Quantum Mechanics

Nicholas Lyu

May 27, 2024

These notes are for the fall 2023 iteration of Harvard's second-semester undergraduate quantum mechanics, Physics 143b, taught by Sonia Paban. The course includes a brief introduction to path integrals, followed by perturbation theory applied to hydrogen energy levels, then quantum dynamics, WKB approximation, scattering, and density operators.

These notes deviate from the course material by

- a section on symmetry and conservation laws, adapted from Griffiths.
- an interaction-picture explanation of time-dependent perturbation theory, adapted from MIT's online lecture notes.
- the adiabatic theorem from Weinberg's *Lectures on Quantum Mechanics*.
- does not include density operators.

A note on notations: $d/dx, \partial/\partial x$ are abbreviated d_x, ∂_x. Summation over a free index which does not appear on the left hand side are occasionally omitted to reduce clutter. Function arguments are occasionally integerchanged with subscripts to reduce clutter.

Contents

1 Path Integrals

1.1 Gaussian Integrals

A single-variable Gaussian integral may be evaluated by a change into spherical coordinates:

$$G(a) = \int_{-\infty}^{\infty} dx \, \exp(-ax^2) = \sqrt{\frac{\pi}{a}} \tag{1.1}$$

More generally, we may consider a general Gaussian integral for a positive definite $n \times n$ matrix A and offset ω.

$$\int_{-\infty}^{\infty} (dx_1 \cdots dx_n) \, \exp\left(-x^T A x + \omega^T x\right) = \exp\left(\frac{1}{4}\omega^T A^{-1} \omega\right) \sqrt{\frac{\pi^N}{\det A}} \tag{1.2}$$

The integral is evaluated by diagonalizing A and completing the square, as below:

$$x^T A x - \omega^T x = \left(x - \frac{A^{-1}\omega}{2}\right)^T A \left(x - \frac{A^{-1}\omega}{2}\right) - \frac{1}{4}\omega^T A^{-1} \omega$$

We may also consider integrating imaginary, oscillating exponentials:

- Put in by hand a convergence factor $\exp(-\delta x^2)$, then take $\delta \to 0$
- Perform the change of variables $x' = \sqrt{-i\alpha}x$

The following integrals from Wikipedia are helpful:

$$\begin{aligned}
\int_{-\infty}^{\infty} d^n x \, \exp\left(-\frac{1}{2}x^T A x + \omega^T x\right) &= \sqrt{\frac{(2\pi)^n}{\det A}} \exp\left(\frac{1}{2}\omega^T A^{-1}\omega\right) \\
\int_{-\infty}^{\infty} d^n x \, \exp\left(-\frac{1}{2}x^T A x + i\omega^T x\right) &= \sqrt{\frac{(2\pi)^n}{\det A}} \exp\left(-\frac{1}{2}\omega^T A^{-1}\omega\right) \\
\int_{-\infty}^{\infty} d^n x \, \exp\left(-\frac{i}{2}x^T A x + i\omega^T x\right) &= \sqrt{\frac{(2\pi i)^n}{\det A}} \exp\left(-\frac{i}{2}\omega^T A^{-1}\omega\right)
\end{aligned} \tag{1.3}$$

1.2 Propagator

Recall that in Lagrangian mechanics, the Lagrangian $\mathcal{L}(q, \dot{q}, t)$ is usually associated with $T - V$. Based on the Lagrangian, one may define the action functional as below, where t_1, t_2 may be omitted if clear from context.

$$S_{t_1,t_2}[q] = \int_{t_a}^{t_b} \mathcal{L}(q(t), \dot{q}(t), t)$$

Example 1.1 (*Classical free particle*). Recall a free point particle with

$$\mathcal{L} = m\dot{x}^2/2$$

The Lagrangian e.o.m and the resulting classical path are

$$m\ddot{x} = 0 \implies x_{\text{cl}}(t) = \frac{x_b - x_a}{t_b - t_a}(x - t_a) + x_a$$

The corresponding classical action is

$$S[x_{\text{cl}}] = \int_{t_a}^{t_b} dt\, \frac{1}{2} m \left(\frac{x_b - x_a}{t_b - t_a}\right)^2 = \frac{m(x_b - x_a)^2}{2(t_b - t_a)}$$

The theorem below shows how the path integral formulation quantum mechanics is based classical Lagrangian mechanics. The following theorem demonstrates its relation to the Hamiltonian formulation of quantum mechanics.

Definition 1.1 (*propagator*). Given the Lagrangian for a system, its **propagator**, or **kernel**, is the following integral over all paths q such that $q(t_a) = x_a, q(t_b) = x_b$

$$K(x_b, t_b, x_a, t_a) = \int D[q]\, \exp\left(\frac{i}{\hbar} S[q]\right) = \int D[q]\, \exp\left(\frac{i}{\hbar} \int_{t_a}^{t_b} dt\, \mathcal{L}(q(t), \dot{q}(t), t)\right) \tag{1.4}$$

Theorem 1.1 (*path integral formulation*). The kernel satisfies

$$K(x_b, t_b, x_a, t_a) = \langle x_b, t_b | x_a, t_a \rangle$$

In other words, the Hamiltonian and Lagrangian formulation of quantum mechanics are compatible in the following way (assuming a time-indepent Hamiltonian)

$$\int D[q]\, \exp\left(\frac{i}{\hbar} \int_{t_a}^{t_b} dt\, \mathcal{L}(q(t), \dot{q}(t), t)\right) = \left\langle x_b \left| \exp\left(-\frac{i}{\hbar}(t_b - t_a) H\right) \right| x_a \right\rangle \tag{1.5}$$

Remark 1.1. Several remarks are in order:

- Every path q contributes a factor with absolute value 1: contributions only differ in phase. Conceptually, the first-order endpoint-preserving variations vanish at the classical path (which satifies the Lagrangian equations of motion), resulting in in-phase contributions, while those paths far from the classical one are easily out of phase.
- The destructive interference far away from the classical path relies on the large value of $\Delta S/\hbar$. This qualifies how quantum mechanics degenerates to classical mechanics in the limit $\hbar \to 0$, or when action scales are large when compared to $\hbar$, as in the case for most macroscopic systems.
- Should we choose to describe our system as an evolving field $\Psi(x, t)$ instead of a path $q(t)$, the path-integral formulation generalizes in a straightforward way:

$$\int D[\Psi] \exp\left(\frac{i}{\hbar} \int d^4x\, \mathcal{L}(\Psi, \dot{\Psi}, t)\right)$$

- We're assuming spinless particles. There are subtle ties to commutativity here.
- The position basis in $K(b,a) = \langle x_b | U(t_b - t_a) | x_a \rangle$ is special. We cannot use the Lagrangian should we choose a different basis for the propagator.

The propagator K determines the dynamics. We take the basis $|x,t\rangle$ and view the system state as defined on the whole space-time, with time evolution via varying t:

$$\begin{aligned} \psi(x,t) = \langle \psi | x,t \rangle &= \langle \psi | \sum\nolimits_{x'} \langle x,t | x',t_0 \rangle | x',t_0 \rangle \\ &= \sum\nolimits_{x'} K(x,t,x',t_0) \langle \psi | x',t_0 \rangle \\ &= \sum\nolimits_{x'} K(x,t,x',t_0) \psi(x',t_0) \end{aligned} \tag{1.6}$$

Alternatively, assuming a time-invariant Hamiltonian and an energy basis $\{|n,t\rangle\}$

$$\begin{aligned} K(x,t,x',t') &= \langle x,t | x',t' \rangle \\ &= \sum\nolimits_n \langle x,t' | n \rangle \langle n | x,t \rangle \\ &= \sum\nolimits_n \exp\left(-\frac{i}{\hbar} E_n (t-t') \right) \psi_n^*(x) \psi_n(x') \end{aligned} \tag{1.7}$$

The propagator satisfies the Schrodinger equation: fixing x', t' (recall equation 1.5)

$$i\hbar \partial_t K(x,t,x',t') = H_t K(x,t,x',t') \tag{1.8}$$

Remark 1.2. The dynamics of the system is captured by a one-parameter family of unitaries U_t, obtained by integrating the exponential of the Hamiltonian (or computing the Schrodinger equation), which send initial states $|\psi_0\rangle$ to $|\psi_t\rangle$. The propagator is simply the representation of this unitary in the position basis. To see why, recall the action of a linear operator A with matrix representation (A_{ij}) in a finite-dimensional Hilbert space

$$(Av)_i = \sum_j A_{ij} v_j$$

The matrix element representation A_{ij} may be viewed instead as a map $A(i,j) = A_{ij}$ and the states similar maps $v(j) = v_j$.

$$(Av)(i) = \sum_j A(i,j) v(j)$$

The direct analogue of this in infinite-dimensional Hilbert space is to replace summing over the discrete index j with integration over a continuous variable x

$$\psi_t(x) = (U_t \, \psi_0)(x) = \int K_{0 \to t}(x,x') \psi_0(x') \, dx'$$

1.3 Integration over paths

Consider the following method of parameterizing all possible paths $(x_a, t_a) \to (x_b, t_b)$. Discretize time by units of ϵ: let $t_0 = t_a, t_N = t_b, N\epsilon = t_b - t_a$, and $t_{j+1} = t_j + \epsilon$.

$$K(b,a) \sim \lim_{\epsilon \to 0, N\epsilon = \Delta t} \int \cdots \int (dx_1 \cdots dx_{N-1}) \exp\left(\frac{i}{\hbar} S[q(x_1 \cdots x_{N-1})]\right) \tag{1.9}$$

Note that x_0, x_N are fixed, so they are not variables to be integrated. Under this parameterization, the values $\{x_1 \cdots x_{N-1}\}$ parameterizes a path q under the following substitution:

$$S[q] = \int_{t_a}^{t_b} \mathcal{L}(q, \dot{q}, t)\, dt = \sum_{j=0}^{N-1} \mathcal{L}\left(x_i, \frac{x_{i+1} - x_i}{\epsilon}, t\right) \tag{1.10}$$

1.4 Separable Lagrangian

Let q_{cl} denote the classical path satisfying Euler-Lagrange equations. Consider the following quantity for an endpoint-preserving perturbation η and time-invariant Lagrangian:

$$\begin{aligned} \mathcal{L}(q_{\text{cl}} + \epsilon\eta, \dot{q}_{\text{cl}} + \epsilon\dot{\eta}) &= \sum_{n=1}^{\infty} \frac{1}{n!} \left[\epsilon \left(\eta \partial_q + \dot{\eta} \partial_{\dot{q}}\right)\right]^n \mathcal{L}(q_{\text{cl}}, \dot{q}_{\text{cl}}, t) \\ &= \left[1 + \epsilon(\eta\partial_q + \dot{\eta}\partial_{\dot{q}}) + \epsilon^2 \left(\eta^2 \partial_q^2 + 2(\eta\partial_q)(\dot{\eta} d_{\dot{q}}) + \dot{\eta}^2 \partial_{\dot{q}}^2\right) + O(\epsilon^3)\right] \mathcal{L}_{\text{cl}} \end{aligned} \tag{1.11}$$

The zeroth-order term denotes the classical action, the first-order term vanishes by the Euler-Lagrange equations, and the second-order terms preserve the quadratic coefficients.

Theorem 1.2 (*quadratic Lagrangians are separable*). For quadratic Lagrangians of the form

$$\mathcal{L}(q, \dot{q}, t) = Aq^2 + B\dot{q}^2$$

Both the Lagrangian and the action separate linearly by classical paths

$$\begin{aligned} \mathcal{L}(q_{\text{cl}} + \eta, \dot{q}_{\text{cl}} + \dot{\eta}) &= \mathcal{L}(q_{\text{cl}}, \dot{q}_{\text{cl}}) + \mathcal{L}(\eta, \dot{\eta}) \\ S[q_{\text{cl}} + \eta] &= S[q_{\text{cl}}] + S[\eta] \end{aligned} \tag{1.12}$$

Theorem 1.3 (*propagator for separable Lagrangian*). When the Lagrangian separates, the propagator in equation 1.4 takes the following form. The path integral over η is agnostic towards x_a, x_b and only depends on $t_b - t_a$ since the Lagrangian is time-invariant.

$$\begin{aligned} K(x_b, t_b, x_a, t_a) &= \int D[q]\, \exp\left(\frac{i}{\hbar} S[q]\right) = \int D[\eta]\, \exp\left(\frac{i}{\hbar} S[q_{\text{cl}} + \eta]\right) \\ &= \exp\left(\frac{i}{\hbar} S_{\text{cl}}\right) \int D[\eta]\, \exp\left(\frac{i}{\hbar} S[\eta]\right) = A(t_b - t_a) \exp\left(\frac{i}{\hbar} S_{\text{cl}}\right) \end{aligned}$$

Example 1.2 (*free particle*). Recall a free particle has Lagrangian $\mathcal{L}(x, \dot{x}) = \frac{1}{2}m\dot{x}$.

$$K(x, t, x', t') = \sqrt{\frac{m}{2\pi i\hbar\Delta t}} \exp\left(\frac{im(x - x')^2}{2\hbar\Delta t}\right) \tag{1.13}$$

Note the appearance of classical action in the spatially dependent exponential term.

Example 1.3 (*simple harmonic oscillator*). Consider the following Lagrangian

$$L = \frac{m\dot{x}^2}{2} - \frac{m\omega^2}{2}x^2$$

The corresponding classical action is

$$S_{\text{cl}} = \frac{m\omega}{2\sin(\omega\Delta t)}\left(\left(x_a^2 + x_b^2\right)\cos(\omega\Delta t) - 2x_a x_b\right)$$

Recalling the simple Harmonic oscillator solution are all real and of the following form

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

Perform this substitution and invoke equation 1.7

$$\sqrt{\frac{m\omega}{\hbar}}x_a \mapsto \xi, \sqrt{\frac{m\omega}{\hbar}}x_b \mapsto \eta$$

$$K = \sqrt{\frac{m\omega}{2\pi\hbar i\sin\omega\Delta t}} \exp\left(\frac{1}{2}(\xi^2 + \eta^2) - \frac{\xi^2 + \eta^2 - 2\xi\eta\exp(-i\Delta t\omega)}{1 - \exp(-2i\Delta t\omega)}\right)$$

The exponential term is the exponential of the classical action.

$$K(b, a) = \sqrt{\frac{m\omega}{2\pi\hbar i\sin\omega\Delta t}} \exp\left(\frac{i}{\hbar}S_{\text{cl}}\right) \tag{1.14}$$

2 Symmetry, Conservation Laws, and Selection Rules

2.1 Operators in quantum theory

2.1.1 Fundamental opertors

The fundamental operators in quantum theory are x, p with

$$(x\,\psi)(x) = x\psi(x), \quad (p\,\psi)(x) = -i\hbar\partial_x$$

They give rise to the canonical commutation relation

$$[x, p] = i\hbar$$

This commutation relation gives rise to vector operator's commutation relations. The momentum operator may be conveniently memorized as using $-\partial_x$ to effect translation in x, using i to keep it skew-Hermitian, using $\hbar$ for units.

2.1.2 Ladder operators

For a harmonic oscillator Hamiltonian

$$H = \frac{1}{2m}\left[p^2 + (m\omega x)^2\right]$$

The raising and lowering opperators of interest are

$$a_\pm = \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp ip + m\omega x\right)$$

They are conjugates of each other and obey the commutation relations

$$[a_-, a_+] = 1, \quad H = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)$$

We can in turn express x, p in terms of the ladder operators

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_+ + a_-), \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(a_+ + a_-)$$

Number operator n is defined by $n = a_+a_-$. We conveniently have (operator on left side)

$$n\psi_n = n\psi_n, \quad a_+\psi_n = \sqrt{n+1}\psi_{n+1}, \quad a_-\psi_n = \sqrt{n}\psi_{n-1}$$

2.1.3 Vector operators

The fundamental commutation relations for vector operators are

$$[V_x, V_y] = i\hbar V_z; \quad [V_y, V_z] = i\hbar V_x; \quad [V_z, V_x] = i\hbar V_y$$

We can define $V^2 = V_x^2 + V_y^2 + V_z^2$, then $[V, V^2] = 0$. We can also define ladder operators

$$V_\pm = V_x \pm iV_y$$

They obey the commutation relations

$$[V^2, V_\pm] = 0, \quad [V_z, V_\pm] = \pm\hbar V_\pm$$

Fix an eigenspace of L^2 with eigenvalue $\hbar^2 l(l+1)$ with dimension $2l+1$, where l can be an integer or half-integer. In this eigenspace,

$$V_z = \hbar \begin{pmatrix} l & & & \\ & l-1 & & \\ & & \ddots & \\ & & & -l \end{pmatrix}, \quad L_x = \frac{1}{2}(V_+ + V_-), \quad L_y = \frac{i}{2}(V_- - V_+)$$

Here the representations of $V_\pm$ are shifted diagonals of $\hbar$.

2.2 Transformation

We first formally consider transformations acting on states.

Definition 2.1 (*translation operator*). We define its action on $\psi(x)$ as

$$T(a)\psi(x) = \psi(x-a)$$

This definition characterizes the action of $T(a)$ on the positional representation of $|\psi\rangle$. In terms of states themselves, the translation operator satisfy, for $|\psi'\rangle = T(a)|\psi\rangle$

$$\langle\psi'|x\rangle = \langle\psi|x-a\rangle$$

Definition 2.2 (*parity operator*). The parity-inverted state $|\psi'\rangle = \Pi|\psi\rangle$ satisfies

$$\langle\psi'|r\rangle = \langle\psi'|-r\rangle$$

Here $|r\rangle$ may be generally understood as a 3d positional basis. Represented spherically:

$$\Pi\psi(r,\theta,\phi) = \psi(r,\pi-\theta,\phi+\pi)$$

Proposition 2.1. For hydrogenic orbitals, $\Pi\psi_{nlm}(r,\theta,\phi) = (-1)^l\psi_{nlm}(r,\theta,\phi)$ We only need consider the angular part. Recall $Y_l^m(\theta,\phi) \propto P_l^m(\cos\theta)\exp(im\phi)$, and $\cos(\pi-\theta) = -\cos\theta$.

Definition 2.3 (*z-rotation operator*). The rotation operator which effects counterclockwise rotation about the z-axis by φ is

$$R_z(\varphi)\psi(r,\theta,\phi) = \psi(r,\theta,\phi-\varphi)$$

Transformations, since they map states to states, must be unitary. They are effectively a basis permutation. For example, translation effects the basis change $|x\rangle \mapsto |x-a\rangle$. One may view this via the equivalence between sliding our state to the right, and sliding the spatial axis to the left while following the center of the axis. By unitarity $T^\dagger = T^{-1}$.

Apart from considering the effect of T on $|\psi\rangle$, define its application on an operator O such that expectation values of O w.r.t. $T|\psi\rangle$ agrees with that of $T(O)$ w.r.t. $|\psi\rangle$. This motivates the following definition.

Definition 2.4 (*operator transformation, invariance*). The effect of transforming operator O by T is $T(O) = T^\dagger OT = T^{-1}OT$. It follows that O is invariant under T if $[O,T]=0$.

$$\langle\psi|T^\dagger OT|\psi\rangle = \langle\psi|T(O)|\psi\rangle \implies T(O) = T^\dagger OT \tag{2.1}$$

2.3 Observables and transformations

Recall that $p = -i\hbar\partial_x$. Assuming that $\psi(x)$ may be expanded as a power-series.

$$\begin{aligned} T(a)\psi(x) = \psi(x-a) &= \sum_{n=0}^{\infty} \frac{(-a)^n}{n!}\partial_x^n\psi(x) \\ &= \sum \frac{1}{n!}\left(\frac{-ia}{\hbar}(-ih\partial_x)\right)^n \psi(x) \end{aligned} \tag{2.2}$$

Definition 2.5 (*exponential of an operator*). We define the exponential of a Hermitian operator as a power-series, with multiplication denoting composition

$$\exp(\alpha O) = \sum_{n=0}^{\infty} \frac{1}{n!}(\alpha O)^n \tag{2.3}$$

This definition is made precise by the formulation of Lie group and Lie algebra, its main property of interest is

$$\partial_\alpha \exp(\alpha O) = \alpha \exp(\alpha O) \tag{2.4}$$

Definition 2.6 (*observables generate transformation*). We say that a Hermitian observable O generates a one-parameter family of transformations $T(a), a \in \mathbb{R}$ if

$$T(a) = \exp\left(-\frac{ia}{\hbar}O\right) \tag{2.5}$$

Equation 2.2 shows that momentum generates axial translation.

More generally, consider a (partial) basis $\{|o\rangle\}$ corresponding to the eigenstates of an observable O and let $\psi(o) = \langle\psi|o\rangle$. The basis is partial in the sense that it is the basis of one of possibly many components of the tensor product Hilbert space (e.g. position and spin). Note that $\psi(o)$ may be a state! Define the effect of the unitary transformation $T_o(a)$ by $|o\rangle \mapsto |o - a\rangle$. Assuming that $\psi(o)$ may be expanded as a power series in terms of o.

$$\psi(o-a) = T_o(a)\psi(o) = \sum_{n=0}^{\infty} \frac{1}{n!}((-a)\,\partial_o)^n \psi(o) = \exp\left(-a\,\partial_o\right)\psi(o) \tag{2.6}$$

Every unitary $T(a)$ is the complex exponential of a Hermitian O which provides the phase factors for the eigenvalues of the unitary. We also have the freedom to choose O up to a phase scaling factor α with both free value and unit:

$$T(a) = \exp\left(\frac{i}{\alpha}Q(a)\right) = \exp\left(-a\,\partial_o\right) \implies Q(a) = aQ = a(i\alpha\,\partial_o) \tag{2.7}$$

Remark 2.1. Equation 2.8 provides another perspective: each Hermitian Q defines an infinitesimal transformation $(1 + iaQ/N)$ when $N \to \infty$. This operator is unitary up to a quadratic order:

$$(1 + iaQ/N)^\dagger\,(1 + iaQ/N) = 1 + O(1/N^2) \tag{2.8}$$

The cumulative action of applying $(1 + iaO/N)$ for N times is $\exp(iaQ)$

Returning to equation 2.7, ∂_o effects the change $|o\rangle \mapsto |o + do\rangle$, so we choose $\alpha = -1/\hbar$.

Theorem 2.2 (*Hamiltonian generates time translation*). $\exp\left(-iHt/\hbar\right)|t_0\rangle = |t_0 - t\rangle$

Proof: this statement is equivalent to Schrodinger's equation.

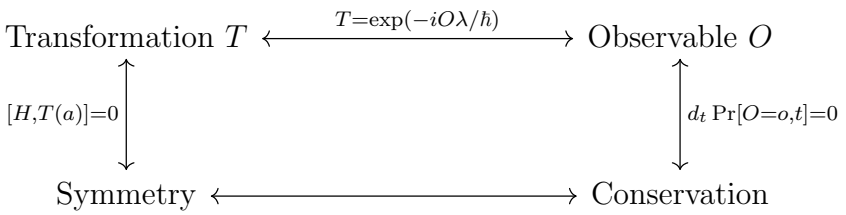
$$\partial_t|\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle$$

Definition 2.7 (*complete set of compatible observables (CSCO)*). A set of Hermitian observables $\{O_j\}$ over a Hilbert space is compatible if they pairwise commute, and complete if for every set of eigenspaces $\{\mathcal{S}_{O_j,\lambda_k}\}$, their intersection has dimension at most 1.

Example 2.1 (*CSCO for central potential*). For any Hamiltonian H which commutes with L, the set H, L_z, L^2 is a complete set of compatible observables. They pairwise commute and E_n, l, m uniquely determine an eigenstate.

2.4 Symmetry and conservation

The key idea of this section is the diagram below.



A system is defined by its time-evolution, which is defined by its Hamiltonian. We first establish the connection between transformation and symmetry.

Definition 2.8 (*continuous symmetry*). A system with Hamiltonian H has continuous symmetry with respect to a family of transformations $T(a)$, parameterized by $a \in \mathbb{R}$, if

$$\forall a \in \mathbb{R}, [H, T(a)] = 0$$

Transformations biject with observables, up to a constant factor. We show that continuous symmetry is equivalent to the conservation of an observable.

Theorem 2.3 (*conservation is equivalent to commutativity*). The probability distribution for observating different values of a Hermitian O is conserved if and only if $[H, O] = 0$.

Proof: suppose $[H, O] = 0$, then the energy eigenstates $|n\rangle$ are also eigenstates of O.

$$|\psi_0\rangle = \sum c_n |n\rangle \implies \Pr[O = o_n, t = 0] = |c_n|^2$$

Under time evolution, the probability distribution is unchanged

$$|\psi_t\rangle = \sum \exp\left(iE_n t/\hbar\right) c_n |n\rangle \implies \Pr[O = o_n, t] = |\exp\left(iE_n t/\hbar\right) c_n|^2 = |c_n|^2$$

Conversely, distribution conservation in particular implies $\langle O \rangle = 0$ (Ehrenfest's theorem):

$$\begin{aligned} d_t \langle O \rangle &= d_t \langle \psi | O | \psi \rangle \\ &= \left(d_t |\psi\rangle\right)^\dagger O |\psi\rangle + \left(O|\psi\rangle\right)^\dagger d_t |\psi\rangle + \partial_t O \\ &= \frac{i}{\hbar} \langle [H, O] \rangle \end{aligned}$$

The expectation value vanishes for all $|\psi\rangle$, so $[H, O] = 0$.

Theorem 2.4 (*continuous symmetry $\iff$ conservation*). For a Hermitian O, the probability distribution for observating different values of O is conserved if and only H has continuous symmetry with respect to the family of transformations generated by O

$$T(a) = \exp(-iaO/\hbar)$$

Proof: $[H, \exp\left(-iaO/\hbar\right)] \iff [H, O] = 0$. Think in the eigenbasis throughout.

Remark 2.2. Theorem 2.4 emphasizes the fundamental stochasticity of quantum mechanics. The true quantum-mechanical counterpart of classical values are not the measured values (which is not conserved), but its distribution.

2.5 Selection rules

Recall that commutativity ensures a simultaneous set of eigenvectors. This constitutes the most basic idea of a selection rule. We recall a result from linear algebra:

Theorem 2.5 (*commutativity is equivalent to shared eigenbasis*). two normal operators A, B commute if and only if they share an eigenbasis.

Proof: Let v be an eigenvector of A with eigenvalue λ, then

$$ABv = BAv = \lambda Bv$$

This means Bv is in the eigenspace of A with eigenvalue λ. Then B maps eigenspaces of A onto themselves. Apply the spectral theorem in each eigenspace.

Selection rules constrain the matrix elements of an operator based on commutativity.

Theorem 2.6 (*Laporte's rule*). Matrix elements of an operator that is odd under parity is nonzero only for states with the same parity. Those for operators invariant under parity is nonzero only for states with different parity.

Proof: Consider an operator O such that $\{O, \Pi\} = 0$ and states $|n\rangle, |m\rangle$ with parity

$$\Pi|n\rangle = p_n|n\rangle, \quad \Pi|m\rangle = p_m|m\rangle, \quad p_n, p_m \in \{-1, 1\}$$

Consider the matrix element

$$\begin{aligned}\langle n|O|m\rangle &= -\left\langle n|\Pi^\dagger O\Pi|m\right\rangle \\ &= -p_m p_n \langle n|O|m\rangle\end{aligned}$$

Rearranging the equation $\langle n|O|m\rangle (1 + p_m p_n) = 0$ implies that states with the same parity ($p_m p_n = 1$) have vanishing matrix elements. The argument proceeds similarly for $[O, \Pi] = 0$.

Remark 2.3. One informal way to remember Laporte's rule is that the matrix elements of O give the transition matrix when O happens to be the Hamiltonian. For a system which cares about parity, only states which have the same parity can evolve into each other.

Definition 2.9 (*vector operator*). Let $R_n(\theta)$ correspond to the transformation of rotating about n by θ, it has a 3×3 matrix representation $D_n(\theta)$. A 3-component vector operator V is a vector operator if for all n, θ

$$R_n^\dagger(\theta) V R_n(\theta) = D_n(\theta) V$$

In other words, the operator transforms spatially. This is equivalent to if V satisfies

$$[L_i, V_j] = i\hbar\epsilon_{ijk} V_k$$

Examples of three such vectors are r, p, L.

Theorem 2.7 (*rotational selection rules for scalars*). A rank-1 operator f satisfying

$$[L_z, f] = [L_\pm, f] = [L^2, f] = 0$$

has matrix elements of the form

$$\langle n', l', m'|f|n, l, m\rangle = \delta_{nn'}\delta_{ll'} \langle n', l \parallel f \parallel n, l\rangle$$

3 Time Independent Perturbation Theory

Suppose we successfully solved for the eigensystem $\{E_n^0, \psi_n^0\}$ for a time-independent Hamiltonian H^0. Perturbation theory approximates the eigensystem for the perturbed Hamiltonian

$$H = H^0 + \lambda H'$$

The key assumption of perturbation theory is that *the eigensystem has a power series expansion in terms of* λ. We use this assumption and the known solutions for $\lambda = 0$ to solve for the perturbed eigensystem at $\lambda = 1$. Concretely,

$$\begin{aligned}\psi_n &= \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\end{aligned}$$

The subscript denotes the eigensystem index and superscript correction order. Substitute into the eigenvalue equation for H to yield

$$(H^0 + \lambda H')(\psi_n^0 + \lambda\psi_n^1 + \cdots) = (E_n^0 + \lambda E_n^1 + \cdots)(\psi_n^0 + \lambda\psi_n^1 + \cdots)$$

By assumption this equation holds independently for every power of λ. In the zeroth order

$$H^0\psi_n^0 = E_n^0\psi_n^0$$

To the first and second orders

$$\begin{aligned}H^0\psi_n^1 + H'\psi_n^0 &= E_n^0\psi_n^1 + E_n^1\psi_n^0 \\ H^0\psi_n^2 + H'\psi_n^1 &= E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0\end{aligned} \tag{3.1}$$

Remark 3.1. The power series expansion assumption of perturbation theory is not generally true. The solutions to a physical system is not generally smooth around $\lambda = 0$, as positive and negative coupling may lead to qualitatively different behaviors (consider a two-body system with attractive compared to repulsive interaction). This manifests mathematically in the divergence of higher-order terms. It is a miracle that we can use the first few terms in the perturbation series with a good conscience in the first place.

3.1 Nondegenerate theory

Take the inner product of the first equation in 3.1 with ψ_n^0 to isolate a component

$$\langle\psi_n^0|H^0|\psi_n^1\rangle + \langle\psi_n^0|H'|\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle$$

Hamiltonian H^0 is Hermitian, so the first terms on both sides of the equation cancel, The first-order energy correction is an matrix element of H' in the orthonormal basis $\{|\psi_n^0\rangle\}$.

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle$$

For the first order eigenstate correction, rewrite equation 3.1 as an equation in ψ_n^1.

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$$

Any solution has freedom under $\psi_n^1 \mapsto \psi_n^1 + \alpha\psi_n^0$. Expand ψ_n^1 in the orthonormal basis

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \tag{3.2}$$

Substitute into the equation

$$\sum_{m \neq n} \left(E_m^0 - E_n^0\right) c_m^{(n)} \psi_m^0 = -(H' - E_n^1)\psi_n^0$$

Again, to isolate components take the inner product with ψ_l^0 for $l \neq n$

$$\left(E_l^0 - E_n^0\right) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle$$

Solve for $c_l^{(n)}$ and substitute into 3.2 yields the first-order eigenfunction corrections

$$|\psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle$$

For E_n^2, consider the second equation in 3.1. Inner product with ψ_n^0 to isolate components

$$\langle \psi_n^0 | H^0 | \psi_n^2 \rangle + \langle \psi_n^0 | H' | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

Again, the first term on both sides cancel, so

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$$

Recall that we excluded ψ_n^0 in the expansion for $\psi_n^1\rangle$ in 3.2 so $\langle \psi_n^0 | \psi_n^1 \rangle = 0$, then putting our results in one place:

$$\begin{aligned} E_n^1 &= \langle \psi_n^0 | H' | \psi_n^0 \rangle \\ |\psi_n^1\rangle &= \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle \\ E_n^2 &= \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \end{aligned} \tag{3.3}$$

3.2 Degenerate theory

In the case of degeneracy, we need to think more rigorously about our solutions:

The first order equation $H^0\psi_n^0 = E_n^0\psi_n^0$ is under-determined: when the eigenspace E_n^0 is of dimension greater than 1, there are many eigenstates which satisfy the first-order equation. The problem when we consider the first-order eigenstate correction

$$|\psi_n^1\rangle = \sum_{m\neq n} \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle$$

It is not defined in case of degeneracy, when $E_n^0 = E_m^0$ for some $n \neq m$. The same holds for the second order energy correction.

One way to make sense of the first-order eigenfunction correction equation is choose a "good" basis for the degenerate eigenspace such that

$$\forall n \neq m, E_n^0 = E_m^0 \implies \langle\psi_m^0|H'|\psi_n^0\rangle = 0$$

This allows us to cancel the zero denominators in 3.3 with a zero enumerator and hope that no higher-order degeneracy exists so the indeterminate form is 0. We need the following definition to make precise what we mean by finding a "good" eigenbasis for H^0 with respect to a perturbation H'.

Definition 3.1 (*subspace projection of an operator*). the projection of an operator $H : V \to V$ onto a subspace $W \subset V$ $H_{|W} : W \to W$ is

$$H_{|W} : W \xrightarrow{\iota} V \xrightarrow{H} V \xrightarrow{P_{V\to W}} W$$

Given an orthonormal basis $\{|i\rangle\}$ for W, the matrix representation of $H_{|W}$ is $W_{ij} = \langle i|H|j\rangle$.

Example 3.1 (*operator in* $\mathbb{C}^3$). The subspace projection of the operator

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

onto the subspace spanned by the first and third basis elements is

$$A_{|\mathrm{span}(e_1,e_3)} = \begin{pmatrix} a_{11} & a_{13} \\ a_{31} & a_{33} \end{pmatrix}$$

Formally, this is done by removing the second row and column.

Definition 3.2 (*good basis for perturbation*). $\mathcal{B} = \{|i\rangle\}$ is "good" basis for perturbing H^0 with respect to H' if, for every eigenspace $W \subset V$ of H with basis $\mathcal{A} \subseteq \mathcal{B}$, the representation of $H'_{|W}$ under $\mathcal{A}$ is diagonal. In other words

$$\forall |m\rangle, |n\rangle \in \mathcal{A}, m \neq n : H'_{mn} = 0$$

Remark 3.2. Finding a good basis is weaker than finding a simultaneous eigenbasis for H^0, H', which does not exist when $[H^0, H'] \neq 0$. A good basis *always* exists by applying the spectral theorem to the projection of H' on each eigenspace of H^0.

The following results helps us find a good basis easily under certain conditions.

Theorem 3.1 (*characterization of commutativity*). Two normal operators A, B commute if and only if they leave the eigenspaces of each other invariant.

Proof: Assume commutativity, and let x be an eigenvector of A with eigenvalue λ, then $BAx = \lambda Bx = A(Bx)$, so Bx is also an eigenvector of A with eigenvalue λ. Conversely, let x_i be an eigenbasis for A such that $Ax_i = \lambda_i x_i, ABx_i = \lambda_i Bx_i$. Given an arbitrary vector $v = c_i x_i$, we have

$$BAv = c_i BAx_i = c_i \lambda_i Bx_i = c_i ABx_i = ABv$$

This applies in particular two Hermitian operators. In a subspace spanned by eigenvectors of A with distinct eigenvalues, commutativity forces H to be diagonal.

Lemma 3.2. Given commuting Hermitian operators H, A, $H_{|W}$ is diagonal for every subspace W spanned by an orthonormal set of eigenvectors of A with distinct eigenvalues.

Proof: By $AH = HA$, $\langle i|H|j\rangle = \lambda_j^{-1}\langle i|AH|j\rangle = \lambda_i^{-1}\langle i|HA|j\rangle$. Since $\lambda_i \neq \lambda_j$, $\langle i|H|j\rangle = 0$.

Note commutativity is not transitive: $[A, H^0] = [A, H'] = 0$ does not imply $[H^0, H'] = 0$. The following theorem is the main result of this section.

Theorem 3.3 (*convenient good basis condition*). Given Hermitian H^0, H'. An eigenbasis $\{|i\rangle\}$ for H^0 is a good basis if there exists an operator A such that $[A, H^0] = [A, H'] = 0$ and each subset of $\{|i\rangle\}$ corresponding to a degenerate subspace of H^0 are eigenvectors of A with distinct eigenvalues.

Proof: Given such an A and mutual eigenbasis $\{|i\rangle\}$ between A, H^0, consider each degenerate eigenspace W of H^0. By the lemma above, $H'_{|W}$ must be diagonal in this basis.

Remark 3.3. The converse to the theorem is not true. Given a good basis and $[A, H^0] = 0$, the fact that $H'_{|W}$ is diagonal for each degenerate eigenspace does not mean that it has to leave it invariant. Consider a good basis b_i which is a shared eigenbasis for H^0, A with eigenvalues λ_i, ρ_i for the two operators respectively. Assume $\lambda_1 = \lambda_2$, then $\rho_1 \neq \rho_2$. It suffices to find a H' whose projection onto the span of b_1, b_2 is diagonal but changes some eigenspace of A. The span of b_1, b_2 belongs to distinct eigenspaces of A by $\rho_1 \neq \rho_2$, the following H' suffices for nonzero H'_{13}, H'_{23}. All representations are in the good basis.

$$H = \begin{pmatrix} \lambda_1 & & \\ & \lambda_2 = \lambda_1 & \\ & & \lambda_3 \end{pmatrix}, \quad A = \begin{pmatrix} \rho_1 & & \\ & \rho_2 \neq \rho_1 & \\ & & \rho_3 \end{pmatrix}, \quad H' = \begin{pmatrix} H'_{11} & & H'_{13} \\ & H'_{22} & H'_{23} \\ & & H'_{33} \end{pmatrix}$$

Remark 3.4. The operator A is usually of two forms:

- a unitary symmetry exhibited by both H^0, H'. The condition in the theorem above boils down to degenerate eigenstates of H^0 having different behaviors under the application of the symmetry. See the example below.

- a Hermitian observable whose eigenstates coincide with energy eigenstates of H^0, H'. The theorem condition translates to degenerate eigenstates of H^0 having different observable values. For example, H, L_z, L^2

Example 3.2 (*oscillator*). Consider a particle in two-dimensional oscillator potential

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(x^2+y^2), \quad H' = \epsilon m\omega^2 xy$$

The first excited state is two-fold degenerate with one basis

$$\psi_0^a = \psi_0\phi_1 = \alpha y \exp\left(-\frac{\beta^2(x^2+y^2)}{2}\right)$$
$$\psi_0^b = \psi_1\phi_0 = \alpha x \exp\left(-\frac{\beta^2(x^2+y^2)}{2}\right)$$

One can show that $H'_{ab} \neq 0$, so this is not a good basis. H has continuous rotational symmetry and reflections, while H' is invariant under $A : (x,y) \mapsto (-x,-y)$ and $A' : (x,y) \mapsto (y,x)$. Both A, A' both commute with H, H'.

- ψ_0^a, ψ_0^b are degenerate eigenvectors of A, so A does not give us a good basis.
- ψ_0^a, ψ_0^b are not eigenvectors of A', but $\frac{1}{\sqrt{2}}(\psi_0^a \pm \psi_0^b)$ are with eigenvalues ± 1. They constitute the desired basis in which H' is diagonal.

4 Structure of Hydrogen

4.1 Fine structure

4.1.1 Relativistic correction to kinetic energy

The lowest-order correction Hamiltonian due to relativistic correction to kinetic energy is

$$H_r' = -\frac{p^4}{8m^3c^2} \tag{4.1}$$

Exploiting the Hermiticity of p, the first-order correction is

$$E_r^1 = -\frac{1}{8m^3c^2}\left\langle p^2\psi | p^2\psi\right\rangle \tag{4.2}$$

For our unperturbed $|\psi\rangle$, which are solved for non-relativistically, $p^2 = 2m(E-V)$, so

$$\begin{aligned} E_r^1 &= -\frac{1}{2mc^2}\left\langle (E-V)^2\right\rangle \\ &= -\frac{1}{2mc^2}\left(E_n^2 - 2E_n\left\langle V\right\rangle + \left\langle V^2\right\rangle\right) \\ &= -\frac{(E_n)^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right] \end{aligned} \tag{4.3}$$

Several quantities which are handy in such evaluations when we use the basis n, l, m_l

$$\left\langle \frac{1}{r}\right\rangle = \frac{1}{n^2a} \quad \left\langle \frac{1}{r^2}\right\rangle = \frac{1}{(l+1/2)n^3a^2} \quad \left\langle \frac{1}{r^3}\right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3} \tag{4.4}$$

The perturbation is spherically symmetric, so L^2, L_z commute with both H, H_r' and $|n,l,m\rangle$ are distinct eigenstates of (L^2, L_z), taken together, allowing us to use nondegenerate perturbation theory. Relativistic correction to the kinetic energy lifts the l-degeneracy. Our complete set of commuting observables (recall 2.7) are H, L^2, L_z, S^2, S_z.

4.1.2 Spin-orbit coupling

From the electron's frame, the proton's motion generates a magnetic field which couples to the electron spin.

$$H_{\text{so}}' = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L} \tag{4.5}$$

The energy spectrum is degenerate in m, m_s yet $[\mathbf{S}\cdot\mathbf{L}, L_z], [\mathbf{S}\cdot\mathbf{L}, S_z] \neq 0$. Therefore we cannot use m, s as our quantum numbers. Consider instead the total angular momentum

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S} \tag{4.6}$$

We propose an addition of angular momentum transformation, which replaces the complete set of commuting observables for a Hamiltonian from L^2, L_z, S^2, S_z with J^2, L^2, S^2, J_z corresponding to quantum numbers j, l, s, m_j. We first need to verify commutativity with H_{so}'.

Proposition 4.1. $[\mathbf{J}, \mathbf{S}\cdot\mathbf{L}] = 0$

Proof: Without loss of generality consider J_z,

$$\begin{aligned}[J_z, \mathbf{S}\cdot\mathbf{L}] &= [S_z + L_z, S_xL_x + S_yL_y + S_zL_z] \\ &= [S_z, S_x]L_x + [S_z, S_y]L_y + [L_z, L_x]S_x + [L_z, L_y]S_y \\ &= S_yL_x - S_xL_y + L_yS_x - L_xS_y = 0\end{aligned}$$

Also note that $\mathbf{S}\cdot\mathbf{L} = \frac{1}{2}(J^2 - L^2 - S^2)$, so H'_{so} commutes with L^2, S^2, J^2, J_z.

Proposition 4.2. H'_{so} commutes with J^2, L^2, S^2, J_z.

Proof: The previous proposition shows that H'_{so} commutes with J_z. To show commutativity with the other observables, note that

$$\mathbf{S}\cdot\mathbf{L} = \frac{1}{2}(J^2 - L^2 - S^2)$$

The three operators L^2, S^2, J^2 pairwise commute.

The eigenvalues of $\mathbf{L}\cdot\mathbf{S}$ are then

$$\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Substituting total spin $s = 1/2$

$$E^1_{\text{so}} = \frac{(E_n)^2}{mc^2}\cdot\frac{n\left[j(j+1) - l(l+1) - 3/4\right]}{l(l+1/2)(l+1)} \tag{4.7}$$

Luckily, this combines neatly with the contribution from the relativistic correction to give the fine structure correction

$$E^1_{\text{fs}} = \frac{(E_n)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right) \tag{4.8}$$

Combined with the Bohr formula, the energy now depend on both n, j.

n	j	l	m_j	degeneracy
1	1/2	$\{0\}$	$\{\pm 1/2\}$	2
2	1/2	$\{0, 1\}$	$\{\pm 1/2\}$	4
	3/2	$\{1\}$	$\{\pm 1/2, \pm 3/2\}$	4
3	1/2	$\{0\}$	$\{\pm 1/2\}$	2
	3/2	$\{1, 2\}$	$\{\pm 1/2, \pm 3/2\}$	8
	5/2	$\{2\}$	$\{\pm 1/2, \pm 3/2, \pm 5/2\}$	6

Table 1: Energy levels of a spin 1/2 particle for $n \leq 3$, arranged in (n, j)

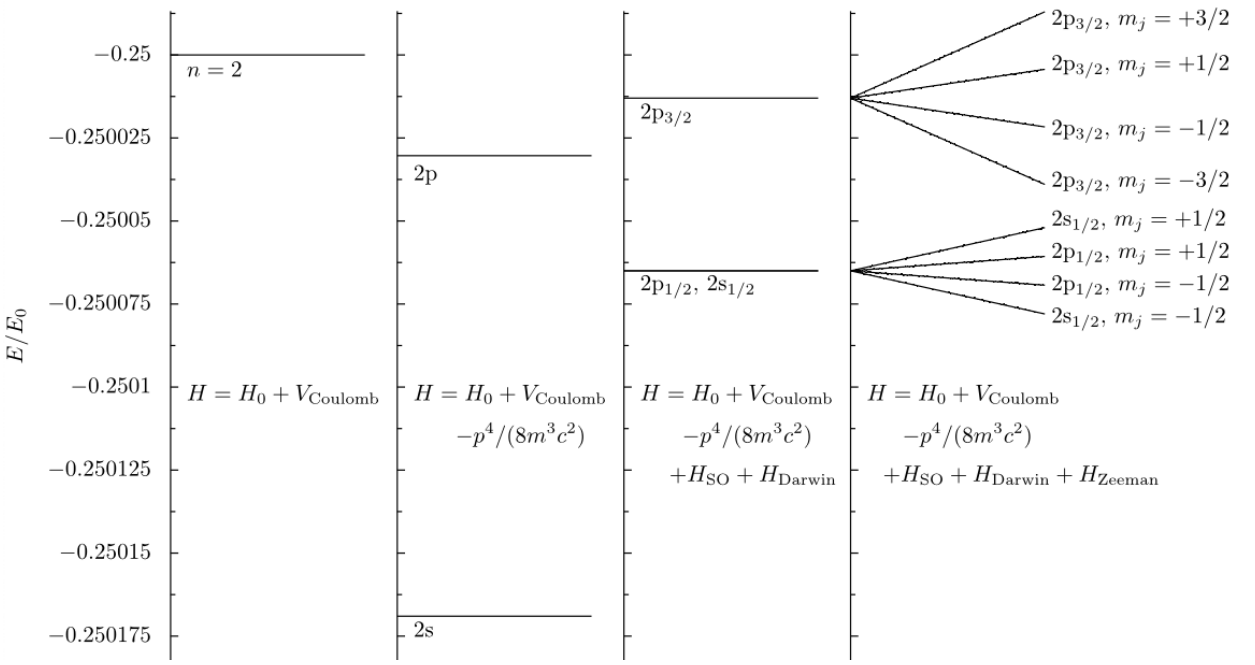


Figure 1: Fine-structure and Zeeman corrections for $n = 2$

$$E_{nj} = -\frac{(E_0)^2}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] \tag{4.9}$$

Our complete set of commuting observables are H, L^2, S^2, J^2, J_z corresponding to quantum numbers n, l, s, j, m_j. Given n, we still have considerable degeneracy in j, l, m_j (table 1).

4.2 Zeeman effect

Zeeman effect characterizes the energy corrections of an atom under external magnetic field.

Definition 4.1 (*gyromagnetic ratio*). The gyromagnetic ratio γ of a system is the ratio between its magnetic moment and angular momentum.

$$\boldsymbol{\mu} = \gamma \mathbf{L}$$

For a classically rotating body, $\gamma = \dfrac{q}{2m}$.

Definition 4.2 (*Bohr magneton*). The Bohr magneton provides the natural unit for gyromagnetic ratio of atomic systems.

$$\mu_B \equiv \frac{e\hbar}{2m_e}$$

For an electron, the gyromagnetic ratio for orbital motion and spin are different: that for

the spin is roughly twice its classical value. Note that $\boldsymbol{\mu}$ scales inversely with mass.

$$\boldsymbol{\mu} = \boldsymbol{\mu}_l + \boldsymbol{\mu}_s = \frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) \tag{4.10}$$

In an external magnetic field $\mathbf{B}$, a hydrogenic atom has the following correction

$$H'_Z = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} \tag{4.11}$$

4.2.1 Weak-field Zeeman effect

When $B \ll B_{\text{int}}$, we let $H^0 = H_{\text{Bohr}} + H'_{fs}$. The zeroth-order eigenstates are given by by L^2, S^2, J^2, J_z. Without loss of generality, let $\mathbf{B} = B\hat{\mathbf{z}}$, then ($Z$ is for Zeeman)

$$H'_Z = \frac{\mu_B B}{\hbar}(L_z + 2S_z) \tag{4.12}$$

After we have thus aligned the external field in the z-direction, the correction H'_Z commutes with our complete set of operators and is diagonal in the l, s, j, m_j basis, in which case

$$\begin{aligned} E^1_Z &= \frac{\mu_B B}{\hbar}\langle L_z + 2S_z \rangle \\ &= \frac{\mu_B B}{\hbar}(J_z + \langle S_z \rangle) \end{aligned} \tag{4.13}$$

We now consider $\langle S_z \rangle$: the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is constant, so the time average of $\mathbf{S}$ is its projection along $\mathbf{J}$ (see Griffiths for detailed explanation)

$$\begin{aligned} \langle S_z \rangle &= \frac{\langle \mathbf{S} \cdot \mathbf{J} \rangle}{J^2} J_z \\ &= \langle \frac{1}{2}\left(J^2 + S^2 - L^2\right) \rangle \frac{\hbar m_j}{j(j+1)} \\ &= \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \hbar m_j \\ &= (g_J - 1) m_j \end{aligned} \tag{4.14}$$

Here we introduced the Landé g-factor g_J. The matrix element for energy correction is

$$\langle n, l, s, j, m_j | H'_Z | n, l, s, j, m_j \rangle = E^1_Z = \mu_B g_J m_j B \tag{4.15}$$

Note that this correction is linear in m_j. Combined with equation 4.9, the energy levels accounting for fine structure and weak-field Zeeman effect is

$$E_{nj} = -\frac{(E_0)^2}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j + 1/2} - \frac{3}{4}\right)\right] + \mu_B g_J m_j B \tag{4.16}$$

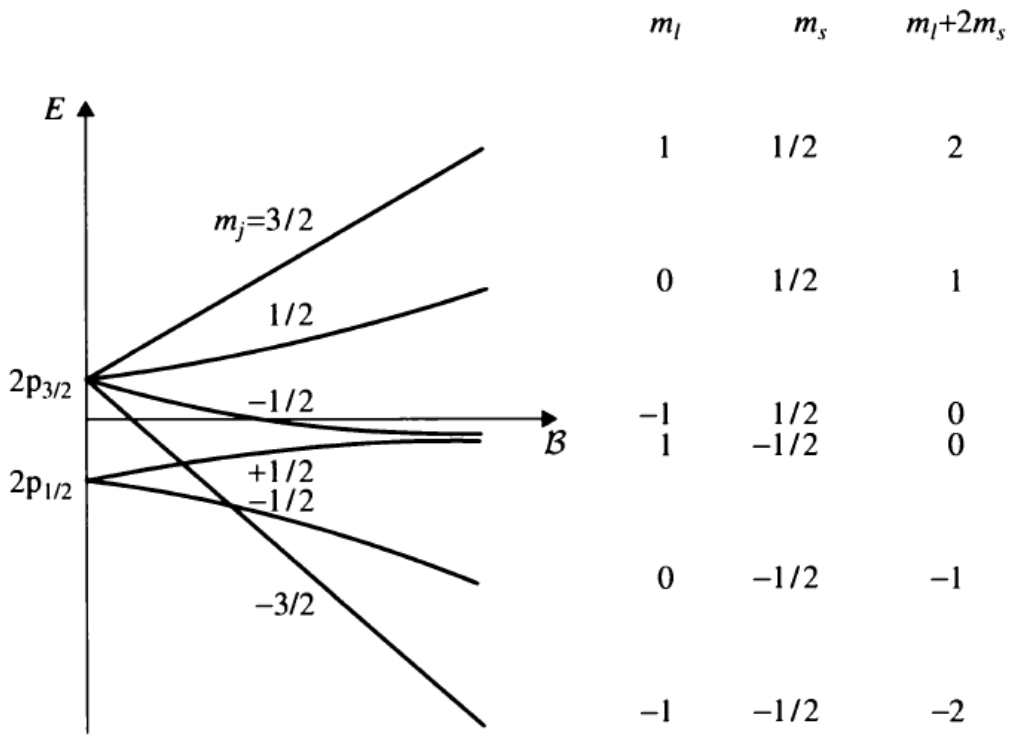


Figure 2: Zeeman effect for $n = 2, l = 1$

4.2.2 Strong-field Zeeman effect

When the external magnetic field dominates the proton's magnetic field, we take $H^0 = H_{\text{Bohr}} + H'_Z$ and H'_{fs} to be the perturbation.

Originally, H_{Bohr} is degenerate in l, s, m_l, m_s, and equation 4.12 suggests that the states with the same $m_l + 2m_s$ are degenerate eigenstates of H^0. To apply non-degenerate perturbation theory, our basis must arise from a set commuting operators complementing H^0, H'_{fs} which additionally lifts the degeneracy in $l, s, m_l + 2m_s$. One such set is L^2, S^2, J^2, J_z.

$$E^1_{\text{fs}} = \langle n, l, m_l, m_s | H'_r + H'_{\text{so}} | n, l, m_l, m_s \rangle \tag{4.17}$$

Here $\langle H'_r \rangle$ commutes with the operators for our basis, so we can use equation 4.3. For the spin-orbit term, $\langle S_z L_z \rangle = \hbar^2 m_l m_s$. Substitute the indeterminate quotient with 1 when $l = 0$.

$$E^1_{\text{fs}} = -\frac{E_0}{n^3}\alpha^2 \left[\frac{3}{4n} - \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \tag{4.18}$$

Equation 4.12 dominates in the strong field regime, while the fine structure characterized by 4.1, 4.5 dominates in the weak field regime. The quantum numbers which distinguish between energy levels in the strong-field regime is then $n, l, s, m_l + 2m_s$, while those in the weak-field regime are n, l, s, j, m_j. The asymptotic slope in the figure above is determined by $m_l + 2m_s$.

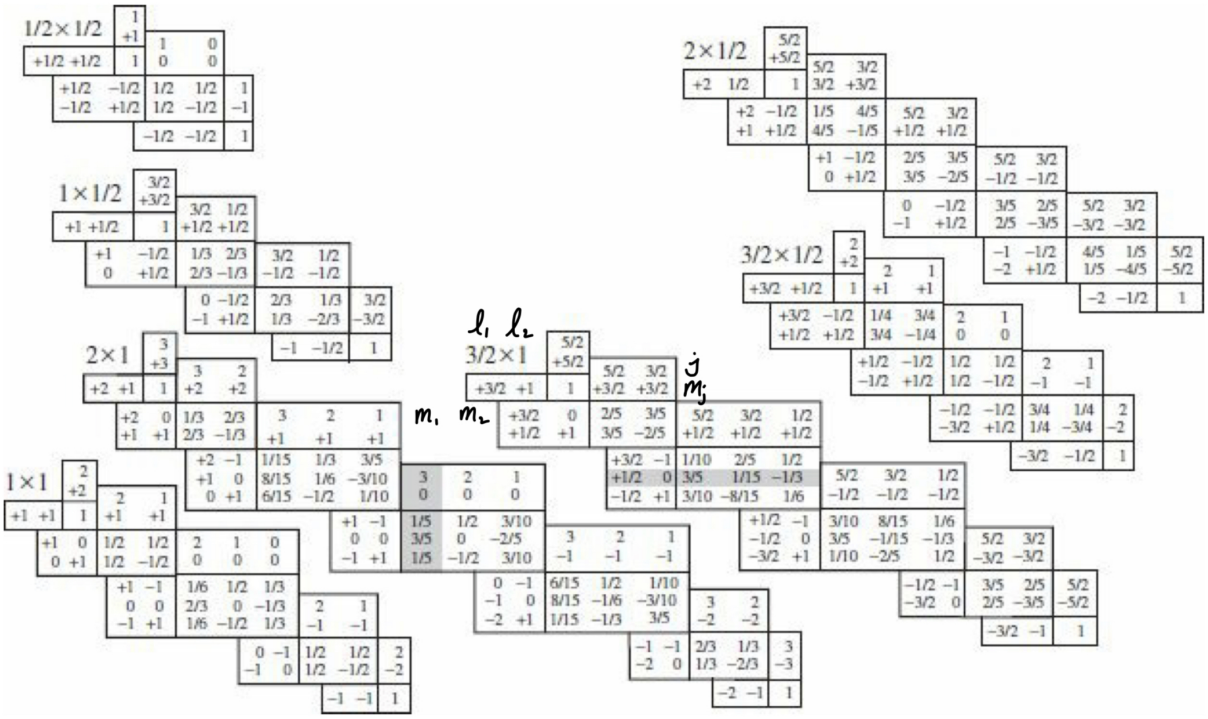


Figure 3: Clebsch-Gordan coefficients

5 Time-dependent Systems

Consider quantum systems whose Hamiltonian may be time-dependent. For most systems, the Hamiltonian consists of a solvable time-independent H^0 and a time-dependent $H'(t)$.

$$H(t) = H^0 + H'(t)$$

When $H'(t)$ is weak compared to H^0, we may resort to time-dependent perturbation theory. Consider H^0 with eigenstates ψ_a, ψ_b and energy E_a, E_b. For an arbitrary state,

$$|\psi\rangle = \sum c_n |n\rangle$$

The time-evolution of a state under $H^0 + H'(t)$ is

$$|\psi(t)\rangle = \sum c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle \tag{5.1}$$

In general, $c_n(t)$ are time-dependent and only constantly 1 when $\partial_t H'(t) = 0$. The probability of finding state in $|n\rangle$ at time t is $|c_n(t)|^2$, which are subject to normalization

$$\sum |c_n(t)|^2 = 1$$

Consider the Schrödinger equation for this system

$$\partial_t |\psi(t)\rangle = -\frac{i}{\hbar}\left[H^0 + H'(t)\right] |\psi(t)\rangle \tag{5.2}$$

Substituting equation 5.1 yields

$$i\hbar\partial_t \left[\sum c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle\right] = \left[H^0 + H'(t)\right] \left[\sum c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle\right]$$

Expanding the left hand side (we suppress summation to avoid clutter)

$$i\hbar\partial_t \left[c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle\right] = i\hbar\dot{c}_n \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle + E_n c_n \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle$$

On the right hand side, the first term cancels with the last term on the left hand side above

$$H^0 \left[c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle\right] = E_n c_n \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle$$

The equation we're left with cannot be directly isolated component-wise for n because $H'(t)$ is not generally diagonal.

$$\sum_n H'(t) c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle = \sum_n i\hbar\dot{c}_n \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle \tag{5.3}$$

To isolate $\dot{c}_m$, apply $\langle m|$ and denote the matrix element $H'_{mn}(t) = \langle m|H'(t)|n\rangle$.

$$\sum_n H'_{mn} \exp\left(-\frac{i}{\hbar} E_n t\right) c_n = i\hbar\dot{c}_m \exp\left(-\frac{i}{\hbar} E_m t\right)$$

Let $\omega_{nm} = (E_n - E_m)/\hbar$, the Schrodinger equation 5.2 may be rewritten exactly as a system of n coupled first-order differential equations

$$\dot{c}_n(t) = -\frac{i}{\hbar} \sum_m H'_{nm}(t) \exp\left(i\omega_{nm} t\right) c_m(t) \tag{5.4}$$

5.1 Interaction Picture

The following section is adapted from these lecture notes from MIT. We may rephrase the derivation in the previous section more concisely in terms of the interaction picture. We adopt a frame in which the energy eigenstates of H^0, as they would normally evolve, remains constant. Formally, consider the transform

$$|\tilde{\psi}(t)\rangle = U(t)^\dagger |\psi(t)\rangle, \quad U(t) \ = \exp\left(-\frac{i}{\hbar}H^0 t\right)$$

Note that $[H^0, U(t)] = 0$, the Schrodinger equation transforms accordingly. We use the subscript to denote time variable to reduce clutter:

$$\begin{aligned}
\partial_t|\tilde{\psi}_t\rangle &= \partial_t\left(U_t^\dagger|\psi_t\rangle\right) = \frac{i}{\hbar}H^0|\tilde{\psi}_t\rangle + U_t^\dagger\left(\partial_t|\psi_t\rangle\right) \\
&= \frac{i}{\hbar}H^0|\tilde{\psi}_t\rangle - U_t^\dagger\left[\frac{i}{\hbar}(H^0 + H'_t)|\psi_t\rangle\right] \\
&= \frac{i}{\hbar}H^0|\tilde{\psi}_t\rangle - \frac{i}{\hbar}\left(U_t^\dagger H^0 U_t\right)\left(U_t^\dagger|\psi_t\rangle\right) - \frac{i}{\hbar}\left(U_t^\dagger H'_t U_t\right)\left(U_t^\dagger|\psi_t\rangle\right) \\
&= -\frac{i}{\hbar}\left(U_t^\dagger H'_t U_t\right)U_t^\dagger|\psi_t\rangle = -\frac{i}{\hbar}\tilde{H}'_t|\tilde{\psi}_t\rangle
\end{aligned} \tag{5.5}$$

This frame change eliminates H^0 and leaves only $\tilde{H}'_t = U_t^\dagger H'_t U_t$. Let $\{c_j(t)\}$ the expansion of the ket in our new frame with respect to the eigenbasis $|\psi_n\rangle$ of H^0

$$|\tilde{\psi}_t\rangle = \sum c_n(t)|\psi_n\rangle$$

These are exactly the de-wiggled coefficients we have introduced in the previous section. We can recover the evolution of the ket in our original frame by $|\psi_t\rangle = U_t|\tilde{\psi}_t\rangle$ by U_t, which is diagonal in this eigenbasis

$$|\psi_t\rangle = U_t\sum c_n(t)|\psi_n\rangle = \sum e^{-iE_n t/\hbar}c_n(t)|\psi_n\rangle$$

In terms of this concrete basis, the Schrodinger equation 5.5 reads

$$\dot{\tilde{c}}_n(t) = \langle\psi_n|\left(\partial_t|\tilde{\psi}_t\rangle\right) = -\frac{i}{\hbar}\sum_m \tilde{c}_m(t)\langle\psi_n|\tilde{H}'_t|\psi_m\rangle$$

We can simplify the matrix element by noting that

$$\langle\psi_n|\tilde{H}'_t|\psi_m\rangle = \langle\psi_n|e^{iH^0 t/\hbar}H'_t e^{-iH^0 t/\hbar}|\psi_m\rangle = e^{i(E_n - E_m)t/\hbar}H'_{nm}(t)$$

This leaves us equation 5.4.

5.2 Time-Dependent Perturbation Theory

So far everything is exact. To obtain a perturbative solution, introduce λ and assume that $|\tilde{\psi}_t\rangle$ can be expanded in λ:

$$\begin{aligned} H_t &= H^0 + \lambda H'_t \\ |\tilde{\psi}_t\rangle &= |\tilde{\psi}^0_t\rangle + \lambda|\tilde{\psi}^1_t\rangle + \lambda^2|\tilde{\psi}^2_t\rangle + \cdots \\ \partial_t|\tilde{\psi}_t\rangle &= -\frac{i}{\hbar}\lambda\tilde{H}'_t|\tilde{\psi}_t\rangle \end{aligned}$$

Equating by powers of λ, the time-derivative of n-th component is coupled to H'_t acting on $(n-1)$-th component.

$$\begin{aligned} \partial_t|\tilde{\psi}^0_t\rangle &= 0 \\ \partial_t|\tilde{\psi}^1_t\rangle &= -\frac{i}{\hbar}\tilde{H}'_t|\psi^0_t\rangle \\ \vdots \quad &= \quad \vdots \\ \partial_t|\tilde{\psi}^{n+1}_t\rangle &= -\frac{i}{\hbar}\tilde{H}'_t|\psi^n_t\rangle \end{aligned} \tag{5.6}$$

Our interacting picture transform degenerates to the identity at $t = 0$. Equating the power series approximation, which holds for all λ, yields the initial conditions

$$\begin{aligned} |\psi_0\rangle &= |\tilde{\psi}^0_0\rangle + \lambda|\tilde{\psi}^1_0\rangle + \cdots \\ |\tilde{\psi}^0_0\rangle &= |\tilde{\psi}^0_t\rangle = |\psi_0\rangle \\ |\tilde{\psi}^n_\sim\rangle &= 0, \quad n > 0 \end{aligned} \tag{5.7}$$

An initial state $|\psi_0\rangle$ gives us the constant $(n = 0)$-th order solutions $|\tilde{\psi}^0_t\rangle$. in the transformed frame, $|\tilde{\psi}_0\rangle$ is constant, i.e. the zeroth order solution evolves only according to H^0. Using the zero initial condition, The following terms in equation 5.6 is solved by succesive integration.

$$\begin{aligned} |\tilde{\psi}^1_t\rangle &= -\frac{i}{\hbar}\int_0^t H'_{t'}|\psi^0_{t'}\rangle\, dt' \\ |\tilde{\psi}^2_t\rangle &= -\frac{i}{\hbar}\int_0^t H'_{t'}|\psi^1_{t'}\rangle\, dt' = -\frac{i}{\hbar}\int_0^t H'_{t'}\left(-\frac{i}{\hbar}\int_0^{t'} H'_{t''}|\psi^0_{t''}\rangle\, dt''\right) dt' \\ &= -\frac{1}{\hbar^2}\int_0^t H'_{t'}\int_0^{t'} H'_{t''}|\psi^0_{t''}\rangle\, dt''\, dt' \\ |\tilde{\psi}^3_t\rangle &= -\frac{i}{\hbar}\int_0^t H'_{t'}|\psi^2_{t'}\rangle\, dt' = \cdots \end{aligned} \tag{5.8}$$

In concrete terms, consider an initial state $|\psi_0\rangle$. We first consider the Fourier expansion of a ket $|\tilde{\psi}_t\rangle$ in the transformed frame in terms of the eigenstates of H^0.

$$|\tilde{\psi}_t\rangle = \sum_k |\tilde{\psi}^k_t\rangle = \sum_{k,j} \tilde{c}^k_j(t)|j\rangle$$

They are related to the Fourier expansion of $|\psi_t\rangle$ in the original frame via

$$\tilde{c}_j^k(t) = \exp\left(-\frac{i}{\hbar}E_j t\right) c_j^k(t)$$

In concrete components, the zeroth order correction is the constant initial condition.

$$|\tilde{\psi}_t^0\rangle = \sum \tilde{c}_j^0(t)|j\rangle = \sum \exp\left(-\frac{i}{\hbar}E_j t\right) c_j^0|j\rangle$$
$$|\psi_t^0\rangle = \exp\left(\frac{i}{\hbar}H^0 t\right)|\tilde{\psi}_0\rangle = |\psi_0\rangle$$

Introduce $\omega_{kj} = \exp(i(E_k - E_j)/\hbar)$, the first-order components read

$$\begin{aligned}
\tilde{c}_k^1(t) = \langle k|\tilde{\psi}_t^1\rangle &= -\frac{i}{\hbar}\langle k|\int_0^t H'_{t'}\sum \exp\left(-\frac{i}{\hbar}E_j t\right) c_j^0|j\rangle\, dt' \\
&= -\frac{i}{\hbar}\sum_j \int_0^t \langle k|H'_{t'}|j\rangle \exp\left(-\frac{i}{\hbar}E_j t\right) c_j^0\, dt' \\
c_k^1 &= -\exp\left(\frac{i}{\hbar}E_k t\right)\tilde{c}_k^1(t) \\
&= -\exp\left(\frac{i}{\hbar}E_k t\right)\frac{i}{\hbar}\sum_j \int_0^t \langle k|H'_{t'}|j\rangle \exp\left(-\frac{i}{\hbar}E_j t\right) c_j^0\, dt' \\
&= -\frac{i}{\hbar}\sum_j c_j(0)\int_0^t \langle k|H'_{t'}|j\rangle \exp(i\omega_{kj})\, dt'
\end{aligned}$$

The second-order components read

$$\begin{aligned}
\tilde{c}_k^2(t) = \langle k|\tilde{\psi}_t^2\rangle &= -\frac{1}{\hbar^2}\int_0^t \langle k|H'_{t'}\int_0^{t'} H'_{t''}|\psi_{t''}^0\rangle\, dt''\, dt' \\
&= -\frac{1}{\hbar^2}\sum_j \int_0^t \langle k|H'_{t'}|j\rangle \int_0^{t'} \langle j|H'_{t''}|\psi_{t''}^0\rangle\, dt''\, dt' \\
&= -\frac{1}{\hbar^2}\sum_{j,l} \int_0^t \langle k|H'_{t'}|j\rangle \int_0^{t'} \langle j|H'_{t''}\exp\left(-\frac{i}{\hbar}E_l t\right) c_l^0|l\rangle\, dt''\, dt' \\
c_k^2(t) &= -\exp\left(\frac{i}{\hbar}E_k t\right)\tilde{c}_k^2(t) \\
&= -\frac{1}{\hbar^2}\sum_{j,l} \int_0^t \exp\left(\frac{i}{\hbar}(E_k - E_j + E_j)t\right)\langle k|H'_{t'}|j\rangle \int_0^{t'} \exp\langle j|H'_{t''}\exp\left(-\frac{i}{\hbar}E_l t\right) c_l^0|l\rangle\, dt''\, dt' \\
&= -\frac{1}{\hbar^2}\sum_{j,l} c_l(0)\int_0^t \exp(i\omega_{kj}t)\langle k|H'_{t'}|j\rangle \int_0^{t'} \exp(i\omega_{jl}t)\langle j|H'_{t''}|l\rangle\, dt''\, dt'
\end{aligned}$$

Taken together and let $H'_{ab}(t) = \langle a|H'(t)|b\rangle$, the second-order approximation is

$$\begin{aligned} c_k(0) &- \frac{i}{\hbar}\sum_j c_j(0)\int_0^t H'_{kj}(t')\exp(i\omega_{kj}t)\,dt' \\ &- \frac{1}{\hbar^2}\sum_{j,l} c_l(0)\int_0^t \exp(i\omega_{kj}t)H'_{kj}(t')\int_0^{t'}\exp(i\omega_{jl}t)H'_{jl}(t'')\,dt''\,dt' \end{aligned} \tag{5.9}$$

Griffiths forgoes the polynomial picture altogether. Substitute $c_m(t) = c_m(0)$ into the right hand side of equation 5.4 to obtain the first order coefficients (not corrections)

$$c_n^{(1)}(t) = c_n(0) - \frac{i}{\hbar}\sum_m c_m(0)\int_0^t H'_{nm}(t')\exp(i\omega_{nm}t')\,dt' \tag{5.10}$$

For the second-order, substitute $c_m(t)$ in equation 5.10 into 5.4.

We wish to emphasize the theme of polynomial approximation in perturbation theory, even in time-dependent systems. We start by introducing a tilde frame which eliminates H^0 and assuming that time-evolution in this frame is expandable in succesive powers of λ. In this frame, the zeroth order solution is constant, and higher-order corrections are coupled to the perturbative action of H' on the immediately lower order. We switch back to the original frame after performing the polynomial approximation.

5.3 Sinusoidal Perturbations

Consider a two-level system with sinusoidal perturbation

$$\begin{aligned} H'(r,t) &= V(r)\cos\omega t \\ H'_{ab}(t) &= \langle\psi_a|V|\psi_b\rangle\cos\omega t = V_{ab}\cos\omega t \end{aligned} \tag{5.11}$$

Assuming initial level a and that diagonal matrix elements vanish, to the first order in 5.9

$$\begin{aligned} c_b(t) &= -\frac{i}{\hbar}V_{ba}\int_0^t \cos\omega t\exp(i\omega_{ba}t)\,dt' \\ &= -\frac{iV_{ba}}{2\hbar}\int_0^t \left[\exp(i(\omega_0+\omega)t') + \exp(i(\omega_0-\omega)t')\right]\,dt' \\ &= -\frac{V_{ba}}{2\hbar}\left[\frac{\exp(i(\omega_0+\omega)t)-1}{\omega_0+\omega} + \frac{\exp(i(\omega_0-\omega)t)-1}{\omega_0-\omega}\right] \end{aligned}$$

Far-detuned frequency have negligible transition rates. Assuming $\omega_0+\omega \gg |\omega_0-\omega|$. Drop the first term. Let $\Delta_\omega = \omega_0 - \omega$

$$\begin{aligned} c_b(t) &\approx -\frac{V_{ba}}{2\hbar}\frac{\exp(i\Delta_\omega t/2)}{\Delta_\omega}\left[\exp(i\Delta_\omega t/2) - \exp(-i\Delta_\omega t/2)\right] \\ &= -i\frac{V_{ba}}{\hbar}\frac{\sin(\Delta_\omega t/2)}{\Delta_\omega}e^{i\Delta_\omega t/2} \end{aligned}$$

The following transition probability should be trusted for $\omega_0 + \omega \gg |\omega_0 - \omega|$ and relatively small probability. The most significant feature is flopping.

$$P_{a\to b}(t) \approx \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2(\Delta_\omega t/2)}{\Delta_\omega^2} \tag{5.12}$$

5.4 Rabi Flopping

Sinusoidal perturbation may be solved exactly if we begin by approximating

$$H'(r,t) = V(r)\cos(\omega t) \to \frac{V}{2} e^{-i\omega t}$$

Here, we ignore the $e^{i\omega t}$ earlier: in the Hamiltonian instead of as a perturbed term. The perturbation under this approximation is not Hermitian, but it allows us to solve equation 5.4. Again, consider a two-level system with $\omega_0 = (E_b - E_a)/\hbar > 0$ starting out in state a, then

$$\dot{c}_a(t) = -\frac{i}{\hbar} H'_{ab}(t) e^{-i\omega_0 t} c_b(t), \quad \dot{c}_b(t) = -\frac{i}{\hbar} H'_{ba}(t) e^{i\omega_0 t} c_a(t)$$

We assume again that diagonal matrix elements vanish. Take another derivative of the equations above to uncouple c_a, c_b.

5.5 Interaction with EM waves

Consider a monochromatic electromagnetic wave incident upon a hydrogenic atom. When its wavelength is long compared to the Bohr radius, to the first order of this ratio, the atom effectively acts as a dipole within a sinusoidally oscillating electric field:

$$H' = -qE_0 z \cos\omega t$$

Then the matrix element for the perturbation reads

$$H'_{ba}(t) = -q\langle\psi_b|z|\psi_a\rangle E_0 \cos\omega t$$

5.5.1 Absorption, Stimulated Emission

The selection rule for spatial components dictate $\Delta l = \pm 1$, so diagonal matrix elements for H' always vanish. Equivalently, note that $z|\psi|^2$ is odd in z. Then the problem is as in 5.11 with $V_{ba} = -q\langle\psi_b|z|\psi_a\rangle E_0$. Substitution into equation 5.12 yields

$$P_{a\to b}(t) = P_{b\to a}(t) = \left(\frac{q\langle\psi_a|z|\psi_b\rangle E_0}{\hbar}\right)^2 \frac{\sin^2(\Delta_\omega t/2)}{\Delta_\omega^2} \tag{5.13}$$

Equal absorption and stimulation probability is by the first-order formula 5.10:

$$H'_{nm} = \overline{H'_{mn}}, \quad \omega_{nm} = -\omega_{mn}$$

The transition probability $P_{a\to b}(t) = |c_b(t)|^2$, computed with initial conditions $c_n(0) = \delta_{na}$.

5.5.2 Spontaneous Emission

We first generalize the perturbation result from a monochromatic, polarized, single-frequency electromagnetic wave to the general case. Recall the energy density of electromagnetic wave

$$u = \frac{\epsilon_0}{2} E_0^2$$

Substitute E_0 with this equation into equation 5.13 yields, for $V_{ab} = q\langle\psi_a|z|\psi_b\rangle$

$$P_{b\to a}(t) = \frac{2u|V_{ab}|^2}{\epsilon_0\hbar^2} \cdot \frac{\sin^2(\Delta_\omega t/2)}{\Delta_\omega^2}$$

Let $du = \rho(\omega)\, d\omega$ denote some distribution of energy-frequency density. When the different components are phase-decorrelated (incoherent), we can conveniently perform the integral over the probability instead of the amplitude, yielding

$$P_{b\to a}(t) = \frac{2|V_{ab}|^2}{\epsilon_0\hbar^2} \int_0^\infty d\omega\, \rho(\omega) \left[\frac{\sin^2(\Delta_\omega t/2)}{\Delta_\omega^2}\right]$$

The bracket term is sharply peaked about $\omega = \omega_0$. We pull $\rho(\omega)$ outside the integral

$$P_{b\to a}(t) \approx \frac{2|V_{ab}|^2}{\epsilon_0\hbar^2}\rho(\omega_0) \int_0^\infty d\omega\, \left[\frac{\sin^2(\Delta_\omega t/2)}{\Delta_\omega^2}\right] = \frac{\pi|V_{ab}|^2}{\epsilon_0\hbar^2}\rho(\omega_0)t$$

Note that integrating over an incoherent frequency spectrum gets rid of the flopping.

Definition 5.1 (*transition rate*). The transition rate between two levels is defined as

$$R_{b\to a} = \partial_t P_{b\to a}$$

The transition rate between two levels in an incoherent spectrum $\rho(\omega)$ with uniform polarization and direction is

$$R_{b\to a} = \frac{\pi}{\epsilon_0\hbar^2}|V_{ab}|^2\rho(\omega_0)$$

Averaging over all propagation and polarization directions introduces a factor of $1/3$ and $z \mapsto \mathbf{r}$ since we are not restricted to the z direction.

$$R_{b\to a} = \frac{\pi}{3\epsilon_0\hbar^2} q^2 |\langle\psi_a|\mathbf{r}|\psi_b\rangle|^2 \rho(\omega_0) = B\rho(\omega_0), \qquad B = \frac{\pi q^2 |\langle\psi_b|\mathbf{r}|\psi_a\rangle|^2}{3\epsilon_0\hbar^2}$$

Denote by A the rate of particles leaving the higher energy level B by spontaneous emission.

$$\begin{aligned} d_t N_b &= -N_b A - N_b R_{b\to a} + N_a R_{a\to b} \\ &= -N_b A - N_b B\rho(\omega_0) + N_a B\rho(\omega_0) \end{aligned}$$

In thermal equilibrium $d_t N_b = 0$, $N_a/N_b = \exp(\hbar\omega_0/k_B T)$. Planck radiation formula gives

$$\rho(\omega_0) = \frac{A}{(N_a/N_b - 1)B} = \frac{A}{(e^{\hbar\omega_0/\tau} - 1)B} = \frac{\hbar\omega_0^3}{\pi^2 c^3 (e^{\hbar\omega/\tau} - 1)}$$

This gives us the spontaneous emission coefficient

$$A = \frac{\omega_0^3 q^2 |\langle \psi_b | \mathbf{r} | \psi_a \rangle|^2}{3\pi\epsilon_0 \hbar c^3}$$

Assuming only spontaneous emission along decay modes with rate coefficients $A_1, A_2, \cdots$ and no replenishing mechanism, the population obeys

$$dN = -\left(\sum A_n\right) N\, dt \implies N(t) = N(0)\exp\left(-\frac{t}{\tau}\right), \quad \tau = \left(\sum A_n\right)^{-1}$$

Here τ is the state's lifetime. Recall the selection rules: matrix elements for a vector $\mathbf{r}$ obeys

$$\begin{aligned} \Delta l = \pm 1, \qquad \Delta m = 0, \pm 1, \quad \text{for any component} \\ \Delta m = 0 \implies \langle n'l'm|x|nlm\rangle = \langle n'l'm|y|nlm\rangle = 0 \\ m' = m \pm 1 \implies \langle n'l'm'|x|nlm\rangle = \pm i\langle n'l'm|y|nlm\rangle = 0, \langle n'l'm'|z|nlm\rangle = 0 \end{aligned}$$

These rules (Griffiths 11.76) are very handy when evaluating transitions rates.

5.6 Bound to Continuum Transitions

We can discretize a continuous energy spectrum by confining the system in a box of size L, use periodic (or impenetratable, the former is usually more convenient) boundary conditions to obtain a discrete spectrum, then take the limit as $L \to \infty$. This gives us the state density $\rho(E)$ with respect to energy. We consider a system, under sinusoidal perturbation, transitioning from a bound state to a continuum state with an energy in finite range ΔE about E_f. Integrating equation 5.12 yields

$$P_{a\to(E_b,\Delta E)}(t) = \int_{E_b-\Delta E/2}^{E_b+\Delta E/2} \frac{|V_{ab}|^2}{\hbar^2}\left[\frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}\right]\rho(E)\, dE$$

Here $\omega_0(E) = (E - E_a)/\hbar$, and $\rho(E)\, dE$ is the number of states of between $E, E + dE$. The bracket quantity is sharply peaked about $E = E_f$ with width $4\pi\hbar/t$. For $t \gg 1$, approximate by pulling $\rho(E)$ out of the integral, which we also extend to infinity

$$P_{a\to E_b}(t \to \infty) = \frac{\pi}{2\hbar}|V_{ab}|^2\rho(E_b)t$$

The transition rate in this limit is known as Fermi's Golden Rule (sinusoidal perturbations)

$$R_{a\to b} = \frac{\pi}{2\hbar}|V_{ab}|^2\rho(E_b) \tag{5.14}$$

Recall that $H'(r,t) = V(r)\cos(\omega t)$ and $V_{ab} = \langle \psi_a | V(r) | \psi_b \rangle$.

5.7 Adiabatic theorem

The reference for this section is Weinberg, *Lectures on Quantum Mechanics, VI.6.*

We consider a parameterized family of Hamiltonians H_s, where s is a slowly varying function $s(t)$ of time. By Hermiticity, H_s is diagonalizable for every s. Given a smooth path s with subscript 0 denote the initial condition $t = 0$, we can track how the eigenbasis $\{|n_s\}$ of H_s smoothly varies with $s(t)$ via a parameterized unitary $U(s)$ such that

$$|n_s\rangle = U(s)|n_0\rangle \implies U_s = \sum_n |n_s\rangle\langle n_0|, \quad U(s_0) = \mathrm{Id}$$

Consider a frame change parameterized by $U(t)$

$$\tilde{H}_s = U_s^\dagger H_s U_s$$

In this frame, the eigenvectors of $\tilde{H}_s$ are constant. Only eigenvalue dependence on s remains

$$\tilde{H}_s|n_0\rangle = U_s^\dagger H_s|n_s\rangle = E_n(s)U_s^\dagger|n_s\rangle = E_n(s)|n_0\rangle$$

Consider the corresponding state transformation (we now suppress $|n_0\rangle = |n\rangle$)

$$|\tilde{\psi}(t)\rangle = U_s^\dagger|\psi(t)\rangle$$

The Schrödinger equation transforms as

$$\begin{aligned}
\partial_t|\tilde{\psi}(t)\rangle &= \left(\partial_t U^\dagger_{s(t)}\right)|\psi(t)\rangle + U_s^\dagger\left(\partial_t|\psi(t)\rangle\right) \\
&= \left(\partial_t U^\dagger_{s(t)}\right)|\psi(t)\rangle + U_s^\dagger\left(-\frac{i}{\hbar}H_s|\psi(t)\right) \\
&= \left(\partial_t U^\dagger_{s(t)}\right)U_s|\tilde{\psi}(t)\rangle - \frac{i}{\hbar}\tilde{H}_s|\tilde{\psi}(t)\rangle \\
&= -\frac{i}{\hbar}\left[\tilde{H}_{s(t)} + \Delta(t)\right]|\tilde{\psi}(t)\rangle
\end{aligned}$$

This looks like the "normal" time-evolution of the frame-shifted state under the frame-shifted Hamiltonian, with an additional term

$$\Delta(t) = i\hbar\left(\partial_t U_{s(t)}\right)^\dagger U_s$$

We introduce another coordinate transform parameterized by the unitary operator $V(t)$ well-defined by the following differential equation, for $-i\tilde{H}_{s(t)}$ correctly skew-Hermitian:

$$\partial_t V(t) = -\frac{i}{\hbar}\tilde{H}_{s(t)}V(t)$$

In the eigenbasis $\{|n_0\rangle\}$ for $\tilde{H}_{s(t)}$ (and also for $H_{s(0)}$) the solution is explicit.

$$\langle n|V(t)|m\rangle = \delta_{nm}\exp\left(-\frac{i}{\hbar}\int_0^t E_n(s(t'))\,dt'\right) = \delta_{nm}\exp\left(i\phi_n(t)\right)$$

Here $\phi_n(t)$ is called the dynamical phse

$$\phi_n(t) = -\frac{1}{\hbar}\int_0^t E_n(s(t'))\,dt'$$

This frame further eliminates dependence on $\tilde{H}_{s(t)}$. Define the transforms

$$|\bar{\psi}_t\rangle = V(t)^\dagger|\tilde{\psi}(t)\rangle = V(t)^\dagger U_s^\dagger|\psi(t)\rangle$$
$$\bar{\Delta}(t) = V(t)^\dagger\Delta(t)V(t)$$

$\tilde{H}_{s(t)}$ and $V(t)$ shares an eigenbasis. Only $\bar{\Delta}(t)$ remains in the Schrödinger equation:

$$\begin{aligned}\partial_t|\bar{\psi}(t)\rangle &= \left(\partial_t V(t)^\dagger\right)|\tilde{\psi}(t)\rangle + V(t)^\dagger\partial_t|\tilde{\psi}(t)\rangle \\ &= \frac{i}{\hbar}\tilde{H}_{s(t)}V(t)^\dagger|\tilde{\psi}(t)\rangle - \frac{i}{\hbar}V(t)^\dagger\left[\tilde{H}_{s(t)}+\Delta(t)\right]|\tilde{\psi}(t)\rangle \\ &= -\frac{i}{\hbar}V(t)^\dagger\Delta(t)|\tilde{\psi}(t)\rangle = -\frac{i}{\hbar}\bar{\Delta}(t)|\bar{\psi}(t)\rangle\end{aligned}$$

Consider the matrix elements of $\overline{\Delta}_{nm}(t)$ under its eigenbasis $\{|n\rangle\}$

$$\begin{aligned}\langle n|\bar{\Delta}(t)|m\rangle &= \langle n|V(t)^\dagger\Delta(t)V(t)|m\rangle = \exp\left(i[\phi_m(t)-\phi_n(t)]\right)\langle n|\Delta(t)|m\rangle \\ &= \langle n|\Delta(t)|m\rangle\exp\left[\frac{i}{\hbar}\int_0^t dt'\,E_n(s(t'))-E_m(s(t'))\right]\end{aligned}$$

In the absence of degeneracy, when the rate of change of $s(t)$ is very small compared to $|E_n(s)-E_m(s)|/\hbar$, any duration that is significant with respect to $\Delta s(t)$ will cause the phase factor to oscillate many times. The only components of $\bar{\Delta}(t)$ which consistently contribute are the diagonal elements, by which

$$\begin{aligned}\bar{\Delta}(t) &= \sum_n\langle n|\bar{\Delta}(t)|n\rangle\,|n\rangle\langle n| = \sum_n\langle n|\Delta(t)|n\rangle\,|n\rangle\langle n| \\ &= \sum_n\langle n|\left[i\hbar\left(\partial_t U_{s(t)}\right)^\dagger U_s\right]|n\rangle\,|n\rangle\langle n| \\ &= i\hbar\sum_n\left(\partial_t\langle n_s|\right)|n_s\rangle\,|n\rangle\langle n| \\ &= \sum\rho_n(t)|n\rangle\langle n|, \quad \rho_n(t) = i\hbar\left(\partial_t\langle n_s|\right)|n_s\rangle\end{aligned}$$

The Schrodinger equation in the bar frame solves to

$$|\bar{\psi}(t)\rangle = \sum_n\exp(i\gamma_n(t))\langle n|\bar{\psi}_0\rangle|n\rangle = \sum_n\exp(i\gamma_n(t))\langle n|\psi_0\rangle|n\rangle$$

In particular, note that $|\bar{\psi}(0)\rangle = |\psi(0)\rangle$ since both transforms are trivial at $t=0$. Here $\gamma_n(t)$ denotes the Berry phase

$$\gamma_n(t) = -\frac{1}{\hbar}\int_0^t\rho_n(t')\,dt'$$

Change back to the original frame, here $V(t)$ introduces $\phi_n(t)$ and U_s effects $|n\rangle \mapsto |n_s\rangle$.

$$\begin{aligned}|\psi(t)\rangle &= U_{s(t)}V(t)|\bar{\psi}(t)\rangle \\ &= \sum_n \exp(i\gamma_n(t))\exp(i\phi_n(t))\langle n|\bar{\psi}_0\rangle|n_s\rangle\end{aligned}$$

Apart from the dynamic and Berry phases $\phi_n(t), \gamma_n(t)$, the adiabatic approximation says that eigenstates vary smoothly with time.

6 WKB Approximation

The WKB approximation is a semiclassical approximation for an eigenstate when the rate of change of the potential is much smaller than the oscillation frequency (momentum) of the eigenstate. Consider the one-dimensional Schrodinger equation again

$$-\frac{\hbar^2}{2m}\partial_x^2\psi(x) + V(x)\psi(x) = E\psi(x)$$

Let $p(x) \equiv \sqrt{2m[E - V(x)]}$, this may be rewritten as

$$\partial_x^2\psi = -\frac{p^2}{\hbar^2}\psi \tag{6.1}$$

Substitute the following solution expression, for A and ϕ real functions:

$$\psi(x) = A(x)\exp[i\phi(x)]$$

Calculate the first and second order derivatives

$$\begin{aligned}\partial_x\psi &= (A' + i\phi')\exp(i\phi)\\ \partial_x^2\psi &= \left[A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2\right]\exp(i\phi)\end{aligned}$$

Substitute into the Schrodinger equation 6.1, we have

$$A'' + 2iA'\phi' + ia\phi'' - A(\phi')^2 = -\frac{p^2}{\hbar^2}A$$

Separate into real and imaginary components:

$$\begin{aligned}A'' - A(\phi')^2 = -\frac{p^2}{\hbar^2}A \iff A'' = A\left[(\phi')^2 - \frac{p^2}{\hbar^2}\right]\\ 2A'(x)\phi'(x) + A(x)\phi''(x) = 0 \iff \partial_x\left(A^2(x)\phi'(x)\right) = 0\end{aligned} \tag{6.2}$$

The second equation implies that $A^2(x)$ is constant, let $\alpha = A^2(x)\phi'(x) \in \mathbb{R}$. Then

$$A(x) = \frac{\alpha}{\sqrt{\phi'(x)}}$$

We're left with solving the real equation with only ϕ. Note that when $V(x)$ is constant, we have the free-particle solution

$$\psi(x) = A\exp\left(\frac{i}{\hbar}px\right), \quad \phi(x) = \frac{1}{\hbar}px$$

WKB makes the following power series expansion of $\phi(x)$ (S_0 has units of action). The variable is in $\hbar^2$ due to $\hbar^2/2m$ term in Schrodinger equation.

$$\phi(x) = \frac{1}{\hbar}\sum_{n=0}^{\infty}\hbar^{2n}S_n(x) = \frac{1}{\hbar}S_0(x) + \hbar S_1(x) + \hbar^3 S_2(x) + \cdots$$

Substitute this into the first equation in 6.2 and equate by powers of $\hbar$. Taking the first term

$$\phi'(x) = \frac{1}{\hbar} S_0'(x) + \hbar S_1'(x)$$
$$A(x) = \frac{\alpha}{\sqrt{\frac{1}{\hbar} S_0'(x) + \hbar S_1'(x)}}$$

Equate in powers of $\hbar$. The first equation in 6.2 is linear in A. The zeroth-order of $\hbar$ becomes

$$\frac{1}{2m} S_0'^2(x) = E - V(x)$$
$$S_0(x) = \pm \int dx\, p(x)$$

The WKB approximation takes this order, the integration bound can arbitrarily chosen for convenience since constants are absorbed into α¿

$$\psi_{\text{WKB}}(x) = \begin{cases} \dfrac{\alpha}{p(x)} \exp\left(\pm \dfrac{i}{\hbar} \displaystyle\int^x dx\, p(x)\right) & p(x) = \sqrt{2m[E - V(x)]} > 0 \\ \dfrac{\alpha}{|p(x)|} \exp\left(\pm \dfrac{1}{\hbar} \displaystyle\int^x |p(x)|\, dx\right) & E < V(x) \end{cases} \tag{6.3}$$

This is equivalent to solving for equation 6.2 with $A'' = 0$. Note that the amplitude scales inversely with classical momentum (velocity) at a point

$$|\psi(x)|^2 \approx \frac{|C|^2}{p(x)}$$

We may approximate the accuracy by plugging this back into the two sides of the Schrodinger equation and noting the differences. It turns out to be the ratio between the characteristic wavelength of the wavefunction versus the potential's rate of change.

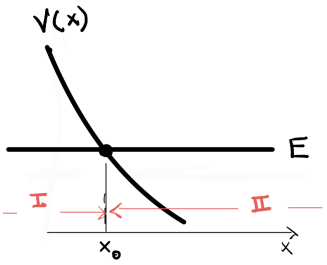
$$\frac{|m\hbar V'(x)|}{p(x)^3} \ll 1$$

The denominator blows up at turning points $E = V(x)$. We can solve for regions around turning points with analytic solutions to a linear approximating potential (airy functions), then patch up with WKB approximations.

6.1 Connection formulas

Assume that there is a classical turning point at x_0

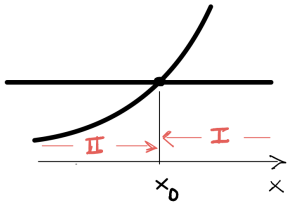
I) When $E > V(x)$ for $x > x_0$



$$\psi(x) = \frac{A}{\sqrt{k_1(x)}} \exp\left(-\int_x^{x_0} dx' \, k_1(x')\right) \longrightarrow \psi(x) = \frac{2A}{\sqrt{k_2(x)}} \cos\left(\int_{x_0}^{x} dx' \, k_2(x') - \frac{\pi}{4}\right) \quad \text{(I)}$$

$$\psi(x) = \frac{A \sin\eta}{\sqrt{k_1(x)}} \exp\left(+\int_x^{x_0} dx' \, k_1(x')\right) \longleftarrow \psi(x) = \frac{A}{\sqrt{k_2(x)}} \cos\left(\int_{x_0}^{x} dx' \, k_2(x') - \frac{\pi}{4} + \eta\right) \quad \text{(II)}$$

II) When $E < V(x)$ for $x > x_0$



$$\psi(x) = \frac{2A}{\sqrt{k_2(x)}} \cos\left(\int_x^{x_0} dx' \, k_2(x') - \frac{\pi}{4}\right) \longleftarrow \psi(x) = \frac{A}{\sqrt{k_1(x)}} \exp\left(-\int_{x_0}^{x} dx' \, k_1(x')\right) \quad \text{(I)}$$

$$\psi(x) = \frac{A}{\sqrt{k_2(x)}} \cos\left(\int_x^{x_0} dx' \, k_2(x') - \frac{\pi}{4} + \eta\right) \longrightarrow \psi(x) = \frac{A \sin\eta}{\sqrt{k_1(x)}} \exp\left(+\int_{x_0}^{x} dx' \, k_1(x')\right) \quad \text{(II)}$$

6.2 Tunneling

Consider scattering across rectangular barrier at $[0, L]$ with surrounding $V = 0$.

$$\psi(x) = \begin{cases} A\exp(ikx) + B\exp(-ikx) & x < 0 \\ \dfrac{C}{\sqrt{|p(x)|}} \exp\left(\dfrac{1}{\hbar}\displaystyle\int_0^x |p(x')|\,dx'\right) + \dfrac{D}{\sqrt{|p(x)|}} \exp\left(-\dfrac{1}{\hbar}\displaystyle\int_0^x |p(x')|\,dx'\right) & 0 < x < L \\ F\exp(ikx) & L < x \end{cases}$$

For large barriers, C must be small so the The tunneling probability related by the decrease of the exponential decay term across the barrier.

$$T = \left|\frac{F}{A}\right|^2 \sim \exp\left(-\frac{2}{\hbar}\int_0^L |p(x)|\,dx\right) \tag{6.4}$$

For general left-incident tunneling with regions $1, 2, 3$ being classically allowed, forbidden, and allowed, respectively. We have

$$\begin{aligned} \psi_1(x) &= A\psi_{\text{WKB},\rightarrow}(x) + B\psi_{\text{WKB},\leftarrow}(x) \\ \psi_2(x) &= C\psi_{\text{WKB},\rightarrow}(x) + D\psi_{\text{WKB},\leftarrow}(x) \\ \psi_3(x) &= F\psi_{\text{WKB},\rightarrow}(x) \end{aligned}$$

This tunneling formula turns out to be useful not only for barriers with 0 surrounding potentials but also general barriers. Using the connection formulas from $3 \to 2 \to 1$ relates A, B as functions of F. The transmission coefficient coincides with equation 6.4. However, the reflection coefficient calculates to $R = |B/A|^2 = 1$. This violates the conservation of probability! We can only trust equation 6.4 for $T \ll 1$.

6.3 Bound approximations

The WKB approximation gives us an approximate wavefunction. Connection formulas give how approximations change across turning points at which a raw approximation would break down. Every confining potential possibly yields bound states. A consistent, normalizable connection of 3 approximations across classical turning points in the regions

- to the left of the confining potential (w.r.t. energy)
- inside the confining potential
- to the right of the confiniing potential

yields the quantization condition for bound state energy.

6.3.1 Two infinite walls

When there are two infinite vertical walls x_-, x_+

$$\int_{x_-}^{x_+} dx\, \sqrt{2m(E - V(x))} = \pi\hbar n, \quad n = 1, 2, \cdots$$

We begin by examining first case with two infinite vertical walls. Use the WKB approximation 6.3 with lower bound at x_-, then

$$\psi_{\text{WKB}}(x_+) = \frac{1}{\sqrt{p(x_+)}} \left(\alpha_1 \sin\phi(x_+) + \alpha_2 \cos\phi(x_+)\right) = 0, \quad \phi(x) = \frac{1}{\hbar}\int_{x_-}^{x} p(x')\, dx'$$

We have $\alpha_2 = 0$ by boundary condition at x_-. The equation above then yields the desired quantization condition $\phi(x_+) = 0$.

Example 6.1 (*finite square well*). Consider a finite square well with $V(x) - V_0$ in $[0, L]$ and zero elsewhere. Applying the first approximation yields

$$\int_0^L dx\, \sqrt{2m(E + V_0)} = L\sqrt{2m(E + V_0)} = \pi n\hbar \implies E = \frac{n^2\pi^2\hbar^2}{2mL^2} - V_0$$

This is equivalent to a vertical shift of the infinite square well solution. While there is no single quantitative metric for how good the approximation is (as opposed to energy ratio), we can estimate by the magnitude of the next term in the expansion.

6.3.2 One infinite wall

When there is one infinite vertical wall at x_-, a smooth classical turning point at x_+

$$\int_{x_-}^{x_+} dx\,\sqrt{2m(E-V(x))} = \pi\hbar\left(n+\frac{3}{4}\right), \quad n=0,1,2,\cdots$$

Begin with an asymptotic formula for the decay on the right side of the potential.

$$\psi_{x>x_+}(x) = \frac{A}{\sqrt{k_1(x)}}\exp\left(-\frac{1}{\hbar}\int_{x_+}^{x} dx'\,k_1(x')\right)$$

Invoke connection at x_+

$$\psi_{x_-<x<x_+}(x) = \frac{2A}{\sqrt{k_2(x)}}\cos\left(\frac{1}{\hbar}\int_{x}^{x_+} dx' k_2(x') - \frac{\pi}{4\hbar}\right)$$

The boundary condition that $\psi_{x_-<x<x_+}(x_-) = 0$ yields

$$\int_{x}^{x_+} dx' k_2(x') = \pi\hbar\left(n+\frac{3}{4}\right)$$

6.3.3 Two smooth turning points

In case of smooth potential with classical turning points at $x_- < x_+$

$$\int_{x_-}^{x_+} dx\,\sqrt{2m(E-V(x))} = \pi\hbar\left(n+\frac{1}{2}\right), \quad n=0,1,2,\cdots$$

Begin with an asymptotic formula for the decay on the right side of the potential

$$\psi_{x>x_+}(x) = \frac{A}{\sqrt{k_1(x)}}\exp\left(-\frac{1}{\hbar}\int_{x_+}^{x} dx'\,k_1(x')\right)$$

Invoke connection at x_+ and manipulate it to fit the connection formula at x_-. Here we temporarily omit $1/\hbar$ to reduce clutter.

$$\begin{aligned}
\psi_{x_-<x<x_+}(x) &= \frac{2A}{\sqrt{k_2(x)}}\cos\left(\int_{x}^{x_+} dx' k_2(x') - \frac{\pi}{4}\right) \\
&= \frac{2A}{\sqrt{k_2(x)}}\cos\left(\left(\int_{x_-}^{x_+} - \int_{x_-}^{x}\right) dx' k_2(x') - \frac{\pi}{4}\right) \\
&= \frac{2A}{\sqrt{k_2(x)}}\cos\left(\int_{x_-}^{x} dx'\,k_2(x') - \left(\int_{x_-}^{x_+} dx' k_2(x') + \frac{\pi}{4}\right)\right) \\
&= \frac{2A}{\sqrt{k_2(x)}}\cos\left(\int_{x_-}^{x} dx'\,k_2(x') - \frac{\pi}{4} - \left(\int_{x_-}^{x_+} dx' k_2(x') - \frac{\pi}{2}\right)\right)
\end{aligned}$$

Invoke the connection formula at x_- again with

$$\eta = \frac{\pi}{2\hbar} - \frac{1}{\hbar}\int_{x_-}^{x_+} dx' k_2(x')$$

In this classically forbidden region, $\psi_{x<x_-}(x)$ must be a decaying function yet the connection yields an increasing exponential. This yields the desired quantization condition $\sin\eta = 0$,

$$\int_{x_-}^{x_+} dx' k_2(x') - \frac{\pi}{2} = n\pi\hbar, \qquad n = 0, 1, 2\cdots$$

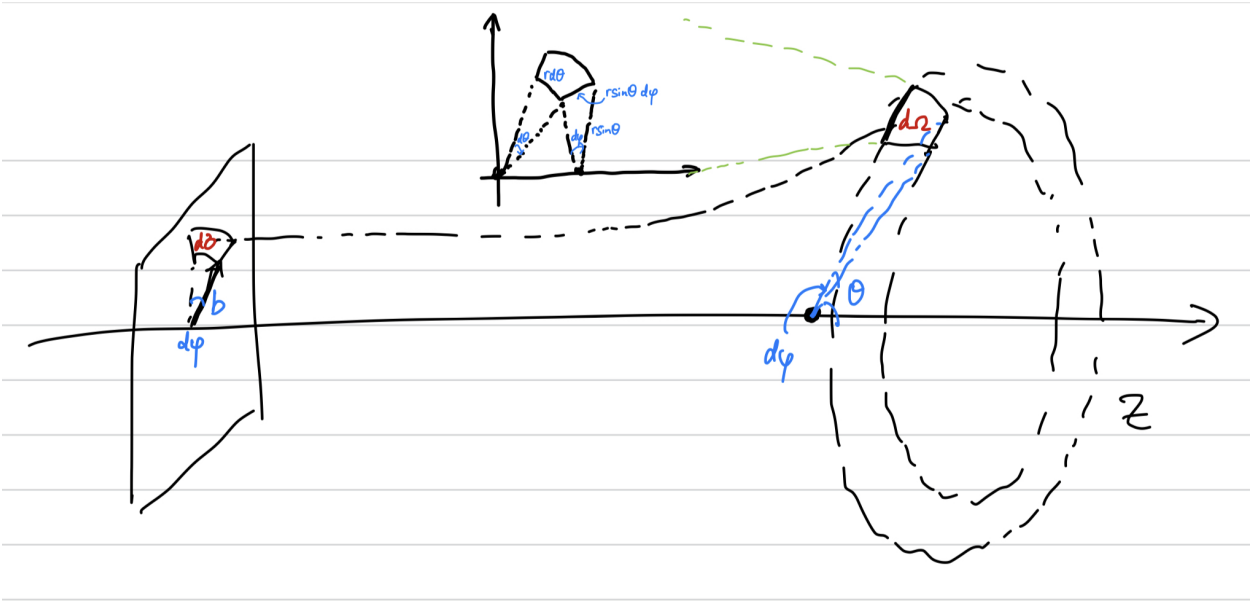
The other quantization formulas follows from a similar procedure, with infinite vertical walls yielding zero boundary condition.

7 Scattering

7.1 Classical scattering

In scattering problems, we assume a spatially and temporally uniform distribution of incoming beams along the incident axis. We also assume cylindrical symmetry parameterized by (z, b, ϕ) denoting height, radius, and azimuthal angle, respectively. Below are the quantities involved in the problem.

- Impact prameter b, scattering angle θ.
- Particles incident within an infinitesimal patch of cross-sectional area $d\sigma = b\,db\,d\varphi$ scatters into a solid angle (normalized area form) $d\Omega = \sin\theta\,d\theta\,d\varphi$.
- Differential cross-section $d_\Omega\sigma = \dfrac{b}{\sin\theta}\,|d_\theta b|$. Usually, the greater θ (more pronounced scattering), the smaller b, thus the absolute sign. $d_\Omega\sigma$ is usually a quantity parameterized by θ. It asks: at angle θ from the scattering center, how much unit solid angle accounts for unit area increase in incident beams?
- The total cross-section $\sigma = \int d_\Omega\sigma\,d\Omega$. It is the total cross-sectional area which will encounter scattering. For classical hard-sphere scattering, this is πR^2.
- The luminosity $\mathcal{L}$ is the experimentally controllable parameter denoting the number of incident particles per unit cross-sectional area, per unit time. We have $dN = \mathcal{L}\,d\sigma$, so $d_\Omega\sigma = \dfrac{1}{\mathcal{L}} d_\Omega N$



7.2 Quantum scattering theory

Assuming that the scattering potential is localized and spherically symmetric, it admits separable solutions

$$\psi(r,\theta,\phi) = \sum_{l,m} \frac{u_{m,l}(r)}{r} Y_l^m(\theta,\phi)$$

Here u satisfies one-dimensional radial equation with effective potential

$$-\frac{\hbar^2}{2m}\partial_r^2 u + \left[V(r) + \frac{\hbar^2}{2m}\frac{L^2}{r^2}\right] u = Eu \tag{7.1}$$

For asymptotically large $kr \gg 1$, the effective potential converges to the radial potential, which gives the general solution

$$\psi(r,\theta,\phi) = \frac{Y_l^m(\theta,\phi)}{r}\left(Ce^{ikr} + De^{-ikr}\right)$$

The outgoing scattering condition eliminates D. Our potential starts out with both polar and azimuthal symmetry. Incidence direction chooses a preferred z-axis and introduces θ dependence by breaking spherical symmetry However, the azimuthally symmetric incidence condition leaves our state ϕ-invariant. The only ϕ-invariant spherical harmonics are those with $m = 0$, so we look for steady state solutions for $r \gg 1$ of the following form:

$$\psi(r,\theta) = A\left[e^{ikz} + \left(\sum_{l=0}^{\infty} c_l Y_l^0(\theta)\right)\frac{e^{ikr}}{r}\right], \quad k = \frac{2mE}{\hbar} \tag{7.2}$$

The spherically normalized amplitudes in parantheses are collected into the *scattering amplitude* $f(\theta)$. The probability flux of a uniform beam through cross-sectional area $d\sigma$ is

$$dP = |\psi_{\text{incident}}|^2\, d\sigma = |A|^2\, d\sigma$$

This is equal to the probability that it scatters into the corresponding solid angle $d\Omega$:

$$dP = |\psi_{\text{scattered}}|^2\, d\Omega = \frac{|Af|^2}{r^2}(r^2\, d\Omega) = |Af|^2\, d\Omega$$

The differential cross-section is correspondingly

$$d_\Omega\sigma = |f(\theta)|^2$$

The subsequent subsections introduce two methods to compute the scattering amplitudes.

7.3 Partial wave analysis

Partial wave analysis allows us to calculate the scattering amplitudes for localized $V(r)$ which *decays faster than* r^2 (this includes finite-range potentials).

Consider equation 7.1 again. When $V(r)$ decays faster than r^{-2}, our space can be split into three regions of interest (note that Coulomb potential is not well-localized in this sense).

- scattering region: $V \neq 0$ and $kr \gg 1$. Here a full consideration is needed.
- intermediate region: $V(r) \approx 0$ but the centrifugal term $\dfrac{\hbar^2}{2m}\dfrac{L^2}{r^2}$ is still nonneglegible. The particle is radially "free".
- radiation zone: $kr \gg 1$, so both $V(r)$ and the centrifugal terms are neglegible. The state in this regime is given by equation 7.2.

We consider the intermediate region, equation 7.1 becomes

$$u(r) = Arj_l(kr) + Brn_l(kr) \tag{7.3}$$

Here n_l, j_l are the spherical Bessel functions which somewhat represents sines and cosines. It is more helpful to change basis to linear combinations of the Bessels representing the analogue of complex exponentials, or the *spherical Hankel functions* which are asymptotically $e^{\pm ikx}/r$

$$h_l^{(1)}(x) \equiv j_l(x) + in_l(x), \quad h_l^{(2)}(x) = j_l(x) - in_l(x)$$

Outgoing solutions are represented by Hankel functions of the first kind, so the intermediate region's state is of the form

$$\psi(r,\theta) = A\left[e^{ikz} + \sum c_{m,l}Y_l^m(r,\theta)R_l(r)\right] = A\left[e^{ikz} + \sum_{l=0}^{\infty} c_l h_l^{(1)}(kr)Y_l^0(\theta)\right]$$

Redefine expansion coefficients with the *l-th partial wave amplitude* $c_l = i^{l+1}k\sqrt{4\pi(2l+1)}a_l$; this parameterization turns out to be useful later. Substituting $Y_l^0(\theta)$ yields

$$\psi(r,\theta) = A\left[e^{ikz} + k\sum_{l=0}^{\infty} i^{l+1}(2l+1)a_l h_l^{(1)}(kr)P_l(\cos\theta)\right]$$

To use consistent spherical coordinates, we need to use Rayleigh's formula

$$e^{ikz} = \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta) \tag{7.4}$$

The intermediate region's state is then of the form

$$\boxed{\psi(r,\theta) = A\sum_{l=0}^{\infty} i^l(2l+1)\left[j_l(kr) + ika_l h_l^{(1)}(kr)\right]P_l(\cos\theta)} \tag{7.5}$$

The l-th partial wave amplitudes a_l are so defined because for large r, the Hankel functions approach $(-i)^{l+1}e^{ikr}/kr$, so equation 7.5 approaches equation 7.2 with

$$f(\theta) = \sum_{l=0}^{\infty} c_l Y_l^0(\theta) = \sum_{l=0}^{\infty}(2l+1)a_l P_l(\cos\theta)$$

The differential cross-section can be computed from the partial wave amplitudes by

$$d_\Omega \sigma(\theta) = |f(\theta)|^2 = \sum_{l,l'} (2l+1)(2l'+1) a_l^* a_{l'} P_l(\cos\theta) P_{l'}(\cos\theta) \tag{7.6}$$

Integrate over the solid angle to obtain the total cross section

$$d_\Omega \sigma(\theta) = |f(\theta)|^2 = 4\pi \sum_{l=0}^{\infty} (2l+1)|a_l|^2 \tag{7.7}$$

When the centrifugal term dominates over the radial potential, the partial wave components are dominated by components with low angular momentum.

For an algorithmic prescription of partial wave analysis:

- Choose a potential cutoff R beyond which to use equation 7.6. Solve for the eigenstates of the potential for $r \leq R$.
- Use matching boundary conditions to evaluate a_l.
- Use the partial wave amplitudes to calculate quantities of interest. If possible, for infinite-range but quickly-decaying potentials take $R \to \infty$.

7.4 Integral form of the eigenvalue equation

The three-dimensional eigenvalue equation for the Hamiltonian may be rewritten as

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r})\psi(\mathbf{r}), \quad k = \frac{\sqrt{2mE}}{\hbar} \tag{7.8}$$

This has the superficial apearance of a Helmholtz equation

$$\left(\nabla^2 + k^2\right)\psi = Q, \quad Q(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r})\psi(\mathbf{r})$$

However, the important difference is that the inhomogeneous term Q now also depends on ψ. Recall that given a Green function $G(\mathbf{r})$ which solves the Helmholtz equation with a delta function "source", integrating it gives the solution to the Helmholtz equation.

$$(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r}) \tag{7.9}$$

While a Green function will not allow us to write the closed form to the eigenvalue equation, it yields an equivalent equation (note that ψ also appears on the right hand side).

$$\psi(\mathbf{r}) = \int d^3\mathbf{r}'\, Q(\mathbf{r}') G(\mathbf{r} - \mathbf{r}')$$

To see that this equation is equivalent to equation 7.8, apply $(\nabla^2 + k^2)$ to both sides.

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = \int d^3\mathbf{r}' \left(\nabla^2 + k^2\right) G(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}') = \int \delta(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}')\, d^3\mathbf{r}' = Q(\mathbf{r})$$

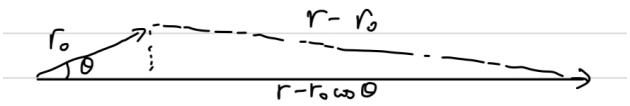


Figure 4: Intuition for $|\mathbf{r} - \mathbf{r}'| \approx r - r' \cos\theta$

One Green function which satisfies equation 7.9 is

$$G(x) = -\frac{e^{ikr}}{4\pi r}$$

The free part of the eigenvalue equation solution is the kernel of $\nabla^2 + k^2$ corresponding to the free-particle solutions. This allows us to write the general integral form of equation 7.8.

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2}\int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}', \quad (\nabla^2 + k^2)\psi_0(\mathbf{r}) = 0 \tag{7.10}$$

7.5 Born Approximation

Suppose V is localized about $\mathbf{r}' = 0$ and we wish to calculate $\psi(\mathbf{r})$ for points far away from the scattering center. The contributing terms all satisfy $|\mathbf{r}'| \ll |\mathbf{r}|$, so

$$|\mathbf{r} - \mathbf{r}'| \approx r - r'\cos\theta = r - \hat{\mathbf{r}} \cdot \mathbf{r}'$$

This is an approximation up to the first order of r'/r. Let $\mathbf{k} = k\hat{r}$, then

$$e^{ik|\mathbf{r}-\mathbf{r}'|} \approx e^{ikr}e^{i\mathbf{k}\cdot\mathbf{r}'} \implies \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \approx \frac{e^{ikr}}{r}e^{-i\mathbf{k}\cdot\mathbf{r}'}$$

Substituting into equation 7.10 with the free solution $\psi_0 = e^{ikz}$ reads

$$\psi(\mathbf{r}) \approx e^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-i\mathbf{k}\cdot\mathbf{r}'}V(\mathbf{r}')\psi(\mathbf{r}')\, d^3\mathbf{r}' \tag{7.11}$$

Equation 7.11 is "exact" to the first order in r'/r, so it is actually exact for the purposes of calculating the scattering amplitudes, which are at asymptotically large r. Equation 7.11 standard form of the eigenstate in the radiation zone. Recall from 7.2 that the scattering amplitudes are the coefficients of Ae^{ikr}/r at large r, we can read off their *exact* values

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2 A}\int e^{-i\mathbf{k}\cdot\mathbf{r}'}V(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}' \tag{7.12}$$

Note that the right hand side contains ψ so this is not a closed form. The Born approximation assumes that the incoming wave is not substantially altered by the scattering, so

$$\psi(\mathbf{r}') \approx \psi_0(\mathbf{r}') = Ae^{ikz'} = Ae^{i\mathbf{k}'\cdot\mathbf{r}'}, \quad \mathbf{k}' = k\hat{z}$$

This yields the first Born approximation for scattering amplitudes. The following holds when *the incident energy is large compared to the potential.*

$$f(\theta,\phi) \approx -\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'}V(\mathbf{r}')d^3\mathbf{r}', \quad \mathbf{k}' = k\hat{z}, \mathbf{k} = k\hat{r}_{\theta,\phi} \tag{7.13}$$

Note that $\mathbf{k}'$ points in the direction of the incident beam, while $\mathbf{k}$ points in the scattering direction. Additionally, *when the energy of the incident beam is low* so that the wavelength is large compared to the scattering region, $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}$ is essentially constant over $\mathbf{r}'$ for which $V(\mathbf{r}')$ is significant, in which case

$$f(\theta,\phi) \approx -\frac{m}{2\pi\hbar^2}\int V(\mathbf{r}')\, d^3\mathbf{r}' \tag{7.14}$$

When the potential is spherically symmetric, the first Born approximation 7.13 may be explicitly evaluated. The following equation does not require low incident energy, only the Born condition that the incident energy is large compared to the potential.

$$f(\theta) \approx -\frac{2m}{\hbar^2\kappa}\int_0^\infty rV(r)\sin(\kappa r)\, dr, \quad \kappa = 2k\sin(\theta/2) \tag{7.15}$$

8 Second Quantization

This section uses Chapter 2 of [1] available here and these lecture notes from ETH.

Particles belong to one of two indistinguishable classes: fermions or bosons, which are antisymmetric and symmetric under particle exchange, respectively. Instead of explicitly symmetrizing a wave function, we can instead adapt our mathematical formulation to inherently account for indistinguishability and even varying number of particles.

Definition 8.1 (*occupation number state*). The occupation number state $|n_1, \cdots\rangle$ denotes n_i fermion or bosons in level i. The total number of particles is given by

$$N = \sum n_i$$

The space of all occupation number states for all N is called Fock space. Explicitly, let $S_\pm$ denote the (anti)-symmetrizer

$$S_\pm |i_1, \cdots, i_N\rangle = \frac{1}{N!} \sum_{P \in S_N} \operatorname{sgn}(P)\, P|i_1, \cdots, i_N\rangle$$

the occupation state is $|n_1, \cdots\rangle_\pm = S_\pm |i_1, \cdots, i_N\rangle$

Proposition 8.1. $\langle n_1, \cdots | n_1' \cdots\rangle = \prod \delta_{n_i, n_i'}, \quad \sum_{n_1, \cdots} |n_1, \cdots\rangle\langle n_1, \cdots| = 1$

Definition 8.2 (*creation and annihilation operators*). The creation and annihilation operators $a_i^\dagger, a_i$ of a particle in level i is defined to be

$$\begin{aligned} a_i^\dagger |\cdots, n_i, \cdots\rangle &= \sqrt{n_i + 1}\, |\cdots, n_i + 1, \cdots\rangle \\ a_i |\cdots, n_i + 1, \cdots\rangle &= \sqrt{n_i + 1}\, |\cdots, n_i, \cdots\rangle \end{aligned}$$

the second equation follows from the first by the adjoint definition.

Theorem 8.2 (*commutation relations*). Consistent symmetrization implies

$$[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0, \quad [a_i, a_j^\dagger] = \delta_{ij} I \qquad \text{(bosons)}$$

$$\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0, \quad \{a_i, a_j^\dagger\} = \delta_{ij} I \qquad \text{(fermions)}$$

They are called the canonical commutation relations (CCRs).

Proof: we consider the fermions first. Given $|n_1, \cdots\rangle = S_-|i_1, \cdots, i_N\rangle$, we have

$$\begin{aligned} a_k^\dagger a_j^\dagger |n_1, \cdots\rangle &= S_-|i_1, \cdots, i_N, j, k\rangle \\ a_j^\dagger a_k^\dagger |n_1, \cdots\rangle &= S_-|i_1, \cdots, i_N, k, j\rangle \end{aligned}$$

Now they differ by a sign since $|i_1, \cdots, i_N, j, k\rangle, |i_1, \cdots, i_N, k, j\rangle$ differ by a transposition $(N+1, N_2)$, so $\{a_i^\dagger, a_j^\dagger\} = 0$. Further note that antisymmetrization annihilates a vector if it contains any duplicate basis, so $n_i = 0, 1$. We omit the rest of the proof.

todo

Corollary 8.1. For fermions, the CCRs imply

$$\begin{aligned} a_j^2 = (a_j^\dagger)^2 = 0, \quad a_j a_j^\dagger = I - a_j^\dagger a_j \\ a_j a_k^\dagger = -a_k^\dagger a_j, \quad a_j a_k = -a_k a_j \end{aligned} \qquad j \neq k$$

For bosons,

$$a_j a_j^\dagger = I + a_j^\dagger a_j, \quad a_j a_k^\dagger = a_k^\dagger a_j, \quad a_j a_k = a_k a_j$$

Let V be the Hilbert space of one particle, then the occupation (Fock) space is $\mathcal{F} \cong V^0 \oplus V^1 \oplus V^2 \oplus \cdots$.

Definition 8.3 (*vacuum and general states*). The vacuum state, denoted $|0\rangle$ or $|\Omega\rangle$, is the state annihilated by all annihilation operators. One can also explicitly write out the occupation number state, for $\zeta = \pm 1$ denoting bosons and fermions, respectively

$$|(n_i)\rangle = \frac{1}{\sqrt{\prod (n_i!)}} \left[\prod (a_i^\dagger)^{n_i}\right] |\Omega\rangle$$

Corollary 8.2. Pauli exclusion principle: for fermions $(a_i^\dagger)^2 = 0$. No single particle state can be occupied by more than one fermion.

Definition 8.4 (*occupation number operator*). the occupation number operator is the Hermitian operator defined by

$$N_i = a_i^\dagger a_i, \quad N_i |(n_i)\rangle = n_i |(n_i)\rangle$$

For both fermions and bosons, it satisfies

$$N_j (a_j^\dagger)^n |\Omega\rangle = n (a_j^\dagger)^n |\Omega\rangle, \quad [N_j, a_{k\neq j}^{(\dagger)}] = 0$$

The total particle number operator is

$$N = \sum a_i^\dagger a_i$$

Note that the level index i implicitly assumes a basis (e.g. position or momentum, or spin along a particular direction). Suppose we wish to change into another basis j.

Proposition 8.3. change of basis formula $a_j^\dagger = \langle i|j\rangle a_i^\dagger, a_j = \langle j|i\rangle a_i$.

Proof: note that single kets $|i\rangle = a_i^\dagger |\Omega\rangle$. Then $|j\rangle = a_j^\dagger |\Omega\rangle$, then

$$|j\rangle = \langle i|j\rangle |i\rangle = \langle i|j\rangle (a_i^\dagger |\Omega) = a_j^\dagger |\Omega\rangle$$

Proposition 8.4. the second quantization of a single-particle operator $O \in \text{End}(V)$ is

$$O = \langle i|O|j\rangle a_i^\dagger a_j$$

Proof: Suppose O is a single-particle operator with eigenbasis $o_\lambda, |\lambda\rangle$. In the second-quantization scheme, it has the representation

$$O = o_\lambda n_\lambda$$

In other words, it counts how many particles are in each of the $|\lambda\rangle$ eigenstates and assigns the proper weights to them. Using a change of basis into arbitrary basis indexed by i or j

$$o_\lambda n_\lambda = \langle\lambda|O|\lambda\rangle a_\lambda^\dagger a_\lambda = \langle\lambda|O|\lambda\rangle\langle i|\lambda\rangle\langle\lambda|j\rangle a_i^\dagger a_j = \langle i|O|j\rangle a_i^\dagger a_j$$

We next consider the second quantization of two-body interaction operators.

Proposition 8.5. $V = \langle i, j|V|k, l\rangle a_i^\dagger a_j^\dagger a_k a_l$

Definition 8.5 (*field operators*). Let $|\mathbf{r}\rangle$ denote a particle localized at $\mathbf{r}$. This constitutes a special basis. Given creation and annihilation operators in some basis indexed by i, denote

$$\langle\mathbf{r}|i\rangle = \phi_i(\mathbf{r})$$

the creation and annihilation operators in the position basis, are called the field operators

$$\hat{\psi}^\dagger(r) = \phi_i^*(\mathbf{r})a_i^\dagger$$