

Notes for Quantum Mechanics 2 course, CMI Autumn 2011
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• These notes (<http://www.cmi.ac.in/~govind/teaching/qm2-o11>) are a continuation of the notes from QM1, available elsewhere on this website. They are very sketchy and aren't a substitute for text books or attendance and taking notes at lectures. Some problems and suggested text books have been listed on the course webpage. Please let me know of any comments or corrections.

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1 Angular momentum (continued)

1.1 Visualization of angular momentum and location in states Y_{lm}

- Classically, suppose we are in a stationary state of angular momentum, i.e., one where \vec{L} points in a fixed direction with fixed magnitude over time. For example, we can be in a classical state where $L_z = 10^5 \hbar, L_y = 0, L_x = 0$. We can visualize this in terms of a rigid body that is rotating with constant angular speed about an axis pointing along \hat{z} . Quantum mechanically, the stationary states may be taken as simultaneous eigenstates $\psi = Y_{lm}$ of L^2 and L_z . In such a state we can imagine the angular momentum vector as having length equal to the square-root of the eigenvalue of L^2 , i.e., $\sqrt{\hbar^2 l(l+1)}$. Moreover, this vector has projection on the z-axis of $\hbar m$. So we know its angle with the z-axis. But that is as much as we can say. We cannot

unambiguously specify its projections on x or y axes since L_x and L_y do not have definite values in this state. To visualize the ‘angular momentum vector’ in this state, we can think of it as the cone of vectors from the origin whose lengths are $\sqrt{\hbar^2 l(l+1)}$ and projection $\hbar m$ on the z -axis. This hand-waving visualization can be a useful aid to memory. There are as many vectors on the cone with x -component of angular momentum equal to $\hbar m_x$ as $-\hbar m_x$. So by symmetry we would expect the expectation value of L_x in the state Y_{lm} to vanish, as it does. It is important to realize that this cone *does not* tell us where the particle is likely to be found, it only gives some crude information on the likely values that may be obtained upon a measurement of various components of angular momentum.

To visualize where the particle is likely to be found if its angular position is measured in state Y_{lm} , we must plot the probability density $|Y_{lm}(\theta, \phi)|^2$ on the surface of a unit sphere in polar coordinates $r = 1, \theta, \phi$. For example, in the S-wave state $Y_{00} = \frac{1}{\sqrt{4\pi}}$, this probability density is constant, indicating that the particle is equally likely to be found at all angular locations. More generally, $Y_{lm}(\theta, \phi) \propto e^{im\phi} P_{lm}(\cos \theta)$. So $|Y_{lm}|^2 \propto |P_{lm}(\theta)|^2$. Thus the angular probability distribution is azimuthally symmetric (independent of ϕ). For example, $|Y_{10}|^2 \propto \cos^2 \theta$. So in this state, the particle is more likely to be found near the north pole ($\theta = 0$) or south pole ($\theta = \pi$), than along the equator $\theta = \pi/2$. Polar plots of $P_{lm}(\theta)$ are given in many text books.

1.2 Rigid Body

- Consider an isotropic rigid body, (i.e., one whose principal moments of inertia are equal) e.g., a spherical ball free to rotate about its center, which is held fixed. Its rotational kinetic energy is $H = \frac{L^2}{2I}$ where I is its moment of inertia about *any* axis passing through its center. Classically, its rotational energy is any positive number, depending on its angular velocity $\omega = L/I$. Quantum mechanically, the spectrum of energies is discrete, $E_l = \frac{l(l+1)\hbar^2}{2I}$ where the angular momentum quantum number $l = 0, 1, 2, \dots$. The corresponding eigenfunctions are the spherical harmonics $Y_{lm}(\theta, \phi)$. The energies are independent of the magnetic quantum number m . This is because of spherical symmetry. All $2l+1$ states Y_{lm} , for $m = -l, \dots, l$, irrespective of their z -component of angular momentum ($L_z Y_{lm} = \hbar m Y_{lm}$) are degenerate in energy.

- For an isotropic rigid body, H , L^2 and L_z commute and are simultaneously diagonal in the basis of spherical harmonics.

- More generally, the rotational kinetic energy of a rigid body free to rotate about a point is $H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}$ where I_1, I_2, I_3 are the principal moments of inertia about the three principal axes of inertia of the body. For an isotropic body, $I_1 = I_2 = I_3$.

- The next simplest case is a top, a rigid body with an axis of symmetry, which we can take as the third principal axis. Then $I_1 = I_2 = I$ and the hamiltonian becomes

$$H = \frac{L_1^2 + L_2^2}{2I} + \frac{L_3^2}{2I_3} = \frac{L^2 - L_3^2}{2I} + \frac{L_3^2}{2I_3}. \quad (1)$$

Written this way, we see that $[H, L^2] = 0$ and $[H, L_3] = 0$, so the hamiltonian is again diagonal in the basis of spherical harmonics. The energy spectrum is

$$E_{lm} = \frac{\hbar^2 l(l+1) - \hbar^2 m^2}{2I} + \frac{\hbar^2 m^2}{2I_3}. \quad (2)$$

Due to lack of isotropy, energy levels now depend on the magnetic quantum number m . The isotropic case is obtained by putting $I_3 = I$.

- For a rigid body without an axis of symmetry, the three moments of inertia are pairwise unequal $I_1 \neq I_2, I_2 \neq I_3, I_3 \neq I_1$. The hamiltonian is

$$H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3} \quad (3)$$

Here $[H, L^2] = 0$ so H and L^2 may be simultaneously diagonalized. But each eigenspace of L^2 (with eigenvalue $\hbar^2 l(l+1)$) is $2l+1$ -fold degenerate. So there are many bases in which L^2 is diagonal. One of these is the basis of spherical harmonics $\langle \theta, \phi | l, m \rangle = Y_{lm}(\theta, \phi)$, in which L_3 is also diagonal¹. But $[H, L_3] \neq 0$, so H is *not* diagonal in the Y_{lm} basis. But all is not lost. Since $[H, L^2] = 0$, H is block diagonal in the Y_{lm} basis, i.e., H has zero matrix elements between states of different l

$$\langle lm | H | l' m' \rangle = f(l, m, m') \delta_{ll'} \quad (4)$$

So we can diagonalize H in each $2l+1$ dimensional eigenspace of L^2 separately. To do so, we first need to know the matrix elements of H and in particular, of L_1 and L_2 or equivalently L_{\pm} in the basis of spherical harmonics.

1.3 Matrix elements of L_{\pm} in the $|lm\rangle$ basis

- Let $|l, m\rangle$ be the normalized simultaneous eigenstates of L^2 and L_z , $\langle lm | l' m' \rangle = \delta_{ll'} \delta_{mm'}$.
- We already know that

$$\begin{aligned} L^2 |lm\rangle &= \hbar^2 l(l+1) |lm\rangle & \text{and} & & L_z |lm\rangle &= \hbar m |lm\rangle \\ \text{So } \langle lm | L^2 | l' m' \rangle &= \hbar^2 l(l+1) \delta_{ll'} \delta_{mm'} & \text{and} & & \langle lm | L_z | l' m' \rangle &= \hbar m \delta_{ll'} \delta_{mm'}. \end{aligned} \quad (5)$$

- Moreover, $L_{\pm} = L_x \pm iL_y$ raise and lower the value of m by one, so for some dimensionless constants C_{lm}^{\pm} we must have

$$L_{\pm} |lm\rangle = \hbar C_{lm}^{\pm} |l, m \pm 1\rangle. \quad (6)$$

To find the C' s we first notice that on account of hermiticity $L_{\pm}^{\dagger} = L_{\mp}$, we have $C_{lm}^{-} = C_{l, m-1}^{+}$. To see this we note that $(L_{-})_{l' m', lm} = (L_{+})_{lm, l' m'}^*$ where

$$(L_{-})_{l' m', lm} = \langle l' m' | L_{-} | lm \rangle = C_{lm}^{-} \delta_{ll'} \delta_{m', m-1} \quad \text{and} \quad (L_{+})_{lm, l' m'}^* = C_{l' m'}^{+*} \delta_{ll'} \delta_{m, m'+1} = C_{l, m-1}^{+*} \delta_{ll'} \delta_{m', m-1} \quad (7)$$

Since these must be equal for all l, l', m, m' we have $C_{lm}^{-} = C_{l, m-1}^{+*}$.

- To find C^{-} , we use the identity $L^2 = L_{+} L_{-} + L_z^2 - \hbar L_z$ to evaluate the elements of the diagonal matrix $\langle l' m' | L^2 | lm \rangle$ in two different ways. We get

$$\begin{aligned} \hbar^2 l(l+1) &= \hbar^2 C_{l, m-1}^{+} C_{lm}^{-} + \hbar^2 m^2 - \hbar^2 m & \Rightarrow & & C_{lm}^{-} C_{l, m-1}^{+} &= l(l+1) - m(m-1) \\ & & \Rightarrow & & |C_{lm}^{-}|^2 &= l(l+1) - m(m-1) \end{aligned} \quad (8)$$

Thus for some phases $e^{i\phi_{lm}}$, we have

$$C_{lm}^{-} = \sqrt{l(l+1) - m(m-1)} e^{-i\phi_{lm}} \quad \text{and} \quad C_{lm}^{+} = \sqrt{l(l+1) - m(m+1)} e^{i\phi_{lm}}. \quad (9)$$

¹Any non-trivial change of basis from Y_{lm} within a $2l+1$ dimensional eigenspace of L^2 will leave L^2 diagonal, but will render L_3 non-diagonal.

It is possible to absorb these phases into the wave functions and take C^\pm to be real.

$$C_{lm}^\pm = \sqrt{l(l+1) - m(m \pm 1)} \quad (10)$$

Thus the matrix elements of L_\pm are

$$\langle l' m' | L_\pm | l m \rangle = \hbar \sqrt{l(l+1) - m(m \pm 1)} \delta_{l'l} \delta_{m', m \pm 1}. \quad (11)$$

Using these we can easily get the matrix elements of L_x and L_y .

1.3.1 E.g.: Matrix representation of angular momenta for $l = 1$

• Let us illustrate with the $l = 1$ subspace which is $2l + 1 = 3$ dimensional and is spanned by the orthonormal spherical harmonics $Y_{1m}(\theta, \phi)$ for $m = 1, 0, -1$ which we denote $|m\rangle$ and represent by the column vectors

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (12)$$

In this basis $L_z|m\rangle = \hbar m|m\rangle$ and $L^2|m\rangle = l(l+1)\hbar^2|m\rangle$ are represented by the diagonal matrices

$$L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad L^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (13)$$

L_\pm have the action $L_\pm|m\rangle = \sqrt{2 - m(m \pm 1)} \hbar |m \pm 1\rangle$ and are adjoints of each other, so

$$\begin{pmatrix} L_+|1\rangle = 0 \\ L_+|0\rangle = \sqrt{2}\hbar|1\rangle \\ L_+|-1\rangle = \sqrt{2}\hbar|0\rangle \end{pmatrix} \Rightarrow L_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad L_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \quad (14)$$

Notice that L_\pm are strictly upper/lower triangular and not hermitian. They are not observables. But using them we find the matrices for L_x and L_y

$$L_x = \frac{L_+ + L_-}{2} = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad L_y = \frac{L_+ - L_-}{2i} = \frac{\hbar}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}. \quad (15)$$

• The eigenvalues of L_z are $\hbar, 0, -\hbar$. Since there is nothing special about the z -direction we should expect the eigenvalues of L_y and L_x to also be the same. Check if this is so!

• However, L_x is not diagonal in the eigenbasis of L_z . Suppose an atom in the $l = 1$ state is in the $m = 0$ eigenstate $|10\rangle$ or $Y_{10}(\theta, \phi)$ of L_z . A measurement of L_x is made. What are the probabilities of various outcomes of the measurement?

• Measurement of L_x can result in any one of the eigenvalues $\hbar m_x = \hbar, 0, -\hbar$, after which the state collapses to the corresponding eigenstate X_+, X_0, X_- , which in this case are (show it!)

$$X_+ = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}, \quad X_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad X_- = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}. \quad (16)$$

The measurement postulate further tells us that the probability of each outcome is the absolute square of the projection of the initial state $|10\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ on the final eigenstate. We find

$$\text{prob}(l_x = 0) = 0, \quad \text{prob}(l_x = \hbar) = \frac{1}{2}, \quad \text{prob}(l_x = -\hbar) = \frac{1}{2}. \quad (17)$$

Interestingly, this means measurement of L_x for a particle in the state $L_z = 0$ cannot result in the value zero while the values $\pm\hbar$ occur with equal probability.

- Problem: using the matrix representations of $L_{x,y,z}$ in the case $l = 1$, find the energy levels (corresponding to $l = 1$) of an anisotropic rigid body with $I_1 = I, I_2 = 2I, I_3 = 3I$ where I is appropriate unit of moment of inertia (dimensions ML^2).

1.4 Coordinate representation of spherical harmonics for $l = 1$

- In the preceding section we did not require the explicit functional forms of the spherical harmonics $Y_{lm}(\theta, \phi)$. But suppose we wanted to know the angular regions where an electron in the state $|1m\rangle$ is likely to be found. Then we need to know $Y_{1m}(\theta, \phi) = \langle \theta, \phi | 1m \rangle$. Of course, we found the functional form of the spherical harmonics by solving the differential equations for the associated Legendre functions. But let us re-obtain Y_{1m} using the algebraic method of raising and lowering operators. We already know the ϕ dependence of Y_{lm} . As it is an eigenfunction of L_z , $Y_{lm}(\theta, \phi) = e^{im\phi} P_{lm}(\theta)$. We begin by finding the state with top-most value of m , Y_{11} . By definition, $L_+ Y_{11} = 0$, so if we denote $Y_{11}(\theta, \phi) = \psi(\theta, \phi)$ whose ϕ dependence is known, then

$$L_+ \psi = \hbar e^{i\phi} (\partial_\theta + i \cot \theta \partial_\phi) \psi = 0 \quad \Rightarrow \quad \psi_\theta + i \cot \theta \psi_\phi = 0 \quad \Rightarrow \quad \psi_\theta - l \cot \theta \psi = 0. \quad (18)$$

We find $\psi = N_{11} e^{i\phi} \sin^l \theta$ for some normalization constant N . In particular, $Y_{11} \propto e^{i\phi} \sin \theta$. The angular probability distribution $|Y_{11}|^2 \propto \sin^2 \theta$ is peaked around the equator $\theta = \pi/2$ while the particle is less likely to be found near the poles. To get the next state, we apply $L_- = L_+^\dagger$. Do this!

$$Y_{10} \propto L_- e^{i\phi} \sin \theta = -\hbar e^{-i\phi} (\partial_\theta - i \cot \theta \partial_\phi) e^{i\phi} \sin \theta = -2\hbar \cos \theta \quad \Rightarrow \quad Y_{10} = N_{10} \cos \theta. \quad (19)$$

Thus $|Y_{10}|^2 \propto \cos^2 \theta$, and the particle is more likely to be found near the poles in this case. We also notice that $Y_{11} \propto e^{i\phi} \sin \theta$ and $Y_{10} \propto \cos \theta$ are orthogonal, as we would expect of eigenstates of L_z with distinct eigenvalues.

- To get $Y_{1,-1}$ we can either apply L_- to Y_{10} or find it by solving $L_- Y_{1,-1} = 0$. Check that both give the same answer! Give polar plots of the absolute squares of all three spherical harmonics $|Y_{1,1}|^2, |Y_{1,0}|^2, |Y_{1,-1}|^2$.

1.5 Anisotropic rigid body

- Recall that for a rigid body without an axis of symmetry, the three moments of inertia are pairwise unequal $I_1 \neq I_2, I_2 \neq I_3, I_3 \neq I_1$. Letting $2I_1 = 1/a, 2I_2 = 1/b$ and $2I_3 = 1/c$, the hamiltonian is $H = aL_1^2 + bL_2^2 + cL_3^2$. H and L^2 may be simultaneously diagonalized, but $[H, L_z] \neq 0$ so the eigenbasis of H is not the spherical harmonic basis. Nevertheless, H is block

diagonal in the spherical harmonic basis and we may separately diagonalize H in each subspace of definite $l = 0, 1, 2, 3, \dots$. Using our knowledge of the angular momentum matrices, the matrix representation of H in the spherical harmonic basis $\{Y_{11}, Y_{10}, Y_{1,-1}\}$ for $l = 1$ is

$$H = \frac{1}{2}\hbar^2 \begin{pmatrix} a+b+2c & 0 & a-b \\ 0 & 2a+2b & 0 \\ a-b & 0 & a+b+2c \end{pmatrix} \quad (20)$$

One eigenvector is obviously $Y_{10} = (0 \ 1 \ 0)^t$ with eigenvalue $\hbar^2(a+b)$. By cyclic symmetry we expect the other two eigenvalues to be $\hbar^2(b+c)$ and $\hbar^2(c+a)$ and the corresponding eigenvectors are

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \rightarrow \hbar^2(a+c); \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \rightarrow \hbar^2(a+b); \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \rightarrow \hbar^2(b+c). \quad (21)$$

In the basis of its eigenvectors H is represented by the diagonal matrix $\Lambda = \hbar^2 \text{diag}(c+a, a+b, b+c)$. Then the unitary transformation that diagonalizes H is the matrix whose columns are the normalized eigenvectors. We are free to choose the order of eigenvectors and have chosen them in such a way that U is not just unitary but also real symmetric.

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix}, \quad HU = U\Lambda \quad \Rightarrow \quad U^\dagger HU = \Lambda \quad (22)$$

So we have found the $l = 1$ energy levels and stationary states of an anisotropic rigid body. The energy eigenstates are

$$\psi_1 = \frac{1}{\sqrt{2}}(Y_{11} + Y_{1,-1}), \quad \psi_2 = Y_{10}, \quad \psi_3 = \frac{1}{\sqrt{2}}(Y_{11} - Y_{1,-1}) \quad (23)$$

L^2 is of course diagonal in the ψ basis, just as it is in the Y_{lm} basis. But L_z is not diagonal in the eigenbasis of H . Indeed, in the ψ basis, it is represented by the matrix $U^\dagger L_z U$ where $L_z = \text{diag}(1, 0, -1)$.

2 Interaction of a particle with an electromagnetic field

- Many of the quantum mechanical properties of atoms, electrons, nuclei, molecules etc are probed through their interaction with electromagnetic fields. E.g., we can measure the angular momentum of electrons in an atom by passing the atom through an inhomogeneous magnetic field. To understand this, we first develop some basic aspects of the interaction of particles with electromagnetic fields.

2.0.1 Charged particle in an electromagnetic field

An electromagnetic field is described by electric $\vec{E}(r, t)$ and magnetic $\vec{B}(r, t)$ fields which may be obtained from scalar $\phi(r, t)$ and vector $\vec{A}(r, t)$ potentials

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \vec{\nabla} \times \vec{A} \quad (24)$$

Suppose a test charge e moves in such an external field (produced by some other charges and currents), then it feels the Lorentz force and follows a trajectory given by Newton's second law

$$m\ddot{\vec{r}} = \vec{F} = e\vec{E} + e\vec{v} \times \vec{B}, \quad (25)$$

Now we wish to derive this equation of motion from a classical Hamiltonian. Having a hamiltonian helps in the passage to the quantum theory. The hamiltonian that does this job is

$$H = \frac{1}{2m} (p - eA)^2 + e\phi = \frac{p \cdot p}{2m} + \frac{e^2 A \cdot A}{2m} - \frac{ep \cdot A}{m} + e\phi. \quad (26)$$

Let us work out Hamilton's equations $\dot{r}_j = \frac{\partial H}{\partial p_j}$, $\dot{p}_j = -\frac{\partial H}{\partial r_j}$ and show that they reduce to the Lorentz force law. Hamilton's equations are

$$m\dot{r}_j = m \frac{\partial H}{\partial p_j} = p_j - eA_j \quad \text{and} \quad -\dot{p}_j = \frac{\partial H}{\partial r_j} = e \frac{\partial \phi}{\partial r_j} + \frac{e^2}{m} A_i \frac{\partial A_i}{\partial r_j} - \frac{e}{m} p_i \frac{\partial A_i}{\partial r_j} \quad (27)$$

We need $m\ddot{r}_j$, which is

$$m\ddot{r}_j = \dot{p}_j - e\dot{A}_j = -e \frac{\partial \phi}{\partial r_j} - \frac{e^2}{m} A_i \frac{\partial A_i}{\partial r_j} + \frac{e}{m} p_i \frac{\partial A_i}{\partial r_j} - e\dot{A}_j. \quad (28)$$

Here $\dot{A}_j = \frac{\partial A_j}{\partial t} + \frac{dr_i}{dt} \frac{\partial A_j}{\partial x_i}$. Let us denote the velocity of the particle by $v_i = \dot{r}_i = \frac{dr_i}{dt}$. Substituting for $p_i = m\dot{r}_i + eA_i$

$$m\ddot{r}_j = eE_j + ev_i \frac{\partial A_i}{\partial r_j} - e(v \cdot \nabla)A_j. \quad (29)$$

From vector calculus,

$$(v \cdot \nabla)A = \nabla(v \cdot A) - v \times (\nabla \times A) \quad (30)$$

Thus

$$m\ddot{r}_j = eE_j + e(v \times B)_j + e \left(v_i \frac{\partial A_i}{\partial r_j} - \frac{\partial(v \cdot A)}{\partial r_j} \right). \quad (31)$$

The term in parentheses vanishes since

$$\frac{\partial v_i}{\partial r_j} = \frac{\partial \dot{r}_i}{\partial r_j} = \frac{d}{dt} \frac{\partial r_i}{\partial r_j} = \frac{d}{dt} \delta_{ij} = 0. \quad (32)$$

Thus, Hamilton's equations for $H = \frac{\pi^2}{2m} + e\phi$ where $\pi = p - eA$ are equivalent to Newton's equation for a particle subject to the Lorentz force in an electromagnetic field. This interaction of a charged particle with an electromagnetic field is called minimal-coupling.

- To get the quantum mechanical hamiltonian, we replace $p \rightarrow -i\hbar\nabla$ to get

$$H = \frac{1}{2m} \left(-i\hbar\vec{\nabla} - e\vec{A} \right)^2 + e\phi = -\frac{\hbar^2\nabla^2}{2m} + \frac{e^2}{2m} \vec{A}^2 - \frac{ie\hbar}{2m} (\nabla \cdot A + A \cdot \nabla) + e\phi \quad (33)$$

Since \vec{A} is real H is hermitian. We will use it later to study an electron in a magnetic field etc.

2.0.2 Magnetic moment interaction

- In addition to charge, a particle (atom, nucleus, electron/proton/neutron) could have an electric and/or magnetic dipole moment. This is particularly important for neutral atoms since dipolar forces dominate in the absence of net charge. An electric dipole feels a torque when in an electric field, but it can also feel a force if the field is inhomogeneous. If a particle has a magnetic dipole moment μ , its energy in a magnetic field is $H_{md} = -\mu \cdot B$, and the corresponding force is $F = \nabla(\mu \cdot B)$. Similarly, if p is the electric dipole moment, the electric dipole energy is $H_{ed} = -p \cdot E$ and force is $F = \nabla(p \cdot E)$. An elementary magnetic dipole moment $\vec{\mu} = I\vec{a}$ can be thought of classically as due to a planar current loop I enclosing an area \vec{a} . For example if a charge q is in a uniform circular orbit of radius r with angular momentum $L = mvr = 2\pi mr^2/T$, it corresponds to a current $I = q/T = qL/2\pi mr^2$. Thus its magnetic moment is $\vec{\mu} = \frac{q\vec{L}}{2m}$. The constant of proportionality, the ratio of magnetic moment to angular momentum $\frac{q}{2m}$ is called the gyromagnetic ratio.

- Suppose we have electrons of angular momentum L in an atom. In a magnetic field \vec{B} , the magnetic dipole energy is

$$H = -\mu \cdot B = \frac{e}{2m} L \cdot B \quad (34)$$

In quantum mechanics, \vec{L} is replaced by the angular momentum operator.

2.1 Measurement of angular momentum using a Stern-Gerlach apparatus

See Sakurai, Griffiths or Bohm. The Stern-Gerlach experiment measures the angular momentum of the electronic state of an atom. A beam of neutral atoms is passed (say in the $+x$ -direction) through a region with an inhomogeneous magnetic field (pointing mainly in the vertical z -direction) and detected on a screen on the $y-z$ plane. Suppose the total angular momentum of the electrons is \vec{L} . The atoms experience a force given by $F = \nabla(\vec{\mu} \cdot \vec{B})$ where the magnetic moment due to the angular momentum of the electrons is $\mu = \frac{e\vec{L}}{2m}$. So $\vec{F} = \mu_x \nabla B_x + \mu_y \nabla B_y + \mu_z \nabla B_z$. If the magnetic field was homogeneous, there would be no force. The magnet is arranged so that the magnetic field is pointing primarily in the vertical z -direction and so that $\frac{\partial B_z}{\partial z}$ is the main contribution. Then the force is approximately in the z -direction and equal to

$$F_z \approx \mu_z \frac{\partial B_z}{\partial z} = \frac{e}{2m} L_z \frac{\partial B_z}{\partial z} \quad (35)$$

Depending on the value of L_z for each atom, it feels a force in the vertical ($\pm z$ direction) and gets deflected from its horizontal path. The screen is far enough from the magnet so that the atoms with different values of L_z get significantly separated by the time they reach the screen. Classically, the angular momenta L_z can take a continuous range of values, and one expects a vertical smear of atoms on the screen, but this is not what is seen. Quantum mechanically, L_z can only take $2l + 1$ discrete values $-\hbar, \dots, \hbar$ if the total angular momentum of the atoms is $l(l + 1)\hbar^2$. And typically, the production of the beam (before entering the magnetic field, say by boiling magnesium atoms from a solid) does not favor any particular value of L_z . So we would expect there to be roughly equal numbers of atoms with each allowed value of L_z . So quantum mechanically one expects certain discrete deflections, leading to $2l + 1$ vertically aligned arrival spots on the screen. Thus, the angular momentum quantum number l can be measured by counting the number of spots. So the S-G experiment gives direct confirmation of the quantization of components of angular momentum.

2.2 Measurement of particle position and path

We can also find the (approximate) location and (approximate) path followed by a particle. This is done, for instance, using a cloud chamber experiment. A particle passes through a gas and ionizes/excites atoms that are within a few atomic diameters from it. The gas is expanded, cools and water vapor condenses on the ionized atoms. The resulting track of condensed water droplets indicates the approximate path of the particle. The presence of water droplets at a spot indicates that the particle must have come within a few atomic diameters of the spot. Due to the scattering against randomly located atoms, the path is jagged and the instantaneous momentum keeps changing direction and is not very precisely determined. In a wave mechanical treatment, the incoming free particle wave packet would gradually spread out in the absence of the gas. Scattering against the atom causes the wave packet to break up to account for the various directions in which the particle could scatter. Of course, only one of these is realized and detected using the track. This wave packet then begins to expand till it scatters against another atom. Thus, the successive scatterings prevent the full broadening of the wave packet. The successive scatterings are like a sequence of rough measurements of position. Each such measurement causes the wave function to collapse to an approximate position eigenstate. Thus, we may track the position of the particle. See Bohm.

2.3 Charged particle in a magnetic field: Landau Levels

See the discussion in Liboff or other books.

Consider a particle of charge e moving in a magnetic field of strength B pointing along \hat{z} . A vector potential that leads to such a magnetic field is $\vec{A} = -yB\hat{x}$. Classically, such a particle executes cyclotron motion which projects to uniform linear motion in the z -direction and uniform circular motion in the x - y plane. The hamiltonian is

$$H = \frac{1}{2m}(p - eA)^2 = \frac{1}{2m} [p_x^2 + e^2 B^2 y^2 + 2eBy p_x + p_y^2 + p_z^2] \quad (36)$$

since $[y, p_x] = 0$. x, z are cyclic coordinates so the momenta p_x, p_z commute with H . The simultaneous eigenstates of p_x and p_z are of the form $C(y)e^{i(k_x x + k_z z)}$ where $C(y)$ is any function of y . So we look for eigenstates of H of this form. We get an eigenvalue problem

$$\frac{1}{2m} [p_y^2 + e^2 B^2 y^2 + 2\hbar k_x e B y + \hbar^2 k_x^2] C(y) = \left(E - \frac{\hbar^2 k_z^2}{2m} \right) C(y) \quad (37)$$

This is of the form of an SHO energy eigenvalue problem

$$\left[\frac{p_y^2}{2m} + \frac{1}{2} m \omega^2 (y - y_0)^2 \right] C(y) = \left(E - \frac{\hbar^2 k_z^2}{2m} \right) C(y) \quad (38)$$

where $\omega = eB/m$ is the cyclotron frequency and $y_0 = \hbar k_x / eB$ is the location of the minimum of the potential. So the energy levels (called Landau levels) are

$$E_{n, k_x, k_z} = \frac{\hbar^2 k_z^2}{2m} + \hbar \omega \left(n + \frac{1}{2} \right). \quad (39)$$

The first term is the kinetic energy of free particle translational motion in the z -direction. The second term comes from the quantum mechanical analogue of circular motion in the x - y plane.

The corresponding eigenstates are familiar from the SHO, they are given in terms of Hermite polynomials \times the gaussian

$$\psi_{k_z, k_x, n}(x, y, z) = A_n \mathcal{H}_n(\xi) e^{-\xi^2/2} e^{i(k_x x + k_z z)}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}}(y - y_0) \quad (40)$$

The energy levels are independent of k_x and therefore are infinitely degenerate. Since $k_x \propto y_0$, this means the energy does not depend on the location of the centre of the cyclotron trajectory which is the location of the gaussian.

In practice, the electron is usually confined to a thin layer of a sample of finite area (say a square of side L in the $x-y$ plane). This means it cannot move in the z -direction. If we impose periodic boundary conditions in the x -direction, $\psi(x=0) = \psi(x=L)$ then the allowed values of k_x must satisfy $k_x L = 2n_x \pi$ for some integer $n_x = 0, \pm 1, \pm 2, \dots$. So the continuously infinite degeneracy in k_x has been reduced to a countably infinite degeneracy. Moreover, $\langle y \rangle = y_0$ (or the center of the classical helix) must lie within the sample (ignoring some edge effects):

$$0 \leq y_0 \leq L \quad \Rightarrow \quad 0 \leq n_x \leq \frac{eBL^2}{h} \quad (41)$$

So the degeneracy is in fact finite and equal to $\frac{eBL^2}{h}$. L^2 is the area of the sample and the total magnetic flux through the sample is $\Phi = BL^2$. On the other hand, $\Phi_0 = h/e$ may be interpreted as an elementary quantum of magnetic flux, and the area it occupies is h/eB . The quantization of magnetic flux is absent in classical electromagnetic theory as the appearance of \hbar suggests. The magnetic flux in most situations studied in classical theory is so large, that the fact that it comes in packets of size h/e is not of any consequence. This is similar to the Planck-Einstein deduction that the energy of light/radiation comes in indivisible packets called photons.

- The degeneracy of electronic energy states is then given by the maximum number of flux quanta that can be accommodated in the sample Φ/Φ_0 . We say that flux is quantized, it comes in multiples of h/e . The applied magnetic field, however, is unrestricted, and we can increase the degeneracy of Landau levels by increasing B or the area of the sample. On the other hand, if the magnetic field or area are so small that $\Phi < \Phi_0$, then within the above approximations, we would say that there can be no magnetic flux penetrating the sample. This is because the degeneracy is zero, and there is no electronic state ‘through which the magnetic flux can pass’. The above calculation would predict that the sample would expel the applied magnetic field, the field lines would have to go around the sample rather than through the sample.

3 Spin angular momentum

In practice, the above prediction of quantum mechanics for the Stern-Gerlach experiment is verified for some atoms, but in other cases, the pattern of spots (or their number) is not quite as expected. One infers that there is a contribution to the angular momentum of the electrons that is not of orbital $\vec{L} = \vec{r} \times \vec{p}$ origin. This additional angular momentum is called spin. There is no such discrepancy if the total electron spin happens to be zero.

Spin was initially discovered (by the work of many physicists, culminating in the work of Goudsmit and Uhlenbeck) through a detailed study of atomic spectral lines. Certain forbidden/additional spectral lines were seen (e.g. where one line was expected, two closely spaced

lines were seen). To account for these, a new ‘spin’ quantum number $m_s = \pm\frac{1}{2}$ was introduced, in addition to the n, l, m quantum numbers used to label the energy levels of the hydrogen atom.

It is interesting to read the translation of a lecture by Goudsmit on the history of the discovery of electron spin, see <http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html>

Subsequently, a theory of spin was developed (among others by Pauli), wherein it is treated as another type of angular momentum. The initial analogy was with the spinning of the Earth about its axis, while orbital angular momentum was compared with the motion of the center of mass of the Earth around the sun. However, no such mechanical model for the spin of the electron has been successful. The electron is point-like to current experimental accuracy and even extended particles like the proton (which are not point-like), have intrinsic spin which has not been explained by mechanical analogies. Quantum mechanical spin is regarded as an ‘intrinsic spin’ represented by a vector observable $\vec{S} = (S_x, S_y, S_z)$. Intrinsic just means not of $r \times p$ origin, i.e., not having to do with movement in three dimensional space. In fact, a massive particle at rest can have a magnetic moment! This magnetic moment must necessarily be of non-orbital origin. Such a magnetic moment is ascribed to its spin. The spin observables are postulated to satisfy the same commutation relations as angular momentum

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \quad (42)$$

Unlike L_i , S_i are not expressible in terms of position and momentum, spin is a new degree of freedom. To make sense of spin in the quantum theory, we need to represent S_i as hermitian operators acting on some Hilbert space of spin states. In fact, we have already learned how to do this in the context of orbital angular momentum. $S^2 = S_x^2 + S_y^2 + S_z^2$ and S_z are simultaneously diagonalizable and their common eigenbasis is denoted $|s, m\rangle$.

$$S^2|sm\rangle = s(s+1)\hbar^2|sm\rangle, \quad S_z|sm\rangle = \hbar m|sm\rangle. \quad (43)$$

$S_{\pm}|sm\rangle = (S_x \pm iS_y)|sm\rangle$ are found to be eigenvectors of S^2 with the same eigenvalue $s(s+1)\hbar^2$, but eigenvectors of S_z with eigenvalue raised/lowered by \hbar , $S_{\pm}|sm\rangle \propto |s, m \pm 1\rangle$. The largest and smallest possible values of m must be s and $-s$ and since S_+ raises m in steps of 1, $2s = N$ for some non-negative integer $N = 0, 1, 2, \dots$. Thus

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \quad \text{and} \quad m = -s, -s+1, \dots, s-1, s. \quad (44)$$

However, unlike for orbital angular momentum where $L_z = -i\hbar\frac{\partial}{\partial\phi}$, S_z is not a differential operator in the coordinates of the particle. There is no restriction on the allowed values of m being integral rather than half integral. Indeed, in nature, s is found to take on both integer and half odd-integer values. s is referred to as the spin of the particle. Unlike the orbital angular momentum quantum number l , a given type of particle (say electron) has a fixed value of spin s , irrespective of its state of motion or location.

Electrons, protons, neutrons, muons, neutrinos, quarks all have spin $s = \frac{1}{2}$. Mesons like pions and kaons have spin zero, as does the proposed Higgs particle. Rho mesons and photons have spin 1, Delta baryons have spin $3/2$, gravitons would have spin two. Atoms as a whole can also have non-zero spin arising collectively from the spins of the electrons protons and neutrons. There are particles with higher spin as well, but we will focus on spin $s = \frac{1}{2}$, which is relevant to electrons.

For each value of spin s , we need to find a representation of the spin observables S_x, S_y, S_z as hermitian operators on some Hilbert space. The relevant Hilbert spaces are $2s + 1$ dimensional. This representation may be built up from the lowest state $|s, -s\rangle$ by repeatedly applying S_+ .

3.1 Spin half: Pauli spin matrices and spinor wave functions

Here the Hilbert space of spin states is $2s + 1 = 2$ dimensional and has basis $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ which are also denoted $|\uparrow\rangle$ and $|\downarrow\rangle$. The general spin state of a spin half particle is $a|\uparrow\rangle + b|\downarrow\rangle$. In this basis,

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \Rightarrow S^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (45)$$

To find the matrix representation of S_x and S_y we recall that

$$S_{\pm}|sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}|s, m\pm 1\rangle. \quad (46)$$

Thus $S_+|\uparrow\rangle = 0, S_+|\downarrow\rangle = \hbar|\uparrow\rangle$ and

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \Rightarrow S_x = \frac{S_+ + S_-}{2} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \text{and} \quad S_y = \frac{S_+ - S_-}{2i} = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

The traceless hermitian matrices $\sigma_i = \frac{2}{\hbar}S_i$ are called Pauli matrices.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (47)$$

Check that they satisfy

$$[\sigma_i, \sigma_j] = 2\sqrt{-1}\epsilon_{ijk}\sigma_k, \quad \text{and} \quad \sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k. \quad (48)$$

If S_z is measured in the above general state $a|\uparrow\rangle + b|\downarrow\rangle$ then the possible values obtained are $\pm\frac{1}{2}\hbar$ with probabilities given by the absolute squares of the projections of the normalized initial state with the corresponding normalized eigenvectors of S_z . These probabilities are $\frac{|a|^2}{|a|^2+|b|^2}$ and $\frac{|b|^2}{|a|^2+|b|^2}$. On the other hand, if we measure S_x , the possible values obtained are again $\pm\frac{1}{2}\hbar$ but with probabilities $\frac{1}{2}|a+b|^2$ and $\frac{1}{2}|a-b|^2$, where we assume the state has been normalized so that $|a|^2 + |b|^2 = 1$.

- The hydrogen atom hamiltonian commutes not just with L^2, L_z but also S^2 and S_z . So we can label stationary states by n, l, m and also s, m_s . Of course $s = \frac{1}{2}$ is fixed for electrons and the energy eigenvalues are independent of l, m, m_s . So accounting for the two possible spin projections of an electron, we revise the **degeneracy of the hydrogen energy levels** to $2n^2$.

3.2 Free spin-half particle

- The energy of a free particle (no electromagnetic field for instance) is found not to depend on its spin. All spin states have the same energy. The hamiltonian is diagonal in spin space

$$H = \frac{\vec{p}^2}{2m} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (49)$$

As a consequence, S^2 and S^z commute with H and p , so we can label the energy eigenstates with the eigenvalues of these compatible observables.

- The states of the particle are now elements of the tensor product $L^2(\mathbb{R}) \otimes \mathbb{C}^2$ of Hilbert spaces for translational and spin degrees of freedom. An example of such a state is

$$e^{-x^2} \begin{pmatrix} 1 \\ 3 \end{pmatrix} + x^2 e^{-x^2} \begin{pmatrix} -1 \\ 10 \end{pmatrix} \quad (50)$$

Among these states, the energy eigenstates with energy eigenvalue $\frac{\hbar^2 \vec{k}^2}{2m}$ are

$$A e^{i\vec{k} \cdot \vec{x}} \begin{pmatrix} a \\ b \end{pmatrix} \quad (51)$$

for any constants A, a, b and any wave vector \vec{k} . In this state, the probability amplitude for finding the particle at position $x = x'$ with up spin is proportional to $A a e^{i\vec{k} \cdot \vec{x}'}$. A basis for this energy eigenspace can be taken as the set of vectors

$$e^{i\vec{k} \cdot \vec{x}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad e^{i\vec{k} \cdot \vec{x}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{for any } \vec{k}. \quad (52)$$

The degeneracy of the energy eigenstates is doubled on account of the additional spin degree of freedom.

3.3 Larmor precession of spin in a magnetic field

Consider a massive spin half particle of charge e (say an electron) at rest in a magnetic field. Associated to the spin, the electron possesses a magnetic moment proportional to the gyromagnetic ratio

$$\vec{\mu}_S = g \frac{e}{2m} \vec{S} = g \frac{e\hbar}{2m} \frac{\vec{S}}{\hbar} = g \mu_b \frac{\vec{\sigma}}{2}, \quad \text{where } \mu_b = \frac{e\hbar}{2m} \text{ is the Bohr magneton.} \quad (53)$$

From classical electrodynamics we expect the g -factor to be $g = 1$, based on a current loop model of a magnetic moment. But the electron spin magnetic moment is not explained by this current loop model. The ‘ g -factor’ associated to electron spin is $g_S \approx 2.0023$, a number which is experimentally determined and also predicted by quantum electrodynamics.

We note that the magnetic moment of an electron due to its orbital angular momentum is as predicted by the classical current loop model

$$\vec{\mu}_L = \frac{e}{2m} \vec{L} = \mu_b \frac{\vec{L}}{\hbar}. \quad (54)$$

So the electron spin gyromagnetic ratio is roughly twice as big as that from orbital angular momentum.

So if an electron is subject to a magnetic field \vec{B} , then its magnetic dipole energy is

$$H = -(\vec{\mu}_S + \vec{\mu}_L) \cdot \vec{B} = \left(g \frac{|e|\hbar}{2m} \vec{S} + \frac{|e|\hbar}{2m} \vec{L} \right) \cdot \vec{B} \quad (55)$$

Now suppose the electron is at rest and $\vec{B} = B_0 \hat{z}$. Then the hamiltonian is (the electron charge $e = -|e|$ is negative)

$$H = -\mu_S \cdot B = \frac{g|e|\hbar B_0}{2m} S_z = \frac{g|e|\hbar B_0}{4m} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \equiv E \sigma_z \quad (56)$$

So the energy eigenstates are the same as those of S_z . The ground state is $|\downarrow\rangle$ with energy $E_{gs} = -E = -\frac{g|e|\hbar B_0}{4m}$ and the excited state is $|\uparrow\rangle$ with energy E . Find the time evolution of an arbitrary initial state. Show that the spin precesses about the vertical axis at a constant rate. Find the precession frequency.

3.4 Rotations generated by angular momentum and spin

We learned that momentum generates infinitesimal translations

$$\psi(x+a) \approx \left(I + \frac{ip a}{\hbar} \right) \psi(x) + \mathcal{O}(a^2) \quad (57)$$

Finite translations are effected by

$$\psi(x+a) = e^{\frac{ipa}{\hbar}} \psi(x); \quad \psi(\vec{r}+\vec{a}) = e^{\frac{i\vec{p}\cdot\vec{a}}{\hbar}} \psi(\vec{r}). \quad (58)$$

Angular momentum generates infinitesimal rotations. A rotation by a small angle $\delta\alpha$ counter clockwise about the axis $\delta\vec{\alpha}$ is given by

$$\psi(\vec{r} + \delta\vec{\alpha} \times \vec{r}) = \left(I + \frac{i\vec{L} \cdot \delta\vec{\alpha}}{\hbar} \right) \psi(\vec{r}). \quad (59)$$

Similarly, a finite rotation is effected by $R_{\vec{\alpha}} = e^{\frac{i\vec{L}\cdot\vec{\alpha}}{\hbar}}$

$$\psi(\vec{r} + \vec{\alpha} \times \vec{r}) = e^{\frac{i\vec{L}\cdot\vec{\alpha}}{\hbar}} \psi(\vec{r}). \quad (60)$$

Of course, rotations do not affect r , they only affect the angles θ, ϕ . So we will focus on the angles and consider a wave function $\psi(\theta, \phi)$. Any such wave function can be expanded as a linear combination of spherical harmonics $\psi(\theta, \phi) = \sum_{lm} c_{lm} \psi_{lm}(\theta, \phi)$. We have seen that the angular momentum operators \vec{L} are each block diagonal in the spherical harmonic basis. This means L_x, L_y, L_z have zero matrix elements between spherical harmonics with different values of l

$$\langle Y_{lm} | L_i | Y_{l'm'} \rangle \propto \delta_{ll'}. \quad (61)$$

So under a rotation, $e^{\frac{i\vec{L}\cdot\vec{\alpha}}{\hbar}} \psi(\theta, \phi)$, if the initial state ψ was one with a definite value of l then the transformed wave function will also have the same value of l .

So let us consider how a p -wave state $\psi(r, \theta, \phi) = aY_{11} + bY_{10} + cY_{1,-1}$ transforms under such rotations. For example, the result of a counter-clockwise rotation by angle α about the z -axis is given by

$$R_{\alpha \hat{z}} (aY_{11} + bY_{10} + cY_{1,-1}) = e^{iL_z \alpha / \hbar} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} ae^{i\alpha} \\ b \\ ce^{-i\alpha} \end{pmatrix}$$

$$R_{\alpha\hat{z}}Y_{11} = e^{i\alpha}Y_{11}, \quad R_{\alpha\hat{z}}Y_{10} = Y_{10}, \quad \text{and} \quad R_{\alpha\hat{z}}Y_{1-1} = e^{-i\alpha}Y_{1-1}. \quad (62)$$

In particular Y_{10} is unaffected by a rotation about z -axis, which is not surprising as it was independent of the azimuthal angle ϕ to begin with. We should have been able to guess the answers using

$$Y_{10} \propto \cos\theta, \quad Y_{1,\pm 1} \propto \sin\theta e^{\pm i\phi}. \quad (63)$$

In particular, we observe that a rotation by $\alpha = 2\pi$ brings us back to the initial state, as we would expect.

- Remark: Rotation of a physical vector can be thought of in two ways. (1) A rotation of the corresponding position vector \vec{r} holding the surroundings (axes) fixed. Or (2) a rotation (by the negative angle) of the ambient space (i.e., the axes) holding \vec{r} fixed. In both points of view, a rotation by $\alpha = 2\pi$ about any axis acts as the identity transformation for any function $\psi(\vec{r})$.

- By analogy with the rotations generated by angular momentum we may consider the transformations generated by spin $e^{\frac{i\vec{S}\cdot\vec{\phi}}{\hbar}}$. For spin half, these become $e^{\frac{i\vec{\sigma}\cdot\vec{\phi}}{2}}$ where $\vec{\sigma}$ is the vector of Pauli matrices. These rotations act on the spin wave function (e.g. $a|\uparrow\rangle + b|\downarrow\rangle$), which however, is not a function of the spatial coordinates.

- So a rotation about an axis in ordinary three dimensional space has two effects. On the one hand, it transforms the coordinate wave function $\psi(\vec{r})$ via the angular momentum operator. It also transforms the spinorial wave function via the spin operator. This transformation generated by spin acts on the ‘internal’ spin degrees of freedom.

- For example, calculate the 2×2 matrix representing a rotation by angle ϕ about the \hat{n} direction, on the spin wavefunction. As a consequence, show that the spin wavefunction changes sign (though it represents the same physical state) under a rotation by 2π , unlike the coordinate wave function.

- Find how an ‘up spin’ $|\uparrow\rangle$ transforms under a rotation by π about the y axis.

4 Addition of angular momenta

4.1 State space and observables for two particle systems

So far we dealt with 1-particle systems (electron in an atom, spin in a magnetic field e.t.c.). Now suppose we have a system of two particles, each of whose space of quantum states are the Hilbert spaces \mathcal{H}_1 and \mathcal{H}_2 . For example, \mathcal{H}_1 could be specified by a basis, i.e., \mathcal{H}_1 is the linear span of a collection of basis vectors, which may be the energy eigenstates of an SHO if we have a particle in one dimension. Similarly, we specify \mathcal{H}_2 as the linear span of a set of basis vectors. Then the space of states of the combined system is the so-called tensor/direct product Hilbert space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. If ψ_n and ϕ_m are a basis for \mathcal{H}_1 and \mathcal{H}_2 respectively, then a basis for $\mathcal{H}_1 \otimes \mathcal{H}_2$ is given by the vectors $\psi_n \otimes \phi_m$. So any state of the combined system is a linear combination of tensor products of basis states of the individual systems.

- This definition is imposed on us by the superposition principle of quantum mechanics. In classical mechanics, the state of a system of 2 particles is given by specifying the state of each particle (x_1, p_1, x_2, p_2) . Analogously in quantum mechanics we might expect the state of the system to be specified by giving the states of each particle, say $|\psi_1\rangle|\phi_2\rangle$. However,

the superposition principle says that these cannot be all the states, since a linear combination of states is also an allowed state. This directly leads to the conclusion that arbitrary linear combinations of product states are allowed states of the combined system. Now the tensor product is merely a notation for writing these product states. The definition of tensor product Hilbert space is merely kinematical, it does not presuppose any particular interaction between the particles.

- E.g., if we have two spin half particles, a basis for their combined spinorial Hilbert space is given by

$$|\uparrow\rangle \otimes |\uparrow\rangle \equiv |\uparrow\uparrow\rangle, \quad |\uparrow\rangle \otimes |\downarrow\rangle \equiv |\uparrow\downarrow\rangle, \quad |\downarrow\rangle \otimes |\uparrow\rangle \equiv |\downarrow\uparrow\rangle, \quad |\downarrow\rangle \otimes |\downarrow\rangle \equiv |\downarrow\downarrow\rangle. \quad (64)$$

We sometimes abbreviate by dropping the \otimes symbol as above. The dimension of the tensor product Hilbert space is the product of dimensions.

- Observables for the two particle system are (hermitian) operators acting on the tensor product Hilbert space. Examples of such operators are tensor products of operators acting on each particle separately. For example, if \vec{S}_1 and \vec{S}_2 are the spin operators for each, then we have the total spin operator

$$\vec{S} = \vec{S}_1 \otimes 1 + 1 \otimes \vec{S}_2 \quad (65)$$

The identity operator for the combined system is $1 \otimes 1$. We often drop the \otimes symbol and suppress the identity operators and write $\vec{S} = \vec{S}_1 + \vec{S}_2$. The z -component of the first spin is $S_{1z} \otimes 1$. The total z -component of spin is $S_z = S_{1z} \otimes 1 + 1 \otimes S_{2z} \equiv S_{1z} + S_{2z}$. A tensor product operator $A \otimes B$ acts on a basis state of the tensor product Hilbert space by

$$(A \otimes B)(u \otimes v) = (Au) \otimes (Bv) \quad (66)$$

The composition of a pair of tensor product operators is given by

$$(A \otimes B)(C \otimes D) = AC \otimes BD \quad (67)$$

This is what you get if you keep in mind that C acts on the state of the first particle followed by A , again on the first particle. Similarly, D acts on the state of the second particle followed by the action of B . For example, the square of total spin works out to be

$$S^2 = (\vec{S}_1 + \vec{S}_2)^2 = S_1^2 \otimes 1 + 1 \otimes S_2^2 + 2\vec{S}_1 \otimes \vec{S}_2. \quad (68)$$

Make sense of this formula and work out how it acts on the above-mentioned tensor product states.

- The tensor product carries a natural inner product induced by the inner products on the individual Hilbert spaces. On basis states, the inner product is

$$\langle u \otimes v, w \otimes z \rangle = \langle u, w \rangle \langle v, z \rangle. \quad (69)$$

4.2 Representation of tensor products of vectors and matrices

- Suppose we have two spin half particles. The individual Hilbert spaces are two dimensional and we can choose their bases to be $\mathcal{H}_1 = \text{span}(\uparrow, \downarrow) = \text{span}(e_1, e_2)$ and $\mathcal{H}_2 = \text{span}(\uparrow, \downarrow) = \text{span}(f_1, f_2)$. These basis vectors are represented by the column vectors

$$e_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad e_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad f_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad f_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (70)$$

The combined Hilbert space is four dimensional and we can choose as a basis (in the following order)

$$\uparrow\uparrow = e_1 \otimes f_1, \quad \uparrow\downarrow = e_1 \otimes f_2, \quad \downarrow\uparrow = e_2 \otimes f_1, \quad \downarrow\downarrow = e_2 \otimes f_2 \quad (71)$$

Then in this basis, the basis vectors themselves can be represented by 4-component column vectors

$$e_1 \otimes f_1 = (1000)^t, \quad e_1 \otimes f_2 = (0100)^t, \quad e_2 \otimes f_1 = (0010)^t, \quad e_2 \otimes f_2 = (0001)^t. \quad (72)$$

We can also arrive at these 4 component column vectors by the following rule for tensor products. This rule is merely a translation of the above choice for ordering the basis vectors

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \otimes \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} a_1 b_1 \\ a_1 b_2 \\ a_2 b_1 \\ a_2 b_2 \end{pmatrix} \Rightarrow e_1 \otimes f_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \text{e.t.c.} \quad (73)$$

On the other hand, tensor products of observables are again linear operators on the combined Hilbert space and should be expressible as 4×4 matrices on the combined Hilbert space. Consider 2 observables

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}. \quad (74)$$

Then the tensor product when it acts on $e_1 \otimes f_1$ is by definition

$$\begin{aligned} (A \otimes B)(e_1 \otimes f_1) &= A e_1 \otimes B f_1 = (a_{11} e_1 + a_{21} e_2) \otimes (b_{11} f_1 + b_{21} f_2) \\ &= a_{11} b_{11} e_1 \otimes f_1 + a_{11} b_{21} e_1 \otimes f_2 + a_{21} b_{11} e_2 \otimes f_1 + a_{21} b_{21} e_2 \otimes f_2. \end{aligned} \quad (75)$$

This allows us to deduce the first column of $A \otimes B$

$$A \otimes B = \begin{pmatrix} a_{11} b_{11} & \cdots \\ a_{11} b_{21} & \cdots \\ a_{21} b_{11} & \cdots \\ a_{21} b_{21} & \cdots \end{pmatrix} \quad (76)$$

Proceeding this way we find the remaining columns of $A \otimes B$ and conclude that

$$A \otimes B = \begin{pmatrix} a_{11} B & a_{12} B \\ a_{21} B & a_{22} B \end{pmatrix}_{4 \times 4}. \quad (77)$$

Use these rules to represent S_z and S^2 as 4×4 matrices and deduce their eigenvectors and corresponding eigenvalues.

4.3 Addition of two spin-half angular momenta

The sum of two spin operators $\vec{S} = \vec{S}_1 + \vec{S}_2$ satisfies the same angular momentum algebra as each of the individual spins. Check that

$$[S_x, S_y] = [S_{1x} + S_{2x}, S_{1y} + S_{2y}] = i\hbar(S_{1z} + S_{2z}) = i\hbar S_z, \quad \text{e.t.c.} \quad (78)$$

In particular we can carry over all our results on the matrix representation of spin observables which depend only on these commutation relations. In particular, $[S^2, S_z] = 0$ and we have raising and lowering operators $S_{\pm} = S_{1\pm} + S_{2\pm}$ which raise or lower the eigenvalue of S_z by \hbar . We may denote the simultaneous eigenstates of S^2 and S_z by $|sm\rangle$ and as before we must have highest/lowest weight states $|ss\rangle, |s, -s\rangle$ that are annihilated by S_{\pm} . Of course, there could be more than one highest weight state labelled by different values of s . From each highest weight state we can build a representation of spin operators by acting repeatedly with S_- . Now we want to know what possible values s can take given that $\vec{S} = \vec{S}_1 + \vec{S}_2$ is the sum of two spin half observables. For each value of s , the allowed values of m will be as before, running from $-s$ to s in steps of one.

Since $|sm\rangle$ is a state of a two-spin system, it must be expressible as a linear combination of tensor products of states of single spins. There are four tensor product basis vectors

$$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \quad (79)$$

We find that all of these are eigenstates of $S_z = S_{1z} + S_{2z}$ which just adds the z -components of the two spins. The corresponding values of m are $1, 0, 0, -1$. So it would appear that the value of s is either 1 or 0, as we will see.

- Now $S_+|\uparrow\uparrow\rangle = 0$. So we can build one representation by successively applying $S_- = S_{1-} + S_{2-}$ to $|\uparrow\uparrow\rangle$

$$S_-|\uparrow\uparrow\rangle = \hbar|\downarrow\uparrow\rangle + \hbar|\uparrow\downarrow\rangle; \quad S_- (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = 2\hbar|\downarrow\downarrow\rangle, \quad S_-|\downarrow\downarrow\rangle = 0. \quad (80)$$

These three basis states are found to be eigenstates of S^2 with eigenvalue $2\hbar^2$ (show this!). Thus we have a spin $s = 1$ three dimensional ‘triplet’ representation on the states

$$|11\rangle = |\uparrow\uparrow\rangle, \quad |10\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |1, -1\rangle = |\downarrow\downarrow\rangle. \quad (81)$$

The remaining orthogonal state with $m = 0$,

$$|00\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (82)$$

is annihilated by both S_- and S_+ and therefore furnishes a 1-dimensional representation of total spin. It is shown to be an eigenstate of S^2 and S_z with eigenvalues 0 and 0. Thus it corresponds to $s = 0, m_s = 0$ and is called the singlet state $|00\rangle$. Notice that the states in the spin-1 triplet representation are symmetric under exchange of particles while the singlet state is anti-symmetric under exchange. This will be exploited when we discuss the Pauli principle.

- To summarize, the total spin of a composite system consisting of two spin half particles can be either $s = 0$ or $s = 1$. This is expressed in the formula $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$. The four dimensional Hilbert space of the composite system splits into the *direct sum* of a one dimensional subspace spanned by the singlet state with $s = 0$ and a three dimensional subspace spanned by the triplet states with $s = 1$.

- The Hilbert space of the combined system has two interesting bases. The first is the ‘uncoupled’ basis of tensor product states $\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$ which are eigenstates of S_{1z}, S_{2z}, S_1^2 and S_2^2 , which are all simultaneously diagonalizable. (In fact S_1^2 and S_2^2 are just proportional to the identity). The uncoupled basis states may be denoted $|s_1, m_1, s_2, m_2\rangle$.

- Then there is the ‘coupled’ basis of eigenstates of S^2, S_z (and S_1^2 and S_2^2) which we could denote $|s, m, s_1, s_2\rangle$. Here $s_1 = s_2 = \frac{1}{2}$ are constant so we usually suppress them. The coupled basis states consist of the triplet and singlet states.
- We can express the basis vectors of the coupled basis as linear combinations of the uncoupled basis vectors and vice versa.

$$|s, m, s_1, s_2\rangle = \sum_{m_1, m_2} C_{m_1, m_2}^{sm} |s_1, m_1\rangle \otimes |s_2, m_2\rangle. \quad (83)$$

The coefficients in these linear combinations are called Clebsch-Gordan coefficients. We have obtained a few of them above.

4.4 Addition of two or more angular momenta

- More generally, we can combine two spins or angular momenta l_1 and l_2 . The result is that the angular momentum l of the combination takes each value from $|l_1 - l_2|$ to $l_1 + l_2$ in integer steps. This is expressed in the formula

$$l_1 \otimes l_2 = (l_1 + l_2) \oplus (l_1 + l_2 - 1) \oplus \cdots \oplus |l_1 - l_2|. \quad (84)$$

For example, if we form a composite system from two spin one particles, the combined system again behaves like a spin system, but with spin either 2 or 1 or 0. The Clebsch-Gordan coefficients for combining angular momenta are tabulated in various quantum mechanics books. To combine three spins, we first combine two of them and then the third and so on.

- This quantum mechanical procedure for finding the resultant spin is to be contrasted with the vector addition formula for combining angular momenta in classical mechanics. However, there is some similarity. Classically, the resultant angular momentum $\vec{L} = \vec{L}_1 + \vec{L}_2$ can take a maximum magnitude equal to $|\vec{L}_1| + |\vec{L}_2|$ when the angular momenta are parallel and a minimal value $||\vec{L}_1| - |\vec{L}_2||$ when the angular momenta are anti-parallel. These maximal and minimal values are analogous to the quantum mechanical result that the maximum angular momentum quantum number is $l_1 + l_2$ and minimal value is $|l_1 - l_2|$. Of course, classically every value in between is also a possibility depending on the relative orientations of the two angular momentum vectors. Quantum mechanically, only certain intermediate values of l are allowed, in integer steps! The classical limit is obtained in the limit of large quantum numbers $l(l+1)\hbar^2 \gg \hbar^2, l_1, l_2 \gg 1$. In this limit, $\sqrt{\hbar^2 l(l+1)} \approx \hbar l \rightarrow |\vec{L}|$ e.t.c. Moreover the size of the small integer steps in units of \hbar is very small compared to the angular momentum and a continuum of values is approximately obtained.

- More generally we may combine any number of spins/angular momenta $s_1 \otimes s_2 \otimes \cdots \otimes s_n$. Then there is a unique (up to normalization) highest weight state (annihilated by S_+) ψ_{hws} with maximal spin projections $S_z |s_1, \cdots, s_n\rangle = \hbar(s_1 + \cdots + s_n) |s_1, \cdots, s_n\rangle$. Applying S_- to this state produces an eigenstate of S_z with eigenvalue $\hbar(s_1 + \cdots + s_n - 1)$ which is \hbar less than maximal. This is the symmetric state

$$\psi_S \propto |s_1 - 1, s_2, \cdots, s_n\rangle + |s_1, s_2 - 1, \cdots, s_n\rangle + \cdots + |s_1, s_2, \cdots, s_n - 1\rangle \quad (85)$$

We may successively apply S_- to this to produce a spin $s_1 + \cdots + s_n$ representation. However the space of states with spin projection \hbar less than maximal is n dimensional with basis

$$|s_1 - 1, s_2, \cdots, s_n\rangle, |s_1, s_2 - 1, \cdots, s_n\rangle, \dots, |s_1, s_2, \cdots, s_n - 1\rangle. \quad (86)$$

Any state ψ in this subspace that is orthogonal to ψ_S is automatically annihilated by S_+ and furnishes a highest weight state for a new spin $s_1 + \dots + s_n - 1$ representation. This procedure is then repeated. Let us see why $S_+\psi = 0$. Since $S_z(S_+\psi) = \hbar(s_1 + \dots + s_n)S_+\psi$, and the space of states with maximal spin projection is one dimensional we must have for some constant c

$$S_+\psi = c\psi_{hws} \quad (87)$$

We will show that $c = 0$ if $\psi \perp \psi_S$. Taking an inner product

$$\langle \psi_{hws} | S_+ | \psi \rangle = \langle \psi_{hws} | c\psi_{hws} \rangle = c \Rightarrow c = \langle S_- \psi_{hws} | \psi \rangle = \langle \psi_S | \psi \rangle = 0. \quad (88)$$

5 Multiparticle systems: Identical particles: bosons & fermions

5.1 Identical and indistinguishable particles

In classical physics we can distinguish a pair of tennis balls since they may not have exactly the same mass or number of fibres. Classical objects may be identified/labelled by their intrinsic properties detected by their different interactions with various measuring devices (like light (for color) or smell or mass). By intrinsic properties we mean charge, mass, shape or inertia tensor etc, not the position or speed of the particle. Even if the masses, shapes and inertia tensors were the same to the accuracy of our devices (i.e., the balls seem identical) we could still distinguish the two tennis balls by keeping track of their historical trajectories $(x(t), p(t))$, ball A was the one that left the factory at 10am on 23/4/10 etc while ball B had a slightly different trajectory (after all we have never found two tennis balls with coincident trajectories even for a short duration).

- The situation with objects needing a quantum mechanical treatment is somewhat different. No experiment so far has been able to distinguish one electron from another, they all have the same mass, charge, spin, magnetic moment and interactions with light, atoms etc. What is more, the possibility of distinguishing two electrons based on their semi-classical trajectories may seem to work approximately for some time, but can easily fail. The electron wave packets, if they come quite close, would overlap, interfere and we would not be able to unambiguously label the electrons when the wave packets separate.
- This is a particularly severe problem when we are dealing with atoms with several electrons. The electrons do not have well-defined orbits, their wave functions overlap and it has not been possible to keep track of which electron is which as time progresses. There are many other examples of identical particles in nature including photons in a black body cavity, neutrons in a neutron star, Rubidium atoms in a laser trap etc.
- Contrast this with the situation with planets in the solar system where we can distinguish them by their color/mass/temperature/support for life/historical trajectories etc. So quantum mechanically electrons are identical and indistinguishable. Of course, not all particles are identical and indistinguishable. We *can* tell a proton apart from an electron by its mass.
- The state of a multi-particle system is a ray in the tensor product Hilbert space. Let us consider two identical particles for simplicity. Since the particles are identical, their individual Hilbert spaces of states can be taken to be the same $\mathcal{H}_1 \cong \mathcal{H}_2$. If ϕ_a is a basis for the individual

Hilbert space, a vector in the tensor product $\mathcal{H}_1 \otimes \mathcal{H}_2$ is of the form

$$\psi(x_1, x_2) = \sum_{a,b} c_{ab} \phi_a(x_1) \otimes \phi_b(x_2) \quad (89)$$

Define the permutation or exchange operator (not to be confused with parity) $P\psi(x_1, x_2) = \psi(x_2, x_1)$ which exchanges the coordinates (and spins if we were keeping track of the spins). Check that this implies that P is hermitian. To implement the identical and indistinguishable nature of the particles, we postulate that the vector ψ and the vector $P\psi$ must represent the same physical state. This implies that

$$\psi(x_1, x_2) = e^{i\theta} \psi(x_2, x_1) \quad (90)$$

for some phase $e^{i\theta}$. We will find that $e^{i\theta} = \pm 1$ are the allowed values, corresponding to bosons and fermions respectively. In particular,

$$P\psi(x_1, x_2) = \psi(x_2, x_1) = e^{-i\theta} \psi(x_1, x_2). \quad (91)$$

From the definition of P we also see that $P^2 = I$ is the identity. Thus we have

$$P^2\psi(x_1, x_2) = \psi(x_1, x_2) \quad \text{and} \quad P^2\psi(x_1, x_2) = e^{-2i\theta} \psi(x_1, x_2). \quad (92)$$

Comparing we find $e^{-2i\theta} = 1$ or $e^{i\theta} = \pm 1$, which means there are only two possibilities

$$\psi(x_1, x_2) = \pm \psi(x_2, x_1) \quad (93)$$

and we say that wavefunctions of a system of two (though it is true also for more than two) identical particles must be either symmetric or antisymmetric under exchange. Note that this applies to all states, not just energy eigenstates!

- In addition we postulate that exchange of particles must be a symmetry of the dynamics, i.e., classically the forces and energy must not be affected by a permutation of the particles (if this weren't true we could distinguish the particles). This means the classical hamiltonian is symmetric

$$H(x_1, p_1; x_2, p_2) = H(x_2, p_2; x_1, p_1) \quad (94)$$

In the quantum theory this means $[P, H] = 0$. Thus, P and H are simultaneously diagonalizable. Energy eigenstates may therefore be chosen to be eigenstates of the exchange operator and must be either symmetric or anti-symmetric functions of the coordinates.

- The symmetric and anti-symmetric functions describe different types of particles. Fermionic particles are those with anti-symmetric wave functions while bosonic particles are those with symmetric wave functions. Electrons in an atom need to be described by anti-symmetric wave functions to match the measured atomic spectra and periodic table. They are fermions. Photons and many isotopes of alkali metal atoms need to be described by symmetric wave functions to match their experimental properties such as Bose condensation. They are bosons. Remarkably, it is found that particles with integer spin $s = 0, 1, 2, \dots$ are bosons and those with half-odd-integer spin $s = \frac{1}{2}, \frac{3}{2}, \dots$ are fermions.

- What is more, $[H, P] = 0$ implies that if the initial state is an eigenstate of P , then it will remain an eigenstate of P under Schrödinger evolution with the same eigenvalue. So a system of identical bosons remains this way at all times. We may build multi-particle wave functions

by taking products of single particle orbitals and either symmetrizing or anti-symmetrizing for bosons and fermions respectively.

- Examples of symmetrized and antisymmetrized wave functions for two particles are

$$\psi_S(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) + \phi_a(x_2)\phi_b(x_1), \quad \psi_A(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) - \phi_a(x_2)\phi_b(x_1). \quad (95)$$

We remark that this anti-symmetric state could also be written as a ‘Slater’ determinant.

$$\psi_A(x_1, x_2) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} \quad (96)$$

Written this way, antisymmetry is equivalent to the statement that the determinant changes sign under a permutation of two columns. This way of writing anti-symmetric states is particularly useful when there are more than two particles.

- Of course, these are just the simplest examples of (anti-)symmetrized wave functions built out of a pair of single particle wavefunctions. More generally we could take linear combinations of (anti-)symmetric wavefunctions to produce new (anti-)symmetric wave functions. E.g. we may build a fermionic state from four one particle wavefunctions

$$\psi_A(x_1, x_2) = N_1 \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} + N_2 \det \begin{pmatrix} \phi_c(x_1) & \phi_c(x_2) \\ \phi_d(x_1) & \phi_d(x_2) \end{pmatrix} \quad (97)$$

- Symmetric and anti-symmetric wave functions have rather different physical features. For example, the probability amplitude to find both particles at the same location $x_1 = x_2 = x$ in an anti-symmetrized state is zero $\psi_A(x, x) = 0$, though it can be non-zero in a symmetrized state. Alternatively $\psi_A = 0$ if $\phi_a = \phi_b = \phi$. This is loosely stated as ‘two identical fermions (e.g. electrons) *cannot* occupy the same 1-particle state ϕ ’. On the other hand, two identical bosons (e.g. photons) *can* occupy the same state. We use this while obtaining the distribution of photons in a black body cavity.

- This property of electrons had been postulated by Pauli (even before the development of Schrodinger’s equation), in an attempt to explain atomic spectra and the periodic table. Pauli’s exclusion principle stated that there was at most one electron per state in an atom. The states could be labelled by the same quantum numbers as appearing in the hydrogen atom n, l, m and an extra quantum number with two possible values. The latter quantum number was subsequently identified as the electron spin projection m_s . Of course, the hydrogen atom stationary state wave functions do not account for electron-electron repulsion, and cannot just be taken over to construct the wave function of a many-electron atom. However, there are ways to do this approximately. In any case, the Pauli-exclusion principle in the form ‘multi-electron wave functions must be anti-symmetric’ under exchange of quantum numbers (coordinates, spins) of any pair of electrons, has stood the test of time.

- For a system of N identical particles, we define the exchange operators which permute the quantum numbers of i^{th} and j^{th} particle (coordinates and spin projections)

$$P_{ij}\psi(\cdots, x_i, \cdots, x_j, \cdots) = \psi(\cdots, x_j, \cdots, x_i, \cdots), \quad \text{for } 1 \leq i, j \leq N. \quad (98)$$

Then each P_{ij} must commute with the hamiltonian. Every energy eigenstate $\psi(x_1, \cdots, x_n)$ can be taken as either symmetric or antisymmetric under *every* such permutation. Symmetric states describe bosons and anti-symmetric ones describe fermions.

- For three identical particles we have three exchange operators P_{12}, P_{23}, P_{31} . Note that $P_{12} = P_{21}$ etc. The action of a permutation operator on a state vector $\psi(x_1, x_2, x_3)$ must produce a state vector that differs from the original one at most by a phase: $P_{ij}\psi = e^{i\theta_{ij}}\psi$. Each permutation operator P_{ij} squares to the identity $P_{ij}P_{ij} = I$, proceeding as before, we find $e^{i\theta_{ij}} = \pm 1$.

- In other words, every state of a system of identical and indistinguishable particles must be an eigenstate of all the P'_{ij} 's with eigenvalues ± 1 . Note that the permutation operators pairwise commute $P_{ij}P_{kl} = e^{i(\theta_{ij}+\theta_{kl})} = P_{kl}P_{ij}$. So they are simultaneously diagonalizable. Now a question arises whether a quantum mechanical system of identical and indistinguishable particles can be in a state where some of the P_{ij} 's have eigenvalue one and some other permutations have eigenvalue minus one. This is not allowed since if there were such a state where, say, $P_{12}\psi = \psi$ and $P_{13}\psi = -\psi$ then we could use these eigenvalues to distinguish between particle 2 and particle 3, violating the indistinguishability. So the only allowed states of identical particles are those that are symmetric under *every* exchange and those that are anti-symmetric under *every* exchange. Moreover, since permutations of particles must be symmetries of the dynamics, we must also have $[P_{ij}, H] = 0$ for all i, j . Thus, the states which are symmetric under every exchange are preserved under time evolution; they are called systems of bosons. The anti-symmetric states are also preserved under time evolution and are called systems of fermions.

- An example of a fermionic state of N particles is given by the Slater determinant, which is constructed using N one particle wave functions ('orbitals'). For $N = 3$ let ϕ_a, ϕ_b, ϕ_c be three one-particle wave functions ('orbitals')

$$\psi_A(x_1, x_2, x_3) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) & \phi_a(x_3) \\ \phi_b(x_1) & \phi_b(x_2) & \phi_b(x_3) \\ \phi_c(x_1) & \phi_c(x_2) & \phi_c(x_3) \end{pmatrix} \quad (99)$$

To build an example of a bosonic state of three identical particles we only need a single 1-particle orbital $\psi_S(x_1, x_2, x_3) = \phi(x_1)\phi(x_2)\phi(x_3)$.

- We may also consider what happens to the state vector of a system of identical particles under permutations that are not simple exchanges of particles. An example is a cyclic permutation of the particles. However, every permutation can be built by composing exchanges, so these new permutations do not contain new information. One finds that wave functions of systems of fermions are anti-symmetric under odd-permutations, such as pairwise exchanges. Under even permutations such as $P_{12}P_{23}$, wave functions of systems of fermions are unchanged. Wave functions of systems of bosons are unchanged under all permutations, irrespective of whether they are even or odd.

5.2 Two spin half electrons in Helium

Consider a pair of spin half fermions, whose orbital motion is not coupled to the spin degrees of freedom, e.g. if the hamiltonian operator is the identity in spin space. This is true for the two electrons in Helium in a non-relativistic treatment where the hamiltonian does not involve any spin-orbit coupling terms:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}. \quad (100)$$

H is symmetric under exchange of the degrees of freedom of the two particles. So it commutes with the exchange operator and we seek simultaneous eigenstates of H and P . We write the total wave function as a product of a spatial and a spin part²

$$\psi(x_1, m_1; x_2, m_2) = \phi(x_1, x_2)\chi(m_1, m_2) \quad (101)$$

$\phi(x_1, x_2)$ is \propto to the probability amplitude for the first particle to be at x_1 and second to be at x_2 irrespective of their spin states. Similarly, $\chi(m_1, m_2)$ is \propto the probability amplitude for the spin projection of the first particle to be $\hbar m_1$ and that of the second particle to be $\hbar m_2$, irrespective of their positions³. Here m_1 and m_2 only take the values $\pm\frac{1}{2}$ while x_1, x_2 are any points in 3d space. In general,

$$\chi = a \uparrow\uparrow + b \uparrow\downarrow + c \downarrow\uparrow + d \downarrow\downarrow \quad \text{where} \quad \chi\left(\frac{1}{2}, \frac{1}{2}\right) = a, \quad \chi\left(\frac{1}{2}, -\frac{1}{2}\right) = b, \dots \quad (102)$$

The Pauli principle of anti-symmetrization states that the total wavefunction must be anti-symmetric under exchange of both coordinate and spin degrees of freedom

$$\psi(x_1, m_1; x_2, m_2) = -\psi(x_2, m_2; x_1, m_1) \quad (103)$$

Now let us look for other operators that commute with both H and P . $H \propto I$ in spin space, so it commutes with the combined spin operators of the two particles S^2 and S_z as well as with S_1^2 and S_2^2 which are each proportional to the identity. All these four spin observables also commute with P . On the other hand, S_{1z} commutes with H but not with P . So in particular, P is *not* diagonal in the uncoupled basis of spin states, but it is diagonal in the coupled basis.

- So we look for energy eigenstates that are simultaneous eigenstates of P , S^2 and S_z . Then there are only two ways to make ψ anti-symmetric: ϕ and χ are symmetric and anti-symmetric respectively or vice-versa.

$${}^1\psi = \phi_S(x_1, x_2)\chi_A(m_1, m_2) \quad \text{or} \quad {}^3\psi = \phi_A(x_1, x_2)\chi_S(m_1, m_2) \quad (104)$$

We have seen that there is only one anti-symmetric 2 particle spin state, the singlet $\chi_A = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ while there are a triplet of symmetric spin states χ_S . In the case of Helium, the spin singlet states are called parahelium and the spin triplet ones orthohelium. Orthohelium states are triply degenerate since the hamiltonian is diagonal in spin space.

- Often we may approximate ϕ by an (anti-)symmetrized combination of single particle wave functions ϕ_1 and ϕ_2 (in general we will need linear combinations of these):

$$\phi_A(x_1, x_2) = \frac{1}{\sqrt{2}}(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)) \quad \text{and} \quad \phi_S(x_1, x_2) = \frac{1}{\sqrt{2}}(\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1))$$

In the Helium atom, these two single particle wave functions ϕ_1, ϕ_2 could be taken as two stationary state wavefunctions of a Hydrogenic atom with nuclear charge $Z = 2$ ⁴. By making different choices for ϕ_1 and ϕ_2 we may search for a state ψ which minimizes the expectation value of the Helium hamiltonian. It turns out that the ground state of the Helium atom is a spin

²If the orbital and spin degrees of freedom were coupled, we would need linear combinations of such product wave functions

³If the spin and coordinate degrees of freedom were coupled, the amplitudes for spin projections could depend on position.

⁴If we ignore the electron-electron repulsion, each electron is in a hydrogenic atom with $Z = 2$.

singlet (parahelium) state $\phi_S\chi_A$ where ϕ_1 and ϕ_2 are both approximately ground state wave functions of hydrogenic atoms. This is why we say Helium has the electronic configuration $1s^2$. The first excited state is a triplet of degenerate orthohelium states etc. To find the eigenfunctions (only $\phi(r_1, r_2)$ remains to be found) we must solve the Schrodinger eigenvalue problem. This is quite hard and one resorts to approximations such as perturbation theory and the variational method. In both approaches, one needs to calculate the expectation value of the the helium hamiltonian. The variational principle states that the ground state energy is the minimal value of $\langle\psi|H|\psi\rangle$ among all unit norm states.

5.3 Coulomb and exchange interactions

To find the ground state of helium, we need to minimize the expectation value of H among all anti-symmetric two particle states. The symmetry /antisymmetry of $\phi_{S,A}$ imply some interesting qualitative features for the expectation value of the interaction energy arising from electrostatic repulsion of electrons. The interaction part of the helium hamiltonian can be written

$$V_I = G(r_1 - r_2) = \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|} \quad (105)$$

Since electrons are identical, $G(r_1 - r_2) = G(r_2 - r_1)$. As discussed in the last section, we are interested in spatial wave functions that are built from a pair of (normalized) one-particle wave functions

$$\phi_{S,A} = \frac{1}{\sqrt{2}} [\phi_a(r_1)\phi_b(r_2) \pm \phi_a(r_2)\phi_b(r_1)] \quad (106)$$

Let us calculate the expectation value of V_I in the states $\phi_{S,A}$ Show that you get

$$\langle V_I \rangle = \int d^3r_1 d^3r_2 G(r_1 - r_2) [|\phi_a(r_1)|^2|\phi_b(r_2)|^2 \pm \Re \phi_a^*(r_1)\phi_b^*(r_2)\phi_a(r_2)\phi_b(r_1)] = V_C \pm V_E \quad (107)$$

The first term V_C is called the Coulomb (or direct) interaction energy while the second term V_E is the exchange interaction energy. Of course, both arise from the Coulomb repulsion of electrons. While the direct Coulomb interaction can be classically interpreted as the energy of a pair of charge clouds, the exchange term has no such simple classical interpretation. Indeed, it is a quantum mechanical effect due to the identical nature of particles and (anti-)symmetry of wave functions. Moreover, the exchange interaction contributes with a different sign according as the spatial wave function is symmetric or anti-symmetric (spin singlet or spin triplet state). The Coulomb energy V_C is clearly positive. In cases where the exchange term is also positive $V_E \geq 0$ (as is the case for Helium) we can conclude that the interaction energy $\langle V_I \rangle$ is greater for ϕ_S than for ϕ_A . So (other things being equal) the spin singlet states $^1\chi_A$ will have a higher energy than the spin triplet states $^3\chi_S$. This is seen in Helium, where typically the spin triplet orthohelium states have a lower energy than the corresponding spin singlet parahelium states constructed from the same pair of single particle states ϕ_a, ϕ_b . There is one notable exception to this rule: the ground state of helium is a spin singlet parahelium state with $\phi_a = \phi_b$. There is no anti-symmetric wave function that can be constructed if $\phi_a = \phi_b$.

6 Perturbation theory for stationary states of time-independent hamiltonians

For most interesting quantum mechanical systems we do not know how to solve the Schrödinger eigenvalue problem for stationary states and energy levels. There are exceptional ‘exactly-solved’

systems such as the free particle, square well, Dirac delta and harmonic oscillator potentials, rigid body with an axis of symmetry, hydrogen atom, charged particle in a constant magnetic field and spin in a magnetic field e.t.c. In some cases, the hamiltonian of interest can be written as $H = H_0 + gH_1$ where H_0 is ‘exactly solved’ and gH_1 is a ‘perturbation’. In some situations, it may be possible to treat the perturbation as small and develop an expansion in powers of g for the energy levels and eigenstates of H by using those of H_0 as a zeroth order approximation. This approach is applied for example in studying the effect of an anharmonic restoring force on a particle in an SHO potential: here $gH_1 = gx^4$. The hydrogen atom in a constant magnetic field $gH_1 = g\vec{L} \cdot \vec{B}$ is another example. Relativistic corrections to the hydrogen atom hamiltonian including the spin-orbit coupling $gH_1 = g\vec{L} \cdot \vec{S}$ can also be treated as a perturbation. An anisotropic rigid body can be treated as a perturbation to a rigid body with an axis of symmetry. The ground state energy of the Helium atom can be estimated by treating the inter-electron repulsion as a perturbation.

- There is another branch of perturbation theory that deals with time-dependent perturbations. This is relevant, for instance, if an atom is exposed to an oscillating electromagnetic field. Time dependent perturbation theory will be discussed later on.
- In effect the method produces an expansion for the energy levels and stationary states of $H = H_0 + gH_1$:

$$E_n = E_n^{(0)} + E_n^{(1)}g + E_n^{(2)}g^2 + \dots \quad \text{and} \quad \psi_n = \psi_n^{(0)} + \psi_n^{(1)}g + \psi_n^{(2)}g^2 + \dots \quad (108)$$

where $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ is the energy spectrum of the unperturbed hamiltonian H_0 .

6.1 Perturbation theory in a simple two state system

Perhaps the simplest instructive example of a perturbative expansion is for an electron spin in a magnetic field $\vec{B} = (B_x, B_y, B_z)$. Here the hamiltonian $H = -\mu \cdot B$ is

$$H = \frac{g|e|\hbar}{4m}\vec{\sigma} \cdot \vec{B} = \frac{g|e|\hbar}{4m} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}. \quad (109)$$

Here we can treat the magnetic interaction due to the field in the $x - y$ plane as a perturbation to the spin in the vertical magnetic field and split the hamiltonian as $H_0 + H_1$ where ($g \approx 2$ is the g-factor)

$$H_0 = \frac{g|e|\hbar B_z}{4m} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad H_1 = \frac{g|e|\hbar}{4m} \begin{pmatrix} 0 & B_x - iB_y \\ B_x + iB_y & 0 \end{pmatrix}. \quad (110)$$

In this case we may read off the energies and stationary states of H_0 and treat H_1 as a perturbation. We will develop a systematic method to calculate corrections to the energies and wavefunctions in the next section. But this problem is so simple that we can solve it explicitly. To avoid writing all the physical constants, let us consider the toy hermitian hamiltonian $H = H_0 + gH_1$ where

$$H_0 = \begin{pmatrix} a & 0 \\ 0 & d \end{pmatrix} \quad \text{and} \quad gH_1 = g \begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix}. \quad (111)$$

Here a, d are real and b is a complex number. g is called a coupling constant and can be regarded as measuring the size of the perturbation.

- The eigenvalues of H_0 are a and d with eigenvectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ respectively.
- The characteristic equation $\det(H - EI) = 0$ allows us to calculate the two energy levels

$$E^2 - (a + d)E + ad - g^2|b|^2 = 0 \quad \Rightarrow \quad E_{\pm} = \frac{1}{2} \left(a + d \pm \sqrt{(a + d)^2 - 4(ad - g^2|b|^2)} \right). \quad (112)$$

Find the corresponding eigenvectors! So far we have made no approximation.

- To understand the nature of a perturbative expansion, let us expand E_{\pm} around the eigenvalues of the unperturbed hamiltonian using the binomial expansion for the square-root

$$E_{\pm} = \frac{a + d}{2} \pm \frac{1}{2} \sqrt{(a - d)^2 + 4g^2|b|^2} = \frac{a + d}{2} \pm \frac{a - d}{2} \left(1 + \frac{2g^2|b|^2}{(a - d)^2} + \dots \right) = \begin{cases} a + \frac{g^2|b|^2}{(a - d)} + \dots \\ d - \frac{g^2|b|^2}{(a - d)} + \dots \end{cases} \quad (113)$$

This expansion for $\sqrt{1 + x^2}$ is valid (converges) when $|x| < 1$

$$\left| \frac{2gb}{a - d} \right| < 1 \quad (114)$$

The physical interpretation is that such a perturbation series provides a good approximation only if (1) the coupling constant g and (2) size of matrix elements of the perturbing hamiltonian in the eigen-basis of H_0 ($|b|$) are sufficiently small and (3) the difference between the unperturbed levels $a - d$ is sufficiently large. If the energy levels of the unperturbed H_0 were degenerate, these series expansions would not be useful. These are general features of such ‘non-degenerate’ perturbative expansions.

- However, even if H_0 had degenerate energy levels $a = d$, we could still get a perturbation series, but of a different sort. If $a = d$, going back to E_{\pm} we find the exact formula

$$E_{\pm} = a \pm g|b|. \quad (115)$$

We see that the perturbing hamiltonian gH_1 breaks the degeneracy of unperturbed levels by an amount proportional to g and the size of the matrix elements of H_1 (namely b). This is generally true. The degeneracy (in magnetic quantum number m) of hydrogen energy levels can be broken by applying a constant magnetic field.

6.2 First order non-degenerate perturbation theory

More generally, suppose we split the hamiltonian $H = H_0 + gH_1$ into an unperturbed (hermitian) H_0 whose spectrum is known and a perturbation gH_1 . We will attempt to obtain the energy levels and eigenstates of H as series in powers of g

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots \quad \text{and} \quad \psi_n = \psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots \quad (116)$$

where $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. Our aim is to find the first order corrections $E_n^{(1)}$ and $\psi_n^{(1)}$. Roughly, we might expect that any change to $\psi_n^{(0)}$ that is in the direction of $\psi_n^{(0)}$ would not change the physical state and can be ignored. In other words, we expect to be able to take $\psi_n^{(1)}$ orthogonal to $\psi_n^{(0)}$.

More precisely, let us assume that the unperturbed states are normalized $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$ and choose to normalize the perturbed eigenstates as well. To order g , the normalization condition reads (dropping the subscript n temporarily)

$$1 \approx \langle \psi_n^0 + g\psi_n^1 | \psi_n^0 + g\psi_n^1 \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + g\langle \psi_n^1 | \psi_n^0 \rangle + g\langle \psi_n^0 | \psi_n^1 \rangle + \mathcal{O}(g^2) \Rightarrow \Re\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0 \quad (117)$$

So the real part of the inner product vanishes. In fact, by a choice of phase, we can also take the imaginary part of the inner product to vanish, i.e. $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0!$ ⁵

- Now the eigenvalue problem for H becomes

$$(H_0 + gH_1) (\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots) = (E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots) (\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots).$$

At the lowest order g^0 this reduces to the unperturbed eigenvalue problem $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. At $\mathcal{O}(g)$,

$$H_0\psi_n^{(1)} + H_1\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}. \quad (120)$$

To isolate $E_n^{(1)}$ let us take the inner product with $\psi_n^{(0)}$,

$$\langle \psi_n^{(0)} | H_0 | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle. \quad (121)$$

Using orthogonality of $\psi_n^{(0)}$ and $\psi_n^{(1)}$ and hermiticity of H_0 we get

$$E_n^{(1)} = \frac{\langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle}{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle} \Rightarrow E_n = E_n^{(0)} + g \frac{\langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle}{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle} + \dots \quad (122)$$

So to first order in perturbation theory, the correction to energy levels is given by the expectation value of the perturbing hamiltonian in the unperturbed state. This justifies our estimation of the separation between ortho and parahelium energy levels by treating the inter-electron Coulomb repulsion as a perturbation.

- Remark: As a consequence of the variational principle, we notice that first order perturbation theory never underestimates the ground state energy:

$$E_0^{\text{1st order}} = E_0^0 + g\langle \psi_0^0 | H_1 | \psi_0^0 \rangle = \langle \psi_0^0 | H_0 + gH_1 | \psi_0^0 \rangle \geq E_0. \quad (123)$$

Here the exact ground state satisfies $H\psi_0 = E_0\psi_0$. By the variational principle E_0 is the minimum of the expectation value of the hamiltonian

$$E_0 = \min_{\|\psi\|=1} \langle \psi | H_0 + gH_1 | \psi \rangle. \quad (124)$$

⁵Suppose $\Im\langle \psi^{(0)} | g\psi^{(1)} \rangle = cg$ for some constant c . Then

$$\langle \psi^{(0)} | g\psi^{(1)} \rangle = icg \approx e^{icg} - 1. \quad (118)$$

Now we may split ψ into a part parallel to $\psi^{(0)}$ and a part perpendicular to it. At order g

$$|\psi\rangle = |\psi^{(0)}\rangle + \langle \psi^{(0)} | g\psi^{(1)} \rangle |\psi^{(0)}\rangle + g|\psi_{\perp}^{(1)}\rangle + \dots \approx e^{icg} |\psi^{(0)}\rangle + g|\psi_{\perp}^{(1)}\rangle + \dots \quad (119)$$

By multiplying $|\psi\rangle$ by the phase e^{-icg} (which does not change its normalization) we may get rid of the phase factor from the first term without affecting the second term to order g . Thus, we may assume that the first order correction to the eigenstates are orthogonal to the unperturbed eigenstates $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$.

6.2.1 First order correction to the eigenstates

- To find $\psi^{(1)}$, it suffices to know its components in any basis. A convenient basis is the orthonormal basis of unperturbed energy eigenstates $\psi_m^{(0)}$. So we wish to express

$$|\psi_n^{(1)}\rangle = \sum_m \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle. \quad (125)$$

The aim is to find the coefficients in this expansion. We already saw in the last section that $\psi_n^{(1)}$ can be chosen not to have any component in the direction of $\psi_n^{(0)}$, so we restrict the sum above to run over $m \neq n$.

- To find $\psi_n^{(1)}$ we return to the eigenvalue equation at order g

$$H_0\psi_n^{(1)} + H_1\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}. \quad (126)$$

Taking the inner product with the m^{th} eigenstate of the unperturbed hamiltonian we get

$$\begin{aligned} \langle \psi_m^{(0)} | H_0 \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H_1 \psi_n^{(0)} \rangle &= \langle \psi_m^{(0)} | E_n^{(0)} \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | E_n^{(1)} \psi_n^{(0)} \rangle \\ \Rightarrow E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle &= E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle. \end{aligned} \quad (127)$$

In the last section, we studied the consequences of this equation when $m = n$ and concluded that $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$, i.e., $\psi_n^{(1)}$ has no component in the direction of $\psi_n^{(0)}$. To find its remaining components, we assume $m \neq n$ and that the unperturbed levels are non-degenerate and get

$$\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \text{for } m \neq n. \quad (128)$$

Thus assuming $E_m^{(0)} \neq E_n^{(0)}$ for $m \neq n$, we find

$$\psi_n = \psi_n^{(0)} + g\psi_n^{(1)}, \quad \text{where } \psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}. \quad (129)$$

So the first order correction to the unperturbed eigenstates is a linear combination of unperturbed eigenstates, weighted by the quotient of the matrix elements of H_1 between unperturbed states and the energy differences $E_n^{(0)} - E_m^{(0)}$. If the unperturbed energy levels $E_n^{(0)} = E_m^{(0)}$ were degenerate, this formula would run into difficulties if $\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle \neq 0$. As long as the unperturbed energy level of interest (n) is non-degenerate, the terms in this sum make sense (for instance, other levels could be degenerate and the formula would still work). So we still need to develop a formula for perturbative corrections to energy levels that are degenerate. We will do this shortly.

- Note also that for fixed n the terms in this sum over m eventually involve division by successively larger energy differences. So we might expect the projections of $\psi_n^{(1)}$ on the highly excited unperturbed states $\psi_m^{(0)}$ to be negligible, provided the matrix elements in the numerator $\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle$ also decrease with growing m .

6.3 Second order correction to the energy

At second order in g the eigenvalue equation becomes

$$H_0\psi_n^2 + H_1\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0. \quad (130)$$

As before, we look at this equation in the orthonormal basis of unperturbed eigenstates by taking the inner product with ψ_m^0 . Using hermiticity of H_0 we get

$$\langle\psi_m^0|H_1\psi_n^1\rangle = E_n^2\delta_{mn} + E_n^1\langle\psi_m^0|\psi_n^1\rangle \quad (131)$$

Specializing to the case $m = n$ allows us to extract E_n^2 since $\langle\psi_n^0|\psi_n^1\rangle = 0$ by a choice of phase:

$$E_n^2 = \langle\psi_n^0|H_1\psi_n^1\rangle \quad (132)$$

Now we substitute the known expression

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle\psi_m^0|H_1|\psi_n^0\rangle\psi_m^0}{E_n^0 - E_m^0} \quad (133)$$

to get

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle\psi_m^0|H_1|\psi_n^0\rangle\langle\psi_n^0|H_1|\psi_m^0\rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|\langle\psi_m^0|H_1|\psi_n^0\rangle|^2}{E_n^0 - E_m^0} \quad (134)$$

We notice that the second order correction to the ground state energy $E_0^{(0)}$ is always negative. This is because the numerators are all absolute squares while the denominators are negative $E_0^0 - E_m^0 < 0$

$$E_{gs}^{(2)} \leq 0. \quad (135)$$

Summary: To second order in the coupling constant, the energy levels are

$$E_n(g) = E_n^0 + g\langle\psi_n^0|H_1|\psi_n^0\rangle + g^2 \sum_{m \neq n} \frac{|\langle\psi_m^0|H_1|\psi_n^0\rangle|^2}{E_n^0 - E_m^0} + \dots \quad (136)$$

6.4 Example: Point-like scatterer in a square-well potential

Let us illustrate perturbative approximations to energy levels with the example of a particle in a 1-dimensional infinite square-well, perturbed by a repulsive delta function. $H = H_0 + gH_1$

$$H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad gH_1 = g\delta\left(x - \frac{L}{2}\right), \quad V(x) = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases} \quad (137)$$

g has dimensions of Energy $\times L$. The unperturbed hamiltonian is parity even about $x = L/2$, and so the unperturbed energy eigenstates are either even or odd about $x = L/2$. The unperturbed spectrum is non-degenerate

$$E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad \psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \dots \quad (138)$$

$n = 1, 3, 5$ correspond to the even states and $n = 2, 4, 6 \dots$ to the odd parity states. The first order correction to the energies

$$E_n^{(1)} = \langle \psi_n^{(0)} | \delta(x - L/2) | \psi_n^{(0)} \rangle = \frac{2}{L} \sin^2(n\pi/2) = \frac{1 - (-1)^n}{L} \quad (139)$$

vanishes for the odd parity states since they vanish where the delta scatterer is located. Thus with in the approximation of first order perturbation theory

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} + \frac{2g}{L} \delta_{n,\text{odd}} \quad (140)$$

The second order correction to energies is

$$E_n^{(2)} = \sum_{p \neq n} \frac{|\langle \psi_p^{(0)} | H_1 | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_p^{(0)}} = \sum_{n \neq p=1}^{\infty} \frac{\sin^2(p\pi/2) \sin^2(n\pi/2) 8m}{(n^2 - p^2)\pi^2\hbar^2} = \frac{2m}{\pi^2\hbar^2} \sum_{n \neq p=1}^{\infty} \frac{1 - (-1)^n - (-1)^p + (-1)^{n+p}}{n^2 - p^2}. \quad (141)$$

Specializing we find that the second order correction to the ground state energy is negative and equal to⁶

$$E_1^{(2)} = -\frac{8m}{\pi^2\hbar^2} \left[\frac{1}{3^2 - 1} + \frac{1}{5^2 - 1} + \frac{1}{7^2 - 1} + \dots \right] = -\frac{8m}{\pi^2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{4n(n+1)} = -\frac{2m}{\pi^2\hbar^2} \quad (142)$$

Thus to second order in perturbation theory, the ground state energy of the perturbed hamiltonian is

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} + \frac{2g}{L} - \frac{2mg^2}{\pi^2\hbar^2} + \mathcal{O}(g^3) \quad (143)$$

Check that the dimensions are correct.

- To understand the quantitative accuracy of this perturbative approximation, let us compare with the exact ground state energy.
- To find the exact energy levels, we solve the Schrodinger equation in the above potential. The boundary conditions are

$$\psi(x \leq 0) = \psi(x \geq L) = 0, \quad \psi\left(\frac{L^+}{2}\right) = \psi\left(\frac{L^-}{2}\right), \quad \psi'\left(\frac{L^+}{2}\right) - \psi'\left(\frac{L^-}{2}\right) = \frac{2mg}{\hbar^2} \psi\left(\frac{L}{2}\right) \quad (144)$$

Like H_0 , the total H is also even about $L/2$, so its eigenstates can be taken as either even or odd. The odd parity states $n = 2, 4, 6, \dots$ of the unperturbed H_0 automatically satisfy these boundary conditions and are seen to be eigenstates of H since they satisfy the free particle Schrodinger equation both to the left and right of the delta scatterer. But the ground state of H is an even parity state which we now determine.

- For $x < L/2$ the solution of the Schrodinger eigenvalue problem with energy $E = \hbar^2 k^2 / 2m$ is $\psi = A \sin kx + B \cos kx$, imposing $\psi(0) = 0$ we get $\psi = A \sin kx$. Thus, the even parity wave functions are

$$\psi_{\text{even}}(x) = \begin{cases} A \sin kx & \text{if } 0 \leq x \leq L/2 \\ A \sin(k(L-x)) & \text{if } L/2 \leq x \leq L. \end{cases} \quad (145)$$

⁶The series is seen to be telescoping when we use partial fractions $\frac{1}{n(n+1)} = \frac{1}{n} - \frac{1}{n+1}$

A will be fixed by normalization and it remains to find the allowed values of k . The continuity of ψ at $L/2$ is guaranteed but the condition on discontinuity of the derivative gives us the condition

$$-Ak \cos(kL/2) - Ak \cos(kL/2) = \frac{2mg}{\hbar^2} A \sin(kL/2) \quad (146)$$

This leads to the transcendental equation

$$-\frac{\hbar^2 k}{mg} = \tan\left(\frac{kL}{2}\right) \quad \text{or} \quad -\kappa = \alpha \tan \kappa, \quad \text{where} \quad \alpha = \frac{mgL}{2\hbar^2} > 0 \quad \text{and} \quad \kappa = \frac{kL}{2}. \quad (147)$$

The allowed energies correspond to solutions $\kappa \neq 0$ of this transcendental equation. The ground state corresponds to the smallest non-trivial solution $\pi/2 \leq \kappa_1 \leq \pi$ as is seen graphically.

- For a quantitative test of perturbation theory, let us restrict to the ground state and use the values

$$\hbar = 1, m = 2, L = 1, g = 1, \alpha = 1. \quad (148)$$

In this case we find that $\kappa_1 \approx 2.02876$ and $k_1 \approx 4.06$ and

$$E_1^{exact} = \frac{\hbar^2 k_1^2}{2m} \approx 4.11586 \quad (149)$$

- On the other hand, our perturbative approximation for the ground state energy is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} + \frac{2g}{L} - \frac{2mg^2}{\pi^2 \hbar^2} + \mathcal{O}(g^3) = \frac{\pi^2}{4} + 2 - \frac{4}{\pi^2} + \dots = 2.4674 + 2 - .405 + \dots = 4.06212 + \dots \quad (150)$$

Thus we see that second order perturbation theory gives an estimate of the ground state energy 4.062 which is within 1.3% of the exact ground state energy ≈ 4.116 ! If g were smaller, the accuracy of perturbation theory would be even better. Moreover we notice that first order perturbation theory ($E_1^{\text{1st order}} \approx 4.46$) overestimates the energy of the g.s. while the second order correction is negative.

6.5 First order degenerate perturbation theory

Suppose $H = H_0 + gH_1$ and we wish to find the correction to a degenerate energy level $E_n^{(0)}$ of H_0 . Since it is degenerate there are several linearly independent eigenvectors of H_0 with eigenvalue E_n^0 . In fact, H_0 is diagonal in *any* basis within the E_n^0 eigenspace. For convenience let us work with orthonormal bases and denote one such orthonormal basis by $\psi_{n\alpha}^0$ where $\alpha = \alpha(n)$ enumerates the degenerate levels

$$H_0 \psi_{n\alpha}^0 = E_n^0 \psi_{n\alpha}^0 \quad (151)$$

Of course, $\psi_{n\alpha}$ are not uniquely determined by H_0 . We will see that the perturbation H_1 helps us to determine the ‘right’ basis within the degenerate subspace. Moreover, we expect the perturbation H_1 to break the degeneracy among the unperturbed levels, since it was found that application of a magnetic field ‘splits’ the degenerate energy levels of hydrogen.

- We wish to expand the energies and eigenstates of H in a series in g

$$E_{n\alpha} = E_n^0 + E_{n\alpha}^1 g + E_{n\alpha}^2 g^2 + \dots \quad \psi_{n\alpha} = \psi_{n\alpha}^0 + \psi_{n\alpha}^1 g + \psi_{n\alpha}^2 g^2 + \dots \quad (152)$$

Now we can't just take over the formula for $E_n^1 = \langle \psi_n^0 | H_1 | \psi_n^1 \rangle$ from non-degenerate perturbation theory since we do not know which of the states $\psi_{n\alpha}^0$ to calculate this expectation value in.

- The eigenvalue problem $H\psi_{n\alpha} = E_{n\alpha}\psi_{n\alpha}$ is (the super-scripts on ψ and E are not powers!)

$$(H_0 + gH_1)(\psi_{n\alpha}^0 + g\psi_{n\alpha}^1 + g^2\psi_{n\alpha}^2 + \dots) = (E_{n\alpha}^0 + gE_{n\alpha}^1 + g^2E_{n\alpha}^2 + \dots)(\psi_{n\alpha}^0 + g\psi_{n\alpha}^1 + g^2\psi_{n\alpha}^2 + \dots).$$

At order g^0 this just says that α labels the degeneracy of the levels with energy E_n^0 :

$$H_0\psi_{n\alpha}^0 = E_n^0\psi_{n\alpha}^0. \quad (153)$$

Due to the degeneracy, we don't know the states $\psi_{n\alpha}$ uniquely, but without much loss of generality, let us suppose the unperturbed eigenstates are orthonormal

$$\langle \psi_{m\beta}^0 | \psi_{n\alpha}^0 \rangle = \delta_{\alpha\beta} \delta_{mn}. \quad (154)$$

At order g^1 we get

$$H_0\psi_{n\alpha}^1 + H_1\psi_{n\alpha}^0 = E_n^0\psi_{n\alpha}^1 + E_{n\alpha}^1\psi_{n\alpha}^0 \quad (155)$$

As before, let us take the inner product with the unperturbed states $\psi_{m\beta}^0$. Using hermiticity of H_0 and orthonormality of unperturbed states we get

$$\langle \psi_{m\beta}^0 | H_1 | \psi_{n\alpha}^0 \rangle = E_{n\alpha}^1 \delta_{mn} \delta_{\alpha\beta} + (E_n^0 - E_m^0) \langle \psi_{m\beta}^0 | \psi_{n\alpha}^1 \rangle. \quad (156)$$

To find $E_{n\alpha}^1$ let us take $m = n$, i.e., focus on a particular degenerate eigenspace of H_0 . Then we have

$$\langle \psi_{n\beta}^0 | H_1 | \psi_{n\alpha}^0 \rangle = E_{n\alpha}^1 \delta_{\alpha\beta}. \quad (157)$$

Bear in mind that we have still not fixed the basis $\psi_{n\alpha}^0$ within the E_n^0 degenerate eigenspace, and nor do we know $E_{n\alpha}^1$. This interesting equation determines them both. It says that the basis $\psi_{n\alpha}^0$ is one in which H_1 is diagonal, and the diagonal entries are the first order corrections to the energy levels $E_{n\alpha}^1$. **In other words, $E_{n\alpha}^1$ are the eigenvalues of H_1 restricted to the degenerate E_n^0 eigenspace of H_0 . And $\psi_{n\alpha}^0$ are the corresponding eigenvectors.** This is the main result of degenerate perturbation theory.

6.5.1 Simplest example of Zeeman effect

The Zeeman effect refers to the experimentally observed shift in atomic energy levels in the presence of a uniform external magnetic field. Let us consider a very simple example of this effect⁷, where a hydrogen atom is placed in an external magnetic field. The magnetic dipole interaction energy is

$$H_{int} = -\boldsymbol{\mu} \cdot \mathbf{B} = \left(\frac{e}{2m} \vec{L} + \frac{e}{m} \vec{S} \right) \cdot \mathbf{B}. \quad (158)$$

Now the unperturbed hamiltonian is just the hydrogen atom hamiltonian $H_0 = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$ whose eigenstates are $|nlm_l\rangle \times$ a spin wave function which we may take to be $|sm_s\rangle$ where $s = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$

$$H_0 |nlm_l sm_s\rangle = -\frac{R}{n^2} |nlm_l sm_s\rangle, \quad n = 1, 2, \dots, l = 0, 1, \dots, n-1, m = -l, \dots, l, m_s = -\frac{1}{2}, \frac{1}{2} \quad (159)$$

⁷We ignore here the effect of the internal magnetic field (due to the motion of the electron in the electric field of the nucleus).

where $R = -me^4/2\hbar^2 = -13.6$ eV is the Rydberg energy. The energy levels are $2n^2$ -fold degenerate. We wish to find the correction to the energy levels due to the magnetic dipole interaction with the uniform external magnetic field, $H = H_0 + H_{int}$. Let us assume that the magnetic field is oriented along the z direction, $B = B_z \hat{z}$. Now it is a fortunate circumstance that

$$H_{int} = \frac{e}{2m}(L_z + 2S_z)B_z \quad (160)$$

is diagonal in the basis of unperturbed energy levels:

$$H_{int}|nlm_l m_s\rangle = \frac{e\hbar}{2m}(m_l + 2m_s)B_z|nlm_l m_s\rangle \quad (161)$$

So the diagonalization of the perturbed hamiltonian within each degenerate subspace of H_0 has already been done. The exact energy eigenstates of $H_0 + H_{int}$ are $|nlm_l m_s\rangle$ with the energies

$$(H_0 + H_{int})|nlm_l m_s\rangle = \left(-\frac{R}{n^2} + \frac{e\hbar}{2m}(m_l + 2m_s)B_z\right)|nlm_l m_s\rangle \quad (162)$$

Thus the unperturbed states with different values of m_l , m_s , which were degenerate in energy are now split in the presence of an external magnetic field. m_l is therefore called the magnetic quantum number.

7 Description of an ensemble of quantum mechanical states by a density matrix

7.1 Pure and mixed ensembles in classical mechanics

See Sakurai or Liboff or a book on statistical mechanics. The state of a classical system of particles is given by specifying the positions and momenta of all the particles. This is the most that classical mechanics allows us to freely specify. Such a state of a classical mechanical system is called a ‘pure’ state, for emphasis. Suppose we prepare several copies of a particle (or system) in the same pure state. Such an ensemble is called a pure ensemble, i.e., an ensemble where each constituent is in the same pure state. This could be a set of identical billiard balls all at rest at height 1m above the floor.

Often we do not know all the coordinates and momenta of particles even in an isolated container of gas, owing to the difficulty of measuring all of these even at the initial instant of time (though it is not forbidden classically). On other occasions, the gas may be in contact with an environment. Owing to the interaction of the system with its very complicated environment, it is not possible to pin down the state of the gas precisely. In such situations, it is hopeless to try to describe the situation of a gas by a pure state (even if it is, strictly speaking, in a pure state).

However, even in such situations, we may be able to say that among all possible pure states of the gas, some are more likely than others. For example, if the gas is in equilibrium in a room maintained at a fixed temperature, we can say that the gas is more likely to be in a state where the molecules are uniformly distributed over the room than all located in one corner. Similarly, the velocities of the gas molecules are more likely to follow the Maxwell-Boltzmann distribution than one where all the velocities are equal and pointing downwards.

In such circumstances, we describe the properties of a box of gas by considering an ensemble of several chambers of gas, each in a possibly different pure state, with different pure states

occurring with different relative probabilities. Then we hope to describe the properties of the original gas box by an ensemble average of the properties in each of the pure states in the various chambers. Such an ensemble of pure states is called a mixed ensemble. Loosely, we say that the gas in the room is in a mixed state. What we mean is that on average, its properties are well approximated by an ensemble average. Thus, a mixed ensemble is a way of saying which pure states are more likely and which are less likely. So a mixed ensemble is an ensemble of pure states with a specification of their relative likelihoods.

Operationally, the specification of a mixed ensemble should allow us to calculate the ensemble average values of observables. For example, we should be able to calculate the average pressure on the walls by averaging over the pressure in each of the possible pure states in the ensemble, weighted by their likelihoods. For a gas in equilibrium at temperature T , the relevant mixed ensemble is the so-called thermal ensemble of Boltzmann that says pure states of high energy are exponentially less likely than pure states of lower energy.

7.2 Pure and mixed ensembles in quantum mechanics

- The most that quantum mechanics allows us to specify about the state of a system is its wave function $\psi(x_S)$ where x_S denotes the degrees of freedom of the system. A quantum system with a wave function is said to be in a (pure) state.
- The measurement postulate implies (among other things) that if we prepare several copies of a system in the same state ψ and make measurements of the observable A , then on average we get the expectation value of A in the state ψ . Such a collection of identically prepared states is called a pure ensemble, where all the states in the ensemble are the same (pure) state.
- More generally, we may consider a so-called mixed ensemble, which contains several copies of the system in possibly different pure states.
- E.g. suppose we pass an unpolarized beam of electrons through a Stern-Gerlach-like apparatus to produce two beams of spin polarized electrons. The electrons in each output beam are in pure spin states. One beam has electrons exclusively in the state \uparrow and the other beam has electrons exclusively in the state \downarrow . Each of these beams is separately a pure ensemble.
- Now we combine the two outputs to form a single beam of electrons. In this new beam, all we know is that 50% of the electrons are polarized spin up and 50% polarized spin down. We can regard this combined beam as a mixed ensemble. If this combined beam is fairly weak, and we isolate the individual electrons, we would not know the state of the individual electrons. Any given electron is equally likely to be in one of two pure spin states \uparrow and \downarrow . Unlike an electron which is in the state $\uparrow + \downarrow$, this electron *does not* have a definitely known wave function and is said to be in a ‘mixed spin state’. Here we are focusing on the spin wave function and not the coordinate degrees of freedom of the electrons.
- Note that the initial unpolarized beam is itself an example of a mixed ensemble. An unpolarized beam is one where there is no preferred direction for the spin vector. For instance it means that if we measure S_z on the electrons in the beam, we will get $\hbar/2$ for half the electrons and $-\hbar/2$ for the other half. It also means that if we measure S_y we will get $\hbar/2$ for half the electrons and $-\hbar/2$ for the other half. The same is true for measurements of S_x on the electrons in such an unpolarized beam.
- Another way in which the concept of a pure state may fail to be adequate is if we have a

quantum system in contact with an environment whose degrees of freedom are denoted x_E . Then the system+environment may have a wave function $\psi(x_S, x_E)$. But it is rarely the case that we can factorize this into a system wave function and an environment wave function $\psi_S(x_S)\psi_E(x_E)$ at all times. In such situations, the system does not have a wave function of its own. It is said to be in a mixed state in which we know less about the system (treated as an entity by itself) than is allowed by quantum mechanics.

- Just as in classical mechanics, we should be able to calculate the average values of observables in any ensemble. QM already tells us how to do this for a pure ensemble. Now consider a mixed ensemble where the normalized pure states ψ_i occur with relative probabilities p_i , with $\sum_i p_i = 1$ where the sum runs over the pure states present in the ensemble. In the next section we will show how to calculate average values of observables in mixed ensembles.

- For example in the above combined beam there are only two distinct pure states in the ensemble, \uparrow and \downarrow with equal populations. The pure states in an ensemble need not be orthogonal, nor do they have to form a basis for the Hilbert space. For example we may have a mixed ensemble of electrons where a third each are in the states \uparrow , \downarrow and $\uparrow + \downarrow$. This example also shows that the number of distinct pure states in an ensemble can exceed the dimension of the Hilbert space.

- Irrespective of the type of ensemble, when we measure an observable A on a constituent of an ensemble, we get an eigenvalue. In a pure ensemble of normalized pure states ψ , we know moreover that we get the eigenvalue a_n with probability $|\langle\phi_n|\psi\rangle|^2$ and the system collapses to the normalized eigenstate ϕ_n of A corresponding to the eigenvalue a_n . This is the famous indeterminacy of quantum mechanics. In a mixed ensemble, there is a further indeterminacy beyond that intrinsic to quantum mechanics. This is because there are several different pure states present in the ensemble. When we measure A for a constituent of a mixed ensemble, we get an eigenvalue a_n but the probability of getting this eigenvalue depends on which pure state the constituent of the ensemble happened to be in. The probability of getting a_n can be written as an ensemble average of the probability in each pure state

$$P(a_n) = \text{probability of getting } a_n = \sum_{i \in \text{ensemble}} p_i |\langle\phi_n|\psi_i\rangle|^2 \quad (163)$$

Check that these probabilities add up to one.

7.2.1 Why the density matrix?

- There is no single wave function that describes all the constituents of a mixed ensemble. But we can still describe such an ensemble by use of a density matrix.

- Suppose we want to predict the average value resulting from measurements of observable A on states in a mixed ensemble consisting of normalized pure states ψ_i occurring with relative frequencies p_i . Quantum mechanics plus ensemble averaging says that it is

$$\langle A \rangle = \sum_i p_i \langle\psi_i|A|\psi_i\rangle \quad (164)$$

Let us insert the identity $I = \sum_n |n\rangle\langle n|$ where $|n\rangle$ is any orthonormal basis for the Hilbert

space. Then

$$\langle A \rangle = \sum_i p_i \sum_{n,m} \langle \psi_i | n \rangle \langle n | A | m \rangle \langle m | \psi_i \rangle = \sum_{mn} A_{nm} \left(\sum_i p_i \langle m | \psi_i \rangle \langle \psi_i | n \rangle \right) \equiv \sum_{mn} A_{nm} \rho_{mn} = \text{tr } A \rho. \quad (165)$$

The quantity within parenthesis is independent of the observable and has been defined to be the density matrix ρ

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| = \sum_i p_i \psi_i \psi_i^\dagger \quad \text{and its matrix elements are} \quad \rho_{mn} = \sum_i p_i \langle m | \psi_i \rangle \langle \psi_i | n \rangle \quad (166)$$

The density matrix is a hermitian operator $\rho^\dagger = \sum_i p_i (\psi_i \psi_i^\dagger)^\dagger = \rho$. It has trace equal to one

$$\text{tr } \rho = \sum_n \rho_{nn} = \sum_i p_i \text{tr } \psi_i \psi_i^\dagger = \sum_i p_i \psi_i^\dagger \psi = \sum_i p_i = 1 \quad (167)$$

since the states ψ_i were assumed to be of norm one.

7.2.2 Pure ensemble density matrices

- In particular, the density matrix of a pure ensemble is got by restricting the sum to a single pure state ψ which occurs with probability $p = 1$. So the density matrix of a pure state ψ is $\rho = |\psi\rangle\langle\psi|$. In other words, the density matrix of a pure state is the outer product of the normalized state vector with itself or the ratio of outer to inner products

$$\rho_\psi^{\text{pure}} = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle} = \frac{\psi\psi^\dagger}{\psi^\dagger\psi} = \frac{\psi\psi^\dagger}{\|\psi\|^2} \quad (168)$$

Here we can regard ψ as a column vector and ψ^\dagger as a row vector.

- The density matrix for a particle in a unit-norm pure state $\psi(x)$ is just the projection operator to the one-dimensional sub-space spanned by ψ , i.e., $\rho = \psi\psi^\dagger = |\psi\rangle\langle\psi|$. We may represent ρ in any orthonormal basis, (say the basis of eigenstates $|n\rangle$ of some observable A like energy, $A|n\rangle = \lambda_n|n\rangle$)

$$\rho_{mn} = \langle m | \psi \rangle \langle \psi | n \rangle = c_m c_n^* \quad (169)$$

where $|\psi\rangle = \sum_n c_n |n\rangle$ and c_n are the components of ψ in the basis $|n\rangle$. In particular, the diagonal elements $\rho_{nn} = |c_n|^2$ give the probabilities that upon a measurement of the observable A , the value λ_n is obtained and the system collapses to the state $|n\rangle$.

- In a pure state, we know the projections c_n of ψ on each basis vector. In a mixed state, the c_n 's are not known with certainty. The normalization of ψ is the condition $\psi^\dagger\psi = 1$ or

$$1 = \langle\psi|\psi\rangle = \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = \sum_n c_n^* c_n = \sum_n \rho_{nn} = \text{tr } \rho. \quad (170)$$

- The fact that a state is pure implies that ρ is a projection operator $\rho^2 = \psi\psi^\dagger\psi\psi^\dagger = \psi\psi^\dagger = \rho$. In fact the density matrix of a pure state is a rank-1 projection operator⁸. In particular, ρ has

⁸A projection to the subspace spanned by the columns of a matrix A is given by $P_A = A(A^\dagger A)^{-1}A^\dagger$. The rank of a projection is the dimension of the subspace to which it projects. An introduction to projection matrices was given in the MP1 lecture notes.

one eigenvalue equal to one and all remaining eigenvalues equal to zero. The 1-eigenspace of ρ is spanned by the pure state ψ . In fact, a pure state can be defined as one whose density matrix is a rank one projection (that projects to the pure state!).

- In addition, for a pure state since $\rho^2 = \rho$ we also have $\text{tr } \rho^2 = \text{tr } \rho = 1$.
- We will see that mixed ensemble density matrices aren't projections and aren't rank one, moreover $\text{tr } \rho^2 < 1$ for a mixed ensemble.

7.2.3 More on mixed ensemble density matrices

- A mixed ensemble can be thought of as an ensemble of pure states, so that the c_n 's are not precisely known but take different values for the various pure states in the ensemble. The elements of the density matrix may be obtained as an ensemble average (this ensemble average is different from the quantum mechanical averaging that we do to find the expectation value of an observable in a given pure state)

$$\rho_{mn} = \overline{c_m c_n^*} \quad (171)$$

Alternatively, the ensemble average can be thought of as an average over the density matrices of each of the pure states in the ensemble weighted by their probabilities (this is how we introduced the concept)

$$\rho = \sum_{i \in \text{ensemble}} p_i |\psi_i\rangle\langle\psi_i| \quad \text{with} \quad \sum_{i \in \text{ensemble}} p_i = 1. \quad (172)$$

Here $p_i \geq 0$ is the probability of occurrence of the pure state $|\psi_i\rangle$ in the ensemble.

- For example, suppose we have a beam of electrons with an isotropic distribution of spin projections (no preferred direction). Then we can describe the spin state of an electron in such an ensemble using a mixed state density matrix. Working in the basis in which S_z is diagonal, both the pure state density matrices $|\uparrow\rangle\langle\uparrow|$ and $|\downarrow\rangle\langle\downarrow|$ are equally likely. Thus the density matrix is

$$\rho = \frac{1}{2} |\uparrow\rangle\langle\uparrow| + \frac{1}{2} |\downarrow\rangle\langle\downarrow| = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (173)$$

Calculate the expectation values of the various components of spin and show that they vanish for this mixed state.

- The same beam with isotropic spin projections can also be described as a mixed ensemble where there are equal numbers of electrons with $S_x = \hbar/2$ as there are electrons with $S_x = -\hbar/2$. If X_{\pm} are the normalized eigenvectors of S_x corresponding to these two eigenvalues, then the density matrix in the basis where S_x is diagonal is given by

$$\rho = \frac{1}{2} X_+ X_+^\dagger + \frac{1}{2} X_- X_-^\dagger \quad (174)$$

By expressing X_{\pm} in terms of \uparrow and \downarrow show that this density matrix is the same as the above density matrix in the basis where S_z is diagonal.

- The density matrix of the mixed ensemble mentioned earlier with a third each of the population in the states \uparrow, \downarrow and $\uparrow + \downarrow$ is

$$\rho_3 = \frac{1}{3} \uparrow\uparrow^\dagger + \frac{1}{3} \downarrow\downarrow^\dagger + \frac{1}{3} \frac{1}{\sqrt{2}} (\uparrow + \downarrow) \frac{1}{\sqrt{2}} (\uparrow^\dagger + \downarrow^\dagger). \quad (175)$$

- Example: Suppose we have a system in thermal equilibrium at temperature T . Then we may describe its properties using a thermal ensemble with (mixed) thermal density matrix. In the basis of energy eigenstates $H|n\rangle = E_n|n\rangle$, the thermal density matrix is

$$\rho = A \sum_{n=0}^{\infty} e^{-E_n/kT} |n\rangle\langle n| \quad \text{where the normalization constant} \quad A^{-1} = \sum_n e^{-E_n/kT} \quad (176)$$

is fixed by the requirement that $\text{tr } \rho = 1$. A thermal density matrix (in the energy basis) corresponds to an ensemble where each pure state $|n\rangle$ of definite energy is present with a probability proportional to the Boltzmann factor $e^{-E_n/kT}$. High energy pure states occur less frequently in the ensemble compared to lower energy pure states. The thermal density matrix at temperature T is $\rho = Ae^{-H/kT}$. The diagonal entries of the density matrix in the energy basis are the relative occupation numbers of the various energy levels of the system at that temperature.

- For a mixed ensemble, ρ is neither a rank-1 matrix nor can it be a projection matrix.
- If a density matrix is a projection operator, then it must be the density matrix of a pure ensemble. Proof: Suppose that a density matrix is a projection $\rho^2 = \rho$. So it projects to a subspace $V \subseteq \mathcal{H}$. Take an o.n. basis ψ_1, \dots, ψ_n for V . Then $\rho = \psi_0\psi_0^\dagger + \dots + \psi_n\psi_n^\dagger$. But then $1 = \text{tr } \rho = n$, this implies $n = 1$. So $\rho = \psi_1\psi_1^\dagger$ must be a pure density matrix and necessarily of rank one.
- If ρ is rank 1, does it have to be pure? Ans: Yes. Why? If ρ is rank one, then $\rho = ab^\dagger$ for some vectors a and b . But $\rho^\dagger = \rho$ so $ab^\dagger = ba^\dagger$. Moreover $\text{tr } \rho = 1$, so $b^\dagger a = 1$, so $b = bb^\dagger a^\dagger = |b|^2 a$. Therefore b is parallel to a . Now define $c = |b|a$, then $\rho = cc^\dagger$, and therefore, ρ is a pure state density matrix.
- Let us see these facts in an example. Suppose a mixed state is formed from an ensemble of *orthonormal pure states* $|n\rangle$

$$\rho = \sum_{n \in \text{ensemble}} P_n |n\rangle\langle n|, \quad \langle n|m\rangle = \delta_{mn}. \quad (177)$$

Then check that $\rho^2 = \sum_n P_n^2 |n\rangle\langle n|$. But for a mixed state, $P_n < 1$ for n in the ensemble, so $P_n^2 < P_n$ for every non-zero P_n . Thus $\rho^2 \neq \rho$ for this mixed state. The rank of a mixed state density matrix in the above example is the number of orthonormal pure states in the ensemble for which $P_n \neq 0$. This is always two or more for a mixed ensemble, and equal to one only for a pure ensemble.

7.2.4 Time evolution of density matrix

- Finally, the time-evolution of a pure state can be expressed in terms of its density matrix

$$i\hbar\dot{\rho} = i\hbar\dot{\psi}\psi^\dagger + i\hbar\psi\dot{\psi}^\dagger = H\psi\psi^\dagger + \psi\psi^\dagger H = [H, \rho]. \quad (178)$$

Alternatively, we can work in a basis

$$i\hbar\partial_t|\psi\rangle = H|\psi\rangle \Rightarrow i\hbar\partial_t\langle n|\psi\rangle = i\hbar\partial_t c_n = \langle n|H|\psi\rangle = \sum_m \langle n|H|m\rangle\langle m|\psi\rangle = \sum_m H_{nm}c_m \quad (179)$$

This implies

$$i\hbar\partial_t\rho_{mn} = i\hbar(c_m\partial_t c_n^* + c_n^*\partial_t c_m) = \sum_p c_n^* H_{mp} c_p - \sum_p c_m H_{pn} c_p^* = \sum_p H_{mp}\rho_{pn} - H_{pn}\rho_{mp} = [H, \rho]_{mn} \quad (180)$$

So the Schrödinger equation for a pure state becomes $i\hbar\frac{\partial\rho}{\partial t} = [H, \rho]$.

- Since each of the pure states in the ensemble evolve according to the Schrodinger equation, the ensemble average mixed density matrix $\rho = \sum_i p_i \rho_i$ also evolves in the same way

$$i\hbar\frac{\partial\rho}{\partial t} = i\hbar\sum_i p_i \frac{\partial\rho_i}{\partial t} = \sum_i p_i [H, \rho_i] = \left[H, \sum_i p_i \rho_i \right] = [H, \rho]. \quad (181)$$

- We recognize that this evolution equation for the density matrix is the quantum mechanical analog of the Liouville equation for the evolution of the phase space density. $\frac{1}{i\hbar}[H, \rho]$ is replaced by the Poisson bracket $\{H, \rho\}$ in classical mechanics.

- The evolution equation for the density matrix also bears a resemblance to the Heisenberg equation of motion of quantum mechanics.

8 Time reversal

8.1 Time reversal in classical mechanics

Newton's law of motion is time-reversal invariant. What we mean by this is that if $x(t)$ is a solution of

$$m\frac{d^2x(t)}{dt^2} = F(x(t)), \quad (182)$$

then $x(-t)$ is also a solution. Indeed let $y(t) = x(-t) = x(t')$ where $t' = -t$. Then

$$\frac{dy(t)}{dt} = \frac{dx(-t)}{dt} = -\frac{dx(t')}{dt'} \Rightarrow \frac{d^2y(t)}{dt^2} = \frac{d^2x(t')}{dt'^2}. \quad (183)$$

But we know that $m\frac{d^2x(t')}{dt'^2} = F(x(t'))$ which implies that

$$m\frac{d^2y(t)}{dt^2} = F(y(t)) \quad (184)$$

So $x(-t)$ satisfies Newton's equation whenever $x(t)$ does. More precisely, if $x(t)$ is a solution of Newton's equation with initial conditions $x(t_1) = x_1$ and $\dot{x}(t_1) = v_1$ and ending up at $x(t_2) = x_2$ with $\dot{x}(t_2) = v_2$, then $y(t) = x(-t)$ is also a solution with initial conditions $y(-t_2) = x_2$, $\dot{y}(-t_2) = -v_2$ and ending up at $y(-t_1) = x_1$, $\dot{y}(-t_1) = -v_1$. So the final state for x becomes the initial state for y after reversing the sign of velocities and vice versa. A movie of the trajectory described by y would look like the movie of x run backwards. The main point is that this backwards movie is also a legitimate solution of Newton's equation. For example, a ball thrown up decelerates and comes to rest at a maximum height. The time reversed trajectory is a ball at rest that falls down and accelerates. One is a solution of Newton's equation if and only if the other is. We may plot this in an $x-t$ diagram.

- Note what this is *not* saying. Suppose a mango is seen to fall (from rest) from a tree 27 minutes after the birth of the nation and hit the ground with velocity 1 m/s, 28 minutes after the birth of the nation. It certainly does not mean that a mango rose up from the ground 28 minutes before the birth of the nation and reached the tree 27 minutes before the birth of the nation. Rather, what it means is that one could (at a time of one's choosing, say 50 min after the birth of the nation) throw a mango up with a velocity of 1 m/s from the point of impact on the ground, and it would follow the reversed path as the earlier mango and reach (with zero instantaneous velocity) the same point on the tree one minute later.

- We say that time reversal is implemented in classical mechanics by reversing the sign of the time variable wherever it appears. As a consequence, velocities and momenta change sign under time reversal, though accelerations do not change sign. Since $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, angular momentum too changes sign under time reversal.

- There are situations where the time reversed trajectory is *not* a solution of Newton's equation. This is the case if the force is not time-reversal invariant. An example of such a force is friction. Another example of such a force is the magnetic part of the Lorentz force $\vec{F} = e\vec{v} \times \vec{B}$. The time-reversed trajectory of a charged particle moving in a *fixed external* magnetic field is in general *not* a solution of Newton's equation $m\vec{r}'' = e\vec{r}' \times B$.

8.2 Time reversal in quantum mechanics

- We need to understand how time-reversal T is implemented in the quantum theory. We would like to promote the time reversal invariance of the classical theory of a free particle or a particle in a potential $V(x)$ to the quantum theory. What ever T is, we wish to find that for a free particle, $T\psi$ is a solution of the SE whenever ψ is a solution.

- For instance, consider a stationary solution of the free particle SE $\psi(x, t) = \sin(kx)e^{-iEt/\hbar}$ where $E = \hbar^2 k^2 / 2m$. Unfortunately, $\psi(x, -t) = \sin(kx)e^{iEt/\hbar}$ is *not* a solution of the SE, as one checks. This means reversal of sign of t is not a symmetry of the SE. But interestingly $\psi^*(x, -t)$ (which happens to be equal to $\psi(x, t)$ in this case), is a solution of the SE! We will exploit this observation soon.

- More generally, consider the SE for a particle in a real potential $V(x)$ with initial condition $\psi(x, t_0) = \psi_0(x)$

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t). \quad (185)$$

Merely changing the sign of t , unfortunately produces an equation different from the SE. $\psi(x, -t)$ satisfies the equation

$$-i\hbar \frac{\partial \psi(x, -t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, -t)}{\partial x^2} + V(x)\psi(x, -t). \quad (186)$$

Due to the first order time derivative in the SE, it is not-invariant if we simply let $t \rightarrow -t$. This is in contrast to Newton's equation that is second order in time and invariant under $t \rightarrow -t$.

- What is more, we found that classically $p \rightarrow -p$ under time reversal. But simply changing the sign of t does not affect $p = -i\hbar \frac{\partial}{\partial x}$ in the quantum theory. So time reversal in quantum mechanics must involve more than just reversing the sign of time.

- However, notice that the above equation is in fact the SE for the complex conjugate wave function. This suggests how to implement time reversal: we must not only reverse the sign of

t but also replace the wave function by its complex conjugate. This combined operation is a symmetry of the SE and is defined as the time-reversal operation in quantum mechanics.

- So let $\phi(x, t) = \psi^*(x, -t) = \psi^*(x, t')$ where $t' = -t$. We will show that $\phi(x, t)$ is a solution of the SE whenever $\psi(x, t)$ is. To see this, note that

$$\frac{\partial \phi(x, t)}{\partial t} = -\frac{\partial \psi^*(x, t')}{\partial t'}, \quad \text{and} \quad \frac{\partial^2 \phi(x, t)}{\partial x^2} = \frac{\partial^2 \psi^*(x, t')}{\partial x^2}. \quad (187)$$

Thus the SE for $\psi(x, t')$ implies the following equation for $\phi(x, t)$

$$-i\hbar \frac{\partial \phi^*(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi^*(x, t)}{\partial x^2} + V(x)\phi^*(x, t). \quad (188)$$

Taking the complex conjugate of this equation we find that $\phi(x, t)$ also solves the SE. So $\psi^*(x, -t)$ is a solution of SE with final state $\psi^*(x, -t_0) = \psi_0^*$ whenever $\psi(x, t)$ is a solution of SE with initial state ψ_0 .

- We say that time-reversal is implemented in quantum theory by reversing the sign of the time variable (wherever it appears) and by taking the complex conjugate of the wave function:

$$(T\psi)(x, t) = \psi^*(x, -t) \quad (189)$$

- Notice that time reversal is an anti-linear operator

$$T(\psi + \phi) = T\psi + T\phi, \quad \text{but} \quad T(\lambda\psi(t)) = \lambda^*\psi^*(-t) = \lambda^*T\psi(t). \quad (190)$$

- As a consequence, $Tp\psi = T(-i\hbar\psi'(x, t)) = i\hbar\frac{\partial}{\partial x}T\psi = -pT\psi$. So $TpT^{-1} = -p$, which is the quantum mechanical version of the reversal of sign of momentum under time reversal. For this ‘reversal of sign’ of p , it was crucial that T involves complex conjugation.

- In fact, the time-reversal operator T is an anti-unitary operator on solutions of the SE. A unitary operator is one which satisfies $\langle U\phi|U\psi\rangle = \langle\phi|\psi\rangle$ for all states ϕ, ψ . On the other hand,

$$\langle T\phi(t)|T\psi(t)\rangle = \langle\phi^*(-t)|\psi^*(-t)\rangle = \langle\phi(-t)|\psi(-t)\rangle^* = \langle\phi(t)|\psi(t)\rangle^* \quad (191)$$

The last equality follows since Schrödinger evolution preserves inner products. Thus $\langle T\phi(t)|T\psi(t)\rangle = \langle\phi(t)|\psi(t)\rangle^*$ for any pair of states ϕ, ψ . Such an operator is called anti-unitary. Thus time-reversal symmetry of the Schrodinger equation is implemented by an anti-unitary operator (unlike other symmetries like parity, space and time translation or rotation invariance, which are implemented by unitary operators $\mathbb{P}, e^{ipx/\hbar}, e^{-iHt/\hbar}$ and $e^{i\vec{L}\cdot\vec{\phi}/\hbar}$).

- While states transform via $\psi \rightarrow T\psi$, under time-reversal, an operator A must transform to TAT^{-1} . For position and momentum we found that $T\mathbf{r}T^{-1} = \mathbf{r}$ and $T\mathbf{p}T^{-1} = -\mathbf{p}$. This is also consistent with the requirements of the correspondence principle (in the Heisenberg picture) and the classical result that under time reversal, $x(t)$ and $p(t)$ go to $x(-t)$ and $-p(-t)$. On the other hand, For orbital angular momentum and spin we must have $T\mathbf{L}T^{-1} = -\mathbf{L}$ and $T\vec{\sigma}T^{-1} = -\vec{\sigma}$. Show that when acting on Pauli matrices, T can be taken as $C\sigma_2$ where C implements complex conjugation $CzC^{-1} = z^*$. Though σ_2 is unitary, C makes T anti-unitary.

- We can formalize our earlier observations. The Schrödinger equation is time-reversal invariant provided the hamiltonian commutes with T . To see this, apply T to the SE $i\hbar\frac{\partial\psi}{\partial t} = H\psi$, assume $TH = HT$ and use anti-linearity of T to get

$$T\left(i\hbar\frac{\partial\psi}{\partial t}\right) = TH\psi \quad \Rightarrow \quad -i\hbar T\left(\frac{\partial\psi}{\partial t}\right) = H(T\psi). \quad (192)$$

Now by definition $T\left(\frac{\partial\psi}{\partial t}\right) = -\frac{\partial T\psi}{\partial t}$ since the sign of time is reversed. So we get

$$i\hbar\frac{\partial(T\psi)}{\partial t} = H(T\psi) \quad (193)$$

In other words, if ψ is a solution of the SE, then so is $T\psi$ provided $[H, T] = 0$. This brings time-reversal invariance on par with the other symmetries of the SE. E.g. for parity we found that if ψ is a solution and $[H, \mathbb{P}] = 0$, then $\mathbb{P}\psi(x) = \psi(-x)$ is also a solution.

• Now let us characterize the (time-independent) hamiltonians $H = \frac{1}{2m}p^2 + V(x)$ that commute with T . First we use $pT = -Tp$ to find $[p^2, T] = ppT - Tpp = -pTp - Tpp = Tpp - Tpp = 0$. So T commutes with the kinetic energy. As for the potential term,

$$[T, V]\psi = T(V\psi) - VT\psi = V^*T\psi - VT\psi \quad (194)$$

So $[T, V] = 0$ iff $V(x) = V^*(x)$. So $H = \frac{p^2}{2m} + V(x)$ commutes with time reversal iff the potential is real.

• In particular, if H is a hermitian hamiltonian that commutes with T and $\psi_n(x)$ is an energy- E_n eigenstate of H , then $T\psi_n(x) = \psi_n(x)^*$ is also an eigenstate with the same energy E_n :

$$H(T\psi_n) = T(H\psi_n) = T(E_n\psi_n) = E_n(T\psi_n). \quad (195)$$

If $\psi(x)$ is real $T\psi(x) = \psi^*(x)$, isn't a linearly independent eigenstate. But if $\psi(x)$ is complex, it is linearly independent. Scattering states in 1d which behave asymptotically like e^{ikx} are complex wave functions representing particles moving rightward at $x = \infty$. The corresponding time-reversed state describes left moving particles of the same energy.

• Let us remark on time-dependent hamiltonians $H = \frac{p^2}{2m} + V(x, t)$ that are time-reversal invariant. By our earlier argument, such a time dependent potential will preserve the T-invariance of Schrodinger's equation iff $[H, T] = 0$. We already know that $[T, p^2] = 0$, so we just need to characterize potentials $V(x, t)$ that commute with T .

$$([T, V]\psi)(x, t) = V^*(x, -t)T\psi - V(x, t)T\psi \quad (196)$$

So $[T, V] = 0$ iff $V(x, t) = V^*(x, -t)$, i.e., the potential itself must be time-reversal invariant.

• The simplest and most common examples of such potentials are real time-independent potentials, a class we have already encountered. But there are other interesting possibilities, such as a real potential that is even under $t \rightarrow -t$. For example,

$$V(\vec{r}, t) = -e\vec{r} \cdot \vec{E}_o \cos \omega t \quad (197)$$

is a time-reversal invariant time-dependent potential. It describes the electric dipole interaction energy between the electron in an atom and the oscillating electric field of light shone on it.

• Let us illustrate how quantum T -invariance reduces to classical time reversal invariance in a simple example. The gaussian wave packet with initial width $a = \sqrt{\langle x^2 \rangle_{\psi(t=0)} - \langle x \rangle_{\psi(t=0)}^2}$ is

$$\psi(x, t) = \frac{1}{(2\pi)^{1/4} \sqrt{a} \sqrt{1 + \frac{i\hbar t}{2ma^2}}} \exp \left\{ -\frac{(x - p_0 t/m)^2}{4a^2 \left(1 + \frac{i\hbar t}{2ma^2}\right)} \right\} \quad (198)$$

is a solution of the free particle SE. In this state $\langle p \rangle = p_o$ and $\langle x \rangle = \frac{p_o t}{m}$. The time reversed wavefunction

$$(T\psi)(x, t) = \psi^*(x, -t) = \frac{1}{(2\pi)^{1/4} \sqrt{a + \frac{i\hbar t}{2ma}}} \exp \left\{ -\frac{(x + p_o t/m)^2}{4(a^2 + \frac{i\hbar t}{2m})} \right\} \quad (199)$$

too is a solution of the free particle SE. Interestingly, we notice that the time-reversed wave function differs from ψ merely by a reversal of the sign of p_o , which is the mean momentum of the state.

- To understand the classical limits of these solutions, we form the coordinate probability densities. Denoting $a(t) = a\sqrt{1 + \frac{t^2 \hbar^2}{4m^2 a^4}}$ we find

$$|\psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}a(t)} e^{-\frac{(x - \frac{p_o t}{m})^2}{2a(t)^2}} \quad \text{and} \quad |(T\psi)(x, t)|^2 = \frac{1}{\sqrt{2\pi}a(t)} e^{-\frac{(x + \frac{p_o t}{m})^2}{2a(t)^2}} \quad (200)$$

In the classical limit (to be studied more carefully in the next section), these represent particles which are located where the gaussian probability densities are peaked. We see that in the classical limit, ψ represents a particle which is moving with trajectory $x(t) = \frac{p_o t}{m}$ while $T\psi$ represents a particle with trajectory $x(t) = -\frac{p_o t}{m}$. These two trajectories are both solutions of the free particle Newton equation $m\ddot{x} = 0$ and are related by classical time reversal $t \rightarrow -t$!

- As in classical mechanics, there are situations in which the Schrödinger equation is not time reversal invariant. This happens when $[H, T] \neq 0$. For a particle in a potential $V(x)$, this can happen only if $V(x)$ is not real. Complex potentials can be used to describe damping, a quantum mechanical analogue of friction. The SE for a charge in a fixed external magnetic field is also not T -invariant.

- Despite the name, time reversal is not concerned with the possibility of traveling backwards in time or with ‘time travel’. However, it does say that the time-reversed Newton equation is the same as the Newton equation (for a wide range of forces) and the same is true of the Schrödinger equation in a real potential. This fact allows us to produce new solutions of these equations from known ones. This is already quite valuable. Based on the knowledge that certain processes occur, T -invariance can be used to predict that certain reversed-processes must also occur. An example is given in the problem set.

8.3 Time reversal invariance of the Schrödinger equation in momentum space

- Recall the definition of momentum space wave function $\tilde{\psi}(k) = \int dx \psi(x) e^{-ikx}$ and $\psi(x) = \int [dk] \tilde{\psi}(k) e^{ikx}$.

- The free particle SE was shown to admit the time reversed wave function $(T\psi)(x, t)$ as a solution iff $\psi(x, t)$ is a solution. A free particle energy eigenstate is $\psi(x) = e^{i(k'x - \omega t)}$, it is also a momentum eigenstate with momentum $p = \hbar k'$. The time reversed wave function is $(T\psi)(x) = e^{i(-k'x - \omega t)}$, it has the same time dependence, so has the same energy $\hbar^2 k'^2/2m$ but it is a state of momentum $-\hbar k'$. In momentum space, the energy eigenstate is given by $\tilde{\psi}(k) = 2\pi\delta(k - k')e^{-i\omega t}$ and it is clearly a state of definite momentum $k = k'$. The time reversed wave function in momentum space is $\widetilde{T\psi}(k, t) = 2\pi\delta(k + k')e^{-i\omega t}$ is a state of opposite momentum $k = -k'$. Notice that in this case, $\widetilde{T\psi}(k, t) = \left(\tilde{\psi}(-k, -t)\right)^*$.

- More generally, if the hamiltonian is time reversal invariant, then $(T\psi)(x, t) = \psi^*(x, -t)$ is a solution iff $\psi(x, t)$ is a solution. The analogous statement is that if $\tilde{\psi}(k, t)$ is a solution of the SE in momentum space, then so is $\widetilde{T\psi}(k, t) = \left(\tilde{\psi}(-k, -t)\right)^*$. The time reversed wave function in momentum space is the Fourier transform of the time reversed wave function in position space.

$$\widetilde{T\psi}(k, t) = \int dx e^{-ikx} (T\psi)(x, t) = \int dx \psi^*(x, -t) e^{-ikx} = \left(\int dx \psi(x, -t) e^{-i(-k)x} \right)^* = \left(\tilde{\psi}(-k, -t) \right)^*.$$

Note that the Fourier transform of the complex conjugate is not the complex conjugate of the Fourier transform in general. Instead, one checks that

$$\widetilde{\psi^*}(k) = \left(\tilde{\psi}(-k) \right)^* \quad (201)$$

Thus, based on our knowledge of position space solution and its time reverse we can state that if $V(x)$ is real, and $\tilde{\psi}(k, t)$ is a soln of SE, then so is $\widetilde{T\psi}(k, t) = \tilde{\psi}(-k, -t)^*$.

- A first principles way to show this directly is to find the appropriate symmetry of the time-dependent Schrodinger equation expressed in momentum space. Suppose

$$\psi(x) = \int [dk] \tilde{\psi}(k) e^{ikx} \quad \text{and} \quad V(x) = \int [dk] \tilde{V}(k) e^{ikx} \quad (202)$$

then the SE $i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x)$ becomes the following equation for the momentum space wave function

$$i\hbar \frac{\partial \tilde{\psi}(k, t)}{\partial t} = \frac{\hbar^2 k^2}{2m} \tilde{\psi}(k, t) + \int [dk'] \tilde{V}(k - k') \tilde{\psi}(k', t) \quad (203)$$

The last term is the *convolution* of the potential with the wave function $\widetilde{V\psi}(k) = \int [dk'] \tilde{V}(k - k') \tilde{\psi}(k', t)$.

- Now we will show that $\tilde{\psi}(-k, -t)^*$ (complex conjugate of the Fourier transform evaluated at $-k, -t$) is also a solution of this equation. Indeed, taking $t \rightarrow -t$ and the complex conjugate we get⁹

$$i\hbar \frac{\partial \tilde{\psi}(k, -t)^*}{\partial t} = \frac{\hbar^2 k^2}{2m} \tilde{\psi}(k, -t)^* + \int [dk'] \tilde{V}(k - k')^* \tilde{\psi}(k', -t)^* \quad (204)$$

But in the presence of a real potential, $V(x)$, we find that in momentum space, $\tilde{V}(l)^* = \tilde{V}(-l)$. So revering the signs of k and the dummy variable k' we find

$$i\hbar \frac{\partial \tilde{\psi}(-k, -t)^*}{\partial t} = \frac{\hbar^2 k^2}{2m} \tilde{\psi}(-k, -t)^* + \int [dk'] \tilde{V}(k - k') \tilde{\psi}(-k', -t)^* \quad (205)$$

In other words, for a real potential, $\tilde{\psi}^*(-k, -t)$ is a solution of the SE iff $\tilde{\psi}(k, t)$ is a solution. This symmetry is time reversal invariance.

- For the free particle, both P and T are symmetries, and $\widetilde{P\psi}(k) = \tilde{\psi}(-k)$. So PT takes the momentum space wave function $\tilde{\psi}(k, t)$ to $\tilde{\psi}(k, -t)^*$. This is not a symmetry for a generic real potential.

⁹If there were no potential this shows that $\tilde{\psi}(k, -t)^*$ is a solution of the free particle SE whenever $\tilde{\psi}(k, t)$ is. This symmetry of the free particle is PT-symmetry.

- There is another quantity that we could consider, the result of applying T to $\tilde{\psi}(k, t)$:

$$\tilde{\psi}(k, t) = \int dx \psi(x, t) e^{-ikx} \Rightarrow T\tilde{\psi}(k, t) = \int dx \psi^*(x, -t) e^{ikx} = \widetilde{\psi^*}(-k, -t) = \left(\tilde{\psi}(k, -t)\right)^* . \quad (206)$$

While this is a correct formula $\widetilde{\psi^*}(-k, -t)$ it is not the physically useful quantity. As shown earlier, for a real potential, if $\tilde{\psi}(k, t)$ is a solution of the SE, then so is $\tilde{\psi}(-k, -t)^*$. This is not the same as the quantity above though it is related (the discrepancy is due to the fact that T is anti-linear and complex conjugation and Fourier transformation do not commute)

$$\text{new time reversed soln of SE} = \widetilde{T\tilde{\psi}}(k, t) = \tilde{\psi}(-k, -t)^* = \widetilde{\psi^*}(k, -t) = T\tilde{\psi}(-k, t). \quad (207)$$

- Let us specialize to $t = 0$. Since a momentum eigenstate $\langle k|k'\rangle = 2\pi\delta(k-k')$ is a real function in momentum space and under time reversal it is mapped to the momentum eigenstate with momentum $-k$ we can say that under time reversal, $T|k'\rangle = |-k'\rangle$. Under time reversal, a position eigenstate (which is a real function) $\langle x|x'\rangle = \delta(x-x')$ localized at $x = x'$ remains a position eigenstate localized at the same point. So $T|x'\rangle = |x'\rangle$.

9 Semiclassical (WKB) approximation

9.1 Semi-classical regime and slowly varying potentials

- Named after Wentzel, Kramers and Brillouin. We wish to approximately solve the time-independent Schrödinger equation for stationary states that are nearly classical.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x). \quad (208)$$

To do this, we wish to exploit the knowledge of some solution of the classical (Hamilton/Newton) equations of motion. In stationary perturbation theory, the zeroth order was a solution of the unperturbed problem. In the semi-classical approximation, the zeroth order is typically a classical solution (in an appropriate form). Classically, the particle is confined to the region x where $E \geq V(x)$. So we focus on this region and postpone phenomena like tunneling through barriers, which are classically forbidden.

- Let us recall which (stationary) states behave more classically than others. If the potential is a constant (as in an infinite square-well of length L in which $V = 0$), $\psi(x) = Ae^{ikx} + Be^{-ikx}$ where $k = \frac{\sqrt{2m(E-V)}}{\hbar}$ and the boundary conditions imply that the stationary states are $\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$. Classically, a particle with non-zero speed spends on average equal times in all subintervals of $[0, L]$ of equal length, as it bounces back and forth against the walls. This uniform distribution is approximated by the probability distribution $|\psi(x)|^2$ of highly excited states. So the classical limit here is the limit of high energies ($E_n \gg V$). This is also the limit of large wave number $k_n = \frac{n\pi}{L}$ compared to $\frac{1}{L}$. This is also the limit where the de Broglie wave length $\lambda_{dB} = \frac{h}{\sqrt{2m(E-V)}} = \frac{2\pi}{k_n} = \frac{2L}{n}$ is small compared to L .

- Notice that L here is the length scale over which the potential changes significantly. More generally, if $V = V(x)$ we say we are in the semi-classical regime if the de Broglie wave length is small compared to the length scale over which the potential varies significantly.

- This is the case, for example for a highly excited state of a particle in an SHO potential. As long as we stay away from the classical turning points, the wave function oscillates rapidly and its wavelength is small. Near the turning points, λ_{dB} diverges and the quantum effects have to be treated more carefully.

- If the potential is varying slowly with x , we may still surmise that the wave function is of the form $Ae^{\pm ipx/\hbar}$ but that $p = h/\lambda$ is no longer the constant $\hbar k$, but varies slowly with x . In other words, this suggests the ansatz $\psi \sim e^{iS(x)/\hbar}$ where for a constant potential, $S(x) = px = \pm x\sqrt{2m(E - V)}$. Before we work out the consequences of this ansatz, let us say more on what we mean by the semi-classical regime and what it means for the potential to be slowly varying.

- If $V = V(x)$, we require that the wavelength is small compared to the length scale over which the potential changes by an amount of the order of the kinetic energy of the particle¹⁰. Indeed, suppose the potential changes by $p^2/2m$ over a length L , then¹¹

$$\frac{p^2}{2m} \approx \delta V \approx \left| \frac{dV}{dx} \right| L \quad \Rightarrow \quad L \approx \frac{p^2}{2m} \left| \frac{dV}{dx} \right|^{-1} \quad (209)$$

Now

$$\lambda \ll L \quad \Rightarrow \quad \frac{2m\lambda}{p^2} \left| \frac{dV}{dx} \right| \ll 1 \quad \text{or} \quad \left| \frac{2mh}{p^3} \frac{dV}{dx} \right| \ll 1 \quad \text{or} \quad \left| \frac{dV}{dx} \right| \ll \frac{\sqrt{2m}}{h} |E - V(x)|^{\frac{3}{2}} \quad (210)$$

This is our condition for semi-classical behavior. It is a condition on the potential, that also involves the energy and depends on x . It is easier to satisfy this condition for a fixed potential and x , if we make E bigger: excited states behave more classically. It is easier to satisfy (for fixed E) where dV/dx is ‘small’. The criterion involves x , so even for fixed $V(x)$ and E there may be some locations where the behavior *is* semi-classical ($E \gg V(x)$), and other locations where it is *not* semi-classical ($E \approx V(x)$). Also, the ‘smaller’ \hbar is, the easier it is to satisfy this condition so in a sense $\hbar \rightarrow 0$ is the classical limit.

- Let us re-derive this condition by thinking in terms of the de Broglie wavelength. For a non-constant $V(x)$, the de Broglie wavelength changes with x . The concept of a wavelength is useful if there are many oscillations with roughly the same wavelength. This is the case if the change in wavelength (over a length of one wavelength) is small compared to the wavelength itself. The change in wavelength over a distance δx is

$$\delta\lambda = \frac{d\lambda}{dx} \delta x. \quad (211)$$

So putting $\delta x = \lambda$, the change in wavelength over a wavelength is $\delta\lambda = \frac{d\lambda}{dx} \lambda$. Thus we require $\left| \frac{\delta\lambda}{\lambda} \right| = \left| \frac{d\lambda}{dx} \right| \ll 1$. We can express this as a condition on the potential using $\lambda =$

¹⁰We need to decide what we mean by potential ‘changes appreciably’. The change in the potential has dimensions of energy and the KE of the particle is a reasonable scale of energy to compare with. Indeed, near the turning points of the SHO, the KE is small, so the length scale over which the potential changes by an amount of the order of the KE is quite small. On the other hand, far away from the turning points the KE is large (for a highly excited state), and the length scale over which the potential changes appreciably compared to the KE is large. So by this definition, the SHO potential is slowly-varying away from the turning points for a highly excited state, and not slowly-varying near the turning points. The corresponding statement about the smallness/largeness of λ_{dB} is a consequence since $\lambda = h/\sqrt{2m(E - V(x))}$ is determined by E and $V(x)$.

¹¹In approximating δV by its first derivative, we assume that L is not so large that this approximation breaks down.

$$h/\sqrt{2m(E - V(x))}.$$

$$\left| \frac{\delta\lambda}{\lambda} \right| = \left| \frac{mh}{p^3} \frac{dV}{dx} \right| \ll 1 \quad (212)$$

This is the same condition for semi-classicality as obtained earlier. So we can either say the potential is slowly varying or the de Broglie wavelength is slowly varying.

9.2 Method of variation of constants for a slowly varying potential

- We motivated the ansatz $\psi = Ae^{iS(x)/\hbar}$ in seeking a solution of the time-independent Schrödinger equation in the semi-classical regime. Without further assumptions, this ansatz (for complex S and real A), does not involve any approximation, it is merely a change of dependent variable from $\psi(x)$ to $S(x)$, in terms of which the eigenvalue problem becomes

$$-\frac{\hbar^2}{2m}\psi'' = (E - V)\psi \quad \Rightarrow \quad -\frac{i\hbar}{2m}S'' + \frac{1}{2m}(S')^2 + V(x) = E. \quad (213)$$

Now we exploit the slowly varying nature of $V(x)$ to assume that $S'(x)$ is slowly varying¹² so that we may ignore $S''(x)$ and approximate the SE by

$$\frac{1}{2m} \left(\frac{\partial S}{\partial x} \right)^2 + V = E \quad (214)$$

Notice that this approximation could also be obtained by letting $\hbar \rightarrow 0$ (assuming $S(x)$ has a finite limit as $\hbar \rightarrow 0$), more on this later. Moreover, the resulting equation is the time-independent Hamilton-Jacobi equation of classical mechanics for the distinguished generating function S of a canonical transformation $S(x, P, t)$ from ‘old’ coordinates x, p to new coordinates X, P in which the new hamiltonian $K(X, P) = H(x, p) + \frac{\partial S}{\partial t} = 0$ vanishes identically. Note that the hamiltonian appearing in the Schrödinger equation is the old hamiltonian H , not K . Moreover, even though $K = 0$, this does not mean that the quantum mechanical energy levels are all zero, K is not a unitary transform of H , they do not have the same spectra. It is just that in the new coordinates ($Q = \frac{\partial S}{\partial P}$ and P), the classical dynamics is as simple as it could be since X and P are both constants of motion $\dot{X} = \frac{\partial K}{\partial P} = 0$ and $\dot{P} = -\frac{\partial K}{\partial X} = 0$. All the complications of the original hamiltonian have been dumped in the transformation from old coordinates (x and $p = \frac{\partial S}{\partial x}$) to new coordinates (X and P). The generating function $S(x)$ in the above H-J equation in fact also depends on the new momenta P , though it is not apparent from (214). This dependence enters through the dependence of S on the constants of integration resulting from solving the time-dependent H-J partial differential equation. The constants of integration can be taken as the constant new momenta.

- In our context, we write the H-J equation in the form $S'(x)^2 = p^2$ and integrate to get

$$S(x) = \pm \int_{x_0}^x p(x) dx' \quad \text{where} \quad p(x) = \sqrt{2m(E - V(x))}. \quad (215)$$

¹²For a constant potential $S'(x) = \hbar k$ is a constant, so now we imagine that this erstwhile ‘constant’ varies with x .

Thus, our crude approximation for the wave function in the semi-classical regime is essentially the exponential of an *abbreviated* action integral¹³

$$\psi(x) = Ae^{\frac{i}{\hbar} \int_{x_0}^x p(x') dx'} + Be^{-\frac{i}{\hbar} \int_{x_0}^x p(x') dx'}. \quad (216)$$

- We will improve on this approximation shortly. But even this crude approximation leads to some interesting consequences such as a simple case of the Bohr-Sommerfeld quantization condition.

- Suppose a particle moves in the 1 dimensional potential $V(x)$ which becomes infinite for $x < 0$ and $x > L$ but is arbitrary for $0 \leq x \leq L$. Then the approximate wave function satisfying the boundary condition $\psi(0) = 0$ is

$$\psi(x) \approx A \sin\left(\frac{S(x)}{\hbar}\right) \quad \text{where} \quad S(x) = \int_0^x p(x') dx'. \quad (217)$$

The boundary condition $\psi(L) = 0$ then becomes $S(L) = n\pi\hbar$ which is the Bohr quantization condition

$$\oint p(x') dx' = 2 \int_0^L p(x') dx' = nh. \quad (218)$$

Use this condition to find a semi-classical approximation to the square-well energy levels.

- Let us continue with the theme of making constants vary. A simple way of improving on this approximation is to suppose that both the amplitude and phase are slowly varying functions. Let us put $\psi(x) = A(x)e^{iS(x)/\hbar}$ in the SE, where we now suppose that both $A(x)$ and $S(x)$ are real. We get

$$-\frac{\hbar^2}{2m} \left(A'' + \frac{i}{\hbar} (2A'S' + AS'') - \frac{AS'^2}{\hbar^2} \right) + V(x)A(x) = EA(x). \quad (219)$$

The real part gives us

$$-\frac{\hbar^2}{2m} \left(A'' - \frac{AS'^2}{\hbar^2} \right) = (E - V(x))A(x) \quad (220)$$

which reduces to the time-independent H-J equation, if we ignore the second derivative of $A(x)$. The solution is $S = \pm \int^x p(x') dx'$ as before. The imaginary part gives us the condition $2A'S' + AS'' = 0$ which means $(A^2S')' = 0$ or $A(x) = \pm \frac{C}{\sqrt{S'}} = \pm \frac{C}{\sqrt{p(x)}}$ for some constant C . The approximate wavefunction is

$$\psi(x) \approx \frac{C_1}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int^x p(x') dx'} + \frac{C_2}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int^x p(x') dx'} \quad \text{where} \quad p(x) = \sqrt{2m(E - V(x))}. \quad (221)$$

This is already a better approximation. The contributing amplitudes are inversely proportional to $\sqrt{p(x)}$. So aside from interference effects, the particle is less likely to be found in a place where its classical velocity is large, as we observed for a particle near the equilibrium point in an SHO potential.

- In the next section, we indicate how to improve on this approximation by developing a systematic expansion that incorporates effects of more rapid variation in the potential.

¹³By absorbing a phase and its conjugate into A and B , the limit of integration x_0 may be set equal to the left turning point of the classical trajectory.

9.3 Semi-classical expansion in powers of \hbar

- To get the Hamilton-Jacobi equation of classical mechanics from the Schrödinger equation, we let $\hbar \rightarrow 0$ after making the ansatz $\psi = Ae^{iS/\hbar}$. So we should expect classical behaviour to emerge in the limit $\hbar \rightarrow 0$.
- To reinforce this idea, let us look at the gaussian wave packet for a free particle in this limit. The probability density of a gaussian wave packet is

$$P(x,t) = |\psi(x,t)|^2 = \frac{1}{\sqrt{2\pi}a(t)} e^{-\frac{(x - \frac{p_o t}{m})^2}{2a(t)^2}} \quad \text{where} \quad a(t) = a\sqrt{1 + \frac{t^2}{\tau^2}} \quad \text{and} \quad \tau = \frac{2ma^2}{\hbar} \quad (222)$$

τ is the characteristic time scale over which the wave packet broadens. The mean momentum of this wave packet is $\langle p \rangle = p_o = \hbar k_o$ and the mean position is $\langle x \rangle = \frac{p_o t}{m}$. We take the limit $\hbar \rightarrow 0$ holding p_o fixed (i.e. the limit of large wave number $k_o = \frac{p_o}{\hbar} \rightarrow \infty$). As $\hbar \rightarrow 0$, $\tau \rightarrow \infty$ and the wave packet does not broaden out. The dispersive effects of wave mechanics die out as $\hbar \rightarrow 0$ and the object behaves like a classical particle of fixed size a . To model a classical point-like particle, we could further let $a \rightarrow 0$ and get the probability density $P(x,t) = \delta(x - p_o t/m)$ as expected of a free point-like particle moving at velocity p_o/m .

- The limit $\hbar \rightarrow 0$ is a very convenient way of approaching the classical limit. \hbar is a dimensional constant, so what we mean by $\hbar \rightarrow 0$ is that certain physical quantities with dimensions of action are very large compared to \hbar . In the above example of a free particle gaussian wave packet, the relevant quantity with dimensions of action is $\frac{2ma^2}{t}$. So the classical limit is the one where we consider times t much shorter than the time-scale τ for quantum mechanical dispersive broadening of the wave packet.

- E.g. 3. For highly excited states of the harmonic oscillator, the quantity $\frac{E_n}{\omega} = \hbar(n + \frac{1}{2})$ with dimensions of action is large compared to \hbar . These states behave semi-classically in many respects.

- E.g. L^2 eigenstates of a rigid body with very large angular momentum quantum number $l \gg 1$ behave semi-classically, the magnitude of their total angular momentum $\sqrt{\hbar^2 l(l+1)}$ is the quantity with dimensions of action, that is large compared to \hbar .

- Spin is somewhat different from angular momentum. A given rigid body or atom can be in states of very different angular momentum quantum number l . So letting $\hbar \rightarrow 0$ and simultaneously $l \rightarrow \infty$ while holding the classical quantity $|\vec{L}| = \sqrt{\hbar^2 l(l+1)}$ fixed is a classical limit. On the other hand, an electron is always a spin $s = \frac{1}{2}$ particle, so for an electron, the eigenvalue of S^2 is always $3\hbar^2/4$ which is not large compared to \hbar^2 . So it does not make direct sense to let the spin quantum number s of an *electron* take any value other than $\frac{1}{2}$, leave alone let it go to infinity.

- However, the limit $\hbar \rightarrow 0$ is not a simple one. The wave function of a free particle $\psi(x) = Ae^{ipx/\hbar}$ does not have a good classical limit $\hbar \rightarrow 0$, holding the classically meaningful quantities x, p fixed. Indeed, the wave function has an essential singularity as $\hbar \rightarrow 0$. However, $-i\hbar \log \psi$ does have a good limit as $\hbar \rightarrow 0$, it tends to the abbreviated action px for a trajectory between positions 0 and x .

- In the case of the SHO, the stationary states are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-\frac{m\omega x^2}{2\hbar}} \quad (223)$$

Here too $\psi(x)$ has an essential singularity at $\hbar = 0$, but $\hbar \log \psi(x)$ has a finite limit $\frac{-m\omega x^2}{2}$ as $\hbar \rightarrow 0$.

- For a general potential, this suggests it isn't a good idea to look for an expansion of $\psi(x)$ in powers of \hbar around a 'classical wave function', since such a thing does not even exist for a free particle. It is better to make the ansatz $\psi = Ae^{iS(x)/\hbar}$ and try to expand $S(x)$ in powers of \hbar . Thus we will seek a solution of the time-independent SE in the form $\psi = Ae^{iS(x,\hbar)/\hbar}$ where $S(x)$ is a (possibly complex) function of x depending on \hbar and A is a constant¹⁴. Then

$$\psi'(x) = \frac{iS'}{\hbar}\psi(x), \quad \psi''(x) = \left(\frac{iS''}{\hbar} - \frac{S'^2}{\hbar^2} \right) \psi(x) \quad (224)$$

and the SE becomes

$$-\frac{\hbar^2}{2m} \left(\frac{iS''}{\hbar} - \frac{S'^2}{\hbar^2} \right) + V(x) = E \quad (225)$$

Now we suppose $S(x)$ is expanded in a series in \hbar

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \dots \quad (226)$$

In effect, we are assuming that $S(x)$ has a finite limit as $\hbar \rightarrow 0$. This is true for the free particle as well as for the highly excited states of many problems we have solved (SHO, square well, delta potential). In fact it is true even for low lying states of many of the problems we have solved (like the SHO above). However, it is not always the case that $S(x, \hbar)$ has a finite limit as $\hbar \rightarrow 0$. Not all states are semi-classical. This is especially true for low lying states such as the ground state of the δ potential well or the hydrogen atom, where

$$\psi_0(x) = \frac{\sqrt{mg}}{\hbar} e^{-mg|x|/\hbar^2} \quad \text{and} \quad \psi_{100}(x) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{me^2 r}{4\pi\epsilon_0 \hbar^2}} \quad \text{where} \quad a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}. \quad (227)$$

For both these ground states, $\hbar \log \psi$ does *not* have a finite limit as $\hbar \rightarrow 0$, though $\hbar^2 \log \psi$ has a finite limit. In both these cases, we anticipate that the above semi-classical approximation may not be accurate. On the other hand, the semi-classical expansion will be seen to be a good approximation in situations where our criterion for the semi-classical regime (slowly varying potential or de Broglie wavelength) is satisfied. In those situations, we may use solutions of the classical HJ equation to obtain accurate semi-classical wave functions.

- Note that we are not claiming that the expansion of $S(x, \hbar)$ in powers of \hbar is convergent. This is true for the free particle where $S(x) = px$. But for most potentials, even in the semi-classical regime, the expansion $S(x, \hbar) = S_0 + S_1 \hbar + S_2 \hbar^2 + \dots$ is *divergent*. Nevertheless, it does provide an excellent asymptotic approximation in many cases.

- Equating coefficients of like powers of \hbar , we get a sequence of differential equations for S_n . At order \hbar^0 we recover the time-independent H-J equation, which is the non-linear differential equation

$$\frac{S'_0(x)^2}{2m} + V(x) = E \quad (228)$$

with solution $S_0(x) = \pm \int_{x_0}^x \sqrt{2m(E - V(x'))} dx' = \pm \int_{x_0}^x p(x') dx'$. This is called the Eikonal approximation or the classical approximation. S_0 is called the Eikonal or (abbreviated) action or Hamilton's principal function.

¹⁴We were in effect beginning to do this when we previously made the ansatz $\psi(x) = A(x)e^{iS(x)/\hbar} = e^{\frac{i}{\hbar}(S(x) - i\hbar \log A(x))}$.

- At order \hbar we get a linear equation for S_1 , into which we substitute the known $S'_0 = p(x)$:

$$S'_1(x)S'_0(x) = \frac{i}{2}S''_0 \Rightarrow S'_1(x) = \frac{i}{2}\frac{S''_0}{S'_0} = \frac{i}{2}(\log S'_0)' = \frac{i}{2}(\log p(x))' \Rightarrow S_1 = \frac{i}{2}\log p(x) + \text{const.}$$

Thus we find at this order of approximation

$$\psi(x) \approx \frac{A_1}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int_{x_0}^x p(x') dx'} + \frac{A_2}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int_{x_0}^x p(x') dx'}. \quad (229)$$

This matches our earlier result. But the present method is more systematic and allows us to find further quantum corrections around the classical limit! What is more, this method can also be applied to regions which the classical trajectory is forbidden from exploring (e.g. tunneling through a barrier).

- Let us find a condition for the validity of the eikonal approximation. Recall that we found upon substituting $S = S_0 + \hbar S_1 + \dots$ and $\psi = e^{iS/\hbar}$ in the Schrodinger eigenvalue problem

$$(S'_0)^2 + \hbar(2S'_0 S'_1 - iS''_0) + \mathcal{O}(\hbar^2) = 2m(E - V(x)). \quad (230)$$

Now for the Eikonal approximation to be good, the order of magnitude of the terms of order \hbar^0 must be large compared to that of the terms of order \hbar . $|(S'_0)^2|$ can be taken as the order of magnitude of the constant terms in \hbar and $|i\hbar S''_0|$ the order of magnitude of the terms of linear in \hbar . So the condition is

$$|(S'_0)^2| \gg |\hbar S''_0| \quad \text{or} \quad \left| \frac{\hbar S''_0}{S'^2_0} \right| \ll 1 \quad (231)$$

This is the same as our earlier criterion for the semi-classical regime, that the potential or de Broglie wavelength be slowly varying $\left| \frac{d\lambda}{dx} \right| \ll 1$:

$$\lambda(x) = \frac{h}{p(x)} = \frac{h}{S'_0} \Rightarrow \left| \frac{d\lambda}{dx} \right| = \left| \frac{h S''_0}{S'^2_0} \right| \ll 1 \quad (232)$$

9.4 Estimation of Tunneling amplitude

- Previously, we tried to use solutions of the classical Hamilton-Jacobi equation to approximately infer the quantum mechanical wave function. This program was applicable in the classically allowed region $E > V(x)$. On the other hand, the wave function can be non-zero even in classically forbidden regions ($E < V(x)$) as in the case of tunneling through a barrier. In such classically forbidden regions, we may still obtain a semiclassical approximation to the wavefunction using the expansion in powers of \hbar developed in the last section. Even if $E < V$, the condition for the semi-classical regime $\left| \frac{d\lambda}{dx} \right| \ll 1$ or $\left| \frac{dV}{dx} \right| \ll \frac{\sqrt{2m}}{\hbar} |E - V(x)|^{\frac{3}{2}}$ can still be satisfied, especially if $E \ll V$ or if $\frac{dV}{dx}$ is small.

- For simplicity let us consider scattering against a barrier in one dimension that extends between $x = -L$ and L , such as a rectangular barrier with an undulating top $V(x) > 0$ for $|x| \leq L$ and $V(x) = 0$ for $|x| > L$. Classically if the energy $E > V_{\max}$, the particle ‘rolls over’ the barrier, but is reflected otherwise. Quantum mechanically, even if $E < V_{\max}$ there can be a non-zero transmission probability due to tunneling. We wish to get a semi-classical estimate for the transmission coefficient in cases where it is small. (After all, it is zero classically.)

- Let us consider scattering from the left with incident energy $E = \hbar^2 k^2 / 2m < V_{max}$. Suppose the repulsive potential is such that there are just two classical turning points ($x_L = -L$ on the left of the barrier and $x_R = L$ on the right) between which $V(x) > E$, as is the case for a rectangular barrier.

- In the classically allowed regions to the left ($\psi(x) = Ae^{ikx} + Be^{-ikx}$) and right ($\psi(x) = Fe^{ikx}$) of the barrier, the WKB approximation gives the exact free particle wave functions since the potential is a constant. The transmission coefficient we wish to find is $|F/A|^2$. Instead of trying to solve the SE in the classically disallowed region, we use the WKB approximation

$$\psi(x) \approx \frac{C'}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int_{x_L}^x p(x') dx'} + \frac{D'}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int_{x_L}^x p(x') dx'} \quad (233)$$

Here $p(x) = \sqrt{E - V(x)}$ is purely imaginary and we may absorb some phases into C' and D' and write

$$\psi(x) \approx \frac{C}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar} \int_{x_L}^x \sqrt{2m(V(x)-E)} dx'} + \frac{D}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar} \int_{x_L}^x \sqrt{2m(V(x)-E)} dx'}. \quad (234)$$

- Since we assumed the tunneling probability is small, the barrier must be high (compared to E) or wide (compared to the de Broglie wavelength of the incident wave). In this case, the coefficient D of the exponentially growing wavefunction must be very small and we ignore it ($D \rightarrow 0$ as the barrier width $L \rightarrow \infty$). This can be motivated by imposing continuity of $\psi(x)$ and its first derivative at the classical turning points x_L, x_R . The attenuation of the wavefunction is approximately

$$\frac{|F|}{|A|} \approx e^{-\frac{1}{\hbar} \int_{x_L}^{x_R} \sqrt{2m(V(x')-E)} dx'} \equiv e^{-\gamma} \quad (235)$$

So the WKB estimate for the transmission probability is

$$T \approx e^{-2\gamma} = e^{-\frac{2}{\hbar} \int_{x_L}^{x_R} \sqrt{2m(V(x')-E)} dx'} \quad (236)$$

We see that as $\hbar \rightarrow 0$, $T \rightarrow 0$ exponentially fast and classically the particle is not transmitted.

- Tunneling was used by Gamow and others to explain the decay of a nucleus to a daughter nucleus by emission of an α ($nnpp$) particle. The strong nuclear forces create something like an attractive finite spherical potential well inside the nucleus for the alpha particle. Outside the nucleus, the alpha particle is repelled by the electrostatic force with the positively charged daughter nucleus. But in order to escape, the alpha particle has to tunnel through a potential barrier. See the discussion in Griffiths or elsewhere.

10 Scattering

10.1 Scattering matrix in one dimension

- Suppose the potential from which we scatter is localized: $V(x) \rightarrow 0$ sufficiently fast as $x \rightarrow \pm\infty$. We seek scattering eigenstates of the Schrodinger operator

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x) = \frac{\hbar^2 k^2}{2m} \psi(x) \quad (237)$$

The asymptotic behavior of the wave function must be of the form

$$\psi(x) \rightarrow \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{as } x \rightarrow -\infty \\ Ce^{ikx} + De^{-ikx} & \text{as } x \rightarrow +\infty \end{cases} \quad (238)$$

A, D represent the incoming amplitudes from $\pm\infty$ while B, C are the amplitudes of scattered plane waves to $\pm\infty$. An aim of scattering theory is to predict the ‘scattering amplitudes’ $B(k), C(k)$ given the incoming amplitudes A and D ¹⁵, the potential and incoming wave number k , by solving the Schrödinger eigenvalue problem.

- What is more, on account of the linearity of the equation, these quantities must be linearly related. Let S be the 2×2 matrix such that

$$\begin{pmatrix} B \\ C \end{pmatrix} = S(k) \begin{pmatrix} A \\ D \end{pmatrix} \quad (239)$$

S is called the scattering matrix. It takes the amplitudes of the incoming plane waves and transforms them into the outgoing plane waves. The matrix elements of S depend on k , the wave number of the incoming waves as well as on the potential. Moreover, S is a unitary matrix, as we will see shortly.

- To find the $S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$ matrix, we need to find its columns (the images of the basis vectors)

$$S \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} S_{11} \\ S_{21} \end{pmatrix}, \quad \text{and} \quad S \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} S_{12} \\ S_{22} \end{pmatrix}. \quad (240)$$

But these we recognize are the scattering problems considered before $A = 1, D = 0$ is scattering of a unit amplitude wave from the far left. So $S_{11} = B/A = r$ and $S_{21} = C/A = t$ are the reflected and transmitted amplitudes for this situation. $A = 0, D = 1$ is the scattering of a unit amplitude wave from the far right. So S_{12} and S_{22} are the transmitted and reflected amplitudes for this situation. Thus, if we know the reflected and transmitted amplitudes for the unit scattering problems from the left and right, we can synthesize the S-matrix. Moreover, if $V(x)$ is even, the transmitted amplitude for unit scattering from the left must be the same as the transmitted amplitude for unit scattering from the right and $S = \begin{pmatrix} r & t \\ t & r \end{pmatrix}$.

- Unitarity of S is the statement that $\langle Su, Sv \rangle = \langle u, v \rangle$ for any pair of vectors u and v . In more detail, $u = \begin{pmatrix} A \\ D \end{pmatrix}$ and $v = \begin{pmatrix} A' \\ D' \end{pmatrix}$ can be any two vectors representing the incoming amplitudes. Then unitarity $SS^\dagger = S^\dagger S = I$ is the statement that inner products (lengths and angles) are preserved:

$$\left\langle \begin{pmatrix} A \\ D \end{pmatrix}, \begin{pmatrix} A' \\ D' \end{pmatrix} \right\rangle = \left\langle S \begin{pmatrix} A \\ D \end{pmatrix}, S \begin{pmatrix} A' \\ D' \end{pmatrix} \right\rangle \quad \text{or} \quad A^*A' + D^*D' = B^*B' + C^*C' \quad (241)$$

To get an idea of why this is true, let us consider first the condition of preservation of norms $\langle u, u \rangle = \langle Su, Su \rangle$ which is the condition $|A|^2 + |D|^2 = |B|^2 + |C|^2$. We recognize this as the conservation of probability current density as shown below.

¹⁵ A, D can be regarded as the two constants of integration of the second order ODE.

- The probability current density (which is proportional to the Wronskian of ψ^* and ψ)

$$j(x, t) = \frac{\hbar}{2mi} (\psi^* \partial_x \psi - \partial_x \psi^* \psi) \quad (242)$$

is shown to be independent of x , $\frac{\partial j}{\partial x} = 0$ by use of the Schrödinger eigenvalue equation. For an eigenstate, $\rho = |\psi|^2$ is time-independent. So the conservation law $\rho_t + j_x = 0$ becomes $j_x = 0$. So

$$j(-\infty) = \frac{\hbar k}{m} (|A|^2 - |B|^2) = j(\infty) = \frac{\hbar k}{m} (|C|^2 - |D|^2) \Rightarrow |A|^2 + |D|^2 = |B|^2 + |C|^2. \quad (243)$$

This shows the diagonal elements of SS^\dagger are 1 (in any basis). See the hw problem for the rest.

- More generally, to show that $A^*A' + D^*D' = B^*B' + C^*C'$, consider two scattering eigenstates ψ_1, ψ_2 of the Schrödinger eigenvalue problem in a real potential with the same energy E and asymptotics

$$\psi_1(x) \rightarrow \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{as } x \rightarrow -\infty \\ Ce^{ikx} + De^{-ikx} & \text{as } x \rightarrow +\infty \end{cases}, \quad \psi_2(x) \rightarrow \begin{cases} A'e^{ikx} + B'e^{-ikx} & \text{as } x \rightarrow -\infty \\ C'e^{ikx} + D'e^{-ikx} & \text{as } x \rightarrow +\infty. \end{cases} \quad (244)$$

Since $V(x)$ is real, ψ_1^* is also an eigenstate with energy E . We construct the Wronskian

$$W(\psi_1^*, \psi_2)(x) = \psi_1^*(x)\psi_2'(x) - \psi_1'^*(x)\psi_2(x). \quad (245)$$

We check that the Wronskian is a constant $W'(x) = 0$ and therefore equate its asymptotic values

$$W(-\infty) = 2ik(A^*A' - B^*B') = W(\infty) = 2ik(C^*C' - D^*D') \quad (246)$$

and conclude that $A^*A' + D^*D' = B^*B' + C^*C'$. In other words, S is unitary.

- Let us look at an example, scattering against a delta-potential well $V(x) = -g\delta(x)$. In this case, for scattering of a unit amplitude plane wave from the left we found that the reflected amplitude is $r = B/A = \frac{i\gamma}{1-i\gamma}$ and the transmitted amplitude is $t = \frac{1}{1-i\gamma}$ where $\gamma = \frac{mg}{\hbar^2 k}$. Thus we find the S-matrix for scattering against a delta well

$$S = \frac{1}{1-i\gamma} \begin{pmatrix} i\gamma & 1 \\ 1 & i\gamma \end{pmatrix}. \quad (247)$$

Check that S is unitary. • The S-matrix contains all the information about the scattering problem. It allows us to predict the amplitudes of the outgoing waves given any configuration of incoming waves. In particular, we can find the reflection and transmission coefficients from S , $T = |t|^2 = |S_{12}|^2$ and $R = |r|^2 = |S_{11}|^2$.

- Moreover, the S-matrix also encodes information about the bound states ('waves' that decay exponentially at infinity). In general, the bound state energies are given by $E = \hbar^2 k^2 / 2m$ for each pole k of the S-matrix that lies on the positive *imaginary* k -axis. In the above example, it has a pole in the upper half of the complex k plane at $k = \frac{img}{\hbar^2}$, which corresponds to the energy of the single bound state $E = \frac{\hbar^2 k^2}{2m} = -\frac{mg^2}{2\hbar^2}$.

- The scattering matrix is unitary, so its eigenvalues are complex numbers of unit magnitude, though they need not be complex conjugates of each other. For an even potential $S = \begin{pmatrix} r & t \\ t & r \end{pmatrix}$ is a

complex symmetric matrix. Unitarity is the pair of conditions $|r|^2 + |t|^2 = 1$ and $rt^* + tr^* = 0$. The eigenvectors of S are $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ with eigenvalues $r + t$ and $r - t$ respectively. Unitarity ensures that $r + t = e^{i\delta_1}$ and $r - t = e^{i\delta_2}$ are complex numbers of unit magnitude. These eigenvectors correspond to incoming amplitudes that scatter to outgoing amplitudes which differ from the incoming ones by a multiplicative phase. δ_1 and δ_2 can be called phase shifts since they encode the shifts in the phases of the incoming amplitudes, due to scattering.

$$S \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (r + t) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = e^{i\delta_1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad S \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (r - t) \begin{pmatrix} 1 \\ -1 \end{pmatrix} = e^{i\delta_2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (248)$$

Asymptotic amplitudes which are eigenvectors of the S-matrix scatter in particularly simple ways with just a change in the asymptotic phase. E.g. the eigenvector $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ corresponds to the situation where plane waves of equal amplitude are incident from both sides of the scatterer. However, the asymptotic amplitudes which are eigenstates of the S-matrix are usually not the most convenient incident amplitudes from an experimental viewpoint, where we send a beam from one side. The situation is worse in three dimensions, where again, we send in plane waves from one side, though the eigenstates of the S-matrix correspond to spherical waves imploding on the target!

10.2 Scattering in three dimensions: differential scattering cross section

- We are interested in scattering by a (spherically symmetric) potential $V(r)$ which vanishes sufficiently fast as $r \rightarrow \infty$. This is two-body scattering after passage to the relative coordinate r . Scattering eigenstates must satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(r)\psi(\vec{r}) = E\psi(\vec{r}). \quad (249)$$

Interesting examples of scattering potentials are (1) Coulomb $V(r) = \frac{\alpha}{r}$, as in Rutherford scattering of positively charged α -particles by a positively charged nucleus; (2) Screened coulomb $V(r) = \frac{\alpha e^{-\mu r}}{r}$ which is usually relevant when the charge of the scattering center is screened by opposite nearby charges, as in a medium; and (3) hard sphere $V(r) = V_0 \theta(r < a)$ as when atoms collide. In most of these situations, we only have access to the particles/waves that are sent in and come out, far from the scattering center. The aim of scattering is to predict the angular distribution of the scattered particles (as $r \rightarrow \infty$), given how the particles are sent in (and with what energy). For simplicity, the incoming particles are usually directed at the scattering center in a single collimated beam of fixed energy.

- For scattering in 3d, the S-matrix is infinite dimensional. Since $V \approx 0$ for large r , the incoming and out-going waves are asymptotically free particle energy eigenstates. We can choose any convenient basis for them. E.g. we could send in plane waves with any wave vector $\vec{k}_{in} = k\hat{n}$ pointing radially inward, so the incoming states are labeled by inward directed unit vectors. For outgoing states we could again use plane waves, now with outward directed wave vectors $\vec{k}_{out} = k\hat{n}'$. The magnitude of the wave vector is the same for elastic scattering. Then the S-matrix relates the incoming amplitudes to the outgoing amplitudes, and in particular, $S(\hat{n}', \hat{n})$ gives the amplitude for an outgoing wave vector pointing along \hat{n}' if the incoming wave vector was pointing along \hat{n} . Unlike the situation in 1d, where the S-matrix was 2×2 , here the S-matrix

has a continuously infinite number of rows and columns (each labeled by points on a sphere). We will not pursue the problem of determining the S-matrix directly. Instead we will repeat what we did in 1d, i.e., consider the standard scattering problem of predicting the outgoing amplitudes given that there is a plane wave incident on the target from the left. But in essence this determines the S-matrix, since the columns of the S-matrix are the outgoing amplitudes in the plane wave basis for each possible radial direction of incoming plane wave, just as we found in one dimension.

- The free particles in the incoming collimated beam are modeled by plane waves with wave vector \vec{k} . For a spherically symmetric $V(r)$ we can take the incoming wave vector $\vec{k} = k\hat{z}$ to be along \hat{z} without loss of generality. If A is a constant with dimensions of $L^{-3/2}$,

$$\psi_{in}(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}} = Ae^{ikz} = Ae^{ikr\cos\theta}. \quad (250)$$

The scattered wave function asymptotically for large r is again that of a free particle. However, the direction of linear momentum is not conserved (translation invariance is broken by the presence of a scattering center located around $r = 0$). The scattered wave is not an eigenstate of linear momentum. In fact, we should expect a scattered wave that is roughly a spherical wave, but whose amplitude is more in the forward direction \hat{z} ($\theta \approx 0$) and varies as θ is increased up to π (back-scattered direction $-\hat{z}$).

- To find the general form the scattered wave function ψ_{sc} can take, we must solve (for large r) the free particle SE for energy eigenvalue $E = \hbar^2 k^2 / 2m$ where k is the magnitude of the incoming wave vector. Let us recall how this is done

$$\left(\frac{p_r^2}{2m} + \frac{L^2}{2mr^2} \right) \psi = \frac{\hbar^2 k^2}{2m} \psi \quad \text{where } p_r = -i\hbar \frac{1}{r} \partial_r r \Rightarrow p_r^2 \psi = -\hbar^2 \frac{1}{r} \frac{\partial^2 r \psi}{\partial r^2}.$$

We proceed by separation of variables and seek a solution in the product form $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. Separation of variables leads to the pair of equations

$$L^2 Y = l(l+1)\hbar^2 Y \quad \text{and} \quad -\frac{\hbar^2}{2m} \frac{1}{r} (rR)'' + \frac{\hbar^2 l(l+1)}{2mr^2} R = \frac{\hbar^2 k^2}{2m} R. \quad (251)$$

We already know the eigenfunctions of L^2 are $Y_{lm}(\theta, \phi)$. In terms of $u = rR$, the radial equation becomes

$$-\frac{\hbar^2}{2m} u'' + \left(\frac{\hbar^2 l(l+1)}{2mr^2} - \frac{\hbar^2 k^2}{2m} \right) u(r) = 0. \quad (252)$$

For very large r ¹⁶, the angular momentum term is subdominant compared to the energy eigenvalue term and we get $-u'' = k^2 u$, so $u(r) = ae^{irk} + be^{-irk}$ or

$$R_{kl}(r) = \frac{ae^{ikr}}{r} + \frac{be^{-ikr}}{r}, \quad \text{as } r \rightarrow \infty \quad (253)$$

So to leading order in this crude approximation, as $r \rightarrow \infty$, the radial wave function is independent of l and consists of a superposition of an outgoing and incoming spherical wave. Since

¹⁶ r large compared to the incoming wavelength $2\pi/k$, more precisely, $kr \gg l(l+1)$. Actually, this is an over simplification and is strictly valid only for $l = 0$. Even for large r , $R(r)$ depends on l in a manner that we will derive soon.

the scattered wave must be outgoing, $b = 0$. The general solution of the free particle eigenvalue problem can be written as a linear combination of separable eigenstates with the same energy

$$\psi(r, \theta, \phi) = \sum_{lm} c_{lm} R_{kl}(r) Y_{lm}(\theta, \phi) \quad (254)$$

As $r \rightarrow \infty$ $R_{kl}(r)$ is independent of l , so the scattered wave can be written as

$$\psi_{sc}(r, \theta, \phi) = a \frac{e^{ikr}}{r} \sum_{lm} c_{lm} Y_{lm}(\theta, \phi) \quad (255)$$

But $a \sum_{lm} c_{lm} Y_{lm}(\theta, \phi)$ just represents an arbitrary function of θ and ϕ which we denote $Af(\theta, \phi)$. Thus for large r , the scattered wave may be written as

$$\psi_{sc}(\vec{r}) = A \frac{e^{ikr}}{r} f(\theta, \phi) \quad \text{or} \quad \psi(\vec{r}) = A e^{ikr \cos \theta} + A \frac{e^{ikr}}{r} f(\theta, \phi). \quad (256)$$

This asymptotic form of the wavefunction is called the scattering boundary condition or Sommerfeld radiation boundary condition. It is a boundary condition in the sense that it says there is no incoming wave from infinity (except for the incident plane wave). In fact it can be regarded as a definition of $f(\theta, \phi)$. $f(\theta, \phi)$ is called the scattering amplitude; it has dimensions of length and we will discuss its physical meaning shortly.

- Before doing so let us improve the above argument by not throwing away the centrifugal repulsion term involving angular momentum. Let us work out the simultaneous eigenstates of energy and angular momentum for the free particle. These are $R_l(r) Y_{lm}(\theta, \phi)$. In terms of $u = rR$ and $\rho = kr$, the radial equation becomes the spherical Bessel equation

$$-\frac{d^2 u_l(\rho)}{d\rho^2} + \frac{l(l+1)}{\rho^2} u_l = u_l \quad (257)$$

The solutions are expressed in terms of the spherical Bessel and spherical Neumann functions

$$R_l(\rho) = a_l j_l(\rho) + b_l n_l(\rho) \quad (258)$$

For $l = 0$, $j_0(\rho) = \frac{\sin \rho}{\rho}$ and $n_0(\rho) = -\frac{\cos \rho}{\rho}$. By a method of Infeld, j_l, n_l for $l = 1, 2, 3, \dots$ can be obtained from j_0, n_0 by applying a raising operator, which raises the value of l without changing the energy $\hbar^2 k^2 / 2m$. This is explored in the problem set. While j_l are finite at $\rho = 0$, n_l diverge at $\rho = 0$. To see this we return to the radial equation

$$-\frac{\hbar^2}{2m} u''(r) + \frac{l(l+1)}{2mr^2} u = \frac{\hbar^2 k^2}{2m} u(r) \quad (259)$$

For small r the energy eigenvalue term may be ignored compared to the centrifugal repulsion to get

$$-u'' + \frac{l(l+1)}{r^2} u = 0 \quad \text{for } r \rightarrow 0. \quad (260)$$

We put the guess $u \sim r^\alpha$ in this equation and get a quadratic equation for α

$$\alpha(\alpha - 1) = l(l + 1) \quad (261)$$

with solutions $\alpha = l + 1$ and $\alpha = -l$. Thus for small r the two solutions behave like $u_l \propto r^{l+1}$ and $u_l \propto r^{-l}$, or in terms of $R = u/r$, the two solutions behave like $j_l \propto \rho^l$ and $n_l \propto \rho^{-l-1}$. Including the proportionality constants,

$$j_l(\rho) \rightarrow \frac{\rho^l}{(2l+1)!!} = \frac{2^l l! \rho^l}{(2l+1)!} \quad \text{and} \quad n_l(\rho) \rightarrow \frac{(2l-1)!!}{\rho^{l+1}} = \frac{(2l)!}{2^l l! \rho^{l+1}} \quad \text{as } \rho \rightarrow 0. \quad (262)$$

Here $(2l+1)!! = (2l+1)(2l-1)(2l-3)\cdots 5\cdot 3\cdot 1$. However both n_l and j_l contain radially ingoing and outgoing parts and both are polynomials in $\sin \rho$, $\cos \rho$ and $\frac{1}{\rho}$. On the other hand, the linear combinations (spherical Hankel functions of first and second kinds) $h_l^\pm(\rho) = j_l(\rho) \pm in_l(\rho)$ are purely outgoing and purely incoming for all ρ . For example, as $\rho \rightarrow \infty$

$$h_l^+(\rho) \rightarrow \rho^{-1} e^{i\rho} (-i)^{l+1} \quad \text{and} \quad h_l^-(\rho) \rightarrow \rho^{-1} e^{-i\rho} i^{l+1}. \quad (263)$$

Similarly, the asymptotic behavior of the spherical Bessel and Neumann functions are

$$j_l(\rho) \rightarrow \rho^{-1} \sin(\rho - l\pi/2) \quad \text{and} \quad n_l(\rho) \rightarrow -\rho^{-1} \cos(\rho - l\pi/2) \quad (264)$$

So we can write an energy $E = \hbar^2 k^2 / 2m$ eigenstate of the free particle hamiltonian as a linear combination of separable angular momentum eigenstates with the same energy

$$\psi(r, \theta, \phi) = \sum_{lm} d'_{lm} R_l(kr) Y_{lm}(\theta, \phi) \quad (265)$$

In particular, the scattered wave must admit such an expansion far from the scattering center where $V \approx 0$. However, the scattering b.c. says that there must not be any incoming spherical wave, so the expansion can only involve the outgoing spherical Hankel functions

$$\psi_{sc}(r, \theta, \phi) = \sum_{lm} d_{lm} h_l^+(kr) Y_{lm}(\theta, \phi) \quad (266)$$

For large kr we use the asymptotic behavior of the spherical Hankel function $h_l^+ \rightarrow (-i)^{l+1} e^{i\rho} / \rho$ to get

$$\psi_{sc} \rightarrow a \frac{e^{ikr}}{r} \sum_{lm} c_{lm} Y_{lm}(\theta, \phi), \quad \text{where} \quad ac_{lm} = \frac{(-i)^{l+1} d_{lm}}{k}. \quad (267)$$

We conclude that the asymptotic behavior of the scattered wave is a spherical wave modulated by a largely arbitrary function $f(\theta, \phi)$ called the scattering amplitude

$$\psi_{sc}(r, \theta, \phi) = A \frac{e^{ikr}}{r} f(\theta, \phi) \quad (268)$$

To understand the physical meaning of f , we compute the probability current density (for large r) of the incoming and scattered waves (the two don't interfere since the incoming beam is assumed to be collimated in a pipe along the z -axis¹⁷. More precisely, for any fixed angle $\theta \neq 0, \pi$, we can always choose r sufficiently large so that the point r, θ, ϕ is located outside the beam pipe both in the back and forward scattering directions)

$$\vec{j} = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \nabla \psi^* \psi) \quad (269)$$

¹⁷Though the pipe is narrow, it is wide enough so that the largest impact parameters of the incoming particles usually exceeds the range of the potential $V(r)$, which is usually very localized.

If $d\vec{S}$ is an infinitesimal surface area vector, then $\vec{j} \cdot d\vec{S}$ is the current across dS and can be interpreted as the number of particles crossing infinitesimal area $d\vec{S}$ per unit time.

- The probability current density of the incident wave Ae^{ikz} is $\vec{j}_{inc} = \frac{\hbar k|A|^2}{m}\hat{z}$. The unit cross-sectional area vector in the direction of the incident beam is \hat{z} , so $\vec{j}_{inc} \cdot \hat{z} = |A|^2\hbar k/m$ is interpreted as the number of particles crossing unit cross-sectional area of the incoming beam per unit time.

- For the scattered wave $\psi_{sc}(r) = Af(\theta, \phi)\frac{e^{ikr}}{r}$, one first checks that for large r ,

$$\nabla\psi \rightarrow Af(\theta, \phi)\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}\right)\hat{r} + \mathcal{O}\left(\frac{1}{r^2}\right) \quad \text{using } \nabla = \hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial\phi} \quad (270)$$

Then one finds

$$\vec{j}_{sc} \rightarrow \frac{|A|^2\hbar k|f|^2}{m} \frac{\hat{r}}{r^2} \quad \text{as } r \rightarrow \infty. \quad (271)$$

Let us find the scattered probability flux across an infinitesimal area element $d\vec{S} = \hat{r}r^2d\Omega$ pointing radially outward. Here $d\Omega = \sin\theta d\theta d\phi$. The scattered probability density current crossing $d\vec{S}$ per unit time (loosely, the number of scattered particles crossing $d\vec{S}$ per unit time) is

$$\vec{j}_{sc} \cdot d\vec{S} = \frac{\hbar k|A|^2|f|^2}{m} d\Omega \quad (272)$$

The scattering amplitude f is not a probability amplitude, $|f|^2$ does not integrate to 1 in general, see below. Note that the scattered flux is zero if $f = 0$, which is the case if $V = 0$. This does not mean that particle number is not conserved in the absence of a potential. In the absence of a potential, there is no scattered wave at all, the incoming plane wave just passes through and all the particles come out with $\theta = 0$ in the form of a plane wave.

- We see that the scattered flux is proportional to the incident flux $\frac{\hbar k|A|^2}{m}$. We define the ratio to be the cross-section for scattering into the angular region $d\Omega$ in the vicinity of $\Omega = (\theta, \phi)$

$$d\sigma(\Omega) = \frac{\vec{j}_{sc} \cdot d\vec{S}}{\vec{j}_{inc} \cdot \hat{z}} = |f|^2 d\Omega \quad (273)$$

$d\sigma$ is proportional to the angular element $d\Omega$, so we define the ratio to be the so-called differential scattering cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2 \quad (274)$$

$\frac{d\sigma}{d\Omega}d\Omega = |f|^2d\Omega$ is the number of particles scattered into the angular region $d\Omega$ per unit time per unit incident flux. So $f(\theta, \phi)$ is the amplitude for *scattering* in the angular direction defined by θ, ϕ . The differential scattering cross section $\frac{d\sigma}{d\Omega} = |f|^2$ has dimensions of an area.

- Classically, $d\sigma/d\Omega$ is the cross sectional area of the incident beam through which incoming particles must pass in order to be *scattered* into the angular region $d\Omega$.

- The total scattering cross-section is defined as the integral of the differential scattering cross section over all directions

$$\sigma = \int \frac{d\sigma}{d\Omega}d\Omega = \int |f(\theta, \phi)|^2 \sin\theta d\theta d\phi. \quad (275)$$

σ has dimensions of area. The total cross section σ can be thought of as the total effective cross-sectional area (normal to the incident beam) presented by the scattering potential. If $V = 0$, the scattering x-section vanishes, there are no scattered particles, yet particle number is conserved since there is an undeflected incoming beam that passes through.

- An aim of scattering theory is to determine the differential scattering cross section, given the potential V . This is called the direct scattering problem. This is the problem we will address. For this, it suffices to find the scattering amplitude $f(\theta, \phi)$, which will depend on the potential V , energy of the incoming waves, m and \hbar . In fact, for a spherically symmetric potential, we have cylindrical symmetry about the z -axis of the incoming beam, so $f(\theta, \phi) = f(\theta)$ must be independent of ϕ .

- There is another interesting problem, the inverse scattering problem, whose aim is to reconstruct the potential given the scattering data (i.e., the differential scattering cross section or scattering amplitudes). This is a much harder problem, but is of great practical importance in fields such as tomography (medical imaging CAT, PET scans, seismic imaging, oil exploration etc.)

10.3 Partial wave expansion

- As mentioned, direction of linear momentum is not conserved in the scattering process, but angular momentum is conserved for a spherically symmetric potential. This suggests we can decompose the scattering problem into different angular momentum sectors labeled by l . Roughly, the component parts of the wave function corresponding to different values of angular momentum quantum number l are the ‘partial waves’. The overall strategy is simple: solve the Schrödinger eigenvalue problem in the potential $V(r)$ with the above scattering boundary condition and determine the scattering amplitude $f(\theta)$. The partial wave expansion is an approach to find $f(\theta)$ as a sum over over partial amplitudes of increasing l . Truncating the partial wave expansion after the first few partial waves provides a good approximation especially for low energy scattering, i.e. where the wavelength $2\pi/k$ of the incoming beam is large compared to the range of the scattering potential a : $ka \ll 1$.

10.3.1 Partial wave amplitudes

- For a spherically symmetric potential $f(\theta, \phi) = f(\theta)$, so we may expand the scattering amplitude

$$f(\theta) = \sum_l (2l + 1) a_l P_l(\cos \theta) \quad (276)$$

in spherical harmonics with $m = 0$: $Y_{l0}(\theta) = \frac{1}{\sqrt{4\pi}} \sqrt{2l + 1} P_l(\cos \theta)$. The factor $(2l + 1)$ is conventional and for later convenience. So to find the scattering amplitude, it suffices to find the (generally complex) *partial wave amplitudes* a_l . a_l have dimensions of length. In many scattering problems, a good approximate cross section is got by retaining just the first few a_l . The differential cross section is

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \sum_{l,l'=0}^{\infty} a_l^* a_{l'} (2l + 1)(2l' + 1) P_l^*(\cos \theta) P_{l'}(\cos \theta). \quad (277)$$

The total scattering cross section is simpler due to orthogonality of Legendre polynomials

$$\int_{-1}^1 P_l(x)P_{l'}(x)dx = \frac{2}{2l+1}\delta_{ll'}. \quad (278)$$

Thus the partial wave expansion for the total cross section is

$$\sigma = \sum_{l'} a_l^* a_{l'} (2l+1)(2l'+1) \int_0^{2\pi} d\phi \int_0^\pi P_l(\cos\theta)P_{l'}(\cos\theta) \sin\theta d\theta = 4\pi \sum_{l=0}^{\infty} (2l+1)|a_l|^2. \quad (279)$$

Note that we have merely chosen to parametrize the angular distribution of scattered amplitudes $f(\theta, \phi)$ as a sum of partial wave amplitudes a_l of definite angular momentum. The problem of direct scattering is to find a_l . We will do this by solving the SE in the presence of the potential and then read off the a_l by considering the asymptotic behavior of the wave function.

10.3.2 Phase shifts

• In fact, it is physically revealing and more economical to express these partial wave amplitudes a_l , in terms of certain scattering phase shifts δ_l given by¹⁸

$$a_l = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{e^{i\delta_l} \sin \delta_l}{k} \quad (280)$$

This is similar to the situation in 1d where we could express the (complex) scattered amplitudes (B, C) for eigenstates of the S-matrix in terms of phase shifted incoming amplitudes (A, D) . Moreover these phases $e^{i\delta_{1,2}}$ were the eigenvalues of the S-matrix. In 3d, the eigenstates of the S-matrix are the spherical harmonics and we have an infinite number of phase shifts δ_l labelled by angular momentum quantum number l . The eigenvalues of the S-matrix are the phases $e^{2i\delta_l}$. To extract the scattering phase shifts, we first need to know the phases of the wave function in the absence of scattering, i.e., the asymptotic phases of the incoming plane wave

• However, the incoming plane wave Ae^{ikz} is not a state of definite angular momentum. Nevertheless, it is a free particle eigenstate. Moreover, the angular momentum (L^2) eigenstates $R_{kl}(r)Y_{lm}(\theta, \phi)$ of the free particle form a complete set and we should be able to expand $e^{ikr \cos \theta}$ as a linear combination of them. Since $e^{ikr \cos \theta}$ is independent of ϕ , we only need the $m = 0$ spherical harmonics, the Legendre polynomials $P_l(\cos \theta)$ and since $e^{ikr \cos \theta}$ is finite at $r = 0$, we don't need the spherical Neumann functions $n_l(kr)$. Thus for some coefficients c_l we must have

$$e^{ikr \cos \theta} = \sum_{l=0}^{\infty} c_l j_l(kr) P_l(\cos \theta). \quad (281)$$

Multiplying by $P_{l'}(\cos \theta)$ and integrating with respect to $\cos \theta$ using the orthogonality of Legendre polynomials, it turns out with some more work, that $c_l = i^l(2l+1)$ (see problem set). Thus we expressed the incoming plane wave as a linear combination of spherical waves of various angular momenta

$$e^{ikr \cos \theta} = \sum_{l=0}^{\infty} i^l(2l+1) j_l(kr) P_l(\cos \theta). \quad (282)$$

¹⁸It is not clear at present why the complex number a_l can be expressed with modulus and phase related in this particular manner. This form will be shown to be a consequence of probability and angular momentum conservation.

The point of this expansion is that in a spherically symmetric potential, angular momentum is conserved, so spherical waves of definite angular momentum scatter independently and in a simple manner.

- Let us look at the behavior of these component spherical waves for large r . Using the asymptotic behavior $j_l(kr) \sim \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right)$, we get for large kr ,¹⁹

$$e^{ikr \cos \theta} \rightarrow \sum_{l=0}^{\infty} \frac{i^l (2l+1) P_l(\cos \theta)}{kr} \sin\left(kr - \frac{l\pi}{2}\right) = \sum_l \frac{(2l+1) P_l(\cos \theta)}{2ikr} \left[e^{ikr} - (-1)^l e^{-ikr} \right]. \quad (283)$$

So the incident plane wave is a superposition of imploding and exploding spherical waves of all angular momenta l , with the specific phases given above. Notice that the coefficients of the imploding and exploding spherical wave have the same absolute magnitude and only differ by the phase $-(-1)^l$. As is explained below, this feature is a consequence of conservation of probability. If the magnitudes of the coefficients were different there would be a net accumulation/deficit of probability at $r = 0$ which is not the case for a plane wave that is just ‘passing through’.

- If $V = 0$, this plane wave would not be modified and is the complete solution of the Schrödinger eigenvalue problem. Comparing Ae^{ikz} with the scattering b.c. the scattering amplitude $f = 0$ if $V = 0$.
- In the presence of a spherically symmetric potential, the spherical waves for different values of l scatter independently due to conservation of angular momentum. For example, if the incoming wave only had $l = 0$, the outgoing wave would also be an S-wave.
- Summarizing, we have merely re-written the scattering boundary condition as a sum of partial waves of definite angular momentum. The scattering b.c. is the statement that the scattering eigenstate wave function for large r must be of the form

$$\psi(\vec{r}) \rightarrow A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right] = A \sum_l (2l+1) P_l(\cos \theta) \left[\frac{e^{ikr} - (-1)^l e^{-ikr}}{2ikr} + \frac{a_l e^{ikr}}{r} \right] \text{ for large } r. \quad (284)$$

- Now we introduce the concept of phase shifts, by thinking about the scattering eigenstate (total wave function, incident plus scattered) in a different way. Any scattering eigenstate for large r must in particular be a free particle eigenstate. For a spherically symmetric potential it can be written as a linear combination of spherical Hankel functions times Legendre polynomials (assuming it is independent of ϕ , which is the case of interest)

$$\psi(r, \theta) = A \sum_l (2l+1) P_l(\cos \theta) \left[\tilde{A}_l h_l^+(kr) + \tilde{B}_l h_l^-(kr) \right] \quad (285)$$

For large kr , we use the asymptotic forms $h_l^\pm \rightarrow \rho^{-1} e^{i\rho(\mp i)^{l+1}}$ to write this as

$$\psi(r, \theta) \rightarrow A \sum_l (2l+1) P_l(\cos \theta) \left[A_l \frac{e^{ikr}}{r} + B_l \frac{e^{-ikr}}{r} \right] \text{ where } A_l = (-i)^{l+1} \frac{\tilde{A}_l}{k}, \quad B_l = i^{l+1} \frac{\tilde{B}_l}{k} \quad (286)$$

¹⁹Use $e^{\pm i l \pi / 2} = (\pm i)^l$. We could also work with the spherical Hankel functions $h_l^\pm(\rho) = j_l(\rho) \pm i n_l(\rho)$ which have the virtue of being purely outgoing and incoming spherical waves. For large ρ , $h_l^\pm(\rho) \rightarrow \rho^{-1} e^{\pm i \rho} (\mp i)^{l+1}$.

A_l and B_l are some coefficients which we now fix. A is the same old constant with dimensions of $L^{-3/2}$. The ingoing spherical wave for each l (at large r) is unaffected by the potential. So this fixes B_l to be the coefficient of the imploding wave in the expansion of e^{ikz} above.

$$B_l = \frac{-(-1)^l}{2ik} \quad (287)$$

What can the coefficients A_l of the outgoing spherical wave be? A_l can receive two contributions: (1) from the outgoing spherical wave in the incoming plane wave (283) & (2) from the scattered wave ψ_{sc} . We will fix A_l by comparison with the scattering boundary condition. But before that we note that it must have the same absolute magnitude as B_l .

- For a real potential, the probability current density $\vec{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \nabla\psi^*\psi)$ for an *eigenstate* of the Schrödinger operator is divergence-free $\nabla \cdot \vec{j} = 0$ since $\frac{\partial \rho}{\partial t} = 0$. In other words, $\int \vec{j} \cdot d\vec{s} = 0$ over any closed surface. In particular, $\int \vec{j} \cdot d\vec{s} = 0$ for a spherical surface at $r = \infty$. For the above ψ , as $r \rightarrow \infty$

$$\vec{j} \rightarrow \frac{\hbar k |A|^2 \hat{r}}{mr^2} \sum_{l'} (2l+1)(2l'+1) P_l(\cos\theta) P_{l'}(\cos\theta) [A_l^* A_{l'} - B_l^* B_{l'}] \quad (288)$$

Using the spherical area element $d\vec{s} = \hat{r} r^2 \sin\theta d\theta d\phi$ we get

$$\int \vec{j} \cdot d\vec{s} = \frac{4\pi\hbar k |A|^2}{m} \sum_l (2l+1) [|A_l|^2 - |B_l|^2] = 0. \quad (289)$$

Conservation of probability implies $\sum_l (2l+1) (|A_l|^2 - |B_l|^2) = 0$. Conservation of angular momentum means there cannot be leakage of probability current between distinct angular momentum sectors. Thus, conservation of probability plus conservation of angular momentum implies that $|A_l| = |B_l|$ for each l . Thus even in the presence of a potential, the amplitude of the outgoing spherical wave A_l can differ from the amplitude of the ingoing spherical wave B_l , only by a multiplicative phase. By convention,

$$A_l = \frac{e^{2i\delta_l}}{2ik} \quad \text{while} \quad B_l = \frac{-(-1)^l}{2ik}. \quad (290)$$

δ_l is called the l^{th} partial wave phase shift, it is real and defined modulo π . In other words, the asymptotic solution of the Schrödinger eigenvalue problem must be of the form

$$\psi(r, \theta) \rightarrow A \sum_l \frac{(2l+1)P_l(\cos\theta)}{2ikr} \left[e^{2i\delta_l} e^{ikr} - (-1)^l e^{-ikr} \right]. \quad (291)$$

Note that this is the total wave function. In particular, the coefficient $e^{2i\delta_l}$ of the exploding wave includes contributions both from ψ_{inc} and ψ_{sc} , but the coefficient of the imploding wave arises entirely from ψ_{inc} .

- The phases of the outgoing partial waves in the total wave function have been shifted by $2i\delta_l$ compared to the un-scattered outgoing waves in e^{ikz} . It is sometimes convenient to write this as

$$\psi(r, \theta) \rightarrow A \sum_{l=0}^{\infty} \frac{i^l (2l+1) P_l(\cos\theta)}{kr} e^{i\delta_l} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right). \quad (292)$$

Comparing with the expansion of $e^{ikz} = \sum_l i^l (2l+1) P_l(j_l)$ where $j_l \rightarrow \frac{\sin(kr - l\pi/2)}{kr}$, we see that the effect of the potential on the total wavefunction is to shift the phase of the sine function by δ_l and \times it by $e^{i\delta_l}$.

- We may also state this in terms of the radial wave function. When $V = 0$, the radial wave function had the asymptotic behavior

$$R_l(kr) \propto \frac{\sin(kr - \frac{l\pi}{2})}{kr} \quad \text{for } kr \gg 1. \quad (293)$$

In the presence of a potential, it has the phase-shifted asymptotic behavior

$$R_l(r) \propto \frac{\sin(kr - \frac{l\pi}{2} + \delta_l)}{kr} \quad \text{for } kr \gg 1. \quad (294)$$

- We now relate the phase shifts δ_l to the partial wave amplitudes a_l by comparing (291) with the known scattering boundary condition

$$\psi(r, \theta) \rightarrow Ae^{ikz} + Af(\theta, \phi) \frac{e^{ikr}}{r} = A \sum_l (2l+1) P_l(\cos \theta) \left[\frac{e^{ikr} + (-1)^l e^{-ikr}}{2ikr} + a_l \frac{e^{ikr}}{r} \right] \quad (295)$$

We find

$$\frac{e^{2i\delta_l}}{2ik} = a_l + \frac{1}{2ik} \Rightarrow a_l = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{e^{i\delta_l} \sin \delta_l}{k}. \quad (296)$$

Having exploited conservation of probability (unitarity) and angular momentum to replace the complex partial wave amplitudes a_l by the real phase shifts δ_l , we write the partial wave expansion for the scattering amplitude and differential cross section as

$$\begin{aligned} f(\theta) &= \sum_{l=0}^{\infty} (2l+1) a_l P_l(\cos \theta) \\ \Rightarrow \frac{d\sigma}{d\Omega} &= |f|^2 = \frac{1}{k^2} \sum_{l,l'} (2l+1)(2l'+1) e^{-i(\delta_l - \delta_{l'})} \sin \delta_l \sin \delta_{l'} P_l(\cos \theta) P_{l'}(\cos \theta). \end{aligned} \quad (297)$$

Integrating, the total cross section becomes

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \equiv \sum_l \sigma_l. \quad (298)$$

The partial x-sections are all non-negative and in particular, σ is bounded below by the S-wave x-section $\sigma \geq \sigma_0$. We also get the so-called ‘unitarity bound’ on the ‘partial cross sections’:

$$\sigma_l \leq \frac{4\pi}{k^2} (2l+1). \quad (299)$$

The unitarity bound is saturated iff the phase shifts are odd multiples of $\pi/2$. So to find the cross section, it suffices to find the scattering phase shifts δ_l , which are dimensionless real quantities depending on the potential and the incoming wave number k . To do so, we must solve the Schrödinger eigenvalue problem in the given potential. Soon, we will do this in some examples.

- More advanced treatments show that for an attractive potential $V(r) < 0$ in 3d, if the S-wave phase shift is small, then it is positive and for a repulsive potential it is negative. Roughly, this is because in a repulsive potential, the particle slows down and is able to accumulate less phase shift while in an attractive potential, it speeds up and accumulates more phase shift compared to a free particle. We will see this in some examples. The quantum mechanical phase shift is related to Wigner’s time-delay.

10.3.3 Semiclassical estimate of relative sizes of phase shifts

- Let us get a rough semi-classical estimate for which phase shifts can be significantly different from zero. Suppose we scatter classical particles of momentum p from a potential that is negligible for $r > a$. Then for impact parameters $b > a$ there is negligible scattering/deflection. The magnitude of angular momentum²⁰ $L = pb$ is proportional to b . So for fixed energy of incoming particles (or fixed momentum p), there will be no scattering if L is too large, i.e. $L > pa$. Semi-classically we write $L = \hbar\sqrt{l(l+1)} \approx \hbar l$ and $p = \hbar k$ and find that partial waves with $l > ka$ suffer no phase shift.

- For very low energy scattering, $ka \ll 1$ and the only partial wave that can have a non-zero phase shift is the $l = 0$ S-wave. The corresponding scattering amplitude is

$$f(\theta) = \frac{1}{k} \sum_l (2l+1) P_l(\cos\theta) e^{i\delta_l} \sin\delta_l \rightarrow \frac{e^{i\delta_0} \sin\delta_0}{k} \quad (300)$$

In particular, for S-wave scattering, the scattering amplitude is spherically symmetric. The incoming wave e^{ikz} contains all angular momenta l . But at low energies, only its S-wave part was scattered, leading to a spherically symmetric outgoing wave with a phase shift.

- A parameter that is often used to characterize the scattering at low energies is the (S-wave) scattering length α defined as

$$\alpha = -\lim_{k \rightarrow 0} f(\theta). \quad (301)$$

As we argued above, at low energies (k small) δ_l for $l \geq 1$ vanish and S-wave scattering dominates. The scattering length α is independent of θ , it is a real parameter with length dimensions, but it can be positive or negative. Often a positive scattering length arises for a repulsive potential and a negative scattering length for an attractive potential as we will see in the examples.

10.3.4 Optical theorem

An immediate consequence of writing the total cross section in terms of the phase shifts is the optical theorem. It relates the total cross section to the imaginary part of the forward scattering amplitude. By forward scattering we mean scattering in the direction $\theta = 0$.

$$f(\theta) = \sum_l (2l+1) P_l(\cos\theta) \frac{e^{i\delta_l} \sin\delta_l}{k} \Rightarrow \Im f(0) = \frac{1}{k} \sum_l (2l+1) \sin^2\delta_l \Rightarrow \sigma = \frac{4\pi}{k} \Im f(0). \quad (302)$$

Here we used $P_l(1) = 1$, which follows from the Rodrigues formula by successive differentiation

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l (x^2 - 1)^l}{dx^l}. \quad (303)$$

²⁰Angular momentum is defined with respect to an origin. We have been using the scattering center $r = 0$ as the origin. However, angular momentum of the projectile is more easily computed with respect to a point (\mathbf{s} in the $-\hat{z}$ direction) far to the left along the beam pipe, since there, the momentum is known to be in the \hat{z} direction. It turns out that the two angular momenta are equal, as we check now. Suppose the incoming particle far to the left has momentum \mathbf{p} directed along \hat{z} at a point \mathbf{r} . We write $\mathbf{r} = \mathbf{s} + \mathbf{b}$ where \mathbf{b} is a ‘vertical’ vector with magnitude equal to the impact parameter. Thus $\mathbf{L}_{\text{origin}} = \mathbf{r} \times \mathbf{p} = \mathbf{s} \times \mathbf{p} + \mathbf{b} \times \mathbf{p} = \mathbf{b} \times \mathbf{p}$ as \mathbf{p} and \mathbf{s} are anti-parallel.

The optical theorem can be thought of as a consequence of unitarity of the S -matrix. The possibility of writing the scattering amplitude in terms of real phase shifts was, after all, contingent on the conservation of probability.

- The optical theorem implies that if the scattering amplitude is real, the total cross section must be zero. If there is non-trivial scattering, the amplitude f cannot be a real function. Moreover, its imaginary part must be +ve in the forward direction. The optical theorem and differential cross section $d\sigma/d\Omega = |f|^2$ together give information on both the real and imaginary parts of f in the forward direction.

10.4 Example: Infinitely hard sphere scattering

This could be used to model scattering of atoms by atoms, where the nuclei strongly repel electrostatically when brought nearby but do not feel much of a force when far apart due to the neutrality of atoms. An infinitely hard sphere refers to a repulsive spherical barrier given by the potential

$$V(r) = \begin{cases} \infty & \text{for } r \leq a \\ 0 & \text{for } r \geq a \end{cases} \quad (304)$$

Classically, the cross section is the cross sectional area seen by a projectile, i.e., $\sigma_{cl} = \pi a^2$. Classically, if the impact parameter $\geq a$, the particle passes undeflected, while if it is less than a , it is deflected according to the law of reflection.

- In QM, the dimensionless quantity ka is a measure of the size of the obstacle relative to the wavelength of the incident wave. Our aim is to find the phase shifts and thereby determine the cross section. The phase shifts δ_l are dimensionless and we will express them in terms of ka . To do so, we must solve the Schrödinger eigenvalue problem for the free particle in the exterior of the hard sphere and impose the scattering boundary condition as $r \rightarrow \infty$ (which defines the phase shifts) and the Dirichlet boundary condition $\psi(r = a) = 0$ on the surface of the sphere.

- The solution of the free particle Schrödinger eigenvalue problem outside the hard sphere is given by $\psi = \sum_{lm} c_{lm} R_l(r) Y_{lm}(\theta, \phi)$ where

$$-\frac{1}{r}(rR_l)'' + \left[\frac{l(l+1)}{r^2} - k^2 \right] R_l = 0, \quad \text{for } r > a \quad (305)$$

The radial function must be a linear combination of spherical Bessel and Neumann functions

$$R_l(r) = \alpha_l j_l(kr) + \beta_l n_l(kr). \quad (306)$$

Imposing $\psi(r = a) = 0$ gives

$$R(a) = 0 \Rightarrow -\frac{\beta_l}{\alpha_l} = \frac{j_l(ka)}{n_l(ka)}. \quad (307)$$

The scattering b.c. at $r = \infty$ which serves to define the phase shifts is

$$\begin{aligned} \psi &\rightarrow A \sum_l (2l+1) P_l(\cos \theta) \frac{i^l e^{i\delta_l}}{kr} \sin \left(kr - \frac{l\pi}{2} + \delta_l \right) \\ &= A \sum_l (2l+1) P_l(\cos \theta) \frac{i^l e^{i\delta_l}}{kr} \left[\sin \left(kr - \frac{l\pi}{2} \right) \cos \delta_l + \cos \left(kr - \frac{l\pi}{2} \right) \sin \delta_l \right] \quad \text{or} \end{aligned}$$

$$R_l(r) \propto \frac{1}{kr} \sin(kr - \frac{1}{2}l\pi + \delta_l) \propto \frac{1}{kr} \left[\sin\left(kr - \frac{l\pi}{2}\right) \cos \delta_l + \cos\left(kr - \frac{l\pi}{2}\right) \sin \delta_l \right]. \quad (308)$$

We must compare this with the behavior of the wave function as $r \rightarrow \infty$,

$$R_l(r) = \alpha_l j_l(kr) + \beta_l n_l(kr) \rightarrow \frac{1}{kr} \left[\alpha_l \sin\left(kr - \frac{l\pi}{2}\right) - \beta_l \cos\left(kr - \frac{l\pi}{2}\right) \right] \quad (309)$$

We get

$$-\frac{\beta_l}{\alpha_l} = \frac{\sin \delta_l}{\cos \delta_l} = \tan \delta_l \quad (310)$$

Now combining with the b.c. at $r = a$ we get a formula for the phase shifts in terms of the physical parameters of the problem k and a

$$\tan \delta_l = \frac{j_l(ka)}{n_l(ka)} \Rightarrow \delta_l = \arctan \frac{j_l(ka)}{n_l(ka)}. \quad (311)$$

The partial wave amplitudes $a_l = \frac{e^{i\delta_l} \sin \delta_l}{k}$ follow as a consequence.

- To understand this result, let us first consider the S-wave phase shift $l = 0$ in which case $j_0(\rho) = \sin \rho/\rho$ and $n_0(\rho) = -\cos \rho/\rho$. For this repulsive potential, the S-wave phase shift is *negative*:

$$\delta_0 = \arctan(-\tan ka) = -ka \quad \text{mod } \pi. \quad (312)$$

The S-wave partial wave amplitude is $a_0 = -k^{-1}e^{-ika} \sin ka$.

- The partial x-sections are $\sigma_l = \frac{4\pi}{k^2}(2l+1)\sin^2 \delta_l$ and the total x-section is the sum of these non-negative partial x-sections. Thus the S-wave scattering x-section is

$$\sigma_0(k) = \frac{4\pi}{k^2} \sin^2 ka \quad (313)$$

So the S-wave x-section is maximal at the longest wavelengths (low energy, ka small)

$$\sigma_0(k \rightarrow 0) = 4\pi a^2 \quad (314)$$

and decreases with growing wave number. In fact, at long wavelengths, the S-wave x-section is equal to the surface area of the hard sphere. So the total x-section (as $k \rightarrow 0$) is at least as big as the area of the sphere. Contrast this with the classical x-section which is equal to πa^2 , the x-sectional area of the hard sphere. So for low energy scattering, the target in wave mechanics looks bigger than for classical particle scattering.

- Moreover the S-wave x-section oscillates within a decreasing envelope as k increases. Interestingly, σ_0 vanishes if $ka = n\pi$. The target is transparent at these energies within the S-wave approximation.

- When is the S-wave approximation good? i.e., when can we ignore the other phase shifts? S-wave scattering dominates at low energies or large incident wavelengths compared to the miniscule size of the obstacle. For a small obstacle $ka \ll 1$ and²¹

$$\tan \delta_l = \frac{j_l(ka)}{n_l(ka)} \rightarrow -\frac{2^{2l}(l!)^2}{(2l)!(2l+1)!} (ka)^{2l+1} \quad (315)$$

²¹We use the behaviors for small ρ : $j_l(\rho) \rightarrow \frac{2^l l!}{(2l+1)!} \rho^l = \frac{\rho^l}{(2l+1)!!}$ and $n_l(\rho) \rightarrow -\frac{(2l)!}{2^l l!} \frac{1}{\rho^{l+1}} = -\frac{(2l-1)!!}{\rho^{l+1}}$.

So as $ka \rightarrow 0$, $\tan \delta_l \rightarrow 0$ for $l = 1, 2, 3, \dots$. So the P,D,F ... wave phase shifts all vanish for very low energy scattering. The S-wave phase shift alone can have a non-zero low energy limit. At low energies, even though the incoming plane wave had all angular momentum components, only its S-wave component gets non-trivially scattered producing a spherically symmetric scattered wave, while higher angular momentum components pass the minuscule obstacle unaffected. The higher angular momentum components of ψ_{inc} , $j_l(\rho) \propto \rho^l$ are suppressed near $\rho = 0$ and do not feel the effects of the obstacle.

- Using the above phase shifts we can construct the scattering amplitude

$$f(\theta) = \frac{1}{k} \sum_l (2l+1) P_l(\cos \theta) e^{i\delta_l} \sin \delta_l \quad (316)$$

In particular, at low energies ($k \rightarrow 0$) $\delta_l = 0$ for $l \geq 1$ and this implies the (S-wave) scattering length is equal to the radius of the obstacle a :

$$\alpha = - \lim_{k \rightarrow 0} f(\theta) = - \lim_{k \rightarrow 0} \frac{e^{-ika} \sin(-ka)}{k} = a \quad (317)$$

For a repulsive potential, the S-wave scattering length is usually positive.

10.5 Finite spherical well: S-wave scattering

- See Liboff for example. Let us consider low wave number scattering against a finite spherical well. This could be used to model scattering of an electron against an atom. The nuclear attraction is effective only within the atom and is effectively screened outside the neutral atom. So we take

$$V(r) = \begin{cases} -V & \text{for } r < a \\ 0 & \text{for } r \geq a. \end{cases} \quad (318)$$

At low energies $ka \ll 1$, it is adequate to truncate the partial wave expansion after the $l = 0$ term and consider S-wave scattering. The aim is to solve the Schrödinger eigenvalue problem in the S-wave sector and read off the S-wave phase shift δ_0 by comparing with the scattering boundary condition. In the S-wave sector $\psi(\vec{r}) = R(r)Y_{00}$ and we only need consider $l = 0$. In the interior of the well, the radial eigenvalue equation for $u = rR$ is

$$-\frac{\hbar^2}{2m} u'' - Vu = \frac{\hbar^2 k'^2}{2m} u \Rightarrow -u'' = k'^2 u \text{ where } k'^2 = k^2 + \frac{2mV}{\hbar^2}. \quad (319)$$

So $R(r < a) = r^{-1} (A \sin k'r + B \cos k'r)$. Since the wave function must be regular at $r = 0$, $B = 0$.

- Outside the well, we have the free particle SE $-u'' = k^2 u$ with solution $u = c_1 \sin kr + c_2 \cos kr$ which can be written as

$$R(r > a) = \frac{B}{r} \sin(kr + \varphi) \quad (320)$$

Comparing with the scattering boundary condition which defines the phase shift, $R(r) \sim \sin(kr - l\pi/2 + \delta_0)$, we conclude that $\varphi = \delta_0$ is just the S-wave phase shift. To find δ_0 we need to impose the continuity of the wave function ψ and its gradient $\nabla\psi$ across the surface $r = a$. Since $\psi = RY_{00}$, we must impose continuity of R and R' . Continuity of R (or u) gives

$$A \sin k'a = B \sin(ka + \delta_0) \quad (321)$$

Continuity of R' upon using continuity of R gives

$$Ak' \cos k'a = Bk \cos(ka + \delta_0) \quad (322)$$

Taking a quotient, we get a relation between δ_0 and the physical parameters of the problem:

$$k' \cot k'a = k \cot(ka + \delta_0(k)) \quad \text{where} \quad k'^2 = k^2 + \frac{2mV}{\hbar^2} \quad (323)$$

In principle, this transcendental equation expresses δ_0 as a function of incident wave number k , V and a . In what follows we find δ_0 approximately in some regimes. These approximations could easily fail and one must check the conclusions for consistency.

- We first consider the case where δ_0 is small. Since ka is also small, in this case, we can approximate $\cot(ka + \delta_0) \approx (ka + \delta_0)^{-1}$ and get²²

$$\delta_0^{\text{approx}}(k) = ka \left(\frac{\tan k'a}{k'a} - 1 \right) \quad \text{when } \delta_0 \text{ and } ka \text{ are small.} \quad (324)$$

Note that when the energy is small compared to the depth of the well $E \ll V$, we may write

$$k'a = a \sqrt{\frac{2mV}{\hbar^2}} \sqrt{1 + \frac{\hbar^2 k^2}{2mV}} \approx \frac{a}{\hbar} \sqrt{2mV} \left(1 + \frac{E}{2V} + \dots \right) \quad \text{where } E = \frac{\hbar^2 k^2}{2m}. \quad (325)$$

So that for small ka and small E/V , we have

$$\delta_0^{\text{approx}}(k) \approx ka \left[\frac{\tan \left[\frac{a}{\hbar} \sqrt{2mV} \left(1 + \frac{E}{2V} \right) \right]}{\frac{a}{\hbar} \sqrt{2mV} \left(1 + \frac{E}{2V} \right)} - 1 \right]. \quad (326)$$

- Let us compute the S-wave scattering amplitude f and cross section σ_0 for small ka and small δ_0 :

$$f(\theta) = \sum_l (2l+1) P_l a_l \approx a_0 = \frac{1}{k} e^{i\delta_0} \sin \delta_0 \quad (327)$$

- When $\delta_0 \ll 1$ we approximate $e^{i\delta_0} \approx 1$ and $\sin \delta_0 \approx \delta_0$ to get

$$f(\theta) \approx a \left(\frac{\tan k'a}{k'a} - 1 \right) \quad \text{and} \quad \sigma_0 \approx 4\pi |a_0|^2 \approx \frac{4\pi \delta_0^2}{k^2} \approx 4\pi a^2 \left(\frac{\tan k'a}{k'a} - 1 \right)^2. \quad (328)$$

As expected, the S-wave scattering amplitude is spherically symmetric. An interesting feature of this approximate S-wave cross section is that it vanishes at energies satisfying the transcendental relation $k'a = \tan k'a \pmod{\pi k'/k}$. At those energies, the target appears transparent to S-waves! Note that at these energies $\delta_0 = 0$ so we are allowed to use our approximate formula for small δ_0 *provided* ka is also small.

- The S-wave scattering length for small δ_0 is obtained from the low energy limit of $f(\theta)$

$$\alpha \approx - \lim_{k \rightarrow 0} f(\theta) = a \left(1 - \frac{\tan a \sqrt{\frac{2mV}{\hbar^2}}}{a \sqrt{\frac{2mV}{\hbar^2}}} \right). \quad (329)$$

²²Note that $g(x) = \tan x - x$ satisfies $g(0) = 0$ and $g'(x) = \tan^2 x \geq 0$, so $\tan x \geq x$ for $0 \leq x \leq \pi/2$. Thus δ_0 is guaranteed to be positive (as is often the case for an attractive potential) for the energy range $0 \leq \sqrt{\frac{2m(E+V)a^2}{\hbar^2}} \leq \pi/2$.

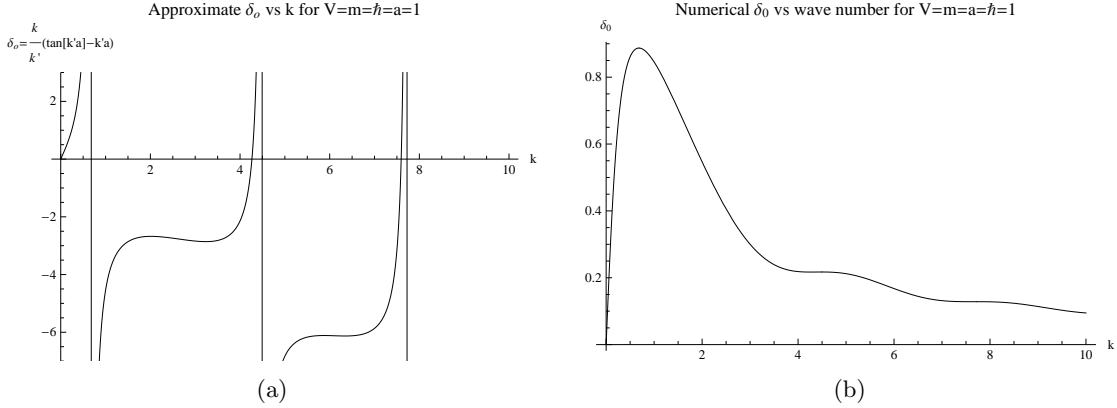


Figure 1: (a) Approx. S-wave phase shift $\delta_0^{\text{approx}} = ka \left(\frac{\tan k'a}{k'a} - 1 \right)$ (valid for small ka and small δ_0) versus k for $V = a = m = \hbar = 1$. For small $k < \frac{1}{2}$ or so, δ_0^{approx} is small (and positive in this case), and the approximation may be relied upon. δ_0^{approx} diverges at the potential S-wave resonances $k'a = (2n + 1)\pi/2$, where the formula cannot be trusted. But periodically, δ_0^{approx} vanishes (mod π) signaling possible transparency to S-wave scattering. Near such k the formula may be trusted provided ka is small. However, the first such possibility for these parameters occurs only at $ka \approx 1.3$ which is not small compared to 1. So this δ_0^{approx} cannot a priori be trusted near these 'higher zeros' of δ_0 (mod π). (b) Numerical solution of transcendental equation for δ_0 for same V, m, a, \hbar . S-wave phase shift does show some local maxima roughly where expected from δ_0^{approx} . It does not vanish anywhere, though the phase shift has local minima. δ_0^{approx} can only be trusted for small k for these parameters.

For $0 \leq a\sqrt{\frac{2mV}{\hbar^2}} \leq \pi/2$, i.e., if the well is not too deep, this scattering length is negative, as is often the case for an attractive potential. Note that this is only an approximate scattering length and is valid only when the S-wave phase shift δ_0 is small.

- The above approximate phase shift $\delta_0^{\text{approx}}(k)$ most dramatically fails to be reliable at those k where the tangent function blows up, i.e., when $k'a \approx (2n + 1)\pi/2$. At those energies, δ_0 is not small and we need to go back and solve $k' \cot k'a = k \cot(ka + \delta_0)$ without assuming δ_0 is small. In fact near such values ($k'a = (2n + 1)\pi/2$), $\cot k'a = 0$ and so $\sin(ka + \delta_0) \approx \pm 1$ which means $\sin(\delta_0) \approx \pm 1$ if $ka \ll 1$. So if ka is small and $k'a$ is near an odd multiple of $\pi/2$, the S-wave scattering phase shift reaches a peak of $\pi/2$ modulo π where the S-wave scattering cross section saturates the unitarity bound

$$\sigma_0^{\text{unitarity bound}} = \frac{4\pi}{k^2} \sin^2 \delta_0 = \frac{4\pi}{k^2} \quad (330)$$

When the S-wave x-section goes through a maximum it is called an S-wave resonance (even if it does not saturate the unitarity bound). The target looks very large at resonant energies. It is as if the incoming particle gets nearly trapped bouncing around the potential well, before eventually escaping to infinity. Note that in atomic scattering, infinity just means a few atomic diameters, by which time the potential would have died out. Also, the time ($\sim 10^{-10}$ s) particles spend in the vicinity of the scattering center can be very small compared to human time scales.

- The case of low energy scattering by a repulsive finite spherical barrier $V > 0$ for $r < a$ is also interesting. See the problem set. In the interior region $r < a$, we have $E < V$ so k' is

replaced by $i\kappa$ where $\hbar^2\kappa^2/2m = V - E$. The S-wave cross section for low energy scattering is

$$\sigma = 4\pi a^2 \left(\frac{\tanh \kappa a}{\kappa a} - 1 \right)^2. \quad (331)$$

When the barrier becomes infinitely high $V \rightarrow \infty$ $\kappa \rightarrow \infty$ and $\tanh \kappa a \rightarrow 1$. We recover the S-wave cross section $\sigma = 4\pi a^2$ for scattering by a hard sphere.

10.6 Born series and approximation

- Max Born's approximation to find the scattering amplitude $f(\theta, \phi)$ is useful especially when the scattering potential $V(\vec{r})$ is weak compared to the energy of the incoming wave $\hbar^2k^2/2m$. In such a situation, the scattered wave is expected to be small compared to the incoming plane wave. So it is useful in the regime of high energies while the partial wave approximation is useful at low energies. Loosely, the Born series is an expansion in powers of the potential V , treated as a perturbation to the kinetic term. V need not be spherically symmetric.

10.6.1 Integral form of the Schrödinger equation and Green's function of the Helmholtz operator

- The starting point for the Born series is a rewriting of the Schrödinger eigenvalue problem as an integral equation. We begin by writing

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = \frac{\hbar^2k^2}{2m}\psi \Rightarrow (\nabla^2 + k^2)\psi = \frac{2mV}{\hbar^2}\psi. \quad (332)$$

$\nabla^2 + k^2$ is the Helmholtz operator and if the rhs $\frac{2mV}{\hbar^2}\psi$ had been a source $\chi(\vec{r})$ independent of $\psi(\vec{r})$, this would be the inhomogeneous Helmholtz equation. Recall that the general solution of an inhomogeneous linear equation $A\psi = \chi$ is given by the sum of a particular solution and the general solution of the homogeneous equation $A\psi = 0$. Though the SE is in fact a homogeneous equation, it pays to think of it as an inhomogeneous Helmholtz equation and treat the rhs $\frac{2mV}{\hbar^2}\psi$ as a small source.

- The idea is to try to invert the operator $\nabla^2 + k^2$ and take it to the rhs. However, $\nabla^2 + k^2$ is not invertible, as it is 'many to one', it has zero eigenvalues. Indeed, it has a large null space consisting of all free particle eigenstates: $(\nabla^2 + k^2)\psi_0 = 0$, e.g., the plane waves $\psi_0(\vec{r}) = e^{i\vec{l}\cdot\vec{r}}$ for *any* vector \vec{l} whose length is $|\vec{l}| = k$. These plane waves span the zero eigenspace of the Helmholtz operator (though we could just as well use angular momentum eigenstates of the free particle with energy $\hbar^2k^2/2m$).

- Though it isn't invertible, we may be able to find a 'right inverse' in the sense of a 'Green's function' $G(r, r')$ satisfying (here ∇ is the gradient in \vec{r} as opposed to the gradient ∇' in \vec{r}')

$$(\nabla^2 + k^2)G(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}'). \quad (333)$$

But such a Green's function is not unique. However, any two Green's functions $G^{(1)}, G^{(2)}$ for the Helmholtz operator differ by a solution ψ_0 of the homogeneous Helmholtz equation

$$[\nabla^2 + k^2] \left(G^{(1)}(\vec{r}, \vec{r}') - G^{(2)}(\vec{r}, \vec{r}') \right) = 0 \Rightarrow G^{(1)}(\vec{r}, \vec{r}') - G^{(2)}(\vec{r}, \vec{r}') = \psi_0(r) \quad (334)$$

We will find a Green's function for the Helmholtz operator shortly. The virtue of having one is that it in effect provides a 'particular solution' of the inhomogeneous Helmholtz equation. In more detail, we may write the 'general solution' of the SE as

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G(\vec{r}, \vec{r}') \frac{2mV(\vec{r}')}{\hbar^2} \psi(\vec{r}') d^3r' \quad (335)$$

where $\psi_0(\vec{r})$ is any solution of $(\nabla^2 + k^2)\psi = 0$, i.e., a free particle energy eigenstate. It is easily checked that this ψ satisfies the SE. However, it is not an explicit solution since ψ appears both on the left and right sides. Nevertheless, it is an integral equation for ψ which looks a bit like the scattering boundary condition if we take $\psi_0 = e^{ikz}$! So we should expect the integral expression on the rhs to tend to the scattered wave for large r .

- We can iterate this expression to get the Born series, which gives a formal solution of the SE:

$$\begin{aligned} \psi(r) = & \psi_o(r) + \int G(r, r') \frac{2mV(r')}{\hbar^2} \psi_o(r') dr' + \iint G(r, r') \frac{2mV(r')}{\hbar^2} G(r', r'') \frac{2mV(r'')}{\hbar^2} \psi_o(r'') dr' dr'' \\ & + \iiint G(r, r') \frac{2mV(r')}{\hbar^2} G(r', r'') \frac{2mV(r'')}{\hbar^2} G(r'', r''') \frac{2mV(r''')}{\hbar^2} \psi_o(r''') dr' dr'' dr''' + \dots \end{aligned} \quad (336)$$

- We still have to find a Green's function for the Helmholtz operator, i.e., any one solution of

$$(\nabla^2 + k^2) G(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}'). \quad (337)$$

We will select a solution that is appropriate to the scattering problem. A priori $G(r, r')$ is a function of six coordinates and it is daunting to find a solution of this partial differential equation that involves derivatives in three of them r, θ, ϕ . However, on account of the translation invariance ($\vec{r} \rightarrow \vec{r} + \vec{b}$) of the Helmholtz operator, we choose to look for a Green's function that depends only on the translation-invariant vector $\vec{r} - \vec{r}'$. So we have gone from 6 to 3 variables. Furthermore, on account of the rotation invariance of the Helmholtz operator²³, we choose to look for a Green's function that depends only on the rotation invariant quantity $s = |\vec{s}| = |\vec{r} - \vec{r}'|$. This reduces the above partial differential Helmholtz operator to an ordinary differential operator. $G(s)$ must satisfy²⁴

$$\frac{1}{s} \frac{d^2 s G(s)}{ds^2} + k^2 G(s) = \delta^3(\vec{s}). \quad (338)$$

Let us first consider the case $s > 0$ where this is a homogeneous linear ODE $(sG)'' + k^2 sG = 0$. The general solution is $G(s) = \frac{Ae^{iks}}{s} + \frac{Be^{-iks}}{s}$. However, we choose $B = 0$ since we will be interested in the outgoing scattered wave. To find A , we look at the behavior for small s , where

²³By rotation-invariance we mean that if $\vec{r}' = (x', y', z') = R\vec{r}$ for a rotation R applied to $\vec{r} = (x, y, z)$, then the formula for the Laplacian $\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is unchanged. It is good to check this first in two dimensions, where $x' = cx - sy$ and $y' = sx + cy$ for $s = \sin \alpha$ and $c = \cos \alpha$ where α is the angle of (counter-clockwise) rotation. Just as translation-invariance is manifest in Cartesian coordinates, rotation-invariance is manifest in spherical polar coordinates. Suppose the rotation is by a counter-clockwise angle α about some axis. Let us choose our coordinate system so the axis of rotation is the z -axis. Then under such a rotation $(r, \theta, \phi) \mapsto (r, \theta, \phi + \alpha)$. Now the laplacian is $\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$. The formula for this differential operator is clearly unchanged under $\phi \rightarrow \phi + \alpha$. Thus the Laplacian is rotation invariant.

²⁴For $G(\vec{r}, \vec{r}') = G(\vec{r} - \vec{r}')$, we can re-cast the derivatives w.r.to \vec{r} as derivatives with respect to \vec{s} since $\frac{\partial G(x-x')}{\partial x} = \frac{\partial G(x-x')}{\partial (x-x')}$.

$G(s) \rightarrow \frac{A}{s}$ independent of k . So to find A , it suffices to consider the case $k = 0$. For $k = 0$, it is easy to show that

$$\nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta^3(\vec{r}) \quad (339)$$

For $r \neq 0$, this is immediate since $\nabla^2 r^{-1} = \frac{1}{r}(rr^{-1})'' = 0$. To check that it is correct also at $r = 0$ we integrate over the interior of a unit sphere and use Stokes theorem:

$$\int \vec{\nabla} \cdot \vec{\nabla} \frac{1}{r} d^3r = \int_{S^2} \vec{\nabla} \frac{1}{r} \cdot \hat{r} r^2 d\Omega = \int -\frac{\hat{r}}{r^2} \cdot \hat{r} r^2 d\Omega = -4\pi. \quad (340)$$

So we conclude that $A = -\frac{1}{4\pi}$. Thus we have found one Green's function for the Helmholtz operator

$$G(s) = -\frac{1}{4\pi} \frac{e^{iks}}{s} \quad \text{or} \quad G(\vec{r} - \vec{r}') = -\frac{1}{4\pi} \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|}. \quad (341)$$

A Green's function is not unique, we can add to this $G(s)$ any solution of the homogeneous equation and get another Green's function. However, for the problem of interest, $G(s)$ is most appropriate, as it satisfies the scattering b.c.

- To summarize, we have written the Schrödinger eigenvalue problem as an integral equation

$$\psi(r) = \psi_0(r) - \frac{1}{4\pi} \int \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} \psi(\vec{r}') d^3r' \quad (342)$$

and iterated it to obtain the Born series (336).

10.6.2 Born approximation

So far we have not made any approximation. Now we apply this to the scattering problem by choosing $\psi_0(r) = e^{i\vec{k} \cdot \vec{r}}$ to be the incoming plane wave with $\vec{k} = k\hat{z}$. Notice that successive terms in the Born series involve higher powers of the potential. We suppose that the potential is weak so that the total wave function does not differ much from the incoming plane wave and truncate the Born series after one iteration. This gives the first Born approximation

$$\psi(r) = e^{i\vec{k} \cdot \vec{r}} - \frac{1}{4\pi} \int \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} e^{i\vec{k} \cdot \vec{r}'} d^3r' + \mathcal{O}(V^2). \quad (343)$$

To find the scattering amplitude, we must extract the asymptotic behavior for large r and compare with the scattering boundary condition

$$-\frac{1}{4\pi} \int \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} e^{i\vec{k} \cdot \vec{r}'} d^3r' \rightarrow f(\theta, \phi) \frac{e^{ikr}}{r}. \quad (344)$$

To extract the large r behavior of the integral, we assume that the potential is localized, so that the integral over \vec{r}' receives non-trivial contributions only for small r' . So we may assume that $r \gg r'$ inside the integral. The simplest possibility is to take $|\vec{r} - \vec{r}'| \approx r$. Within this crude approximation the scattering amplitude is independent of θ and ϕ (below $\vec{k} = k\hat{z}$ for a plane wave incident from the left)

$$f_{crude}(\theta, \phi) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \tilde{V}(-\vec{k}) \quad \text{where} \quad \tilde{V}(\vec{k}) = \int V(\vec{r}') e^{-i\vec{k} \cdot \vec{r}'} d^3r'. \quad (345)$$

Though too crude, it indicates that the scattering amplitude is proportional to the Fourier transform of the potential, which we will see is a general feature of the Born approximation.

- To do justice to the first Born approximation and extract the angular dependence of the scattering amplitude, we need a better approximation for $|\vec{r} - \vec{r}'|$. We write

$$|\vec{r} - \vec{r}'|^2 = r^2 - 2\vec{r} \cdot \vec{r}' + r'^2 = r^2 \left(1 - 2\frac{\vec{r} \cdot \vec{r}'}{r^2} + \frac{r'^2}{r^2} \right) \Rightarrow |\vec{r} - \vec{r}'| = r \left(1 - 2\frac{\vec{r} \cdot \vec{r}'}{r^2} + \frac{r'^2}{r^2} \right)^{\frac{1}{2}} = r - \hat{r} \cdot \vec{r}' + \mathcal{O} \left(\frac{r'^2}{r^2} \right).$$

Using $|\vec{r} - \vec{r}'| \approx r - \hat{r} \cdot \vec{r}'$ in the first Born approximation, we get²⁵

$$\psi(r) \approx e^{i\vec{k}_i \cdot \vec{r}} - \frac{1}{4\pi} \frac{2m}{\hbar^2} \frac{e^{ikr}}{r} \int V(\vec{r}') e^{-i(\vec{k}_f - \vec{k}_i) \cdot \vec{r}'} d^3r' \quad (346)$$

where we defined $\vec{k}_i = \vec{k}$ for the incoming wave vector and an²⁶ outgoing wave vector $\vec{k}_f = k\hat{r}$ in the direction defined by θ, ϕ . From this we can read off the scattering amplitude

$$f(\theta, \phi) = f(\hat{k}_f) = f(\hat{r}) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \tilde{V}(\vec{k}_f - \vec{k}_i) = -\frac{m}{2\pi\hbar^2} \tilde{V}(\vec{q}). \quad (347)$$

This is the first Born approximation for the scattering amplitude and is valid even if V isn't spherically symmetric. The vector $\vec{q} = \vec{k}_f - \vec{k}_i$ is called the momentum transfer. The main result of the Born approximation is that the scattering amplitude $f(\hat{r})$ is proportional to the Fourier transform of the potential with respect to the momentum transfer $\vec{q} = k\hat{r} - \vec{k}$.

- The Born approximation gives a solution to the direct scattering problem valid at high energies. In treating the potential term in the hamiltonian $H = \frac{p^2}{2m} + V$ as a perturbation, V has been assumed to be small compared to the free particle energy, which is the energy of the incoming particle in the beam. This is what allows us to replace $\psi(\vec{r}')$ under the integral by the free particle $\psi_0(\vec{r}')$.

- The Born approximation also gives a partial result in inverse scattering: a way to extract the potential if the scattering amplitude is known.

- In the limit of zero momentum transfer $\vec{q} \rightarrow 0$, the Born scattering amplitude simplifies. In this limit, the scattering amplitude is spherically symmetric and sensitive only to the integral of the potential:

$$f_{\vec{q} \rightarrow 0}(\hat{r}) = -\frac{m}{2\pi\hbar^2} \tilde{V}(0) = -\frac{m}{2\pi\hbar^2} \int V(\vec{r}') d^3r'. \quad (348)$$

10.6.3 Born approximation for spherically symmetric potential

- For a spherically symmetric potential, the Born approximation for the scattering amplitude may be simplified. If $\vec{k} = k\hat{z}$ and $\vec{k}_f = k\hat{r}$, then from the isosceles triangle, the momentum

²⁵In the denominator we use the crude approximation $|\vec{r} - \vec{r}'| \approx r$. This is because $|\vec{r} - \vec{r}'|^{-1} \approx \frac{1}{r} \left(1 - \frac{\hat{r} \cdot \vec{r}'}{r} \right)^{-1} \approx \frac{1}{r} \left(1 + \frac{\hat{r} \cdot \vec{r}'}{r} + \dots \right) \approx \frac{1}{r} + \frac{\hat{r} \cdot \vec{r}'}{r^2}$. The 2nd term is $\sim r^{-2}$ for $r \rightarrow \infty$ and wouldn't contribute to $f(\theta, \phi)$, which is the coefficient of $\frac{e^{ikr}}{r}$ for large r .

²⁶ $\vec{k}_f = k\hat{r}$ is not the wave vector of a plane wave. The outgoing wave is a spherical wave. \hat{k}_f is just a convenient notation for the unit vector \hat{r} in the direction in which we are interested in finding $f(\theta, \phi)$. But it is a reasonable notation, since in an experiment, we would detect a outgoing scattered free particle at angular location θ, ϕ with momentum $\hbar\vec{k}_f$.

transfer $\vec{q} = \vec{k}_f - \vec{k}_i$ is seen to have a magnitude $q = 2k \sin \frac{\theta}{2}$. To evaluate the Fourier transform of the potential

$$\tilde{V}(\vec{q}) = \int e^{-i\vec{q}\cdot\vec{r}'} V(r') r'^2 dr' \sin \theta' d\theta' d\phi' \quad (349)$$

we pick the \hat{z}' axis to point in the direction of \vec{q} so that $\vec{q} \cdot \vec{r}' = qr' \cos \theta'$ and get

$$\tilde{V}(q) = \int V(r') e^{-iqr' \cos \theta'} r'^2 \sin \theta' dr' d\theta' d\phi' \quad (350)$$

We can perform the θ' integral by the substitution $t = \cos \theta'$

$$\int_0^\pi e^{-iqr' \cos \theta'} \sin \theta' d\theta' = \int_{-1}^1 e^{-iqr't} dt = \frac{2 \sin qr'}{qr'} \quad (351)$$

Thus the Fourier transform of a spherically symmetric potential is rotationally invariant in momentum space as well

$$\tilde{V}(\vec{q}) = \tilde{V}(q) = \frac{4\pi}{q} \int_0^\infty V(r') r' \sin qr' dr' \quad (352)$$

Thus the scattering amplitude in the first Born approximation is

$$f(\theta, \phi) = -\frac{2m}{\hbar^2 q} \int_0^\infty V(r) r \sin qr dr \quad \text{where } q = 2k \sin \frac{\theta}{2}. \quad (353)$$

10.6.4 Rutherford scattering

• In the case of Rutherford scattering of charge q_1 against charge q_2 , the potential is $V(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r}$, and

$$\tilde{V}(q) = \frac{q_1 q_2}{\epsilon_0 q} \int_0^\infty \sin qr dr = \frac{q_1 q_2}{\epsilon_0 q^2} \int_0^\infty \sin \rho d\rho \quad (354)$$

However, the dimensionless oscillatory integral appearing above is not absolutely convergent. In the absence of additional (physical) input we could assign any numerical value to it. However aside from this numerical constant, if we put $q = 2k \sin \theta/2$, we see that the cross section $|\frac{m}{2\pi\hbar^2} \tilde{V}(q)|^2$ resembles the Rutherford cross section. We have already encountered difficulties with the Coulomb potential in that its total scattering cross section is infinite classically. The Coulomb potential does not die off fast enough as $r \rightarrow \infty$ for us to be able to legitimately treat the incoming and scattered particles as free. This is reflected in the above ambiguity in defining the Fourier transform of the Coulomb potential. However, in many physical situations, the Coulomb potential is screened beyond a screening length. So we can treat the Coulomb potential as the $\mu \rightarrow 0$ limit of a screened Coulomb (or Yukawa) potential

$$V(r) = \alpha \frac{e^{-\mu r}}{r} \quad \text{where } \alpha = \frac{q_1 q_2}{4\pi\epsilon_0}. \quad (355)$$

μ^{-1} is called the screening length. For $r > \mu^{-1}$, the Coulomb potential is effectively screened by the exponential damping factor. For the Yukawa potential, we find

$$\tilde{V}(q) = \frac{4\pi}{q} \int_0^\infty \frac{\alpha e^{-\mu r}}{r} r \sin qr dr = \frac{4\pi\alpha}{\mu^2 + q^2}. \quad (356)$$

Putting $\alpha = q_1 q_2 / 4\pi\epsilon_0$ in the limit $\mu \rightarrow 0$ we get for the Coulomb potential

$$\tilde{V}(q) \rightarrow \frac{q_1 q_2}{\epsilon_0} \frac{1}{q^2}. \quad (357)$$

Putting $q = 2k \sin(\theta/2)$ we get the limiting scattering amplitude in the Born approximation

$$f(\theta, \phi) \approx -\frac{2m}{\hbar^2} \frac{q_1 q_2}{4\pi\epsilon_0} \frac{1}{q^2} = -\frac{q_1 q_2}{16\pi\epsilon_0 E} \frac{1}{\sin^2 \theta/2} \quad (358)$$

where $E = \hbar^2 k^2 / 2m$. The differential cross section for Coulomb scattering in the Born approximation is found to match Rutherford's result from classical mechanics

$$\frac{d\sigma}{d\Omega} = |f|^2 \approx \left(\frac{q_1 q_2}{16\pi\epsilon_0 E} \right)^2 \frac{1}{\sin^4 \theta/2}. \quad (359)$$

Scattering in the forward direction dominates, but there is significant scattering through wide angles as well, as found in Rutherford's alpha scattering experiment.

11 Time-dependent hamiltonians and perturbation theory

- Suppose an atom is exposed to electromagnetic radiation for a certain duration (e.g. shine monochromatic light (e.g. laser) beam on an atom). How does it affect the atom? The atom is typically in a stationary state before the light was turned on. An interesting question is whether the atom will make a transition to another given stationary state and the rate of such transitions. In effect, from the time the laser is turned on, the hamiltonian of the atom has been perturbed by a time-dependent interaction of the electron with the oscillating electromagnetic field of the light beam²⁷. Since the atom is neutral, this interaction energy is to leading order in the multipole expansion, given by the electric dipole energy $-\vec{p} \cdot \vec{E}$ where \vec{p} is the electric dipole moment of the atom and $\vec{E} = \vec{E}_o \cos(\vec{k} \cdot \vec{r} - \omega t)$ is the electric field in the electromagnetic wave. For a hydrogen atom, $\vec{p} = e\vec{r}$ where \vec{r} is the position vector of the electron (with respect to the nucleus) and $e < 0$ its charge. The magnetic force $e\vec{v} \times \vec{B}$ is smaller than the electric force $e\vec{E}$ by a factor of v/c . This is because, in an EM wave, the amplitudes are related by $B_o = E_o/c$ and $v/c \ll 1$ for electrons in an atom. So we ignore the magnetic force.

- The wavelength of visible light ($\sim 400 - 700$ nm) is much larger than the size of atoms (~ 0.1 nm), so the electromagnetic field can be assumed spatially constant over the atom, but its time-dependence cannot be ignored. Indeed, as we learned from atomic spectroscopy, the frequency of visible (or UV/IR) light is such that $h\nu$ is of the order of the (electron volt) energy differences between atomic energy levels. What is more, atomic transitions occur in about a nano-second, while the time period of visible light is about $T = 10^{-15}$ s, so the time dependence of the electromagnetic wave cannot be ignored.

- Here we develop techniques to treat physical situations where a time-dependent perturbation $gH_1(t)$ is applied to a system in a stationary state of its time-independent hamiltonian H_0 . In the above example, we may treat the electric dipole interaction energy as a perturbation since the electric field in the light beam is typically much smaller (in commercial lasers used in eye

²⁷We are treating the electron quantum mechanically but the light as a classical electromagnetic wave rather than as photons.

surgery, it is about $10^7 - 10^8$ V/m) than the electric field felt by the electrons due to the nucleus $\sim \frac{13.6\text{V}}{0.053\text{nm}} \sim 10^{11}\text{V/m}$.

- Time dependent perturbations can be of various sorts. E.g. (1) periodic as in the case of monochromatic light shone on an atom. (2) adiabatic, where we have a perturbation which is very slowly varying compared to the time scales associated with H_0 , (3) impulsive, where the perturbation lasts only a very short time as when an X-ray pulse is shone on an atom, possibly ionising it, or when a fast charged particle passes by an atom (4) sudden, for example where a sudden perturbation is applied resulting in a new time-independent hamiltonian. This happens when a neutron in the nucleus of an atom beta decays leaving behind a new isotope with a different atomic number.

- We will not solve these problems in detail, but will develop some of the formalism to treat them and illustrate with simple examples. In all cases, the main quantity of interest is the probability of transitions induced by the time-dependent perturbation.

11.1 Sudden perturbation: strong short-lived time dependence

A heavy isotope of hydrogen Tritium (npe) is unstable to beta decay $n \rightarrow p^+ + e^- + \bar{\nu}_e$. The resulting beta particle (electron) typically has a large kinetic energy (~ 1000 eV) and escapes from the atom in quick time²⁸. The anti-neutrino also escapes very fast leaving behind a Helium-3 ion (${}^3_2\text{He}^+$ npe, He-3 is a very stable isotope of Helium, no decay has been observed). The beta decay process happens almost instantaneously compared to atomic time-scales and in effect the hamiltonian of the system has suddenly changed from that of Tritium to that of a Helium ion. We are concerned with the electron wave function. Initially the Tritium atom was in one of its stationary states ψ_i^T (most often, its ground state). We would like to know the probability of a transition to any of the stationary states of ${}^3_2\text{He}^+$ after the decay.

- Such a sudden and drastic perturbation to a system, which takes it from one time-independent hamiltonian to another time-independent one can be modeled by

$$H(t) = \begin{cases} H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} & \text{for } t < 0 \\ H_1 = \frac{p^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r} & \text{for } t > 0 \end{cases} \quad (360)$$

So the hamiltonian operator behaves a bit like a step function with a finite discontinuity at $t = 0$. We wish to find the wave function after the sudden change (i.e. at $t = 0^+$), given that the system was in a stationary state of H_0 prior to the perturbation i.e., at $t = 0^-$. The Schrödinger equation $i\hbar\frac{\partial\psi}{\partial t} = H(t)\psi(t)$ can be usefully written as an integral equation

$$|\psi(t)\rangle = |\psi(0^-)\rangle - \frac{i}{\hbar} \int_0^t H(t')|\psi(t')\rangle dt' \quad (361)$$

Now we wish to take $t \rightarrow 0^+$. Though the hamiltonian suffers a sudden change, the change in each of its matrix elements is finite at $t = 0$, so the integral should vanish as $t \rightarrow 0^+$ (provided the wave function itself does not suffer an infinite discontinuity at $t = 0$). Thus we have

$$\lim_{t \rightarrow 0^+} |\psi(t)\rangle = \lim_{t \rightarrow 0^-} |\psi(t)\rangle \quad (362)$$

²⁸The beta particle is not mono-energetic, there is a continuous distribution of electron energies and neutrino energies up to about 18 KeV. On rare occasions, where the beta particle has very low energy, it may be captured by the He-3 ion to form a He-3 atom resulting only in a mono-energetic $\bar{\nu}_e$ escaping.

and the wave function is continuous at $t = 0$. Taking the projection on $|x\rangle$, for any fixed x , the wavefunction cannot have a finite discontinuity as t crosses 0. In other words, the change to the nucleus happened so fast that the electron wave function did not have time to change from its initial state ψ_i^T . Now, after the decay, the electron finds itself near a He-3 nucleus and if a measurement of the energy is made, one of the energy levels $E_n^{He_3^+}$ of He_3^+ is obtained, and the electron wave function collapses to the corresponding eigenstate $\psi_n^{He_3^+}$. The transition probability is

$$P_{i\text{-tritium} \rightarrow n\text{-}He_3^+} = |\langle \psi_n^{He} | \psi_i^T \rangle|^2 \quad (363)$$

Note that the energy difference between initial and final electronic states contributes to the energies of the emitted beta particle and anti-neutrino. To evaluate these transition probabilities we need to know the corresponding wave functions of Tritium and He_3^+ . We know them since they are both hydrogenic atoms with $Z = 1$ and $Z = 2$. The He-3 nucleus (npp, $Z = 2$) has twice the nuclear charge as the Tritium nucleus (nnp, $Z = 1$), so the Tritium atom (in its ground state) is much larger than the Helium ion (in its ground state). Indeed, the Bohr radius of a hydrogenic atom is $a = \frac{4\pi\epsilon_0\hbar^2}{mZe^2}$. So though the g.s. of He-3 is the most likely final state, it is also likely to make a transition to an excited state of He-3. The electronic energy difference (along with the nuclear mass defect) is carried away by the β -electron and $\bar{\nu}_e$.

- A sudden perturbation of this sort resulting in an abrupt and permanent change in the hamiltonian was not analyzed by treating the perturbation as small. But there are many situations where the perturbation may be treated as small. Let us develop a method to deal with such perturbations.

11.2 First order time-dependent perturbation theory

- Suppose a quantum system is initially in a stationary state $\psi_i^{(0)}$ of the hamiltonian H_0 . A time dependent perturbation $gH_1(t)$ is turned on at time $t = 0$ so that the total hamiltonian for $t \geq 0$ is

$$H(t) = H_0 + gH_1(t) \theta(t > 0) \quad (364)$$

We want to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H(t)\psi(t) \quad \text{with initial condition} \quad \psi(x, t = 0) = \psi_i^{(0)}(x). \quad (365)$$

We assume the stationary states of H_0 are known

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}, \quad \text{are orthonormal} \quad \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}, \quad (366)$$

non-degenerate and form a complete set. So we expand the wavefunction at subsequent times as

$$\psi(t) = \sum_n c_n(t) \psi_n^{(0)} \quad \text{where normalization requires} \quad \sum_n |c_n|^2 = 1. \quad (367)$$

In general, the coefficients $c_n(t)$ are complex and time-dependent. In the absence of the perturbation ($g = 0$), we know $c_n(t)$. So we expect

$$c_n(t) = c_n(0)e^{-iE_n^{(0)}t/\hbar} (1 + \mathcal{O}(g)) \quad (368)$$

In the presence of the perturbation, the SE becomes for $t > 0$,

$$i\hbar \sum_m \dot{c}_m(t) \psi_m^{(0)} = (H_0 + gH_1) \sum_m c_m(t) \psi_m^{(0)}. \quad (369)$$

Taking the inner product with $\psi_n^{(0)}$ we get

$$i\hbar \dot{c}_n(t) = c_n(t) E_n^{(0)} + g \sum_m \left\langle \psi_n^{(0)} | H_1(t) | \psi_m^{(0)} \right\rangle c_m(t). \quad (370)$$

This is a system of coupled first order ODEs for the coefficients $c_n(t)$. We know how they behave in the absence of the perturbation, so let us absorb the unperturbed harmonic time dependence and define

$$d_n(t) = c_n(t) e^{iE_n^{(0)}t/\hbar}. \quad (371)$$

Then d_n satisfy the system of ordinary differential equations

$$\dot{d}_n(t) = -\frac{i}{\hbar} \sum_m \left\langle \psi_n^{(0)} | gH_1(t) | \psi_m^{(0)} \right\rangle e^{-i(E_m^{(0)} - E_n^{(0)})t/\hbar} d_m(t) \quad (372)$$

with initial conditions $d_n(0) = c_n(0) = \delta_{ni}$ (since the system was initially in the eigenstate $|\psi_i\rangle$). We will solve this system of equations for $d_n(t)$ essentially in a series in powers of g , $d_n(t) = \delta_{ni} + \mathcal{O}(g)$. To do so, it is convenient to write this as a system of integral equations. Integrating once,

$$d_n(t) = \delta_{ni} - \frac{i}{\hbar} \int_0^t dt' \sum_m \left\langle \psi_n^{(0)} | gH_1(t') | \psi_m^{(0)} \right\rangle e^{-i(E_m^{(0)} - E_n^{(0)})t'/\hbar} d_m(t') \quad (373)$$

So far we haven't made any approximation. The advantage of this formulation is that d_n is expressed as a zeroth order part plus a term of order g . We may solve this by iteration.

- To get a sense for what an iterative solution is, let us look at a toy version of this. Consider the equation $x = 1 + gx$ whose solution is $x = (1 - g)^{-1}$. For $|g| < 1$, we may expand the solution in a series $x = 1 + g + g^2 + \dots$. We could have obtained this series solution by iteration. The n^{th} iterate is given by

$$x^{(n)} = 1 + gx^{(n-1)}. \quad (374)$$

In favorable cases, the first few iterates already give a good approximation. In this case, the first few iterative approximations are

$$x^{(0)} = 1, \quad x^{(1)} = 1 + g, \quad x^{(2)} = 1 + g(1 + g) = 1 + g + g^2, \quad x^{(3)} = 1 + g(1 + g + g^2) = 1 + g + g^2 + g^3. \quad (375)$$

We see that we can recover the power series solution by iteration.

- Returning to (373), the first iterate involves putting the zeroth order solution $d_m = \delta_{mi}$ on the rhs. Thus to first order in g we have

$$d_n(t) = \delta_{ni} - \frac{gi}{\hbar} \int_0^t dt' \left\langle \psi_n^{(0)} | H_1(t') | \psi_i^{(0)} \right\rangle e^{-i(E_i^{(0)} - E_n^{(0)})t'/\hbar} + \mathcal{O}(g^2). \quad (376)$$

This tells us how the initial state $\psi_i^{(0)}$ evolves in time, since

$$\psi(t) = \sum_n c_n(t) \psi_n^{(0)} = \sum_n d_n(t) e^{-iE_n^{(0)}t/\hbar} \psi_n^{(0)} \quad \text{and} \quad \psi(0) = \psi_i^{(0)}. \quad (377)$$

$d_n(t)e^{-iE_n^{(0)}t/\hbar}$ is the component of the state at time t that is in the direction of the unperturbed eigenstate $\psi_n^{(0)}$. If the perturbation is switched off at time t , and a measurement of energy H_0 is made, then $|d_n(t)|^2$ is the probability of getting the value $E_n^{(0)}$. So $|d_n(t)|^2$ is the probability that the system makes a transition from initial state i to final state n due to the perturbation. If $i \neq n$, this transition probability is just the absolute square of the above time-integral of the matrix element of the perturbing hamiltonian between initial and final states

$$P(i \rightarrow n \neq i; t) = \frac{g^2}{\hbar^2} \left| \int_0^t dt' \left\langle \psi_n^{(0)} \left| H_1(t') \right| \psi_i^{(0)} \right\rangle e^{-i(E_i^{(0)} - E_n^{(0)})t'/\hbar} \right|^2 + \mathcal{O}(g^3) \quad (378)$$

The probability that the final state is the same as the initial state $i = n$ can be estimated to order g^2 by using the normalization of the wave function $\sum_n |c_n(t)|^2 = \sum_n |d_n|^2 = 1$. So²⁹

$$P(i \rightarrow i; t) = 1 - \sum_{n \neq i} P(i \rightarrow n, t). \quad (380)$$

- To go further, we must specify the perturbing hamiltonian $H_1(t)$. We will study some special cases.

11.3 Connection to time-independent perturbation theory

- Let us first consider a perturbation gH_1 that is slowly withdrawn $e^{-t/\tau}gH_1\theta(t > 0)$. This allows us to make contact with the results of time-independent perturbation theory for $H_0 + gH_1$.

- As before, we begin at $t = 0$ with a stationary state $\psi_i^{(0)}$ of H_0 . The eigenstates of H_0 , $\psi_n^{(0)}$ and energies $E_n^{(0)}$ are assumed known. Suppose the small perturbing hamiltonian $gH_1(t)$ is switched on at $t = 0$. Here $g \ll 1$ is dimensionless. Moreover, $H_1(t)$ is assumed to be slowly varying with time and eventually turned off. The time scale over which $H_1(t)$ varies is called τ . This may be relevant to an atom in a weak magnetic field that is introduced, and then slowly turned off. After it is turned off, the system is again governed by the hamiltonian H_0 and if a measurement of energy is made after a long time $t \gg \tau$, one of the values $E_f^{(0)}$ is obtained. In other words, the perturbation $gH_1(t)$ may induce a transition from an initial eigenstate i to a final eigenstate f of H_0 .

- To model such a situation, let us assume all the matrix elements of $H_1(t)$ have the same time dependence (which may be given by how we turn off the current in the coil producing the magnetic field), which we take for simplicity of calculations to be

$$H_1(t) = H_1 e^{-t/\tau} \quad \text{for } t > 0 \text{ and } \tau \text{ large} \quad (381)$$

²⁹Merely squaring the approximate formula for $d_i(t)$ (376) does not give the correct answer, as the term of order g^2 (say γg^2) in d_i that we have *not computed*, also contributes! Let $I = \int_0^t dt' \langle \psi_i | H_1(t') | \psi_i \rangle \in \mathbb{R}$, then

$$d_i(t) = 1 - \frac{igI}{\hbar} + \gamma g^2 + \dots \Rightarrow |d_i|^2 = 1 + \frac{g^2 I^2}{\hbar^2} + 2g^2 \Re \gamma + \mathcal{O}(g^3). \quad (379)$$

In fact, if we do not account for this term γg^2 , it would even appear that the probability to remain in the state i exceeds 1! Stated differently, normalization puts a constraint on what $\Re \gamma$ can be.

We are interested in the transition probability to another stationary state $\psi_f^{(0)}$ of H_0 after a time t . Slowly turned off means τ is large in the sense that

$$\tau \gg \frac{\hbar}{|E_f^{(0)} - E_i^{(0)}|}. \quad (382)$$

In particular, we are looking for a transition to a different energy level, $i \neq f$.

- The component of $\psi(t)$ in the direction of the f^{th} eigenstate of H_0 is $d_f(t)e^{-iE_f^{(0)}t/\hbar}$ where

$$\begin{aligned} d_f(t) &= \delta_{fi} - \frac{i}{\hbar} \left\langle \psi_f^{(0)} \left| gH_1 \right| \psi_i^{(0)} \right\rangle \int_0^t dt' e^{-i(E_i^{(0)} - E_f^{(0)} - \frac{i}{\tau})t'/\hbar} + \mathcal{O}(g^2) \\ &= \delta_{fi} - \frac{1}{\hbar} \left\langle \psi_f^{(0)} \left| gH_1 \right| \psi_i^{(0)} \right\rangle \frac{1 - e^{-t/\tau} e^{-i(E_i^{(0)} - E_f^{(0)})t/\hbar}}{\frac{E_i^{(0)} - E_f^{(0)}}{\hbar} - \frac{i}{\tau}} + \mathcal{O}(g^2). \end{aligned} \quad (383)$$

So far, we have not made use of the slow removal of the perturbation nor the largeness of t . Let us focus on the transition probability after a long time $t \gg \tau$ when the perturbation has been turned off and the hamiltonian is again H_0 . Using $\tau \gg \hbar/(|E_i^{(0)} - E_f^{(0)}|)$ in the denominator and $t \gg \tau$ in the numerator,

$$|d_f(t \gg \tau)|^2 \rightarrow \left| \frac{\left\langle \psi_f^{(0)} \left| gH_1 \right| \psi_i^{(0)} \right\rangle}{E_i^{(0)} - E_f^{(0)}} \right|^2 \quad \text{for } i \neq f \text{ and small } g. \quad (384)$$

Therefore the transition probability is the absolute square of the ratio of the matrix element of the (time-independent) perturbing hamiltonian H_1 between initial and final states and the difference in energies. We recognize this factor from the formula for the first order correction to the wave function arising in non-degenerate perturbation theory:

$$\psi_i = \psi_i^{(0)} + g\psi_i^{(1)}, \quad \text{where } \psi_i^{(1)} = \sum_{f \neq i} \frac{\langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \psi_f^{(0)}}{E_i^{(0)} - E_f^{(0)}}. \quad (385)$$

Starting from $\psi_i^{(0)}$, due to the effect of H_1 , it is as if the system evolved approximately into the corresponding stationary state $\psi_i^{(0)} + g\psi_i^{(1)}$ of $H_0 + gH_1$. The perturbation was turned off by waiting a long time $t \gg \tau$ and we asked for the probability that a measurement of energy causes the system to collapse to the final eigenstate $f \neq i$ of H_0 . This probability is approximately given by the absolute square of the component of $\psi_i^{(0)} + g\psi_i^{(1)}$ in the direction of $\psi_f^{(0)}$. This was what we computed in first-order non-degenerate time-independent perturbation theory.

11.4 Impulse approximation

- Here we consider a system in a stationary state subject to a sudden effect that is withdrawn quickly. For example, a fast electron may pass near a hydrogen atom, or an X-ray pulse may be shone on an atom for a short duration of time. These impulsive perturbations may end up

ionizing the atom or exciting it to a new stationary state. We model an impulse at $t = 0$ by the hamiltonian

$$H = H_0 + gH_1\delta(t) \quad (386)$$

H_1 could be quite a big change compared to H_0 , so one wonders if perturbation theory is applicable. But the change only lasts a short time and it is the integrated effect that enters the formula for the transition probability, so perturbation theory could serve as a good approximation. For $t > 0$ we find

$$d_f(t > 0) = \delta_{fi} - \frac{ig}{\hbar} \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle e^{-i(E_i^{(0)} - E_f^{(0)})\frac{t}{\hbar}} + \dots \Rightarrow P(i \rightarrow f \neq i, t) = \frac{g^2}{\hbar^2} \left| \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \right|^2 + \dots \quad (387)$$

In particular, there can be no transition to final state f in the impulse approximation, if the perturbing hamiltonian has zero matrix element $(H_1)_{fi}$ between the initial and final states.

11.5 Harmonic perturbation

The effect of electromagnetic radiation on an atom is primarily due to the electric dipole interaction between the oscillating electric field of the EM wave and the dipole moment of the atom. For monochromatic light, the electric field $\vec{E} = \vec{E}_0 \cos \omega t$ varies sinusoidally with time but is roughly constant over the dimensions of the atom (whose hamiltonian is H_0), so

$$gH_1 = -e\vec{r} \cdot \vec{E}_0 \cos \omega t \quad (388)$$

Note that the electromagnetic wave may be due to light that is shone on the atom or could also arise from light emitted by the atom. Even if light isn't shone on the atom by an external agency, there are virtual photons present due to quantum fluctuations of the vacuum and these could interact with the atom.

- We will consider a general sinusoidal perturbation of the form

$$H = H_0 + gH_1 \cos \omega t \quad (389)$$

If we denote the energies of the initial and final eigenstates of H_0 as $E_{i,f}^{(0)} = \hbar\omega_{i,f}$, then

$$\begin{aligned} d_f &= \delta_{fi} - \frac{ig}{\hbar} \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \int_0^t e^{-i(\omega_i - \omega_f)t'} \cos \omega t' dt' + \mathcal{O}(g^2) \\ &= \delta_{fi} + \frac{g}{2\hbar} \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \left[\frac{e^{-i(\omega_i - \omega_f + \omega)t} - 1}{\omega_i - \omega_f + \omega} + \frac{e^{-i(\omega_i - \omega_f - \omega)t} - 1}{\omega_i - \omega_f - \omega} \right] + \mathcal{O}(g^2). \end{aligned} \quad (390)$$

To understand this result of perturbation theory, we ask for what angular frequency of the perturbation $\omega > 0$ (e.g. what color of incident light) the transition probability from initial state i to final state f is significant. This happens if the denominator of one of the two terms is nearly zero. If $\omega \approx \omega_f - \omega_i$, this corresponds to absorption of a photon by the atom in making a transition to an excited state. If $\omega \approx \omega_i - \omega_f$, this corresponds to decay of the atom from an excited state to a lower energy level while emitting a photon. In either case, one of the two terms dominates and we have the transition probability from state i to state $f \neq i$ given by (± refer to absorption and emission respectively)

$$P_{i \rightarrow f}(t) \approx \frac{g^2}{4\hbar^2} \left| \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \right|^2 \frac{|e^{i(\Delta\omega \mp \omega)t} - 1|^2}{(\Delta\omega \mp \omega)^2} = \frac{g^2}{\hbar^2} \left| \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \right|^2 \frac{\sin^2\left(\frac{\Delta\omega \mp \omega}{2}t\right)}{(\Delta\omega \mp \omega)^2} \text{ for } \omega \approx \pm\Delta\omega. \quad (391)$$

We used $|e^{i\theta} - 1|^2 = 4 \sin^2(\theta/2)$ and denoted the change in angular frequency as $\Delta\omega = \omega_f - \omega_i$.

- P is a probability in the sense that $\sum_f P_{i \rightarrow f} = 1$. However, P is not in general a probability distribution in the t or ω variables. $\int dt P(t) = \infty$ and $\int P(\omega) d\omega \neq 1$ in general.

- An interesting feature of this formula is the possibility of stimulated emission. Suppose there are two levels at energies $\hbar\omega_1 < \hbar\omega_2$ (say the g.s. and an excited state) and we shine light of frequency nearly equal to $\omega_2 - \omega_1$ on a population of such atoms which are mostly in the g.s. Atoms that are in state E_1 are then likely (with probability $P_{1 \rightarrow 2}$) to absorb photons and get excited to state E_2 . On the other hand, suppose many of the atoms were originally in the ‘population inverted’ excited state E_2 and we stimulate them by shining light of frequency $\omega \approx \omega_2 - \omega_1$. Then with the same probability as before, $P_{2 \rightarrow 1} = P_{1 \rightarrow 2}$, those atoms are likely to *emit* photons of frequency $\omega_2 - \omega_1$. So the emitted photons have roughly the same frequency as the stimulating photons. This is called stimulated emission. It leads to a cascade since a single photon can stimulate an atom to emit a photon of the same frequency and we have two photons. These two photons can stimulate two other atoms to emit, producing 4 photons, all of the same frequency $\omega_2 - \omega_1$. The laser is based on this phenomenon of stimulated emission.

- The above formula says that the probability of the system being found in final state f at time t oscillates slowly in time with a frequency $\Delta\omega \mp \omega$, which by assumption is much smaller than ω . So we may maximize our chances of finding the atom in state f by waiting till time T_n given by one of

$$T_n = \frac{(2n+1)\pi}{\Delta\omega \mp \omega}, \quad n = 0, 1, 2, \dots \quad (392)$$

For small times $t \ll \frac{2\pi}{\Delta\omega \mp \omega}$, the probability of a transition grows quadratically with time.

- On the other hand, suppose we fix a time t . Notice that as the frequency of light ω is tuned off from the ‘resonant’ frequency $\pm\Delta\omega$, the probability of a transition decays rapidly (quadratically in $\frac{1}{\Delta\omega \mp \omega}$). In fact, let us consider the ‘average transition rate per unit time’,

$$\frac{P_{i \rightarrow f}(t)}{t} \approx \frac{g^2}{\hbar^2} \left| \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \right|^2 \frac{\sin^2\left(\frac{1}{2}(\Delta\omega \mp \omega)t\right)}{(\Delta\omega \mp \omega)^2 t}. \quad (393)$$

If we wait a time t large compared to the period of this oscillatory behavior $\frac{2\pi}{\Delta\omega \mp \omega}$, then the transition rate gets more sharply peaked at $\omega = \pm\Delta\omega$. Indeed, using a representation of the Dirac Delta function³⁰

$$\frac{2}{\pi} \lim_{t \rightarrow \infty} \frac{\sin^2 \frac{1}{2} \Omega t}{\Omega^2 t} = \delta(\Omega), \quad \text{and putting } \Omega = \Delta\omega \mp \omega, \quad (394)$$

we get for a harmonic perturbation that lasts for a long time $0 \leq t \leq T$ ³¹

$$\lim_{T \rightarrow \infty} \frac{P_{i \rightarrow f}(t)}{T} \approx \frac{g^2}{4\hbar^2} \left| \langle \psi_f^{(0)} | H_1 | \psi_i^{(0)} \rangle \right|^2 2\pi \delta(\Delta\omega \mp \omega). \quad (395)$$

³⁰Let $D_t(\omega) = \frac{2}{\pi} \frac{\sin^2(\omega t/2)}{\omega^2 t}$. Then we see that $D_t(\omega) \rightarrow 0$ as $t \rightarrow \infty$ for any $\omega \neq 0$. Moreover, at $\omega = 0$, $D_t(0) = \frac{t}{2\pi} \rightarrow \infty$ as $t \rightarrow \infty$. So as $t \rightarrow \infty$, $D_t(\omega)$ tends to a distribution supported at $t = 0$. To show it is the Dirac delta distribution we need to show $\lim_{t \rightarrow \infty} \int_{\mathbb{R}} D_t(\omega) d\omega = 1$, but in fact this integral $U(t) = \int_{\mathbb{R}} D_t(\omega) d\omega = 1$ for all $t > 0$. First by rescaling $\omega = \phi/t$ we see that $U(t) = U(1)$. So it only remains to show that $U(1) = \frac{1}{\pi} \int_{\mathbb{R}} \frac{\sin^2 x}{x^2} dx = 1$. This may be established using contour integration.

³¹Here $\omega > 0$ and $\Delta\omega = \omega_f - \omega_i$. Absorption: $-\text{sign}, \Delta\omega > 0$ and $\omega \approx \Delta\omega$. Emission $+\text{sign}, \omega_f < \omega_i$, $\omega \approx -\Delta\omega$.

This is called Fermi's Golden rule. For a harmonic perturbation, the average transition rate after a long time is proportional to the absolute square of the perturbing hamiltonian between initial and final states, and is significant only when the frequency of the perturbation matches the gap between the levels.

11.5.1 Selection rules for transitions due to dipole radiation

- Returning to where we began, one of the most significant early results of quantum mechanics is that an atom does not radiate in a stationary state. E.g. in a stationary state of the hydrogen atom, though ψ changes with time, the charge density $\rho(\vec{r}, t) = e|\psi(\vec{r})|^2$ is time-independent where e is the electron charge. From E & M a static charge distribution does not radiate. This solved the classical problem of instability of an atom to radiation. In E & M we learn that the simplest and dominant type of radiation is dipole radiation, arising from a time-dependent electric dipole moment vector. The expectation value of the dipole moment of the hydrogen atom in a stationary state ψ_{nlm} is not just time-independent but zero: $e\langle nlm|\vec{r}|nlm\rangle = e\int \vec{r}|\psi(\vec{r})|^2 d^3r = 0$ ³². So there is no dipole radiation (absorbed/emitted) for an 'isolated' atom in a stationary state.

- But even atoms in stationary states often collide with neighboring atoms or with photons and emit and absorb radiation by making transitions between electronic stationary energy levels. In the dipole approximation, the perturbing hamiltonian is

$$gH_1 \cos \omega t = -\vec{d} \cdot \vec{E}_0 \cos \omega t, \quad \text{where} \quad \vec{d} = e\vec{r} \quad (396)$$

is the dipole moment. For instance let us consider light polarized along \hat{z} , $\vec{E}_0 = E_0\hat{z}$. Then the probability of a transition from $i \rightarrow f$

$$P_{i \rightarrow f}(t) = \frac{e^2 E_0^2}{\hbar^2} |\langle \psi_f | z | \psi_i \rangle|^2 \frac{\sin^2 \frac{1}{2}(\Delta\omega \mp \omega)t}{(\Delta\omega \mp \omega)^2}. \quad (397)$$

Let us specialize to the case of hydrogen. For such a transition to take place (by the absorption/emission of light polarized along \hat{z}), the matrix element $\langle n'l'm' | z | nlm \rangle$ must be non-zero. More generally, the relevant matrix elements are $\langle n'l'm' | \vec{r} | nlm \rangle$ where $\vec{r} = (r_1, r_2, r_3) = (x, y, z)$. If this matrix element is zero, a dipole transition is forbidden at first order in perturbation theory. We may factorize these matrix elements into three integrals using $\psi_{nlm} \propto R_{nl}(r)P_{lm}(\cos \theta)e^{im\phi}$:

$$\langle n'l'm' | r_i | nlm \rangle \propto \int R_{n'l'm'}(r)^* R_{nlm}(r) r^3 dr \int_0^{2\pi} d\phi e^{i(m-m')\phi} \int_0^\pi P_{l'm'}(\cos \theta)^* P_{lm}(\cos \theta) \frac{x_i}{r} \sin \theta d\theta. \quad (398)$$

The r -integral just alters the intensity of the radiation for a given transition. But the θ or ϕ integrals could vanish. For example, for $x_3 = z = r \cos \theta$ the matrix element is zero if $m' \neq m$:

$$\langle n'l'm' | z | nlm \rangle \propto \int_0^{2\pi} e^{i(m-m')\phi} \int_0^\pi P_{l'm'}(\cos \theta)^* P_{lm}(\cos \theta) \sin \theta \cos \theta d\theta \propto \delta_{mm'}. \quad (399)$$

³²There is no preferred direction picked out by $|\psi_{nlm}|^2 \propto |R_{nl}(r)|^2 |P_{lm}(\theta)|^2$. More precisely, $|\psi(-\vec{r})|^2 = |\psi(\vec{r})|^2$ so that the charge distribution is symmetric under $\vec{r} \rightarrow -\vec{r}$. Under $\hat{r} \rightarrow -\hat{r}$ ($\theta, \phi \rightarrow \pi - \theta, \pi + \phi$) Since $|\psi|^2$ is independent of ϕ we only need to examine the transformation of $P_{lm}(\theta)$ under $\theta \rightarrow \pi - \theta$ which is the same as $\cos \theta \rightarrow -\cos \theta$. $P_{lm}(x)$ are found to be either even or odd in $x = \cos \theta$. $P_{lm} = (1 - x^2)^{|m|/2} d_x^{|m|} P_l(x)$ and $P_l(x)$ are themselves alternatively even and odd in x . In either case $|P_{lm}|^2$ is symmetric under $\theta \rightarrow \pi - \theta$. E.g., state $nlm = 210$: $|R(r) \cos \theta|^2$ is larger along the polar z -axis $\theta = 0$, but is symmetric under $z \rightarrow -z$, so there is no preferred direction for $\langle \vec{d} \rangle$ to point in.

For \hat{z} polarized light the transition probability is zero unless $m = m'$. This is the simplest selection rule.

- For light polarized in the x - y plane, it is convenient to consider the matrix elements of $x \pm iy = r \sin \theta e^{\pm i\phi}$ (from which the matrix elements of x and y may be obtained by adding and subtracting.)

$$\langle n'l'm'|x \pm iy|nlm\rangle \propto \int_0^{2\pi} e^{\pm i\phi} e^{i(m-m')\phi} d\phi \propto \delta_{m',m\pm 1}. \quad (400)$$

Thus for light polarized in the x - y plane, we have the selection rule $m' = m \pm 1$ or $\langle n'l'm'|x|nlm\rangle = \langle n'l'm'|y|nlm\rangle = 0$. This may be understood if we assume the photon γ has spin one, and therefore $S_z^\gamma = 0$ or $\pm\hbar$. So by conservation of the z -component of angular momentum, the change in electronic L_z , i.e., Δm_l , must be 0 or ± 1 .

- One also obtains another selection rule $l' = l \pm 1$ by considering the θ -integral in the matrix elements $\langle n'l'm'| \frac{x_i}{r} |nlm\rangle$. This rule is a consequence of two general facts. (1) Harmonics $P_{l'm'}$ and P_{lm} of distinct angular momenta l, l' (but same m) are orthogonal; and (2) $\frac{x_i}{r} \times$ a harmonic of order l can be expressed as a linear combination of harmonics of order $l - 1$ and $l + 1$.

- In the case of z -polarization we already know that $m' = m$ so we need only consider the integral

$$\langle n'l'm'|z|nlm\rangle \propto \delta_{mm'} \int P_{l'}^m(\cos \theta) P_l^m(\cos \theta) \cos \theta \sin \theta d\theta \quad (401)$$

Using the recursion & orthogonality relations for associated Legendre functions (in Liboff's conventions)

$$(2l + 1) \cos \theta \times P_l^m = (l + m)P_{l-1}^m + (l - m + 1)P_{l+1}^m \quad \text{and} \quad \int P_{l'}^m P_l^m \sin \theta d\theta \propto \delta_{ll'} \quad (402)$$

we find

$$\langle n'l'm'|z|nlm\rangle \propto \delta_{m'm} [(l + m)\delta_{l',l-1} + (l - m + 1)\delta_{l',l+1}] \quad (403)$$

In other words, for \hat{z} -polarized light, transitions are forbidden unless $m' = m$ and $l' - l = \pm 1$.

- Similarly, we now show that $\langle n'l'm'|x|nlm\rangle$ and $\langle n'l'm'|y|nlm\rangle$ vanish if $m' - m \neq \pm 1$ (already shown) and $l' - l \neq \pm 1$. Let us consider the matrix element of $x + iy = r \sin \theta e^{i\phi}$:

$$\langle n'l'm'|x + iy|nlm\rangle \propto \int P_{l'}^{m'} P_l^m \sin^2 \theta d\theta \int e^{i(m-m'+1)\phi} d\phi \quad (404)$$

and utilize the recursion relation

$$(2l + 1) \sin \theta \times P_l^m = P_{l-1}^{m+1} - P_{l+1}^{m+1} \quad (405)$$

and above orthogonality condition to find

$$\langle n'l'm'|x + iy|nlm\rangle \propto \delta_{m',m+1} \int (P_{l'}^{m+1} P_{l-1}^{m+1} - P_{l'}^{m+1} P_{l+1}^{m+1}) d\cos \theta \propto \delta_{m',m+1} (\delta_{l',l-1} - \delta_{l',l+1}). \quad (406)$$

The matrix element of $x + iy$ vanishes if $m' \neq m - 1$ and $l' \neq l \pm 1$. As for $x - iy$ we do something similar, though the recursion relation is used on the primed indices

$$(2l' + 1) \sin \theta \times P_{l'}^{m'} = P_{l'-1}^{m'+1} - P_{l'+1}^{m'+1} \quad (407)$$

so that

$$\begin{aligned}\langle n'l'm'|x - iy|nlm\rangle &\propto \delta_{m',m-1} \int P_{l'}^{m'} \sin\theta P_l^m d\cos\theta \propto \delta_{m',m-1} \int (P_{l'-1}^m - P_{l'+1}^m) P_l^m d\cos\theta \\ &\propto \delta_{m',m-1} [\delta_{l'-1,l} - \delta_{l'+1,l}]\end{aligned}\quad (408)$$

• Thus, for dipole radiation, we must have the selection rules $l' = l \pm 1$. We can understand this if we assume the photon has spin one. So the composite of an electron with orbital angular momentum l and a photon of spin one behaves as a system with angular momentum $l' = l - 1$ or $l' = l$ or $l' = l + 1$. But the $l \rightarrow l$ transition has zero matrix element (as shown above or by the parity argument below) and we have the selection rules

$$\Delta m = 0, \pm 1, \quad \text{and} \quad \Delta l = \pm 1. \quad (409)$$

We could turn the argument around to infer that photons have spin one, based on the observation that atoms make transitions with $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$ accompanied by emission/absorption of single photons.

• One consequence is that the transition $1S \rightarrow 2S$ is forbidden at first order. Similarly, the $2S$ level is stable against emission of dipole radiation in first order of perturbation theory, since there is no lower level to go to. This accounts for the experimentally observed long life-time of the $2S$ level. Dipole transitions between a pair of S-wave states are forbidden for the same reason. The $2P$ state 211 can decay to the g.s. 100 by emitting a photon but it can't 'decay' to 200 since there is no energy difference. But 211 can decay/be excited to 210 by emission/absorption of a photon when the two levels are split in the presence of a magnetic field.

11.5.2 Use of parity to obtain a selection rule

• As an example to illustrate the use of parity, let us show that if $l' = l$, then the matrix element $\langle n'l'm'|r_i|nlm\rangle$ must vanish for each of the components of \vec{r} .

• First we note that if $|f\rangle$ and $|g\rangle$ are states of opposite parity, (say without loss of generality) $\mathbb{P}f = f, \mathbb{P}g = -g$, then $\langle f|g\rangle = 0$. This is because $\mathbb{P}^2 = I$ and $\mathbb{P} = \mathbb{P}^\dagger$, so

$$\langle f|g\rangle = \langle f|\mathbb{P}^2|g\rangle = \langle \mathbb{P}f|\mathbb{P}g\rangle = -\langle f|g\rangle \quad \Rightarrow \quad \langle f|g\rangle = 0. \quad (410)$$

So states of opposite parity are orthogonal. We will show that $r_i\psi_{nlm}(r, \theta, \phi)$ and $\psi_{n'l'm'}(r, \theta, \phi)$ are states of opposite parity. This will imply that the matrix elements of the electric dipole energy vanishes between states with the same value of l . Thus there cannot be any electric dipole transition between them at first order in perturbation theory.

• Now parity acts by $(r_1, r_2, r_3) \mapsto (-r_1, -r_2, -r_3)$. In spherical coordinates this is $\mathbb{P} : (r, \theta, \phi) \mapsto (r, \pi - \theta, \pi + \phi)$. Now $\psi_{nlm} = R_{nl}(r)P_{lm}(\cos\theta)e^{im\phi}$ where

$$P_{lm}(x) = (1 - x^2)^{|m|/2} d_x^{|m|} \frac{1}{(2l)!!} d_x^l (x^2 - 1)^l \quad (411)$$

Under parity $x = \cos\theta \rightarrow -x = -\cos\theta$. So it is seen that $P_{lm}(-x) = (-1)^{l+|m|}P_{lm}(x)$. On the other hand $\mathbb{P}e^{im\phi} = (-1)^m e^{im\phi}$. Since $(-1)^{m+l+|m|} = 1$ we find that

$$\mathbb{P}Y_{lm} = (-1)^l Y_{lm} \quad \text{and} \quad \mathbb{P}\psi_{nlm} = (-1)^l \psi_{nlm}. \quad (412)$$

Furthermore, $r_i\psi_{nlm}$ has parity opposite to that of ψ_{nlm} since r_i changes sign under parity:

$$\mathbb{P}r_i\psi_{nlm} = -(-1)^l r_i\psi_{nlm}. \quad (413)$$

So we conclude that $\psi_{n'l'm'}$ and $r_i\psi_{nlm}$ which have the same value of l are states of opposite parity. So their inner product vanishes and we have the selection rule $l' \neq l$ for dipole radiation!