

A Review of Quantum Mechanics

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I. The Rise of Quantum Mechanics

($e_G^2 = e^2/4\pi\epsilon_0$ in Gaussian units). Hence

1.1 Physics & quantum physics:

Physics = objective description of recurrent physical phenomena

Quantum physics = “quantized” systems with both wave and particle properties

$$E = T + U = \frac{U}{2} = -T. \quad (5)$$

Bohr’s two *quantum postulates* (*L quantization* and *quantum jump* on photon emission):

$$\begin{aligned} \mathbf{L} &= mva = n\hbar, \quad n = 1, 2, \dots, \\ h\nu &= E_{n_i} - E_{n_f}. \end{aligned} \quad (6)$$

1.2 Scientific discoveries:

Facts → Theory/Postulates → Facts

For ground state:

1.3 Planck’s black body radiation:

Failure of classical physics:

$$\begin{aligned} \text{Emissivity} &= \frac{1}{4}uc, \quad \lambda_{\max}T = \text{const}, \\ \text{energy density} &= u = \rho_\nu \langle E \rangle, \\ \langle E \rangle_{\text{exp}} &\neq k_B T, \end{aligned} \quad (1)$$

$$\begin{aligned} E_1 &= \frac{U_1}{2} = -\frac{e_G^2}{2a} = -13.6 \text{ eV} \\ &= -T_1 = -\frac{\hbar^2}{2ma^2}, \\ a &= \frac{\hbar^2}{me_G^2} = 0.53 \text{ \AA} \quad (\text{Bohr radius}), \end{aligned} \quad (7)$$

(ρ_ν = density of states in frequency space).

For excited states:

Planck hypothesis of *energy quantization* ($E_n = n h\nu$) explains observation:

$$r_n = n^2 a, \quad E_n = \frac{E_1}{n^2}. \quad (8)$$

$$\langle E \rangle = \frac{h\nu \sum_{n=0}^{\infty} n e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}, \quad (2)$$

where $x = h\nu/(k_B T)$.

1.6 Compton scattering:

Energy-momentum conservation for a photon of lab energy $E = hc/\lambda$ scattered from an electron (of mass m) initially at rest in the lab (before=LHS, after=RHS; 1=photon, 2= recoiling e):

$$\begin{aligned} \mathbf{p} &= \mathbf{p}_1 + \mathbf{p}_2, \\ E + mc^2 &= E_1 + \sqrt{m^2 c^4 + p_2^2 c^2}. \end{aligned} \quad (9)$$

1.4 Einstein’s photoelectric effect:

Photoelectrons ejected from a metal by absorbed light of frequency ν have maximum energy:

$$E = h\nu - W(\text{work function}) \quad (3)$$

that depends on the frequency ν of light and not its intensity.

Photon scattered into lab angle θ has longer wavelength λ_1 :

$$\begin{aligned} \lambda_1 - \lambda &= \lambda_e(1 - \cos \theta), \quad \text{where} \\ \lambda_e &= \frac{h}{mc} = \frac{hc}{m^2 c^4} = 2.4 \text{ pm} \end{aligned} \quad (10)$$

is the *electron Compton wavelength*.

1.5 Bohr’s atomic model:

Electron of mass m in a classically stable circular orbit of radius $r = a$ and velocity v around the atomic nucleus:

$$\frac{mv^2}{r} = \frac{e_G^2}{r^2}, \quad \text{or} \quad T = -\frac{U}{2}, \quad (4)$$

1.7 de Broglie’s matter wave:

Massive matter and massless light satisfy the same energy-momentum and momentum-wavelength relations

$$\begin{aligned} E^2 &= p^2 c^2 + m^2 c^4, \\ p &= \hbar k = \frac{h}{\lambda}. \end{aligned} \quad (11)$$

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Thus moving matter is postulated to be a wave with a motional *de Broglie* wavelength $\lambda = h/p$, leading to the diffraction maxima for both matter and light of

$$\begin{aligned} \text{2-sided formula:} \quad & 2d \sin \theta = n\lambda, \\ \text{1-sided formula:} \quad & D \sin \theta = n\lambda. \end{aligned}$$

II. Waves and quantum waves

Classical and quantum waves have identical mathematical properties.

2.1 Waves in physics:

Waves rise and fall, travel, have *coherence in space and in time*, interfere, and diffract.

Two classes of waves:

- (a) Inertial waves in massive media: ocean waves, sound waves, vibrations of violin strings;
- (b) *Noninertial* waves in vacuum: EM waves, matter waves.

2.2 Mathematical description of waves:

The **1-dimensional wave equation** (1DWEq)

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \right) \Psi(x, t) = 0 \quad (12)$$

is an *equation of state* that gives a *wave function* $\Psi(x, t)$ describing an unfolding event in spacetime. The wave equation is a partial differential equation (PDE) because it depends on more than one variable, here the two variables x and t .

In contrast, the solution $x(t)$ of an *equation of motion* such as a Newton equation describes how a single point $x(t)$ on an object evolves in time. Similarly, a snapshot of an object is not necessarily a wave. A wave function $\Psi(x, t)$ is needed to describe a wave's coherent structure in *both space and time*.

However, a wave (any wave) can have particle properties if a point x can be defined on it such that one can describe how its position changes in time.

The wave equation (12) describes *linear* waves satisfying the **superposition principle** that a sum of solutions is also a solution :

$$\Psi = a_1 \Psi_1 + a_2 \Psi_2. \quad (13)$$

Traveling waves:

- (a) $f(x - vt)$ = a wave traveling to the right (+x),
- (b) $g(x + vt)$ = a wave traveling to the left (-x),
- (c) the composite wave $a_1 f(x - vt) + a_2 g(x + vt)$ is also a wave.

LDEs (linear DEs) with **constant coefficients** have exponential solutions:

$$\begin{aligned} \frac{d}{dx} e^{ikx} &= ik e^{ikx}, \\ \frac{d}{dt} e^{-i\omega t} &= -i\omega e^{-i\omega t}. \end{aligned} \quad (14)$$

These DE are called **eigenvalue equations** because the constant ik is called an *eigenvalue* of the differential operator d/dx , while the solution e^{ikx} is called its *eigenfunction* belonging to its eigenvalue ik .

The 1DWEq (12) has four distinct (i.e., linearly independent) eigenfunctions:

$$\Psi(x, t) = e^{\pm i(kx \pm \omega t)}. \quad (15)$$

Energy in both classical and quantum waves is carried by the intensity or energy flux

$$I \propto |\Psi|^2. \quad (16)$$

Its quadratic dependence on Ψ is responsible for the **interference** between two traveling waves $\Psi_i = A_i e^{i\theta_i}$ with real A_i :

$$\begin{aligned} |\Psi_1 + \Psi_2|^2 &= |\Psi_1|^2 + |\Psi_2|^2 + 2\text{Re}(\Psi_1^* \Psi_2) \\ &= A_1^2 + A_2^2 + 2A_1 A_2 \cos(\Delta s), \end{aligned}$$

$$\text{where} \quad \Delta s = \Delta k \left[x - \left(\frac{\Delta \omega}{\Delta k} \right) t \right]. \quad (17)$$

In the limit $\Delta k \rightarrow 0$,

$$\begin{aligned} \frac{d\omega}{dk} &= v_g = \text{group velocity} \\ &\neq v = \frac{\omega}{k} = \text{wave velocity}. \end{aligned} \quad (18)$$

Examples: Certain waves satisfy the relation $\omega = Ak^p$. Then $v_g/v = p$. Specific examples are $p = 2$ for transverse vibrations of a thick bar, $p = 3/2$ for short ripples moving under surface tension, and $p = 1/2$ for long waves on deep sea.

The result (17) is similar in structure to the squared length of a sum of two vectors in space that intersect at an angle θ :

$$|\mathbf{A}_1 + \mathbf{A}_2|^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos \theta, \quad (19)$$

Two waves of the same amplitude traveling in opposite directions interfere form a **standing wave**:

$$\begin{aligned} \Psi &= A[\cos(kx - \omega t) + \cos(kx + \omega t)] \\ &= 2A \cos(kx) \cos(\omega t) \end{aligned} \quad (20)$$

with *factorized* space and time dependences.

2.3 Matter-wave quantization:

Light wave of momentum p and energy $E = pc$ is described by the wave function:

$$e^{i(kx - \omega t)} = e^{i[(p/\hbar)x - (E/\hbar)t]}. \quad (21)$$

de Broglie and Schrödinger suggested that the RHS expression holds also for **matter waves** so that:

$$\begin{aligned} \left(\frac{\hbar}{i} \frac{\partial}{\partial x}\right) e^{i(p/\hbar)x} &= \hat{p} e^{i(p/\hbar)x} = p e^{i(p/\hbar)x}, \\ \left(i\hbar \frac{\partial}{\partial t}\right) e^{-i(E/\hbar)t} &= \hat{H} e^{-i(E/\hbar)t} = E e^{-i(E/\hbar)t}. \end{aligned} \quad (22)$$

The differential operators that appear are called the momentum operator \hat{p} and the Hamiltonian (or energy) operator \hat{H} , respectively.

Commutation relations: The rules of differential calculus dictates that a differential operator does not commute with its own variable:

$$\begin{aligned} \frac{\partial}{\partial x} x &= 1 + x \frac{\partial}{\partial x}, \quad \text{or} \quad \left[\frac{\partial}{\partial x}, x\right] = 1; \\ \frac{\partial}{\partial t} t &= 1 + t \frac{\partial}{\partial t}, \quad \text{or} \quad \left[\frac{\partial}{\partial t}, t\right] = 1. \end{aligned} \quad (23)$$

These results give the **fundamental commutators** of wave mechanics

$$[\hat{p}, x] = \frac{\hbar}{i}, \quad [\hat{H}, t] = i\hbar. \quad (24)$$

2.4 Wave packet and the uncertainty principle:

A **wave packet** is a superposition of waves of the type (21)

$$f(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i[kx - \omega(k)t]} dk, \quad (25)$$

with a linear superposition function $g(k)$ sometimes called a *spectral amplitude*.

Expectation value (= mean value) of a property $A(x, t)$ of the wave:

$$\begin{aligned} \langle A(x, t) \rangle &\equiv \int_{-\infty}^{\infty} \rho_P(x, t) A(x, t) dx, \quad \text{where} \\ \rho_P(x, t) &= \frac{|f(x, t)|^2}{\int_{-\infty}^{\infty} |f(x, t)|^2 dx} \end{aligned} \quad (26)$$

is the normalized *probability density* of finding the wave at the spacetime point (x, t) .

The expectation value of a time-independent property $B(k)$ of the wave can be calculated by using the spectral amplitude $g(k)$:

$$\begin{aligned} \langle B(k) \rangle &\equiv \int_{-\infty}^{\infty} \tilde{\rho}_P(k) B(k) dk, \quad \text{where} \\ \tilde{\rho}_P(k) &= \frac{|g(k)|^2}{\int_{-\infty}^{\infty} |g(k)|^2 dx} \end{aligned} \quad (27)$$

is the normalized probability density of finding the wave in “ k space”. (We shall not consider more complicated properties that also depend on the time t or the energy E .)

Uncertainty relations: A wave of any kind satisfies the uncertainty relation

$$\begin{aligned} \Delta x \Delta k &\geq \frac{1}{2}, \quad \text{where} \\ (\Delta x)^2 &= \langle (x - \bar{x})^2 \rangle, \quad \bar{x} = \langle x \rangle, \\ (\Delta k)^2 &= \langle (k - \bar{k})^2 \rangle, \quad \bar{k} = \langle k \rangle. \end{aligned} \quad (28)$$

The expression for matter waves is usually written as the Heisenberg *uncertainty principle*:

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \quad (29)$$

Spreading wave packets: A Gaussian wave packet has the spectral amplitude

$$g(k) = e^{-\alpha k^2}, \quad \text{with} \quad \Delta k = \frac{1}{2\sqrt{\alpha}}. \quad (30)$$

It gives rise to a wave function at time $t = 0$ of

$$f(x, t = 0) \propto e^{-x^2/(4\alpha)}, \quad \text{with} \quad \Delta x = \sqrt{\alpha}. \quad (31)$$

Hence the wave packet at time $t = 0$ has the minimal uncertainty product of

$$\Delta x \Delta k = \frac{1}{2}. \quad (32)$$

For $t \neq 0$, however, the uncertainty product could be greater than the minimal value of $1/2$. This happens if the system is *dispersive*, meaning a nonzero second Taylor coefficient β in the following expansion:

$$\begin{aligned} \omega(k) &\approx \omega(k = 0) + k \left. \frac{d\omega}{dk} \right|_0 + \frac{1}{2} k^2 \left. \frac{d^2\omega}{dk^2} \right|_0 \\ &= \omega(0) + kv_g + \frac{1}{2} k^2 \beta. \end{aligned} \quad (33)$$

The resulting approximate wave function at any time t can then be evaluated to the closed form

$$\begin{aligned} f(x, t) &\propto e^{-x_t^2/(4\alpha_t)}, \quad \text{with} \\ x_t &= x - v_g t, \quad \alpha_t = \alpha + \frac{i\beta}{2} t. \end{aligned} \quad (34)$$

Thus the position x of the wave moves in time with the group velocity

$$v_g = \left. \frac{d\omega}{dk} \right|_0. \quad (35)$$

Its position uncertainty increases in time to

$$\Delta x(t) = \frac{|\alpha_t|}{\sqrt{\alpha}} = \sqrt{\alpha} \left[1 + \left(\frac{\beta t}{2\alpha} \right)^2 \right]^{1/2}. \quad (36)$$

For a massive particle in free space $E^2 = p^2c^2 + m^2c^4$. Hence

$$\beta = \hbar \frac{d^2 E}{dp^2} = \hbar \frac{m^2 c^6}{E^3} \neq 0. \quad (37)$$

Thus the spatial width of the Gaussian packet of a massive particle spreads out in both positive and negative times.

III. Wave mechanics

Wave mechanics describes physics by using the Schrödinger wave eq. and its wave functions.

3.1 Schrödinger wave equation (SchWEq) :

First quantization: The classical E-p relation $E^2 = p^2c^2 + m^2c^4$ is quantized into a wave equation by replacing E, p by the differential operators

$$\begin{aligned} E &\rightarrow \hat{H} = i\hbar \frac{\partial}{\partial t} \\ p &\rightarrow \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} : \end{aligned} \quad (38)$$

$$\left(i\hbar \frac{\partial}{\partial t} \right)^2 \Psi(x, t) = \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 c^2 + m^2 c^4 \right] \Psi, \quad (39)$$

where the wave function $\Psi(x, t)$ has to be added for the operators to operate on. In this way, a classical state of motion “spreads out” into a wave structure.

Nonrelativistic limit: Likewise, the NR energy $E = T + V = p^2/2m + V$ (not containing the rest energy mc^2) is quantized into the SchWEq:

$$\left(i\hbar \frac{\partial}{\partial t} \right) \Psi(x, t) = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 + V(x) \right] \Psi, \quad (40)$$

Commutation relations: A differential operator does not commute with its variable. Hence

$$[\hat{p}, x] = \frac{\hbar}{i}, \quad [\hat{H}, t] = i\hbar. \quad (41)$$

Group velocity: $E^2 = p^2c^2 + m^2c^4 \Rightarrow EdE = c^2pdp$. Hence

$$vv_g = \frac{E}{p} \left(\frac{dE}{dp} \right) = c^2. \quad (42)$$

3.2 Born’s interpretation of $|\Psi|^2$:

The squared wave function gives the **probability density** of finding system at spacetime location (x, t) :

$$|\Psi(x, t)|^2 = \rho_P(x, t) \quad (43)$$

in the sense that the probability for finding the state somewhere in space at time t is

$$\begin{aligned} P(t) &= \int_{-\infty}^{\infty} \rho_P(x, t) dx \\ &= \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1. \end{aligned} \quad (44)$$

By choosing $P(t) = 1$, the wave function is said to be *normalized*.

3.3 Conservation of $|\Psi|^2$:

The probability density can be moved around, but cannot be created or destroyed in the absence of explicit creative or destructive physical processes:

$$\begin{aligned} 0 &= \frac{d}{dt} \rho_P(x, t) = \left(\frac{\partial}{\partial t} + \frac{dx}{dt} \frac{\partial}{\partial x} \right) \rho_P(x, t) \\ &= \frac{\partial}{\partial t} \rho_P(x, t) + \frac{\partial}{\partial x} j_P(x, t). \end{aligned} \quad (45)$$

This is called the *continuity equation* for the *conserved* probability current density

$$j_P(x, t) = v \rho_P(x, t), \quad (46)$$

where $v = dx/dt$.

IV. Wave mechanics in one spatial dimension

Wave mechanics is applied to simple one-dimensional problems to illustrate how the SchWEq is solved and how its wave character affects the properties of a system.

4.1 Solving the Schrödinger wave equation (SchWEq) :

Separation of variables: Since solutions are unique up to a superposition, we may look for a solution of the factorized form

$$\Psi(x, t) = \psi(x)\phi(t). \quad (47)$$

Then

$$\frac{\psi(x)\hat{H}\phi(t)}{\psi(x)\phi(t)} = \frac{\phi(t)\left(\frac{\hat{p}^2}{2m} + V\right)\psi(x)}{\phi(t)\psi(x)} = E. \quad (48)$$

On simplification, the first expression is clearly a function of t only, while the middle expression is a function of x only. Hence the *separation constant* E must be a constant independent of t or x .

The PDE can thus be broken up into two ordinary DEs:

$$\begin{aligned} \hat{H}\phi(t) &= \left(i\hbar \frac{\partial}{\partial t} \right) \phi(t) = E\phi(t), \\ \left[\frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 + V(x) \right] \psi(x) &= E\psi(x), \end{aligned} \quad (49)$$

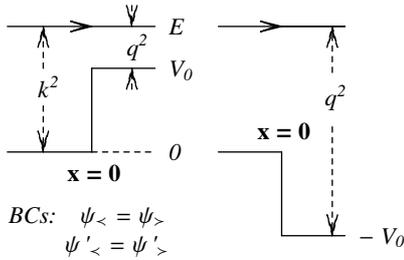


FIG. 1: Wave numbers and wave functions at a potential step.

where E appears in both ODEs as the **energy eigenvalue**. The first ODE gives the time-dependent factor

$$\phi_E(t) = e^{-i(E/\hbar)t}, \quad (50)$$

but the second equation is a second-order ODE whose solution requires the imposition of two

Boundary conditions at a suitable boundary $x = x_0$:

$$\begin{aligned} \psi_{<}(x_0) &= \psi_{>}(x_0), \\ \psi'_{<}(x_0) &\equiv \left. \frac{d}{dx} \psi_{<}(x) \right|_{x_0} = \psi'_{>}(x_0). \end{aligned} \quad (51)$$

Note that if the first BC is violated, $\psi'(x_0)$ becomes infinite and the DE (differential eq.) cannot be satisfied. If the second BC is violated, $\psi''(x_0)$ becomes infinite. The DE also cannot be satisfied, except for the special case where $V(x_0)$ has a compensating infinity at x_0 .

4.2 Particle in a box of length L :

With the two BCs $\psi(0) = \psi(L) = 0$, the solutions turn out to be the *same* as those describing classical vibrations of a violin string of length L :

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad (52)$$

for a normalized wave function.

4.3 Potential step:

Figure 1 shows a particle of mass m incident from the left with energy E . The wave numbers k, q are defined as follows:

$$E = \frac{\hbar^2 k^2}{2m}, \quad E - V = \frac{\hbar^2 q^2}{2m}; \quad (53)$$

or $k^2 = q^2 - k_0^2$, where $k_0^2 = 2mV_0/\hbar^2$. The particle's matter wave is partially reflected at the boundary $x = 0$, and partially transmitted across it (with no further reflection downstream):

$$\begin{aligned} x < 0: & \quad \psi_{<}(x) = e^{ikx} + B e^{-ikx}, \\ x > 0: & \quad \psi_{>}(x) = A_T e^{iqx}. \end{aligned} \quad (54)$$

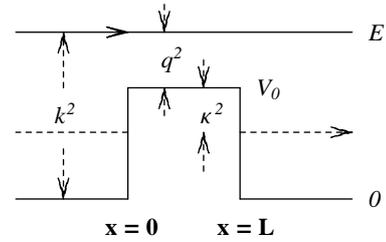


FIG. 2: Wave numbers for a rectangular potential barrier.

Its probability current density is conserved across the boundary:

$$\begin{aligned} j_{<} &= \frac{\hbar k}{m} (1 - |B|^2) \\ &= j_{>} = \frac{\hbar q}{m} |A_T|^2. \end{aligned} \quad (55)$$

Its reflection and transmission coefficients at the boundary are:

$$R = |B|^2, \quad T = 1 - R. \quad (56)$$

4.4 Potential barrier:

A particle of incident energy E higher than the height V_0 of a rectangular potential barrier is partially reflected and partially transmitted by a potential barrier. The wave functions for $x < 0$ before the barrier and for $x > L$ after the barrier remain the same as Eq.(54), but the presence of the second boundary at $x = L$ causes reflected waves to be present in the barrier region

$$0 < x < L: \quad \psi_{<}(x) = C e^{ikx} + D e^{-ikx}. \quad (57)$$

The two boundary conditions at the second boundary $x = L$ are enough to determine the two extra coefficients C and D . The reflection coefficient remains $R = |B|^2$, but its value is changed. The transmission coefficient is

$$T = 1 - R = \frac{1}{1 + \left(\frac{k^2 - q^2}{2kq}\right)^2 \sin^2(qL)}. \quad (58)$$

Quantum tunneling: The formula for T works even when the energy E falls below the height V_0 of the potential barrier, as shown in Fig. 2. Then $q^2 = -\kappa^2 < 0$, and $q = i\kappa$ becomes purely imaginary. The function $[\sin(qL)/q]^2$ in the formula is *analytically continued* to the function $[\sinh(\kappa L)/\kappa]^2$. The resulting transmission coefficient T across the finite barrier is shown in Fig. 3. The fact that T does not vanish for $E < E_0$, as it does in classical mechanics, is called *quantum tunneling*. Note that tunneling can occur only when the barrier thickness is finite.

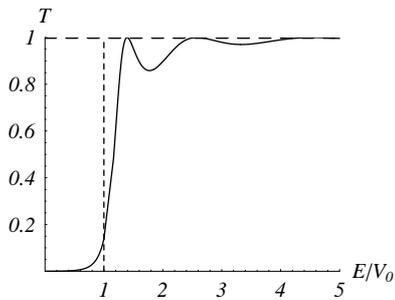


FIG. 3: Transmission coefficient across a rectangular potential barrier.

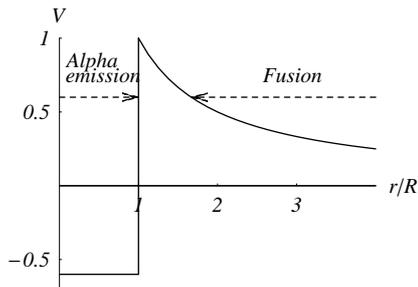
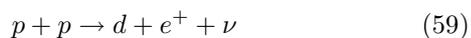


FIG. 4: Tunneling across the Coulomb barrier in α decay and in nuclear fusion.

4.5 Applications of quantum tunneling:

Alpha decay: An α particle inside a nucleus feels an attractive nuclear potential. As the α particle leaves the nucleus in alpha decay, it sees the repulsive Coulomb potential outside the nucleus. These two potentials combine to form a potential barrier that the α particle must tunnel through on its way out, as illustrated in Fig. 4. The decay probability is thus fT , the product of the frequency f of the α particle's hitting the inside wall of the potential barrier and the transmission coefficient T through the potential barrier (that gives the tunneling probability per attempt).

Nuclear fusion: is just the time reversed situation of emission. Here a charged particle, say a proton, is trying to enter a nucleus from the outside by tunneling through its very high and thick Coulomb potential barrier. The transmission coefficient is typically very small, but increases very rapidly with the energy E . If a number of atomic nuclei are exposed to a gas of protons of increasing temperature, the high-energy tail of the Boltzmann energy distribution of the proton gas will allow more and more protons to get into atomic nuclei to initiate nuclear fusion reactions. For example, the pp reaction



(where e^+ is the positron and ν is a particle called

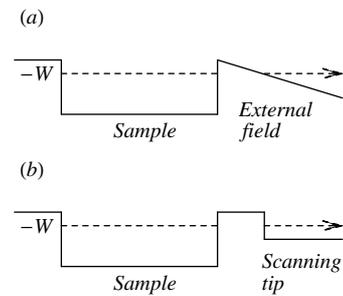


FIG. 5: Tunneling through a finite potential barrier (a) in cold emission, and (b) in a scanning tunneling microscope.

the electron neutrino) powers the conversion of mass into solar energy in the interior of the Sun. The reaction rate depends on the temperature T as T^4 .

The luminosity of a star usually increases as M^3 of its mass M , or T^{24} of its central temperature. Such an unusually strong dependence led Bethe in 1938 to look for another source of hydrogen burning. He discovered that this alternative route is a certain CNO cycle that involves certain carbon, nitrogen and oxygen isotopes in intermediate steps.

Cold emission: Electrons are bound in metals by their work function W . However, they can be induced to tunnel out of the metal by applying an external electric field to change the potential to a triangular penetrable potential, as illustrated in Fig. 5(a).

In **scanning tunneling microscopes**, the tunneling is induced by the proximity of the scanning tip, as shown in Fig. 5(b). Since the tunneling current increases greatly as the thickness of the potential barrier decreases, one has a very sensitive device for mapping the geometrical shape of a surface down to atomic dimensions.

4.6 Bound states in a potential well:

If $V(x) \rightarrow \text{constant}$ as $x \rightarrow \pm\infty$, the lower of these two constant values is usually taken to be the zero of the energy scale. Two situations can then be realized:

- (a) A system with $E > 0$ has continuous energy spectrum with wave functions that are *not* localized or square-integrable, while
- (b) a system with $E < 0$ has a discrete energy spectrum with localized wave functions that are *square-integrable*. The resulting physical states are called bound states in a potential well.

The wave numbers associated with a bound state in an attractive one-dimensional square-well potential

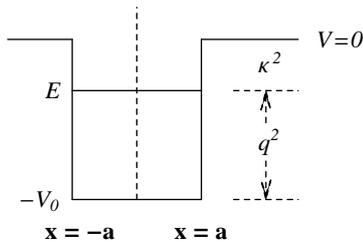


FIG. 6: Wave numbers associated with a bound state in an attractive square-well potential.

are summarized in Fig. 6, where

$$|E| = -E = \frac{\hbar^2 \kappa^2}{2m}, \quad E - V = \frac{\hbar^2 q^2}{2m}. \quad (60)$$

Such an attractive one-dimensional potential has at least one bound state, the ground state of even parity whose wave function is proportional to $\cos qx$. This is because such a wave function already “bends” over at the boundaries, and can always be matched to a decreasing exponential function outside the potential well.

V. The mathematical structure of quantum mechanics

Physical states in quantum mechanics are linear waves. Both quantum states and classical linear waves can be superposed to form other waves, in the same way that ordinary vectors in space can be added to form other vectors.

5.1 Fourier transform (FT):

The superposition principle for linear wave functions (solutions of linear wave equations) is formalized in the methods of Fourier series and Fourier transforms (FT). Both methods and their generalizations are used in quantum mechanics.

The **FT** of a wave function $f(x)$ in one spatial variable x is defined by the integral

$$\mathcal{F}\{f(x)\} \equiv g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx. \quad (61)$$

For example,

$$\mathcal{F}\left\{\frac{d}{dx}f(x)\right\} = ikg(k) \rightarrow \left(\frac{ip}{\hbar}\right)g(k). \quad (62)$$

Thus the momentum operator $\hat{p} = (\hbar/i)\partial/\partial x$ yields the momentum value $p = \hbar k$ associated with the spectral amplitude $g(k)$.

Fourier inversion formula:

$$\mathcal{F}^{-1}\{g(k)\} \equiv f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx} dk. \quad (63)$$

This is how a wave packet is constructed, namely by taking a linear superposition of waves. Also

$$\mathcal{F}^{-1}\left\{\frac{d}{dk}g(k)\right\} = -ixf(x). \quad (64)$$

Thus a position operator $\hat{x} = i\partial/\partial k$ gives the value of the position x associated with the wave function $f(x)$.

The FT shows that waves can be described either by wave functions $f(x)$ in space, or by their spectral amplitudes $g(k)$ in k -space. Functions of one space can be constructed from those in the other space. Hence wave properties are completely specified either in ordinary space or in k -space, a “simplification” that follows from a wave’s coherent structure.

Table I gives some simple examples of FTs.

Dirac δ -function: Since

$$\mathcal{F}^{-1}\{\mathcal{F}\{f(x)\}\} = f(x), \quad (65)$$

we find (by writing out the two integral transforms on the LHS in two steps) that

$$\int_{-\infty}^{\infty} \delta(x-x')f(x')dx' = f(x), \quad (66)$$

where

$$\delta(x-x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk \quad (67)$$

TABLE I: Some Fourier transforms.

Property	If $f(x)$ is	then $\mathcal{F}\{f(x)\}$ is
	$f(x)$	$g(k)$
	$e^{-\alpha x^2}$	$\frac{1}{\sqrt{2\alpha}} e^{-\frac{k^2}{4\alpha}}$
	unit step function ^a	$-\frac{1}{\sqrt{2\pi}} \frac{2}{k} \sin ka$
Derivatives	$\left(\frac{d}{dx}\right)^n f(x)$	$(ik)^n g(k)$
Derivatives	$(-ix)^n f(x)$	$\left(\frac{d}{dk}\right)^n g(k)$
Translation	$f(x-a)$	$e^{-ika} g(k)$
Attenuation	$f(x)e^{-\alpha x}$	$g(k-i\alpha)$
CC ^b	Real	$g^*(k) = g(-k)$
	Real and even	$g^*(k) = g(-k) = g(k)$
	Real and odd	$g^*(k) = g(-k) = -g(k)$

^afrom $-a$ to a

^bComplex conjugation

is called a Dirac δ -function.

Dirac has given a simple intuitive construction of his δ -function as a rectangular function of width ϵ and height $1/\epsilon$ with a unit area under it:

$$\delta(x - x') = \lim_{\epsilon \rightarrow 0} \begin{cases} 1/\epsilon, & \text{when } |x - x'| \leq \epsilon/2, \\ 0, & \text{otherwise.} \end{cases} \quad (68)$$

5.2 Operators and their eigenfunctions:

When a differential operator operates on its **eigenfunction**, it gives a function that is proportional to the eigenfunction itself:

$$\begin{aligned} \hat{p} e^{ikx} &= \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) e^{ikx} = \hbar k e^{ikx}, \\ \hat{x} e^{-i(x/\hbar)p} &= \left(i\hbar \frac{\partial}{\partial p} \right) e^{-ixp/\hbar} = x e^{-ixp/\hbar}. \end{aligned} \quad (69)$$

The proportionality constant is called its eigenvalue.

Two functions or eigenfunctions can be combined into an **inner product**:

$$\begin{aligned} (\phi, \psi) &\equiv \int_{-\infty}^{\infty} \phi^*(x) \psi(x) dx \\ &= \int_{-\infty}^{\infty} g_\phi^*(k) g_\psi(k) dk. \end{aligned}$$

Dirac denotes this inner product by the bracket symbol $\langle \phi | \psi \rangle$.

5.3 Dirac notation:

Functions in function space and states of a physical system in quantum mechanics are mathematically similar to vectors in space. Dirac emphasizes this similarity using a mathematical notation that works for vectors, functions and quantum states.

A vector (function, state) can be expanded in terms of basis vectors (functions, states). Dirac distinguishes between two kinds of vectors (functions, states) – column vectors (functions, ket states) and row vectors (complex-conjugated functions, bra states), where the name bra and ket comes from the two parts of the word “bracket”:

$$\begin{aligned} |\psi\rangle &= \text{ket} = \psi_1|1\rangle + \psi_2|2\rangle \\ &= \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \text{column vector} \\ \langle\phi| &= \text{bra} = \phi_1^*\langle 1| + \phi_2^*\langle 2| \\ &= (\phi_1^*, \phi_2^*) = \text{row vector} \\ &= |\phi\rangle^\dagger, \end{aligned} \quad (70)$$

For simple vectors, the basis states $|1\rangle$ and $|2\rangle$ are just the unit basis vectors usually denoted \mathbf{e}_1 and \mathbf{e}_2 , respectively. The \dagger symbol is called an adjoint operation. It combines the matrix operation of

transposition with the complex conjugation of all “matrix elements”.

The **Dirac bracket** $\langle \phi | \psi \rangle$ is a scalar product of vectors or an inner product of functions

$$\langle \phi | \psi \rangle = (\phi_1^*, \phi_2^*) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \phi_1^* \psi_1 + \phi_2^* \psi_2, \quad (71)$$

where the complex conjugation on the bra components is needed to keep the self scalar product $\langle \psi | \psi \rangle$ nonnegative. For two orthonormal vectors or states:

$$\langle i | j \rangle = \delta_{ij}. \quad (72)$$

Eigenbras and eigenkets: One goes beyond simple vector spaces by using the eigenfunctions of operators such as position \hat{x} and momentum \hat{p} . In fact, we immediately associate their eigenfunctions with abstract **eigenstates** in the following eigenbra or eigenket form:

$$\begin{aligned} \hat{x}|x\rangle &= x|x\rangle, & \langle x|\hat{x} &= x^*\langle x| = x\langle x|, \\ \hat{p}|p\rangle &= p|p\rangle, & \langle p|\hat{p} &= p^*\langle p| = p\langle p|, \end{aligned} \quad (73)$$

where the eigenvalues x and p are real, as is true for all physical observables, i.e., properties that can be measured experimentally. The eigenvalues x and p normally range continuously from $-\infty$ to ∞ .

Projection and quantum destructive measurement: A simple 2-dimensional vector $|A\rangle$ can be decomposed into its components $A_i = \langle i | A \rangle$ with respect to the basis $|i\rangle$:

$$\begin{aligned} |A\rangle &= |1\rangle A_1 + |2\rangle A_2 \\ &= \left(\sum_{i=1}^N |i\rangle \langle i| \right) |A\rangle. \end{aligned} \quad (74)$$

In a similar way, an N -dimensional vector space is made up of the N one-dimensional subspaces projected out by the *projection operators*

$$\mathcal{P}_i = \mathcal{M}_i = |i\rangle \langle i| \quad (75)$$

in the sense that

$$\mathcal{P}_i |A\rangle = A_i |i\rangle \quad (76)$$

leaves only that part of the vector that is in this i th subspace. \mathcal{P}_i is also called a *measurement symbol* (hence \mathcal{M}_i). This measurement is not a classical nondestructive measurement but a quantum *destructive* measurement that destroys all other components of the original vector $|A\rangle$. The projection collapses the state $|A\rangle$ into just the part $A_i |i\rangle$ in the i th subspace.

Completeness relations: The original vector $|A\rangle$ can be restored by adding up all its projections

$A_i|i\rangle$. Hence an identity operator can be constructed for this linear vector space

$$\mathbf{1} = \sum_{i=1}^N |i\rangle\langle i| \quad (77)$$

for discrete basis states that satisfy the orthonormality relation $\langle i|j\rangle = \delta_{ij}$.

The idea of *completeness* or *closure* holds also for eigenstates of operators such as \hat{x} and \hat{p} that have continuous eigenvalues:

$$\begin{aligned} \mathbf{1} &= \int_{-\infty}^{\infty} |x\rangle\langle x| dx \\ &= \int_{-\infty}^{\infty} |p\rangle\langle p| dp. \end{aligned} \quad (78)$$

The resulting basis states $|x\rangle$ or $|p\rangle$ are said to be continuous basis states.

Representations: A discrete representation is a specification of a vector (or state) $|A\rangle$ by its components A_i in a discrete basis. A continuous representation uses the continuous basis states $|x\rangle$ to give the components $A(x) = \langle x|A\rangle$ in the expansion

$$|A\rangle = \int_{-\infty}^{\infty} dx |x\rangle A(x). \quad (79)$$

Wave functions: The (position) wave function of a state or wave $|\psi\rangle$ is just its component $\psi(x) = \langle x|\psi\rangle$ in the position representation. Its component $\psi(p) = \langle p|\psi\rangle$ in the momentum representation is called its *momentum* wave function. A wave function can be expanded into an arbitrary discrete representation of basis states $|i\rangle$

$$\begin{aligned} \langle x|\psi\rangle \equiv \psi(x) &= \sum_{i=1}^N \langle x|i\rangle \langle i|\psi\rangle \\ &= \sum_{i=1}^N \phi_i(x) \psi_i, \end{aligned} \quad (80)$$

where $\phi_i(x) = \langle x|i\rangle$ is the wave function of the basis state $|i\rangle$. Incidentally, N must be infinite to match the number of points on the straight line.

A wave function can also be expanded in another continuous representation, say the momentum representation:

$$\begin{aligned} \langle x|\psi\rangle = \psi(x) &= \int_{-\infty}^{\infty} dp \langle x|p\rangle \langle p|\psi\rangle \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{dp}{\hbar} e^{i(p/\hbar)x} \psi(p). \end{aligned} \quad (81)$$

This is just the inverse Fourier transform relation.

Dirac δ -function: The equivalence

$$\begin{aligned} \psi(x) &= \int_{-\infty}^{\infty} \delta(x-x') \psi(x') dx' \\ = \langle x|\psi\rangle &= \int_{-\infty}^{\infty} \langle x|x'\rangle \langle x'|\psi\rangle dx' \end{aligned} \quad (82)$$

shows that

$$\langle x|x'\rangle = \delta(x-x'). \quad (83)$$

It immediately follows that the Dirac δ -function can be represented in infinitely many ways. For example,

$$\langle x|x'\rangle = \sum_{i=1}^N \langle x|i\rangle \langle i|x'\rangle = \sum_{i=1}^N \phi_i(x) \phi_i^*(x'). \quad (84)$$

Quantum measurement and wave-function collapse:

Electrons emitted from a source pass through a single slit and fall on a distant observing screen on the other side of the slit. As a coherent matter wave, *each* electron forms a diffraction pattern on the observing screen in the direction y of the diffraction pattern. (Diffraction = spreading of a wave into the geometrical shadow regions.)

A detector of acceptance Δy placed at position $y = d$ on the observing screen detects electrons from signals of their passage through the detector. If $\psi(y') = \langle y'|\psi\rangle$ is the wave function of self-diffracting electrons normalized in some way, the part that enters the detector is

$$\Delta\psi(d) = \int_{d-\Delta y/2}^{d+\Delta y/2} dy' |y'\rangle \langle y'|\psi\rangle. \quad (85)$$

The probability of an electron entering the detector is

$$\Delta P(d) = \int_{d-\Delta y/2}^{d+\Delta y/2} dy' |\psi(y')|^2. \quad (86)$$

Note that the electron described by the wave function $\psi(y)$ can be anywhere on the screen before the detection. However, once it is known to have gone into the detector, e.g., by the detector signal it generates, its wave function has *collapsed* into $\Delta\psi(d)$. This is how a quantum measurement can modify the state itself.

5.4 Operators and their matrix elements: Matrix mechanics

Operators as matrices: Operators can be visualized as matrices because they satisfy matrix operations. Hence quantum mechanics is also called **matrix mechanics**. For example, an operator \hat{A} acting on a state always gives another state:

$$\hat{A}|\psi\rangle = c|\phi\rangle \quad (87)$$

in much the same way that a square matrix multiplying a column vector always gives another column vector. It can happen occasionally that the result is actually proportional to the original state $|\psi\rangle$

$$\hat{A}|a\rangle = a|a\rangle. \quad (88)$$

These special states are called the **eigenstates** of \hat{A} . The proportionality constants a are called their *eigenvalues*. Note how the eigenvalue a is used to label the eigenstate $|a\rangle$ itself. This operator equation is called an *eigenvalue equation*.

Noncommuting operators: Operators, like matrices, do not generally commute. For example,

$$[\hat{p}, \hat{x}] = \frac{\hbar}{i}. \quad (89)$$

In matrix mechanics, commutators like this specify the fundamental wave nature of the matter waves described by these operators. It is the starting point from which other results can be derived. In contrast, the wave property of matter is described in wave mechanics by postulating the quantization rule

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad (90)$$

and the wave function $\psi(x)$ on which \hat{p} operates.

Operator matrix elements: Operators like matrices have matrix elements. The matrix elements of a matrix or operator \hat{M} can be expressed conveniently in the Dirac notation as

$$M_{ij} = \langle i|\hat{M}|j\rangle, \quad (91)$$

a two-sided *representation* in terms of a suitable basis $|i\rangle$. A 2×2 matrix or operator can thus be written in operator form as

$$\begin{aligned} \hat{M} &= M_{11}|1\rangle\langle 1| + M_{12}|1\rangle\langle 2| \\ &+ M_{21}|2\rangle\langle 1| + M_{22}|2\rangle\langle 2|. \end{aligned} \quad (92)$$

The ket-bra combinations on the RHS are themselves operators or square matrices. The off-diagonal operators are the *transition* operators

$$|\psi\rangle\langle\phi| = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} (\phi_1^* \phi_2^*) = \begin{pmatrix} \psi_1\phi_1^* & \psi_1\phi_2^* \\ \psi_2\phi_1^* & \psi_2\phi_2^* \end{pmatrix}, \quad (93)$$

while the diagonal operators (with $\phi = \psi$) are projection operators.

An operator in the representation of its own eigenstates is a diagonal matrix. Thus

$$\begin{aligned} \langle x|\hat{x}|x'\rangle &= \langle x|x'\rangle x' = x'\delta(x-x') \\ \langle x|\hat{p}|x'\rangle &= \langle x|x'\rangle \left(\frac{\hbar}{i} \frac{d}{dx'}\right) = \delta(x-x') \left(\frac{\hbar}{i} \frac{d}{dx'}\right) \end{aligned} \quad (94)$$

Note how the operator \hat{p} becomes a diagonal differential operator in the x -representation, and how it comes out to the right of the Dirac bracket to *avoid* operating on it. The Hamiltonian operator too has interesting diagonal representations:

$$\langle E|\hat{H}|E'\rangle = \begin{cases} \langle E|E'\rangle E' = \delta(E-E')E', & \text{if continuous} \\ \langle n|n'\rangle E_{n'} = \delta_{nn'}E_{n'}, & \text{if discrete.} \end{cases} \quad (95)$$

Eigenvalue eq. as wave eq.: Matrix mechanics can be shown to be equivalent to wave mechanics by writing the operator eigenvalue equation $\hat{H}|\Psi_E\rangle = E|\Psi_E\rangle$ as a Schrödinger wave equation:

$$\begin{aligned} E\langle x|\Psi_E\rangle &= \langle x|\hat{H}|\Psi_E\rangle \\ &= \int_{-\infty}^{\infty} dx' \langle x|x'\rangle \left[\frac{\hat{p}^2}{2m} + V(\hat{x}) \right] x' \Psi_E(x') \\ &= \int_{-\infty}^{\infty} dx' \delta(x-x') \left[\frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx'} \right)^2 + V(x') \right] \\ &\quad \times \Psi_E(x') \\ &= \left[\frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 + V(x) \right] \Psi_E(x). \end{aligned} \quad (96)$$

5.5 Hermitian operators and physical observables:

Hermitian operator: is one for which

$$\hat{H}^\dagger = \hat{H}^{T*} = \hat{H} \text{ (itself)}. \quad (97)$$

It has the important properties that

- (a) Eigenvalues are real.
- (b) Eigenstates can be orthonormalized.

Physical observables can have only real values. Hence they are described by Hermitian operators in quantum mechanics.

Dirac notation: For any operator \hat{A} :

$$\begin{aligned} \langle\phi|\hat{A}\psi\rangle &= \int_{-\infty}^{\infty} \phi^\dagger(x) [\hat{A}\psi](x) dx \\ &= \int_{-\infty}^{\infty} \{[\hat{A}^\dagger\phi](x)\}^\dagger \psi(x) dx \\ &= \langle\hat{A}^\dagger\phi|\psi\rangle. \end{aligned} \quad (98)$$

The Hermiticity of an operator \hat{H} is confirmed by the equality $\langle\phi|\hat{H}|\psi\rangle = \langle\hat{H}\phi|\psi\rangle$ of the two distinct integrals involved. Note that if $\phi(x)$ is a column wave function (called a spinor), the transposition part of the adjoint operator will come into play to change it into a row spinor.

5.6 One-dimensional harmonic oscillator:

The 1DHO problem can be solved elegantly in matrix mechanics. First write its Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \quad (99)$$

in the compact form

$$\begin{aligned} \hat{h} &= \frac{\hat{H}}{\hbar\omega} = \frac{1}{2}(\hat{q}^2 + \hat{y}^2), \\ \text{where } \hat{y} &= \frac{\hat{x}}{x_0}, \\ \hat{q} &= \frac{x_0}{\hbar}\hat{p} = \frac{1}{i}\frac{d}{dy}. \end{aligned} \quad (100)$$

Here the oscillator length $x_0 = \sqrt{\hbar/m\omega}$ is defined by the equation

$$\hbar\omega = m\omega^2 x_0^2. \quad (101)$$

The dimensionless position and momentum operators do not commute:

$$[\hat{q}, \hat{y}] = 1/i. \quad (102)$$

The dimensionless Hamiltonian \hat{h} can be factorized:

$$\begin{aligned} \hat{h} &= \hat{a}^\dagger\hat{a} + \frac{1}{2}, \\ \text{where } \hat{a} &= \frac{1}{\sqrt{2}}(\hat{y} + i\hat{q}) \\ \hat{a}^\dagger &= \frac{1}{\sqrt{2}}(\hat{y} - i\hat{q}) \end{aligned} \quad (103)$$

are called the *step-down* and *step-up* operators, respectively. They do not commute

$$[\hat{a}, \hat{a}^\dagger] = 1. \quad (104)$$

Number operator and its eigenstates: The number operator $\hat{N} = \hat{a}^\dagger\hat{a}$ is Hermitian. It has real eigenvalues n that can be used to label its eigenstates

$$\hat{N}|n\rangle = n|n\rangle. \quad (105)$$

It then follows that $|n\rangle$ is also an energy eigenstate:

$$\hat{H}|n\rangle = (n + \frac{1}{2})\hbar\omega|n\rangle. \quad (106)$$

The eigenvalue n of the number operator is a non-negative number or integer 0, 1, 2, ... This important quantization property follows from non-negative nature of its Hamiltonian (meaning that $\langle\hat{H}\rangle \geq 0$) and from the nonzero commutators

$$[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger, \quad [\hat{N}, \hat{a}] = -\hat{a}. \quad (107)$$

The commutators show that \hat{a}^\dagger and \hat{a} change the state $|n\rangle$ as follows:

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad \hat{a}|n\rangle = \sqrt{n}|n-1\rangle. \quad (108)$$

Oscillator quanta: The *quantum number* n (qu. no. = any number used to label a quantum state) gives the number of oscillator energy quanta, each of energy $\hbar\omega$, that can be emitted from that state. Thus \hat{a}^\dagger increases the number of energy quanta in the state by 1, and is called a *creation* operator, while the *destruction* operator \hat{a} decreases n by 1. Physical processes that causes the absorption or emission of energy quanta can be expressed in terms of these operators.

The ground state which by definition cannot emit any energy has the qu. no. $n = 0$. It has a zero-point energy $\hbar\omega/2$ that comes from the wave spreading of its wave function from the classical point $x = 0$ of stable equilibrium.

Wave functions: The impossibility of energy emission from the ground state is stated by the operator equation

$$\hat{a}|0\rangle = 0. \quad (109)$$

Its y -representation gives the first-order differential equation for the ground-state (GS) wave function:

$$\left(y + \frac{d}{dy}\right)\phi_0(y) = 0. \quad (110)$$

The resulting normalized GS wave function is

$$\phi_0(y) = \alpha_0 e^{-y^2/2}, \quad \text{where } \alpha_0 = \frac{1}{\pi^{1/4}}. \quad (111)$$

Excited states can be created by adding energy quanta to the GS:

$$|n\rangle = \left[\frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\right]|0\rangle. \quad (112)$$

Consequently, its wave function can be constructed by successive differentiations of the GS wave function:

$$\begin{aligned} \phi_n(y) &= \langle y | \left[\frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\right] |0\rangle \\ &= \frac{\alpha_0}{\sqrt{2^n n!}} \left(y - \frac{d}{dy}\right)^n e^{-y^2/2}. \end{aligned} \quad (113)$$

Operators in the number representation: In the number representation $|n\rangle$, the only nonzero matrix elements of \hat{a} and \hat{a}^\dagger lie along the diagonal one line away from the main diagonal of the matrix:

$$\hat{a} = \begin{pmatrix} 0 & \sqrt{1} & 0 & \dots \\ 0 & 0 & \sqrt{2} & \dots \\ 0 & 0 & 0 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}, \quad \hat{a}^\dagger = \begin{pmatrix} 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}. \quad (114)$$

Hence the dimensionless position and momentum operators are the square matrices

$$\hat{y} = \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & \sqrt{1} & 0 & \cdot \\ \sqrt{1} & 0 & \sqrt{2} & \cdot \\ 0 & \sqrt{2} & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix},$$

$$\hat{q} = \frac{1}{i\sqrt{2}}(\hat{a} - \hat{a}^\dagger) = \frac{1}{i\sqrt{2}} \begin{pmatrix} 0 & \sqrt{1} & 0 & \cdot \\ -\sqrt{1} & 0 & \sqrt{2} & \cdot \\ 0 & -\sqrt{2} & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}. \quad (115)$$

5.7 Uncertainty principle:

The quintessential wave property described by the Heisenberg uncertainty principle takes on a surprisingly elegant form in matrix mechanics: If the square uncertainty of the expectation value of a physical observable \hat{A} in the quantum state $|\psi\rangle$ is defined as

$$(\Delta A)^2 = \langle (\hat{A} - \bar{A})^2 \rangle_\psi, \quad (116)$$

then the product of uncertainties of two physical observables \hat{A} and \hat{B} in the *same* quantum state satisfies the inequality

$$(\Delta A)(\Delta B) \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle_\psi \right|. \quad (117)$$

Simultaneous eigenstates: $|a, b\rangle$ exist for commuting operators \hat{A} and \hat{B} :

$$\hat{A}|a, b\rangle = a|a, b\rangle, \quad \hat{B}|a, b\rangle = b|a, b\rangle. \quad (118)$$

Then $\Delta A = 0 = \Delta B$.

5.8 Classical correspondence:

Bohr's correspondence principle: Quantum mechanics reproduces classical mechanics in the limit of large quantum numbers. *Example:* The probability density of quantum state $|n\rangle$ of the 1DHO agrees with the classical value:

$$\lim_{n \rightarrow \infty} |\psi_n^{\text{QM}}(x)|^2 \rightarrow \rho^{\text{CM}}(x). \quad (119)$$

For a periodic system of period T , the classical probability density can be defined in terms of the probability $dP(x)$ of finding the classical point mass within a width dx of the position x during a moment dt in time t :

$$dP(x) = \rho^{\text{CM}}(x) dx = \frac{2}{T} dt, \quad \text{or}$$

$$\rho^{\text{CM}}(x) = \frac{2}{v(x)T}, \quad (120)$$

where $v(x) = dx/dt$ is the velocity at position x . See Fig. 4-18, 19 of Bransden/Joachain for a comparison between quantum and classical ρ s for the 1DHO.

Ehrenfest's theorem: The expectation value of a physical observable satisfies a classical equation of motion. The expectation value of an operator $\hat{A}(t)$ in the time-dependent state

$$|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\Psi(0)\rangle \quad \text{is} \quad (121)$$

$$\langle \hat{A}(t) \rangle_t \equiv \langle \Psi(t) | \hat{A}(t) | \Psi(t) \rangle$$

$$= \langle \Psi(0) | e^{i\hat{H}t/\hbar} \hat{A}(t) e^{-i\hat{H}t/\hbar} | \Psi(0) \rangle. \quad (122)$$

A time differentiation of the three time factors generates three terms:

$$\frac{d}{dt} \langle \hat{A}(t) \rangle_t = \left\langle \frac{\partial \hat{A}(t)}{\partial t} \right\rangle_t + \frac{i}{\hbar} \langle [\hat{H}, \hat{A}(t)] \rangle_t. \quad (123)$$

Examples:

$$\frac{d}{dt} \langle \hat{x} \rangle_t = \frac{i}{\hbar} \langle [\hat{H}, \hat{x}] \rangle_t = \frac{1}{m} \langle \hat{p} \rangle_t;$$

$$\frac{d}{dt} \langle \hat{p} \rangle_t = \frac{i}{\hbar} \langle [\hat{H}, \hat{p}] \rangle_t = - \left\langle \frac{d\hat{V}}{d\hat{x}} \right\rangle_t. \quad (124)$$

VI. Quantum mechanics in three spatial dimensions

Different directions in space are independent of one another in quantum mechanics in the sense that

$$[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = [\hat{x}_i, \hat{p}_j] = 0, \quad \text{if } i \neq j. \quad (125)$$

QM problems in three-dimensional space can be solved by using methods of both wave and matrix mechanics.

6.1 Separation of variables in rectangular coordinates:

If a Hamiltonian $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3$ is separable into terms referring to different dimensions in rectangular coordinates, its energy eigenstates can be factorized into the product states $|n = n_1 n_2 n_3\rangle = |n_1\rangle |n_2\rangle |n_3\rangle$, one in each spatial dimension:

$$\hat{H} |n_1 n_2 n_3\rangle = (E_1 + E_2 + E_3) |n_1 n_2 n_3\rangle. \quad (126)$$

The method works for other operators too:

$$\hat{p}^2 |p_1 p_2 p_3\rangle = (p_1^2 + p_2^2 + p_3^2) |p_1 p_2 p_3\rangle. \quad (127)$$

Examples:

- (a) 3-dim HO: $E_n = \hbar\omega(n+3/2)$, $n = n_1 + n_2 + n_3$.
- (b) Free particle: $p^2 = p_1^2 + p_2^2 + p_3^2$ in the state $|p_1 p_2 p_3\rangle$.
- (c) Particle in a box of sides L_i : The discrete momentum spectrum is defined by the quantum numbers $n_i = k_i L_i / \pi = 1, 2, \dots$

6.2 Separation in spherical coordinates:

Kinetic energy: In the spherical coordinates $\mathbf{r} = (r, \theta, \phi)$, $\hat{\mathbf{p}}^2$ separates into a radial part and an angular part:

$$\hat{\mathbf{p}}^2 = \hat{p}_r^2 + \frac{\hat{\mathbf{L}}^2}{r^2},$$

$$\text{where } \hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

$$= \hat{L}_x \mathbf{e}_x + \hat{L}_y \mathbf{e}_y + \hat{L}_z \mathbf{e}_z \quad (128)$$

is the orbital angular momentum operator. Note that the position and momentum operators in a typical term of $\hat{\mathbf{L}}$ such as $\mathbf{e}_x \hat{y} \hat{p}_z$ commute because they refer to different directions in space. However, $\hat{\mathbf{L}}$ is quite a different type of operator from $\hat{\mathbf{r}}$ or $\hat{\mathbf{p}}$, because its components \hat{L}_i do not commute with one another:

$$[\hat{L}_i, \hat{L}_j] = i\hbar \hat{L}_k, \quad (i, j, k \text{ in RH order}). \quad (129)$$

On the other hand,

$$[\hat{\mathbf{L}}^2, \hat{L}_i] = 0, \quad \text{for any component } i. \quad (130)$$

The two commuting operators $\hat{\mathbf{L}}^2, \hat{L}_z$ can be used to define the simultaneous eigenstate $|\ell m\rangle$:

$$\begin{aligned} \hat{\mathbf{L}}^2 |\ell m\rangle &= \hbar^2 \ell(\ell + 1) |\ell m\rangle, \\ \hat{L}_z |\ell m\rangle &= \hbar m |\ell m\rangle, \end{aligned} \quad (131)$$

where ℓ and m are called the orbital (angular momentum) and magnetic quantum numbers, respectively. This eigenstate describes completely an angular state in spherical coordinates. The resulting angular wave function

$$\langle \theta \phi | \ell m \rangle = Y_{\ell m}(\theta, \phi) \quad (132)$$

is called a *spherical harmonic*.

In the position representation, the \hat{L}_z equation can be written as the differential equation

$$\left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) Y_{\ell m}(\theta, \phi) = m Y_{\ell m}(\theta, \phi). \quad (133)$$

The solutions in the variable ϕ are

$$Y_{\ell m}(\theta, \phi) = f(\theta) e^{im\phi}. \quad (134)$$

These solutions are periodic in ϕ with a period of 2π :

$$e^{im(\phi+2\pi)} = e^{im\phi}. \quad (135)$$

Hence m must be an integer ($0, \pm 1, \pm 2, \dots$). It will turn out that ℓ is a nonnegative integer bounded from below by $|m|$.

The kinetic energy operator in spherical coordinates is

$$\hat{T} = \hat{T}_r + \hat{T}_L = \frac{1}{2m} \left(\hat{p}_r^2 + \frac{\hat{\mathbf{L}}^2}{r^2} \right), \quad (136)$$

Central potential: Central potentials are spherically symmetric and depend only on the radial distance from the center of potential (or force):

$$V = V(r) \neq f(\theta, \phi). \quad (137)$$

For central potentials, the Hamiltonian separates in the radial and angular coordinates

$$\hat{H} = (\hat{T}_r + \hat{V}) + \hat{T}_L. \quad (138)$$

As a result, the wave function of definite energy E factorizes as follows:

$$\psi_{E\ell m}(\mathbf{r}) = \langle \mathbf{r} | E \ell m \rangle = R_{E\ell}(r) Y_{\ell m}(\theta, \phi). \quad (139)$$

The radial factor satisfies the Schrödinger equation

$$\begin{aligned} \left\{ \frac{1}{2m} \left[\hat{p}_r^2 + \frac{1}{r^2} \hbar^2 \ell(\ell + 1) \right] + V(r) \right\} R_{E\ell}(r) \\ = E R_{E\ell}(r), \end{aligned} \quad (140)$$

where

$$\begin{aligned} \hat{p}_r^2 &= -\hbar^2 \nabla_r^2 = -\hbar^2 \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right) \\ &= -\hbar^2 \frac{1}{r} \left(\frac{d^2}{dr^2} \right) r. \end{aligned} \quad (141)$$

Note that the wave function $R_{E\ell}(r)$ depends on ℓ as well as the energy eigenvalue E . An energy eigenstate in three-dimensional space has only three state labels.

Laplace equation: of electrostatics is also important in QM because its solutions describe the quantum states of a static or resting free particle ($V = 0, p = 0$ and $E = 0$):

$$\nabla^2 \psi(\mathbf{r}) = 0. \quad (142)$$

The solutions regular at the origin $r = 0$ are the *solid spherical harmonics* (or harmonic polynomials)

$$\mathcal{Y}_{\ell m}(\mathbf{r}) = r^\ell Y_{\ell m}(\theta, \phi). \quad (143)$$

Solutions of the Laplace equations are sometimes called *harmonic functions*.

The solutions in rectangular coordinates are simpler. They are all rectangular polynomials with terms of the form $x^{n_1} y^{n_2} z^{n_3}$ having the same degree $n = n_1 + n_2 + n_3$. All rectangular polynomials

TABLE II: Rectangular polynomials and solid spherical harmonics.

n	Rect. Poly.	Harmonic?	Number	$\mathcal{Y}_{\ell m}$?
0	1	Y	1	\mathcal{Y}_{00}
1	z	Y	3	$\mathcal{Y}_{1m=0}$ $m = \pm 1$
	$x \pm iy$	Y		
2	$2z^2 - x^2 - y^2$	Y	5	$\mathcal{Y}_{2m=0}$ $m = \pm 1$ $m = \pm 2$
	$z(x \pm iy)$	Y		
	$(x \pm iy)^2$	Y		
	$x^2 + y^2 + z^2$	N		
			1	—

can be written in the spherical form with definite ℓ, m :

$$r^n Y_{\ell m}(\theta, \phi) = \begin{cases} \text{harmonic,} & \text{if } \ell = n \\ \text{non-harmonic,} & \text{if } \ell < n \end{cases}, \quad (144)$$

but only those where the power n of r is equal to the degree ℓ of $Y_{\ell m}$ are solutions of the Laplace equation.

Because ∇^2 is simple in rectangular coordinates, the result

$$\nabla^2 x^{n_1} = \frac{d^2}{dx^2} x^{n_1} = n_1(n_1 - 1)x^{n_1-2} \quad (145)$$

can be used to determine if any rectangular polynomial is a harmonic function. *Examples* are given in Table II. Functions with definite m include:

$$\begin{aligned} m = \pm 1: & \quad x \pm iy = r \sin \theta e^{\pm i\phi} \\ m = 0: & \quad z, \quad x^2 + y^2. \end{aligned} \quad (146)$$

All solid spherical harmonics can be built from these two classes of functions.

6.3 Three-dimensional harmonic oscillator:

Rectangular coordinates: The Hamiltonian of the 3DHO is separable in rectangular coordinates:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{1}{2}m\omega^2 \hat{\mathbf{r}}^2 = \hat{H}_1 + \hat{H}_2 + \hat{H}_3. \quad (147)$$

Consequently, its energy eigenstates are factorable:

$$|n_1 n_2 n_3\rangle = \left[\frac{(\hat{a}_1^\dagger)^{n_1}}{\sqrt{n_1!}} \right] \left[\frac{(\hat{a}_2^\dagger)^{n_2}}{\sqrt{n_2!}} \right] \left[\frac{(\hat{a}_3^\dagger)^{n_3}}{\sqrt{n_3!}} \right] |000\rangle. \quad (148)$$

All possible rectangular polynomials made up of the components \hat{a}_i^\dagger of the vector operator $\hat{\mathbf{a}}^\dagger$ can create a 3DHO state. Their energy eigenvalues are

$$\begin{aligned} E_n &= (n + \frac{3}{2})\hbar\omega, \quad \text{where} \\ n &= n_1 + n_2 + n_3 = 0, 1, 2, \dots \end{aligned} \quad (149)$$

Spherical coordinates: The energy eigenstates are

$$|n\ell m\rangle \propto (\hat{\mathbf{a}}^\dagger)^{2\nu} \mathcal{Y}_{\ell=-2\nu, m}(\hat{\mathbf{a}}^\dagger) |000\rangle, \quad \nu = 0, 1, \dots \quad (150)$$

All the states shown in Table II with x replaced by the operator \hat{a}_1^\dagger , etc., are valid 3DHO states. The degeneracy of these states is thus

$$D(n) = \frac{1}{2}(n+1)(n+2) = \sum_{\ell=\text{even or odd}}^n (2\ell+1). \quad (151)$$

6.4 Plane wave in free space:

Three-dimensional plane waves have the product wave functions

$$\begin{aligned} e^{i\mathbf{k}\cdot\mathbf{r}} &= e^{i(k_x x + k_y y + k_z z)} \\ &= \sum_{\ell=0}^{\infty} A_{\ell 0} R_{E\ell}(r) Y_{\ell 0}(\theta, \phi) \\ &= \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) j_\ell(kr) P_\ell(\cos \theta) \end{aligned} \quad (152)$$

where the choice $\mathbf{k} = k\mathbf{e}_3$ makes explicit the axial symmetry of the wave function about the propagation direction \mathbf{e}_k .

The *spherical Bessel* function $j_\ell(\rho = kr)$ that appears is the solution of the radial equation

$$\left[-\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d}{d\rho} \right) + \frac{\ell(\ell+1)}{\rho^2} - 1 \right] j_\ell(\rho) = 0. \quad (153)$$

It has simple properties when $\rho \rightarrow 0$ and ∞ . The *Legendre polynomials* $P_\ell(\cos \theta)$ are those used in electrostatics.

6.5 Hydrogen atom:

Similarity with the Bohr model: In wave mechanics, the energy expectation values will turn out to satisfy the Bohr-model relations

$$\begin{aligned} E &= T + U = \frac{U}{2} = -T, \\ E_n &= \frac{E_1}{n^2}, \\ E_1 &= -\frac{e_G^2}{2a}, \quad T_1 = \frac{\hbar^2}{2ma^2}, \end{aligned} \quad (154)$$

where n is the principal (or Bohr) quantum number, and a is the Bohr radius.

Differences from the Bohr model: The single circular orbit of radius $a_n = n^2 a$ of the Bohr model spreads out into states of quantum numbers n, ℓ, m , with $0 \leq \ell < n$. This result is consistent with the spherical symmetry of the electrostatic attraction between the electron and the proton. The degeneracy of states is then

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell+1) = n^2. \quad (155)$$

Wave functions: are

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi). \quad (156)$$

The radial functions $R_{n\ell}$ are functions of

$$\rho = \kappa r, \quad \text{where} \quad \frac{\hbar^2 \kappa^2}{2m} = -E. \quad (157)$$

Then

$$R_{n\ell}(\rho) = \frac{u_{n\ell}(\rho)}{\rho} = \rho^\ell e^{-\rho} v(\rho) \quad (158)$$

can be written in two other forms with each function satisfying a different differential equation:

$$\nabla_r^2 R_{n\ell}(r) = \left[\frac{\ell(\ell+1)}{r^2} - \left(\frac{2m}{\hbar^2} \right) \frac{e_G^2}{r} + \kappa^2 \right] R_{n\ell},$$

$$u_{n\ell}''(\rho) = \left[\frac{\ell(\ell+1)}{\rho^2} - \frac{\rho_0}{\rho} + 1 \right] u_{n\ell},$$

$$\rho v''(\rho) + 2(\ell+1-\rho)v' + (\rho_0 - 2\ell - 2)v = 0. \quad (159)$$

where $\rho_0 = 2/\kappa a$ and $v'(\rho) = dv(\rho)/d\rho$. All solutions have

$$\rho_0 = 2n, \quad \text{giving} \quad E_n = \frac{E_1}{n^2}, \quad (160)$$

in agreement with the Bohr model.

Polynomials $v_\nu(\rho)$: The factor $v(\rho)$ in Eq.(158) is a polynomial of ρ :

- (a) $v_0(\rho) = 1$ gives solutions with $\ell = n - 1$,
- (b) $v_1(\rho) = \rho - c$ (a constant) gives solutions with $\ell = n - 2$,
- (c) polynomials of degree ν , namely

$$v_\nu(\rho) = \sum_{j=0}^{\nu} c_j \rho^j, \quad (161)$$

give solutions with $\ell = n - 1 - \nu$.

Hydrogen states: The properties of the states of the hydrogen atom are summarized in Table III. The spectroscopy notation used is:

$$[\ell] = s, p, d, f, \dots \quad \text{for} \quad \ell = 0, 1, 2, 3, \dots \quad (162)$$

The spectroscopic symbol for a quantum state is $2s+1[\ell]_j$, giving the spin degeneracy $2s+1$, the orbital angular momentum $[\ell]$ and the total spin quantum number j .

VII. Spin and statistics

The study of orbital angular momentum states leads us to intrinsic spins and quantum statistics.

TABLE III: States of the hydrogen atom. The radial wave functions are expressed in terms of the dimensionless distance $\tilde{r} = r/a$.

n	E_n	ℓ	m	Spect.Symbol	$R_{n\ell}(\tilde{r})$
1	E_1	0	0	1s	$e^{-\tilde{r}}$
2	$E_1/4$	1	$0, \pm 1$	2p	$\tilde{r}e^{-\tilde{r}/2}$
		0	0	2s	$(1 - \tilde{r}/2)e^{-\tilde{r}/2}$
n	E_1/n^2	$\ell_{\max} = n - 1$		$n[\ell_{\max}]$	$\tilde{r}^{\ell_{\max}} e^{-\tilde{r}/n}$
		ℓ		$n[\ell]$	

7.1 Angular momentum:

The orbital angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} = \hat{L}_x \mathbf{e}_x + \hat{L}_y \mathbf{e}_y + \hat{L}_z \mathbf{e}_z \quad (163)$$

is very different from $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ because its components do not commute with one another:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, \quad \text{or} \quad \hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar \hat{\mathbf{L}}. \quad (164)$$

However, every component \hat{L}_i commutes with

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \quad (165)$$

The angular momentum states $|\ell m\rangle$ are the simultaneous eigenstate of the two commuting operators $\hat{\mathbf{L}}^2, \hat{L}_z$:

$$\begin{aligned} \hat{\mathbf{L}}^2 |\ell m\rangle &= \hbar^2 \ell(\ell+1) |\ell m\rangle, \\ \hat{L}_z |\ell m\rangle &= \hbar m |\ell m\rangle, \end{aligned} \quad (166)$$

The nature of these states can be studied by using the

Ladder operators: for angular momentum states

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y. \quad (167)$$

These operators have the structure of

$$x \pm iy = r \sin \theta e^{\pm i\phi} \quad (168)$$

that in wave functions have the magnetic quantum numbers $m = \pm 1$. Hence \hat{L}_\pm can be called the $m = \pm 1$ components of $\hat{\mathbf{L}}$ in spherical coordinates. Operators and states are both matrices, though states are not square matrices. They can be multiplied together. In spherical coordinates, the m value of a product of functions or matrices is the sum of the m values of the individual functions or matrices. Hence we expect that $\hat{L}_\pm |\ell m\rangle$ to be a state of magnetic quantum number $m \pm 1$, respectively.

Before demonstrating this result, let us first note however that the ladder operators, like their constituent rectangular components of \hat{L}_x, \hat{L}_y , commute with $\hat{\mathbf{L}}^2$ itself. Hence they do not change the orbital quantum number ℓ when acting on the state $|\ell m\rangle$. However, they too do not commute with \hat{L}_z :

$$[\hat{L}_z, \hat{L}_\pm] = \pm \hbar \hat{L}_\pm. \quad (169)$$

These commutators can be used to show explicitly that \hat{L}_+ is the step-up operator for m , increasing its value by 1, while the step-down operator \hat{L}_- decreases m by 1:

$$|\phi_\pm\rangle = \hat{L}_\pm |\ell m\rangle = A_{\ell m} |\ell m \pm 1\rangle. \quad (170)$$

$A_{\ell m}$ can be found by calculating the normalization $\langle \phi_\pm | \phi_\pm \rangle$ using

$$\hat{\mathbf{L}}^2 - \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2 = \hat{L}_\mp \hat{L}_\pm \pm \hbar \hat{L}_z. \quad (171)$$

The result is

$$\hat{L}_\pm |\ell m\rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} |\ell m \pm 1\rangle. \quad (172)$$

Possible ℓm values: m^2 is bounded because

$$\langle \hat{L}_z^2 \rangle < \langle \hat{\mathbf{L}}^2 \rangle, \quad \text{or} \quad m^2 < \ell(\ell+1). \quad (173)$$

Hence $m_{\min} \leq m \leq m_{\max}$. From Eq.(172):

$$\begin{aligned} \hat{L}_+ |\ell m_{\max}\rangle &= 0 \quad \Rightarrow \quad m_{\max} = \ell, \\ \hat{L}_- |\ell m_{\min}\rangle &= 0 \quad \Rightarrow \quad m_{\min} = -\ell. \end{aligned} \quad (174)$$

So the total number of steps N on the ladder is

$$m_{\max} - m_{\min} = 2\ell = N - 1. \quad (175)$$

Assuming that ladders with any number of steps exist in nature, one finds

$$\text{Odd } N = 2\ell + 1 \quad \Rightarrow \quad \ell = \frac{N-1}{2} = \text{integer},$$

$$\text{Even } N = 2s + 1 \quad \Rightarrow \quad s = \frac{N-1}{2} = \text{half integer}. \quad (176)$$

The orbital quantum numbers ℓs are integers because they are also the integer degrees of the harmonic polynomials $\mathcal{Y}_{\ell m}$. The half-integer s 's are the spin quantum numbers of an intrinsic spin angular momentum $\hat{\mathbf{S}}$. The word ‘‘spin’’ is also used for any angular momentum.

Angular-momentum representations: $\hat{\mathbf{L}}^2, \hat{L}_z$ and therefore also $\hat{L}_\pm, \hat{L}_x, \hat{L}_y$ are $N \times N$ matrices for those states with N steps in their ladder.

Example: For spin $s = 1/2$, the ladder has only two steps, with spin states ‘‘up’’ and ‘‘down’’. Then the spin operators are 2×2 matrices: $\hat{\mathbf{S}}^2 = (3/4)\hbar^2 \text{diag}(1, 1)$. The **Pauli spin matrices** are the components of $\hat{\boldsymbol{\sigma}} = 2\hat{\mathbf{S}}/\hbar$:

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad (177)$$

7.2 Addition of angular momenta:

Product states: Two angular momentum operators $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are independent if $[\hat{L}_i, \hat{S}_j] = 0$. The simultaneous eigenstates of the commuting operators $\hat{\mathbf{L}}^2, \hat{L}_z, \hat{\mathbf{S}}^2, \hat{S}_z$ are the product states

$$|\ell m_\ell s m_s\rangle = |\ell m_\ell\rangle |s m_s\rangle. \quad (178)$$

They have the degeneracy

$$d(\ell, s) = (2\ell + 1)(2s + 1). \quad (179)$$

Coupled states: Two independent angular momenta $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ can be added to the total angular momentum:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \quad (180)$$

The four operators $\hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{\mathbf{J}}^2, \hat{J}_z$ can be shown to commute among themselves. Hence their simultaneous eigenstates $|\ell s j m\rangle$ exist:

$$\begin{aligned} \hat{\mathbf{L}}^2 |\ell s j m\rangle &= \hbar^2 \ell(\ell+1) |\ell s j m\rangle, \\ \hat{\mathbf{S}}^2 |\ell s j m\rangle &= \hbar^2 s(s+1) |\ell s j m\rangle, \\ \hat{\mathbf{J}}^2 |\ell s j m\rangle &= \hbar^2 j(j+1) |\ell s j m\rangle, \\ \hat{J}_z |\ell s j m\rangle &= \hbar m |\ell s j m\rangle. \end{aligned} \quad (181)$$

Clebsch-Gordan coefficients: The two distinct ways (product or coupled) of specifying the states of two angular momenta are related by a change of representation:

$$\begin{aligned} |\ell s j m\rangle &= \left(\sum_{m_\ell m_s} |\ell m_\ell s m_s\rangle \langle \ell m_\ell s m_s | \right) |\ell s j m\rangle, \\ |\ell m_\ell s m_s\rangle &= \left(\sum_j |\ell s j m\rangle \langle \ell s j m | \right) |\ell m_\ell s m_s\rangle, \end{aligned} \quad (182)$$

where each sum involves only one summation index because $m_\ell + m_s = m$. The transformation (Clebsch-Gordan) coefficients are chosen real, and therefore

$$\langle \ell s j m | \ell m_\ell s m_s \rangle = \langle \ell m_\ell s m_s | \ell s j m \rangle. \quad (183)$$

Examples: Two spin 1/2 states can be coupled to a total spin of $S = 1$ or 0:

$$\begin{aligned} |\tfrac{1}{2} \tfrac{1}{2} S M = 11\rangle &= |\uparrow\uparrow\rangle, \quad |\tfrac{1}{2} \tfrac{1}{2} 1 - 1\rangle = |\downarrow\downarrow\rangle, \\ |\tfrac{1}{2} \tfrac{1}{2} 1 0\rangle &= \frac{1}{\sqrt{2}} |\uparrow\downarrow + \downarrow\uparrow\rangle; \\ |\tfrac{1}{2} \tfrac{1}{2} 0 0\rangle &= \frac{1}{\sqrt{2}} |\uparrow\downarrow - \downarrow\uparrow\rangle, \end{aligned} \quad (184)$$

where \uparrow (\downarrow) denotes the spin up (down) magnetic state of the spin 1/2 system.

Vector model: The length J of the vector sum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ satisfies a *triangle inequality*:

$$|L - S| \leq J \leq L + S, \quad \text{but}$$

$$j_{\min} = |\ell - s| \leq j \leq j_{\max} = \ell + s, \quad (185)$$

for quantum angular momenta involves the quantum numbers.

Construction of total angular momentum states: The j th ladder of states has $2j + 1$ steps. The topmost state $m = \ell + s$ of the longest ladder $j_{\max} = \ell + s$ is simply

$$|\ell s \ell + s \ell + s\rangle = |\ell \ell s s\rangle. \quad (186)$$

Then step down to find the remaining states on the ladder:

$$\begin{aligned} \hat{J}_- |\ell s j m\rangle &= \hbar \sqrt{j(j+1) - m(m-1)} |\ell s j m - 1\rangle \\ &= (\hat{L}_- + \hat{S}_-) \sum_{m_\ell m_s} |\ell m_\ell s m_s\rangle \\ &\quad \times \langle \ell m_\ell s m_s | \ell s j m \rangle, \end{aligned} \quad (187)$$

where the RHS is a sum over two terms involving $\hat{L}_- |\ell m_\ell\rangle$ and $\hat{S}_- |s m_s\rangle$, respectively.

The topmost state of the next ladder with $j = \ell + s - 1$ is the remaining or unconstructed state with $m = \ell + s - 1$. It is constructed by orthonormalization from $|\ell s \ell + s \ell + s - 1\rangle$, using the product representation. By convention, its overall phase is taken to be the Wigner (aka Condon-Shortley) phases. The other states on the ladder are found by stepping down. This construction method works for all the remaining j ladders.

7.3 Identical particles in quantum mechanics:

Spin-statistics theorem: Identical particles of integer (half integer) spins satisfy the Bose-Einstein (Fermi-Dirac) statistics. They are called bosons (fermions).

Two identical particles are indistinguishable in their probability densities

$$\rho(2, 1) = \rho(1, 2), \quad (188)$$

but their wave functions may differ by a negative sign

$$\Psi(2, 1) = \pm \Psi(1, 2) \quad \text{for} \quad \begin{cases} \text{bosons} \\ \text{fermions} \end{cases}. \quad (189)$$

Boson (Fermion) wave functions are symmetric (antisymmetric) in the particle labels.

Examples: If α, β are *single-particle* (s.p.) states:

$$\Psi_{\alpha\beta}(1, 2) \propto [\psi_\alpha(1)\psi_\beta(2) \pm \psi_\alpha(2)\psi_\beta(1)]. \quad (190)$$

TABLE IV: electronic structure of the elements. The quantum numbers of some atomic ground states are also given as the spectroscopic symbol $^{2S+1}[L]_J$.

Z	Element	Spatial Configuration	Ground State
1	H	1s	$^2S_{1/2}$
2	He	(1s) ²	1S_0
3	Li	(He)2s	$^2S_{1/2}$
4	Be	(He)(2s) ²	1S_0
5	B	(He)(2s) ² 2p	$^2P_{1/2}$
6	C	(He)(2s) ² (2p) ²	
7	N	(He)(2s) ² (2p) ³	
8	O	(He)(2s) ² (2p) ⁴	
9	F	(He)(2s) ² (2p) ⁵	$^2P_{3/2}$
10	Ne	(He)(2s) ² (2p) ⁶	1S_0

If $\beta = \alpha$ is the same s.p. state:

$$\begin{aligned} \text{Bosons : } \Psi_{\alpha\alpha}(1, 2) &= \psi_\alpha(1)\psi_\alpha(2) \neq 0, \quad \text{but} \\ \text{Fermions : } \Psi_{\alpha\alpha}(1, 2) &= 0. \end{aligned} \quad (191)$$

These important results are called:

Bose-Einstein condensation: The ground state of a system of identical bosons is one where every boson is in the lowest energy single-particle state.

Pauli exclusion principle: No two identical fermions can populate the same single-particle state.

Many identical particles: The wave function of N identical bosons is symmetric under any permutation of the N particle labels. For identical fermions, the wave function changes sign under an odd permutation of the N particle labels, but remains unchanged under an even permutation.

7.4 The Periodic Table:

Electronic structure of the elements: is summarized in Table IV:

Helium atom: Its two electrons with spins pointing \uparrow and \downarrow can populate the same 1s spatial state. They complete the principal qu. no. $n = 1$ shell. The shell n can accommodate $2n^2$ electrons.

To get the lowest energy, both electrons in the He ground state (GS) occupy the lowest s.p. spatial state $n\ell m = 100$. The total wave function

$$\begin{aligned} \Psi_0(1, 2) &= \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\chi_{SM=00}(1, 2) \\ &= -\Psi_0(2, 1) \end{aligned} \quad (192)$$

must be antisymmetric in the two fermion labels 1 and 2. Hence the spin “function” χ (not a “state”) for the total intrinsic spin must be the antisymmetric function with $S = 0$.

The atomic Hamiltonian

$$\hat{H}(1, 2) = -\frac{Ze_G^2}{r_1} - \frac{Ze_G^2}{r_2} + \frac{e_G^2}{r_{12}} \quad (193)$$

gives the GS energy (with $Z = 2$)

$$E_0(\text{He}) \approx -Z^3 E_R + E_{12} \approx -109 \text{ eV} + 30 \text{ eV}. \quad (194)$$

where $E_R = 13.6 \text{ eV}$ is the Rydberg energy.

Closed subshells: The m_s value of the spin state $|sm_s\rangle$ changes when the quantization axis \mathbf{e}_z changes direction. However, if all m_s states are filled by $2s + 1$ particles, they will remain filled when the arbitrarily chosen direction \mathbf{e}_z changes. Hence the total M_S is 0, and this *unique* state of $2s + 1$ particles has $S = 0$. Similarly, the complete filling of the $2\ell + 1$ states of different m_ℓ gives a *unique* spherical symmetric spatial system of $2\ell + 1$ particles that has $L = M_L = 0$. This is why the ground states of He, Be and Ne are all 1S_0 states.

Spin-orbit interaction: The atomic Hamiltonian contains a relativistic term $A_{LS}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, $A_{LS} > 0$. It gives a negative (attractive) energy of $-(A_{LS}/2)(\ell + 1)$ for the s.p. state with the total angular momentum $j = \ell - 1/2$. For the $j = \ell + 1/2$ state on the other hand, the energy is repulsive, namely $(A_{LS}/2)\ell$. This explains why the B ground state in the spatial $2p$ configuration has the quantum numbers $^2P_{1/2}$ of the lowest-energy single electron state outside the closed $n = 1$ shell and the closed $2s$ subshell.

The F ground state is one electron short of the closed $n = 2$ shell. The lowest energy is obtained by putting the missing electron or *hole* in the higher $j = 3/2$ state to give a $^2P_{3/2}$ ground state, i.e., leaving a higher state unpopulated by populating all the lower-energy states in the $2p$ subshell.

7.5 Free Fermi gas:

Box normalization: For a particle extending over all space, the plane-wave wave functions $e^{i\mathbf{k}\cdot\mathbf{r}}$ are not square-integrable. This feature causes awkwardness including the appearance of Dirac δ -functions. The problem can be circumvented by subdividing space into identical cubes of sides L satisfying a periodic boundary condition (BC). The wave functions in each identical cube can then be normalized.

One-dimensional space: The periodic BC

$$\phi_{k_x}(x + L) = e^{ik_x(x+L)} = \phi_{k_x}(x) = e^{ik_x x} \quad (195)$$

gives the discrete spectrum

$$k_x L = 2\pi n_x, \quad \text{with } n_x = 0, \pm 1, \pm 2, \dots \quad (196)$$

and the normalized wave functions

$$\phi_{k_x}(x) = \frac{1}{\sqrt{L}} e^{ik_x x}. \quad (197)$$

The corresponding states $|n_x\rangle$ can be labeled by the qu. no. n_x . They form a discrete basis for wave functions in the representative 1D box.

Three-dimensional space: The normalized 3D wave functions in the representative cube are

$$\langle \mathbf{r} | \mathbf{n} \rangle = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \text{where } k_i = \frac{2\pi}{L} n_i, \quad (198)$$

and $\mathbf{n} = n_1 n_2 n_3$.

Fermi gas: For identical fermions, each spatial state can be populated at most singly (the spin degeneracy being treated separately). Then \mathbf{n} is called a (vector) occupation number. A free particle of mass m has energy $E_k = \sqrt{(\hbar k)^2 c^2 + m^2 c^4}$. So the lowest energy state of a free Fermi gas of N fermions in the cube is one where the states of lowest k or occupation number $n = |\mathbf{n}|$ are populated. With spatial isotropy (spherical symmetry), the occupation pattern is that of a sphere in \mathbf{n} or \mathbf{k} space of radius $k = k_F$:

$$\begin{aligned} N &= \int dN = \int d^3 \mathbf{n} = \left(\frac{L}{2\pi}\right)^3 \int d^3 \mathbf{k} \\ &= \int_0^{k_F} \left(\frac{dN}{dk}\right) dk = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k_F^3. \end{aligned} \quad (199)$$

Here

$$\frac{dN}{dk} = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 \quad (200)$$

is called the *density of states* in k -space. The radius of the Fermi sphere in k -space

$$k_F = (6\pi^2 \rho_{\#})^{1/3}, \quad \text{where } \rho_{\#} = \frac{N}{L^3}, \quad (201)$$

is called the Fermi momentum. It does not depend on the size of the cube. For electrons with their spin degeneracy $d(s) = 2$, the total electron number is $N_e = 2N$.

The energy per particle in a free Fermi gas is

$$\begin{aligned} \frac{E}{N} &= \langle E_k \rangle_{\text{gas}} = \frac{\int \left(\frac{dN}{dk}\right) E_k dk}{\int \left(\frac{dN}{dk}\right) dk} \\ &= \begin{cases} (3/5)\epsilon_F, & \text{if nonrelativistic;} \\ (3/4)\hbar c k_F, & \text{if very relativistic.} \end{cases} \end{aligned} \quad (202)$$

The nonrelativistic energy

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \quad (203)$$

at the surface $k = k_F$ of the Fermi sphere is called the (NR) Fermi energy.

Chandrasekhar limit: A white dwarf star contains Z protons, Z electrons and $A - Z$ neutrons. The main contributions to its energy are the repulsive kinetic energy of the highly relativistic electron gas and the attractive gravitational potential

energy of its mass M . Both energies are inversely proportional to R , the radius of the star, but they have different M dependences:

$$E_{\text{Tot}} = b \frac{M^{4/3}}{R} - c \frac{M^2}{R} \begin{cases} > 0, & \text{unbound,} \\ = 0, & \text{critical,} \\ < 0, & \text{collapse.} \end{cases} \quad (204)$$

The white dwarf will collapse gravitationally if its mass exceeds the critical mass

$$M_c = \left(\frac{b}{c}\right)^{3/2}. \quad (205)$$

VIII. Approximation methods for time-independent problems

Few problems in quantum mechanics are exactly solvable. We first consider some approximation methods for Hamiltonians that are *time-independent*.

8.1 Time-independent perturbation theory:

2×2 **matrices:** can be diagonalized exactly. The Hermitian matrix

$$H = \begin{pmatrix} 0 & b \\ b & a \end{pmatrix}, \quad (206)$$

where both a and b are real, has the eigenvalues and orthonormal eigenvectors

$$\begin{aligned} E_{1,2} &= \frac{1}{2}(a \mp \Delta E), \\ \Delta E &= \sqrt{a^2 + 4b^2} \approx a + 2\frac{b^2}{a}; \\ \psi_1 &= \begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix}, \quad \psi_2 = \begin{pmatrix} -\sin \theta \\ \cos \theta \end{pmatrix}, \\ \tan \theta &= \frac{E_1}{b} \approx -\frac{b}{a}. \end{aligned} \quad (207)$$

Many problems of physical interest involving only two dominant states can be solved approximately by this method.

Perturbation theory: Let the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$ contains a main part \hat{H}_0 whose energy eigenvalues $E_n^{(0)}$, eigenfunctions ϕ_n or eigenstates $|n\rangle$ are already known. If a complicated but weak perturbation \hat{H}' is now added to the system, the eigenvalue equation

$$(\hat{H}_0 + \lambda \hat{H}')\psi_n = E_n \psi_n \quad (208)$$

can be solved by a systematic expansion in powers of λ that can be set back to its numerical value of 1 at the end of the expansion.

This λ expansion is done in both E_n and ψ_n :

$$\begin{aligned} &(\hat{H}_0 + \lambda \hat{H}') \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \dots \right) \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \dots \right) \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \dots \right). \end{aligned} \quad (209)$$

The equation is solved by equating terms of the same power of λ on the two sides of the equation:

$$\begin{aligned} \lambda^0 : \quad &\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad \Rightarrow \quad \psi_n^{(0)} = \phi_n, \\ \lambda^1 : \quad &E_n^{(1)} = H'_{nn}, \\ &\psi_n^{(1)} = - \sum_{k \neq n} \frac{H'_{kn}}{E_k^{(0)} - E_n^{(0)}} \phi_k, \end{aligned}$$

$$\text{where} \quad H'_{kn} = \langle k | \hat{H}' | n \rangle. \quad (210)$$

8.2 Calculation of $E_n^{(1)}$:

Many perturbations are made up of sums of factorable terms of the type

$$\hat{H}' = Q(r) \hat{A} \quad (211)$$

involving a radial factor $Q(r)$ and an angle-spin factor \hat{A} for a system with intrinsic spin \mathbf{S} . Then

$$\begin{aligned} E_n^{(1)} &= Q_{n\ell} \langle \hat{A} \rangle_\alpha, \\ \text{where} \quad Q_{n\ell} &= \int_0^\infty |R_{n\ell}(r)|^2 Q(r) r^2 dr, \\ \alpha &= \ell m_\ell s m_s \quad \text{or} \quad \ell s j m. \end{aligned} \quad (212)$$

Examples:

$$\begin{aligned} \langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle &= \frac{1}{2} \langle \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \rangle_{\ell s j m}, \\ \langle \hat{L}_z + 2\hat{S}_z \rangle_{\ell m_\ell s m_s} &= (m_\ell + 2m_s) \hbar, \\ \langle \hat{S}_z \rangle_{\ell s j m} &= \frac{\hbar m}{\hbar^2 j(j+1)} \langle \hat{\mathbf{J}} \cdot \hat{\mathbf{S}} \rangle_{\ell s j m}. \end{aligned} \quad (213)$$

8.3 Variational method:

Variational principle: For any wave function ψ :

$$E_\psi = \langle \hat{H} \rangle_\psi \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0(\text{GS}). \quad (214)$$

The approximate wave function ψ gives a higher energy when it contains excited-state components of higher energies.

Variational wave function: is any wave function carrying a number of parameters b that can be varied in order to minimize the energy

$$E(b) = \frac{\langle \psi(b) | \hat{H} | \psi(b) \rangle}{\langle \psi(b) | \psi(b) \rangle}. \quad (215)$$

The energy minimum $E(b_0)$ where $dE(b)/db = 0$ is the best variational estimate because it is closest to the true ground-state (GS) energy E_0 .

He atom: The ee repulsion between the two electrons in the He atom can be eliminated approximately by reducing the actual nuclear charge $Z = 2$ to the effective charge $z \approx 27/16$.

Hartree mean-field screening: In an atom with Z electrons, the mutual ee interactions can be replaced by a mean field experienced by each electron characterized by an effective nuclear charge of

$$z(r) = \begin{cases} Z, & \text{for } r \rightarrow 0 \\ 1, & \text{for } r \rightarrow \infty \end{cases} \quad (216)$$

8.4 WKB approximation:

Since any complex number can be written in the amplitude-phase form $Ae^{i\phi}$, one can look for a solution of the 1D Schrödinger wave equation in this amplitude-phase form. The WKB approximation is a semi-classical result used between the two classical turning points x_1 and x_2 of the potential $V(x)$ where the local wave number

$$k(x) = \sqrt{\frac{2m}{\hbar^2}[E - V(x)]} \quad (217)$$

is real. It is obtained by ignoring the $A''(x) = d^2A(x)/dx^2$ term. Then

$$\begin{aligned} \psi(x) &= A(x)e^{i\phi(x)} \\ &\approx \psi_{WKB}(x) = \frac{C}{\sqrt{k(x)}} e^{\pm i \int_{x_1}^x k(x') dx'}. \end{aligned} \quad (218)$$

WKB quantization: At a turning point where the potential has a finite slope, the wave function can penetrate into the classically forbidden region where the local wave number becomes purely imaginary $k \rightarrow i\kappa$. Under this *analytic continuation*, the amplitude factor becomes complex, $A \propto 1/\sqrt{k} \rightarrow e^{-i\pi/4}/\sqrt{k}$, thereby contributing an additional phase of $-\pi/4$. The resulting WKB-modified Bohr-Sommerfeld quantization condition is

$$\int_{x_1}^{x_2} k(x) dx = \left(n - \frac{m}{4}\right) \pi, \quad n = 1, 2, \dots, \quad (219)$$

where m is the number of turning points where the potential is *not* an ∞ wall. The resulting WKB energies are often quite good. They even agree with the exact energies in the case of the one-dimensional harmonic oscillator potentials.

IX. Approximation methods for time-dependent problems

Time-dependent problems are more complicated partly because one has to keep track of the time evolution of a state, but mostly because the Hamiltonian itself might be time-dependent.

9.1 The time-dependent two-state problem:

is exactly solvable for the time-independent Hamiltonian (206). Let a state be prepared initially as

$$|\psi\rangle \equiv |\Psi(t=0)\rangle = d_1|\psi_1\rangle + d_2|\psi_2\rangle, \quad (220)$$

where $|\psi_i\rangle$ are the time-independent eigenstates of \hat{H} . Then it evolves at time t into

$$\begin{aligned} |\Psi(t)\rangle &= e^{-i\hat{H}t/\hbar}|\psi\rangle = d_1|\Psi_1(t)\rangle + d_2|\Psi_2(t)\rangle \\ &= d_1e^{-iE_1t/\hbar}|\psi_1\rangle + d_2e^{-iE_2t/\hbar}|\psi_2\rangle. \end{aligned} \quad (221)$$

Unperturbed basis: It is often useful to express $|\Psi(t)\rangle$ in terms of the *time-dependent* unperturbed basis states

$$\begin{aligned} |\Phi_1(t)\rangle &= e^{-iE_1^{(0)}t/\hbar} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \\ |\Phi_2(t)\rangle &= e^{-iE_2^{(0)}t/\hbar} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned} \quad (222)$$

of energies $E_1^{(0)} = 0$ and $E_2^{(0)} = a$:

$$|\Psi(t)\rangle = c_1(t)|\Phi_1(t)\rangle + c_2(t)|\Phi_2(t)\rangle. \quad (223)$$

The probabilities $|c_i(t)|^2$ can be found by using the energy eigenstates

$$\psi_1 = \begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix}, \quad \psi_2 = \begin{pmatrix} -\sin \theta \\ \cos \theta \end{pmatrix} \quad (224)$$

in Eq.(221):

$$\begin{aligned} |c_1(t)|^2 &= |d_1 \cos \theta - d_2 e^{-i\Delta\omega t} \sin \theta|^2, \\ |c_2(t)|^2 &= |d_1 \sin \theta + d_2 e^{-i\Delta\omega t} \cos \theta|^2, \end{aligned} \quad (225)$$

where $\Delta\omega = (E_2 - E_1)/\hbar$. These probabilities are in general functions of t . Indeed, their time dependences betray the fact that the ϕ_i are not energy eigenstates, for otherwise they will be stationary states with time-independent probabilities.

The expansion (223) is particularly interesting when the basis states $|\phi_i\rangle$ are themselves physically observable, as happens in

Neutrino oscillations: Neutrinos come in three distinct varieties or “flavors”: ν_e, ν_μ, ν_τ , associated with the electron e , muon μ and tau τ , respectively. Although they are physically distinct from one another, they are not mass eigenstates (energy eigenstates at zero momentum). The mass eigenstates are linear combinations of these neutrino basis states of different flavors. For this reason, the flavor probabilities are not constants of motion, but instead they oscillate in time.

Solar neutrino oscillations: The neutrinos initially produced in the solar interior where masses are converted to energy are $\nu_e = \phi_1$, and not $\nu_\mu = \phi_2$, i.e., $c_2(t=0) = d_1 \sin \theta + d_2 \cos \theta = 0$, or $d_1 = \cos \theta$, $d_2 = -\sin \theta$. Allowing only oscillation into ν_μ for simplicity, the probabilities for finding ν_e and ν_μ at a later time t are

$$\begin{aligned} |c_1(t)|^2 &= 1 - \sin^2 2\theta \sin^2(\Delta\omega t/2), \\ |c_2(t)|^2 &= \sin^2 2\theta \sin^2(\Delta\omega t/2). \end{aligned} \quad (226)$$

The neutrinos may have very small masses, so that

$$E_i \approx p_i c + \frac{m_i^2 c^3}{2p_i}. \quad (227)$$

The the probability for finding ν_e of energy E at a distance $L = ct$ from the Sun is

$$\begin{aligned} |c_1(t)|^2 &= 1 - \sin^2 2\theta \sin^2 [A(\Delta m^2 c^4)L/E]; \\ \Delta m^2 &= |m_1^2 - m_2^2|, \\ A &= \frac{1}{4\hbar c} = 1.27 \text{ GeV}(\text{eV})^{-2}\text{km}^{-1}. \end{aligned} \quad (228)$$

Experimental data for solar neutrinos of energies *broadly* distributed around a mean value of $E = 3 \text{ MeV}$ give

$$(\Delta m^2)c^4 = 7.3 \times 10^{-5} (\text{eV})^2, \quad \tan^2 \theta = 0.41. \quad (229)$$

9.2 Time-dependent perturbation theory:

Expansion in exact eigenstates: Suppose $\hat{H} \neq \hat{H}(t)$, and its energy eigenvalues E_j and eigenstates $|\psi_j\rangle$ are known. Then any arbitrary quantum state at time t can be expanded in terms of these energy eigenstates:

$$|\Psi(t)\rangle = \sum_{j=1}^N d_j |\Psi_j(t)\rangle = \sum_j d_j e^{-iE_j t/\hbar} |\psi_j\rangle. \quad (230)$$

Expansion in basis states: This same state can also be expanded in terms of a known set of basis states $|\Phi_n(t)\rangle = e^{-iE_n^{(0)}t/\hbar} |\phi_n\rangle$ that are eigenstates of a known Hamiltonian \hat{H}_0 of energies $E_n^{(0)}$:

$$|\Psi(t)\rangle = \sum_n c_n(t) |\Phi_n(t)\rangle = \sum_n c_n(t) e^{-iE_n^{(0)}t/\hbar} |\phi_n\rangle \quad (231)$$

It happens occasionally that both $|\psi\rangle$ and $|\phi\rangle$ states are physically observable. Then it is of interest to express one observational probabilities in terms of the other expansion coefficients. For example,

$$|c_n(t)|^2 = \left| \sum_{j=1}^N U_{nj} d_j e^{-iE_j t/\hbar} \right|^2, \quad (232)$$

is a generalization of what is done for neutrino oscillations to higher dimensions. Here U , with

$$U_{nj} = \langle \phi_n | \psi_j \rangle, \quad (233)$$

is an $N \times N$ unitary matrix if both sets of states are normalized. U is then made up of the eigenstates $|\psi_j\rangle$ stored columnwise.

TD perturbation: The expansion (231) can also be used if $\hat{H} = \hat{H}_0 + \hat{H}'$ contains a time-dependent

(TD) perturbation \hat{H}' . Unfortunately, the TD expansion coefficients $c_n(t)$ must be obtained more laboriously by actually solving the TDSchEq

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (\hat{H}_0 + \lambda \hat{H}') |\Psi(t)\rangle. \quad (234)$$

The resulting differential equations (DEs) of motion for $c_k(t)$,

$$i\hbar \dot{c}_b(t) = \lambda \sum_k H'_{bk} e^{i\omega_{bk}t} c_k(t), \quad (235)$$

are a set of coupled first-order DEs that can be solved easily in a PC. Here $\omega_{bk} = (E_b^{(0)} - E_k^{(0)})/\hbar$.

Systematic TD perturbation theory: is concerned with the Taylor expansion in λ (eventually set to 1):

$$c_b(t) = c_b^{(0)}(t) + \lambda c_b^{(1)} + \dots \quad (236)$$

Eq.(235) can then be separated term by term into separate equations for $c_b^{(n)}$:

$$\begin{aligned} \lambda^0 \text{ terms: } & i\hbar \dot{c}_b^{(0)}(t) = 0 \Rightarrow c_b^{(0)}(t) = \text{const}, \\ \lambda^1 \text{ terms: } & i\hbar \dot{c}_b^{(1)}(t) = \sum_k H'_{bk} e^{i\omega_{bk}t} c_k^{(0)}, \dots \end{aligned} \quad (237)$$

These first-order DEs in time can be integrated directly, making it easy to calculate first-order wave functions in TD perturbation theory.

Sinusoidal perturbation: Let the sinusoidal perturbation

$$\hat{H}' = \hat{V} \cos \omega t, \quad 0 \leq t \leq t_0 \quad \text{only}, \quad (238)$$

be turned on for a finite period of time. After the perturbation has ceased, a state initially in $|\phi_a\rangle$ will find itself in the state $|\phi_b\rangle$, $b \neq a$, with the probability

$$\left| c_b^{(1)}(t \geq t_0) \right|^2 \approx \left| \frac{V_{ba}}{2} \right|^2 j_0^2(z) \frac{t_0^2}{\hbar^2}, \quad (239)$$

$$\begin{aligned} \text{where } \quad z &= \frac{1}{2}(\omega_{ba} \pm \omega)t_0, \\ j_0(z) &= \sin(z)/z, \\ \omega_{ba} &= [E_b^{(0)} - E_a^{(0)}]/\hbar. \end{aligned} \quad (240)$$

Thus most of the excitations are close to the two states $|\phi_b\rangle$ with energies $E_b^{(0)} = E_a^{(0)} \pm \hbar\omega$.

Golden rule: The transition rate during the interaction lasting a time t_0 from a state a to a *group of states* b is thus

$$\begin{aligned} W_{ba} &\equiv \frac{1}{t_0} \int_{-\infty}^{\infty} |c_b^{(1)}|^2 \rho_b d(\hbar\omega_{ba}) \\ &\approx \frac{2\pi}{\hbar} \left| \frac{V_{ba}}{2} \right|^2 \rho_b, \end{aligned} \quad (241)$$

where $\rho_b = dN_b/dE_b$ is the density of final states.

Example: The Bohr transition of an atomic electron from a higher atomic state b to a lower state a with the emission of a photon of energy $\hbar\omega = E_b^{(0)} - E_a^{(0)}$ is caused by the electric dipole interaction

$$\hat{H}' = \hat{V} \cos(\omega t). \quad (242)$$

Here $\hat{V} = -\boldsymbol{\epsilon} \cdot \hat{\mathbf{D}} E_0$ is the electric-dipole interaction between the electric dipole operator $\hat{\mathbf{D}} = q\hat{\mathbf{r}}$ of the atomic electron and the electric field $\mathbf{E} = \boldsymbol{\epsilon} E_0$ of the emitted photon. The latter can be obtained from the photon energy density in a cube of side L :

$$\frac{\hbar\omega}{L^3} = \frac{\epsilon_0 E_0^2}{2}, \quad (243)$$

where ϵ_0 is the permittivity of free space. When \hat{H}' is used in the Golden Rule, the resulting transition rate is the Einstein coefficient for spontaneous photon emission by the atom:

$$A = W_{ba} = \frac{4}{3} \left(\frac{\omega^3}{c^3 \hbar} \right) \left(\frac{1}{4\pi\epsilon_0} \right) |\mathbf{D}_{ba}|^2, \quad (244)$$

9.3 Sudden, adiabatic and impulsive perturbations:

In **sudden perturbation**, the Hamiltonian changes suddenly by a *finite* amount to the final value \hat{H}_a . If the change is so sudden that the state $|\psi\rangle$ at $t = 0$ has not changed, the state at times $t > 0$ is just

$$\begin{aligned} |\Psi(t)\rangle &= e^{-i\hat{H}_a t/\hbar} |\psi\rangle \\ &= \sum_n e^{-iE_n^{(a)} t/\hbar} |\phi_n\rangle \langle \phi_n | \psi \rangle \\ &= \sum_n |\Phi_n(t)\rangle \langle \phi_n | \psi \rangle. \end{aligned} \quad (245)$$

Adiabatic perturbation: When a time-dependent Hamiltonian $\hat{H}(t)$ changes very slowly in time, we expect the instantaneous eigenvalues $E_n^{(t)}(t)$ and eigenstates $|\psi_n^{(t)}\rangle$ defined by the eigenvalue equation

$$\hat{H}(t) |\psi_n^{(t)}\rangle = E_n^{(t)}(t) |\psi_n^{(t)}\rangle \quad (246)$$

to give a good approximation. That is

$$E_n(t) \approx E_n^{(t)}(t), \quad (247)$$

a result known as the adiabatic theorem.

If one watches the system for a sufficiently long time, however, sooner or later additional features will appear. They can be described conveniently by using the time-dependent basis $|\psi_k^{(t)}\rangle$:

$$|\Psi(t)\rangle = \sum_k c_k(t) e^{-(i/\hbar) \int_0^t E_k^{(t')}(t') dt'} |\psi_k^{(t)}\rangle. \quad (248)$$

The new features include the appearance of a geometrical phase φ_n^{geo} and of transitions to other states $k \neq n$.

Impulsive perturbation: An impulsive perturbation contains a δ -function in time:

$$\hat{H}'(x, t) = \hat{A}(x) \delta(t). \quad (249)$$

The TDSE can be solved exactly to show that the δ -function makes the state discontinuous at $t = 0$:

$$|\Psi(0_+)\rangle = \left(1 - \frac{\hat{A}}{2i\hbar} \right)^{-1} \left(1 + \frac{\hat{A}}{2i\hbar} \right) |\Psi(0_-)\rangle, \quad (250)$$

X. Applications

In this chapter, we see how quantum problems of great physical interest have been solved exactly or approximately.

10.1 Solving special matrix eigenvalue problems:

Special matrices of arbitrarily large dimensions of great physical interest can sometimes be solved analytically by symmetry considerations.

To begin, it is easy to verify by inspection the eigenvalues and eigenvectors of the Pauli matrix σ_x :

$$\begin{aligned} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} &= \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \\ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} &= - \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \end{aligned} \quad (251)$$

Indeed, three simple rules often go a long way in finding the eigenvectors and eigenvalues of certain Hermitian matrices:

- The vector $\mathbf{v}_1 = (1, 1, \dots, 1)$, where all components are 1, is an eigenvector of a matrix where the matrix elements of each row is a permutation of those of the first row. Its eigenvalue E_1 is just the sum of the matrix elements of any row.
- Eigenvectors of a Hermitian matrix can be made orthogonal to one another.
- The sum of eigenvalues is equal to the trace of the matrix.

Example 1: The vector $\mathbf{v}_1 = (1, 1, 1)$ is an eigenvector of the 3×3 matrix $((0,1,1), (1,0,1), (1,1,0))$, with eigenvalue $E_1 = 2$. The three vectors $\mathbf{v}_2 = (2, -1, -1)$, $\mathbf{v}_3 = (-1, 2, -1)$, $\mathbf{v}_4 = (-1, -1, 2)$ are all orthogonal to \mathbf{v}_1 , but not linearly independent of one another. Each has the eigenvalue -1. The orthogonal eigenvectors can be taken to be \mathbf{v}_1 , \mathbf{v}_2 , and $\mathbf{v}_5 = (\mathbf{v}_3 - \mathbf{v}_4)/3 = (0, 1, -1)$.

Example 2: The vectors \mathbf{v}_1 , \mathbf{v}_2 and \mathbf{v}_5 are also the orthogonal eigenvectors of the Hermitian matrix $((1,1,1),(1,1,1),(1,1,1))$, with the eigenvalues 3, 0, and 0, respectively. This is a special case of the general result that two matrices M_1 and M_2 have common eigenvectors if

$$M_2 = M_1 + aI, \quad (252)$$

where I is the identity matrix. Since the parameter a can be complex, we see that non-Hermitian matrices can also have orthogonal eigenvectors.

Example 3: The arbitrarily large $N \times N$ matrix whose matrix elements are all 1's has one "collective" eigenvector $\mathbf{v}_1 = (1, 1, \dots, 1)$ with eigenvalue N . The remaining eigenvalues are all 0. The orthogonal eigenvectors can be chosen to be $\mathbf{v}_2 = (N-1, -1, -1, \dots, -1)$, $\mathbf{v}_3 = (0, N-2, -1, \dots, -1)$, ..., $\mathbf{v}_N = (0, 0, \dots, 0, 1, -1)$.

BCS theory of superconductivity: can be understood conceptually by using a large dimensional $N \times N$ matrix Hamiltonian with the same small negative matrix element $-\epsilon$ everywhere. All eigenstates have energy 0, except the collective eigenstate $\mathbf{v}_1 = (1, 1, \dots, 1)$ that has energy $\Delta = -\epsilon N$. The energy gap Δ that separates the ground state from the excited states makes it hard for the system to be excited. If the ground state contains current-carrying electrons, then at sufficiently low temperatures (below a certain critical temperature T_c), these electrons cannot lose energy by inelastic collisions with the crystal lattice in the conductor. When this happens, both dissipation and resistivity vanish, and the medium becomes superconducting. (BCS = Bardeen, Cooper and Schrieffer who discovered this fundamental theory of superconductivity.)

10.2 Stark effect in an external electric field:

A charge q moved a distance z against a constant external electric field $\mathbf{E} = \mathcal{E}\mathbf{e}_z$ has the (dipole) interaction energy

$$E' = -q \int \mathbf{E} \cdot d\mathbf{r} = -q\mathcal{E}z. \quad (253)$$

The resulting perturbing Hamiltonian is

$$\hat{H}' = -\mathcal{E}\hat{D}_z, \quad \text{where } \hat{\mathbf{D}} = q\hat{\mathbf{r}} \quad (254)$$

is called the electric dipole operator of the charge. This operator is odd in parity, changing sign when $z \rightarrow -z$. Hence all first-order energies vanish:

$$E_n^{(1)} = \langle n | \hat{H}' | n \rangle = 0. \quad (255)$$

Since $z = r \cos \theta$ is independent of the azimuthal angle ϕ , \hat{D}_z has magnetic quantum number $m = 0$.

Hence \hat{H}' has nonzero matrix elements only between two *opposite-parity* states i, j with the same magnetic quantum number: $m_i = m_j$.

Example: In the $n = 2$ shell of the hydrogen atom, there are four states: $n\ell m = 200; 210, 21 \pm 1$. \hat{H}' connects only the two opposite-parity $m = 0$ states. For these two states alone, it takes the form of a 2×2 matrix $b((01), (1, 0))$ whose eigenstates are

$$E_{1,2} = \mp b: \quad \psi_{1,2} = \frac{1}{\sqrt{2}}(\phi_{200} \pm \phi_{210}). \quad (256)$$

Their energies $E_{1,2}$ thus move away from the undisturbed energy of the two states with $m = \pm 1$ by an amount proportional to b , which is proportional to \mathcal{E} . [The state $|\ell m\rangle$ has parity $(-1)^\ell$.]

10.3 Aharonov-Bohm effect:

Gauge transformation: In classical electromagnetism (EM) the electric and magnetic fields are uniquely defined, but the EM potential (the scalar potential φ and vector potential \mathbf{A}) are not unique. They can change by a gauge transformation

$$\begin{aligned} \mathbf{A} &\rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda, \\ \varphi &\rightarrow \varphi' = \varphi - \frac{\partial\Lambda}{\partial t}, \end{aligned} \quad (257)$$

where Λ is any scalar field, without changing the EM fields

$$\begin{aligned} \mathbf{B} &= \nabla \times \mathbf{A}, \\ \mathbf{E} &= -\nabla\varphi - \frac{\partial\mathbf{A}}{\partial t}. \end{aligned} \quad (258)$$

Relativistic electrodynamics: The basic dynamical variable in classical mechanics is the 4-momentum $(\mathbf{p}, iE/c)$. To add EM, one needs an EM 4-vector. There is a unique qualifying candidate: the EM 4-potential $(\mathbf{A}, i\varphi/c)$. Hence electrodynamics for a particle of mass m and charge q can be built up from the sum $(\mathbf{p} - q\mathbf{A}, i(E - q\varphi)/c)$. This combination transforms like a 4-vector under Lorentz transformations, thus guaranteeing the correct result in different inertial frames. As a result, the EM 4-potential plays a more fundamental role in quantum mechanics than the EM fields.

The energy-momentum relation for relativistic electrodynamics is then

$$(E - q\varphi)^2 = (\mathbf{p} - q\mathbf{A})^2 c^2 + m^2 c^4. \quad (259)$$

One can find from this the nonrelativistic kinetic energy T_{NR} :

$$\begin{aligned} T &\equiv E - mc^2 \\ &\approx T_{NR} = q\varphi + \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2. \end{aligned} \quad (260)$$

Quantum electrodynamics: We are now in a position to quantize the mechanical terms in NR

electrodynamics, leaving the EM potential unquantized for simplicity:

$$\hat{H} = \frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A})^2 + \hat{V} + q\varphi. \quad (261)$$

Aharonov-Bohm phase: The EM interaction resides primarily in the phase (or gauge) of quantum wave functions. For the special case where $\varphi = 0$, this important result can be demonstrated readily by showing that the wave function ψ in the presence of the vector potential \mathbf{A} differs from the wave function ψ' without \mathbf{A} by an \mathbf{A} -dependent phase g :

$$\psi(\mathbf{r}) = e^{ig}\psi'(\mathbf{r}). \quad (262)$$

If true, the phase factor e^{ig} serves the purpose of removing the \mathbf{A} dependence from the Schrödinger equation when moved to the left of a “gauged” factor:

$$\left(\frac{\hbar}{i}\nabla - q\mathbf{A}\right)e^{ig}\psi'(\mathbf{r}) = e^{ig}\left(\frac{\hbar}{i}\nabla\right)\psi'(\mathbf{r}). \quad (263)$$

Since

$$\left(\frac{\hbar}{i}\nabla\right)e^{ig}\psi'(\mathbf{r}) = e^{ig}\left[\hbar(\nabla g) + \frac{\hbar}{i}\nabla\right]\psi'(\mathbf{r}), \quad (264)$$

g has to satisfy the differential equation

$$\hbar\nabla g = q\mathbf{A}, \quad \text{or} \quad \hbar dg = q\mathbf{A} \cdot d\mathbf{r}. \quad (265)$$

Hence

$$g = \frac{q}{\hbar} \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}', \quad (266)$$

where the line integral is in general *path-dependent*. The integral is then said to be *non-integrable*. This non-integrability can be made explicit by integrating around a closed circuit c once and simplifying the result with the help of Stokes’s theorem:

$$\begin{aligned} g &= \frac{q}{\hbar} \oint_c \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}' \\ &= \frac{q}{\hbar} \int_{\mathbf{S}} (\nabla \times \mathbf{A}) \cdot d\mathbf{S} = \frac{q}{\hbar} \Phi, \end{aligned} \quad (267)$$

where the total magnetic flux Φ across the surface \mathbf{S} enclosed by the circuit c depends on the magnetic field $\nabla \times \mathbf{A}$ on and *inside* c . Such a dependence on properties of the system outside the path c shows why quantum mechanics in particular, and waves more generally, describe nonlocal phenomena that are spread out in space.

Magnetic flux quantization: Suppose the path c is located in a region free of any EM field, then the wave function must return to its original value

after one complete circuit. Hence its Aharonov-Bohm phase can only be an integral multiple of 2π :

$$g = 2\pi n = \frac{q\Phi}{\hbar}, \quad \text{or} \quad \Phi = n\Phi_0. \quad (268)$$

As a result, the magnetic flux enclosed by c can only exist in integral multiples of a quantized unit flux $\Phi_0 = h/q$. Experimental measurement determines that $q = -2e$ in superconductors, thus showing that the super current is carried by pairs of electrons, now called Cooper pairs.

Gauge interactions: Other fundamental interactions also work through the phase of quantum wave functions. Hence they are called gauge interactions. Indeed, the information contained in the phase of a wave function is usually more important than that contained in its amplitude. A picture of Snow White can be made to appear in our eye as a coherent wave. One can take the phase information from Snow White’s wave function and use it with the amplitude part of the wave function from a picture of Happy, one of the seven dwarfs. A composite wave like this has been constructed theoretically. Believe it or not, one sees Snow White in the resulting hybrid picture, and not the dwarf.

10.4 Magnetic resonance:

Rabi measured the magnetic moments of atomic states by finding the Zeeman splitting of the energies of different magnetic substates by *resonance matching*. Atomic magnetic moments are traditionally expressed as $g\mu_B$ in units of the Bohr magneton $\mu_B = e\hbar/2m$, the theoretical value g being called the Landé g factor. The Hamiltonian involved is

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad (269)$$

where $\hat{H}_0 = \hat{H}_1 + \hat{H}_{LS} + \hat{H}_2$ contains the usual NR Hamiltonian \hat{H}_1 , the relativistic spin-orbit term \hat{H}_{LS} , and the Zeeman Hamiltonian

$$\begin{aligned} \hat{H}_2 &= -\hat{\mathbf{M}} \cdot \mathbf{B}_z \\ &= \frac{g\mu_B B_z}{\hbar} \hat{J}_z = \omega_0 \hat{J}_z \end{aligned} \quad (270)$$

that gives the splitting between the magnetic substates of the same j . Finally a small oscillatory magnetic field is applied in the x -direction to give a perturbing Hamiltonian

$$\hat{H}' = \omega_x \hat{J}_x \cos(\omega t), \quad \text{where} \quad \hbar\omega_x = g\mu_B B_x. \quad (271)$$

This perturbation causes transitions between the magnetic substates. Any quantum state

$$\begin{aligned} |\Psi(t)\rangle &= \sum_m c_m(t) |\Phi_m(t)\rangle \\ &= \sum_m c_m(t) e^{-i\omega_m t} |\phi_m\rangle, \end{aligned} \quad (272)$$

where $\omega_m = E_m^{(0)}/\hbar$, can be expressed in term of the unperturbed states $|\Phi_m(t)\rangle$. The time-dependent expansion coefficient $c_m(t)$ then satisfies the TD-SchEq

$$i\hbar\dot{c}_m(t) = \sum_k H'_{mk} e^{i\omega_{mk}t} c_k(t), \quad (273)$$

where $\omega_{mk} = \omega_m - \omega_k$.

Example: The problem can be solved approximately for $c_m(t)$ for the atomic $n[\ell]_j = 2p_{1/2}$ configuration that has only two magnetic substates ϕ_{\pm} of energies $E_{\pm}^{(0)} = \pm\hbar\omega_0/2$. For example, if the system is initially in the upper state ($c_+ = 1, c_- = 0$), then the probability of finding the system in the upper and lower states at a later time t are respectively:

$$\begin{aligned} P_{++} &= |c_+|^2 = \cos^2(\omega_R t/2) + \sin^2 \chi \sin^2(\omega_R t/2), \\ P_{-+} &= |c_-|^2 = \cos^2 \chi \sin^2(\omega_R t/2), \quad \text{where} \end{aligned} \quad (274)$$

$$\begin{aligned} \omega_R &= \sqrt{(\Delta\omega)^2 + (\omega_x/2)^2}, \quad \Delta\omega = \omega_0 - \omega, \\ \sin \chi &= \frac{\Delta\omega}{\omega_R}, \quad \cos \chi = \frac{\omega_x/2}{\omega_R}. \end{aligned} \quad (275)$$

Magnetic resonance: As the applied frequency ω passes the Zeeman frequency ω_0 , the minimum population of the ϕ_+ state falls sharply to 0 at ω_0 and then rises sharply back up to ≈ 1 again, thus giving a clear signal for the measurement of ω_0 . The third frequency ω_x controls the period τ of oscillation of the population between the two magnetic substates. At full resonance ($\omega = \omega_0$), one finds $\tau = 4\pi/\omega_x$.

XI. Scattering theory

Information about the dynamical properties of microscopic systems like atoms, nuclei and particles can be obtained by scattering beams of projectiles from targets containing them, as first demonstrated by Rutherford, Geiger and Marsden who elucidated atomic structure by scattering α particles from a gold foil.

11.1 The scattering cross sections:

The differential cross section

$$\frac{d\sigma}{d\Omega} = \frac{1}{L} \frac{d\mathcal{R}}{d\Omega} \quad (276)$$

is the angular distribution $d\mathcal{R}/d\Omega$ of the reaction rate \mathcal{R} per unit luminosity L . L itself is the product IN_T , where I is the *flux* or current density of the incident beam (number of incoming particles per second per cross sectional area of the beam, or \dot{N}_i/a for a beam of uniform cross section a) and N_T is the number of target particles illuminated by this beam. L depends on both beam and target. $d\Omega$

is the differential solid angle in a suitable inertial frame.

Example: Two beams of the same cross sectional area A collide head-on where their paths cross each other. Each beam is made up of bunches of N_i ($i = 1, 2$) particles per bunch. The target can be taken to be one bunch of N_2 particles in beam 2. Then the effective incident flux is $I = fN_1/A$, where f is the frequency of collision between bunches.

Rutherford cross section: For the scattering of α -particles of charge $Z_1 = 2$ from an atomic nucleus of charge Z_2 , Rutherford found from classical mechanics that in the CM frame

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \left(\frac{d}{4}\right)^2 \frac{1}{\sin^4(\theta/2)}, \\ \text{where} \quad d &= \frac{Z_1 Z_2 e_G^2}{T_{CM}}, \end{aligned} \quad (277)$$

is the distance of closest approach (or turning point) for head-on collision at the NR kinetic energy T_{CM} in the CM frame. Note that for backscattering $\theta = \pi$, the Rutherford differential cross section $d^2/16$ gives a direct measurement of the position d of the classical turning point.

Total cross section: is proportional to the total reaction rate:

$$\sigma = \int d\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int \frac{d\mathcal{R}}{L} = \frac{\mathcal{R}}{L}. \quad (278)$$

11.2 Quantum theory of scattering in a nutshell:

Partial-wave expansion: of a plane wave into spherical waves of good angular momentum ℓ around the origin of coordinates has the Rayleigh form:

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\ell=0}^{\infty} i^{\ell} (2\ell+1) P_{\ell}(\cos\theta) j_{\ell}(kr), \\ r \rightarrow \infty &\sum_{\ell=0}^{\infty} i^{\ell} (2\ell+1) P_{\ell}(\cos\theta) \frac{i}{2k} \\ &\times \left[\frac{e^{-i(kr-\ell\pi/2)}}{r} - \frac{e^{i(kr-\ell\pi/2)}}{r} \right] \end{aligned} \quad (279)$$

This is the time-independent wave function of a *stationary* scattering state. The time-dependent wave function carries an additional time factor $e^{-i\omega t}$, where $\omega = \hbar k^2/2m$. The additional time factor shows that the wave function e^{-ikr}/r describes an *ingoing* spherical wave collapsing towards the origin, while the wave function e^{ikr}/r describes an *outgoing* spherical wave expanding out from the origin.

Scattered wave: When a target particle is placed at the origin of coordinates, the radial part j_{ℓ} of the

wave function (279) will be replaced by the function $R_\ell(r)$ from the SchEq with a potential in it. At large distances r , the ingoing waves are still collapsing towards the origin, and therefore do not know if a potential is present there. In elastic scatterings, an outgoing spherical wave has the same normalization as before, and can be changed at most by a phase, here taken to be $2\delta_\ell$, that resides in a phase factor $S_\ell = e^{2i\delta_\ell}$ called an S -matrix element:

$$\begin{aligned} \psi(\mathbf{r}) &\underset{r \rightarrow \infty}{\sim} \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) P_\ell(\cos\theta) \frac{i}{2k} \\ &\times \left[\frac{e^{-i(kr-\ell\pi/2)}}{r} - S_\ell \frac{e^{i(kr-\ell\pi/2)}}{r} \right] \\ &= \psi_{\mathbf{k}}(\mathbf{r}) + \psi_{sc}(\mathbf{r}) \quad \text{where} \end{aligned} \quad (280)$$

$$\begin{aligned} \psi_{sc}(\mathbf{r}) &\underset{r \rightarrow \infty}{\sim} \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) P_\ell(\cos\theta) \\ &\times \left(\frac{S_\ell - 1}{2ik} \right) \frac{e^{i(kr-\ell\pi/2)}}{r} \\ &= f(\theta) \frac{e^{ikr}}{r}. \end{aligned} \quad (281)$$

is the scattered wave function, the additional wave function generated by the potential. Containing only outgoing spherical waves, it can be written asymptotically ($r \rightarrow \infty$) in terms of an angle-dependent quantity called the *scattering amplitude*

$$f(\theta) = \sum_{\ell=0}^{\infty} (2\ell+1) f_\ell P_\ell(\cos\theta),$$

$$\text{where} \quad f_\ell = \frac{S_\ell - 1}{2ik} = \frac{1}{k} e^{i\delta_\ell} \sin \delta_\ell \quad (282)$$

if the scattering is elastic, meaning that the phase shift δ_ℓ is real.

Flux: or probability current density is

$$\mathbf{j} = \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*) \approx \mathbf{j}_{\mathbf{k}} + \mathbf{j}_{sc}, \quad (283)$$

where $\mathbf{j}_{\mathbf{k}} = \hbar \mathbf{k} / m$ is the flux of the plane wave, and

$$\mathbf{j}_{sc} = \frac{\hbar k}{m} \mathbf{e}_{\mathbf{r}} \frac{|f(\theta)|^2}{r^2} \quad (284)$$

is the flux of the scattered wave at large distances.

Differential cross section: A detector of area $dA = r^2 d\Omega$ then measures the differential cross section

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{1}{L_{\mathbf{k}}} \frac{d\mathcal{R}}{d\Omega} = \frac{1}{\hbar k / m} (\mathbf{j}_{sc} \cdot \mathbf{e}_{\mathbf{r}}) \frac{dA}{d\Omega} \\ &= |f(\theta)|^2. \end{aligned} \quad (285)$$

Total cross section: is the result integrated over the solid angle $d\Omega$:

$$\begin{aligned} \sigma_{\text{tot}} &= \int \left(\frac{d\sigma}{d\Omega} \right) d\Omega = \int f^*(\theta) f(\theta) d\Omega \\ &= \sum_{\ell} \sigma_{\text{tot},\ell}, \end{aligned} \quad (286)$$

where the two sums over ℓ , one from each f , has been simplified to only one sum by using the orthogonality relation for Legendre polynomials

$$\int_{-1}^1 P_\ell(\cos\theta) P_{\ell'}(\cos\theta) d\Omega = \frac{4\pi}{2\ell+1} \delta_{\ell\ell'}, \quad \text{and} \quad (287)$$

$$\sigma_{\text{tot},\ell} = \frac{4\pi}{k^2} (2\ell+1) \sin^2 \delta_\ell. \quad (288)$$

Optical theorem: If δ_ℓ is real, one finds that

$$\begin{aligned} \text{Im} f(\theta=0) &= \sum_{\ell} (2\ell+1) \text{Im} f_\ell = \sum_{\ell} (2\ell+1) \frac{\sin^2 \delta_\ell}{k} \\ &= \frac{k}{4\pi} \sigma_{\text{tot}}. \end{aligned} \quad (289)$$

This theorem holds even when the phase shift $\delta_\ell = \alpha_\ell + i\beta_\ell$ becomes complex.

11.3 Breit-Wigner resonance:

The partial-wave total cross section $\sigma_\ell = \sigma_{\ell, \text{max}} \sin^2 \theta_\ell$ reaches a maximum value of $\sigma_{\ell, \text{max}} = (4\pi/k^2)(2\ell+1)$ whenever $\delta_\ell(k) = \pi/2$. This maximum value is called the *unitarity limit*.

If $\delta_\ell(E)$ rises through $\delta_\ell(E = E_R) = \pi/2$ sufficiently rapidly, a Taylor expansion about $E = E_R$ needs to be taken only to the terms

$$\delta_\ell \approx \frac{\pi}{2} + (E - E_R) \left. \frac{d\delta_\ell}{dE} \right|_{E_R}. \quad (290)$$

$$\text{Then} \quad \tan \delta_\ell \approx -\frac{\Gamma/2}{E - E_R}, \quad \text{where}$$

$$\frac{\Gamma}{2} = \frac{1}{(d\delta_\ell/dE)_{E_R}} > 0. \quad (291)$$

Resonance: In the neighborhood of a resonance, the partial-wave total cross section has the simple E -dependence:

$$\begin{aligned} \sigma_\ell &= \sigma_{\ell, \text{max}} \frac{\tan^2 \delta_\ell}{1 + \tan^2 \delta_\ell} \\ &= \sigma_{\ell, \text{max}} \frac{(\Gamma/2)^2}{(E - E_R)^2 + (\Gamma/2)^2}. \end{aligned} \quad (292)$$

This function has a sharp maximum at $E = E_R$ and falls rapidly to half its maximal value at $E - E_R = \pm \Gamma/2$. Hence Γ is called the *resonance width* (or full width at half maximum, FWHM).

Decaying state: The partial-wave scattering amplitude near resonance has the simple form

$$\begin{aligned} f_\ell &= \frac{1}{k} e^{i\delta_\ell} \sin \delta_\ell = \frac{1}{k} \frac{1}{\cot \delta_\ell - i} \\ &= \frac{1}{k} \frac{-\Gamma/2}{(E - E_R) + i\Gamma/2}. \end{aligned} \quad (293)$$

At the complex energy $E = E_R - i\Gamma/2$, the time-dependent probability density decays exponentially

$$\begin{aligned} |\Psi(\mathbf{r}, t)|^2 &= |\psi(\mathbf{r}) e^{-i(E_R - i\Gamma/2)t/\hbar}|^2 \\ &= |\psi|^2 e^{-\Gamma t/\hbar}. \end{aligned} \quad (294)$$

11.4 Yukawa's theory of interactions:

Yukawa showed in 1935 that both the Coulomb interaction mediated by the exchange of massless photons between charges, and the strong or nuclear interaction mediated by the exchange of massive bosons called mesons, can be derived from quantum mechanics.

Klein-Gordon equation: The Einstein energy-momentum relation $E^2 = \mathbf{p}^2 c^2 + m^2 c^4$ can be quantized into the Klein-Gordon equation in free space:

$$\hat{H}^2 \Phi(\mathbf{r}, t) = (\hat{\mathbf{p}}^2 c^2 + m^2 c^4) \Phi(\mathbf{r}, t), \quad (295)$$

where $\hat{H} = i\hbar\partial/\partial t$ and $\hat{\mathbf{p}} = (\hbar/i)\nabla$. The resulting wave functions Φ oscillates in time as $e^{-iEt/\hbar}$. These free-space solutions are said to be on the *energy shell*, because the E - \mathbf{p} relation is satisfied on a spherical shell in \mathbf{p} -space.

Static solutions of the KG equation: The KG equation does not have time-independent solutions in free space, because these solutions have $E = 0$ and therefore cannot satisfy Einstein's E - \mathbf{p} relation. Yukawa showed that there are static (hence energy-nonconserving) solutions near a point charge q located at the origin that satisfy the inhomogeneous DE:

$$(\hat{\mathbf{p}}^2 c^2 + m^2 c^4) \phi(\mathbf{r}) = 4\pi(\hbar c)^2 q \delta(\mathbf{r}), \quad (296)$$

For $m = 0$, the Yukawa equation simplifies to the Poisson equation

$$\nabla^2 \phi(\mathbf{r}) = -4\pi q \delta(\mathbf{r}). \quad (297)$$

One can show with the help of Gauss's theorem (or Gauss's law in electrostatics) that the resulting static wave function of a massless photon around a point charge that vanishes at $r = \infty$ is

$$\phi(\mathbf{r}) = \frac{q}{r}. \quad (298)$$

This is just the Coulomb potential around the point charge q (in Gaussian units, or $q = q_{SI}/\sqrt{4\pi\epsilon_0}$).

The photon in question cannot propagate freely. It can only exist momentarily around its point source (the point charge), and is then said to be a *virtual* photon. In Feynman's diagrammatic language, the Coulomb interaction arises from the emission of a virtual photon by a source (the q here) and its absorption by a test charge at distance r from it, or vice versa.

The virtual particle in Yukawa's theory of interactions is a boson, otherwise it cannot be emitted because of the conservation of fermion number. A virtual boson that is massive satisfies the Yukawa equation

$$(\nabla^2 - \mu^2)\phi(\mathbf{r}) = -4\pi g \delta(\mathbf{r}), \quad (299)$$

where the unit of charge is now denoted g , and $\mu = mc/\hbar$ is the inverse reduced Compton wavelength. The solution of this DE that vanishes at $r = \infty$ can be shown to be the Yukawa potential

$$\phi(\mathbf{r}) = \frac{g}{r} e^{-\mu r}. \quad (300)$$

Nuclear forces: were known in 1937 to have a range of $1/\mu \approx 1.4$ fm. (fm = 10^{-15} m.) This fact allowed Yukawa to predict that these forces are caused by the exchange of bosons of mass $m = \mu\hbar/c \approx 140$ MeV/ c^2 . Such strongly interacting bosons, now called π mesons or pions, were discovered in 1947.

11.5 Scattering at low energies:

Impact parameter: In classical mechanics, a particle impacting at a transverse distance b (the impact parameter) from the center of a square-well potential of range R will not "see" the potential if $b > R$. If the incident momentum in the center-of-mass frame is \mathbf{p} , the interaction vanishes when the angular momentum $\ell = \mathbf{r} \times \mathbf{p}$ exceeds the value $\ell_{\max} = \text{Max}(kR/\hbar)$, where $\text{Max}(z)$ is the largest integer in z .

The wave spreading in quantum mechanics makes the connection between ℓ and b less sharply defined, but it remains true that the scattering phase shift δ_ℓ vanishes sharply when $\ell > \ell_{\max}$. Consequently,

$$f(\theta) \approx \sum_{\ell=0}^{\ell_{\max}} (2\ell+1) f_\ell P_\ell(\cos\theta), \quad (301)$$

Hence at sufficiently low energies, the S-wave ($\ell = 0$) term dominates:

$$\sigma_{\text{tot}} \approx 4\pi \frac{\sin^2 \delta_0}{k^2} = \frac{4\pi}{k^2 + k^2 \cot^2 \delta_0}. \quad (302)$$

The fact that the leading Taylor term for $\ell = 0$ is independent of k comes from the properties of the scattering wave function.

Effective-range expansion:

$$k \cot \delta_0 = -\frac{1}{a(k)} = -\frac{1}{a_0} + \frac{1}{2}r_0 k^2 + \dots, \quad (303)$$

where a_0 is called the scattering length and r_0 is called the effective range.

11.6 Phase shifts for finite-range potentials:

Radial wave function: The wave function in the presence of a potential V is

$$\psi(\mathbf{r}) = \sum_{\ell=0}^{\infty} i^\ell (2\ell + 1) P_\ell(\cos \theta) \frac{u_\ell(r)}{kr}, \quad (304)$$

where the radial wave function u_ℓ satisfies the radial wave equation

$$\frac{d^2 u_\ell}{dr^2} + \frac{2\mu}{\hbar^2} (E - V) u_\ell - \frac{\ell(\ell + 1)}{r^2} u_\ell = 0. \quad (305)$$

where μ is the reduced mass in the center-of-mass system.

Attractive S-wave square-well potential: For $\ell = 0$ in an attractive square-well potential of depth V_0 , the radial wave equation is

$$\begin{aligned} \text{For } r < R: \quad & \frac{d^2 u_{\text{in}}}{dr^2} + \kappa^2 u_{\text{in}} = 0, \\ & u_{\text{in}} = \sin(\kappa r); \end{aligned} \quad (306)$$

$$\begin{aligned} \text{For } r > R: \quad & \frac{d^2 u_{\text{out}}}{dr^2} + k^2 u_{\text{out}} = 0, \\ & u_{\text{out}} = \sin(kr + \delta_0); \end{aligned} \quad (307)$$

$$k^2 = \frac{2mE}{\hbar^2}, \quad \kappa_0^2 = \frac{2mV_0}{\hbar^2}, \quad \kappa^2 = k^2 + \kappa_0^2. \quad (308)$$

The phase shift δ_0 is determined by matching the inside and outside logarithmic derivatives $\mathcal{L}_{\text{in}} = \mathcal{L}_{\text{out}}$ at $r = R$, where $\mathcal{L} = (du/dr)/u$, to give

$$\begin{aligned} \frac{1}{\kappa} \tan \kappa R &= \frac{1}{k} \tan(kR + \delta_0), \quad \text{or} \\ \delta_0 &= \tan^{-1} \left(\frac{k}{\kappa} \tan \kappa R \right) - kR. \end{aligned} \quad (309)$$

Levinson's theorem: If there are m bound states inside the potential,

$$\delta_\ell(k = 0) = m\pi, \quad (310)$$

except for an S-wave bound state at $E = 0$, which contributes only $\pi/2$, half of the normal contribution.

11.7 Born approximation for two-particle scatterings:

The Born (or first Born) approximation for the scattering of two particles is a first-order TDPT that can be obtained from the

Golden rule: A weak two-body interaction

$$\hat{H}' = \hat{V} e^{-i\omega t} + \hat{V}^\dagger e^{i\omega t} \quad (311)$$

causes the scattering from an initial two-particle state i to a final two-particle state f within the solid angle $d^2\Omega_f$ around the final relative momentum \mathbf{k}_f . The transition rate is given, in first-order TDPT, by the Golden Rule:

$$\begin{aligned} \frac{dw_{fi}}{d\Omega} &= \frac{2\pi}{\hbar} |\langle f | \hat{V} | i \rangle|^2 \frac{\rho_f(E)}{4\pi} \\ &= \frac{\mu_f (\hbar k_f)}{(2\pi)^2 \hbar^4} \left(L^3 |\langle f | \hat{V} | i \rangle|^2 \right). \end{aligned} \quad (312)$$

Here μ_j, k_j are the reduced mass and relative momentum, respectively, in the state $j (= i, f)$ of the two-body system in a cube of side L , and the density of final state factor is

$$\frac{\rho_f(E)}{4\pi} = \left(\frac{L}{2\pi} \right)^3 \frac{k^2 dk}{dE}. \quad (313)$$

The scattering is elastic if $k_f = k_i$, and inelastic if k_f, k_i .

The resulting **differential scattering cross section**

$$\frac{d\sigma_{fi}}{d\Omega} \equiv \frac{1}{J_{\text{inc}}} \left(\frac{dw_{fi}}{d\Omega} \right) \quad (314)$$

is just the transition rate per unit incident flux (or current density), which is

$$J_{\text{inc}} = \frac{v_i}{L^3} = \frac{\hbar k_i}{\mu_i L^3} \quad (315)$$

in a cube of side L . Note that J_{inc} has the expected dimension of $\text{m}^{-2}\text{s}^{-1}$. The final result for the Born approximation can be written compactly as

$$\frac{d\sigma_{fi}}{d\Omega_f} = \frac{\mu_i \mu_f}{(2\pi)^2 \hbar^4} \left(\frac{k_f}{k_i} \right) |\tilde{V}(q)|^2, \quad (316)$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, and

$$\tilde{V}(q) \equiv L^3 \langle f | \hat{V} | i \rangle = \int e^{-i\mathbf{q}\cdot\mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} \quad (317)$$

is obtained by using the plane-wave wave functions in the relative coordinate \mathbf{r} normalized to one particle in a cube of side L :

$$\langle \mathbf{r} | i \rangle = \frac{1}{L^{3/2}} e^{i\mathbf{k}_i \cdot \mathbf{r}}, \quad \langle f | \mathbf{r} \rangle = \frac{1}{L^{3/2}} e^{-i\mathbf{k}_f \cdot \mathbf{r}}. \quad (318)$$

Thus the cross section in the Born approximation can be calculated directly from the Fourier transform $\tilde{V}(\mathbf{q})$ of the interaction potential $V(\mathbf{r})$.

Examples of $\tilde{V}(\mathbf{q})$ are those from the δ -shell and the Yukawa potentials:

$$\begin{aligned} V(r) = A_0\delta(r - R) &\Rightarrow \tilde{V}(q) = A_0\frac{4\pi R}{q}\sin(qR); \\ V(r) \propto \frac{e^{-\alpha r}}{r} &\Rightarrow \tilde{V}(q) \propto \frac{4\pi}{\alpha^2 + q^2}. \end{aligned} \quad (319)$$