Quantum Mechanics II

Chapter 12: Rotational Invariance and Angular Momentum

12.1 Translations in Two Dimensions

The generators of infinitesimal translations along the x and y directions are

$$P_x \xrightarrow[\text{basis}]{\text{coordinate}} -i\hbar\frac{\partial}{\partial x} \quad \text{and} \quad P_y \xrightarrow[\text{basis}]{\text{coordinate}} -i\hbar\frac{\partial}{\partial y}$$

We can generalize this in terms of a vector operator

$$\vec{P} = P_x\vec{i} + P_y\vec{j}$$

$\hat{n}\cdot\vec{P} = P_{\hat{n}}$ ← generator of translations along $\hat{n}$

Recall that a finite translation operator is recovered through exponentiation of infinitesimal operators

$$T(a) = e^{-iaP_{\hat{a}}/\hbar} = e^{-i\vec{a}\cdot\vec{P}/\hbar}$$

Since P_x and P_y commute we can conclude the commutativity of x and y translations

12.2 Rotations in Two Dimensions

Classically we can represent a rotation of ϕ as

$$\begin{bmatrix} x \\ y \end{bmatrix} \to \begin{bmatrix} \bar{x} \\ \bar{y} \end{bmatrix} = \underbrace{\begin{bmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{bmatrix}}_{R(\phi\hat{k})} \begin{bmatrix} x \\ y \end{bmatrix}$$

We let $U[R(\phi\hat{k})]$ be the operator associated with this rotation

$$|\psi\rangle \xrightarrow[U[R]]{} |\psi_R\rangle = U[R]|\psi\rangle$$

The rotated state obeys the expectations of the classical rotation

$$\langle X\rangle_R = \langle X\rangle\cos\phi - \langle Y\rangle\sin\phi$$
$$\langle Y\rangle_R = \langle X\rangle\sin\phi - \langle Y\rangle\cos\phi$$

Analogous for momenta

We can also define $U[R]$ based on its action on eigenkets

$$U[R]|x,y\rangle = |x\cos\phi - y\sin\phi,\ x\sin\phi + y\cos\phi\rangle$$

To explicitly construct $U[R]$ we begin with an infinitesimal rotation $\varepsilon_z\vec{k}$

$$U[R(\varepsilon_z\vec{k})] = I - \frac{i\varepsilon_z L_z}{\hbar}$$ ← generator of infinitesimal rotations

$$U[R]|x,y\rangle = |x - \varepsilon_z y,\ x\varepsilon_z + y\rangle$$

Therefore,

$$\langle xy|\left(I - \frac{i\varepsilon_z L_z}{\hbar}\right)|\psi\rangle = \psi(x + y\varepsilon_z,\ y - x\varepsilon_z)$$

We can then expand each side to order ε_z

$$\langle xy|I|\psi\rangle - \frac{i\varepsilon_z}{\hbar}\langle xy|L_z|\psi\rangle = \psi(x,y) + \frac{\partial\psi}{\partial x}(y\varepsilon_z) + \frac{\partial\psi}{\partial y}(-x\varepsilon_z)$$

$$\langle xy|L_z|\psi\rangle = \left[x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)\right]\psi(x,y)$$

We then recover the form of L_z, generator of infinitesimal rotations

$$L_z \xrightarrow[\text{basis}]{\text{coordinate}} x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)$$

$$L_z = XP_y - YP_x$$

We can alternatively discover this form by exploring commutator relations between X, Y, P_x, P_y and L_z

Recall that a finite operator is recovered through exponentiation of a infinitesimal operator

$$U[R(\phi\hat{k})] = \lim_{N\to\infty}\left(I - \frac{i}{\hbar}\frac{\phi}{N}L_z\right)^N = \exp\left(\frac{-i\phi L_z}{\hbar}\right)$$

To make L_z more tractable we can represent it in polar coordinates

$$L_z \xrightarrow[\text{coordinate basis}]{} -i\hbar\frac{\partial}{\partial\phi}$$

By doing so we can recognize exponention creates the desired rotation

$$\exp\left(-i\phi_0 L_z/\hbar\right) \xrightarrow{\text{Substitution}} \exp\left(-\phi_0\frac{\partial}{\partial\phi}\right)$$

$$\exp\left(-\phi_0\frac{\partial}{\partial\phi}\right)\psi(\rho,\phi) = \psi(\rho,\phi-\phi_0)$$

L_z is conserved in a problem with rotational invariance if

$$U^\dagger[R]\,H(X,P_x;Y,P_y)\,U[R] = H(X,P_x;Y,P_y)$$

Consequently,

$$[L_z, H] = 0$$

This implies

- An experiment and its rotated version will produce the same outcome if H is rotationally invariant
- There exists a common basis for H and L_z

12.3 The Eigenvalue Problem of L_z

Let's find the eigenfunctions of L_z

$$L_z|l_z\rangle = l_z|l_z\rangle \xrightarrow[\text{coordinate basis}]{} -i\hbar\frac{\partial\psi_{l_z}(\rho,\phi)}{\partial\phi} = l_z\psi_{l_z}(\rho,\phi)$$

This produces

$$\psi_{l_z}(\rho,\phi) = R(\rho)\,e^{il_z\phi/\hbar}$$

$R(\rho)$ is an arbitrary normalizable function

Next, we can impose the hermiticity constraint (← real eigenvalues (observables))

$$\langle\psi_1|L_z|\psi_2\rangle = \langle\psi_2|L_z|\psi_1\rangle^*$$

$$\int_0^\infty\int_0^{2\pi}\psi_1^*\left(-i\hbar\frac{\partial}{\partial\phi}\right)\psi_2\,\rho\,d\rho\,d\phi = \left[\int_0^\infty\int_0^{2\pi}\psi_2^*\left(-i\hbar\frac{\partial}{\partial\phi}\right)\psi_1\,\rho\,d\rho\,d\phi\right]^*$$

Integrating by parts gives us the following condition

$$\psi(\rho,0) = \psi(\rho,2\pi)$$

Imposing this condition on our above L_z eigenfunctions results in

$$1 = e^{2\pi i l_z/\hbar}$$

Consequently,

$$l_z = m\hbar \qquad m = 0,\pm1,\pm2,\dots$$

m is the magnetic quantum number

The existence of the $R(\rho)$ term implies that l_z is not sufficient in determining the state

Since H commutes with L_z we can use this to specify the state by finding simultaneous eigenfunctions

State is determined by energy and angular momentum in a rotationally invariant problem

To proceed we introduce the following functions

$$\Phi_m(\phi) = (2\pi)^{-1/2}e^{im\phi}$$

where $\int_0^{2\pi}\Phi_m^*(\phi)\Phi_{m'}(\phi)\,d\phi = \delta_{mm'}$

non-degenerate eigenfunctions of L_z if ρ didn't exist

Let's consider a rotationally invariant problem where $V = V(\rho)$. Our Hamiltonian eigenvalue equation is

$$\left[\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right) + V(\rho)\right]\varphi_E(\rho,\phi) = E\,\varphi_E(\rho,\phi)$$

(μ: mass)

Recall that our generic eigenfunction with eigenvalue $m\hbar$ is

$$\varphi_m(\rho,\phi) = R(\rho)(2\pi)^{-1/2}e^{im\phi} = R(\rho)\,\Phi_m(\phi)$$

Since H commutes with L_z we can require the following to be an eigenfunction of H

$$\varphi_{Em}(\rho,\phi) = R_{Em}(\rho)\,\Phi_m(\phi)$$

We can now feed this form into our earlier Hamiltonian eigenvalue equation

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{d\rho^2} + \frac{1}{\rho}\frac{d}{d\rho} - \frac{m^2}{\rho^2}\right) + V(\rho)\right]R_{Em}(\rho) = ER_{Em}(\rho)$$ ← purely radial equation

Φ_m provide the angular part of the wavefunction for a rotationally invariant Hamiltonian

12.4 Angular Momentum in Three Dimensions

In three dimensions we find L_x and L_y in addition to L_z (↖ generators in x and y directions)

$$L_x = YP_z - ZP_y$$
$$L_y = ZP_x - XP_z$$
$$L_z = XP_y - YP_x$$

If we subject a point to a series of infinitesimal rotations and match coefficients in the corresponding quantum operator relation, we recover

$$\left.\begin{aligned}[L_x, L_y] &= i\hbar L_z\\ [L_y, L_z] &= i\hbar L_x\\ [L_z, L_x] &= i\hbar L_z\end{aligned}\right\} \quad \vec{L}\times\vec{L} = i\hbar\vec{L} \quad \text{or} \quad [L_i, L_j] = i\hbar\sum_{k=1}^{3}\varepsilon_{ijk}L_k$$

Next, we define total angular momentum squared

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

where

$$[L^2, L_i] = 0$$

Once again for a finite rotation we can recover the form through exponentiation

$$U[R(\vec{\theta})] = \lim_{N\to\infty}\left(I - \frac{i}{\hbar}\frac{\theta}{N}\hat{\theta}\cdot\vec{L}\right)^N = e^{-i\theta\cdot\vec{L}/\hbar}$$

If we have a rotationally invariant hamiltonian

$$[H, L_i] = 0 \quad \text{and} \quad [H, L^2] = 0$$

L^2 and each L_i component is conserved

Cannot find common eigenbasis for H and all L_i, just H, L^2 and one L_i

12.5 The Eigenvalue Problem for L^2 and L_z

We can solve this similarly to the harmonic oscillator

Begin by assuming a common basis between L^2 and L_z

$$L^2|\alpha\,\beta\rangle = \alpha|\alpha\,\beta\rangle \quad \text{and} \quad L_z|\alpha\,\beta\rangle = \beta|\alpha\,\beta\rangle$$

Next, we define raising and lowering operators

$$L_\pm = L_x \pm i L_y$$

which satisfies the following commuting relations

$$[L_z, L_\pm] = \pm \hbar L_\pm \qquad \text{and} \qquad [L^2, L_\pm] = 0$$

$L_\pm$ raises/lowers eigenvalues of L_z by $\hbar$ but leave L^2 untouched

$$L_z(L_+|\alpha\beta\rangle) = (L_+L_z + \hbar L_+)|\alpha\beta\rangle \qquad \text{and} \qquad L^2 L_+|\alpha\beta\rangle = L_+L^2|\alpha\beta\rangle = \alpha L_+|\alpha\beta\rangle$$
$$= (L_+\beta + \hbar L_+)|\alpha\beta\rangle$$
$$= (\beta+\hbar) L_+|\alpha\beta\rangle$$

Notice that the above relations show that $L_+|\alpha\beta\rangle$ is proportional to $|\alpha, \beta+\hbar\rangle$

$$L_+|\alpha\beta\rangle = C_+(\alpha,\beta)|\alpha,\beta+\hbar\rangle$$
$$L_-|\alpha\beta\rangle = C_-(\alpha,\beta)|\alpha,\beta-\hbar\rangle$$

Existence of $L_\pm$ implies eigen states $|\alpha,\beta+1\rangle, |\alpha,\beta+2\rangle, \ldots$ and $|\alpha,\beta-1\rangle, |\alpha,\beta-2\rangle, \ldots$

Classical intuition says that these values cannot be unbounded

Consider the QM relation

$$\langle\alpha\beta| L^2 - L_z^2 |\alpha\beta\rangle = \langle\alpha\beta| L_x^2 + L_y^2 |\alpha\beta\rangle$$

Since $L_x^2 + L_y^2$ is positive semi-definite

$$\alpha - \beta^2 \geq 0$$
$$\alpha \geq \beta^2$$

Since we have an upper bound on β we conclude that there exists a state $|\alpha\beta_{max}\rangle$ such that

$$L_+|\alpha\beta_{max}\rangle = 0 \leftarrow \text{can't be raised}$$

Now we can apply the lowering operator L_-

$$0 = L_-L_+|\alpha\beta_{max}\rangle$$
$$= (L^2 - L_z^2 - \hbar L_z)|\alpha\beta_{max}\rangle \qquad \Rightarrow \qquad \alpha = \beta_{max}(\beta_{max}+\hbar)$$
$$= (\alpha - \beta_{max}^2 - \hbar\beta_{max})|\alpha\beta_{max}\rangle$$

We can apply the same reasoning to find β_{min}

$$0 = L_-|\alpha\beta_{min}\rangle = L_+L_-|\alpha\beta_{min}\rangle$$
$$= (L^2 - L_z^2 + \hbar L_z)|\alpha\beta_{min}\rangle \qquad \Rightarrow \qquad \alpha = \beta_{min}(\beta_{min}-\hbar)$$
$$= (\alpha - \beta_{min}^2 + \hbar\beta_{min})|\alpha\beta_{min}\rangle$$

We can now conclude

$$\beta_{min} = -\beta_{max}$$

Assume it took k steps to transition from $|\alpha\beta_{min}\rangle$ to $|\alpha\beta_{max}\rangle$

$$\beta_{max} - \beta_{min} = 2\beta_{max} = \hbar k$$

$$\beta_{max} = \frac{\hbar k}{2} \qquad k = 0,1,2,\ldots$$

Therefore,

$$\alpha = \beta_{max}(\beta_{max}+\hbar) = \hbar^2\left(\frac{k}{2}\right)\left(\frac{k}{2}+1\right)$$

We refer to $\frac{k}{2} = \frac{\beta_{max}}{\hbar}$ as the angular momentum of the state

α is the square of magnitude of angular momentum

Notice that for odd k we produce L_z eigenvalues that are half integer multiples of $\hbar$

This is a reflection of a general operator that commutes as defined above

The true L_z operator imposes the integer result from above

In fact L_z operator only applies to rotations of scalar wavefunctions

If we consider vector wavefunctions rotations involve two parts

i) Rotating the vector at x,y,z by $\delta\vec{\theta}$ ← S_z (Spin Angular momentum)

ii) Reassigning (x',y',z') ← L_z (Orbital Angular Momentum)

With this in mind the true generator of infinitesimal rotations takes the form

$$J_i = L_i + S_i$$

We know that J must obey the same commutation relations

$$J \times J = i\hbar J$$

← L is special case when φ is scalar

To generalize our results lets switch to J

$$J^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle \qquad j = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots$$

$$J_z |jm\rangle = m\hbar |jm\rangle \qquad m = j, j-1, \ldots -j$$

j is the angular momentum of the state

When $J=L$

$$L^2 |lm\rangle = l(l+1)\hbar^2 |lm\rangle \qquad l = 0, 1, \ldots$$

$$L_z |lm\rangle = m\hbar |lm\rangle \qquad m = -l, \ldots, l$$

To find the actual eigen state we must determine the matrix forms of the operators

Recall the form $J_\pm |jm\rangle = C_\pm (j,m) |j, m\pm 1\rangle$

Next, consider the adjoint

$$\langle jm| J_- = C^*(j,m) \langle j, m+1|$$

We can put these together

$$\langle jm| J_- J_+ |jm\rangle = |C_+(j,m)|^2 \langle j, m+1 | j, m+1\rangle$$

$$= |C_+(j,m)|^2$$

$$\langle jm| J^2 - J_z^2 - \hbar J_z |jm\rangle = |C_+(j,m)|^2$$

Now we can solve for our constant

$$|C_+(j,m)|^2 = j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2$$

$$= \hbar^2 (j-m)(j+m+1)$$

$$C_+(j,m) = \left[\hbar^2 (j-m)(j+m+1)\right]^{1/2}$$

Analogous reasoning produces

$$C_-(j,m) = \hbar \left[(j+m)(j-m+1)\right]^{1/2}$$

Finally, we recover

$$J_\pm |jm\rangle = \hbar \left[(j \mp m)(j \pm m + 1)\right]^{1/2} |j, m\pm 1\rangle$$

↑ $2j+1$ states for J_z

With this equation in hand we can solve the matrix elements of J_x and J_y

$$\langle j'm' | J_x | jm\rangle = \langle j'm'| \frac{J_+ + J_-}{2} | jm\rangle = \frac{\hbar}{2}\left[\delta_{jj'}\delta_{m'm+1}\left[(j-m)(j+m+1)\right]^{1/2} + \delta_{jj'}\delta_{m'm-1}\left[(j+m)(j-m+1)\right]^{1/2}\right]$$

$$\langle j'm' | J_y | jm\rangle = \langle j'm'| \frac{J_+ - J_-}{2i} | jm\rangle = \frac{\hbar}{2i}\left[\delta_{jj'}\delta_{m'm+1}\left[(j-m)(j+m+1)\right]^{1/2} + \delta_{jj'}\delta_{m'm-1}\left[(j+m)(j-m+1)\right]^{1/2}\right]$$

We can pull out matrix forms from these relations

The matricies are block diagonal since j is constant under the action of $J_\pm$

commutation relation holds by block

We can't simply recover finite rotations by exponentiating J since they are infinite dimensional

However, since J is block diagonal so will its exponentiation

We can focus on rotation by consider block matricies of the associated subspaces W_j

$$D^{(j)}[R(\theta)] = \exp\left[-\frac{i\vec{\theta}\cdot\vec{J}^{(j)}}{\hbar}\right] = \sum_0^\infty \left(\frac{-i\theta}{\hbar}\right)^n \left(\hat{\theta}\cdot J^{(j)}\right)^n \cdot \frac{1}{n!}$$

Each subspace W_j is invariant under rotations and irreducible

Angular momentum doesn't change w/ rotations

Can't change basis within W_j and retain block diagonal property

Rotational invariance causes degeneracy but degenerate states are not always rotations of eachother

Next, lets represent L^2 and L_z in the coordinate basis

Consider the topmost state $|ll\rangle$

$$L_+|ll\rangle = 0$$

In coordinate basis

$$L_\pm \longrightarrow \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right)$$

spherical coordinates

If we let $\varphi_l^l(r,\theta,\phi)$ represent the eigenfunction of $|ll\rangle$

$$\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\varphi_l^l(r,\theta,\phi) = 0$$

We also know that $\varphi_l^l(r,\theta,\phi)$ is an eigenfunction of L_z w/ eigenvalue $l\hbar$

$$\varphi_l^l(r,\theta,\phi) = U_l^l(r,\theta)\,e^{il\phi}$$

Plugging this expression into the $|ll\rangle$ eigenfunction for L_+ results in

$$\left(\frac{\partial}{\partial\theta} - l\cot\theta\right)U_l^l = 0$$

$$U_l^l(r,\theta) = R(r)(\sin\theta)^l$$

nailed down by rotationally invariant Hamiltonian

Instead consider the class of functions that would be unique non-degenerate solutions in the absence of radial coordinate

$$Y_l^l(\theta,\phi) = (-1)^l\left[\frac{(2l+1)}{4\pi}\right]^{1/2}\cdot\frac{1}{2^l l!}(\sin\theta)^l e^{il\phi}$$

We can apply the lowering operator to discover Y_l^{l-1}

$$Y_l^{l-1}(\theta,\phi) = \frac{1}{(2l)^{1/2}}\cdot\frac{(-1)}{\hbar}\left[\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\right]Y_l^l$$

Continuing this procedure we can recover the spherical harmonics

$$Y_\ell^m(\theta,\phi) = (-1)^\ell \left[\frac{(2\ell+1)!}{4\pi}\right]^{1/2} \cdot \frac{1}{2^\ell \ell!} \left[\frac{(\ell+m)!}{(2\ell)!\,(\ell-m)!}\right]^{1/2} e^{im\phi} (\sin\theta)^{-m} \cdot \frac{d^{\ell-m}}{d(\cos\theta)^{\ell-m}} (\sin\theta)^{2\ell}$$

We can expand any arbitrary $\psi(r,\theta,\phi)$ as a series of r-dependent coefficients

$$\psi_r(r,\theta,\phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} C_\ell^m(r)\, Y_\ell^m(\theta,\phi)$$

$$C_\ell^m(r) = \int Y_\ell^{m*}(\theta,\phi)\,\psi(r,\theta,\phi)\,d\Omega$$

$C_\ell^m(r)$ can be interpreted as the amplitude of finding a particle at radial distance r with angular momentum ℓ m

Spherical harmonics can be further simplified by introducing Legendre Polynomials

$$Y_\ell^m(\theta,\phi) = \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}\right]^{1/2} (-1)^m e^{im\phi} P_\ell^m(\cos\theta)$$

12.6 Solution of Rotationally Invariant Problems

When potentials only have radial dependence the schrodinger equation in spherical coordinates takes the form

$$\left[\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + V(r)\right]\psi_E(r,\theta,\phi) = E\,\psi_E(r,\theta,\phi)$$

Since $[H,\vec{L}^2]=0$ in a spherically symmetric potential, we can find simultaneous eigenfunctions of H, L^2 and L_z

$$\psi_{E\ell m}(r,\theta,\phi) = R_{E\ell m}(r)\, Y_\ell^m(\theta,\phi)$$

Radial Schrodinger Equation under spherical symmetry

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2}\right) + V(r)\right] R_{E\ell} = E R_{E\ell}$$

We can simplify this equation by introducing $R_{E\ell} = \frac{U_{E\ell}}{r}$

$$\left[\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right)\right] U_{E\ell} = 0$$

↑ repulsive centrifugal barrier

Imposing hermiticity conditions on the eigenvalue equation of $U_{E\ell}$ and considering boundary conditions yields the limit

$$U_{EL} \xrightarrow[r\to 0]{} 0$$

As $r \to \infty$ we face two possibilities

1. $E > 0$: Particle classically escapes to infinity
   U_E oscillates as $r \to \infty$
2. $E < 0$: Particle is bound
   U_E falls exponentially as $r \to \infty$

Skipped Detailed Explaination of U_{EL} behavior

Chapter 13: Hydrogen Atom

13.1 The Eigenvalue Problem

We can reduce this two body to an electron moving in the field of an immobile proton

The potential due to our proton is $V(r) = -e^2/r$

The corresponding schrodinger equation

$$\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2}\right)\right] U_{El} = 0$$

$$\psi_{Elm}(r,\theta,\phi) = \frac{U_{El}(r)}{r} Y_l^m(\theta,\phi)$$

We have the asymptotic behavior of U_{El}

$$U_{El} \underset{r\to\infty}{\sim} \exp\left[-(2mW/\hbar^2)^{1/2} r\right]$$

$W = -E$ is the binding Energy

$$U_{El} \underset{r\to 0}{\sim} r^{l+1}$$

To simplify our calculations we can introduce the following dimensionless variables

$$\rho = (2mW/\hbar^2)^{1/2} r$$

such that

$$U_{El} = e^{-\rho} v_{El}$$

Our expression for v becomes

$$\frac{d^2v}{d\rho^2} - 2\frac{dv}{d\rho} + \left[\frac{e^2\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right] v_{El} = 0$$

$$\lambda = (2m/\hbar^2 W)^{1/2}$$

We can substitute in a power series representation of ρ

$$v_{El} = \rho^{l+1} \sum_{k=0}^{\infty} c_k \rho^k$$

Produces the following recursion relation

$$\frac{c_{k+1}}{c_k} = \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - l(l+1)}$$

As $k \to \infty$ our recursive relation approaches $\frac{c_{k+1}}{c_k} \to 2/k$

To prevent the series from blowing up we look to terminate the series for some k

$$e^2\lambda = 2(k+l+1)$$

In terms of Energy this is equivalent to

$$E = -W = \frac{-me^4}{2\hbar^2(k+l+1)} \quad \text{for } k = 0,1,2,\ldots \quad l = 0,1,2,\ldots$$

We refer to this value as the principle quantum number

$$n = k+l+1$$

In this notation our allowed energies are

$$E_n = \frac{-me^4}{2\hbar^2 n^2} \quad n = 1,2,3,\ldots$$

For a given n the allowed values of l are

$$l = n-k-1 = n-1, n-2, \ldots 0 \longrightarrow \text{degeneracy at each } n \text{ is } n^2$$

degeneracies at each l indicates an additional symmetry

At this point it is natural to introduce a natural unit of energy for energy levels of the hydrogen atom

$$R_y = \frac{me^4}{2\hbar^2} \longrightarrow E_n = \frac{-R_y}{n^2}$$

Rydberg

For a given n and l we can determine the wavefunction

$$V_l \propto \rho^{l+1} \cdot \text{polynomial of degree } n-l-1$$

Laguerre Polynomial

$$L_{n-l-1}^{2l+1}(2\rho)$$

$$R_{nl}(\rho) = e^{-\rho} L_{n-l-1}^{2l+1}(2\rho)$$

We can also introduce the bohr radius, a natural distance for the hydrogen atom

$$a_0 = \frac{\hbar^2}{me^2}$$

Recall that $\rho = \left(\frac{2mW}{\hbar^2}\right)^{1/2} r = \frac{me^4}{\hbar^2 n} r$

so $R_{nl} \sim e^{-r/na_0} \left(\frac{r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$

As $r \to \infty$

$$R_{nl} \underset{r\to\infty}{\sim} r^{n-1} e^{-r/na_0}$$

Given a wavefunction of this form, what is prob of finding the electron a radial distance r away?

$$\psi_{n,n-1,m} \propto e^{-r/na_0} r^{n-1} Y_{n-1}^m(\theta,\phi)$$

$$\int P(r) r^2 dr\, d\Omega \propto e^{-2r/na_0} r^{2n} dr$$

This value is maximized when

$$\frac{d}{dr}\left(e^{-2r/na_0} r^{2n}\right) = 0$$

$$r = n^2 a_0$$

Bohr radius is most probable value of r when $n=1$ (ground state)

For higher n we consider $\langle r \rangle$

$$\langle r \rangle_{nlm} = \frac{a_0}{2}\left[3n^2 - l(l+1)\right]$$

13.2 The Degeneracy of the Hydrogen Spectrum

Symmetries in H imply conservation of the generators of the symmetries

Coulomb potential is special in that it conserves the Runge-Lenz vector

$$\vec{n} = \frac{\vec{p} \times \vec{l}}{m} - \frac{e^2}{r}\vec{r}$$

In quantum theory we have an operator N that commutes w/ H

$$N = \frac{1}{2m}\left[P \times L - L \times P\right] - \frac{e^2 R}{(x^2+y^2+z^2)^{1/2}}$$

Recall that degeneracy in m is given by the fact that L is conserved

consequently $[L_z, H] = 0$ and we can raise/lower m at a given l without changing E

There must therefore be an operator built from N that raises/lowers l to produce n degeneracies

13.3 Numerical Estimates and Comparison with Experiment

Useful Estimates

$$\hbar c \simeq 2000 \text{ eV Å}$$

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}$$

α: fine structure constant

$$mc^2 \simeq 0.5 \text{ MeV}$$

Bohr Radius Estimate

$$a_0 \simeq \frac{\hbar^2}{me^2} = \frac{\hbar c}{mc^2}\left(\frac{\hbar c}{e^2}\right) = \frac{2000 \cdot 137}{0.5 \cdot 10^6} \text{ Å} \simeq 0.55 \text{ Å}$$

Energy Level Estimates

$$R_y = \frac{me^4}{2\hbar^2} = \frac{mc^2}{2}\left(\frac{e^2}{\hbar c}\right)^2 \approx \frac{0.25 \cdot 10^6}{137^2} \text{ eV} \simeq 13.3 \text{ eV}$$

$$E_n = -\frac{R_y}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

13.4 Multielectron Atoms in the Periodic Table

It is impossible to treat multielectron atoms analytically

Instead we rely on approximations such as the Hartree approximation

Hartree Approximation

- Assume each electron obeys one-particle schrodinger equation
- Assume potential energy is given by $V = -e\,\phi(r)$ ← from nucleus and other electrons
- Each electron is assigned a prob distribution from which electronic contribution is $-e \cdot$ probability density
- Guess potential $\phi_0(r)$ and compute allowed eigenstates
  - fill up in increasing energy obeying pauli exclusion principle
- Compute $\phi_1(r)$ according to electronic configuration from $\phi_0(r)$
- Repeat until $\phi_0(r)$ is sufficiently close to $\phi_1(r)$

Chapter 14: Spin

14.1 Introduction

Spin has no classical counterpart so we can't easily obtain a spin operator or write down a Hamiltonian

Most spins can be solved similarly except for photon spin which requires relativistic considerations

14.2 What is the Nature of Spin?

Spin is best understood as a form of angular momentum but one that is distinct from L

Intrinsic angular momentum

14.3 Kinematics of Spin

Infinitesimal rotation of a wavefunction occurs in two parts

1) Each spatial point is reassigned to its rotated point ← coordinate transformation
2) Components of the wavefunction are transformed into linear combinations of eachother ← Vector transformation

L is responsible for 1) but S is responsible for 2)

$$|\psi'\rangle = \left[I - \frac{i\epsilon}{\hbar}\left(L_z + S_z\right)\right]|\psi\rangle$$

$$= \left[I - \frac{i\epsilon}{\hbar} J_z\right]|\psi\rangle$$

$$J = L + S$$

↖ generator of infinitesimal rotations

Since J operators are generators of rotation they must obey

$$[J_i, J_j] = i\hbar \sum_k \varepsilon_{ijk} J_k$$

Furthermore, we know that L and S commute as they act on different parts of the wavefunction

act on x,y,z ↗ ↖ act on $1,\dots,n$

$$[L_i, L_j] + [S_i, S_j] = i\hbar\left[\sum_k \varepsilon_{ijk} L_k + \sum_k \varepsilon_{ijk} S_k\right]$$

$$\Downarrow$$

$$[S_i, S_j] = i\hbar \sum_k \varepsilon_{ijk} S_k$$

empirically S_i only takes $\pm\hbar/2$

Earlier, we solved for J_x, J_y and J_z. We can find the form of S in each 2×2 block matrix

$$S_x = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad S_y = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad S_z = \pm\hbar/2\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

We describe an electron through a two-component wave function called a spinor

$$\psi = \begin{bmatrix} \varphi_+(x,y,z) \\ \varphi_-(x,y,z) \end{bmatrix} = \varphi_+\begin{bmatrix} 1 \\ 0 \end{bmatrix} + \varphi_-\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$\varphi_- = 0,\ \varphi_+ \neq 0 \Rightarrow S_z = \hbar/2$

$\varphi_+ = 0,\ \varphi_- \neq 0 \Rightarrow S_z = -\hbar/2$

$$P|\psi\rangle = 0,\ L_z|\psi\rangle = 0 \text{ but } S_z|\psi\rangle \neq 0$$

Spinors are two complex component objects

Orbital Angular momentum can be modified via an external field but spin cannot

$$S^2 = \hbar^2\begin{bmatrix} (1/2)(1/2+1) & 0 \\ 0 & (1/2)(1/2+1) \end{bmatrix} = \frac{3}{4}\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

↖ Eigenvalue

Hilbert space can be understood as direct product of infinite dimension space and a two dimensional space

$$V_e = V_o \otimes V_s \qquad |xyzs_z\rangle = |xyz\rangle \otimes |s_z\rangle$$

Suppose the orbital degree of freedom evolves independently of the spin degree of freedom

$$H = H_0 + H_S \quad \leftarrow \text{Seperable hamiltonian}$$

In this case we can focus on the 2-D hilbert space

Any ket $|s,s_z\rangle = |s,m\rangle$

$$|s,m\rangle = |1/2, 1/2\rangle \xrightarrow{S_z} \begin{bmatrix}1\\0\end{bmatrix}$$

$$|s,m\rangle = |1/2, -1/2\rangle \xrightarrow{S_z} \begin{bmatrix}0\\1\end{bmatrix}$$

Basis

$$|\chi\rangle = \alpha|1/2, 1/2\rangle + \beta|1/2, -1/2\rangle \xrightarrow{S_z} \begin{bmatrix}\alpha\\\beta\end{bmatrix}$$

Normalization condition: $1 = |\alpha|^2 + |\beta|^2$

We refer to the eigenstates $|\hat{n}, \pm\rangle$ of $\hat{n}\cdot S$ with eigenvalues of $\pm\hbar/2$ as spin up/down in the direction $\hat{n}$

Suppose $\hat{n}$ points in the direction θ, ϕ

$$\hat{n}_z = \cos\theta$$
$$\hat{n}_x = \sin\theta\cos\phi$$
$$\hat{n}_y = \sin\theta\sin\phi$$

$$\hat{n}\cdot S = \hat{n}_x S_x + \hat{n}_y S_y + \hat{n}_z S_z$$

$$= \frac{\hbar}{2}\begin{bmatrix}\cos\theta & \sin\theta e^{-i\phi}\\ \sin\theta e^{i\phi} & -\cos\theta\end{bmatrix}$$

$$|\hat{n}, up\rangle = \begin{bmatrix}\cos(\theta/2)e^{-i\phi/2}\\ \sin(\theta/2)e^{i\phi/2}\end{bmatrix} \quad \text{and} \quad |\hat{n}, down\rangle = \begin{bmatrix}-\sin(\theta/2)e^{-i\phi/2}\\ \cos(\theta/2)e^{i\phi/2}\end{bmatrix}$$

Pauli Matricies are operators in the 2-D Hilbert Space

$$S = \frac{\hbar}{2}\sigma$$

$$\sigma_x = \begin{bmatrix}0&1\\1&0\end{bmatrix} \quad \sigma_y = \begin{bmatrix}0&-i\\i&0\end{bmatrix} \quad \sigma_z = \begin{bmatrix}1&0\\0&-1\end{bmatrix}$$

Properties of Pauli Matricies

1) Anti-commutative

$$[\sigma_i, \sigma_j]_+ = 0 \quad \text{or} \quad \sigma_i\sigma_j = -\sigma_j\sigma_i \quad i\neq j$$

2) Cyclic Permutations

$$\sigma_x\sigma_y = i\sigma_z$$

3) Traceless

$$\mathrm{Tr}\,\sigma_i = 0$$

4) Square of Pauli Matrix

$$\sigma_i^2 = I$$

$$(\hat{n}\cdot\sigma)^2 = I$$

5) Combining 1 and 4

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij} I$$

6) Combining 5 and 2

$$[\sigma_x, \sigma_y] = 2i\sigma_z \quad \leftarrow \text{cyclic permutations}$$

7) Product of Pauli Operators

$$(A\cdot\sigma)(B\cdot\sigma) = A\cdot B\, I + i(A\times B)\cdot\sigma$$

↖ vectors/operators that commute w/ σ

8) Trace of Product of Matricies

$$\mathrm{Tr}(\sigma_i\sigma_j) = 2\delta_{ij}$$

If we consider the identity matrix as σ_0 or the 4th pauli matrix we see that

σ_α matricies are linearly independent

Therefore we can write any 2x2 matrix M as

$$M = \sum m_\alpha \sigma_\alpha$$

$$m_\alpha = \frac{1}{2}\mathrm{Tr}(M\sigma_\alpha)$$

↖ real if M is hermetian

Rotation Operators

$$U[R(\theta)] = e^{-i\theta\cdot S/\hbar} = e^{-i\theta\cdot\sigma/2}$$ ← general form

$$= \exp\left[-i\left(\frac{\theta}{2}\right)\hat{\theta}\cdot\sigma\right]$$

$$= \sum_{n=0}^{\infty}\left(\frac{-i\theta}{2}\right)^n \cdot \frac{1}{n!}(\hat{\theta}\cdot\sigma)^n$$

even coefficients disappear

$$= I + \left(\frac{-i\theta}{2}\right)\hat{\theta}\cdot\sigma + \frac{1}{2!}\left(\frac{-i\theta}{2}\right)^2 I + \frac{1}{3!}\left(\frac{-i\theta}{2}\right)\hat{\theta}\cdot\sigma + \cdots$$

Combing in terms of I and $\hat{\theta}\cdot\sigma$

$$U[R(\theta)] = \cos(\theta/2)I - i\sin(\theta/2)\hat{\theta}\cdot\sigma$$

14.4 Spin Dynamics

Recall from magnetostatics that the torque on a current loop I in a magnetic field B is given by

$$T = \mu \times B$$ ← Torque acts to rotate the loop until μ and B are parallel

$$\mu = \frac{I\cdot A}{c} e_\perp$$

magnetic moment; perpendicular to plane of loop

Imagine a small particle of mass m and charge q moving in a circular orbit of r

$$I = \frac{qv}{2\pi r}$$ ← charge flow past any point per second

Consequently,

$$\mu = \frac{qv}{2\pi r}\cdot\frac{\pi r^2}{c} = \frac{qvr}{2c} = \frac{q}{2mc}\cdot l$$ ← magnitude of angular momentum

$\frac{q}{2mc}$: gyromagnetic ratio γ

When μ originates from angular momentum, T will create a precession of μ around B

$$T = \frac{dl}{dt} = \mu\times B = \gamma(l\times B)$$

For a small time step Δt

$$\Delta l = \gamma(l\times B)\Delta t$$

$$= \gamma l B\sin\theta\,\Delta t$$

Since Δl is perpendicular to l, the tip of l moves

$$\Delta\phi = \frac{-\Delta l}{l\sin\theta} = (-\gamma B)\Delta t$$

$$\omega_0 = -\gamma B$$

↖ precession frequency

Consider the Hamiltonian of a particle of mass m and charge q in a magnetic field

$$H = \frac{|P|^2}{2m} - \frac{q}{2mc}(P\cdot A + A\cdot P) + \frac{q^2|A|^2}{2mc^2}$$

$$A = \frac{B}{2}(-yi + xj)$$

$$\nabla\times A = \vec{B} = B\vec{k}$$

Assuming that B is small and noticing that $(P\cdot A)|\psi\rangle \longrightarrow (A\cdot P)|\psi\rangle$

$$H_{int} = -\frac{q}{2mc}(2A\cdot P)$$

$$= -\frac{q}{2mc}\cdot\frac{B}{2}(-yP_x + xP_y)$$

$$= -\frac{q}{2mc}L\cdot B = -\mu\cdot B$$

$$\mu = \frac{q}{2mc}L$$

Along the z-axis we see

$$\mu_z = \frac{q}{2mc}L_z = \frac{q\hbar}{2mc}(0, \pm1, \pm2, \ldots)$$

↑ Bohr magneton

Spin Magnetic Moment

We can represent any operator in V_s as a linear combination of I and S

$$\mu = \gamma S \quad \text{(orbital case)}$$
$$= g\left(\frac{-e}{2mc}\right) S$$

Plugging back into our earlier hamiltonian

$$H_{int} = -\mu \cdot B = \frac{ge}{2mc} S \cdot B = \frac{ge\hbar}{4mc} \sigma \cdot B$$

intrinsic magnetic moment is $g/2$ magnetons

Experiment finds $g \approx 2$

gyromagnetic ratio for spin is twice as much as orbital angular momentum

Quantum Electrodynamics arrives at a theoretical prediction on par w/ experimental result

Returning to our Hamiltonian

$$H = -\mu \cdot B = -\gamma S \cdot B$$
$$\gamma = -\frac{e}{mc}$$

The time evolution of a state is given by

$$|\varphi(t)\rangle = U(t)|\varphi(0)\rangle$$
$$U(t) = e^{-iHt/\hbar} = e^{i\gamma t(S\cdot B)/\hbar}$$

Recall that $\exp(-i\theta \cdot S/\hbar)$ acts to rotate by θ

Therefore $U(t)$ simply acts to rotate the state by $-\gamma Bt$

$\langle S \rangle$ will precess around B with frequency $\omega_0 = -\gamma B$

Paramagnetic Resonance

A classical magnetic moment μ in a field $\vec{B}_0 = B_0 \vec{k}$ will precess around $\vec{B}_0$ with a frequency $\omega_0 = -\gamma B_0$

If we view this process from a frame rotating at ω parallel to B_0, the observed frequency will be

$$\omega_r = \omega_0 - \omega = -\gamma B_0 - \omega = -\gamma(B_0 + \omega/\gamma)$$

Effective field in this rotating frame is

$$B_r = B_0 + \omega/\gamma$$

For a more general magnetic field

$$B = B\cos\omega t\, \vec{i} - B\sin\omega t\, \vec{j} + B_0 k$$

At $t = 0$

$$\mu(0) = \mu\vec{k}$$

Let's consider $\vec{B}$ from the perspective of a frame that rotates at a frequency $\vec{\omega} = -\omega\vec{k}$

rotating component of B is "frozen"

$$\vec{B}_r = B\, i_r + (B_0 - \omega/\gamma)\vec{k}$$

(i_r: unit vector in the rotating frame; reduced effective B)

μ will precess around B_r at a frequency

$$\omega_r = -\gamma B_r$$
$$|\omega_r| = \gamma\left[B^2 + (B_0 - \omega/\gamma)^2\right]^{1/2}$$

For the time evolution of $\mu_z(t)$

$$\mu_z(t) = \mu\cos^2\alpha + \mu\sin^2\alpha\cos\omega_r t$$
$$= \mu_z(0)\left[\frac{(\omega_0-\omega)^2}{(\omega_0-\omega)^2 + \gamma^2B^2} + \frac{\gamma^2B^2\cos\omega_r t}{(\omega_0-\omega)^2 + \gamma^2B^2}\right]$$

← Invariant under z rotations

At paramagnetic resonance $\omega = \omega_0$, $\vec{B}_r = B\vec{i}_r$, $\alpha = \pi/2$

cone becomes a circle and M_z oscillates with the largest amplitude M and Frequency γB

If we apply a 90° pulse, a rotating field at resonance frequency s.t.

$$\gamma B \tau = \pi/2$$

the magnetic moment will swing back into the x-y plane

14.5 Return of Orbital Degrees of Freedom

Let's return to the case where H is seperable

$$H = H_0 + H_s$$

In the hydrogen Atom the Coulomb interaction is independent of spin

$$|n\ell m m_s = +\tfrac{1}{2}\rangle \rightarrow \varphi_{n\ell m}(r,\theta,\phi)\,\chi_+$$

$$|n\ell m m_s = -\tfrac{1}{2}\rangle \rightarrow \varphi_{n\ell m}(r,\theta,\phi)\,\chi_-$$

For a hydrogen atom in a weak magnetic field $\vec{B} = B\vec{k}$

$$H = H_{coulomb} - \left(\frac{-eB}{2mc}\right)L_z - \left(\frac{eB}{mc}\right)S_z$$

← Proton's coupling is small compared to electron

H is diagonalized by same states as before

$$H|n\ell m m_s\rangle = \left[\frac{-R_y}{n^2} + \frac{eB\hbar}{2mc}\left(m + 2m_s\right)\right]|n\ell m m_s\rangle$$

↖ new eigenvalues

Increased Degeneracy!

In a multielectron atom the contributions from all the electrons increase the number of spectral lines (Zeeman Effect)

Chapter 15: Addition of Angular Momentum

15.1 A simple Example

Consider the operator $S = S_1 + S_2$

↖ total angular momentum operator

$$S_z = S_{1z} + S_{2z}$$

With this in hand we can solve for the respective eigenvalues and vectors

$$S_z|++\rangle = (S_{1z} + S_{2z})|++\rangle = \hbar|++\rangle$$
$$S_z|+-\rangle = 0|+-\rangle$$
$$S_z|-+\rangle = 0|-+\rangle$$
$$S_z|--\rangle = -\hbar|--\rangle$$

} Only 3 allowed values

$$S_z \longrightarrow \hbar \begin{matrix} ++ & +- & -+ & -- \end{matrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

two fold degeneracy in $S_z = 0$ $\quad \alpha|+-\rangle + \beta|-+\rangle$

Now we can take a look at $S^2 = S_1^2 + S_2^2 + 2S_1 \cdot S_2$

$$S^2 \longrightarrow \hbar^2 \begin{matrix} ++ & +- & -+ & -- \end{matrix} \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}$$

Notice that $|++\rangle$ and $|--\rangle$ are eigenstates of S^2 while $|+-\rangle$ and $|-+\rangle$ are not

$\frac{|+-\rangle + |-+\rangle}{2^{1/2}}$ $(s=1)$

are eigenstates of S^2 (verify by explicit computation)

$\frac{|+-\rangle - |-+\rangle}{2^{1/2}}$ $(s=0)$

Allowed values for total spin are $s=1$ and $s=0$

Allowed values for S_z are $\hbar, 0,$ and $-\hbar$

Recall that s_i takes values $1/2$ while $m_i = \pm 1/2$

We can now recover the eigenstates of the above states

$|s=1 \; m=1, \; s_1=1/2 \; s_2=1/2\rangle = |++\rangle$

$|s=1 \; m=0, \; s_1=1/2 \; s_2=1/2\rangle = 2^{-1/2}\left[|+-\rangle + |-+\rangle\right]$

$|s=1 \; m=-1, \; s_1=1/2 \; s_2=1/2\rangle = |--\rangle$

} Triplets

$|s=0 \; m=0, \; s_1=1/2 \; s_2=1/2\rangle = 2^{-1/2}\left[|+-\rangle - |-+\rangle\right]$ ← Singlet

] represent states with well defined angular momentum total-s basis

The problem of adding angular momenta is essentially a change of basis from one that diagonalizes $(S_1^2, S_2^2, S_{1z}, S_{2z})$ to one that diagonalizes (S^2, S_z, S_1^2, S_2^2)

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$$

(3 dimensions; 1 dimension; 2 Dimensions; 2 dimensions)

Direct product of two spin $1/2$ Hilbert spaces is the direct sum of spin-1 space and a spin-0 space

Rotation matricies in the product space can be block diagonalized by changing to the total-s basis

Total-s states obey symmetry rules

- Triplets are symmetric
- Singlets are antisymmetric

For a complete state vector to maintain traditional symmetry relations we multiply by the opposite symmetry

$$|w_1 w_2, s\rangle \otimes \frac{|+-\rangle - |-+\rangle}{2^{1/2}}$$

$$|w_1 m_1, w_2 m_2, A\rangle = \begin{cases} |w_1 w_2, A\rangle \otimes \begin{cases} |\uparrow\uparrow\rangle \\ \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{2^{1/2}} \\ |\downarrow\downarrow\rangle \end{cases} \end{cases}$$

15.2 The General Problem

Consider the general problem of adding two angular momenta J_1 and J_2

The total j-kets are

$$|jm, j_1 j_2\rangle \quad \text{where} \quad j_1 + j_2 \geq j \geq j_1 - j_2, \quad j \geq m \geq -j$$

We can generalize the previous section for j_1 and j_2

1) maximal $m = j_1 + j_2$ is taken to be a product ket

$$|j_1 + j_2, j_1 + j_2\rangle = |j_1 j_1, j_2 j_2\rangle$$

↑ maximal projections along z-axis

2) The remaining m states are found via lowering

$$J_- |j_1 + j_2, j_1 + j_2\rangle = \hbar [2(j_1 + j_2)]^{1/2} |j_1 + j_2, j_1 + j_2 - 1\rangle$$

$$\Downarrow$$

$$|j_1 + j_2, j_1 + j_2 - 1\rangle = \frac{1}{[2(j_1 + j_2)]^{1/2} \hbar} \cdot (J_{1-} + J_{2-}) |j_1 j_1, j_2 j_2\rangle$$

↓ Application of lowering operator

$$= \frac{1}{[2(j_1 + j_2)]^{1/2} \hbar} \left[\hbar (2j_1)^{1/2} |j_1 (j_1 - 1), j_2 j_2\rangle + \hbar (2j_2)^{1/2} |j_1 j_1, j_2 (j_2 - 1)\rangle \right]$$

$$= \left(\frac{j_1}{j_1 + j_2} \right)^{1/2} |j_1 (j_1 - 1), j_2 j_2\rangle + \left(\frac{j_2}{j_1 + j_2} \right)^{1/2} |j_1 j_1, j_2 (j_2 - 1)\rangle$$

3) Repeat this process for remaining $j_1 + j_2$ states

4) In the remaining $j_1 + j_2 - n$ states we face the problem of duplicity

$m = j_1 + j_2 - 1$ can be a linear combination of $|j_1 j_1, j_2 (j_2 - 1)\rangle$ and $|j_1 (j_1 - 1), j_2 j_2\rangle$

The linear combination must be normalized and orthogonal to other states formed from the same kets

We can consequently write the total j-kets as

$$|jm, j_1 j_2\rangle = \sum_{m_1} \sum_{m_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | jm, j_1 j_2\rangle$$

↑ $\langle j_1 m_1, j_2 m_2 | jm\rangle$

Clebsh-Gordon or vector addition coefficients are the corresponding coefficients in the summation

Properties

1) $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $j_1 - j_2 \leq j \leq j_1 + j_2$

2) $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $m_1 + m_2 = m$

3) They are real } convention

4) $\langle j_1 j_1, j_2 (j - j_1) | jj\rangle$ is positive } convention

5) $\langle j_1 m_1, j_2 m_2 | jm\rangle = (-1)^{j_1 + j_2 - j} \langle j_1 (-m_1), j_2 (-m_2) | j (-m)\rangle$

Consider the addition of L and S

More specifically, consider an electron bound to a proton in a state of orbital angular momentum l

$$J = L + S = l \pm 1/2$$

$$|j=\ell+1/2, m\rangle = \alpha\,|\ell, m-1/2; 1/2, 1/2\rangle + \beta\,|\ell, m+1/2; 1/2, -1/2\rangle$$

$$|j=\ell+1/2, m\rangle = \alpha'\,|\ell, m-1/2; 1/2, 1/2\rangle + \beta'\,|\ell, m+1/2; 1/2, -1/2\rangle$$

Orthonormality applies the following constraints

$$\alpha^2 + \beta^2 = 1$$

$$\alpha'^2 + \beta'^2 = 1$$

$$\alpha\alpha' + \beta\beta' = 0$$

By demanding

$$J^2\,|j=\ell+1/2, m\rangle = \hbar^2(\ell+1/2)(\ell+3/2)\,|j=\ell+1/2, m\rangle$$

we can deduce

$$\frac{\beta}{\alpha} = \left(\frac{\ell+1/2-m}{\ell+1/2+m}\right)^{1/2}$$

Putting everything together

$$|j=\ell\pm 1/2, m\rangle = \frac{1}{(2\ell+1)^{1/2}}\left[\pm(\ell+1/2\pm m)^{1/2}\,|\ell, m-1/2; 1/2, 1/2\rangle + (\ell+1/2\mp m)^{1/2}\,|\ell, m+1/2; 1/2, -1/2\rangle\right]$$

Chapter 16: The Variational and WKB Methods

16.1 The Variational Method

The mean energy level $E[\psi]$ cannot be less than the lowest energy state E_0

$$E[\psi] \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

The idea is that we can calculate $E[\psi]$ for each ψ in our space and select the lowest value as our ground state

In practice this isn't feasible so we focus on a subspace of the vectors parameterized by a set of variables $(\alpha, \beta, \gamma, \ldots)$

We then find the values $\alpha_0, \beta_0, \gamma_0 \ldots$ that minimize E.

We take this value as an upper bound on E_0

Coulomb Potential Example

$V = -\frac{e^2}{r}$ $\longrightarrow$ ground-state wavefunction should have no angular momentum, no nodes, and behave like r^0 as $r \to 0$ and vanish at $r \to \infty$ (Why?)

We select a solution of the form

$$\varphi(r, \theta, \phi, \alpha) = e^{-\alpha r^2}$$

$$E(\alpha) = \frac{\int \left[e^{-\alpha r^2} \left(-\frac{\hbar^2}{2m} \cdot \frac{1}{r} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{e^2}{r} \right) e^{-\alpha r^2} \right] r^2 \, dr}{\int e^{-2\alpha r^2} r^2 \, dr} = \frac{3\hbar^2 \alpha}{2m} - \left(\frac{2}{\pi}\right)^{1/2} 2e^2 \alpha^{1/2}$$

minimized @ $a_0 = \left(\frac{me^2}{\hbar^2}\right)^2 \cdot \frac{8}{9\pi}$

$E(\alpha_0) = -0.85 \, R_y$ ← slightly above true energy

Ground State Helium Example

Hamiltonian in coordinate basis

$$H \to \frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

(r_1, r_2: radial coordinates; r_{12}: radial separation)

If we ignore the repulsive term

$$\varphi = \varphi_{100}(r_1)\varphi_{100}(r_2)$$

$$\varphi_{100} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$ ← singlet state is suppressed

$e^2 \to Ze^2$, $Z = 2$

$$= \frac{Z^3}{\pi a_0^3} e^{-Z(r_1 + r_2)/a_0}$$

Associated Energy

$$E = 2\left(-\frac{m(Ze^2)^2}{2\hbar^2}\right) \simeq -108.8 \text{ eV}$$

True value is -78.6 eV

Variational Method + Repulsive Interaction

$$\varphi = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1 + r_2)/a_0}$$ ← variable Z

$$E(Z) = \frac{\left[\int \varphi(r_1, r_2, Z)\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}\right] \times \varphi(r_1, r_2, Z) \, d^3r_1 \, d^3r_2\right]}{\int |\varphi(r_1, r_2, Z)|^2 \, d^3r_1 \, d^3r_2} = -2 R_y \left[4Z - Z^2 - \tfrac{5}{8}Z\right]$$

Minimum at $Z = 2 - 5/16$ ⟶ ~ 77.5 eV

Even poor approximations of ψ can give good energy estimates

For example, consider $|\psi\rangle = |E_0\rangle + |\delta\psi\rangle$

$$|\delta\psi\rangle = |\delta\psi_\parallel\rangle + |\delta\psi_\perp\rangle$$
$$= \alpha|E_0\rangle + |\delta\psi_\perp\rangle$$

$$E[\psi] = \frac{E_0|1+\alpha|^2 + \langle\delta\psi_\perp|H|\delta\psi_\perp\rangle}{|1+\alpha|^2 + \langle\delta\psi_\perp|\delta\psi_\perp\rangle} = E_0 + O(\delta\psi_\perp)^2$$

↖ Second order error

Eigenkets of H are stationary points of $E[\psi]$

To get bounds on higher energy states we consider trial states in whose expansion $|E_0\rangle, \ldots |E_n\rangle$ do not appear
↖ as estimated via variational methods

16.2 The Wentzel-Kramers-Brillouin Method

Consider a particle of energy E moving in constant potential

$$\varphi(x) = \varphi(0)\, e^{\pm ipx/\hbar} \qquad p = [2m(E-V)]^{1/2}$$

general solution is a combination of $\pm$ waves

$$\lambda = \frac{2\pi\hbar}{p}$$

Suppose V varies slowly. Over a small region φ will still behave like a plane wave

$$\lambda(x) = \frac{2\pi\hbar}{p(x)} = \frac{2\pi\hbar}{[2m(E-V(x))]^{1/2}}$$

To recover the accumulated phase shift from $x = x_0$ to $x = x$ is given by

$$\varphi(x) = \varphi(x_0)\exp\left[\pm(i/\hbar)\int_{x_0}^{x} p(x')\,dx'\right]$$

wavelength at a point x only makes sense if δx over λ is negligible

Our goal is to solve

$$\left[\frac{d^2}{dx^2} + \frac{1}{\hbar^2}p^2(x)\right]\varphi(x) = 0$$

We can generally write

$$\varphi(x) = \exp[i\phi(x)/\hbar]$$

Putting the two together

$$-\left(\frac{\phi'}{\hbar}\right)^2 + \frac{i\phi''}{\hbar} + \frac{p^2(x)}{\hbar^2} = 0$$

We can approximate ϕ via a powerseries in $\hbar$

$$\phi = \phi_0 + \hbar\phi_1 + \hbar^2\phi_2 + \cdots$$

As $\hbar \to 0$ the wavelength estimate $\lambda = \frac{2\pi\hbar}{p} \to 0$

Every potential is slowly varying in this limit

WKB approximation retains the first two terms in the expansion

$$\phi = \phi_0 + \hbar\phi_1$$

$$\frac{-(\phi_0')^2 + p^2(x)}{\hbar^2} + \frac{i\phi_0'' - 2\phi_1'\phi_0'}{\hbar} + O(\hbar^0) = 0$$

We can first focus on the $1/\hbar^2$ term

$$\phi_0' = \pm p(x) \quad \text{or} \quad \phi_0(x) = \pm\int^x p(x')\,dx'$$

Consequently,

$$\varphi(x) = \varphi(x_0)\exp\left[\pm(i/\hbar)\int_{x_0}^{x} p(x')\,dx'\right]$$

Next, let's apply the $1/\hbar$ term

$$i\phi_0'' = 2\phi_1''\phi_0'$$

$$\frac{\phi_0''}{\phi_0'} = -2i\phi_1'$$

$$\ln\phi_0' = -2i\phi_1 + c$$

$$\phi_1 = +i\ln(\phi_0')^{1/2} + \frac{c}{2i} = i\ln p^{1/2} + \tilde{c}$$

The wavefunction now takes the form

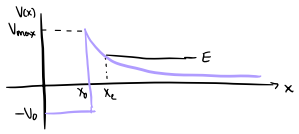
$$\varphi(x) = \varphi(x_0)\left[\frac{p(x_0)}{p(x)}\right]^{1/2} \exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right]$$

The condition for WKB approximation is as follows

$$\left|\frac{\varphi_0''}{\hbar}\right| << \left|\frac{\varphi_0'}{\hbar}\right|^2$$ ← higher order $\hbar$ terms are less important than lower ones

Tunneling Amplitudes

Consider a particle trapped in a well



We can apply the mechanics of the WKB method to solve the tunneling probability

Ratio between pt. of escape and well barrier : $\varphi(x_2) = \varphi(x_0)\exp\left(\underbrace{\frac{1}{\hbar}\int_{x_0}^{x_2} i\left[2m(V(x)-E)\right]^{1/2}dx}_{-\gamma/2}\right)$

A particle inside the well has velocity $v = \frac{[2m(E+V_0)]^{1/2}}{m}$ and bangs against outer wall with $f = \frac{v}{2x_0}$

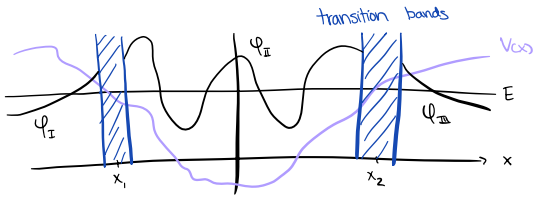
Each collision further has an escape probability of $e^{-\gamma}$

$$R = \frac{[2m(E+V_0)]^{1/2}}{2mx_0}e^{-\gamma}$$ ← prob escape in 1 second

mean lifetime: $\tau = 1/R$

Bound States

WKB method can also be adapted for bound state energies and wavefunctions



x_1 and x_2 are the classic turning points for systems with energy E

φ_I and φ_{III} will take the form of a damped exponential

$$\varphi_{III}(x) \sim \frac{1}{[2m(V(x)-E)]^{1/2}}\exp\left(-\frac{1}{\hbar}\int_{x_2}^{x}\left\{2m[V(x')-E]\right\}^{1/2}dx'\right)$$

In region 2 we assume oscillatory behaviour

$$\varphi_{II}(x) = \frac{A}{[p(x)]^{1/2}}\cos\left[\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + B\right]$$

real parameters A, B replace complex parameters $\varphi(x_0)$

Neither of our estimates are applicable at the turning points as $p(x)^{-1/2}$ and $[2m(V(x)-E)]^{-1/2}$ blow up in their limits

wavelength tends towards infinity

To remedy this issue we define transition areas around x_1 and x_2

In this region we assume V(x) can be approximated by a linear function

$$V(x) \simeq V(x_1) + V'(x-x_1)$$
$$= E + V'\cdot(x-x_1)$$

We then match these potentials to the respective damped oscillations and oscillatory functions

For example,

$$\varphi_{II}(x) = \frac{A}{[p(x)]^{1/2}}\cos\left[\frac{1}{\hbar}\int_{x_1}^{x} p(x')dx' - \frac{\pi}{4}\right]$$ ← near x_1

$$\varphi_{II}(x) = \frac{A'}{[p(x)]^{1/2}}\cos\left[\frac{1}{\hbar}\int_{x_2}^{x} p(x')dx' + \frac{\pi}{4}\right]$$ ← near x_2

For the functions to coincide we require $A = A'$ in magnitude and the phase difference to be a multiple of π

$$\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' - \frac{1}{\hbar}\int_{x_2}^{x} p(x')\,dx' - \frac{\pi}{2} = n\pi \qquad n = 0, 1, \ldots$$

quantization of energy

when n is even $A = A'$ but when n is odd, $A = -A'$

WKB method works better for larger n

WKB wavefunction has n nodes

If we assume that ψ_{II} vanishes in the classical regions then the wavefunction must undergo an integer number of half-cycles in $x_1 \le x \le x_2$

Bohr-Sommerfeld Quantization:

$$\int_{x_1}^{x_2} p(x)\,dx = (n+1)\hbar\pi \qquad n = 0, 1, 2, \ldots$$

Since ψ doesn't actually vanish at the turning points we find that the number of cycles is some what less than $n+1$

WKB method in 3-dimensions to solve radial equation in a rotationally invariant problem

When $\ell = 0$ there is no centrifugal barrier

$$U(r) \sim \frac{1}{[p(r)]^{1/2}} \sin\left[\frac{1}{\hbar}\int_0^r p(r')\,dr'\right] \qquad p = [2m(E - V(r))]^{1/2}$$

quantization condition

$$\int_0^{r_{max}} p(r)\,dr = \left(n + \tfrac{3}{4}\right)\hbar\pi \qquad n = 0, 1, 2, \ldots$$

barrier at $r = 0$ is infinite

Dependent on $V(r)$ at origin and $\ell = 0$ (centrifugal barrier)

Chapter 17: Time-Independent Perturbation Theory

17.1 The Formalism

Suppose we know the solution to H^0 but want to find $H = H^0 + H^2$ for a relatively small H^2

H^0: unperturbed Hamiltonian; H^2: perturbation

Assume that for every eigenket $E_n^0 = |n^0\rangle$ of H^0 there is an analagous eigenket $|n\rangle$ with energy E_n for H

We write the eigenkets and eigenvalues of H as a perturbation series

$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + \cdots$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + \cdots$$

Superscript k gives the power of H^1 that it is expected to be proportional to

Let's begin by considering the eigenvalue equation

$$H|n\rangle = E_n|n\rangle$$

$$(H_0 + H_1)\left(|n^0\rangle + |n^1\rangle + \cdots\right) = \left(E_n^0 + E_n^1 + \cdots\right)\left(|n^0\rangle + |n^1\rangle + \cdots\right)$$

order of a term is given by sum of subscripts

The general approach is to sequentially solve the eigenvalue equation

First, consider the H^0 term ← 0^{th} order dependence on H^1

$$H^0|n^0\rangle = E_n^0|n^0\rangle$$

↖ Easy to solve

Next, consider the first order terms

$$H^0|n^1\rangle + H^1|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$$

We can now dot both sides with $\langle n^0|$

$$\langle n^0|H_0|n^1\rangle + \langle n^0|H^1|n^0\rangle = E_n^0\langle n^0|n^1\rangle + E_n^1\langle n^0|n^0\rangle$$

$$\cancel{\langle n^0|E_n^0|n^1\rangle} + \langle n^0|H^1|n^0\rangle = \cancel{E_n^0\langle n^0|n^1\rangle} + E_n^1$$

$$E_n^1 = \langle n^0|H^1|n^0\rangle$$ ← Expectation value!

"First order change in energy is the expectation value of H^1 in the unperturbed state"

For an arbitrary eigenket m^0 where $m \neq n$, let's consider the dot product of $\langle m^0|$ with the above expression

$$\langle m^0|H^0|n^1\rangle + \langle m^0|H^1|n^0\rangle = E_n^0\langle m^0|n^1\rangle$$

$$\langle m^0|n^1\rangle = \frac{\langle m^0|H^1|n^0\rangle}{E_n^0 - E_m^0}$$

Since $m \neq n$ we determine the components of $|n^1\rangle$ in the H^0 eigenbasis except for the component parallel to $|n^0\rangle$

We solve this missing term by imposing the normality condition

$$1 = \langle n|n\rangle = \left(\langle n^0| + \langle n_\perp^1| + \langle n_\parallel^1|\right) + \left(|n^0\rangle + |n_\perp^1\rangle + |n_\parallel^1\rangle\right)$$

$$= \langle n^0|n^0\rangle + \langle n_\parallel^1|n^0\rangle + \langle n^0|n_\parallel^1\rangle + \text{higher order terms}$$

$\langle n_\perp^1|n^0\rangle$ terms vanish

$$0 = \langle n_\parallel^1|n^0\rangle + \langle n^0|n_\parallel^1\rangle + \text{higher order terms}$$

This implies that

$$\langle n^0|n_\parallel^1\rangle = i\alpha \quad \text{for } \alpha \text{ real}$$

In first order approximations

$$1 + i\alpha = e^{i\alpha}$$

Putting it all together

$$|n\rangle = |n^0\rangle e^{i\alpha} + \sum_{m \neq n} \frac{|m^0\rangle\langle m^0|H^1|n^0\rangle}{E_n^0 - E_m^0}$$

$e^{i\alpha}$: just a phase change

$$= |n^0\rangle + |n^1\rangle$$

$|n^1\rangle$: orthogonal to $|n^0\rangle$, proportional to H^1 first power

Second Order Part

$$H^0|n^2\rangle + H^1|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$$

Applying the same dotting $\langle n^0|$ and applying results from $|n^1\rangle = |n_\perp^1\rangle$

$$E_n^2 = \langle n^0|H^1|n^1\rangle$$

$$= \sum_{m \neq n} \frac{|\langle n^0|H^1|m^0\rangle|^2}{E_n^0 - E_m^0}$$

For $|n'\rangle$ to be small compared to $|n^0\rangle$

$$\left| \frac{\langle m^0|H'|n^0\rangle}{E_n^0 - E_m^0} \right| \ll 1$$

17.2 Some Examples

Consider a particle of charge q and mass m in a harmonic oscillator potential

$$V = \frac{1}{2} m\omega^2 x^2$$

Suppose we apply an external magnetic field of magnitude f along the x-axis

$$\phi = -fx \qquad V = -qfx$$

Our corresponding Hamiltonian takes the form

$$H = H^0 + H' = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 - qfx$$

We can calculate the first order shift in energy

$$E_n^1 = \langle n^0|H'|n^0\rangle = -qf\langle n^0|x|n^0\rangle = 0$$

We see that E_n^1 vanishes by noticing that X has no diagonal element

$$X = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^\dagger)$$

Alternatively, if we consider the coordinate basis

$$E_n^1 = -qf \int (\psi_n^0)^* x \psi_n^0 \, dx$$

$$= -qf \int |\psi_n^0|^2 x \, dx$$

↑ even function

Next, we can find the perturbed eigenket

$$|n\rangle = |n^0\rangle + \sum_{m \neq n} \frac{|m^0\rangle\langle m^0| - qf\left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^\dagger)|n^0\rangle}{E_n^0 - E_m^0}$$

$$= |n^0\rangle + qf\left(\frac{1}{2m\hbar\omega^3}\right)^{1/2} \left[(n+1)^{1/2}|(n+1)^0\rangle - n^{1/2}|(n-1)^0\rangle\right]$$

↑ Up to the first order the perturbation mixes $|n^0\rangle$ w/ states above and below it

Second order energy shift

$$E_n^2 = \langle n^0|H'|n'\rangle = \sum_{m \neq n} \frac{|\langle m^0|H'|n^0\rangle|^2}{E_n^0 - E_m^0}$$

$$= q^2 f^2 \cdot \frac{\hbar}{2m\omega}\left(\frac{n+1}{-\hbar\omega} + \frac{n}{\hbar\omega}\right) = -\frac{q^2 f^2}{2m\omega^2}$$

Stark Effect

Consider a ground state hydrogen atom in a constant electric field $E = \mathcal{E}k$

We can represent this perturbation as

$$H' = e\mathcal{Z}\mathcal{E} \qquad \leftarrow \text{solving classically}$$

1st Order energy shift from Ground state

$$E_{100}^1 = \langle 100|e\mathcal{Z}\mathcal{E}|100\rangle = 0$$

↑ parity arguments

2nd Order energy shift from ground state

$$E_{100}^2 = \sum_{n\ell m}{}' \frac{e^2\mathcal{E}^2 |\langle n\ell m|\mathcal{Z}|100\rangle|^2}{E_{100}^0 - E_{n\ell m}^0} \leftarrow -Ry\left(1 - \tfrac{1}{n^2}\right)$$

$$= \sum_{n=2}^{\infty} \frac{e^2\mathcal{E}^2 |\langle n00|\mathcal{Z}|100\rangle|^2}{E_1^0 - E_n^0}$$

Since the magnitude of the energy difference increases with n, we can write the following inequality

$$|E_{100}^2| \leq \frac{e^2\mathcal{E}^2}{|E_1^0 - E_2^0|} \sum_{n\ell m}{}' |\langle n\ell m|\mathcal{Z}|100\rangle|^2$$

We can rewrite $\sum_{n\neq m}{}' |\langle n|m|z|100\rangle|^2 = \langle 100|z^2|100\rangle - \langle 100|z|100\rangle^2$

which is equal to a_0^2

Putting the pieces together

$$|E_{100}^2| \leq \frac{e^2\mathcal{E}^2}{|(\frac{e^2}{2a_0})(1-\frac{1}{4})|}\, a_0^2 \leq \frac{8a_0^3\mathcal{E}^2}{3}$$

We can get a lower bound by retaining the first energy term

$$|E_{100}^2| \geq \frac{e^2\mathcal{E}^2}{3e^2/8a_0}\, |\langle 210|z|100\rangle|^2$$

$\approx 0.55\, a_0^2$

Alternatively, we can try to find a Ω s.t.

$$H'|n^0\rangle = [\Omega, H^0]|n^0\rangle$$

For the Stark effect

$$\Omega = -\frac{ma_0 e\mathcal{E}}{\hbar^2}\left(\frac{r^2\cos\theta}{2} + a_0 r\cos\theta\right)$$

(coordinate basis)

$$|E_{100}^2| = |\langle 100|H'\Omega|100\rangle - 0|$$

$$= (0.84)\cdot\frac{8}{3}a_0^3\mathcal{E}^2$$

17.3 Degenerate Perturbation Theory

When $E_n^0 = E_m^0$ the condition for perturbation expansion is impossible

$$\left|\frac{\langle m^0|H'|n^0\rangle}{E_n^0 - E_m^0}\right| \ll 1$$

In degenerate space small perturbations produce vastly different results

Our goal is to select a basis that diagonalizes H' in the degenerate space of H^0

Let's once again consider the stark effect for $n=2$

We can no longer claim that the first-order shift is 0 since

$$\langle 2lm|e\mathcal{E}z|2lm\rangle = 0$$

Instead we need to find the basis in the $n=2$ sector that diagonalizes H'

From selection rules

$$H' \longrightarrow \begin{array}{c|cccc} nlm & 200 & 210 & 211 & 21\text{-}1 \\ \hline 200 & 0 & \Delta & 0 & 0 \\ 210 & \Delta & 0 & 0 & 0 \\ 211 & 0 & 0 & 0 & 0 \\ 21\text{-}1 & 0 & 0 & 0 & 0 \end{array}$$

$$\Delta = \langle 200|e\mathcal{E}z|210\rangle = -3e\mathcal{E}a_0$$

Notice that H' is $\Delta\cdot\sigma_x$ in the $m=0$ sector. We can consequently see that the eigenvalues are $\pm\Delta$ and eigenstates are $\frac{[|200\rangle \pm |210\rangle]}{2^{1/2}}$

For $|m|=1$ the old states $|2,1,\pm1\rangle$ diagonalize H'

Results

1) Zeroth-order states stable under perturbation are $|21\pm1\rangle$ and $\frac{[|200\rangle \pm |210\rangle]}{2^{1/2}}$

2) First-order shift in E^1 is 0 for first two states and $\pm\Delta$ for next two

Stable states for E^1 are a mix of $l=0$ and $l=1$ implying indefinite parity

Fine Structure Example

The Coulomb potential alone does not sufficiently explain interactions between a proton and electron

These are actual fine-structure corrections that produce energy shifts proportional to $\alpha^2\cdot$ coulomb binding energy

Under relativistic considerations

$$T = (c^2p^2 + m^2c^4)^{1/2} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + O(p^6)$$

↑ Extra term H_r

Since H_r is rotationally invariant, it is diagonal in the $|nlm\rangle$ basis

$$E_T^1 = -\frac{1}{8m^3c^2}\langle n\ell m|\, p^4 |n\ell m\rangle$$

$$p^4 = 4m^2\left(\frac{p^2}{2m}\right)^2 = 4m^2\left(H^0 + \frac{e^2}{r}\right)^2$$

$$E_T^1 = \frac{-1}{2mc}\left[(E_n^0)^2 + 2E_n^0 e^2\left\langle\frac{1}{r}\right\rangle_{n\ell m} + e^4\left\langle\frac{1}{r^2}\right\rangle_{n\ell m}\right]$$

$2E_n^0$ ↑ ; $\frac{4E_0^2 n}{\ell+1/2}$ ↑

$$= -\frac{1}{2}(mc^2)\alpha^4\left[-\frac{3}{4n^4} + \frac{1}{n^3(\ell+1/2)}\right]$$

The other relativistic effect to consider is called spin-orbit interaction

From the rest frame of an electron moving at velocity v, the proton produces a magnetic field by moving at $-v$

$$B = -\frac{e}{c}\frac{\vec{v}\times\vec{r}}{r^3}$$

Spin-orbit energy is the interaction between the electron and this field

$$\mathcal{H}_{s.o.} = -\mu\cdot B = \frac{e}{mcr^3}\mu\cdot(p\times r) = -\frac{e}{mc}\cdot\frac{\mu\cdot l}{r^3}$$ ← classical

$$H_{s.o} = \frac{e^2}{m^2c^2r^3}\, S\cdot L$$ ← Quantum

In reality the quantum hamiltonian is half as big since rest frame of electron doesn't have a constant velocity

↑ Thomas factor

First, we must find a basis that diagonalizes $H_{s.o.}$ ← states for a given n are degenerate

$$H_{s.o.} = \frac{e^2}{4m^2c^2r^3}\left[J^2 - L^2 - S^2\right]$$

$$\langle j'\, m'\, \ell'\, 1/2|\, H_{s.o.}\,|\, j\, m\, \ell\, 1/2\rangle = \delta_{jj'}\delta_{mm'}\delta_{\ell\ell'}\frac{e^2}{4m^2c^2}\left\langle\frac{1}{r^3}\right\rangle\hbar^2\left[j(j+1) - \ell(\ell+1) - 3/4\right]$$

We can then recover the first-order energy perturbation

$$E_{s.o.}^1 = \frac{\hbar^2e^2}{4m^2c^2}\left\langle\frac{1}{r^3}\right\rangle_{n\ell}\begin{bmatrix}\ell\\ -(\ell+1)\end{bmatrix}$$ ↖ $J = \ell \pm 1/2$

$$= \frac{1}{4}mc^2\alpha^4\,\frac{\begin{Bmatrix}\ell\\ -(\ell+1)\end{Bmatrix}}{n^3\ell(\ell+1/2)(\ell+1)}$$

Total Fine Structure Shift

$$E_{f.s.}^1 = E_T^1 + E_{so}^1 = -\frac{mc^2\alpha^2}{2n^2}\cdot\frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)$$

Chapter 18: Time-Dependent Perturbation Theory

18.1 The Problem

Consider the perturbative solution class given by the Hamiltonian

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

18.2 First-Order Perturbation Theory

Since the eigenkets of H^0 make a basis, we can represent any wavefunction as

$$|\psi(t)\rangle = \sum_n c_n(t)\,|n^0\rangle$$

If $H' = 0$ then $c_n(t) = c_n(0)\,e^{-iE_n^0 t/\hbar}$

We write our equation w/ similar form

$$|\psi(t)\rangle = \sum_n d_n(t)\,e^{-iE_n^0 t/\hbar}\,|n^0\rangle$$

↖ changes under $H' \longrightarrow$ power series of H'

To recover $d_f(t)$ we hit both sides by $\left[i\hbar\frac{\partial}{\partial t} - H^0 - H'\right]$

$$0 = \sum_n \left[i\hbar\dot{d}_n - H'(t)d_n\right] e^{-iE_n^0 t/\hbar}\,|n^0\rangle$$

Next, we dot each side by $\langle f_0|\,e^{iE_f^0 t/\hbar}$

$$i\hbar\dot{d}_f = \sum_n \langle f^0|H'(t)|n^0\rangle\, e^{i\omega_{fn}t}\, d_n(t)$$

$$\omega_{fn} = \frac{E_f^0 - E_n^0}{\hbar}$$

Consider when $t=0$ and the system is in the state $|i^0\rangle$

$$d_n(0) = \delta_{ni}$$

If we want to characterize $d_f(t)$ we consider orders of H'

Zeroth-Order

$$\dot{d}_f = 0$$ ← ignore RHS above expression since H' is explicit

First-Order

$$\dot{d}_f = \frac{-i}{\hbar}\langle f^0|H'(t)|i^0\rangle\, e^{i\omega_{fi}t}$$ ← uses zeroth-order d_n

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar}\int_0^t \langle f^0|H'(t')|i^0\rangle\, e^{i\omega_{fi}t'}\,dt'$$

↖ requires $|d_f(t)| \ll 1 \quad (f \neq i)$

Can plug-in first order estimate to find second-order

Consider a one-dimensional harmonic oscillator in the ground state $|0\rangle$ of the unperturbed hamiltonian at $t=-\infty$

Further consider a perturbation of the form

$$H'(t) = -e\mathcal{E}\,X\,e^{-t^2/\tau^2}$$

Find the probability that the oscillator occupies the state $|n\rangle$ at $t=\infty$

$$d_n(\infty) = \frac{i}{\hbar}\int_{-\infty}^{\infty}(-e\mathcal{E})\langle n|X|0\rangle\, e^{-t^2/\tau^2}\, e^{i\omega t}\,dt$$

$$X = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a + a^\dagger)$$

Since H' is proportional to X only $d_1(\infty) \neq 0$

$$d_1(\infty) = \frac{ie\,\mathcal{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\int_{-\infty}^{\infty} e^{-t^2/\tau^2}\, e^{i\omega t}\,dt$$

$$= \frac{ie\mathcal{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\cdot\left(\pi\tau^2\right)^{1/2}e^{-\omega^2\tau^2/4}$$

Therefore,

$$P_{0\to1} = |d_1|^2 = \frac{e^2\mathcal{E}^2\pi\tau^2}{2m\omega\hbar}\,e^{-\omega^2\tau^2/2}$$

The Sudden Perturbation

Consider a hamiltonian perturbation occuring over a small time interval

As this interval approaches 0

$$|\varphi_{after}\rangle - |\varphi_{before}\rangle = \frac{-i}{\hbar}\int_{-\varepsilon/2}^{\varepsilon/2} H(t)\,|\varphi(t)\rangle\,dt \longrightarrow 0$$

↖ on the order of ε

Instantaneous change in H produces no instantaneous change in $|\psi\rangle$

Consider a 1s electron bound to a nucleus of charge Z which undergoes β-decay by emitting a relativistic electron and changing charge to Z+1

$$\tau \simeq \frac{a_0}{Zc}$$ ← approximate time for electron to exit n=1 shell

Characteristic time for 1s electron

$$T \simeq \frac{\text{size of state}}{\text{velocity of } e^-} \simeq \frac{a_0/Z}{Z\alpha c} = \frac{a_0}{Z^2\alpha c}$$

Consequently

$$\tau/T = Z\alpha$$

For small Z we can apply the sudden approximation and conclude the state doesn't change

Not eigenstate of Z+1

The Adiabatic Perturbation

Consider a hamiltonian that changes very slowly from $H(0)$ to $H(\tau)$

Adiabatic theorem claims that if the rate of change is sufficiently slow, then the system will end in the corresponding eigenket $|n(\tau)\rangle$ of $H(\tau)$

Example 1: Particle in a Box

Consider a particle in a box of length $L(0)$

Adiabatic theorem states that if the box expands sufficiently slowly then the particle will be in the n^{th} state of $L(\tau)$ given that it was in the n^{th} state of $L(0)$

Semi-classical momentum is given by

$$p \simeq \hbar/L$$

Time to complete an oscillation is on the order

$$T \simeq \frac{L}{v} = \frac{mL}{p} \simeq \frac{mL^2}{\hbar}$$

Expansion/Contraction is slow if the length of change of box per cycle over Length is smaller than 1

$$\frac{|\Delta L|_{\text{per cycle}}}{L} \simeq \frac{\left|dL/dt\right| mL^2}{\hbar L} = \frac{m}{\hbar}\left|\frac{dL}{dt}\right| \ll 1$$

$$\frac{v_{walls}}{v_{particle}} \ll 1$$

Alternatively we can estimate T as

$$T \sim \frac{1}{\omega_{min}}$$ ↖ smallest transition frequency between i and f

$$\omega_{fi} = \frac{E_f^0 - E_i^0}{\hbar}$$

Since $E_n^0 = \frac{n^2\hbar\pi^2}{2mL^2}$ we can argue that energy differences are on the order of $\frac{\hbar^2}{mL^2}$

$$T \sim \frac{1}{\omega_{min}} \simeq \frac{mL^2}{\hbar}$$

Example 2: Perturbed Oscillator

Consider a perturbation of the following form

$$H'(t) = -e\mathcal{E}x e^{-t^2/\tau^2}$$

As $\tau \to \infty$ the system becomes adiabatic

This further implies

$$w\tau \gg 1 \quad , \quad \tau \gg 1/w$$

which aligns with semi-classical estimate

We can use the formulation of the adiabatic perturbation to recover the time-independent result

Consider a potential of the form

$$H(t) = H^0 + e^{t/\tau} H'$$

H^0 @ $t=-\infty$ $\qquad$ H^0+H @ $t=0$

The first order projection along $|m^0\rangle$ for $m \neq n$ at $t=0$ is given by

$$d_m(0) = \frac{-i}{\hbar} \int_{-\infty}^{0} \langle m^0|H'|n^0\rangle e^{t/\tau} e^{i\omega_{mn}t} dt$$

$$= \frac{(-i/\hbar)\langle m^0|H'|n^0\rangle}{1/\tau + i\omega_{mn}}$$

Letting $\tau \to \infty$ we recover

$$\langle m^0|n\rangle = \frac{\langle m^0|H'|n^0\rangle}{E_n^0 - E_m^0}$$

We define large τ s.t. $|1/\tau| \ll |\omega_{min}|$

It returns that $\tau \approx 1/\omega_{min}$ is a reasonable measure for the natural timescale of the system

If the system is near degenerate a very large τ is required to hold the system adiabatic

The Periodic Perturbation

Consider a time-dependent perturbation of the form

$$H'(t) = H' e^{-i\omega t}$$

At time t we can describe the amplitude of perturbation from $|i^0\rangle$ to $|f^0\rangle$ via

$$d_f(t) = \left(\frac{-i}{\hbar}\right) \int_0^t \langle f^0|H'|i^0\rangle e^{i(\omega_{fi}-\omega)t'} dt'$$

$$= \frac{-i}{\hbar}\langle f^0|H'|i^0\rangle \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi}-\omega)}$$

Probability consequently takes the form

$$P_{i\to f} = |d_f|^2 = \frac{1}{\hbar^2}|\langle f^0|H'|i^0\rangle|^2 \left[\frac{\sin\left((\omega_{fi}-\omega)t/2\right)}{(\omega_{fi}-\omega)\frac{1}{2}t}\right]^2 t^2$$

Notice that the function roughly goes as $\frac{\sin^2 x}{x^2}$ which is only interesting for $\Delta x \approx \pi$

We can impose this condition and find

$$|(\omega_{fi}-\omega)t/2| \lesssim \pi$$

$$E_f^0 t = (E_i^0 t + \hbar\omega t) \pm 2\hbar\pi$$

$$E_f^0 - E_i^0 = \hbar\omega\left(1 \pm \frac{2\pi}{\omega t}\right)$$

For small t the system doesn't fully process the periodic perturbation and doesn't respond accordingly

If we apply the potential for a long time

$$d_f = \lim_{T\to\infty} \frac{-i}{\hbar} \int_{-T/2}^{T/2} H'_{fi} e^{i(\omega_{fi}-\omega)t'} dt' = -\frac{2\pi i}{\hbar} H'_{fi}\, \delta(\omega_{fi}-\omega)$$

Skipping calculation of $P_{i\to f}$ and subsequent conversion to $R_{i\to f}$ we can find the average transition rate

$$R_{i\to f} = \frac{P_{i\to f}}{T} = \frac{2\pi}{\hbar}\left|\langle f^0|H'|i^0\rangle\right|^2 \delta\left(E_f^0 - E_i^0 - \hbar\omega\right)$$

Fermi's Golden Rule

18.3 Higher Orders in Perturbation Theory

Skipped

18.4 A General Discussion of Electromagnetic Interactions

Classical Electrodynamics

Lorentz force gives the response of matter in an EM field

$$F = q\left(\vec{E} + \frac{v}{c}\times\vec{B}\right)$$

Maxwell's Equations give us the response of fields to the charges

$$\nabla\cdot\vec{E} = 4\pi\rho \qquad \nabla\cdot\vec{B} = 0$$

$$\nabla\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \nabla\times\vec{B} = \frac{1}{c}\frac{\partial\vec{E}}{\partial t} + \frac{4\pi}{c}\vec{j}$$

ρ is charge density

j is current density

We relate current and charge density via the continuity equation

$$\nabla\cdot\vec{j} + \frac{\partial\rho}{\partial t} = 0$$

We introduce $\vec{A}$ s.t. $\vec{A}$ is the curl of $\vec{B}$

$$\vec{B} = \nabla\times\vec{A}$$

We can plug this definition into Maxwell's equations and recover

$$\nabla\times\left(E + \frac{1}{c}\frac{\partial A}{\partial t}\right) = 0$$

Next we apply the gradient property $\nabla\times\nabla\phi = 0$ to write the parenthetical statement as a gradient

$$E = -\frac{1}{c}\frac{\partial A}{\partial t} - \nabla\phi$$ ← Equivalent Algebraic Expression

We can apply some clever manipulations and relate A and ϕ as follows:

$$\nabla^2\phi + \frac{1}{c}\frac{\partial}{\partial t}(\nabla\cdot A) = -4\pi\rho$$

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} - \nabla\left(\nabla\cdot A + \frac{1}{c}\frac{\partial\phi}{\partial t}\right) = -\frac{4\pi\vec{j}}{c}$$

We can alter our produced potentials without changing E or B

$$A' = A - \nabla\Lambda$$

$$\phi' = \phi + \frac{1}{c}\frac{\partial\Lambda}{\partial t}$$

↖ Gauge transformations

Λ is an arbitrary function

↖ gauge parameter

Gauge transformations don't effect the potentials E and B ↙ gauge invariance

For a free EM field, we can select the Coulomb gauge such that

$$\nabla\cdot A = 0$$

$$\phi = 0$$

Under these conditions our equations of motion reduce to

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = 0$$ ← EM waves travel at speed c w/ solutions $A = A_0\cos(k\cdot r - \omega t)$

$$\nabla\cdot\dot{A} = 0$$

$$\nabla \cdot A = 0$$

These equations also tell us that electromagnetic waves are transverse

$$E = -\frac{1}{c}\frac{\partial A}{\partial t} = -\left(\frac{\omega}{c}\right) A_0 \sin(k \cdot r - \omega t)$$

$$B = \nabla \times A = -(k \times A_0)\sin(k \cdot r - \omega t)$$

} mutually perpendicular and have the same magnitude

We can thus solve for energy flow across a unit area

$$|S| = \frac{c}{4\pi}|(E \times B)| = \frac{\omega^2}{4\pi c}|A_0|^2 \sin^2(k \cdot r - \omega t)$$

$$S_{av} = \frac{\omega^2}{8\pi c}|A_0|^2$$

Chapter 19: Scattering Theory

19.1 Introduction

Scattering is a useful technique in understanding quantum forces and particles

19.2 Recapitulation of One-Dimensional Scattering and Overview

The general question is posed as: "If a beam of nearly monoenergetic particles w/ mean momentum $\langle p \rangle = \hbar k_0$ are incident from the far left on a potential $V(x)$ that tends to 0 as $|x| \to \infty$ what fraction T will get transmitted and what fraction R will be Reflected?"

If momentum space wavefunctions are sufficiently peaked then we can focus on k_0 instead of the shape

Mathematically we represent the situation as a combination of wavepackets ψ_k which are eigenfunctions of H

$$\psi_k \xrightarrow[x \to -\infty]{} Ae^{ikx} + Be^{-ikx}$$

Ae^{ikx}: incident wave; Be^{-ikx}: Reflected wave

$$\xrightarrow[x \to \infty]{} Ce^{ikx}$$

Ce^{ikx}: transmitted wave

With this form in mind we can propogate the wavefunction

time-dependence: $e^{-iEt/\hbar}$ $\quad E = \frac{\hbar^2 k^2}{2m}$

As $t \to \infty$ we can recover R and T from the norm of the wavefunction

In three dimensions we have additional considerations

ρ: impact parameter is the coordinate in the plane perpendicular to k_0

distribution is not uniform until $\rho \to \infty$ but instead when ρ is $>>$ range of the potential

Generally we are interested in solving the differential cross section

$$\frac{d\sigma(\theta,\phi)}{d\Omega} d\Omega = \frac{\text{number of particles scattered into } d\Omega/\text{sec}}{\text{number incident/sec / area in } \rho \text{ plane}}$$

We can solve this quantity

1) Finding mean momentum $\langle p \rangle = \hbar k_0$ and mean impact parameter $\langle \rho \rangle$

2) Expand wavepacket in terms of eigenfunctions of H

$$\psi_k = \psi_{inc} + \psi_{sc}$$

ψ_{inc}: incident wave; ψ_{sc}: scattered wave

3) Propogate wavefunction through time-dependence factor and expansion coefficients $a(k)$

$$e^{-iEt/\hbar} \quad \text{w/} \quad E = \frac{\hbar^2 k^2}{2m}$$

4) As $t \to \infty$ we can find the probability current density associated w/ our wavefunction

We can then integrate this quantity for the cone $d\Omega$

Since for sufficiently sharp momentum peaks probability only depends on $\hbar k_0$ and $\langle \rho \rangle$ we can represent this probability as $P(\rho, k_0 \to d\Omega)$

5) Now we can consider a beam of particles with $\eta(\rho)$ particles per second per unit area in the ρ plane

$$\eta(d\Omega) = \int P(\rho, k_0 \to d\Omega)\, \eta(\rho)\, d^2\rho$$ ← # of particles in $d\Omega$

When $\eta(\rho) = \eta$ (constant) the expression simplifies

$$\frac{d\sigma}{d\Omega}\,d\Omega = \frac{n(d\Omega)}{n} = \int P(\rho, k_0 \to d\Omega)\, d^2\rho$$

The time-dependent picture simplifies to the time-independent approach since as the wavepacket broadens it enters a steady state configuration ψ_{k_0}

↑ plane wave so ρ dependence is removed

Let's revisit the form of our wavefunction

$$\psi_k = e^{ikz} + \psi_{sc}(r, \theta, \phi)$$

While we don't know the form of ψ_{sc} we know that far from the origin it obeys the free particle equation

$$(\nabla^2 + k^2)\psi_{sc} = 0 \qquad (r \to \infty)$$

The general solution for a free particle gives us

$$\psi_{sc} \xrightarrow[r\to\infty]{} \sum_l \sum_m \left(A_l j_l(kr) + B_l n_l(kr)\right) Y_l^m(\theta, \phi)$$

Neumann functions

$$j_l(kr) \longrightarrow \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr}$$

$r \to \infty$

$$n_l(kr) \longrightarrow \frac{\cos\left(kr - \frac{l\pi}{2}\right)}{kr}$$

Since we require $\frac{A_l}{B_l} = -i$ so that our wave is outgoing $\left(\frac{e^{ikr}}{kr}\right)$

It follows that

$$\psi_{sc} \to \frac{e^{ikr}}{kr} \sum_l \sum_m (-i)^l (-B_l) Y_l^m(\theta, \phi)$$

$r \to \infty$

$$\psi_{sc} \to \frac{e^{ikr}}{kr} f(\theta, \phi)$$

Putting it together

$$\psi_k \xrightarrow[r\to\infty]{} e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r}$$

↑ Scattering Amplitude

The next step is to solve for current densities j_{sc} and j_{inc}

Since current density is only associated w/ ψ_k it includes cross terms between e^{ikz}

Notice that as $r \to \infty$ ψ_{sc} is negligible due to the $1/r$ term

$$|j_{inc}| = \left| \frac{\hbar}{2\mu i} \left(e^{-ikz} \nabla e^{ikz} - e^{ikz} \nabla e^{-ikz} \right) \right|$$

$$= \frac{\hbar k}{\mu}$$

For j_{sc} we consider in the limit as $r \to \infty$ for $\theta \neq 0$

$$j_{sc} = \frac{\hbar}{2\mu i} \left(\psi^*_{sc} \nabla \psi_{sc} - \psi_{sc} \nabla \psi^*_{sc} \right)$$

$$\nabla = e_r \frac{\partial}{\partial r} + e_\theta \frac{\partial}{r \partial \theta} + e_\phi \frac{1}{r \sin\theta} \frac{\partial}{\partial \theta}$$

As $r \to \infty$ the last two terms die off

So,

$$\frac{\partial}{\partial r} f(\theta, \phi) \frac{e^{ikr}}{r} = f(\theta, \phi)\, ik \frac{e^{ikr}}{r} + O\left(\frac{1}{r^2}\right)$$

Finally,

$$j_{sc} = \frac{e_r}{r^2} |f|^2 \frac{\hbar k}{\mu}$$

Probability flows into $d\Omega$ at

$$R(d\Omega) = j_{sc} \cdot e_r r^2 d\Omega$$

$$= |f|^2 \frac{\hbar k}{\mu} d\Omega$$

With our j_{inc}

$$\frac{d\sigma}{d\Omega} d\Omega = \frac{R(d\Omega)}{j_{inc}} = |f|^2 d\Omega$$

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

19.3 The Born Approximation (Time-Dependent Description)

For a sufficiently broad wavepacket we can estimate it via a plane wave

We can describe its behavior post scattering through the propagator

$$S = \lim_{\substack{t_f \to \infty \\ t_i \to -\infty}} U(t_f, t_i)$$

S matrix

Probability a particle enters the detector with opening angle $d\Omega$ is given by

$$P(p_i \to d\Omega) = \sum_{p_f \text{ in } d\Omega} |\langle p_f | S | p_i \rangle|^2$$ ← prob final momentum lies in cone $d\Omega$

If we evaluate S to the first order seeing V as a perturbation, we can apply Fermi's Golden Rule

$$R_{i\to d\Omega} = \frac{dP(p_i \to d\Omega)}{dt}$$

$$= \frac{2\pi}{\hbar}\left[\int_0^\infty |\langle p_f|V|p_i\rangle|^2 \delta\left(\frac{p_f^2}{2m} - \frac{p_i^2}{2m}\right) p_f^2\, dp_f\right] d\Omega$$

$$= \frac{2\pi}{\hbar} |\langle p_f|V|p_i\rangle|^2 m p_i\, d\Omega$$

Transition rate is the rate of flow of probability into $d\Omega$

Probability comes in at the rate

$$j_{inc} = \frac{\hbar k}{m}\left(\frac{1}{2\pi\hbar}\right)^3 \text{ sec}^{-1}\,\text{area}^{-1}$$

We can now find the differential cross section

$$\frac{d\sigma}{d\Omega} d\Omega = \frac{R_{i\to d\Omega}}{j_{inc}} = (2\pi)^4 m^2 \hbar^2 |\langle p_j|V|p_i\rangle|^2 d\Omega$$

$$\frac{d\sigma}{d\Omega} = \left|\frac{m}{2\pi\hbar^2}\int e^{-iq\cdot r'} V(r')\, d^3r'\right|^2$$

$\hbar q = p_f - p_i$

↖ momentum transfered to the particle

Comparing expressions for the differential cross section we can recover the form of f

$$f(\theta,\phi) = \frac{-m}{2\pi\hbar^2}\int e^{-iq\cdot r'} V(r')\, d^3r'$$

↗

Born Approximation

When we choose spherically symmetric potentials

$$f(\theta,\phi) = \frac{-m}{2\pi\hbar^2}\int e^{-iqr'\cos\theta} V(r')\, d(\cos\theta)\, d\phi'\, r'^2\, dr'$$

$$= \frac{-2m}{\hbar^2}\int \frac{\sin qr'}{q} V(r')\, r'\, dr'$$

$$= f(\theta)$$

19.4 Born Again (The Time-Independent Description)

Omitted

19.5 The Partial Wave Expansion

We can represent our function $f(\theta)$ in terms of Legendre polynomials

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

$$P_\ell(\cos\theta) = \left(\frac{4\pi}{2\ell+1}\right)^{1/2} Y_\ell^0$$

We refer to $a_\ell(k)$ as the ℓ^{th} partial wave amplitude

We can understand a_ℓ as the measure of scattering in the angular momentum ℓ sector

Result of conservation of angular momentum in a spherically symmetric potential (Each ℓ component scatters independently)

In practice only low ℓ values have significant amplitudes

For a uniform beam of particles in a cylinder of radius ρ

we find angular momentum $\hbar\ell = \hbar k\rho$

if the potential has a range of r_0 particles with $\rho > r_0$ will "miss" the target

$$\ell_{max} = k\rho_{max} \simeq kr_0$$

Next we explore how to recover $a_\ell(k)$ from a given potential $V(r)$

Consider a free particle

$$j_\ell(kr) \xrightarrow[r\to\infty]{} \frac{\sin(kr - \ell\pi/2)}{kr}$$

In our wave expansion

$$e^{ikz} \longrightarrow \frac{1}{2ik}\sum_{\ell=0}^{\infty} i^\ell (2\ell+1)\left(\frac{e^{i(kr-\ell\pi/2)}}{r} - \frac{e^{-i(kr-\ell\pi/2)}}{r}\right) P_\ell(\cos\theta)$$

$i = e^{i\pi/2}$

$$= \frac{1}{2ik}\sum_{\ell=0}^{\infty} (2\ell+1)\left(\frac{e^{ikr}}{r} - \frac{e^{-(ikr-\ell\pi)}}{r}\right) P_\ell(\cos\theta)$$

As we apply a potential we must retain the same $r\to\infty$ behavior

We can introduce a phase shift

$$R_\ell(r) = \frac{u_\ell(r)}{r} \xrightarrow[r\to\infty]{} \frac{A_\ell \sin\left[kr - \ell\pi/2 + \delta_\ell(k)\right]}{r}$$

(phase shift)

Our wavefunction now takes the form

$$\psi_k(r) \longrightarrow \sum_{\ell=0}^{\infty} A_\ell \frac{\left(e^{i(kr-\ell\pi/2+\delta_\ell)} - e^{-i(kr-\ell\pi/2+\delta_\ell)}\right) P_\ell(\cos\theta)}{r}$$

Since $V(r)$ only produces an outgoing wave, the incoming wave must match the free particle

$$A_\ell = \frac{2\ell+1}{2ik} e^{i(\ell\pi/2+\delta_\ell)}$$

Plugging into the above wavefunction

$$\psi_k(r) \longrightarrow e^{ikz} + \left[\sum_{\ell=0}^{\infty} (2\ell+1)\left(\frac{e^{2i\delta_\ell}-1}{2ik}\right) P_\ell(\cos\theta)\right]\frac{e^{ikr}}{r}$$

Therefore,

$$a_\ell(k) = \frac{e^{2i\delta_\ell} - 1}{2ik}$$

Phase shift does not alter probability currents but changes angular distribution

We refer to this shift as the partial wave S matrix

$$S_\ell(k) = e^{2i\delta_\ell(k)}$$

We can rewrite the partial wave coefficients

$$a_\ell(k) = \frac{e^{i\delta_\ell} \sin\delta_\ell}{k}$$

Consequently, f takes the form

$$f(\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{i\delta_\ell} \sin\delta_\ell\, P_\ell(\cos\theta)$$

The cross-section is now

$$\sigma = \int |f|^2 d\Omega = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell$$

↳ Orthogonality of Legendre polynomials

For a given ℓ we can consider its cross section

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell$$

Each of these cross-sections are bounded by the unitary bound

$$\sigma_\ell < \sigma_\ell^{max} = \frac{4\pi}{k^2}(2\ell+1)$$

saturated when $\delta_\ell = \frac{n\pi}{2}$ for odd n

Optical Theorem

$$\sigma = \frac{4\pi}{k}\,\mathrm{Im}\, f(0)$$ ← proof as exercise lol

Example: Hard Sphere

Consider a sphere given by the following potential

$$V(r) = \begin{cases} \infty & r < r_0 \\ 0 & r > r_0 \end{cases}$$

Inside the sphere the radial function vanishes and outside it is given by the free-particle solution

$$R_\ell(r) = A_\ell j_\ell(kr) + B_\ell n_\ell(kr)$$

Require $R_\ell(r_0) = 0$ for continuity

Continuity requirements impose

$$\frac{B_\ell}{A_\ell} = -\frac{j_\ell(kr_0)}{n_\ell(kr_0)}$$

Recalling the asymptotic forms of j_ℓ and n_ℓ

$$R_\ell(r) \longrightarrow \frac{1}{kr}\left[A_\ell \sin(kr - \ell\pi/2) - B_\ell \cos(kr - \ell\pi/2)\right]$$

$$= \frac{(A_\ell^2 + B_\ell^2)^{1/2}}{kr}\left[\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)\right]$$

$$\delta_\ell = \tan^{-1}\left(\frac{-B_\ell}{A_\ell}\right) = \tan^{-1}\left[\frac{j_\ell(kr_0)}{n_\ell(kr_0)}\right]$$

When $\ell = 0$ $\quad \delta_0 = -kr_0$

In general repulsive potentials give negative phase shifts while attractive potentials produce positive phase shifts

↑ slow particle down

Resonances

Sometimes, in the region $k = k_0$ δ_ℓ rapidly rise from $n\pi$ to $(n+1)\pi$

$$\delta_\ell = \delta_b + \tan^{-1}\left(\frac{\Gamma/2}{E_0 - E}\right)$$

↑ background phase $\simeq n\pi$

The corresponding cross section is given by ← neglecting δ_b

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell$$

↑ Breit-Wigner form

$$= \frac{4\pi}{k^2}(2\ell+1)\frac{(\Gamma/2)^2}{(E_0 - E)^2 + (\Gamma/2)^2}$$

Forms a bell shaped curve with max height σ_ℓ^{max} and half-width $\Gamma/2$

$\Gamma/2$ depends on k as $\Gamma/2 = (kr_0)^{2\ell+1}\gamma$ ← k constant

More generally σ_ℓ is found by

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\frac{[\gamma(kr_0)^{2\ell+1}]^2}{(E - E_0)^2 + [\gamma(kr_0)^{2\ell+1}]^2}$$

When $\ell \neq 0$ σ_ℓ is damped by the $k^{4\ell}$ factor except near E_0 where the denominator neutralizes it

We can think of the phenomena of resonance in terms of the S-matrix

$$S_\ell(k) = e^{2i\delta_\ell} = \frac{e^{i\delta_\ell}}{e^{-i\delta_\ell}} = \frac{1 + i\tan\delta}{1 - i\tan\delta} = \frac{E - E_0 - i\Gamma/2}{E - E_0 + i\Gamma/2}$$

Resonance corresponds to a pole in the complex plane

$$E = E_0 - i\Gamma/2 \quad \text{or} \quad k = k_0 - i\eta/2$$

$E_0 = \frac{\hbar^2 k_0^2}{2m}$ and $\Gamma = \frac{\eta\hbar^2 k_0}{m}$

Since Γ and η are small the pole is close to the real axis ← valid near $E = E_0$ on real axis

To understand what this implies let's consider bound states w.r.t the S matrix

$$R_{kl}(r) \xrightarrow[r\to\infty]{} \frac{Ae^{ikr}}{r} + \frac{Be^{-ikr}}{r}$$ } is real and positive

$$\Rightarrow \quad e^{2i\delta_l} = S_l(k) = \frac{A}{B}$$ ← outgoing amplitude, ← incoming amplitude

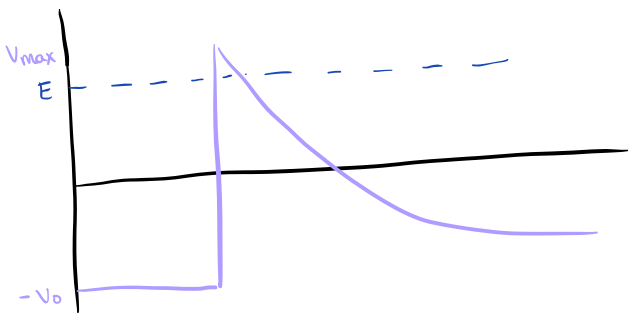
When k is complex we find bound states at $B=0$ or $S_l(k)=\infty$

Poles of $S_l(k)$ are bound states

Since bound states have time dependence we can argue that resonance does as well

$$e^{-i(E_0 - i\Gamma/2)t/\hbar} = e^{-iE_0t/\hbar}\, e^{-\Gamma t/2\hbar}$$

After a time of order $\tau = 1/\Gamma$ the bound state is gone ← particle escapes to infinity



Particle with $E>0$ will occassionally tunnel into the well and stay for $\tau = 1/\Gamma$ and then tunnel out to ∞

↑ Metastable or quasi-bound state

Chapter 20: The Dirac Equation

The dirac formulation of quantum mechanics includes relativistic considerations

20.1 The Free-Particle Dirac Equation

Consider a free particle w/ the following Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m}$$

We can apply the following substitutions to recover schrodinger's equation

$$p \to \hat{p} \qquad \mathcal{H} = i\hbar\frac{\partial}{\partial t}$$

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \frac{\hat{p}^2}{2m}|\psi\rangle$$

Einstein gives us the relativistic equivalent for the Hamiltonian

$$\mathcal{H} = (c^2p^2 + m^2c^4)^{1/2}$$

Our new version of the schrodinger equation is given by

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = (c^2\hat{p}^2 + m^2c^4)^{1/2}|\psi\rangle$$

In the momentum basis the equation takes the form

$$i\hbar\frac{\partial\psi}{\partial t} = mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \cdots\right)\psi(p,t)$$

← power series expansion of square root

Converting to the coordinate basis each $p^2 \rightarrow (-\hbar^2 \nabla^2)$

Space and time are on different orders

To account for this we can write our Hamiltonian as

$$\mathcal{H}^2 = c^2 p^2 + m^2 c^4$$

This form results in

$$\frac{\partial^2 |\psi\rangle}{\partial t^2} = \left(\frac{-c^2 \underline{P}^2}{\hbar^2} - \frac{m^2 c^4}{\hbar^2} \right) |\psi\rangle$$

In the coordinate basis

$$\left[\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 + \left(\frac{mc^2}{\hbar} \right)^2 \right] \psi = 0$$ ← Klein-Gordon Equation

This form is scalar and only applicable for spinless particles

In the Dirac formulation we assume the square rooted quantity is the perfect square of a quantity linear in $\underline{P}$

$$c^2 p^2 + m^2 c^4 = (c\alpha_x P_x + c\alpha_y P_y + c\alpha_z P_z + \beta mc^2)^2$$

$$= (c\alpha \cdot \underline{P} + \beta mc^2)^2$$

We can solve for α and β by matching the RHS and LHS

$$\alpha_i^2 = \beta^2 = 1$$

$$\alpha_i \alpha_j + \alpha_j \alpha_i = [\alpha_i, \alpha_j]_+ = 0 \quad i \neq j$$

$$\alpha_i \beta + \beta \alpha_i = [\alpha_i, \beta]_+ = 0$$

α and β are 4×4 hermetian matricies

$$\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix} \qquad \beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

σ and I are 2×2 matricies

Dirac Equation

$$\frac{i\hbar \partial |\psi\rangle}{\partial t} = (c\alpha \cdot \underline{P} + \beta mc^2) |\psi\rangle$$

Since α, β are 4×4 matricies $|\psi\rangle$ must have 4 components

↖ Lorentz Spinor

20.2 Electromagnetic Interaction of the Dirac Particle

The classical Hamiltonian for electromagnetic potentials for a particle of charge q

$$\mathcal{H} = \left[(p - qA/c)^2 + m^2 c^4 \right]^{1/2} + q\phi$$

The corresponding quantum equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \left[c\alpha \cdot (\underline{P} - qA/c) + \beta mc^2 + q\phi \right] \psi$$

Set $\phi = 0$ and consider energy eigenstates

$$\psi(t) = \psi e^{-iEt/\hbar}$$

Our quantum equation yields

$$E\psi = (c\alpha \cdot \pi + \beta mc^2) \psi$$

$$\pi = \underline{P} - \frac{qA}{c}$$ ← kinetic momentum operator

We can express ψ as two two-component spinors

$$\psi = \begin{pmatrix} \chi \\ \phi \end{pmatrix}$$

From the eigenvalue equation

$$\begin{bmatrix} E - mc^2 & -c\sigma \cdot \pi \\ -c\sigma \cdot \pi & E + mc^2 \end{bmatrix} \begin{bmatrix} \chi \\ \phi \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$(E-mc^2)\chi - c\sigma\cdot\pi\phi = 0$$
$$(E+mc^2)\phi - c\sigma\cdot\pi\chi = 0$$

We can solve the spinors in terms of eachother

$$\phi = \left(\frac{c\sigma\cdot\pi}{E+mc^2}\right)\chi$$

At low velocities we can write the denominator as

$$E+mc^2 = E_s + 2mc^2$$

$E_s = E-mc^2$ is the energy of the schrodinger equation

$$E_s << 2mc^2 \quad \text{so} \quad E+mc^2 \simeq 2mc^2$$

The numerator is on the order mvc, so

$$\left|\frac{\phi}{\chi}\right| \cong \frac{1}{2}\left(\frac{v}{c}\right) << 1$$

(small component / Large component)

Continuing in the non-relativistic domain

$$\phi = \frac{\sigma\cdot\pi}{2mc}\chi$$

With this in hand we can plug into our expressions for the spinors

$$E_s\chi = c\sigma\cdot\pi\phi = \frac{(\sigma\cdot\pi)(\sigma\cdot\pi)}{2m}\chi \leftarrow \text{Pauli Equation}$$

Using the following identities

$$\sigma\cdot A\sigma\cdot B = A\cdot B + i\sigma A\times B \quad \text{and} \quad \pi\times\pi = \frac{iq\hbar}{c}B$$

$$\left[\frac{(p-qA/c)^2}{2m} - \frac{q\hbar}{2mc}\sigma\cdot B\right]\chi = E_s\chi$$

spin ½ particle with $g=2$

Hydrogen Fine Structure

We can apply the dirac equation when

$$V = e\phi = -e^2/r \leftarrow \text{electron in the hydrogen atom}$$

Our coupled equations take the form

$$(E-V-mc^2)\chi - c\sigma\cdot P\phi = 0$$
$$(E-V+mc^2)\phi - c\sigma\cdot P\chi = 0$$

We can express ϕ as

$$\phi = (E-V+mc^2)^{-1}c\sigma P\chi$$

Plugging this into our second equation

$$(E-V-mc^2)\chi = c\sigma\cdot P\left[\frac{1}{E-V+mc^2}\right]c\sigma\cdot P\chi$$

If we use the non-relativistic estimate $E-V+mc^2 \to 2mc^2$

$$E_s\chi = \left[\frac{P^2}{2m}+V\right]\chi$$

← non-relativistic schrodinger equation

To see the fine structure we must go to order $(V/c)^4$ in $(E-V+mc^2)^{-1}$

$$\frac{1}{E-V+mc^2} = \frac{1}{2mc^2+E_s-V} = \frac{1}{2mc^2}\left(1+\frac{E_s-V}{2mc^2}\right)^{-1}$$
$$\simeq \frac{1}{2mc^2}\left(1-\frac{E_s-V}{2mc^2}\right) = \frac{1}{2mc^2} - \frac{E_s-V}{4m^2c^4}$$

The eigenvalue equation now takes the form

$$E_s \chi = \left[\frac{p^2}{2m} + V - \frac{\sigma \cdot p \, (E_s - V) \, \sigma \cdot p}{4m^2 c^2} \right] \chi$$

Still require $E_s - V$ to order v^2/c^2

Remainder skipped

20.3 More on Relativistic Quantum Mechanics

Relativity allows for particle production given sufficient energy

Quantum Mechanics allows arbitrarily large energy violations over short periods

The marriage of the two ideas produces issues in the form of negative energy solutions

Consider the Free-particle Dirac Equation

$$i \frac{\partial \psi}{\partial t} = (\alpha \cdot p + \beta m) \psi \qquad (\hbar = c = 1)$$

Plane wave solutions take the form

$$\psi = w(p) \, e^{i(p \cdot r - Et)}$$

↑ spinor w/ no spacetime dependence

The planewave satisfies

$$Ew = (\alpha \cdot p + \beta m) w$$

$$\begin{bmatrix} E-m & -\sigma \cdot p \\ -\sigma \cdot p & E+m \end{bmatrix} \begin{bmatrix} \chi \\ \phi \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

Particle at rest ↘

If $p = 0$ the equation decouples

$(E-m)\chi = 0 \rightarrow E = m$ ← particle at rest has energy m and described by arbitrary spinor

$(E+m)\phi = 0 \rightarrow E = -m$

When $p \neq 0$

$$\chi = \frac{\sigma \cdot p}{E-m} \phi$$

$$\phi = \frac{\sigma \cdot p}{E+m} \chi$$

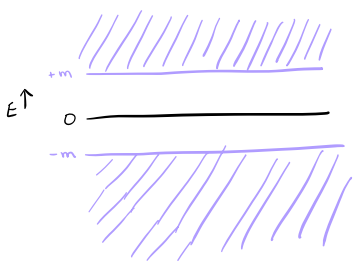
Equivalently,

$$\frac{p^2}{E^2 - m^2} = 1$$

$$E^2 = p^2 + m^2$$

$$E = \pm \sqrt{p^2 + m^2}$$

Continuous bands of energy from $+m$ to ∞ and from $-m$ to ∞



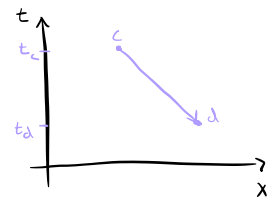
Dirac postulated that all negative-energy states were occupied by an unobservable sea of negative electrons

Holes in the "electron sea" are actually just positrons

Dirac's solution only works for particles w/ spin due to pauli's exclusion principle

Feynman proposed that negative energy particles travel backwards through time

Consider a particle that is created at space time c and travels backward to d



positron created at d and destroyed at c

As an observer who travels forward through time we see

1) $t < t_d$: Nothing
2) $t = t_d$: $-|E|$ and charge e^- are destroyed
   World goes up by E and e
3) $t = c$: Negative energy is created, charge e^- is created
   Destroys positron
4) $t > t_c$: Nothing

We can represent anti-particle particle pair addition as scattering through time under this scheme

We can write the schrodinger propagator as

$$U_s = \sum_n \varphi_n(x)\,\varphi_n^*(x')\,e^{-iE_n(t-t')}$$

Each term satisfies the schrodinger equation so we have

$$\left(i\frac{\partial}{\partial t} - H\right) U_s = 0$$

U_s can also propagate backwards so we add the restriction

$$G_s = \theta(t-t')\,U_s$$

$$\left(i\frac{\partial}{\partial t} - H\right) G_s = \left[i\frac{\partial}{\partial t}\,\theta(t-t')\right] \sum_n \varphi_n(x)\,\varphi_n^*(x')\,e^{-iE_n(t-t')}$$

$$= i\,\delta(t-t')\,\delta^3(x-x')$$
$$= i\,\delta^4(x-x') \qquad x = (t, x)$$

In Dirac Theory, the propagator behaves similarly

$$\left(i\frac{\partial}{\partial t} - H^0\right) G_D = i\,\delta^4(x-x')$$

H^0: dirac free-particle hamiltonian

$$G_D = \theta(t-t')\left(\sum_{n^-} + \sum_{n^+}\right)$$

n^-, n^+: pos/neg energy eigenfunctions

Since G_D isn't unique we can subtract any solution for all times

Feynman Propagator:

$$G_F^0(x,x') = \theta(t-t') \sum_{n^+} - \theta(t'-t) \sum_{n^-}$$

↑ subtracting all negative-energy solutions for all times

This propagator propagates positive solutions forward and negative solutions backward