $\hat{H}_0$ is the harmonic oscillator Hamiltonian corresponding to the harmonic potential V_0. Thus, the basis functions satisfy

$$\hat{H}_0 \phi_i(q) = \epsilon_i \phi_i(q). \tag{2.32}$$

The linear variational method turn the Schrödinger equation into a matrix eigenvalues problem

$$\boldsymbol{H} \boldsymbol{c} = E \boldsymbol{c}, \tag{2.33}$$

where the column vector $\boldsymbol{c}$ contains the expansion coefficients and the Hamiltonian matrix elements are given by

$$H_{i,j} \equiv \langle \phi_i | \hat{H} | \phi_j \rangle = \epsilon_i \delta_{i,j} + \langle \phi_i | \Delta V | \phi_j \rangle. \tag{2.34}$$

Formally, the energies E are found as zeros of the characteristic polynomial, i.e., the determinant

$$|\boldsymbol{H} - E\boldsymbol{I}| = 0, \tag{2.35}$$

where $\boldsymbol{I}$ is the identity matrix with $I_{i,j} = \delta_{i,j}$. For each solution $E = E_v$ the corresponding eigenvector $\boldsymbol{c}_v$ is found as the non-trivial solution of the singular set of linear equations

$$(\boldsymbol{H} - E_v \boldsymbol{I}) \boldsymbol{c}_v = \boldsymbol{0}. \tag{2.36}$$

The energies E_v are *upper limits* of the exact solutions of the Schrödinger equation.

2.3   Rotational levels of diatomic molecules

The above harmonic approximation and variational methods are directly applicable to a rotating diatomic molecule when applied to the *effective* potential, i.e., the potential including the centrifugal term [see Eq. (2.16)]

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}. \tag{2.37}$$

A more approximate method is to find the vibrational wave function χ_v for $l = 0$ only and compute the rotational energy with first order perturbation theory. This gives the energy levels

$$E_{vl} \approx E_v + \langle \chi_v | \frac{\hbar^2 l(l+1)}{2\mu r^2} | \chi_v \rangle = E_v + B_v l(l+1), \tag{2.38}$$

with rotational constant

$$B_v = \frac{\hbar^2}{2\mu} \langle \phi_v | r^{-2} | \phi_v \rangle. \tag{2.39}$$

The rotational constant can be further approximated as

$$B_v \approx \frac{\hbar^2}{2\mu} r_v^{-2}, \tag{2.40}$$

where

$$r_v = \langle \phi_v | r | \phi_v \rangle. \tag{2.41}$$

In the harmonic approximation $r_v = r_e$, the equilibrium distance.

2.4   Morse oscillator

The Morse potential is a more realistic model for a diatomic Born-Oppenheimer potential than the harmonic approximation, but is still has analytic solutions for vibrational wave functions and energies. The Morse potential is given by

$$V_{\mathrm{M}}(r) = V_e + D_e[1 - e^{-\alpha(r-r_e)}]^2. \tag{2.42}$$

It is easy to verify that the minimum of this potential occurs at $r = r_e$ with $V_{\mathrm{M}}(r_e) = V_e$. For large r the Morse potential approaches the value $V_e + D_e$. The force constant of the harmonic approximation to the Morse potential is

$$k = \left. \frac{\partial^2 V(r)}{\partial r^2} \right|_{r=r_e} = 2D_e \alpha^2. \tag{2.43}$$

The exact energies are given by

$$E_v = \hbar\omega_0 (v + \frac{1}{2}) - \frac{[\hbar\omega_0(v + 1/2)]^2}{4D_e}, \tag{2.44}$$

where $\omega_0 = \sqrt{\frac{k}{\mu}}$ as in the harmonic approximation. The Morse oscillator has only a finite number of bound states, and this expression is only valid for vibrational quantum numbers v for which $E_v > E_{v-1}$. The vibrational wave functions can be found in the original paper by Philip Morse [1].

Since there are only a finite number of bound states, the analytic solutions do not form a complete set. This must be kept in mind when using Morse oscillator functions as basis functions in a variational calculation. The problem can be ameliorated by using r_e, α, and D_e as nonlinear variational parameters.

2.5   Numerical approach to one-dimensional bound states

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

$$r_i = r_0 + i\Delta, \quad \text{with } i = 1, 2, \ldots, n, \tag{2.45}$$

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

$$c_i = \chi(r_i). \tag{2.46}$$

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

$$V(r_i)\chi(r_i) = V(r_i)c_i, \tag{2.47}$$

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

$$V_{i,j} = V(r_i)\delta_{i,j}. \tag{2.48}$$

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

$$\frac{\partial^2}{\partial r^2}\chi(r)|_{r=r_i} \approx \frac{\chi(r_{i-1}) - 2\chi(r_i) + \chi(r_{i+1})}{\Delta^2} = \frac{c_{i-1} - 2c_i + c_{i+1}}{\Delta^2}. \tag{2.49}$$

Hence, the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} \tag{2.50}$$

is represented by the matrix

$$\boldsymbol{T} = -\frac{\hbar^2}{2\mu\Delta^2}\begin{pmatrix} -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & 1 & -2 & 1 & \\ & & 1 & \ddots & \end{pmatrix}, \tag{2.51}$$

or, in components

$$T_{i,j} = -\frac{\hbar^2}{2\mu\Delta^2}(\delta_{i+1,j} - 2\delta_{i,j} + \delta_{i,j+1}). \tag{2.52}$$

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

$$\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V} \tag{2.53}$$

and the eigenvectors and eigenvalues can be found by solving the matrix eigenvalue equation as in Eqs. (2.33)-(2.36).

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

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

$$\psi(r) = \sin(k_{\max}r - \varphi) \tag{2.54}$$

with

$$\frac{\hbar^2 k_{\max}^2}{2\mu} = T_{\max} \tag{2.55}$$

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

$$k_{\max}\lambda_{\min} = 2\pi. \tag{2.56}$$

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

$$\Delta_{\min} \approx \frac{\lambda_{\min}}{4}. \tag{2.57}$$

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

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

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

Chapter 3

Time-dependent Schrödinger equation

The motion of nuclei is most naturally described by the time dependent Schrödinger equation. To be specific, we consider a diatomic molecule in its ground state, set in motion through excitation by light. The ground-state vibrational wave function is $\chi_0(r)$ has *zero-point* energy, but it is still called *stationary*, because it is an eigenstate of the nuclear Hamiltonian

$$\hat{H}_0 = \hat{T} + V_0(r), \tag{3.1}$$

where $V_0(r)$ is the ground state potential and $\hat{T}$ the nuclear kinetic energy operator. Without going into the details of the interaction between light and molecules, we imagine that the molecule is put into an electronically excited state by a short laser-pulse. The vibrational wave function $\widetilde{\chi}_0(r)$ - assuming it has not changed during the excitation - will no longer be and eigenstate of

$$\hat{H} = \hat{T} + V(r), \tag{3.2}$$

where $V(r)$ is the potential for the electronically excited state. The nuclear wave function at time t_0, the time of the excitation, is equal to ground vibrational wave function

$$\psi(r, t_0) = \widetilde{\chi}_0(r). \tag{3.3}$$

The wave function at later times, $\psi(r, t)$, is found by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(r, t)}{\partial t} = \hat{H}\psi(r, t). \tag{3.4}$$

If the photon energy put into the molecule it is not sufficient to break the bond, we may use the vibrational wave functions $\chi_v(r)$ of the electronically excited state as a basis to expand $\psi(r, t)$ using time-dependent coefficients $c_v(t)$,

$$\psi(r, t) = \sum_v \chi_v(r) c_v(t), \tag{3.5}$$

where the vibrational wave functions are solutions of

$$\hat{H}\chi_v(r) = \epsilon_v \chi_v(r). \tag{3.6}$$

At time t_0 we have

$$\psi(r, t_0) = \widetilde{\chi}_0(r) = \sum_v \chi_v(r) c_v(t_0) \tag{3.7}$$

The expansion coefficients at time t_0 are found by projection with the vibrational wave functions, assuming they form an orthonormal set

$$\langle \chi_v | \widetilde{\chi}_0 \rangle = \langle \chi_v | \sum_{v'} \chi_{v'}(r) c_{v'}(t_0) \rangle = \sum_{v'} \delta_{v,v'} c_{v'}(t_0) = c_v(t_0). \tag{3.8}$$

To find the expansion coefficients at later times, we substitute the expansion of $\psi(t, r)$ [Eq. (3.5)] into the Schrödinger equation (3.4)

$$i\hbar \frac{\partial}{\partial t} \sum_v \chi_v(r) c_v(t) = \hat{H} \sum_v \chi_v(r) c_v(t) = \sum_v \epsilon_v \chi_v(r) c_v(t). \tag{3.9}$$

This equation may be rewritten as

$$\sum_v \chi_v(r) [i\hbar \frac{\partial}{\partial t} c_v(t) - \epsilon_v c_v(t)] = 0 \tag{3.10}$$

and since the vibrational wave functions are linearly independent all the terms in the sum must be zero, i.e.,

$$i\hbar \frac{\partial}{\partial t} c_v(t) = \epsilon_v c_v(t). \tag{3.11}$$

Alternatively, one may arrive at this equation by projecting Eq. (3.9) with $\chi_v(r)$. The solution is

$$c_v(t) = e^{-\frac{i}{\hbar} \epsilon_v (t - t_0)} c_v(t_0). \tag{3.12}$$

Substituting this back into the expansion [Eq. (3.5)] and using Eq. (3.8) for the coefficients at t_0 gives

$$\psi(r, t) = \sum_v \chi_v(r) e^{-\frac{i}{\hbar} \epsilon_v (t - t_0)} \langle \chi_v | \widetilde{\chi}_0 \rangle. \tag{3.13}$$

3.1   Time-dependent Schrödinger equation in arbitrary basis

Above we expanded the time-dependent wave function $\psi(r, t)$ in a basis of eigenfunctions $\chi_v(r)$ of the Hamiltonian $\hat{H}$. Here, we expand $\psi(r, t)$ in an arbitrary orthonormal basis $\{\phi_1(r), \ldots, \phi_n(r)\}$

$$\psi(r, t) = \sum_i \phi_i(r) d_i(t). \tag{3.14}$$

Substituting this expansion into the time-dependent Schrödinger equation (3.4) and projecting with the basis functions ϕ_i gives

$$i\hbar \frac{\partial}{\partial t} d_i(t) = \sum_j \langle \phi_i | \hat{H} | \phi_j \rangle d_j(t), \tag{3.15}$$

or, in matrix-vector notation

$$i\hbar \frac{\partial}{\partial t} \boldsymbol{d}(t) = \boldsymbol{H} \boldsymbol{d}(t). \tag{3.16}$$

To solve this set of coupled, first-order, linear differential equations, we first determine the eigenvalues λ_i and eigenvectors $\boldsymbol{u}_i$ of the Hamiltonian matrix $\boldsymbol{H}$

$$\boldsymbol{H}\boldsymbol{u}_i = \lambda_i \boldsymbol{u}_i. \tag{3.17}$$

This approach is equivalent to using the above method, with vibrational wave functions obtained with the linear variational method. We first rewrite the eigenvalue problem in matrix notation

$$\boldsymbol{H}\left[\boldsymbol{u}_1 \boldsymbol{u}_2 \ldots \boldsymbol{u}_n\right] = \left[\boldsymbol{u}_1 \boldsymbol{u}_2 \ldots \boldsymbol{u}_n\right] \begin{pmatrix} \lambda_1 & & \\ & \ddots & \\ & & \lambda_n \end{pmatrix} \tag{3.18}$$

or

$$\boldsymbol{H}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{\Lambda} \tag{3.19}$$

where $\boldsymbol{\Lambda}$ is the diagonal matrix with matrix elements

$$\Lambda_{i,j} = \lambda_i \delta_{i,j}. \tag{3.20}$$

Assuming that the eigenvectors $\boldsymbol{u}_i$ are orthonormal, we find

$$\boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{I}, \tag{3.21}$$

because

$$(\boldsymbol{U}^\dagger \boldsymbol{U})_{i,j} = \boldsymbol{u}_i^\dagger \boldsymbol{u}_j = \langle \boldsymbol{u}_i | \boldsymbol{u}_j \rangle = \delta_{i,j}. \tag{3.22}$$

Since the columns of the matrix $\boldsymbol{U}$ are linearly independent and the matrix is square it is nonsingular, i.e., it has an inverse. Multiplying Eq. (3.21) with $\boldsymbol{U}^{-1}$ from the right gives

$$\boldsymbol{U}^\dagger = \boldsymbol{U}^{-1} \tag{3.23}$$

and so $\boldsymbol{U}$ is a unitary matrix. We express the expansion coefficient vector in this the basis of eigenvectors,

$$\boldsymbol{d}(t) = \boldsymbol{U}\boldsymbol{c}(t). \tag{3.24}$$

Substituting this basis transformation into Eq. (3.16) and multiplying from the left with $\boldsymbol{U}^\dagger$ gives

$$i\hbar \frac{\partial}{\partial t} \boldsymbol{U}^\dagger \boldsymbol{U}\boldsymbol{c}(t) = \boldsymbol{U}^\dagger \boldsymbol{H}\boldsymbol{U}\boldsymbol{c}(t) \tag{3.25}$$

or

$$i\hbar \frac{\partial}{\partial t} \boldsymbol{c}(t) = \boldsymbol{\Lambda}\boldsymbol{c}(t). \tag{3.26}$$

If we write this in components we are back at equation (3.12), with the eigenvalues λ_i corresponding to the vibrational energies ϵ_v. At t_0, we can find the expansion coefficient again by projection,

$$d_i(t_0) = \langle \phi_i | \widetilde{\chi}_0 \rangle. \tag{3.27}$$

Using

$$\boldsymbol{c}(t_0) = \boldsymbol{U}^\dagger \boldsymbol{d}(t_0) \tag{3.28}$$

we find the explicit expression of the time-dependent expansion coefficients as

$$\boldsymbol{d}(t) = \boldsymbol{U} \begin{pmatrix} e^{-\frac{i}{\hbar}\lambda_1(t-t_0)} & & \\ & \ddots & \\ & & e^{-\frac{i}{\hbar}\lambda_n(t-t_0)} \end{pmatrix} \boldsymbol{U}^\dagger \boldsymbol{d}(t_0). \tag{3.29}$$

3.2   Matrix exponentiation

The time-dependent Schrödinger equation expressed in a basis, Eq. (3.16) can also be written as

$$\frac{\partial}{\partial t}\boldsymbol{d}(t) = -\frac{i}{\hbar}\boldsymbol{H}\boldsymbol{d}(t). \tag{3.30}$$

For sufficiently small time steps τ we can approximate

$$\boldsymbol{d}(t+\tau) \quad \approx \quad \boldsymbol{d}(t) + \tau\frac{\partial}{\partial t}\boldsymbol{d}(t) \tag{3.31}$$

$$= \quad \boldsymbol{d}(t) - \frac{i}{\hbar}\tau\boldsymbol{H}\boldsymbol{d}(t) \tag{3.32}$$

$$= \quad (\boldsymbol{I} - \frac{i}{\hbar}\tau\boldsymbol{H})\boldsymbol{d}(t). \tag{3.33}$$

As a numerical approach this is more efficient than the previous method, since it involves only a matrix-vector multiplication, which requires in the order of n^2 operations (n being the dimension of the basis), rather than the order n^3 required for diagonalization. However, it can only be used for short times. For larger time intervals τ may be divided into m smaller time steps τ/m, for which the short-time propagator can be used. Mathematically, we get the exact result by taking the limit of $m \to \infty$,

$$\boldsymbol{d}(t+\tau) = \lim_{m\to\infty}(\boldsymbol{I} - \frac{i\tau}{m\hbar}\boldsymbol{H})^m\boldsymbol{d}(t). \tag{3.34}$$

Since the Hamiltonian matrix $\boldsymbol{H}$ commutes with the identity matrix $\boldsymbol{I}$ this limit can be evaluated with the exact same method one would use when the dimension of the space were one - i.e. when $\boldsymbol{H}$ would be a number and $\boldsymbol{d}$ had only a single component. The result is

$$\boldsymbol{d}(t+\tau) = \sum_{k=0}^{\infty}\frac{1}{k!}(-\frac{i}{\hbar}\boldsymbol{H}\tau)^k\boldsymbol{d}(t) \tag{3.35}$$

Here, one may recognize the Taylor expansion of the exponential function

$$e^x = \sum_{k=0}^{\infty}\frac{1}{k!}x^k. \tag{3.36}$$

By defining a function of a matrix through the Taylor expansion of that function, we may write

$$\boldsymbol{d}(t+\tau) = e^{-\frac{i}{\hbar}\boldsymbol{H}\tau}\boldsymbol{d}(t). \tag{3.37}$$

In general, for a function defined by a polynomial expansion

$$f(x) = \sum_k c_k x^k \tag{3.38}$$

we may define the corresponding matrix function

$$f(\boldsymbol{A}) \equiv \sum_k c_k \boldsymbol{A}^k. \tag{3.39}$$

If the matrix $\boldsymbol{A}$ is *normal*, i.e., if it commutes with its Hermitian conjugate

$$[\boldsymbol{A}, \boldsymbol{A}^\dagger] = \boldsymbol{0}, \tag{3.40}$$

it has a complete set of orthonormal eigenvectors. Note that Hermitian matrices $\boldsymbol{H}$ satisfy this condition, since $\boldsymbol{H}^\dagger = \boldsymbol{H}$, but it also hold for *anti*-Hermitian matrices $\boldsymbol{A} = i\boldsymbol{H}$, for which $\boldsymbol{A}^\dagger = -\boldsymbol{A}$. With the eigenvectors collected in the unitary matrix $\boldsymbol{U}$ and the corresponding eigenvalues in the diagonal matrix $\boldsymbol{\Lambda}$,

$$\boldsymbol{A}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{\Lambda} \tag{3.41}$$

we may write $\boldsymbol{A}$ as

$$\boldsymbol{A} = \boldsymbol{U}\boldsymbol{\Lambda}\boldsymbol{U}^\dagger. \tag{3.42}$$

The square of the matrix may now be evaluated as

$$\boldsymbol{A}^2 = \boldsymbol{A}\boldsymbol{A} = (\boldsymbol{U}\boldsymbol{\Lambda}\boldsymbol{U}^\dagger)(\boldsymbol{U}\boldsymbol{\Lambda}\boldsymbol{U}^\dagger) = \boldsymbol{U}\boldsymbol{\Lambda}^2\boldsymbol{U}^\dagger \tag{3.43}$$

and for an arbitrary power we find

$$\boldsymbol{A}^k = \boldsymbol{U}\boldsymbol{\Lambda}^k\boldsymbol{U}^\dagger. \tag{3.44}$$

Hence, the matrix-polynomial Eq. (3.39) can be evaluated as

$$
\begin{aligned}
f(\boldsymbol{A}) &= \sum_k c_k \boldsymbol{U}\boldsymbol{\Lambda}^k\boldsymbol{U}^\dagger & (3.45) \\[2mm]
&= \boldsymbol{U}\left(\sum_k c_k \boldsymbol{\Lambda}^k\right)\boldsymbol{U}^\dagger & (3.46) \\[2mm]
&= \boldsymbol{U}\begin{pmatrix} \sum_k c_k \lambda_1^k & & \\ & \ddots & \\ & & \sum_k c_k \lambda_n^k \end{pmatrix}\boldsymbol{U}^\dagger & (3.47) \\[2mm]
&= \boldsymbol{U}\begin{pmatrix} f(\lambda_1) & & \\ & \ddots & \\ & & f(\lambda_n) \end{pmatrix}\boldsymbol{U}^\dagger. & (3.48)
\end{aligned}
$$

From this general expression we can immediately obtain equation (3.29) of the previous section by noting that the eigenvalues of $-\frac{i}{\hbar}\boldsymbol{H}(t - t_0)$ are $-\frac{i}{\hbar}\lambda_i(t - t_0)$, and so matrix exponentiation is equivalent to the other methods. Note, however, that algorithms exist to exponentiate a matrix, without computing eigenvalues and eigenvectors first [6].

3.3   Free particles in one dimension

The Hamiltonian $\hat{H}_0$ for a free particle with mass μ, moving in one dimension (x) consists of just the kinetic energy operator

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}. \tag{3.49}$$

We call it a "free particle" because the potential is zero. The time-independent Schrödinger equation for this Hamiltonian is

$$\hat{H}_0 \Psi(x) = E\Psi(x), \tag{3.50}$$

and it is easy to find the solutions $\Psi(x)$

$$\Psi(x) = Ne^{-ikx}, \tag{3.51}$$

where the so called wave vector k is related to the energy E by

$$E = \frac{\hbar^2 k^2}{2\mu}. \tag{3.52}$$

The problem with these solutions is that they cannot be normalized, since the integral

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 \, dx \tag{3.53}$$

does not exist ("is infinite") for any normalization factor $N \neq 0$. To give meaning to these wave functions we will first derive analytic solutions of the time-dependent Schrödinger equation for a free particle. This derivation will be more complicated, but we will find solutions that can be normalized, so the interpretation of the result will be straightforward.

3.4   Gaussian wave packets

The time-dependent Schrödinger equation for a free particle moving in one dimension is

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \Psi(x,t). \tag{3.54}$$

We will derive normalizable solutions that can be written in exponential form

$$\Psi(x,t) = e^{f(x,t)}, \tag{3.55}$$

where $f(x,t)$ is a complex function. To simplify the notation we will use a dot to denote the derivative with respect to time (t), and a prime to denote the derivative with respect to the position x and we will drop the (x,t) arguments. Dividing Eq. (3.4) by $i\hbar$ then gives

$$\dot{\Psi} = \frac{i\hbar}{2\mu} \Psi''. \tag{3.56}$$

For the time derivative we have

$$\dot{\Psi} = \dot{f}e^f = \dot{f}\Psi, \tag{3.57}$$

the first derivative of Ψ with respect to x gives

$$\Psi' = f'e^f \tag{3.58}$$

and the second derivate is

$$\Psi'' = f''e^f + (f')^2 e^f = [f'' + (f')^2]\Psi. \tag{3.59}$$

Substituting Eqs. (3.57) and (3.59) into the Schrödinger equation (3.56) gives

$$\dot{f}\Psi = \frac{i\hbar}{2\mu}[f'' + (f')^2]\Psi. \tag{3.60}$$

This equation is satisfied if

$$\dot{f} = \frac{i\hbar}{2\mu}[f'' + (f')^2]. \tag{3.61}$$

It turns out that this equation has solutions that can be written in this form:

$$f(x, t) = -\frac{1}{2}\alpha_t(x - vt)^2 + ikx + c_t, \tag{3.62}$$

where α_t and c_t are functions of time, and v and k are constants. It may not be immediately obvious that a solution can be written like this, but given the functional form is not difficult to derive the expressions for α_t and c_t and find an interpretation of the parameters v, k, α_t, and c_t. In particular, we will find that v has the meaning of the (average) velocity of the wave packet, $\hbar k = \mu v \equiv p$ is its linear momentum and c_t keeps the wave packet normalized as a function of time.

To verify Eq. (3.62) we first write the left-hand side (lhs) and the right-hand side (rhs) of Eq. (3.61) as second degree polynomials in x. The lhs is equal to:

$$\dot{f} = -\frac{1}{2}\dot{\alpha}_t(x - vt)^2 + \alpha_t v(x - vt) + \dot{c}_t \tag{3.63}$$

$$= -\frac{1}{2}\dot{\alpha}_t x^2 + (\dot{\alpha}_t t + \alpha_t)vx - \frac{1}{2}\dot{\alpha}_t v^2 t^2 - \alpha_t v^2 t + \dot{c}_t. \tag{3.64}$$

For the rhs we have:

$$f' = -\alpha_t(x - vt) + ik = -\alpha_t x + \alpha_t vt + ik \tag{3.65}$$

$$f'' = -\alpha_t \tag{3.66}$$

$$(f')^2 = \alpha_t^2 x^2 - 2\alpha_t(\alpha_t vt + ik)x + (\alpha_t vt + ik)^2 \tag{3.67}$$

Equating the terms with x^2 in Eq. (3.61) gives:

$$-\frac{1}{2}\dot{\alpha}_t = \frac{i\hbar}{2\mu}\alpha_t^2 \tag{3.68}$$

or

$$\dot{\alpha}_t = -\frac{i\hbar}{\mu}\alpha_t^2. \tag{3.69}$$

We will solve this first order differential equation for α_t below.

Equating the terms linear in x gives [see Eqs. (3.61), (3.64), and (3.67)]

$$(\dot{\alpha}_t t + \alpha_t)v = \frac{i\hbar}{2\mu}(-2\alpha_t^2 vt - 2\alpha_t ik). \tag{3.70}$$

On the lhs we can replace $\dot{\alpha}_t$ by substituting Eq. (3.69) and we can simplify the rhs:

$$-\frac{i\hbar}{\mu}\alpha_t^2 tv + \alpha_t v = -\frac{i\hbar}{\mu}\alpha_t^2 vt + \frac{\hbar}{\mu}\alpha_t k, \tag{3.71}$$

which shows that the parameters v and k must be related through:

$$v = \frac{\hbar k}{\mu}. \tag{3.72}$$

Since mass times velocity is linear momentum, $\mu v = p$, we just found that $\hbar k = p$, as we announced above. Note that for a free moving particle we do not expect the velocity or the momentum to change in time, and indeed v and k are constants.

Finally, from the terms independent of x we get:

$$\underbrace{-\frac{1}{2}\dot{\alpha}_t v^2 t^2 - \alpha_t v^2 t + \dot{c}_t}_{A_t} = \underbrace{\frac{i\hbar}{2\mu}[(\alpha_v vt + ik)^2 - \alpha_t]}_{B_t} \tag{3.73}$$

or

$$\dot{c}_t = B_t - A_t \tag{3.74}$$

After solving α_t (see below) we know B_t and A_t, so c_t can be found by integration:

$$c_t = c_0 + \int_0^t (B_t - A_t)\, dt. \tag{3.75}$$

Since the Hamiltonian is Hermitian, the normalization of the wave function should not change in time, and we can check the expression for α_t and c_t by computing the norm:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = \int_{-\infty}^{\infty} \Psi(x,t)^* \Psi(x,t) dx = \int_{-\infty}^{\infty} e^{-\Re[\alpha_t](x-vt)^2 + 2\Re[c_t]}\, dx, \tag{3.76}$$

where $\Re[\ldots]$ stands for the real part of the argument and the result should be time independent.

Derivation of expression for α_t

Here we solve Eq. (3.69), with $\alpha = \alpha_t$,

$$\frac{d\alpha}{dt} = -C\alpha^2, \quad \text{with } C = \frac{i\hbar}{\mu}. \tag{3.77}$$

Separation of variables gives

$$\frac{d\alpha}{\alpha^2} = -C\, dt \tag{3.78}$$

Integration from some initial $t = 0$ for which $\alpha = \alpha_0$ to time t gives

$$\int_{\alpha_0}^{\alpha_t} \frac{1}{\alpha^2}\, d\alpha = -\int_0^t C dt, \tag{3.79}$$

which gives

$$-\left.\frac{1}{\alpha}\right|_{\alpha_0}^{\alpha_t} = -Ct \tag{3.80}$$

or

$$-\frac{1}{\alpha_t} + \frac{1}{\alpha_0} = -Ct, \tag{3.81}$$

which may be rewritten as

$$\alpha_t = \frac{\alpha_0}{1 + \frac{i\hbar}{\mu}t\alpha_0}. \tag{3.82}$$

First note that for $t = 0$ we get $\alpha_t = \alpha_0$, as it should be. Furthermore, over time the absolute value of α_t becomes smaller and for $t \gg \frac{\mu}{\hbar}$ we get

$$\alpha_t \simeq \frac{\mu}{i\hbar t} \quad \to 0 \quad (\text{for } t \to \infty). \tag{3.83}$$

This shows that over time $|\alpha_t|$ gets smaller, i.e., the wave packet spreads. To make this statement more quantitative we first note that the spread of the wave packet Δx actually depends on the *real* part of α_t

$$\Delta x \approx \frac{1}{\sqrt{\Re[\alpha]}} \tag{3.84}$$

If we take α_0 to be real, then we find for the real part of α_t,

$$\Re(\alpha_t) = \frac{\alpha_0}{1 + \frac{\hbar^2}{\mu^2}t^2\alpha_0^2} \tag{3.85}$$

For $t \gg \frac{\mu}{\hbar\alpha_0}$ we can ignore the 1 in the denominator of this equation and we find

$$\Delta x \approx \frac{\hbar t\sqrt{\alpha_0}}{\mu} \tag{3.86}$$

This shows that eventually the width of the wave packet will be increasing linearly in time. Also, if α_0 is large the wave packet is initially very narrow, but for large times it will be wider.

3.5   Expectation values of Gaussian wave packets

It is left as an exercise to show that the expectation value of the position x is

$$\langle x \rangle \equiv \frac{\langle \Psi(x,t)|x|\Psi(x,t)\rangle}{\langle \Psi(x,t)|\Psi(x,t)\rangle} = vt. \tag{3.87}$$

Here, the wave function is given by Eqs. (3.55), (3.62), and (3.82). Note that the expression for c_t is not needed. Also, the expectation value of the linear momentum:

$$\langle \hat{p} \rangle = \langle \frac{\hbar}{i}\frac{\partial}{\partial x} \rangle = \hbar k. \tag{3.88}$$

Even more work: solve c_t integral Eq. (3.75) and show that $\langle \Psi(x,t)|\Psi(x,t)\rangle$ is a constant.

3.6   Middle of the wave packet

Since α_t becomes very small after a long time, the wave function $\Psi(x,t)$ near $x = vt$ looks like
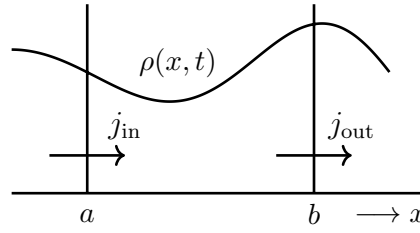
$$\Psi(x,t) \simeq e^{ikx+c_t}. \tag{3.89}$$

Figure 3.1: The particle density $\rho(x,t)$ as a function of position x for time t. The fluxes at a and b are j_{in} and j_{out}.

The interpretation of the wave packet suggests that $\Psi(x,t)$, at least in this region near $x = vt$, describes particles that move with velocity v. Neglecting the term with $\alpha_t(x - vt)^2$ in Eq. (3.62) we note that $f \approx ikx + c_t$ and 3.61 becomes

$$\dot{f} = \frac{i\hbar}{2\mu}(f')^2, \tag{3.90}$$

from which we find

$$\dot{c}_t = -\frac{i}{\hbar}\frac{\hbar^2 k^2}{2\mu}. \tag{3.91}$$

Since $\hbar k = p = \mu v$, we may rewrite $\frac{\hbar^2 k^2}{2\mu} = \frac{1}{2}\mu v^2$, which is the kinetic energy (E_0) of a particle with mass μ moving at a velocity v. Solving Eq. (3.91) by integration we find

$$c_t = c_0 - \frac{i}{\hbar}E_0 t \tag{3.92}$$

so at large t for $x \approx vt$ we may write $\Psi(x,t)$ as

$$\Psi(x,t) \simeq e^{c_0} e^{ikx} e^{-\frac{i}{\hbar}E_0 t} \tag{3.93}$$

This wave function cannot be valid for all x, since it cannot be normalized, but the x-dependent part e^{ikx} is a solution of the time-independent Schrödinger equation at energy E_0,

$$(\hat{H} - E_0)e^{ikx} = 0 \tag{3.94}$$

and it can also be easily verified that $\Psi(x,t)$ is solution of the time-dependent Schrödinger equation. Since the wave packet spreads out over time, the region for which Eq. (3.93) becomes larger and larger, so it is very tempting to use such functions to describe free particles with energy E_0, even though they cannot be normalized. In the next section we will introduce the concept of *flux*, which will help us to work with solutions of the time-independent Schrödinger equations that cannot be normalized.

3.7   Flux in one dimension

We consider a particle moving along a one-dimensional Cartesian coordinate. The *particle density* $\rho(x,t)$ gives the probability density of finding a particle at coordinate x at time t

(Fig. 3.1). The probability $P_{ab}(t)$ of finding the particle in the interval $[a, b]$ at time t is found by integrating the particle density over that interval

$$P_{ab}(t) = \int_a^b \rho(x, t)\, dx. \tag{3.95}$$

The change in time of the probability of finding a particle in the interval is related to the fluxes j_a and j_b through

$$\frac{d}{dt} P_{\text{ab}}(t) = j_a - j_b \tag{3.96}$$

To find the quantum mechanical expression for flux we express the particle density in terms of the wavefunction $\Psi(x, t)$:

$$\rho(x, t) = |\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t) \tag{3.97}$$

and we determine its time derivative from the time-dependent Schrödinger equation:

$$\frac{d}{dt} P_{\text{ab}}(t) = \frac{d}{dt} \int_a^b \Psi^*(x, t)\Psi(x, t)\, dx = \int_a^b \left[\Psi^*(x, t)\frac{d}{dt}\Psi(x, t) + \Psi(x, t)\frac{d}{dt}\Psi^*(x, t) \right]\, dx. \tag{3.98}$$

From the time-dependent Schrödinger equation we have

$$\frac{d}{dt}\Psi(x, t) = -\frac{i}{\hbar}\hat{H}\Psi(x, t) \tag{3.99}$$

and its complex conjugate

$$\frac{d}{dt}\Psi^*(x, t) = \frac{i}{\hbar}\hat{H}\Psi^*(x, t) \tag{3.100}$$

so we have

$$\frac{d}{dt} P_{\text{ab}}(t) = -\frac{i}{\hbar} \int_a^b \left[\Psi^*(x, t)\hat{H}\Psi(x, t) - \Psi(x, t)\hat{H}\Psi^*(x, t) \right] dx. \tag{3.101}$$

The Hamiltonian for a particle with mass μ moving in a potential $V(x)$ is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x). \tag{3.102}$$

First, we note that the potential, if we assume that it is real, does not contribute to the integral

$$\int_a^b \left[\Psi^*(x, t)V(x)\Psi(x, t) - \Psi(x, t)V(x)\Psi^*(x, t) \right] dx = 0. \tag{3.103}$$

If the potential has a negative imaginary part the Hamiltonian is not Hermitian and the potential can "absorb" particles. In a time-dependent calculation this means that the norm of the wave function would not be conserved.

For the kinetic energy term we find

$$\frac{d}{dt} P_{\text{ab}}(t) = \frac{i\hbar}{2\mu} \int_a^b \left[\Psi^*(x, t)\frac{\partial^2}{\partial x^2}\Psi(x, t) - \Psi(x, t)\frac{\partial^2}{\partial x^2}\Psi^*(x, t) \right] dx. \tag{3.104}$$

To evaluate the integral, we use the following relation that holds for any two functions $f(x)$ and $g(x)$ with derivative f' and g':

$$\frac{d}{dx}(fg' - gf') = f'g' + fg'' - (g'f' + gf'') = fg'' - gf'' \tag{3.105}$$

so

$$\int_a^b (fg'' - gf'')dx = \int_a^b \frac{d}{dx}(fg' - gf')dx = (fg' - gf')\big|_a^b. \tag{3.106}$$

Applying this relation to Eq. (3.104) gives

$$\frac{d}{dt}P_{\mathrm{ab}}(t) = \frac{i\hbar}{2\mu}\left[\Psi^*(x,t)\frac{d}{dx}\Psi(x,t) - \Psi(x,t)\frac{d}{dx}\Psi^*(x,t)\right]_a^b \tag{3.107}$$

$$= -\frac{\hbar}{\mu}\mathrm{Im}\left[\Psi^*(x,t)\frac{d}{dx}\Psi(x,t)\right]_a^b \tag{3.108}$$

$$= j_a - j_b, \tag{3.109}$$

where we define the flux at x

$$j_x = \frac{\hbar}{\mu}\mathrm{Im}\left[\Psi^*(x,t)\frac{d}{dx}\Psi(x,t)\right]. \tag{3.110}$$

3.8   The Ehrenfest theorem

Combining Eqs. (3.72), (3.87), and (3.88) shows that for a Gaussian wave packet moving in free space

$$\langle x\rangle = vt = \frac{\langle p\rangle}{\mu}t. \tag{3.111}$$

So the expectation values of position and momentum behave as for a classical particle. This is a special case of the much more general Ehrenfest theorem, which holds for arbitrary wave packets, and is also valid if the potential in not zero: *the expectation values of observables satisfy classical equations of motion.*

Consider the time-dependence of the expectation value of some observable $\hat{A}$ for a particle moving in one dimension as described by some wavepacket $\Psi(x,t)$

$$\frac{d}{dt}\langle\Psi(x,t)|\hat{A}|\Psi(x,t)\rangle = \langle\dot{\Psi}(x,t)|\hat{A}|\Psi(x,t)\rangle + \langle\Psi(x,t)|\hat{A}|\dot{\Psi}(x,t)\rangle \tag{3.112}$$

$$= \frac{i}{\hbar}\langle\Psi(x,t)|[\hat{H},\hat{A}]|\Psi(x,t)\rangle \tag{3.113}$$

or, written more compactly,

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{A}]\rangle. \tag{3.114}$$

If we take

$$\hat{H} = \frac{p^2}{2\mu} + V(x) \tag{3.115}$$

and use

$$[\hat{H}, x] = \frac{1}{2\mu}[p^2, x] = \frac{1}{2\mu}\{p[p, x] + [p, x]p\} = \frac{\hbar}{i\mu}p \tag{3.116}$$

$$[\hat{H}, p] = \frac{1}{2\mu}[V, p] = -\frac{\hbar}{i}\frac{d}{dx}V, \tag{3.117}$$

we find

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p \rangle}{\mu} \tag{3.118}$$

$$\frac{d}{dt}\langle p \rangle = -\left\langle \frac{dV}{dx} \right\rangle. \tag{3.119}$$

These equations of motion correspond to Hamiltons classical equations of motion

$$\frac{d}{dt}x = \frac{\partial H(p, x)}{\partial p} = \frac{p}{\mu} \tag{3.120}$$

$$\frac{d}{dt}p = -\frac{\partial H(p, x)}{\partial x} = -\frac{\partial V}{\partial x}, \tag{3.121}$$

where the classical Hamiltonian is defined by

$$H(p, x) = \frac{p^2}{2\mu} + V(x). \tag{3.122}$$

Chapter 4

Time-independent scattering in one dimension

4.1 Some properties and examples of flux

The first example is a free particle in 1-D:

$$\Psi_1(x) = Ne^{ikx}, \tag{4.1}$$

where N is a constant, we find

$$j_1 = \frac{\hbar}{\mu}\text{Im}\left[N^*e^{-ikx}\frac{d}{dx}Ne^{ikx}\right] = |N|^2\frac{\hbar k}{\mu}. \tag{4.2}$$

The momentum is given by $p = \hbar k$, it is related to the velocity v through $p = \mu v$, and for the density we have $\rho(x) = |\Psi(x)|^2 = |N|^2$, so we get a relation that is also valid in classical mechanics:

$$j = \rho v. \tag{4.3}$$

As a second example we look at

$$\Psi_2(x) = ae^{ikx} + be^{-ikx}, \tag{4.4}$$

which has a flux

$$j_2 = \frac{\hbar k}{\mu}(|a|^2 - |b|^2). \tag{4.5}$$

This result may suggest that the flux of the sum of two wave functions is equal to the fluxes of these wave functions, but in general that is not correct. A counter example can be constructed from $\Psi_1(x)$, by writing it as a sum

$$\Psi_1(x) = N\cos(kx) + i\sin(kx) \tag{4.6}$$

From the definition [Eq. 3.110] it follows immediately that the flux of a real wave function is zero. The flux is also zero for a wave function that can be written as an arbitrary complex *constant* factor times a real wave function.

In general, for a wave function with a real part $f(x)$ and an imaginary part $g(x)$,

$$\Psi(x) = f(x) + ig(x) \tag{4.7}$$

we find

$$j = \frac{\hbar}{\mu}\text{Im}\left\{[f(x) - ig(x)]\frac{d}{dx}[f(x) + ig(x)]\right\} = \frac{\hbar}{\mu}(fg' - f'g). \tag{4.8}$$

The factor

$$W(f, g) = fg' - f'g \tag{4.9}$$

is called the *Wronskian* of the functions f and g. If the Hamiltonian is real, and Ψ is a solution of the 1-D Schrödinger equation with energy E, then f and g are both solution with energy E. In this case the Wronskian of f and g, and hence the flux j are constant. This can be seen in two ways. First consider the derivative of the Wronskian:

$$\frac{d}{dx}W(f, g) = f'g' + fg'' - f''g - f'g' = fg'' - f''g. \tag{4.10}$$

For f and g we have:

$$-\frac{\hbar^2}{2\mu}f''(x) + V(x)f(x) = Ef(x) \tag{4.11}$$

$$-\frac{\hbar^2}{2\mu}g''(x) + V(x)f(x) = Eg(x). \tag{4.12}$$

If we multiply the first of these two equations with $g(x)$ and the second with $f(x)$ and we take the difference of the two equations we get

$$\frac{\hbar^2}{2\mu}(g''f - f''g) = 0 \tag{4.13}$$

and we find that the Wronskian $W(f, g)$, and hence the flux j, is constant.

An easier way to show that a solution $\Psi(x)$ of the time-independent Schrödinger equation has constant flux starts with Eq. (3.101). Again, assuming the Hamiltonian is real, both Ψ and Ψ^* have energy E, and the right-hand side of the equation is zero. This means that the probability $P_{\text{ab}}(t)$ of finding a particle in interval $[a, b]$ is constant in time, and hence the flux $j_a = j_b$ [see Eqs. (3.106)] for each a and b, or, in other words, j is constant.

This result shows that if a solution of the time-independent Schrödinger equation has a node, i.e., for some x we have $\Psi(x) = 0$, then its flux must be zero at x, and, hence, everywhere.

4.2   Boundary conditions for 1-D scattering problems

We start with an example from elementary quantum mechanics that has an analytic solution, a "stream of particles" with energy E and mass μ, scattered by a step potential:

$$V(x) = \begin{cases} V_a, & \text{for } x > 0. \\ V_b, & \text{for } x < 0, \end{cases} \tag{4.14}$$

We assume the particles are incoming from the right, and particles may be reflected at $x = 0$, or transmitted. Hence, for $x > 0$ the wave function consists of an incoming and a reflected part

$$\Psi_a(x) = e^{-ik_a x} - e^{ik_a x} R, \quad (x > 0), \tag{4.15}$$

with reflection coefficient R. The minus sign for the reflection term is just a convention: with this choice $R = 1$ if $V_b = \infty$. For $x < 0$ we only have a transmitted wave

$$\Psi_b(x) = e^{-ik_b x} T, \quad (x < 0), \tag{4.16}$$

where T is the transmission amplitude. The wave numbers k_a and k_b are the positive solutions of

$$\frac{\hbar^2 k_i^2}{2\mu} = E - V_i, \quad \text{for } i = a, b. \tag{4.17}$$

The flux of the transmitted wave is $j_b = \frac{\hbar k_b}{\mu} |T|^2$. The incoming flux, by which we mean the flux of the wave function without the step in the potential, i.e., for $V_b = V_a$, is given by $j_{\text{in}} = \frac{\hbar k_a}{\mu}$. With the step potential the reflected part will be nonzero, and the flux will be

$$j_a = j_{\text{in}} - \frac{\hbar k_a}{\mu} |R|^2. \tag{4.18}$$

Since flux must be conserved, we must have $j_a = j_b$, or

$$1 - |R|^2 = \frac{k_b}{k_a} |T|^2. \tag{4.19}$$

The amplitudes R and T can be found from the condition that the wave function and its first derivative must be continuous at $x = 0$. The transmission probability is given by

$$P_{a \leftarrow b} = \frac{j_b}{j_{\text{in}}} = \frac{k_b}{k_a} |T|^2. \tag{4.20}$$

Note that as a result of conservation of flux [Eq. (4.19)], this probability must be between 0 and 1.

4.3   Numerical solution for 1-D tunneling problem

We consider a one-dimensional potential barrier, e.g.,

$$V(x) = V_m e^{-\alpha x^2}. \tag{4.21}$$

Classically, if the scattering energy E is less than the maximum of the potential, $E < V_m$, all particles will be reflected, and otherwise all particles are transmitted. Quantum mechanically, *tunneling* may occur for $E < V_m$, while part of the wave may still be reflected if $E > V_m$.

The boundary conditions are similar to the step-potential problem in the previous Section with $V_a = V_b = 0$, but Eq. (4.15) now applies for $x \ll 0$, where we have $V(x) \approx 0$, and similarly Eq. (4.16) now applies for $x \gg 0$.

In the region where the potential is not negligible, we will solve the Schrödinger equation numerically, representing the wave function by its values $\Psi_i \equiv \Psi(x_i)$ on an equally spaced grid

$$x_i = x_0 + i\Delta, \quad i = 1, \ldots, N, \tag{4.22}$$

and using the second order finite difference approximation for the kinetic energy operator, just as we did for bound states in Section 2.5. The grid will have to cover the entire range where the potential is nonnegligible, so $x_0 \ll 0$ and $x_N \gg 0$, and the step size Δ must be taken small compared to the smallest Broglie wave length in the problem. Since the time-independent Schrödinger equation is a second order differential equation, we need two boundary conditions. Initially, we do not know the reflection coefficient R, so we cannot apply boundary conditions at x_N. For $x \ll 0$ we also do not know T, but we know the *ratio* of $\Psi(x)$ for two points. Hence, we introduce the Q-matrices defined by

$$\Psi_{i-1} = Q_i\Psi_i, \quad i = 1, 2, \ldots, N, \tag{4.23}$$

For $i = 1$ we have

$$e^{-ikx_0}T = Q_1 e^{-ikx_1}T, \tag{4.24}$$

or

$$Q_1 = e^{ik(x_1 - x_0)} = e^{ik\Delta}. \tag{4.25}$$

The 1-d time independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x) - E \right]\Psi(x) = 0 \tag{4.26}$$

can be rewritten as

$$\Psi''(x) = W(x)\Psi(x) \tag{4.27}$$

where

$$W(x) = \frac{2\mu}{\hbar^2}[V(x) - E]. \tag{4.28}$$

Using the second order finite difference approximation [as in Eq. (2.49)], we find

$$\Psi_i'' = \frac{\Psi_{i-1} - 2\Psi_i + \Psi_{i+1}}{\Delta^2} = W_i\Psi_i, \tag{4.29}$$

where $W_i \equiv W(x_i)$. This gives the three-term recursion relation

$$\Psi_{i-1} - (\Delta^2 W_i + 2)\Psi_i + \Psi_{i+1} = 0. \tag{4.30}$$

We can relate both Ψ_{i-1} and Ψ_{i+1} to Ψ_i using the Q-matrices defined in Eq. (4.23)

$$Q_i\Psi_i - (\Delta^2 W_i + 2)\Psi_i + Q_{i+1}^{-1}\Psi_i = 0, \tag{4.31}$$

which gives the two-term recursion relation

$$Q_i - (\Delta^2 W_i + 2) + Q_{i+1}^{-1} = 0. \tag{4.32}$$

Since we know Q_1, we can get *propagate* the Q-matrices:

$$Q_{i+1} = (\Delta^2 W_i + 2 - Q_i)^{-1}, \quad \text{for } i = 1, \ldots, N - 1. \tag{4.33}$$

Once we have computed Q_N we can match it to the $x \gg 0$ boundary condition of the wave function

$$\Psi_{N-1} = Q_N \Psi_N \tag{4.34}$$

or, with Eq. (4.15),

$$e^{-ik_a x_{N-1}} - e^{ik_a x_{N-1}} R = Q_N(e^{-ik_a x_N} - e^{ik_a x_N} R) \tag{4.35}$$

which we can solve for R

$$R = [e^{ik_a x_{N-1}} - Q_N e^{ik_a x_N}]^{-1}[e^{-ik_a x_{N-1}} - Q_N e^{-ik_a x_N}]. \tag{4.36}$$

Having found the reflection coefficient R, we can obtain the wave function Ψ_N at the last grid point from Eq. (4.15). Assuming we stored the matrices Q_i during the propagation, we can compute the wave function recursively with Eq. (4.23), propagating backwards, i.e., with $i = N, N-1, \dots, 1$. To complete the calculation we can find the transmission amplitude T from

$$\Psi_0 = e^{-ik_b x_0} T \tag{4.37}$$

and we can check numerically the relation between $|T|$ and $|R|$ as given by Eq. (4.19).

Chapter 5

Multichannel collinear scattering

Collinear scattering is an approximation where all atoms move on a straight line. The classic[7, 8, 9] example is the vibrational excitation of H_2 by He

$$H_2(v) + He \rightarrow H_2(v') + He. \tag{5.1}$$

We will take the coordinate of the atom as x_A, and the coordinates of the atoms in the molecules as x_B and x_C. The mass of the atom is m_A and the mass of the molecule is $m_{BC} = m_B + m_C$. The center-of-mass of the molecule is

$$x_{BC} = \frac{m_B x_B + m_C x_C}{m_{BC}} \tag{5.2}$$

and the center-of-mass of the complex is

$$X_{COM} = \frac{m_A x_A + m_{BC} x_{BC}}{m_A + m_{BC}}. \tag{5.3}$$

In these Cartesian coordinates, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m_A}\frac{\partial^2}{\partial x_A^2} - \frac{\hbar^2}{2m_B}\frac{\partial^2}{\partial x_B^2} - \frac{\hbar^2}{2m_C}\frac{\partial^2}{\partial x_C^2} + V_{\text{Cart}}(x_A, x_B, x_C). \tag{5.4}$$

The first step is to introduce *Jacobi coordinates*, or *scattering coordinates*:

$$r = x_B - x_C \tag{5.5}$$
$$R = x_A - x_{BC} \tag{5.6}$$

Assuming the potential is invariant under translation of all three atoms, we can transform the potential to Jacobi coordinates by taking the center of mass of the molecule as the origin, so $x_A = R$, and

$$V(R, r) = V_{\text{Cart}}(R, \frac{m_C}{m_{BC}}r, -\frac{m_B}{m_{BC}}r). \tag{5.7}$$

We assume that the interaction between the atom and the molecule approaches zero for large distance, so the diatomic potential is given by

$$V_{BC}(r) = \lim_{R \to \infty} V(R, r) \tag{5.8}$$

and the interaction potential is defined by

$$\Delta V(R, r) = V(R, r) - V_{BC}(r). \tag{5.9}$$

The Hamiltonian in Jacobi coordinates then becomes

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \hat{H}_{BC}(r) + \Delta V(R, r), \tag{5.10}$$

with the reduced mass of the complex

$$\mu^{-1} = m_A^{-1} + m_{BC}^{-1} \tag{5.11}$$

and the Hamiltonian of the diatom is

$$\hat{H}_{BC} = -\frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2} + V_{BC}(r), \tag{5.12}$$

with μ_{BC} the reduced mass of the molecules BC,

$$\mu_{BC}^{-1} = m_B^{-1} + m_C^{-1}. \tag{5.13}$$

The Schrödinger equation in Jacobi coordinates can now be rewritten as

$$\frac{\partial^2}{\partial R^2}\Psi(R, r) = \frac{2\mu}{\hbar^2}\left[\hat{H}_{BC}(r) + \Delta V(R, r) - E\right]\Psi(R, r). \tag{5.14}$$

The vibrational wave functions of the diatom are solutions of

$$\hat{H}_{BC}\phi_n(r) = \epsilon_n\phi_n(r). \tag{5.15}$$

We consider energy well below the dissociation energy of the molecule BC, and we assume that the functions $\phi_n(r)$ approximate a complete set, so we can use these functions to expand the scattering wave functions

$$\Psi(R, r) = \sum_{n'}\phi_{n'}(r)c_{n'}(R). \tag{5.16}$$

The terms in this expansion for which the vibrational energies are less than the total energy, $\epsilon_n < E$, are called the *open channels*. To get converged results, we may also have to include *closed channels*. The closed channels have vibrational energies $\epsilon_n > E$, so they cannot contribute asympotically (i.e., at large R), but in the interaction region, where $\Delta V(R, r)$ is not negligible, they can.

To define the boundary conditions, we assume that the interaction potential is sufficiently repulsive at short range (i.e., for small R) so that we may assume that the wave function can be set to zero for some value R_0,

$$\Psi(R_0, r) = 0. \tag{5.17}$$

For large R the boundary conditions are

$$\Psi_n(R, r) \simeq \underbrace{-\phi_n(r)v_n^{-1/2}e^{-ik_nR}}_{\text{incoming}} + \underbrace{\sum_{n'}\phi_{n'}(r)v_{n'}^{-1/2}e^{ik_{n'}R}S_{n',n}}_{\text{outgoing}}. \tag{5.18}$$

There are several differences compared to single channel scattering. The wavenumber k_n depends on the vibrational state (n) of the molecule, since the kinetic energy is equal to the total energy minus the energy of the molecule:

$$\frac{\hbar^2 k_n^2}{2\mu} = E - \epsilon_n. \tag{5.19}$$

Furthermore, the wave function Ψ_n is labeled with the vibrational state of the molecule *before* the collision, i.e., the state of the *incoming* wave. After the collision, there can be contributions to the wave function from open channels, so the outgoing wave is a sum over channels. The contribution of final state $\phi_{n'}$ for a given initial state ϕ_n, is given by the $\boldsymbol{S}$-matrix element $S_{n',n}$. The $\boldsymbol{S}$-matrix is a complex symmetric unitary matrix, i.e., $\boldsymbol{S} = \boldsymbol{S}^T$ (or $S_{n',n} = S_{n,n'}$), and $\boldsymbol{S}^\dagger \boldsymbol{S} = \boldsymbol{S}\boldsymbol{S}^\dagger = \mathbf{1}_{m \times m}$, where m is the number of open channels. The unitarity is the result of using flux-normalized waves: we included the factors $v_n^{-1/2}$, with the velocities $v_n = \hbar k_n/\mu$. The probability of scattering into final vibrational state $\phi_{n'}$ for given initial state n is

$$P_{n',n} = |S_{n',n}|^2. \tag{5.20}$$

The sum of each column of $\boldsymbol{P}$ is one, since $\boldsymbol{S}$ is unitary. If the interaction potential is zero, and we take $R_0 = 0$, i.e., we assume that the potential is infinitely repulsive for $R < 0$, then one can easily check that the functions $\Psi_n(R,r)$ with $\boldsymbol{S} = \mathbf{1}_{m \times m}$ are solutions of the time-independent Schrödinger equation.

To find a solution in the general case, we insert the expansion Eq. (5.16) into Eq. (5.14) and project from the left with $\langle \phi_n |$. Using the orthonormality of the vibrational wave functions $\langle \phi'_n | \phi_n \rangle = \delta_{n',n}$ we obtain

$$\frac{\partial^2}{\partial R^2} c_n(R) = \sum_{n'} W_{n',n}(R) c_{n'}(R), \tag{5.21}$$

where

$$W_{n',n}(R) = \frac{2\mu}{\hbar^2} \left[(\epsilon_n - E)\delta_{n',n} + \langle \phi_{n'} | \Delta V(R,r) | \phi_n \rangle \right]. \tag{5.22}$$

In matrix notation, the coupled-channels equation becomes

$$\boldsymbol{c}''(R) = \boldsymbol{W}(R)\boldsymbol{c}(R). \tag{5.23}$$

We can find a numerical solution as before: we introduce an equally spaced grid $\{R_i = R_0 + i\Delta, \ i = 1, \ldots, N\}$, we define the expansion coefficients for the wave function on the grid, $\boldsymbol{c}_i = \boldsymbol{c}(R_i)$ and we introduce the Q-matrices as real, square, matrices of dimension $n_{\text{tot}} = n_{\text{open}} + n_{\text{closed}}$ (the number of open channels plus the number of closed channels), that satisfy $\boldsymbol{c}_{i-1} = \boldsymbol{Q}_i \boldsymbol{c}_i$. For the second derivative we use the second order finite difference approximation

$$\boldsymbol{c}''(R_i) = \frac{\boldsymbol{c}_{i-1} - 2\boldsymbol{c}_i + \boldsymbol{c}_{i+1}}{\Delta^2} \tag{5.24}$$

and we arrive at the matrix equivalent of Eq. (4.33)

$$\boldsymbol{Q}_{i+1} = (\Delta^2 \boldsymbol{W}_i + 2 - \boldsymbol{Q}_i)^{-1}, \quad \text{for } i = 1, \ldots, N-1. \tag{5.25}$$

where $\boldsymbol{W}_i = \boldsymbol{W}(R_i)$. At short range the boundary condition for the Q-matrix becomes $\boldsymbol{Q}_1 = \boldsymbol{0}_{n_{\text{tot}} \times n_{\text{tot}}}$, because we require the wave function to be zero at $R = R_0$. To match the wave function to its analytic long range form, we rewrite Eq. (5.18) as

$$\Psi_n(R, r) \simeq \sum_{n'} \phi_{n'}(r) \left[-v_{n'}^{-1/2} e^{-ik_{n'}R} \delta_{n'n} + v_{n'}^{-1/2} e^{ik_{n'}R} S_{n',n} \right] \equiv \sum_{n'} \phi_{n'}(r) C_{n',n}(R). \quad (5.26)$$

In matrix notation, the boundary conditions for the expansion coefficients can be written as

$$\boldsymbol{C}(R) = -\boldsymbol{U}(R) + \boldsymbol{V}(R)\boldsymbol{S} \quad (5.27)$$

where $\boldsymbol{U}(R)$ is a diagonal matrix with incoming waves on the diagonal

$$U_{n',n}(R) = v_{n'}^{-1/2} e^{-ik_{n'}R} \delta_{n'n} \quad (5.28)$$

and its complex conjugate, $\boldsymbol{V}(R) \equiv \boldsymbol{U}^*(R)$, contains outgoing waves. After propagating the Q-matrix to R_N, the S-matrix is found by solving the set of linear equations

$$-\boldsymbol{U}_{N-1} + \boldsymbol{V}_{N-1}\boldsymbol{S} = \boldsymbol{Q}_N \left(-\boldsymbol{U}_N + \boldsymbol{V}_N \boldsymbol{S} \right) \quad (5.29)$$

i.e.,

$$\boldsymbol{S} = \left(\boldsymbol{V}_{N-1} - \boldsymbol{Q}_N \boldsymbol{V}_N \right)^{-1} \left(\boldsymbol{U}_{N-1} - \boldsymbol{Q}_N \boldsymbol{U}_N \right). \quad (5.30)$$

This only solves the hypothetical problem of particles moving on a straight line, but the numerical approach will turn out to be suitable in a general three-dimensional collision problem as well.

Chapter 6

Elastic scattering

6.1 Classical equations of motion

We will set up the classical equations of motion to describe the collision of two atoms, A and B, with masses m_A and m_B and three-dimensional Cartesian coordinates $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$. We assume that the interaction potential, $V(r)$, is *isotropic*, i.e., that it only depends on the distance $r \equiv |\boldsymbol{R}_B - \boldsymbol{R}_A|$. The kinetic energy in Cartesian coordinates is

$$T = \frac{1}{2}m_A \dot{\boldsymbol{R}}_A \cdot \dot{\boldsymbol{R}}_A + \frac{1}{2}m_B \dot{\boldsymbol{R}}_B \cdot \dot{\boldsymbol{R}}_B, \tag{6.1}$$

where the central dot denotes a scalar product and the dot in $\dot{\boldsymbol{r}}$ denotes the time derivative. As in Chapter 2 we switch to Jacobi coordinates $(\boldsymbol{X}, \boldsymbol{r})$, where $\boldsymbol{X}$ is the center of mass [Eq. (2.2)] and $\boldsymbol{r} = \boldsymbol{R}_B - \boldsymbol{R}_A$. The kinetic energy in these coordinates is

$$T = \frac{1}{2}M_{\text{tot}} \dot{\boldsymbol{X}} \cdot \dot{\boldsymbol{X}} + \frac{1}{2}\mu \dot{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}}, \tag{6.2}$$

with the total mass M_{tot} and the reduced mass μ given by Eqs. (2.5) and (2.6). In order to use the classical Hamilton's equations of motion we introduce *conjugate momenta* $\boldsymbol{P}$ and $\boldsymbol{p}$. They are defined as derivatives of the kinetic energy with respect to the velocities $\dot{\boldsymbol{X}}$ and $\dot{\boldsymbol{r}}$, i.e., for Cartesian components $i = x, y, z$,

$$P_i \equiv \frac{\partial T}{\partial \dot{X}_i} = M_{\text{tot}} \dot{X}_i \tag{6.3}$$

$$p_i \equiv \frac{\partial T}{\partial \dot{r}_i} = \mu \dot{r}_i, \tag{6.4}$$

or, in vector notation

$$\boldsymbol{P} = M_{\text{tot}} \dot{\boldsymbol{X}} \tag{6.5}$$

$$\boldsymbol{p} = \mu \dot{\boldsymbol{r}}. \tag{6.6}$$

The classical Hamiltonian can now be expressed in coordinates $(\boldsymbol{X}, \boldsymbol{r})$ and their conjugate momenta $(\boldsymbol{P}, \boldsymbol{p})$

$$H(\boldsymbol{X}, \boldsymbol{r}, \boldsymbol{P}, \boldsymbol{p}) = T + V(r) = \frac{P^2}{2M_{\text{tot}}} + \frac{p^2}{2\mu} + V(r), \tag{6.7}$$

where $P = |\boldsymbol{P}|$ and $p = |\boldsymbol{p}|$. The equation of motion for the center-of-mass $\boldsymbol{X}$ and its conjugate momenta $\boldsymbol{P}$ is

$$\dot{X}_i = \frac{\partial H}{\partial P_i} \tag{6.8}$$

$$\dot{P}_i = -\frac{\partial H}{\partial X_i} \tag{6.9}$$

i.e.,

$$\dot{\boldsymbol{X}} = \frac{1}{M_{\text{tot}}} \boldsymbol{P} \tag{6.10}$$

$$\dot{\boldsymbol{P}} = \boldsymbol{0}. \tag{6.11}$$

Similarly, for the relative motion, we find

$$\dot{\boldsymbol{r}} = \frac{1}{\mu} \boldsymbol{p} \tag{6.12}$$

$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla} V(r). \tag{6.13}$$

Clearly Eqs. (6.10) and (6.12) are consistent with the definitions of the momenta in Eqs. (6.5) and (6.6). Using $\dot{\boldsymbol{p}} = \mu \ddot{\boldsymbol{r}}$ and the force $\boldsymbol{F} \equiv -\boldsymbol{\nabla} V$, the last equation becomes Newton's equation of motion

$$\boldsymbol{F} = \mu \ddot{\boldsymbol{r}}. \tag{6.14}$$

The advantage of Hamilton's equations of motion is that they take the same form in any coordinate system, see, e.g., the textbook on classical mechanics by Goldstein [10]. Also, using momenta instead of velocities can help to make the relation to quantum mechanics a little easier to understand.

Since the potential depends only on the length of the vector $\boldsymbol{r}$, we have for the components of the force

$$F_i = -\frac{\partial}{\partial r_i} V(r) = -\frac{\partial r}{\partial r_i} \frac{\partial V(r)}{\partial r}. \tag{6.15}$$

From $r = \sqrt{r_x^2 + r_y^2 + r_z^2}$ we find

$$\frac{\partial r}{\partial r_i} = \frac{r_i}{r} \tag{6.16}$$

and in vector notation

$$\dot{\boldsymbol{p}} = \boldsymbol{F} = -\frac{1}{r} \frac{\partial V(r)}{\partial r} \boldsymbol{r}. \tag{6.17}$$

We now have the equations of motion, but we can gain more insight and simplify the equations by introducing the orbital angular momentum vector

$$\boldsymbol{l} \equiv \boldsymbol{r} \times \boldsymbol{p}. \tag{6.18}$$

First, we derive that $\boldsymbol{l}$ is conserved, i.e., its time derivative is zero:

$$\dot{\boldsymbol{l}} = \dot{\boldsymbol{r}} \times \boldsymbol{p} + \boldsymbol{r} \times \dot{\boldsymbol{p}} \tag{6.19}$$

$$= \frac{1}{\mu} \underbrace{\boldsymbol{p} \times \boldsymbol{p}}_{=\boldsymbol{0}} - \frac{1}{r} \frac{\partial V(r)}{\partial r} \underbrace{\boldsymbol{r} \times \boldsymbol{r}}_{=\boldsymbol{0}} = \boldsymbol{0}. \tag{6.20}$$

From the definition of l [Eq. (6.18)] it follows that $r \perp l$ and $p \perp l$, i.e., the position vector r and the momentum p are always in a plane perpendicular to l. This plane is called the *scattering plane*. In a Cartesian coordinate system where the scattering plane is the x, y-plane and introducing polar coordinates (r, ϕ) we have

$$r = r \begin{pmatrix} \cos\phi \\ \sin\phi \\ 0 \end{pmatrix} = r\hat{r} \tag{6.21}$$

The velocity in this coordinate system is

$$\dot{r} = \dot{r}\hat{r} + r\dot{\phi} \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \equiv \dot{r}\hat{r} + r\dot{\phi}\hat{r}_\perp \tag{6.22}$$

and the kinetic energy is

$$T = \frac{1}{2}\mu\dot{r} \cdot \dot{r} = \frac{1}{2}\mu(\dot{r}^2 + r^2\dot{\phi}^2). \tag{6.23}$$

The conjugate momenta are

$$p_r \equiv \frac{\partial T}{\partial \dot{r}} = \mu\dot{r} \tag{6.24}$$

$$p_\phi \equiv \frac{\partial T}{\partial \dot{\phi}} = \mu r^2 \dot{\phi}. \tag{6.25}$$

In this coordinate system the angular momentum only has a z-component and it is easy to verify that $l_z = \mu r^2 \dot{\phi}$, so $p_\phi = l_z$. Since $l_z^2 = l^2$, the Hamiltonian can be written as:

$$H = \frac{p_r^2}{2\mu} + \underbrace{\frac{l^2}{2\mu r^2} + V(r)}_{\equiv V_{\text{eff}}(r)}. \tag{6.26}$$

The first term on the right-hand side is the *radial kinetic energy* and the second term is called the *centrifugal term*. Since l is a constant we can define an effective potential $V_{\text{eff}}(r)$ as the sum of the interaction potential $V(r)$ and the centrifugal term. Finding $r(t)$ is equivalent to solving a one-dimensional problem for the effective potential,

$$\dot{p}_r = -\frac{\partial H}{\partial r} \tag{6.27}$$

or

$$\mu\ddot{r} = -\frac{\partial V_{\text{eff}}(r)}{\partial r}. \tag{6.28}$$

The angle can be found from Eq. (6.25)

$$\dot{\phi} = \frac{l_z}{\mu r^2}. \tag{6.29}$$

This equation shows that $\dot{\phi}r^2$ is a constant. For planetary orbits this is known as *Kepler's second law*.

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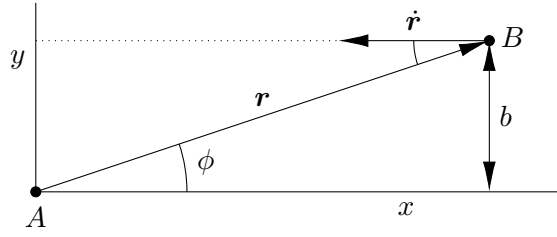
Figure 6.1: Initial condition of the classical trajectory.

As initial condition of the trajectory at time t_0 we start with a large value of r, where we assume $V(r)$ to be negligible, and we take the initial velocity $\boldsymbol{r}(t_0)$ parallel to the x-axis, but with opposite sign. From $\boldsymbol{l} = \mu \boldsymbol{r} \times \dot{\boldsymbol{r}}$ we find

$$l_z = \mu v b, \tag{6.30}$$

where v is the velocity $v \equiv |\dot{\boldsymbol{r}}|$ and b is called the *impact parameter*, which is equal to the initial y-component of $\boldsymbol{r}(t_0)$. The impact parameter may also be defined as the nearest approach between the atoms A and B if the interaction potential were zero and they would move in a straight line.

Chapter 7

Elastic scattering in quantum mechanics

7.1   Free particles in 3D

The time-independent Schrödinger equation for a particle with mass μ in three dimensions

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r}). \tag{7.1}$$

The Cartesian coordinates of the particle are

$$\boldsymbol{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{7.2}$$

and the Laplacian in 3D is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{7.3}$$

Solutions are products of one-dimensional solutions

$$\Psi(\boldsymbol{r}) = Ne^{ik_x x}e^{ik_y y}e^{ik_z z} = Ne^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{7.4}$$

By substituting this *plane wave* into Eq. (7.1) we find the energy

$$E = \frac{\hbar^2}{2\mu}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2\mu}. \tag{7.5}$$

The *flux* in three dimensions $\boldsymbol{j}$ is a vector with three components

$$\boldsymbol{j} = \begin{pmatrix} j_x \\ j_y \\ j_z \end{pmatrix} = \frac{\hbar}{\mu} \begin{pmatrix} \mathrm{Im}[\Psi^*(\boldsymbol{r})\frac{\partial}{\partial x}\Psi(\boldsymbol{r})] \\ \mathrm{Im}[\Psi^*(\boldsymbol{r})\frac{\partial}{\partial y}\Psi(\boldsymbol{r})] \\ \mathrm{Im}[\Psi^*(\boldsymbol{r})\frac{\partial}{\partial z}\Psi(\boldsymbol{r})] \end{pmatrix} = \frac{\hbar}{\mu}\mathrm{Im}[\Psi^*(\boldsymbol{r})\boldsymbol{\nabla}\Psi(\boldsymbol{r})] = N^2\frac{\hbar\boldsymbol{k}}{\mu} = |\Psi|^2\frac{\boldsymbol{p}}{\mu} = \rho\boldsymbol{v}, \tag{7.6}$$

where we introduced the momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$, the velocity $\boldsymbol{v}$, and the density $\rho = |\Psi|^2$. Since the density has units of *particles per volume* and the velocity is in *distance per time*, the flux now has units *particles per area per time*.

We can also solve the problem using spherical polar coordinates (r, θ, ϕ), [Chapter 2, Eq. (2.7)]. The Schrödinger equation becomes

$$[\hat{H}_0 - E]\Psi(r, \theta, \phi) = 0 \tag{7.7}$$

with the Hamiltonian of the free particle

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2}. \tag{7.8}$$

Just as for the diatomic molecule [Eq. (2.12)] we can factorize the wave function in a radial part $\chi_k(r)/r$ and spherical harmonics $Y_{l,m}(\theta, \phi)$ for angular part

$$\Psi_{k,l,m}(r, \theta, \phi) = \frac{1}{r}\chi_{k,l}(r)Y_{l,m_l}(\theta, \phi). \tag{7.9}$$

As before, we included the factor $1/r$ in the expansion, because the volume element in spherical coordinates is $d\tau = r^2 \sin(\theta)dr\, d\theta\, d\phi$. To find the equation for $\chi_{k,l}$ we substitute the expansion in the Schrödinger equation, project the equation onto spherical harmonics, and multiply from the left by r:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} - E\right]\chi_{k,l}(r) = 0. \tag{7.10}$$

For large r, the centrifugal term becomes negligible, and the equation becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - E\right]\chi_{k,l}(r) = 0, \tag{7.11}$$

so we find two solutions

$$\chi_{k,l}^{\pm}(r) = Ne^{\pm ikr}, \tag{7.12}$$

with energy $E = \frac{\hbar^2 k^2}{2\mu}$. Any linear combination of spherical waves with the same energy is a solution of the Schrödinger equation, so we can write an arbitrary solution with energy E at large r as

$$\Phi_E^{(\pm)}(r, \theta, \phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\Psi_{k,l,m}(r, \theta, \phi)c_{k,l,m} = N\frac{e^{\pm ikr}}{r}f(\theta, \phi), \tag{7.13}$$

where $f(\theta, \phi)$ is some linear combination of spherical harmonics. For reasons that become clear below, it is called the **scattering amplitude**.

7.1.1   Flux in spherical polar coordinates

To evaluate the flux in spherical polar coordinates we need the gradient operator ∇ in spherical polar coordinates. Denoting the Cartesian coordinates $[x, y, z]$ as $[r_1, r_2, r_3]$ and the spherical polar coordinates $[r, \theta, \phi]$ as $[q_1, q_2, q_3]$, we have

$$\nabla_i \equiv \frac{\partial}{\partial r_i} = \sum_{j=1}^{3}\frac{\partial q_j}{\partial r_i}\frac{\partial}{\partial q_j} = \sum_j J_{i,j}\frac{\partial}{\partial q_j}, \tag{7.14}$$

where we introduced the 3×3 Jabobian matrix $\boldsymbol{J}$ with elements

$$J_{i,j} = \frac{\partial q_j}{\partial r_i}. \tag{7.15}$$

Since we have expressions for r_i as functions of the spherical polar coordinates $r_i(\boldsymbol{q})$, it is a little easier to compute instead

$$\widetilde{J}_{i,j} = \frac{\partial r_i}{\partial q_j}. \tag{7.16}$$

It is easy to see the $\widetilde{\boldsymbol{J}}$ is the inverse of the Jacobian $\boldsymbol{J}$:

$$\frac{\partial q_j}{\partial q_i} = \delta_{i,j} = \sum_k \frac{\partial q_j}{\partial r_k}\frac{\partial r_k}{\partial q_i} = \sum_{k=1}^{3} J_{j,k}\widetilde{J}_{k,i} = \delta_{j,i}. \tag{7.17}$$

Inverting the matrix $\widetilde{\boldsymbol{J}}$ to get $\boldsymbol{J}$ is easier than it sounds, since the columns of $\boldsymbol{J}$ are orthogonal for orthogonal curvilinear coordinates such as spherical polar coordinates. From Eq. (2.7) we find

$$\widetilde{\boldsymbol{J}} = \begin{pmatrix} \cos\phi\sin\theta & r\cos\phi\cos\theta & -r\sin\phi\sin\theta \\ \sin\phi\sin\theta & r\sin\phi\cos\theta & r\cos\phi\sin\theta \\ \cos\theta & -r\sin\theta & 0 \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{r}} & \hat{\boldsymbol{f}}_\theta \hat{\boldsymbol{f}}_\phi \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & r\sin\theta \end{pmatrix}, \tag{7.18}$$

where the matrix $\begin{pmatrix} \hat{\boldsymbol{r}} & \hat{\boldsymbol{f}}_\theta \hat{\boldsymbol{f}}_\phi \end{pmatrix}$ is orthonormal. So, for the transpose of $\boldsymbol{J}$ we find

$$\boldsymbol{J}^T = \widetilde{\boldsymbol{J}}^{-T} = \begin{pmatrix} \hat{\boldsymbol{r}} & \dfrac{\hat{\boldsymbol{f}}_\theta}{r} & \dfrac{\hat{\boldsymbol{f}}_\phi}{r\sin\theta} \end{pmatrix} \tag{7.19}$$

and we find for the gradient

$$\boldsymbol{\nabla} = \hat{\boldsymbol{r}}\frac{\partial}{\partial r} + \frac{1}{r}\hat{\boldsymbol{f}}_\theta\frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta}\hat{\boldsymbol{f}}_\phi\frac{\partial}{\partial\phi}. \tag{7.20}$$

If we use this result to compute the flux of the spherical wave $\Psi_{k,l,m}(r,\theta,\phi)$ for large r, we see that the components in the direction $\hat{\boldsymbol{f}}_\theta$ and $\hat{\boldsymbol{f}}_\phi$ are smaller by a factor $1/r$ compared to the $\hat{\boldsymbol{r}}$ component. So, for sufficiently large r we find that the flux of $\Psi_E^{(\pm)}(r,\theta,\phi)$ is

$$\boldsymbol{j} = \hat{\boldsymbol{r}}\frac{\hbar}{\mu}\mathrm{Im}\left[\Psi_E^{(\pm)}(r,\theta,\phi)^*\frac{\partial}{\partial r}\Psi_E^{(\pm)}(r,\theta,\phi)\right] = \pm\hat{\boldsymbol{r}}N^2\frac{\hbar k}{\mu}\frac{|f(\theta,\phi)|^2}{r^2}. \tag{7.21}$$

7.2   Boundary conditions for elastic scattering

Having expressions for the free particle in Cartesian coordinates and in spherical polar coordinates and the corresponding fluxes (at least at large r), we can write down the boundary conditions for elastic scattering. Before the collision, a stream of incoming particles can be described by a plane wave.

$$\Psi_{\mathrm{in}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{7.22}$$
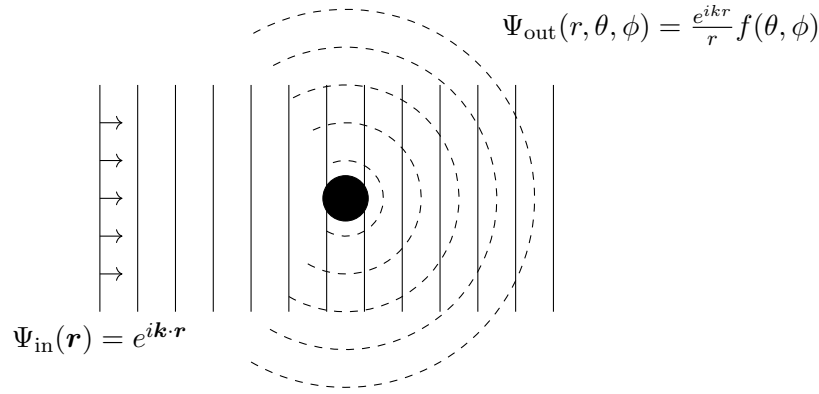
Figure 7.1: Boundary conditions for elastic scattering.

After the collision the particles will move away from the scattering center, so they can be described by spherical waves, so the boundary conditions for large r are

$$\Psi(\boldsymbol{r}) \simeq \underbrace{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}_{\text{incoming}} + \underbrace{\frac{e^{ikr}}{r}f(\theta,\phi)}_{\text{outgoing}}, \tag{7.23}$$

as illustrated in Fig. (7.1). The corresponding flux is

$$\boldsymbol{j} = \underbrace{\frac{\hbar}{\mu}\boldsymbol{k}}_{\text{incoming}} + \underbrace{\frac{\hbar k}{\mu}\frac{|f(\theta,\phi)|^2}{r^2}\hat{\boldsymbol{r}}}_{\text{outgoing}} \tag{7.24}$$

Here, we left out the cross term that arises from the interference between the incoming and the outgoing part of the wave function. This can be justified in several ways. One way is to assume that in incoming wave is not really infinitely wide, so that at sufficiently large r the outgoing wave no longer overlaps with the incoming wave (except in the forward direction).

Remember that the flux is expressed as particles *per time per area*. As the spherical wave spreads out, the particles are spread over an ever larger area and the flux goes to zero as $1/r^2$. However, the area corresponding to a solid angle $d\Omega = \sin\theta d\theta d\phi$ at a distance r is $r^2 d\Omega$, so we define the outgoing flux in particles *per time per solid angle* as

$$j_{\text{out}}(\theta,\phi) = \frac{\hbar k}{\mu}|f(\theta,\phi)|^2 d\Omega \tag{7.25}$$

The incoming flux is expressed per area

$$j_{\text{in}} = \frac{\hbar k}{\mu} \tag{7.26}$$

The ratio of outgoing flux and incoming flux is called the ***differential cross section***

$$\frac{d\sigma}{d\Omega}(\theta,\phi) = \frac{j_{\text{out}}}{j_{\text{in}}} = |f(\theta,\phi)|^2, \tag{7.27}$$

which has units of *area*. When the incoming wave is along the z-axis and the potential is isotropic then the system has **cylinder symmetry**, and the cross section is independent of ϕ. In that case the differential cross section a function of θ only and $f(\theta, \phi)$ can be written as $f(\theta)$,

$$\frac{d\sigma}{d\Omega}(\theta) = |f(\theta)|^2. \tag{7.28}$$

7.3 Partial wave expansion

So far, the boundary conditions are expressed in Cartesian coordinates for the incoming wave and in spherical polar coordinates for the outgoing wave. Since angular momentum is conserved for the isotropic potential that we will consider, the spherical polar coordinates are preferred, so we rewrite the incoming wave in those coordinates. To simplify the problem we define the z-axis to be parallel to the wave vector so that $\boldsymbol{k} = k\boldsymbol{e}_z$, and the wave function becomes independent of the ϕ angle. With $\boldsymbol{k} \cdot \boldsymbol{r} = k\boldsymbol{e}_z \cdot \boldsymbol{r} = kr\cos\theta$ we can now expand the plane wave in Legendre polynomials of $\cos\theta$

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} a_l(kr)P_l(\cos\theta). \tag{7.29}$$

Using the orthogonality of Legendre polynomials,

$$\int_{-1}^{1} P_l(x)P_{l'}(x)dx = \frac{2}{2l+1}\delta_{ll'} \tag{7.30}$$

we can find the expansion coefficients $a_l(kr)$ by projection, with $x \equiv kr$ and $z \equiv \cos\theta$,

$$a_l(x) = \frac{2l+1}{2}\int_{-1}^{1} e^{ixz}P_l(z)\,dz. \tag{7.31}$$

For $l = 0$ we have $P_0(z) = 1$ and we find

$$a_0(x) = \frac{1}{2}\int_{-1}^{1} e^{ixz}dz = \frac{1}{2}\frac{e^{ixz}}{ix}\Big|_{z=-1}^{z=1} = \frac{1}{2}\frac{e^{ix} - e^{-ix}}{ix} = \frac{\sin(x)}{x} = j_0(x). \tag{7.32}$$

The complete expansion is given by

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta), \tag{7.33}$$

where j_l is a spherical Bessel function of the first kind. These functions are the regular solutions of the radial Schrödinger equation for a free particle [Eq. (7.10)], where "regular" means that they are finite at $r = 0$. For large r they behave like

$$j_l(kr) \simeq \frac{\sin(kr - \frac{l\pi}{2})}{kr} = \frac{i}{2k}\left[\frac{e^{-i(kr-\frac{l\pi}{2})}}{r} - \frac{e^{i(kr-\frac{l\pi}{2})}}{r}\right], \tag{7.34}$$

where we have written the real functions as a sum on incoming and outgoing spherical waves. We now make the following key observation: if the potential is nonzero only the spherical

outgoing part of the wave function can change as a result of the scattering, since the wave function must satisfy the boundary conditions given by Eq. (7.23). Thus, for large r, the solution of the Schrödinger equation can be written as

$$\Psi(r,\theta,\phi) = \frac{i}{2k} \sum_{l=0}^{\infty} i^l (2l+1) \frac{\psi_l(kr)}{r} P_l(\cos\theta) \tag{7.35}$$

where the *partial wave* $\psi_l(kr)$ satisfies the boundary condition

$$\psi_l(kr) \simeq e^{-i(kr-\frac{l\pi}{2})} - e^{i(kr-\frac{l\pi}{2})} S_l. \tag{7.36}$$

If we set the "S-matrix" S_l to one, we recover the asymptotic form of the expansion of a free particle wave function [Eq. (7.33)]. Thus, if the potential is nonzero, S_l may deviate from one. To see this more clearly we define the "T-matrix" as

$$T_l = 1 - S_l \tag{7.37}$$

and we separate the part of the wave function that depends on T_l

$$\Psi(r,\theta,\phi) \simeq e^{ikr\cos\theta} + \frac{i}{2k} \sum_{l=0}^{\infty} i^l (2l+1) \frac{e^{i(kr-\frac{l\pi}{2})}}{r} T_l P_l(\cos\theta). \tag{7.38}$$

By comparing this expression with the boundary condition in Eq. (7.23) we find this expression for the scattering amplitude

$$f(\theta,\phi) = \frac{i}{2k} \sum_{l=0}^{\infty} (2l+1) T_l P_l(\cos\theta), \tag{7.39}$$

where we used

$$e^{-i\frac{l\pi}{2}} = \left(e^{i\frac{\pi}{2}}\right)^{-l} = i^{-l}. \tag{7.40}$$

We can now evaluate the differential cross section as the square of the absolute value of the scattering amplitude, see Eq. (7.28).

The ***integral cross section*** is found by integrating over all angles

$$\sigma_{\text{tot}} = \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \, |f(\theta)|^2. \tag{7.41}$$

Using the orthogonality relation of Legendre polynomials, Eq. (7.30) we find

$$\sigma_{\text{tot}} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)|T_l|^2. \tag{7.42}$$

7.4   Numerical method for elastic scattering

Just as for bound states of a diatomic molecule, the angular momentum quantum is conserved, i.e., l is a good quantum number, and we can solve the radial Schrödinger equation for each

partial wave with angular momentum l separately. Thus, the function $\psi_l(kr)$ in Eq. (7.35) must be a solution of

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - E \right]\psi_l(kr) = 0 \tag{7.43}$$

and it must satisfy the boundary condition given in Eq. (7.36). Since the wave function $\Psi(r,\theta,\phi)$ must be finite, and we included a factor $1/r$ in Eq. (7.35), the function $\psi_l(kr)$ must be zero for $r = 0$. We can use the same numerical approach as in Chapter 4.3, by introducing a "Q-matrix" [Eq. (4.23)] and deriving a two term recursion relation for it [Eq. (4.33)].

7.5   Alternative boundary conditions

The S-matrix boundary condition in Eq. (7.36) was derived using the long range behavior of spherical Bessel functions j_l [Eq. (7.34)]. Numerically, this is not the most convenient form: one has to propagate to a large value of r where the approximation is sufficiently accurate. To converge the result one has to propagate to a larger distance as a check, but then the numerical error in the propagation becomes larger. That, in turn, means that one has to re-check the propagation step size. Thus, numerically, it is better to use the exact long range form of the free waves. For this purpose, spherical Hankel functions $h_l^{(1)}$ and $h_l^{(2)}$ can be used instead of the exponential functions (with $z = kr$):

$$h_l^{(1)}(z) = j_l(z) + iy_l(z) \simeq \frac{-ie^{i(z-l\frac{\pi}{2})}}{z} \tag{7.44}$$

$$h_l^{(2)}(z) = j_l(z) - iy_l(z) \simeq \frac{ie^{-i(z-l\frac{\pi}{2})}}{z}, \tag{7.45}$$

where the $y_l(z)$ are *spherical Bessel functions of the second kind*. Thus, we have the exact expression

$$j_l(kr) = \frac{h_l^{(2)}(kr) + h_l^{(1)}(kr)}{2}, \tag{7.46}$$

where the $h_l^{(2)}$ are the incoming waves and the $h_l^{(1)}$ are the outgoing waves. Instead of Eq. (7.36) we can now use

$$\Psi_l(kr) \simeq (-2ikr)\left[h_l^{(2)}(kr) + h_l^{(1)}(kr)S_l \right]. \tag{7.47}$$

Asymptotically, these are the same boundary conditions as before. However, in a calculation we can now match the propagated solution to the free wave at the point where the potential becomes negligible compared to the scattering energy and we no longer have to worry about the approximation of the free waves at finite value of r.

Chapter 8

Inelastic scattering

We consider the collision of diatomic molecules A and B,

$$A(v_a, j_a, m_a) + B(v_b, j_b, m_b) \to A(v'_a, j'_a, m'_a) + B(v'_b, j'_b, m'_b). \tag{8.1}$$

where v_a is the vibrational quantum number of molecule A, j_a is its total angular momentum quantum number, and m_a is the quantum number corresponding to the projection of the angular momentum of molecule A on the space-fixed z-axis, and v_b, j_b, and m_b are the corresponding quantum numbers for molecule B.

For compactness we will denote the molecular eigenstates in Dirac notation by

$$|\boldsymbol{n}_a\rangle \equiv |v_a j_a m_a\rangle \tag{8.2}$$

$$|\boldsymbol{n}_b\rangle \equiv |v_b j_b m_b\rangle \tag{8.3}$$

and the corresponding energies are $\epsilon_{\boldsymbol{n}_a}$ and $\epsilon_{\boldsymbol{n}_b}$. We further shorten the notation by introducing

$$|\boldsymbol{n}\rangle \equiv |\boldsymbol{n}_a\rangle |\boldsymbol{n}_b\rangle \tag{8.4}$$

$$\epsilon_{\boldsymbol{n}} \equiv \epsilon_{\boldsymbol{n}_a} + \epsilon_{\boldsymbol{n}_b}. \tag{8.5}$$

Before the collision molecules A and B are described by plane waves with wave vectors $\boldsymbol{k}_a$ and $\boldsymbol{k}_b$, respectively, so the incoming wave in Dirac notation is

$$\Psi_{\boldsymbol{n}_a \boldsymbol{k}_a; \boldsymbol{n}_b \boldsymbol{k}_b}(\boldsymbol{r}_a, \boldsymbol{r}_b) = \underbrace{|\boldsymbol{n}_a\rangle |\boldsymbol{n}_b\rangle}_{|\boldsymbol{n}\rangle} e^{i(\boldsymbol{k}_a \cdot \boldsymbol{r}_a + \boldsymbol{k}_b \cdot \boldsymbol{r}_b)}, \tag{8.6}$$

where $\boldsymbol{r}_a$ and $\boldsymbol{r}_b$ are the center-of-mass of molecule A and B, respectively.

As before, we introduce center-of-mass coordinates for the complex $\boldsymbol{X}$ [as in Eq. (2.2)] and $\boldsymbol{r} \equiv \boldsymbol{r}_b - \boldsymbol{r}_a$. The exponent in the plane wave can be written in these coordinates using

$$\boldsymbol{k}_a \cdot \boldsymbol{r}_a + \boldsymbol{k}_b \cdot \boldsymbol{r}_b = \boldsymbol{k}_a \cdot \left(\boldsymbol{X} - \frac{m_b}{m_a + m_b} \boldsymbol{r} \right) + \boldsymbol{k}_b \cdot \left(\boldsymbol{X} + \frac{m_a}{m_a + m_b} \boldsymbol{r} \right) \tag{8.7}$$

$$= (\boldsymbol{k}_a + \boldsymbol{k}_b) \cdot \boldsymbol{X} + \frac{m_a \boldsymbol{k}_b - m_b \boldsymbol{k}_b}{m_a + m_b} \cdot \boldsymbol{r} \tag{8.8}$$

$$= \boldsymbol{k}_{\text{com}} \cdot \boldsymbol{X} + \boldsymbol{k} \cdot \boldsymbol{r}. \tag{8.9}$$

In a center-of-mass frame $\boldsymbol{X} = \boldsymbol{0}$ and the total energy of the system is given by

$$E = \frac{\hbar^2 k_{\boldsymbol{n}}^2}{2\mu} + \epsilon_{\boldsymbol{n}}, \tag{8.10}$$

where μ is the reduced mass. We label $k_{\boldsymbol{n}}$ with the quantum numbers $\boldsymbol{n}$, because we assume that the total energy is fixed, so that the kinetic energy depends on the states of the atoms. Although the magnitude $k_{\boldsymbol{n}}$ depends on the state of the molecules, the directions are the same

$$\boldsymbol{k}_{\boldsymbol{n}} = k_{\boldsymbol{n}} \hat{\boldsymbol{k}}. \tag{8.11}$$

We can now write the flux-normalized plane wave in the center-of-mass frame with the molecules in quantum state $\boldsymbol{n}$ as

$$|\Psi_{\boldsymbol{n}}^{(in)}(\boldsymbol{r})\rangle = |\boldsymbol{n}\rangle \, v_{\boldsymbol{n}}^{-1/2} \, e^{i\boldsymbol{k}_{\boldsymbol{n}}\cdot\boldsymbol{r}}, \tag{8.12}$$

where the $v_{\boldsymbol{n}}$ is the velocity given by $v_{\boldsymbol{n}} = \hbar k_{\boldsymbol{n}}/\mu$. In inelastic scattering the states of the molecules can change, so the **boundary conditions** are given by

$$|\Psi_{\boldsymbol{n}}(\boldsymbol{r})\rangle \simeq |\boldsymbol{n}\rangle \, v_{\boldsymbol{n}}^{-1/2} \, e^{i\boldsymbol{k}_{\boldsymbol{n}}\cdot\boldsymbol{r}} + \sum_{\boldsymbol{n}'} |\boldsymbol{n}'\rangle v_{\boldsymbol{n}'}^{-1/2} \frac{e^{ik_{\boldsymbol{n}'}r}}{r} f_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}}), \tag{8.13}$$

where $f_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}})$ is the **scattering amplitude** for excitation from initial state $\boldsymbol{n}$ to final state $\boldsymbol{n}'$, for products moving in the direction $\hat{\boldsymbol{r}}$, while $\hat{\boldsymbol{k}}$ is the initial direction of the relative velocity. Again, the hat in $\hat{\boldsymbol{r}}$ indicates it is a unit vector and $\boldsymbol{r} = r\hat{\boldsymbol{r}}$.

To find the expression for the scattering amplitude we first expand the incoming plane wave in partial waves,

$$|\Psi_{\boldsymbol{n}}^{(\text{in})}(\boldsymbol{r})\rangle = |\boldsymbol{n}\rangle v_{\boldsymbol{n}}^{-1/2} \sum_{l=0}^{\infty} i^l (2l+1) j_l(k_{\boldsymbol{n}} r) P_l(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{r}}), \tag{8.14}$$

As before, we rewrite the asymptotic form of the spherical Bessel functions of the first kind as the sum of an incoming and outgoing part for large r,

$$j_l(k_{\boldsymbol{n}} r) \simeq \frac{1}{2ik_{\boldsymbol{n}}} \left[\underbrace{-\frac{e^{-i(k_{\boldsymbol{n}} r - l\frac{\pi}{2})}}{r}}_{\text{in}} + \underbrace{\frac{e^{i(k_{\boldsymbol{n}} r - l\frac{\pi}{2})}}{r}}_{\text{out}} \right]. \tag{8.15}$$

Furthermore, we use the **spherical harmonic addition theorem**, to factor the Legendre polynomial into products of spherical harmonics that depend on either the orientation of $\boldsymbol{r}$, or the direction of the incoming wave $\hat{\boldsymbol{k}}_{\boldsymbol{n}}$

$$P_l(\hat{\boldsymbol{k}}_{\boldsymbol{n}} \cdot \hat{\boldsymbol{r}}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{lm}(\hat{\boldsymbol{r}}) Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.16}$$

Substituting Eqs. (8.15) and (8.16) into Eq. (8.14) gives

$$|\Psi_{\boldsymbol{n}}^{(\text{in})}(\boldsymbol{r})\rangle = \frac{2\pi}{ik_{\boldsymbol{n}}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} |\boldsymbol{n}\rangle Y_{lm}(\hat{\boldsymbol{r}}) v_{\boldsymbol{n}}^{-1/2} \left[\underbrace{-\frac{e^{-i(k_{\boldsymbol{n}} r - l\frac{\pi}{2})}}{r}}_{\text{in}} + \underbrace{\frac{e^{i(k_{\boldsymbol{n}} r - l\frac{\pi}{2})}}{r}}_{\text{out}} \right] i^l Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.17}$$

We see that the outgoing part is

$$\frac{2\pi}{ik_{\boldsymbol{n}}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} |\boldsymbol{n}\rangle Y_{lm}(\hat{\boldsymbol{r}}) v_{\boldsymbol{n}}^{-1/2} \frac{e^{i(k_{\boldsymbol{n}}r-l\frac{\pi}{2})}}{r} i^l Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.18}$$

In the derivation of the expression for the scattering amplitude for elastic scattering, we introduced the factor S_l in the outgoing part. For inelastic scattering, however, l is not a good quantum number, so l can change as a result of the anisotropic interaction potential, but also the states of the molecules can change. Therefore, we replace the spherically outgoing part for each term with a given l and m by

$$\frac{2\pi}{ik_{\boldsymbol{n}}} \sum_{\boldsymbol{n}'} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} |\boldsymbol{n}'\rangle Y_{l'm'}(\hat{\boldsymbol{r}}) v_{\boldsymbol{n}'}^{-1/2} \frac{e^{i(k_{\boldsymbol{n}'}r-l'\frac{\pi}{2})}}{r} S_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m} \, i^l \, Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.19}$$

The result is

$$|\Psi_{\boldsymbol{n}}^+(\boldsymbol{r})\rangle \simeq \frac{2\pi}{ik_{\boldsymbol{n}}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{\boldsymbol{n}'} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} |\boldsymbol{n}'\rangle v_{\boldsymbol{n}'}^{-1/2} Y_{l'm'}(\hat{\boldsymbol{r}})$$
$$\left[-\frac{e^{-i(k_{\boldsymbol{n}'}r-l'\frac{\pi}{2})}}{r} \delta_{\boldsymbol{n}'\boldsymbol{n}} \delta_{l'l} \delta_{m'm} + \frac{e^{i(k_{\boldsymbol{n}'}r-l'\frac{\pi}{2})}}{r} S_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m} \right] i^l Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.20}$$

As before, we define the $\boldsymbol{T}$-matrix

$$S_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m} = \delta_{\boldsymbol{n}'\boldsymbol{n}} \delta_{l'l} \delta_{m'm} - T_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m}, \tag{8.21}$$

such that setting all $\boldsymbol{T}$-matrix elements to zero results in the $\boldsymbol{S}$-matrix being equal to the identity matrix, and the wave function becomes a plane wave where the molecule remains in the initial state $|\boldsymbol{n}\rangle$. Substituting this relation into Eq. (8.20) and comparing the result to the boundary condition Eq. (8.13) gives the expression for the scattering amplitude

$$f_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}}) = \frac{2\pi i}{k_{\boldsymbol{n}}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} i^{l-l'} Y_{l'm'}(\hat{\boldsymbol{r}}) T_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m} Y_{l,m}^*(\hat{\boldsymbol{k}}). \tag{8.22}$$

Since all the channels are flux normalized, the **state-to-state differential cross section (DCS)** is given by

$$\sigma_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \boldsymbol{k}) = |f_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}})|^2. \tag{8.23}$$

This is the most detailed information that we obtain on the cross sections. When we are interested only in the final state of the molecule, but not the direction it is moving in, we integrate the DCS over all final directions $\hat{\boldsymbol{r}}$ to obtain the state-to-state integral cross sections (ICS),

$$\sigma_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{k}}) = \iint \sigma_{\boldsymbol{n}',\boldsymbol{n}}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}}) d\hat{\boldsymbol{r}}. \tag{8.24}$$

Note for the integral over directions written in spherical polar coordinates is

$$\iint d\hat{\boldsymbol{r}} \equiv \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta = \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta. \tag{8.25}$$

In a bulk gas, collisions occur from any direction, so we may take the average of all incoming directions $\hat{\boldsymbol{k}}$

$$\sigma_{\boldsymbol{n'},\boldsymbol{n}} = \frac{1}{4\pi} \iint \sigma_{\boldsymbol{n'},\boldsymbol{n}}(\hat{\boldsymbol{k}})d\hat{\boldsymbol{k}} = \frac{\pi}{k_{\boldsymbol{n}}^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} |T_{\boldsymbol{n'}l'm';\boldsymbol{n}lm}|^2. \tag{8.26}$$

Notice that the general approach for obtaining less detailed information is found by (i) taking the *average* over *initial* states or directions and (ii) *summation* or *integration* over all *final* states or directions that we do not want to distinguish.

We can use the present derivation of cross sections for ro-vibrational transitions in molecule-molecule collisions also to describe the simpler process of *atom - diatom rotationally inelastic collisions*. First, we drop the the quantum numbers v_a, j_a, and m_a, i.e., we assume A to be the atom. We also drop v_b and assume molecule B remains in its vibrational ground state, and we replace j_b and m_b by j and m_j, respectively, for a more compact notation. Furthermore, we assume the molecule is prepared in a rotational state with quantum number j before the collision, but all substates m are equally likely, and also we are only interested in the final rotational state j', but do not care about the distribution of the final m' substates. The expression for the cross section then becomes

$$\sigma(j',j) = \frac{\pi}{k_j^2(2j+1)} \sum_{m_j'=-j'}^{j'} \sum_{m_j=-j}^{j} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \sum_{l'=0}^{\infty} \sum_{m_l'=-l'}^{l'} |T_{j'm_j'l'm_l';jm_jlm_l}|^2. \tag{8.27}$$

8.0.1 Properties of the $\boldsymbol{S}$-matrix

The $\boldsymbol{S}$-matrix is complex symmetric,

$$\boldsymbol{S}^T = \boldsymbol{S} \tag{8.28}$$

this is a consequence of what is called **"microscopic reversibility"**. The $\boldsymbol{T}$-matrix has the same property. From the expression of the integral cross section, Eq. (8.26) we find

$$\sigma_{\boldsymbol{n'},\boldsymbol{n}}k_{\boldsymbol{n}}^2 = \sigma_{\boldsymbol{n},\boldsymbol{n'}}k_{\boldsymbol{n'}}^2, \tag{8.29}$$

i.e., the cross section matrix is not symmetric, but $\sigma_{\boldsymbol{n'},\boldsymbol{n}}$ and $\sigma_{\boldsymbol{n},\boldsymbol{n'}}$ are related by the ratio of the kinetic energies in state $|\boldsymbol{n}\rangle$ and $|\boldsymbol{n'}\rangle$ for a given total energy E.

The $\boldsymbol{S}$-matrix is also unitary

$$\boldsymbol{S}^{\dagger}\boldsymbol{S} = \boldsymbol{1}. \tag{8.30}$$

This is a consequence of flux conservation. It shows that for any given initial state $\boldsymbol{n}$ with partial wave l, m we have

$$\sum_{\boldsymbol{n'}l'm'} |S_{\boldsymbol{n'},l',m';\boldsymbol{n},l,m}|^2 = 1 \tag{8.31}$$

8.1 Coupled channels equation

As before, we expand the wave function in the channel basis, with r-dependent coefficients. The dependence of the wave function on the orientation $\hat{\boldsymbol{r}}$ is described by an expansion in

spherical harmonics $Y_{lm}(\hat{\boldsymbol{r}})$, so these functions have to be included in the channel basis:

$$\Psi_{\boldsymbol{n},lm}(\boldsymbol{r}) = \frac{1}{r}\sum_{\boldsymbol{n}'l'm'}|\boldsymbol{n}'\rangle Y_{l'm'}(\hat{\boldsymbol{r}})U_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m}(r). \tag{8.32}$$

To find the coupled channels equation, we substitute this expansion into the time-independent Schrödinger equation and project onto the channel basis. Furthermore, we separate the Hamiltonian into a radial kinetic energy and the remainder

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \Delta\hat{H}, \tag{8.33}$$

where the last term includes the molecular Hamiltonians and the interaction potential

$$\Delta\hat{H} = \hat{H}_a + \hat{H}_b + \Delta V(r,\hat{\boldsymbol{r}},\boldsymbol{r}_a,\boldsymbol{r}_b) \tag{8.34}$$

and the interaction potential vanishes for large r

$$\lim_{r\to\infty}V(r,\hat{\boldsymbol{r}},\boldsymbol{r}_a,\boldsymbol{r}_b) = 0. \tag{8.35}$$

Multiplying the resulting equation with $2\mu r/\hbar^2$ gives

$$\boldsymbol{U}''(r) = \boldsymbol{W}(r)\boldsymbol{U}(r), \tag{8.36}$$

where the matrix elements of $\boldsymbol{W}$ are given by

$$W_{\boldsymbol{n}',l',m';\boldsymbol{n},l,m}(r) = \frac{2\mu}{\hbar^2}\langle\boldsymbol{n}',l',m'|\Delta\hat{H}-E|\boldsymbol{n},l,m\rangle, \tag{8.37}$$

and the integral is over all coordinates, except r. We impose the boundary conditions for large r

$$U_{\boldsymbol{n}'l'm';\boldsymbol{n}ln}(r) \simeq v_{\boldsymbol{n}'}^{-\frac{1}{2}}\left[-e^{-i(k_{\boldsymbol{n}'}r-l'\frac{\pi}{2})}\delta_{\boldsymbol{n}'\boldsymbol{n}}\delta_{l'l}\delta_{m'm} + e^{-i(k_{\boldsymbol{n}'}r-l'\frac{\pi}{2})}S_{\boldsymbol{n}'l'm';\boldsymbol{n}lm}\right], \tag{8.38}$$

so that we can write the full solution satisfying the boundary conditions of Eq. (8.20) as

$$|\Psi_{\boldsymbol{n}}^+(\boldsymbol{r})\rangle = \frac{2\pi}{ik_{\boldsymbol{n}}}\sum_{\boldsymbol{n}'}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}|\boldsymbol{n}'\rangle Y_{l'm'}(\hat{\boldsymbol{r}})\frac{U_{\boldsymbol{n}'l'm';\boldsymbol{n}lm}(r)}{r}i^l Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{8.39}$$

Solving the coupled channels equation numerically can be done with the algorithm that we described for multichannel collinear scattering in Chapter 5. Matching the wave function to the asymptotic form to extract the $\boldsymbol{S}$-matrix is also very similar, but of course the phase factors $e^{\pm il\frac{\pi}{2}}$ must be included in the incoming and outgoing waves.

When there are no external fields, the Hamiltonian is invariant under rotations, or, in other words, the total angular momentum is conserved. This may be exploited to give a huge reduction in both CPU time and memory usage of a coupled channels. The next chapter gives the required angular momentum theory. Also, the theory in the next chapter can be used to prove the spherical harmonic addition theorem that we already used [Eq. (8.16)].

Chapter 9

Angular momentum theory

9.1   Unitary transformations in place and time

Angular momentum and rotation are closely connected. To better understand this relation, it is instructive to first have a look at a simpler problem: translation of functions in 1D. Figure 9.1 shows a function $f(x)$ translated to the right over a (positive) distance a to give function $g(x)$,

$$g(x) \equiv (\hat{T}_a f)(x) = f(x - a). \tag{9.1}$$

We note that translating the function to the right corresponds to applying the inverse operation to the argument. This is called the *Wigner convention*. We can derive an explicit expression for the translation operator $\hat{T}_a$ from the Taylor expansion

$$f(x - a) = f(x) - af'(x) + \frac{1}{2}a^2 f''(x) + \dots \tag{9.2}$$

$$= \sum_{n=0}^{\infty} \frac{(-a)^n}{n!} \frac{\partial^n}{\partial x^n} f(x) \tag{9.3}$$

$$= e^{-a\frac{\partial}{\partial x}} f(x) \tag{9.4}$$

so we may define

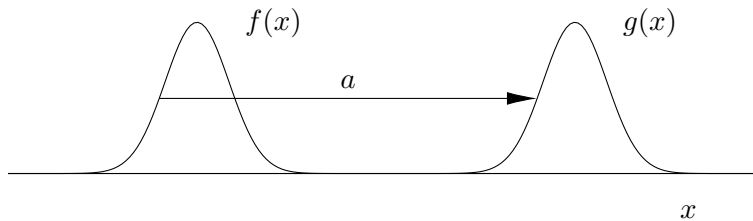$$\hat{T}_a \equiv e^{-a\frac{\partial}{\partial x}}. \tag{9.5}$$

Figure 9.1: Translation of a function: $g(x) = f(x - a)$.

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

$$\langle \frac{\partial}{\partial x} f | g \rangle = -\langle f | \frac{\partial}{\partial x} g \rangle. \tag{9.6}$$

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

$$\hat{p}_x \equiv \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{9.7}$$

so

$$\hat{T}_a = e^{-a\frac{\partial}{\partial x}} = e^{-\frac{i}{\hbar} a \hat{p}_x}. \tag{9.8}$$

Mathematically, solving the time-dependent Schrödinger equation may be thought of as a translation of the wave function in time,

$$\Psi(\boldsymbol{r}, t+\tau) = e^{\tau \frac{\partial}{\partial t}} \Psi(\boldsymbol{r}, t) \tag{9.9}$$

$$= e^{-\frac{i}{\hbar} \hat{H} \tau} \Psi(\boldsymbol{r}, t), \tag{9.10}$$

where we used $\frac{\partial}{\partial t} = -\frac{i}{\hbar} \hat{H}$ in the second step, and again we see that an anti-Hermitian operator $(i\hat{H})$ in the exponential gives a unitary operator.

Next, we consider translation in 3D. We can translate a function over a vector

$$\boldsymbol{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \lambda \hat{\boldsymbol{n}}, \tag{9.11}$$

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

$$\hat{T}(\boldsymbol{a}) = e^{-\frac{i}{\hbar} a_x \hat{p}_x} \, e^{-\frac{i}{\hbar} a_y \hat{p}_y} \, e^{-\frac{i}{\hbar} a_z \hat{p}_z} \tag{9.12}$$

$$= e^{-\frac{i}{\hbar} \lambda \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{p}}}. \tag{9.13}$$

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

$$[\hat{p}_x, \hat{p}_y] = [\hat{p}_x, \hat{p}_z] = [\hat{p}_y, \hat{p}_z] = 0. \tag{9.14}$$

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

9.2   Rotation operator

The rotation operator in 3D around a unit vector $\hat{\boldsymbol{n}}$ over an angle α is given by

$$\hat{R}(\boldsymbol{n}, \alpha) = e^{-\frac{i}{\hbar} \alpha \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{l}}}, \tag{9.15}$$

where the angular momentum vector operator is given by

$$\hat{\boldsymbol{l}} = \boldsymbol{r} \times \hat{\boldsymbol{p}} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \times \begin{pmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \end{pmatrix} = \begin{pmatrix} \hat{l}_x \\ \hat{l}_y \\ \hat{l}_z \end{pmatrix}. \tag{9.16}$$

To check this expression, we first consider a rotation around the z-axis, i.e., $\hat{\boldsymbol{n}} = \boldsymbol{e}_z$,

$$\hat{R}(\boldsymbol{e}_z, \alpha) = e^{-\frac{i}{\hbar}\alpha \boldsymbol{e}_z \cdot \hat{\boldsymbol{l}}} = e^{-\frac{i}{\hbar}\alpha \hat{l}_z} \tag{9.17}$$

The $\hat{l}_z$ operator is given by

$$\hat{l}_z = x\hat{p}_y - y\hat{p}_x \tag{9.18}$$
$$= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{9.19}$$

We introduce polar coordinates

$$x = r\cos\phi\sin\theta \tag{9.20}$$
$$y = r\sin\phi\sin\theta \tag{9.21}$$
$$z = r\cos\theta. \tag{9.22}$$

The $\hat{l}_z$ operator in polar coordinates is given by

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}, \tag{9.23}$$

so the rotation operator is

$$\hat{R}_z(\alpha) \equiv \hat{R}(\boldsymbol{e}_z, \alpha) = e^{-\alpha\frac{\partial}{\partial\phi}}. \tag{9.24}$$

Applying this operator to a wave function expressed in spherical polar coordinates amounts to a tranlation of the ϕ coordinate

$$\hat{R}_z(\alpha)\Psi(r, \theta, \phi) = \Psi(r, \theta, \phi - \alpha). \tag{9.25}$$

Although this only verifies the expression for the rotation operator in Eq. (9.15) for rotations around the z-axis, it is easy to see that it will work for any rotation axis $\hat{\boldsymbol{n}}$, since the scalar product $\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{l}}$ in the exponent is invariant under rotations of the coordinate frame – so we can always choose a coordinate frame where $\boldsymbol{n}$ is the z-axis.

There is one very important difference between rotation and translation: the momentum operators commute [Eq. (9.14)], but the angular momentum operators do not. Essentially everything in angular momentum theory derives from these commutation relations. In the next section we will summarize the elementary results without derivations, since they can be found in most books on quantum mechanics.

9.3   Rotations in $\mathbb{R}^3$

Rotating a vector $\boldsymbol{x}$ around a normalized vector $\hat{\boldsymbol{n}}$ over an infinitesimal angle ϵ gives

$$\boldsymbol{R}(\hat{\boldsymbol{n}}, \epsilon)\boldsymbol{x} = \boldsymbol{x} + \epsilon\hat{\boldsymbol{n}} \times \boldsymbol{x}. \tag{9.26}$$

The cross product is given by

$$\hat{\boldsymbol{n}} \times \boldsymbol{x} = \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \times \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} n_2 x_3 - n_3 x_2 \\ n_3 x_1 - n_1 x_3 \\ n_1 x_2 - n_2 x_1 \end{pmatrix} \tag{9.27}$$

$$= \begin{pmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \tag{9.28}$$

$$\equiv \boldsymbol{N}\boldsymbol{x} \tag{9.29}$$

so we may write

$$\boldsymbol{R}(\hat{\boldsymbol{n}}, \epsilon) = (\boldsymbol{1}_{3\times3} + \epsilon \boldsymbol{N})\boldsymbol{x}, \tag{9.30}$$

where $\boldsymbol{1}_{3\times3}$ is the 3×3 identity matrix. The rotation operator is unitary

$$\boldsymbol{R}^T \boldsymbol{R} = (\boldsymbol{1} + \epsilon \boldsymbol{N})^T (\boldsymbol{1} + \epsilon \boldsymbol{N}) \tag{9.31}$$

$$= \boldsymbol{1} + \epsilon(\boldsymbol{N}^T + \boldsymbol{N}) + \epsilon^2 \boldsymbol{N}^T \boldsymbol{N} \tag{9.32}$$

$$= \boldsymbol{1} + O(\epsilon^2) \tag{9.33}$$

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

$$\boldsymbol{N}^T = -\boldsymbol{N}. \tag{9.34}$$

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

$$\boldsymbol{R}(\hat{\boldsymbol{n}}, \phi) = \lim_{n\to\infty} \boldsymbol{R}(\hat{\boldsymbol{n}}, \frac{\phi}{n})^n = \lim_{n\to\infty} (\boldsymbol{1} + \frac{\phi}{n}\boldsymbol{N})^n = e^{\phi \boldsymbol{N}}. \tag{9.35}$$

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

$$\boldsymbol{N} = n_1 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + n_2 \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} + n_3 \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{9.36}$$

$$= n_1 \boldsymbol{N}_1 + n_2 \boldsymbol{N}_2 + n_3 \boldsymbol{N}_3 \tag{9.37}$$

$$= \boldsymbol{n} \cdot \underline{\boldsymbol{N}} \tag{9.38}$$

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

$$[\boldsymbol{N}_1, \boldsymbol{N}_2] = \boldsymbol{N}_3, \tag{9.39}$$

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

$$[\boldsymbol{N}_i, \boldsymbol{N}_j] = \sum_{k=1}^{3} \epsilon_{i,j,k} \boldsymbol{N}_k. \tag{9.40}$$

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

$$\underline{\boldsymbol{L}} \equiv i\hbar \underline{\boldsymbol{N}} \tag{9.41}$$

for which the components satisfy the commutation relations

$$[\boldsymbol{L}_i, \boldsymbol{L}_j] = i\hbar \sum_{k=1}^{3} \epsilon_{i,j,k} \boldsymbol{L}_k. \tag{9.42}$$

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

$$\boldsymbol{R}(\hat{\boldsymbol{n}}, \phi) = e^{-\frac{i}{\hbar}\phi \hat{\boldsymbol{n}} \cdot \underline{\boldsymbol{L}}}. \tag{9.43}$$

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

$$\hat{R}(\hat{\boldsymbol{n}}, \phi)\Psi(\boldsymbol{r}) = \Psi[\boldsymbol{R}(\hat{\boldsymbol{n}}, -\phi)\,\boldsymbol{r}] \tag{9.44}$$

or explicitly,

$$\left(e^{-\frac{i}{\hbar}\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{l}}} \Psi \right)(\boldsymbol{r}) = \Psi \left(e^{\frac{i}{\hbar}\phi \hat{\boldsymbol{n}} \cdot \underline{\boldsymbol{L}}}\,\boldsymbol{r} \right). \tag{9.45}$$

9.4 Summary of elementary angular momentum theory

The commutation relations of the angular momentum operators are

$$[\hat{l}_i, \hat{l}_j] = i\hbar \sum_{k=1}^{3} \epsilon_{i,j,k} \hat{l}_k. \tag{9.46}$$

In this notation the labels i, j, and k, can be 1, 2, or 3, and they correspond to the components x, y, and z.

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \tag{9.47}$$

commutes with $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$. Since, in particular, $[\hat{l}^2, \hat{l}_z] = 0$, these two Hermitian operators have a common set of eigenvectors, which we will denote in Dirac notation with $|lm\rangle$

$$\hat{l}^2|lm\rangle = \hbar^2 l(l+1)|lm\rangle, \qquad\qquad l = 0, 1, \dots \tag{9.48}$$

$$\hat{l}_z|lm\rangle = \hbar m|lm\rangle, \qquad\qquad m = -l, -l+1, \dots, l \tag{9.49}$$

For orbital angular momentum, the l quantum number must be integer. The commutation relations also allow half integer quantum numbers, which can describe, e.g., electron spin. The angular momentum states are not eigenfunctions of $\hat{l}_x$ and $\hat{l}_y$. To find the action of these operators on the angular momentum states it is convenient to introduce the *ladder operators* $\hat{l}_+$ and $\hat{l}_-$,

$$\hat{l}_\pm \equiv \hat{l}_x \pm i\hat{l}_y. \tag{9.50}$$

When acting on angular momentum states, they change the m quantum number:

$$\hat{l}_\pm|lm\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)}|l, m \pm 1\rangle. \tag{9.51}$$

The action of the $\hat{l}_x$ and $\hat{l}_y$ operators can then be found by expressing them in ladder operators

$$\hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-) \tag{9.52}$$

$$\hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-). \tag{9.53}$$

We assume that the angular momentum states are orthonormal

$$\langle lm|l'm'\rangle = \delta_{ll'}\delta_{mm'}. \tag{9.54}$$

9.5 Wigner rotation matrices

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

$$\hat{R}(\boldsymbol{n}, \phi)|lm\rangle = e^{-\frac{i}{\hbar}\phi \boldsymbol{n}\cdot\hat{\boldsymbol{l}}}|lm\rangle. \tag{9.55}$$

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

$$\hat{R}(\boldsymbol{n}, \phi)|lm\rangle = \sum_{m'=-l}^{(l)} |lm'\rangle D^{(l)}_{m'm}(\boldsymbol{n}, \phi), \tag{9.56}$$

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

$$\hat{R}|lm\rangle = \sum_{m'=-l}^{l} |lm'\rangle D^{(l)}_{m'm}(\hat{R}). \tag{9.57}$$

By projecting the equation from the left with $\langle lm'|$ and using the orthonormality of the angular momentum states [Eq. (1.12)] we find an explicit expression for the D-matrix elements

$$D^{(l)}_{m',m}(\hat{R}) = \langle lm'|\hat{R}|lm\rangle. \tag{9.58}$$

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

$$D^{(l)}_{m',m}(\boldsymbol{e}_z, \phi) = \delta_{m'm}e^{-im\phi}. \tag{9.59}$$

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

$$D^{(l)}_{m',m}(\boldsymbol{e}_y, \beta) = \langle lm'|e^{-\frac{i}{\hbar}\beta\hat{l}_y}|lm\rangle, \tag{9.60}$$

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

$$\boldsymbol{L}_y(m, m') = \langle lm|\hat{l}_y|lm'\rangle \tag{9.61}$$

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

$$\boldsymbol{D}^{(l)}(\boldsymbol{e}_y, \beta) = e^{-\frac{i}{\hbar}\beta \boldsymbol{L}_y}. \tag{9.62}$$

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

$$\boldsymbol{D}^{(l)}(\hat{R}_1 \hat{R}_2) = \boldsymbol{D}^{(l)}(\hat{R}_1) \boldsymbol{D}^{(l)}(\hat{R}_2). \tag{9.63}$$

It is left as an exercise to derive this from the definition of the Wigner D-matrices in Eq. (9.57). From the definition one also finds the representation of the identity operator $\hat{1}$ (a rotation over zero degrees) is the identity matrix,

$$\boldsymbol{D}^{(l)}(\hat{1}) = \boldsymbol{1}_{(2l+1)\times(2l+1)}. \tag{9.64}$$

From the representation property Eq. (9.63) one can derive many useful relations, e.g., where $\hat{1}$ is the identity operator, i.e., some rotation over 0 degrees. Rotations are unitary operators

$$\hat{R}\hat{R}^\dagger = \hat{1} \tag{9.65}$$

or

$$\hat{R}^{-1} = \hat{R}^\dagger \tag{9.66}$$

and their representations have the same properties,

$$\boldsymbol{D}^{(l)}(\hat{R}^{-1}) = [\boldsymbol{D}^{(l)}(\hat{R})]^{-1} = [\boldsymbol{D}^{(l)}(\hat{R})]^\dagger. \tag{9.67}$$

9.6   Wigner $\boldsymbol{D}$-matrix elements as wave functions

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

$$\hat{R}_1 \boldsymbol{D}^{(l)}(\hat{R}_2) \equiv \boldsymbol{D}^{(l)}(\hat{R}_1^{-1}\hat{R}_2) \tag{9.68}$$

$$= \boldsymbol{D}^{(l)}(\hat{R}_1)^\dagger \boldsymbol{D}^{(l)}(\hat{R}_2). \tag{9.69}$$

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

$$\hat{R}_1 \underbrace{D_{mk}^{(l),*}(\hat{R}_2)}_{|(k)lm\rangle} = \sum_{m'=-l}^{l} \underbrace{D_{m'k}^{(l),*}(\hat{R}_2)}_{|(k)lm'\rangle} D_{m'm}^{(l)}(\hat{R}_1). \tag{9.70}$$

By comparing this equation to Eq. (9.57) we find the complex conjuagates of $\boldsymbol{D}$-matrix elements transform exactly as angular momentum states

$$\hat{R}|(k)lm\rangle = \sum_{m'=-l}^{l} |(k)lm'\rangle D_{m'm}^{(l)}(\hat{R}), \tag{9.71}$$

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

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9.7   Euler angles

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

$$\hat{R}(\hat{\boldsymbol{n}}, \phi) = \hat{R}(\boldsymbol{e}_z, \alpha)\hat{R}(\boldsymbol{e}_y, \beta)\hat{R}(\boldsymbol{e}_z, \gamma) \equiv \hat{R}(\alpha, \beta, \gamma). \qquad (9.72)$$

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

$$\boldsymbol{D}^{(l)}(\alpha, \beta, \gamma) \equiv \boldsymbol{D}^{(l)}[\hat{R}(\alpha, \beta, \gamma)]. \qquad (9.73)$$

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

$$D_{mk}^{(l)}(\alpha, \beta, \gamma) = e^{-im\alpha} d_{mk}^{(l)}(\beta) e^{-ik\gamma} \qquad (9.74)$$

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

$$d_{mk}^{(l)}(\beta) \equiv \langle lm | e^{-\frac{i}{\hbar}\beta \hat{l}_y} | lk \rangle. \qquad (9.75)$$

It is left as an exercise to show that this matrix is real [*hint: use Eqs. (9.62), (9.61), (9.53), and (9.50)*].

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

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma \, D_{mk}^{(l),*}(\alpha, \beta, \gamma) D_{m'k'}^{(l')}(\alpha, \beta, \gamma) = \frac{8\pi^2}{2l+1} \delta_{mm'} \delta_{kk'} \delta_{ll'}. \qquad (9.76)$$

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

$$C_{lm}(\theta, \phi) \equiv D_{m,0}^{(l),*}(\phi, \theta, 0) = e^{im\phi} d_{m,0}^{(l)}(\theta) \qquad (9.77)$$

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

$$P_l(\cos\theta) = C_{l,0}(\theta, 0). \qquad (9.78)$$

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

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta, \phi), \qquad (9.79)$$

it is eay to show that

$$C_{lm}(0, 0) = \delta_{m,0}, \qquad (9.80)$$

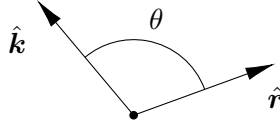whereas the Y_{lm}'s are normalized by condition Eq. (2.15).

Figure 9.2: Coordinates in derivation of spherical harmonic addition theorem.

9.8   Spherical harmonics addition theorem

To derive the spherical harmonic addition theorem, we first define the directions $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{k}}$ by rotating the $\boldsymbol{e}_z$ unit vector.

$$\hat{\boldsymbol{r}} = \boldsymbol{R}_1 \boldsymbol{e}_z \tag{9.81}$$

$$\hat{\boldsymbol{k}} = \boldsymbol{R}_2 \boldsymbol{e}_z, \tag{9.82}$$

where $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ are 3×3 orthonormal matrices (with determinant $+1$). We may now write the cosine of the angle between these two vectors as

$$\cos\theta = \hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{k}} \tag{9.83}$$

$$= \boldsymbol{R}_1 \boldsymbol{e}_z \cdot \boldsymbol{R}_2 \boldsymbol{e}_z \tag{9.84}$$

$$= \boldsymbol{e}_z \cdot \boldsymbol{R}_1^\dagger \boldsymbol{R}_2 \boldsymbol{e}_z. \tag{9.85}$$

We now define the Euler angles α, β, and γ by expressing $\boldsymbol{R}_1^\dagger \boldsymbol{R}_2$ in zyz-Euler angles

$$\boldsymbol{R}_1^\dagger \boldsymbol{R}_2 = \boldsymbol{R}_z(\alpha) \boldsymbol{R}_y(\beta) \boldsymbol{R}_z(\gamma). \tag{9.86}$$

We may now rewrite $\cos\theta$ as (Figure 9.2)

$$\cos\theta = \boldsymbol{e}_z \cdot \boldsymbol{R}_z(\alpha) \boldsymbol{R}_y(\beta) \boldsymbol{R}_z(\gamma) \boldsymbol{e}_z \tag{9.87}$$

$$= \boldsymbol{e}_z \cdot \boldsymbol{R}_y(\beta) \boldsymbol{e}_z \tag{9.88}$$

$$= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \sin\beta \\ 0 \\ \cos\beta \end{pmatrix} \tag{9.89}$$

$$= \cos\beta, \tag{9.90}$$

so $\theta = \beta$. Without having to find the angles α and γ, we can already evaluate Wigner D-matrix elements with $m = k = 0$,

$$D_{0,0}^{(l)}(\boldsymbol{R}_1^\dagger \boldsymbol{R}_2) = D_{0,0}^{(l)}[\boldsymbol{R}_z(\alpha) \boldsymbol{R}_y(\beta) \boldsymbol{R}_z(\gamma)] = D_{0,0}^{(l)}(\alpha, \theta, \gamma) = P_l(\cos\theta). \tag{9.91}$$

The representation property of D-matrices gives

$$D_{0,0}^{(l)}(\boldsymbol{R}_1^\dagger \boldsymbol{R}_2) = \sum_m D_{0,m}^{(l)}(\boldsymbol{R}_1^\dagger) D_{m,0}^{(l)}(\boldsymbol{R}_2) \tag{9.92}$$

$$= \sum_m D_{m,0}^{(l),*}(\boldsymbol{R}_1) D_{m,0}^{(l)}(\boldsymbol{R}_2) \tag{9.93}$$

$$= \sum_m C_{lm}(\hat{\boldsymbol{r}}) C_{lm}^*(\hat{\boldsymbol{k}}). \tag{9.94}$$

[Exercise: show that $D_{m,0}^{(l),*}(\boldsymbol{R}) = C_{lm}(\hat{\boldsymbol{r}})$ when $\hat{\boldsymbol{r}} = \boldsymbol{R}\boldsymbol{e}_z$]. Changing from Racah normalized spherical harmonics to normal regular harmonics we find the spherical harmonics addition theorem,

$$P_l(\cos\theta) = \frac{4\pi}{2l+1}\sum_{lm} Y_{lm}(\hat{\boldsymbol{r}})Y_{lm}^*(\hat{\boldsymbol{k}}). \tag{9.95}$$

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