The following lecture notes for PHYS 414, Quantum Mechanics II, are the sole property of Glenn Agnolet, Physics Department, Texas A&M University. They are not to be copied or distributed without the consent of the author.
Electromagnetic Radiation

Consider the normal modes for electromagnetic waves within a metal box. Within the box $\nabla \cdot E = 0$ (no change) and the $E$ and $B$ fields must satisfy the wave equation. At the surface of the walls the tangential component of $E$ must vanish (infinite conductivity).

The normal modes for a cube of side length $L$ can be written as:

$$E^{(1)}(\mathbf{r}) = \frac{1}{k} \mathbf{\hat{r}} \times \left\{ \hat{z} \cos(k_x x) \cos(k_y y) \sin(k_z z) \right\} e^{-i\omega t}$$

$$= \left[ -\hat{z} \left\{ \frac{k_y}{k} \cos(k_x x) \sin(k_y y) \sin(k_z z) \right\} 
\quad + \hat{y} \left\{ \frac{k_y}{k} \sin(k_y y) \cos(k_x x) \sin(k_z z) \right\} \right] e^{-i\omega t}$$

AND:

$$E^{(2)}(\mathbf{r}) = \frac{1}{k} \mathbf{\hat{z}} \times (\nabla \times \left\{ \hat{z} \sin(k_x x) \sin(k_y y) \right\}) e^{-i\omega t}$$

where $k^2 = k_x^2 + k_y^2 + k_z^2 = \omega^2 / c^2$ and to satisfy the boundary conditions:

$$k_x = \frac{\pi n_x}{L}, \quad k_y = \frac{\pi n_y}{L}, \quad k_z = \frac{\pi n_z}{L} \quad n_x, n_y, n_z = 0, 1, 2, 3, 4, \ldots$$

Thus there are two unique modes which are degenerate in frequency. Each is uniquely determined by specifying $k_x, k_y$ and $k_z$.

To count the number of modes we note that each mode can be indicated by its position in $k$-space (i.e. $k_x, k_y, k_z$) each point indicating the 2 degenerate modes.

Since the density of points is $1$ per $(\pi L)^3$ the number of modes with frequency less than $\omega$ is just the volume of the 1st octant in $k$-space divided by $(\pi L)^2$ (times 2 for the degeneracy).
\[ N = \frac{2 \cdot \frac{1}{2} \left( \frac{4}{3} \pi k^3 \right) \cdot \left( \frac{1}{\lambda} \right)^3}{3} \cdot \frac{\pi L^3 k^3}{3 \pi^3} \cdot \frac{k^3}{3 \pi^2} \cdot \frac{L^3 \omega^3}{3 \pi^3 C^3} \]

The number of modes per unit volume with frequency between \( \omega \) and \( \omega + d\omega \) is then

\[ dN = \rho(\omega) d\omega = \frac{\omega^2 d\omega}{\pi^2 C^3} \]

Because of the complexity of the \( E \) fields of the normal modes we usually see this argument using periodic boundary conditions.

In free space we expect solutions for \( E \) to have the form

\[ E = E_0 e^{i(k \cdot r - \omega t)} \]

with \( E_0 \perp k = (k_x, k_y, k_z) \) and \( k^2 = \omega^2 / c^2 \).

To impose periodic boundary conditions we require that

\[ E(x+L, y+L, z+L) = E(x, y, z) \text{ for arbitrary } x, y, z. \]

Upon substituting this implies that

\[ e^{i k_x L} = 1, \quad e^{i k_y L} = 1, \quad \text{and } e^{i k_z L} = 1 \]

or

\[ k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad \text{and } k_z = \frac{2\pi n_z}{L}. \]

As before each state is uniquely determined by the \( k \) values only now we allow the \( n \) values to take on both positive and negative values. (This allows forward and backward propagating waves.)

Thus the number of modes with frequency less than \( \omega \) becomes..
\[ N = \left[ \frac{\frac{4}{3} \pi k^3}{(2\pi L)^3} \right] = \frac{\frac{4}{3} k^3}{6\pi^2} \]

which is off by a factor of 2 from our previous result!

But we forgot to include the degeneracy due to the orientation of the B field. (Two independent polarizations).

Thus the density of states is the same as before:

\[ dN = \beta(\omega) d\omega = \frac{\omega^2 d\omega}{\pi^2 c^3} \]

From statistical mechanics the probability of a mode being occupied depends upon the temperature:

\[ n = \frac{\omega^2 d\omega}{\pi^2 c^3} \left[ e^{\frac{\omega}{kT}} - 1 \right]. \]
Einstein coefficients.

Place some atoms within the box. Each atom can be in either of two
states. One has energy $E_1$; the other $E_2$, with $E_2 > E_1$ and $E_2 - E_1$.

At some temperature $T$, the electromagnetic waves (or photons) should
be able to stimulate transitions between the two states of the atom. In fact
the radiation field must be in thermal equilibrium with the atom. Assume there are
$N_1$ atoms in state $E_1$ and $N_2$ atoms in state $E_2$.

One can consider three processes.

1. The atom can de-excite from the state $E_2$ to the state $E_1$ spontaneously.
   If $A_2 \rightarrow 1$ is the probability per unit time that the atom spontaneously
de-excite then

   \[ N_2 A_2 \rightarrow 1 \] represents the number of atoms per unit time which
   spontaneously de-excite.

2. The atom can also de-excite due to the perturbation of the electromagnetic
   field. Taking $C_2 \rightarrow 1$ to be the probability per unit time that the atom
   de-excites due to the presence of a single photon, then the total rate of
   atoms which are stimulated to de-excite are

   \[ N_2 \int C_2 \rightarrow 1 N(w) f(kw - kw_0) dw = N_2 C_2 \rightarrow 1 N(w_0) \]

   where $N(w)dw$ is the number density of photons with frequency between
   $w$ and $w + dw$.

3. Similarly the number of atoms per unit time which are excited
   and absorb a photon can be written as

   \[ N_1 \int B_1 \rightarrow 2 N(w) f(kw - kw_0) dw = N_1 B_1 \rightarrow 2 N(w_0) \]

If we require a balance between the rate of exiting atoms and
de-exiting atoms, (detailed balance for thermal equilibrium) then
\[ N, B_1 \rightarrow 2 N(\omega_0) = N, A_2 \rightarrow 1 + N, C_2 \rightarrow 1 N(\omega_0) \]

or

\[ N(\omega_0) = \frac{A_2 \rightarrow 1}{(N/N_B) B_1 \rightarrow 2 - C_2 \rightarrow 1} = \frac{A_2 \rightarrow 1 / B_1 \rightarrow 2}{(N/N_B) - C_2 \rightarrow 1 / B_1 \rightarrow 1} \]

Now the numbers of \( N_1 \) and \( N_2 \) atoms is given by thermal statistical mechanics as

\[ N_1 = N_0 e^{-E_1/kT} \quad \text{and} \quad N_2 = N_0 e^{-E_2/kT} \]

or \( N_1/N_2 = e^{(E_2-E_1)/kT} \)

or \( N_1/N_2 = e^{\hbar \omega_0/kT} \)

Substituting we find

\[ N(\omega_0) d\omega = \frac{A_2 \rightarrow 1 / B_1 \rightarrow 2}{e^{\hbar \omega_0/kT} - C_2 \rightarrow 1 / B_1 \rightarrow 2} d\omega \]

which looks very much like our previous expression

\[ \frac{\hbar^2 d\omega}{\kappa^2 c^2} = \frac{1}{\left[ e^{\hbar \omega/kT} - 1 \right]} \]

if we identify \( C_2 \rightarrow 1 = B_1 \rightarrow 2 \) (That the transition rate probability are equal seems consistent with our results from time-dependent perturbation theory (for harmonic potentials), and \( A_2 \rightarrow 1 / B_1 \rightarrow 2 = \frac{\omega^2}{\kappa^2 c^2} \)

Now this is interesting by the requirement of thermal equilibrium the spontaneous rate of de-excitation can be calculated from the absorption coefficient!
Let us now return to the calculation of the electromagnetic modes within the box. Again using the periodic boundary conditions, we saw that the modes have the form of

\[ E \sim e^{i(k \cdot r - \omega t)}. \]

Let us start by writing down the appropriate vector potential.

\[ A = \hat{e} a \cos(k \cdot r - \omega t) \]

- here we use the real part since the phase is important in Q.M. and our Hamiltonian should be real

\[ E = -\frac{\partial A}{\partial t} = -\hat{e} a \omega \sin(k \cdot r - \omega t) \]

\[ B = \nabla \times A = -\hat{e} \times \nabla [a \cos(k \cdot r - \omega t)] + a \cos(k \cdot r - \omega t) \cdot \hat{e} \]

\[ B = -a \sin(k \cdot r - \omega t) \cdot (k \times \hat{e}) \]

Note: to correspond to an electromagnetic wave \( B \) must be \( \perp \) to \( E \) and so \( k \perp \hat{e} \) or \( k \cdot \hat{e} = 0 \).

The energy density of these waves within our box is given by

\[ \frac{1}{2} \varepsilon \varepsilon_0 E^2 + \frac{1}{2} \mu_0 B^2 = \frac{1}{2} \varepsilon_0 a^2 \omega^2 \sin^2(k \cdot r - \omega t) + \frac{1}{2} \mu_0 k^2 a^2 \sin^2(k \cdot r - \omega t) \]

Since \( \omega = ck \)

\[ \text{Taking the time average we get} \quad \frac{\varepsilon_0 a^2 \omega^2}{2}. \]
The number of photons per unit volume then becomes
\[ \frac{1}{2} \frac{E_0 a^2 w^2}{\hbar \omega} = \frac{1}{2} \frac{E_0 a^2 \omega}{\hbar} \]
Thus we assign a value to \( a \) to correspond to 1 photon per unit volume.
\[ a = \sqrt{\frac{2\hbar}{E_0 \omega}} \]

For time dependent perturbation theory we found that for a harmonic potential \( \Phi_i = V(r) \cos \omega t \)
\[ |\alpha_i f|^2 = \frac{1}{k^2} \frac{V_i f^2 s_m^2 \left( \frac{w - w_i f}{2} \right)^2}{(w - w_i f)^2} \]
\[ t w_i f = E_f - E_i \]
and that the corresponding Hamiltonian rate is
\[ \frac{d\rho}{dt} = \frac{\hbar}{2k} |V_i f^2 \rho (E_i + \hbar \omega) \]
\[ \rho = \frac{\hbar}{2k} |<E_i V(r) | E_i>|^2 \rho(E_f) \]
In our present situation what is the perturbation corresponding to \( V(r) \)?

Since \( \Phi_i = \frac{1}{2m} (p - \mathbf{A})^2 + g \phi \quad \nabla \cdot \mathbf{A} = 0 \)
\[ = \frac{1}{2m} \left[ p^2 - 2g \mathbf{A} \cdot \mathbf{p} + g^2 \mathbf{A}^2 \right] + g \phi \]
Now \( \phi \) is the electrostatic potential which determines the energy states of the system \( (g \phi = \frac{e^2}{4\pi\epsilon_0} \) in the hydrogen atom).
When we consider the results for a single photon, then we can ignore the \( A^2 \) term in deference to the linear terms and so

\[
\psi(E) = -\frac{\hbar A \cdot p}{m} = -(\frac{\hbar}{m}) \cos(k \cdot r - \omega t) \langle \hat{e} \cdot p \rangle
\]

As before, we can write this into two terms.

\[
\psi(E) = -\left(\frac{\hbar A}{m}\right) \left\{ e^{i(k \cdot r - \omega t)} + e^{-i(k \cdot r - \omega t)} \right\} \langle \hat{e} \cdot p \rangle
\]

which correspond to stimulated emission or absorption of a photon. The transition rate then becomes (of the emission term for example),

\[
\Gamma = \frac{\hbar}{2\pi} \left(\frac{\hbar A}{m}\right)^2 |< E_f | e^{i(k \cdot r \cdot \hat{e} \cdot p)} | E_i >|^2 \rho(E_f)
\]

but \( A^2 = \frac{2\hbar}{E_0 \omega} \) and assume \( A = -e \) we have

\[
\Gamma = \frac{\hbar^2}{m^2 \omega} \left(\frac{e^2}{4\pi \hbar^2} \right) |< E_f | e^{i(k \cdot r \cdot \hat{e} \cdot p)} | E_i >|^2 \rho(E_f)
\]

Now when we go to calculate the density of states we must in principle count the total number of final photon-atom states. However, since the state of the recoiling atom is completely specified by the direction and momentum of the photon we need only count the number of photons emitted in a given direction.

When we did our original counting we did not care on which direction the waves were traveling. But since the direction of the wave is specified by \( k_x, k_y, k_z \), the number of photons going in the \( k \) direction with energy between \( E_0 \) and \( E_0 + \hbar \omega \) is
Number of modes with energy less than $E$

$$N = \frac{L^3 \omega^3}{3\pi^2 c^3} = \frac{L^3 E^3}{3\pi^2 c^3 k^3}$$

The number of modes per unit volume with $E < E_i < E + dE$

$$\frac{E^2 dE}{\pi^2 c^3 k^3}$$

The number of modes per unit volume with $E < E_i < E + dE$ and have $k_i$ within the solid angle $d\Omega$

$$\frac{E^2 dE d\Omega}{4\pi^3 c^3 k^3}$$

The density of modes of one polarization with $E < E_i < E + dE$ and $0 \leq k_i$ within $d\Omega$

$$\frac{E^2 dE d\Omega}{8\pi^3 c^3 k^3}$$

Using this restricted density of states we have.

$$d\tilde{Q} = \frac{4\pi^2}{m^2 w} \left( \frac{e^2}{4\pi\epsilon_0} \right) \left| \left< E_f \left| e^{ik\cdot r} (\hat{e} \cdot \hat{p}) \right| E_i \right> \right|^2 \frac{E^2}{8\pi^3 c^3 k^3} d\Omega$$

or if $tw = E$.

$$d\tilde{Q} = \frac{\omega}{2m^2 \pi c^3 k} \left( \frac{e^2}{4\pi\epsilon_0} \right) \left| \left< E_f \left| e^{ik\cdot r} (\hat{e} \cdot \hat{p}) \right| E_i \right> \right|^2 d\Omega.$$
Approximation:

\[ \gamma = \frac{\omega}{2\pi \hbar e^3} k \left( \frac{e^2}{\lambda} \right) \left| \langle E_f | e^{i \hbar \mathbf{p}} (\mathbf{e} \cdot \mathbf{p}) | E_i \rangle \right|^2 d\Omega. \]

For atomic systems, the wave length corresponding to a transition between two states \( E_i, E_f \) is much longer than the size of the atom itself.

\[ \lambda \gg \text{"size of atom"} \]

Since \( |E_f\rangle \) and \( |E_i\rangle \) are only non-zero for \( |\mathbf{k}\rangle \) within the exponential, we can take \( \langle \mathbf{e} \cdot \mathbf{p} | \mathbf{k} \rangle \) small. (Actually, only within the matrix element can one say it is small.)

Therefore, we can write

\[ \langle E_f | e^{i \hbar \mathbf{p}} (\mathbf{e} \cdot \mathbf{p}) | E_i \rangle = \langle E_f | (1 + i \mathbf{e} \cdot \mathbf{k} + \frac{(i \mathbf{e} \cdot \mathbf{k})^2}{2} \cdots ) (\mathbf{e} \cdot \mathbf{p}) | E_i \rangle \]

\[ \approx \langle E_f | \mathbf{e} \cdot \mathbf{p} | E_i \rangle + \mathcal{O}(\mathbf{k} \mathbf{p}) \]

Let us consider the first term in the expansion:

\[ \langle E_f | \mathbf{e} \cdot \mathbf{p} | E_i \rangle = \mathbf{e} \cdot \langle E_f | \mathbf{p} | E_i \rangle \]

since \( \mathbf{e} \) has no connection to the eigenstates \( |E_i\rangle \) or \( |E_f\rangle \).

Now note that

\[ \langle E_f | \mathbf{p} | E_i \rangle = \frac{\langle f | E_f \mathbf{r} - \mathbf{r} E_i | i \rangle}{E_f - E_i} = \frac{\langle f | [\mathbf{h}, \mathbf{r}] | i \rangle}{E_f - E_i} \]

but \[ [\mathbf{h}, \mathbf{r}] = \left[ \frac{\mathbf{p}^2}{2m}, \mathbf{r} \right] = \frac{\hbar \mathbf{W}}{2m} [\mathbf{p}, \mathbf{r}] + [\mathbf{p}, \mathbf{r}] \frac{\mathbf{p}}{2m} \]

\[ = \frac{2\mathbf{p}}{2m} (-i\mathbf{k}) = -i \frac{\hbar \mathbf{p}}{m}. \]
and so \( \langle E_f | v | E_i \rangle = \frac{i}{\hbar} \langle E_f | p | E_i \rangle \) and
\[
\langle E_f \mid \hat{e} \cdot p \mid E_i \rangle \mid^2 = \hbar^2 \omega^2 \mid \hat{e} \cdot \langle E_f \mid v \mid E_i \rangle \mid^2
\]
so that
\[
d\hat{\Omega}_{E_i} = \left( \frac{e^2}{4\pi \hbar} \right) \frac{\omega^3}{2\pi c^3 k} \mid \hat{e}_i \cdot \langle E_f \mid v \mid E_i \rangle \mid^2 d\omega
\]
where I have explicitly put in that this is the transition rate for a specific \( \hat{e}_i \) polarzation.

To compare this expression for the transition rate to a similar formula for the classical power radiated from an oscillating dipole we need to integrate over the two possible values of the polarization.

To compute \( d\hat{\Omega}_{E_i} \) we must integrate over the internal coordinates corresponding to the "atom". However for simplicity we may choose our axis to conform to the vectors \( \hat{k} \), \( \hat{e}_1 \), and \( \hat{e}_2 \).

Consider our \( z \)-axis to align along \( \hat{k} \) and the \( x \) and \( y \) axes to lie along \( \hat{e}_1 \) and \( \hat{e}_2 \).

Then \( \langle E_f \mid v \mid E_i \rangle = \langle E_f \mid x \mid E_i \rangle \hat{x} + \langle E_f \mid y \mid E_i \rangle \hat{y} + \langle E_f \mid z \mid E_i \rangle \hat{z} \)
looks like a vector; but remember \( \langle E_f \mid x \mid E_i \rangle \) will in general be complex. We can define a vector in space however by taking the square root of their absolute values.

\[
\hat{\mathbf{V}} = \left[ 1 \langle E_f \mid x \mid E_i \rangle^2 \right]^{\frac{1}{2}} \hat{x} + \left[ 1 \langle E_f \mid y \mid E_i \rangle^2 \right]^{\frac{1}{2}} \hat{y} + \left[ 1 \langle E_f \mid z \mid E_i \rangle^2 \right]^{\frac{1}{2}} \hat{z}
\]
\[
= M_x \hat{x} + M_y \hat{y} + M_z \hat{z}
\]
which will point in some direction with respect to $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$.

Calculating the transition rates then

$$d\hat{P}_{\hat{e}_1} = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{\omega^3}{2\pi c^3 k} M_x^2 \, d\Omega$$

and

$$d\hat{P}_{\hat{e}_2} = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{\omega^3}{2\pi c^3 k} M_y^2 \, d\Omega$$

Since these two polarizations are independent we add the transition rates to obtain the total transition rate:

$$d\hat{P} = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{\omega^3}{2\pi c^3 k} (M_x^2 + M_y^2) \, d\Omega$$

But $\sqrt{M_x^2 + M_y^2}$ is just the projection of the length of $\hat{v}$ onto the $x,y$ plane.

and so

$$M_x^2 + M_y^2 = \sin^2 \theta \frac{v^2}{c^2} \hat{\hat{v}}$$

Note: very bad notation!

and

$$d\hat{P} = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{\omega^3}{2\pi c^3 k} \sin^2 \theta \frac{v^2}{c^2} \, d\Omega$$

If we multiply by the energy/photon ($\hbar \omega$) we get the total power radiated into the solid angle:

$$\hat{P} = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{\hbar \omega}{2\pi c^3} \sin^2 \theta \frac{v^2}{c^2} \, d\Omega$$

Note: all $k$'s have vanished from our answer suggesting we can calculate this classically!
In fact the angular dependence is that of a classical radiating dipole

\[
\begin{align*}
\text{direction of } \mathbf{d} &= \int x' \rho(x') \, d^3x' \\
\rho(x') &= \text{change density}
\end{align*}
\]

Then the power emitted into the solid angle \(d\Omega\) becomes

\[
d\dot{Q} = \frac{\omega^4}{8\pi (\omega \tau_0)^2} c^3 \left| (\mathbf{n} \times \mathbf{d}) \times \mathbf{n} \right|^2 \, d\Omega
\]

where \(\mathbf{n}\) is the direction of \(d\Omega\).

Comparing our two expressions we see that the identification becomes

\[
|d\mathbf{d}|^2 = |2\varepsilon \langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^2
\]

where \(|\langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^2\) again implies

\[
|\langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^2 = |\langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^4 + |\langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^2 + |\langle \mathbf{E}_f | \mathbf{v} | \mathbf{E}_i \rangle|^2
\]

Note: The extra factor of 2 is from the use of real potentials (see Jackson Chapter 9. (9.1))

Can this oscillating dipole be seen quantum mechanically? Yes!

Consider as an example the system in the ground state of an infinite potential well.

\[
\psi_i = \sqrt{2L} \sin \frac{\pi x}{L} e^{-i\mathbf{E}_i t/\hbar} = \psi_i(x) e^{-i\mathbf{E}_i t/\hbar}
\]
If a photon passes an atom then the vector potential will cause a
perturbation of the form (in the dipole approximation).

\[-\frac{2a}{m} \cos \omega t \hat{e} \cdot \mathbf{p}_x\]

for some time \( \Delta \). After time \( \Delta \) the Hamiltonian will again be the
original \( H_0 \).

If \( k\Delta = E_2 - E_1 \), then after time \( \Delta \) there will be a significant
mixing of the 1st excited state to the original ground state.

\( a_2 \neq 0 \) (but time independent).

The total state of the system will then be

\[ \Psi = \Psi_1(x) e^{-iE_1t/k} + a_2 \Psi_2(x) e^{-iE_2t/k} \]

The total probability density \( |\Psi|^2 \) has the form:

\[ |\Psi|^2 = |\Psi_1|^2 + 2a_2 \Psi_1^\dagger \Psi_2 + 2 \text{Re} \ a_2^* \Psi_1^\dagger \Psi_2 e^{i(E_2-E_1)t/k} \]

\text{time independent} \quad \text{oscillates in time.}

For illustration if \( a_2 = 1 \) then the second term will oscillate as \( \cos \omega t \)
so seen on the next page.

If \( \Psi \) represents a charged particle you will see an effective
oscillation change.

\[ 0 \quad \longleftrightarrow \quad 0 \]

\[ 0 \quad \longleftrightarrow \quad 0 \]

If \( \Psi_1 \) represents a charged particle you will see an effective
oscillation change.
\[ |4_1|^2 \]

\[ |4|^2 \quad t = 0 \]

\[ t = \frac{\pi}{2} = \left(\frac{\pi}{2}\right) \frac{\tau}{(E_2 - E_1)} \]

\[ |4|^2 \quad t = \frac{\pi}{2} = \pi \frac{\tau}{(E_2 - E_1)} \]

\[ \text{charge oscillates with frequency } \omega. \]
- CONNECTION WITH EINSTEIN COEF.

The coefficient $B_{1 \rightarrow 2}$ is related to the transition rate for the system making a transition from state 1 to state 2 (absorbing a photon).

In particular $B_{1 \rightarrow 2} N(\omega)$ is the total transition rate. (where $N(\omega) = (\omega^2/\kappa^2 c^3)$).

Our calculate transition rate $d\mathcal{P} = (\frac{e^2}{4\pi\epsilon_0}) \frac{\omega^3}{2\pi c^3 \kappa} \sin^2 \theta \ 1\Omega \ d\Omega$ can be integrated to give us the total rate.

$$B_{1 \rightarrow 2} N(\omega) = \int d\mathcal{P} = \int d\Omega \ (\frac{e^2}{4\pi\epsilon_0}) \frac{\omega^3}{2\pi c^3 \kappa} \sin^2 \theta \ 1\Omega \ d\Omega$$

$$= (\frac{e^2}{4\pi\epsilon_0}) \left( \frac{\omega^3}{2\pi c^3 \kappa} \right) 1\Omega^2 \int_0^{2\pi} \int_0^{\pi} \sin \theta \ d\theta \ d\phi \ \sin^2 \theta$$

Note: Since $|\psi_1(\mathbf{r},t)|^2 = (\frac{3}{8\pi}) \sin^2 \theta$, we have

$$\int d\Omega \ \sin^2 \theta = (\frac{5\pi}{3})$$

$$B_{1 \rightarrow 2} N(\omega) = \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{4}{3} \frac{\omega^3}{c^3 \kappa} \right) 1\Omega^2$$

$$B_{1 \rightarrow 2} = \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{4}{3} \frac{\omega^3}{c^3 \kappa} \right) 1\Omega^2$$

The spontaneous transition rate is therefore

$$A_{2 \rightarrow 1} = \frac{\omega^2}{\kappa^2 c^3} \cdot B_{1 \rightarrow 2} = \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{4}{3} \frac{\omega^3}{c^3 \kappa} \right) 1\Omega^2$$

$A_{2 \rightarrow 1}$ is the spontaneous transition rate for decay. If there were $N$ atoms in the excited state then the number decaying per unit time would be

$$dN = -A_{2 \rightarrow 1} N \ d\tau \quad \text{or} \quad N(t) = N(t_0) e^{-\left(A_{2 \rightarrow 1}\right) \tau}$$
or \( N(t) = N(t=0) \left( \frac{1}{2} \right)^{t/\tau_\text{H}} \) where \( \tau_\text{H} = \frac{1}{A_2 \to 1} \) so the half-life time

The above relations should equally apply to a single atom. In fact the electric field of the emitted radiation should have the following form:

\[
E(t) = e^{i \omega t} e^{-t/\tau_\text{H}} = e^{i \omega t} e^{-t/2A_2 \to 1}
\]

(the factor of 2 is included since \( A_2 \to 1 \) is characteristic time for the energy).

Taking the Fourier transform to get the profile of this wave in frequency space:

\[
f(\omega) = \int_0^\infty dt \, e^{-i \omega t} E(t) = \int_0^\infty dt \, e^{i \omega t - t/2A_2 \to 1}
\]

\[
f(\omega) = \frac{1}{i(\omega_0 - \omega) - \frac{1}{2A_2 \to 1}}.
\]

The intensity as a function of frequency is then

\[
I(\omega) \propto |f(\omega)|^2 = \frac{1}{(\omega_0 - \omega)^2 + \left(\frac{1}{2A_2 \to 1}\right)^2}
\]

\[
I(\omega)
\]

\[
\Delta \omega = \frac{1}{2A_2 \to 1}
\]

Spectral line width \( \Delta \lambda = \frac{\lambda \Delta \omega}{\omega} \).
Note: one could have also use the measurement uncertainty principle to obtain the line width.

Since the characteristic life-time of the state is \( \tau = \frac{1}{A_{2\rightarrow1}} \), then the uncertainty in the energy of the state must be

\[ \Delta E \geq \hbar k \]

and so the resulting photon must have a spectral width of

\[ \Delta \omega \sim \frac{1}{\tau} \]
Selection Rules.

Assume \( H \) commutes with \( L^2 \) and \( L_z \) so that both have good quantum numbers. In each state \( E_i \), \( E_f \) has a unique angular momentum state \( |l, m_i \rangle \).

Remember the transition rule depends on the matrix element \( \hat{e} \cdot \langle E_f | l \rangle | E_i \rangle \).

1. \( \hat{e} = \hat{z} \)

Consider \( \langle E_f | L_z, z \rangle | E_i \rangle \)

Since \( L_z = x p_y - y p_x \), \([L_z, z] = 0\) and so

\[
\langle E_f | [L_z, z] | E_i \rangle = 0 = \langle E_f | L_z \rangle (L_z z - z L_z) | E_i \rangle
\]

\[
0 = \langle E_f \hat{q}_f m_f | (L_z z - z L_z) | E_i \rangle \langle E_i | \rangle
\]

\[
0 = \hat{k} (m_f - m_i) \langle E_f \hat{q}_f m_f | L_z | E_i \rangle \langle E_i | \rangle
\]

Therefore either \((m_f - m_i) = 0\) or the matrix element vanishes. So for states with \((m_f - m_i) \neq 0\) dipole transitions are not possible.

Conclusion: Selection rule \( \hat{e} = \hat{z} \quad \Delta m = 0 \)

2. \( \hat{e} = \hat{x} \pm i \hat{y} = \hat{x}_z \)

Note \( [L_z, x] = [x p_y, x] - [y p_x, x] = -y [p_x, x] \)

\[
[L_z, x] = -i k y
\]

Similarly \([L_z, y] = -i k x \) and so.

\[
[L_z, x \pm iy] = i k (y \pm i (-x)) = \pm k (x \pm iy)
\]

Therefore consider \( \langle E_f \hat{q}_f m_f | [L_z, x \pm iy] | E_i \rangle \langle E_i | \rangle \)
\[
\langle E_f \ell_f m_f \mid [L, x \pm iy] \mid E_i \ell_i m_i \rangle = \pm \langle E_f \ell_f m_f \mid k(x \pm iy) \mid E_i \ell_i m_i \rangle \\
\langle E_f \ell_f m_f \mid L \pm (x \pm iy)^2 \mid E_i \ell_i m_i \rangle = \pm k \langle E_f \ell_f m_f \mid x \pm E_i \ell_i m_i \rangle
\]

\[
(m_f - m_i) \langle E_f \mid x \pm E_i \rangle = \pm k \langle E_f \mid x \pm E_i \rangle
\]

\[
(m_f - m_i \neq \pm 1) \langle E_f \mid x \pm E_i \rangle = 0.
\]

Again, if \( m_f - m_i \neq \pm 1 \) then \( \langle E_f \mid x \pm E_i \rangle = 0 \) and no dipole

Conclusion: \( \hat{e} \cdot \hat{x} \pm i \hat{y} \) \( \Delta m = \pm 1 \)

Conclude \( \langle E_f \ell_f m_f \mid [L^2, [L, x]] \mid E_i \ell_i m_i \rangle \)

where,

\[
[L^2, [L, x]] = z k^2 (L^2 x_i + x_i L^2)
\]

\[
\langle E_f \ell_f m_f \mid [L^2, [L, x]] \mid E_i \ell_i m_i \rangle = z k^2 \langle E_f \ell_f m_f \mid (L x_i + x_i L) \mid E_i \ell_i m_i \rangle
\]

\[
(l_f (l_f + 1) - l_i (l_i + 1)) k^2 \langle E_f \ell_f m_f \mid [L^2, x] \mid E_i \ell_i m_i \rangle
\]

\[
\left[ (l_f (l_f + 1) - l_i (l_i + 1)) \right]^2 k^4 \langle E_f \mid x \mid E_i \rangle = z k^2 \left[ l_f (l_f + 1) + l_i (l_i + 1) \right] \langle E_f \ell_f m_f \mid x \mid E_i \ell_i m_i \rangle
\]

\[
\left[ l_f^2 - l_i^2 + l_f - l_i \right]^2 - 2 \left[ l_f^2 + l_f - l_i^2 + l_i \right] \langle E_f \mid x \mid E_i \rangle = 0
\]

\[
\left[ (l_f - l_i)^2 (l_f + l_i + 1)^2 - \left( (l_f + l_i + 1) - (l_f - l_i)^2 - 1 \right) \right] \langle E_f \mid x \mid E_i \rangle = 0
\]

\[
\left[ (l_f + l_i + 1)^2 \left[ (l_f - l_i)^2 - 1 \right] - \left[ (l_f - l_i)^2 - 1 \right] \right] \langle E_f \mid x \mid E_i \rangle = 0
\]
\[
\left\{ \begin{array}{c}
\left( (l_f + l_i + 1)^2 - 1 \right) \left( (l_f - l_i)^2 - 1 \right) \langle E_f | x_i | E_i \rangle = 0
\end{array} \right.
\]

Note: \( l_f > 0 \) \( l_i > 0 \), so the first term only vanishes for \( l_f = l_i = 0 \). Otherwise, it is positive.

Ignoring this case for the moment, the matrix element \( \langle E_f | x_i | E_i \rangle \) must vanish unless

\[
(l_f - l_i)^2 - 1 = 0 \quad \text{or} \quad l_f = l_i \pm 1 \quad \text{or} \quad \Delta l = 1.
\]

The case for which \( l_f = l_i = 0 \) can be ignored, since both states have spherical symmetry \( l = 0 \) and therefore the matrix element must vanish. Note it also vanishes because of parity.

**Selection Rules:** Electric Dipole

\( \Delta l = \pm 1 \) \quad (no \( l = 0 \rightarrow l = 0 \))

\( \Delta m = 0, \pm 1 \)

What about \( \Delta S \)? (Since \( \mathbf{H} \) interacts \( = -\frac{8}{\hbar} \mathbf{A} \cdot \mathbf{P} \) does not involve any spin operators; the perturbation cannot mix different \( S \) states, and so \( \Delta S = 0 \). Alternatively, one can say that since \( \mathbf{H}_{\text{total}} \) commutes with \( \mathbf{S} \), the spin angle \( \theta_{\text{spin}} \) must be conserved.)
Physical significance of $\hat{E}_x + i\hat{E}_y$

Remember $A = \hat{E}_0 \sin(k \cdot r - wt)$ and

$$E = -\frac{\text{d}A}{\text{d}t} = \hat{E}_0 \text{aw} \cos(k \cdot r - wt)$$

$$E = \frac{\hat{E}_0 \text{aw}}{2} \left[ e^{i(k \cdot r - wt)} + e^{-i(k \cdot r - wt)} \right]$$

where the second term corresponds to stimulated emission and the first term to absorption.

Choosing the second term for our discussion then $\hat{E}_x + i\hat{E}_y$ corresponds to

$$E_{xt} = \frac{\omega \text{aw}}{2} \left[ \hat{E}_x e^{-i(k \cdot r - wt)} + i\hat{E}_y e^{-i(k \cdot r - wt)} \right]$$

$$= \frac{\omega \text{aw}}{2} \left[ \hat{E}_x e^{-i(k \cdot r - wt)} + \hat{E}_y e^{-i(k \cdot r - wt + \frac{\pi}{2})} \right]$$

If we assume the wave is travelling in the $z$-direction then $k \cdot r = k z$

Then in the $z=0$ plane

$$\text{Re} \left[ E_{xt}(z=0, t) \right] = \frac{\omega \text{aw}}{2} \left[ \hat{E}_x \cos wt + \hat{E}_y \cos (wt + \frac{\pi}{2}) \right]$$

For a fixed plane the $E$-field appears to rotate clockwise as I look at the photon coming towards me.

This is called **RIGHT-CIRCULARLY POLARIZED LIGHT**
Similarly

$E_x = \hat{\epsilon} \cdot \vec{e}$

$t = 0$

$t = \frac{\pi}{2} W$

$t = \pi W$

This configuration is called **left-circularly polarized light**

The name right or left circularly polarized light comes from considering how the electric field spiral in space as it travels.

![Diagram of light polarization](image)

Right-handed spiral

Re-examining the selection rules in this "light" we see that
Here the photon must carry away $-1\hbar$ of any momentum along the $z$-axis in order to conserve any momentum.

For this case the photon must carry away $+1\hbar$ units of any momentum along the $z$-axis to conserve the total any momentum.

Consider what happens when these photons hit a metal plate.

Electrons rotate in the plane of the metal with any momenta pointing in the $-z$-axis.

Similarly for $\text{LCP}$

Electrons now travel in the plane with positive any momenta along the $z$-axis!
Does this general argument about conservation of any mom. apply as well to the $\mathbf{g}$ case?

For this polugation, $\Delta M = 0$. Thus the photon can not be emitted along the $z$-axis. However the photon can be emitted in the $x$-$y$ plane since it would have no projection of any mom. along the $z$-axis.

Angular Distribution

Consider an atom with $l=1$ and $m_z=1$ and that it has probability $P$ that it will emit a LCP photon in the $+z$-direction.

How can we calculate the probability that it will emit a photon in some other direction (say at an angle $\theta$ from the $z$-axis).

Although the atom is in the state $|l=1, m_z=1\rangle$, it can also be written in terms of the eigenstates of $L_z'$, where $z'$ is the $z'$-direction of a rotated $x', y', z'$ coordinate system.

One way to obtain this new coordinate system is to rotate by an angle $\phi$ about the $x$-axis.

Since the Rotation operator $R(\hat{\mathbf{u}}, \phi) = e^{i \phi \hat{\mathbf{u}}}$ rotates a state by an angle $\phi$ about the $\hat{\mathbf{u}}$ direction in terms of the original basis, the operator $R(\hat{\mathbf{n}}_z, \phi)$ can be thought as giving the original state in terms of the basis given by rotating the coordinate system by $\phi$ about $\mathbf{n}_z$. 
From our previous work then

\[ R(-\theta, x) | 1 \rangle | 1 \rangle = \frac{1}{2} (1 + \cos \theta) | 1 \rangle | 1 \rangle - \frac{i}{\sqrt{2}} \sin \theta | 10 \rangle | 1 \rangle - \frac{i}{\sqrt{2}} \sin \theta | 11 \rangle | 1 \rangle \]

\[ R(-\theta, x) | 1 \rangle | 0 \rangle = -\frac{i}{\sqrt{2}} \sin \theta | 11 \rangle | 0 \rangle + \cos \theta | 10 \rangle | 0 \rangle - \frac{i}{\sqrt{2}} \sin \theta | 11 \rangle | 0 \rangle \]

\[ R(-\theta, x) | 1 \rangle | -1 \rangle = \frac{1}{2} (1 - \cos \theta) | 11 \rangle | 1 \rangle - \frac{i}{\sqrt{2}} \sin \theta | 10 \rangle | 1 \rangle + \frac{i}{\sqrt{2}} \sin \theta | 11 \rangle | 1 \rangle \]

Therefore the original state described in the old coordinate system \((x,y,z)\) can be thought of existing in the rotated coordinate system \((x',y',z')\) but with different probabilities of being in the principle \(L^2\) eigenstates.

Since in the rotated frame the atom has the probability of \(\frac{1}{4} (1 + \cos \theta)^2\) of being in the \( | 1 \rangle | 1 \rangle\) state, with the probability of emitting a photon (LCP) along the \(+z\) direction still being \(P\), we see that the overall probability of emitting a photon in a direction rotated from the original \(z\) by an angle \(\theta\) is

\[ P \frac{1}{4} (1 + \cos \theta)^2 \]

Similarly if we were originally in the \( | 1 \rangle | 0 \rangle | -1 \rangle\) state the probability of emitting a photon with RCP will have an angular distribution of

\[ \frac{(1 - \cos \theta)^2}{4} \]
But previously we said that the angular distribution of dipole radiation has a $\sin^2 \theta$ dependence.

The difference occurs because this Hamilton corresponds to a circulating change in the $x$-$y$ plane. Thus can be treated as two single dipoles in perpendicular directions.

Each dipole radiates with the $\sin^2 \theta$ pattern, but the angles must be properly defined.

For dipole 1, the direction chosen is always perpendicular to the dipole, and therefore radiates with a $\sin^2 \frac{\theta}{2} = 1$ pattern.

For dipole 2, the direction shown is rotated by an angle $(\frac{\pi}{2} - \theta)$ from the direction of the dipole, and therefore should radiate as

$$\sin^2 \left( \frac{\pi}{2} - \theta \right) = \cos^2 \theta$$

However, since these two dipoles radiate coherently (there is a fixed phase relation between them), we must add the amplitudes which produce the results found above, i.e.,

$$\left( 1 \pm \cos \theta \right)^2$$

To calculate the above pattern from the definition of the transition rates, we first need to establish a means of describing an arbitrary $\vec{k}$ and $\vec{e}_1$ and $\vec{e}_2$ vectors.
Consider the following definitions:
\[ \hat{\mathbf{r}} = \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z} \]
\[ \hat{\mathbf{e}}_1 = -\sin \phi \hat{x} + \cos \phi \hat{y} \]
\[ \hat{\mathbf{e}}_2 = \cos \phi \cos \theta \hat{x} + \cos \phi \sin \theta \hat{y} + \sin \phi \hat{z} \]

The vector \( \hat{\mathbf{r}} \) which represents the direction of the photon is described by
the angles \( \theta \) and \( \phi \) to give the standard orientation in 3-D. (i.e.,
the photon is directed into the solid angle. \( \sin \theta \, d\phi \, d\theta = d\Omega \).)

The two linearly polarized vectors are chosen such that
\[ \hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_1 = 0 \quad \text{and} \quad \hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_2 = 0. \]

For convenience one \( (\hat{\mathbf{e}}_1) \) is chosen to lie in the \( x-y \) plane.

To describe the radiation pattern of the transition \( 111 \rightarrow 100 \)
in terms of circularly polarized light we must use the appropriate
circular polarization vector \( \hat{\mathbf{e}} \):
\[ \hat{\mathbf{e}}_+ = \hat{\mathbf{e}}_1 + i \hat{\mathbf{e}}_2 \quad \text{Right Circularly Polarized.} \]
\[ \hat{\mathbf{e}}_- = \hat{\mathbf{e}}_1 - i \hat{\mathbf{e}}_2 \quad \text{Left Circularly Polarized.} \]

As before we must calculate the matrix element
\[ \hat{\mathbf{e}} \cdot \langle E_{\mathbf{f} \mathbf{\ell} m \mathbf{f}'} | \mathbf{e} \rangle | E_{\mathbf{f} \mathbf{\ell} m \mathbf{f}'} \rangle \]
\[ = \hat{\mathbf{e}} \cdot \langle E_{\mathbf{f} \mathbf{\ell} m \mathbf{f}'} \mathbf{x} \mathbf{x} + \mathbf{y} \mathbf{y} + \mathbf{z} \mathbf{z} | E_{\mathbf{f} \mathbf{\ell} m \mathbf{f}'} \rangle \]

Because the states of the atom can be described in terms of the
angular momenta states it is convenient to rewrite \( \mathbf{x} \), \( \mathbf{y} \), and \( \mathbf{z} \)
in terms of the spherical harmonics.
\[ x = \left( \frac{2\pi}{3} \right)^{1/2} r \left[ Y_{i-1}^{'} - Y_{i-1}^{'} \right] \]
\[ y = i \left( \frac{2\pi}{3} \right)^{1/2} r \left[ Y_{i-1}^{'''} + Y_{i-1}^{'''} \right] \]
\[ z = \left( \frac{\sqrt{2}}{3} \right)^{1/2} r Y_{i-1}^{'} \]

For the problem \[ |11\rangle \rightarrow |00\rangle \] we see that only matrix elements of \( x \) and \( y \) will be non-zero.

\[ \langle E_f l_f = 0 m_f = 0 | x | E_i l_i = 1 m_i = 1 \rangle \]
\[ = \left( \frac{2\pi}{3} \right)^{1/2} \langle E_f l_f = 0 | E_i \rangle \langle 00 | Y_{i-1}^{'} - Y_{i-1}^{'} | 11 \rangle \]
\[ = -i \left( \frac{2\pi}{3} \right)^{1/2} \langle E_f l_f = 0 | E_i \rangle \left( \frac{1}{4\pi} \right)^{1/2} \]

and

\[ \langle E_f l_f = 0 m_f = 0 | y | E_i l_i = 1 m_i = 1 \rangle \]
\[ = i \left( \frac{2\pi}{3} \right)^{1/2} \langle E_f l_f = 0 | E_i \rangle \langle 00 | Y_{i-1}^{'} + Y_{i-1}^{'} | 11 \rangle \]
\[ = -i \left( \frac{2\pi}{3} \right)^{1/2} \langle E_f l_f = 0 | E_i \rangle \left( \frac{1}{4\pi} \right)^{1/2} \]

(Remembering that \( Y_i^{'} = - (Y_i^{-1})^{*} \) and so

\[ A_{11} \cdot \langle E_f l_f = 0 m_f = 0 | r | E_i l_i = 0 m_i = 0 \rangle = \]
\[ - \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{2\pi}{3} \right)^{1/2} \langle E_f l_f = 0 | E_i \rangle \left\{ \left( -\sin \theta \pm i \cos \theta \cos \phi \right) + i \left( \cos \theta \pm i \cos \theta \sin \phi \right) \right\} \]

Taking the absolute value square:

\[ \frac{1}{6} \langle E_f l_f = 0 | E_i \rangle |^2 \left( -\left( \sin \theta \right)(1 \pm \cos \phi) + i \left( \cos \theta \right)(1 \pm \cos \phi) \right)^2 \]

\[ \frac{1}{6} \langle E_f l_f = 0 | E_i \rangle |^2 \left( \sin^2 \theta + \cos^2 \theta \right)(1 \pm \cos \phi)^2 \]

\[ \frac{1}{6} \langle E_f l_f = 0 | E_i \rangle |^2 \left( 1 \pm \cos \phi \right)^2 \]
A similar calculation can be made for a $\Delta m = 0$ transition.

If the $11,0^+$ state emits a photon with probability $P$ in the $x-y$ plane. Again by looking in the rotated coordinate frame the probability of being in the $110, l_z = 0$ state is

\[ |\cos \beta|^2 \]

For $l_z = 1, m_z = 0$,

Reverting back to the angle from the $z$-axis we see that the probability becomes:

\[ P \cos^2 \beta \]

as expected for a linear dipole.

As before we can also do this by plugging in our general expressions for $\hat{E}_z$ and $\mathbf{r}$. From the form of the wavefunction of the initial state, $(x, y, 0)$, only the $z$ component will be non-zero. One can immediately see then that we get a $\sin^2 \theta$ angular distribution for $\hat{E}_z$. 
Higher order terms in the transition probability.

What happens when one includes the next order term in the expansion of $e^{ik\cdot r}$?

$$\langle E_f | e^{ik\cdot r} \hat{e}\cdot p | E_i \rangle = \langle E_f | \hat{e}\cdot p | E_i \rangle + i \langle E_f | (k\cdot r)(\hat{e}\cdot p) | E_i \rangle$$

Dipole Transition

Note that

$$(k\cdot r)(\hat{e}\cdot p) = \frac{1}{2} \left[ (k\cdot r)(\hat{e}\cdot p) - (k\cdot p)(\hat{e}\cdot r) \right] + \frac{1}{2} \left[ (k\cdot r)(\hat{e}\cdot p) + (k\cdot p)(\hat{e}\cdot r) \right]$$

and $(a\times b), (c\times d) = (a\cdot c)(b\cdot d) - (a\cdot d)(b\cdot c)$

The first term therefore becomes $\frac{1}{2} \left[ (k\times \hat{e}) \cdot (p\times \hat{p}) \right]$ where we identify the $p\times p$ as our usual definition of the total orbital angular momentum. When combined with the $\frac{e}{2m}$ prefactor this is interpreted as the magnetic moment of the orbital part of the wavefunction and so is called a magnetic dipole term.

Selection Rules.

Unlike the vector $\vec{r}$, $\vec{L}$ is a pseudovector and does not change sign upon changing parity. The magnetic dipole transition therefore connects states with the same parity.

The selection rules for $L$ and $M_L$ are obtained by considering when matrix elements of $L_x, L_y$ and $L_z$ or $L^+ , L^-$ and $L_z$ are non-zero.
\[ \langle E_f | l_m | E_i | l_i \rangle \]

Clearly \( \Delta l = 0 \) (since \( L \) does not change \( l \)) and \( \Delta m = \pm 1, 0 \).

**Angular Distribution**

Using the same general arguments as employed for the analogous of the "components" of \( \langle E_f | \mathbf{r} | E_i \rangle \) one can conclude that the radiation pattern again has a similar distribution.

- Alternatively one can use the general arguments on conservation of angular momentum along the \( z \)-axis to get the same results.
- Also direct calculations can be used from the general form of \( k \hat{e} \) and \( \hat{e} \).

The second term is a bit more complicated

\[
\frac{1}{2} \left[ \left( \mathbf{k} \cdot \mathbf{r} \right) (p \cdot \hat{e}) + (k \cdot p) (\mathbf{r} \cdot \hat{e}) \right]
\]

\[ = \frac{1}{2} \left[ \mathbf{k} \cdot (\mathbf{r} \mathbf{p} + \mathbf{p} \mathbf{r}) \cdot \hat{e} \right] \]

As before using the fact that the states are eigenstates of the unperturbed Hamiltonian we have that

\[ k \cdot \langle E_f | \mathbf{r} \mathbf{p} + \mathbf{p} \mathbf{r} | E_i \rangle \cdot \hat{e} = \text{i} m \omega \mathbf{k} \cdot \langle E_f | \mathbf{r} \mathbf{p} | E_i \rangle \cdot \hat{e} \]
Consider the dyadic \( \mathbf{V} \) which has nine components \( \{ x \mathbf{p}, x \mathbf{q}, \ldots \} \).

How does this object behave under rotations? If we were making a rotation about the \( z \)-axis by an angle \( \theta \) we would have for the vector \( \mathbf{v} \):

\[
\begin{align*}
2 & \rightarrow 2' \\
x & \rightarrow x' \cos \theta + y' \sin \theta \\
y & \rightarrow -x' \sin \theta + y' \cos \theta \\
z & \rightarrow z'
\end{align*}
\]

or

\[
\begin{pmatrix}
  x' \\
  y' \\
  z'
\end{pmatrix} =
\begin{pmatrix}
  \cos \theta & \sin \theta & 0 \\
  -\sin \theta & \cos \theta & 0 \\
  0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix}
\]

or

\[
\mathbf{v}' = A_{ij} \mathbf{v}_j \text{ where } A_{ij} = \text{dr}_{ij}
\]

(Note: by convention repeated indices are summed over).

In general for a rotation about an arbitrary axis all elements of \( A_{ij} \) will be non-zero.

Since the vector \( \mathbf{p} \) also transforms as \( \mathbf{v} \) we have

\[
(\mathbf{v} \mathbf{p})_d = A_{ik} A_{jk} (\mathbf{v}' \mathbf{p}')_{kl} = A_{ik} (\mathbf{v}' \mathbf{p})_{KL} A_{Ld}
\]

Any object which exhibits this behavior is called a tensor of rank 2.

\[
T_{ij} = A_{ik} T_{kl} A_{lj}^T
\]

(Note: the transformation \( A_{ij} = \text{dr}_{ij} \) could be other types of coordinate changes and is not restricted to rotations).

The above equations show how the 9 components of the tensor of 2\(^{\text{rd}}\) rank transform amongst themselves under various transformations.

If we restrict ourselves to only rotations and reflections they we find that some of the 9 components only do not mix with other elements. Alternately one finds that there exists subsets of elements which transform only amongst themselves.
Taking our \((\mathbf{M} \cdot \mathbf{P})_{ij}\), we find

- The trace \((\mathbf{M} \cdot \mathbf{P})_{ii} = xPx + yPy + zPz = (\mathbf{P} \cdot \mathbf{P})\) is just a scalar and is therefore invariant under rotations (tensor of rank 0).

- The asymmetric part of \((\mathbf{M} \cdot \mathbf{P})_{ij} - (\mathbf{M} \cdot \mathbf{P})_{ji}\) produces 3 unique combinations
  \[
  \begin{align*}
  xPy - yPx \\
  yPz - zPy \\
  zPx - xPz
  \end{align*}
  \]
  which you should recognize as the angular momentum vector. This object therefore transforms like a vector under rotations (tensor of rank 1).

- The remaining components form a traceless symmetric part which still transforms as a second rank tensor

  \[
  \frac{1}{2} \left[ (\mathbf{M} \cdot \mathbf{P})_{ij} + (\mathbf{M} \cdot \mathbf{P})_{ji} \right] = \frac{1}{2} (\mathbf{P} \cdot \mathbf{P})
  \]

Alternatively, one could treat these as spherical tensors of rank 0, 1, and 2, each of which transforms like the spherical harmonics with \(l=0, 1, \text{ and } 2\).

Starting with \((\mathbf{M} \cdot \mathbf{P})\) made of objects which each transform like \(Y_{lm}\), we have 9 objects. But the product of 2 \(Y_{lm}\)'s can be reduced by the rules of the addition of angular momentum to give us new states of angular momentum. \(\text{if}\)

\[
 l_1 = 1 \quad \otimes \quad l_2 = 1 \quad \text{(has 9 states)} \quad \text{produces} \quad 9 \quad \text{states}
\]
of \(l = 0 \quad (1) \quad l = 1 \quad (3) \quad \text{and} \quad l = 2 \quad (5) \quad \text{.} \)
In classical EM the quadrupole moment tensor is defined as

$$Q_{ij} = \int \rho(x') \left[ 3x_i x_j - r^2 \delta_{ij} \right] d^3x'$$

Within the integral we find terms such as:

$$3xy \quad 3yz \quad 3zx \quad 3x^2-r^2 \quad 3y^2-r^2 \quad 3z^2-r^2$$

Of these the last three are not linearly independent since $r^2=x^2+y^2+z^2$

Sometimes the 4th and 5th terms are combined to give

$$3(x^2-y^2) \quad \text{and} \quad (r^2-3z^2)$$

(which illustrates that of the three only 2 are linearly independent).

Thus our terms within the matrix element have a similar form as the components of the quadrupole tensor.

$$\mathbf{k} \cdot \langle E_f | r \cdot p + p \cdot r | E_i \rangle \cdot \hat{e} = \frac{imw}{k} \mathbf{k} \cdot \langle E_f | \mathbf{r} | E_i \rangle \cdot \hat{e}$$

Although the above matrix element appears to have 9 separate possible terms, only 5 of linearly independent since $\mathbf{k}$ is perpendicular to $\hat{e}$.

The selection rules for the quadrupole matrix element can be determined by using the dipole selection rules.

Consider $\langle E_f | m_f | xy | E_i | m_i \rangle$
By inserting an entire set of states we can use the dipole selection rules.

Since \( \sum_n \left| E_{n_{lm}} \right> \left< E_{n_{lm}} \right| = 1 \) then

\[
\left< E_f | x y | E_i \right> \equiv \sum_n \left< E_f \left| m_f \right| \times \left| E_{n_{lm}} \right> \left< E_{n_{lm}} \right| \left. y \right| E_i \left| m_i \right> \right.
\]

Since \( \left< E_f \left| m_f \right| \times \left| E_{n_{lm}} \right> = 0 \) unless \( m_f - m_i = \pm 1 \) and \( \left< E_{n_{lm}} \right| \left. y \right| E_i \left| m_i \right> = 0 \) unless \( l_i - l_n = \pm 1 \) and \( m_i - m_n = \pm 1 \) then the entire will be zero unless

\[ l_f - l_i = \pm 2 \text{ or } 0 \]

\[ m_f - m_i = \pm 2 \text{ or } 0 \]

Similarly we can analyze matrix elements which contain \( x \): i.e.

\[
\left< E_f | x Z | E_i \right> = \sum_n \left< E_f \left| m_f \right| \times \left| E_{n_{lm}} \right> \left< E_{n_{lm}} \right| \left. x Z \right| E_i \left| m_i \right> \right.
\]

The selection rules for a \( Z \) matrix are that \( \left< E_{n_{lm}} \right| \left. x Z \right| E_i \left| m_i \right> = 0 \) unless \( l_n - l_i = \pm 1 \) and \( m_i = m_n \). So that by combining it with the \( x \) selection rules we obtain

\[ l_f - l_i = \pm 2, 0 \]

and

\[ m_f - m_i = \pm 1 \]

An alternative approach to obtaining these selection rules (and to actually calculate the values of the matrix elements) is to replace \( r_{xy} \) by the spherical harmonics.
\[ xy = r^2 \sin^2 \phi \cos \phi \sin \theta = -i \left( \frac{2\pi}{\sqrt{15}} \right)^{\frac{3}{2}} r^2 \left[ Y_2^2 - Y_2^{-2} \right] \]

\[ yz = r^2 \sin^2 \phi \cos \phi \sin \theta = +i \left( \frac{2\pi}{\sqrt{15}} \right)^{\frac{3}{2}} r^2 \left[ Y_2^1 + Y_2^{-1} \right] \]

\[ x^2 - y^2 = r^2 \sin^2 \phi \cos^2 \theta - r^2 \sin^2 \phi \cos^2 \theta = 2 \left( \frac{2\pi}{\sqrt{15}} \right)^{\frac{3}{2}} r^2 \left[ Y_2^0 \right] \]

\[ 3x^2 - r^4 = r^2 (3 \cos^2 \phi - 1) = 4 \left( \frac{\pi}{\sqrt{5}} \right)^2 r^2 Y_2^0 \]

The matrix element \( \langle Ef \mid l_f m_f \mid l_i \mid E_i m_i \rangle \) therefore reduced to

and integral containing

\[ \int d\Omega \ Y_{l_f}^{m_f} Y_{l_i}^{m_i} \]

One can see that \( Y_{l_i}^{m_i} \) can be rewritten using the rules of addition of angular momentum into states with total \( l = |l_i + 2| \ldots |l_i - 2| \) and total \( z \) component \( m = m_i \).

The selection rules for \( \Delta l = \pm 2, 0 \) and \( \Delta m = 0, \pm 1, \pm 2 \) following from the orthogonality of \( Y_{l_f}^{m_f} \) with the resulting states. (Note: \( \Delta l = \pm 1 \) can be excluded due to the requirement of parity.)

For example if \( l_i = 0 \) \( m_i = 0 \) then the above integral is non-zero only for \( m_f = m \) and \( l_f = 2 \). Thus \( \Delta l = \pm 2 \) and \( m_f = \pm 2, \pm 1 \) or 0.

The selection rules for electric quadrupole radiation is just

\[ \Delta l = 0, 2 \quad \Delta m = 0, \pm 1, \pm 2 \quad \Delta S = 0 \quad \Delta m_S = 0 \]

and as before no \( l = 0 \) to \( l = 0 \) Hamiltonian. \( \Delta \text{Parity} = 0 \).
But wait! If photons only have \( \pm h \) of angular momentum along their direction of propagation, how can one obtain an atom whose angular momentum along the \( z \)-axis changes by \( \Delta M = \pm 2 \)?

Since the radiation term in the Hamiltonian is linear in \( \hat{A} \) one can only be treated situations with only one photon.

The explanation is that the total angular momentum of the system is conserved, which includes the any mom. of both the atom and photon. Just like a particle can have both intrinsic as well as orbital angular mom., the photon can have in addition to its intrinsic spin of \( \pm \hbar \), it can have orbital angular momentum so its total angular momentum along its axis of propagation is \( \pm 2\hbar \). Thus a photon emitted in a \( \Delta M = \pm 2 \) transition will have a more complicated distribution.

-Note: To treat the photon field correctly one would need to expand the vector field (\( \mathbf{E} \& \mathbf{B} \) fields) in terms of the Vector Spherical Harmonics.

Angular dependence of Quadrupole Radiation

Again using our coordinate system for \( \mathbf{k}, \hat{\mathbf{e}}_z = \hat{\mathbf{e}}_1 + i\hat{\mathbf{e}}_2 \) we have

\[
\hat{\mathbf{k}} = \sin\theta \cos\phi \mathbf{\hat{x}} + \sin\theta \sin\phi \mathbf{\hat{y}} + \cos\theta \mathbf{\hat{z}}
\]

\[
\hat{\mathbf{e}}_1 = -\sin\phi \mathbf{\hat{x}} + \cos\phi \mathbf{\hat{y}}
\]

\[
\hat{\mathbf{e}}_2 = \cos\theta \cos\phi \mathbf{\hat{x}} + \cos\theta \sin\phi \mathbf{\hat{y}} - \sin\theta \mathbf{\hat{z}}
\]

and

\[
\sum_{i=1}^{2} \left| \mathbf{k} \cdot \langle \mathbf{E}_f | \mathbf{M}_f | \mathbf{E}_i \rangle \cdot \hat{\mathbf{e}}_i \right|^2
\]
Consider a $\Delta l = 2$ $\Delta m = 0$ transition $|E_f\rangle \rightarrow \gamma_2^0$ and $|E_i\rangle \rightarrow \gamma_0^0$.

Then from our expressions for $\rho_{ij}$ in terms of the $\gamma_{m_i}^0$'s we see that only $\gamma_2^0$ will have non-zero matrix elements. Thus:

$$\sum_k |k_i\langle E_f | \gamma_2^0 | E_i\rangle|^2 \propto \sum_k |k_z\langle E_f | \gamma_2^0 | E_i\rangle e_z|^2$$

$$\propto \left[ | \cos \theta \sin \phi |^2 + | i \cos \theta \sin \phi |^2 \right] = 2 \cos^2 \theta \sin^2 \phi.$$

Choosing $\Delta l = 2$ $\Delta m = \pm 1$ one finds an angular distribution

$$(1 - 3 \cos^2 \theta + 4 \cos^4 \phi).$$

And finally for $\Delta l = 2$ $\Delta m = \pm 2$,

$$(1 - \cos^4 \phi).$$
Consider a transition from $Y_2^2$ to $Y_0^0$. This is a bit more complicated since more than one element of $N_1 N_2$ contributes and therefore must be added with the correct phase.

Looking back at our list of $N_1 N_2$ (in terms of the $Y_j$'s) we see that only $xy$, $yx$, $x^2$, and $y^2$ should contribute. (They all contain a term proportional to $Y_0^0$.)

So that

$$\langle E_f | xy | E_i \rangle = -i \left( \frac{2\pi i}{\alpha} \right)^{\frac{N}{2}} \langle E_f | r^2 | E_i \rangle$$
$$\langle E_f | yx | E_i \rangle = -i \left( \frac{2\pi i}{\alpha} \right)^{\frac{N}{2}} \langle E_f | r^2 | E_i \rangle$$
$$\langle E_f | x^2 | E_i \rangle = \left( \frac{2\pi i}{\alpha} \right)^{\frac{N}{2}} \langle E_f | r^2 | E_i \rangle$$
$$\langle E_f | y^2 | E_i \rangle = -\left( \frac{2\pi i}{\alpha} \right)^{\frac{N}{2}} \langle E_f | r^2 | E_i \rangle$$

Except for factors of $\pm 1$, they all have the same prefactor. So let us concentrate on the angular dependence which arises from the $\hat{k}$ and $\hat{n}$ factors.

$$\hat{k} \cdot \langle E_f | N_1 N_2 | E_i \rangle \cdot (\hat{l} \cdot \hat{m})$$

$xy$:

$$-i \left\{ \sin \theta \cos \phi (\cos \theta \pm i \cos \phi \sin \phi) \right\}$$

$yx$:

$$-i \left\{ \sin \theta \sin \phi (-\sin \phi \pm i \cos \phi \cos \phi) \right\}$$

$x^2$:

$$+ \left\{ \sin \theta \cos \phi (-\sin \phi \pm i \cos \phi \cos \phi) \right\}$$

$y^2$:

$$- \left\{ \sin \theta \sin \phi (\cos \phi \pm i \cos \phi \sin \phi) \right\}$$

Collecting terms:

$$\pm 2 \sin \theta \cos \phi (\cos \theta \sin \phi) - 2 \sin \phi (\cos \theta \sin \phi)$$

$$+ i \left[ - \sin \theta (\cos^2 \phi - \sin^2 \phi) \pm \sin \theta \cos \phi (\cos^2 \phi - \sin^2 \phi) \right].$$
or

\[ \sin \theta (-1 \pm \cos \theta) \left[ \sin 2\theta \mp i \cos 2\theta \right], \]

Taking the absolute value squared we obtain:

\[ \sin^2 \theta (-1 \pm \cos \theta)^2 (\sin^2 \theta \mp \cos^2 \theta) = \sin^2 \theta (-1 \pm \cos \theta)^2 \]

But the above expression is for \( \hat{E}_2 = \hat{E}_1 \pm i \hat{E}_1 \). Summing the contribution from each polarization:

\[ \sin^2 \theta (-1 + \cos \theta)^2 + \sin^2 \theta (-1 - \cos \theta)^2 \]

\[ \sin^2 \theta (1 + \cos^2 \theta) = (1 - \cos^2 \theta)(1 + \cos^2 \theta) = [1 - \cos^4 \theta] \]

which agrees with our prediction, for \( \delta \theta = 2, \delta \eta = 2 \). Similarly \( \delta \theta = 1, \delta \eta = 1 \) can be calculated.
Consequences of symmetry

Helium Atom:

\[
\frac{\hbar^2}{2m} \left( -\nabla_1^2 - \frac{2e^2}{4\pi \varepsilon_0 r_1} \right) + \frac{\hbar^2}{2m} \left( -\nabla_2^2 - \frac{2e^2}{4\pi \varepsilon_0 r_2} \right) + \frac{e^2}{4\pi \varepsilon_0 r_{12}}
\]

electron #1

electron #2

electron-electron interaction

Ignoring the interaction of the two electrons, the ground state (orbital) wave function is given by:

\[
\Psi_{\text{ground}} = \Psi_{1S(1)} \Psi_{1S(2)}
\]

Each electron is in the hydrogenic ground state orbital \( n=1, l=0, m=0 \):

\[
\Psi_{1S} = \frac{1}{\sqrt{\pi} \alpha_0^3} e^{-r/\alpha_0}
\]

This wave function is symmetric. The total wave function must be antisymmetric. This is accomplished by the spin wave function. For the two electrons the possible spin wave functions are:

\[
S = 0 \quad \frac{1}{\sqrt{2}} (\Psi_{+1} \Psi_{-2} - \Psi_{+2} \Psi_{-1}) \quad \text{antisymmetric}
\]

\[
S = 1 \quad \Psi_{+1} \Psi_{+2} + \Psi_{+2} \Psi_{-1} \quad \text{symmetric}
\]
Although in principle 4 states are available only the antisymmetric $S=0$ is allowed!

\[ \psi_{\text{ground}} = \left[ \Psi_{1s(1)} \Psi_{1s(2)} \right] \times \left[ \frac{1}{\sqrt{2}} (\Psi_{+}(1) \Psi_{-}(2) - \Psi_{-}(1) \Psi_{+}(2)) \right] \]

\[ \text{sym. antisym.} \]

The energy of this state is given by (ignoring electron interaction).

\[ E_{\text{ground}} = E_1 + E_1 = -\frac{Z^2 R}{\xi^2} - \frac{Z^2 R}{1^2} \]

\[ = 2 \left[ -(4)(13.6\text{eV}) \right] = -108.8\text{eV}. \]

True ground state energy: \(-78.62\text{eV}\), which is larger as one might expect if one includes the electrostatic energy of the two electrons.

Estimate of the electronic electrostatic energy is given by perturbation theory:

\[ \Delta E_{\text{electrostatic}} = \left\langle \Psi_{1s(1)} \Psi_{1s(2)} \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \Psi_{1s(1)} \Psi_{1s(2)} \right\rangle \]

\[ = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left| \Psi_{1s(1)} \right|^2 \left| \Psi_{1s(2)} \right|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} \]

which can be rewritten as.
\[ \Delta E = \int dV_2 \, \epsilon \rho_2(r_2) \, V(r_2) \]

where \[ V(r_2) = \int dV_1 \, \frac{\epsilon}{4\pi\varepsilon_0} \, |\Psi_{1s}(r_1)|^2 \, \frac{1}{|r_1 - r_2|} \]

is the effective electrical potential produced by a charge density of \[ \epsilon |\Psi_{1s}(r_1)|^2 \]

\[ \rho_2(r_2) \] is the charge density of the second electron.

Since \[ |\Psi_{1s}(r_1)|^2 \] are spherically symmetric, we can use the fact that the potential inside and outside a spherically charged shell is known.

\[
V(r_2) = \int_0^\infty 4\pi r_1^2 dr_1 \frac{\epsilon}{4\pi\varepsilon_0} \left(\frac{\hbar^2}{\alpha_0}\right)^\frac{3}{2} e^{-2r_1/\alpha_0} \frac{1}{|r_1 - r_2|} \\
= \int_0^{r_2} 4\pi r_1^2 dr_1 \frac{\epsilon}{4\pi\varepsilon_0} \left(\frac{\hbar^2}{\alpha_0}\right)^\frac{3}{2} e^{-2r_1/\alpha_0} \frac{1}{r_2} \\
+ \int_{r_2}^\infty 4\pi r_1^2 dr_1 \frac{\epsilon}{4\pi\varepsilon_0} \left(\frac{\hbar^2}{\alpha_0}\right)^\frac{3}{2} e^{-2r_1/\alpha_0} \frac{1}{r_1}
\]

Alternatively, we can use the identity
\[
\frac{1}{|r_1 - r_2|} = \frac{1}{r_2} \sum_{\eta=0}^{\infty} (\frac{r_1}{r_2})^\eta P_\eta (\cos \chi)
\]
where $\theta$ is the angle between the vector $\vec{r}_1$ and $\vec{r}_2$.

Note: $\chi^m_\ell (\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{\pi \ell(\ell+1)}} P^m_\ell (\cos \theta) e^{im\phi}$

where $P^m_\ell (\cos \theta) = P^m_\ell (\cos \theta)$.

Doing these integrals we have.

$\Delta E_{1s^2} = \frac{3\ell}{4} Z R$, $= 34.0$ eV.

$E_{1s^2} = -108.8 \text{ eV} + 34.0 \text{ eV} = -74.8 \text{ eV}$. ($E_{true} = -78.62 \text{ eV}$).

One might expect our result to be slightly too high since we have not yet allowed the electrons to respond to their mutual repulsion.

For example if we chose for our trial wave function

$\psi_{\text{trial}} = \frac{1}{\sqrt{a_0}} \left( \frac{2}{a_0} \right)^3 - 2^* (r_1 + r_2)/a_0$

and used variational technique to estimate the ground state energy we get.

$\frac{2^*}{E_{\text{variational}}} = -77.38 \text{ eV}$. (even better).

Note: the $Z$ in the Hamiltonian remains a $Z$ (and not $2^+$).
Correlation effects.

Assume the two electrons shield each other differently

\[ \psi(r_1, r_2) = N e^{-\frac{Z(1+\nu)}{\alpha_0} r_1/\alpha_0} e^{-\frac{Z(1-\nu)}{\alpha_0} r_2/\alpha_0} \]

Symmetrizing the wave function (keep \( S=0 \) state)

\[ \psi_{sm}(r_1, r_2) = N' \left\{ e^{-\frac{Z(1+\nu)}{\alpha_0} r_1/\alpha_0} e^{-\frac{Z(1-\nu)}{\alpha_0} r_2/\alpha_0} + e^{-\frac{Z(1-\nu)}{\alpha_0} r_1/\alpha_0} e^{-\frac{Z(1+\nu)}{\alpha_0} r_2/\alpha_0} \right\} \]

Using the variation technique one can solve for the values of \( \nu, Z' \) which minimize the total energy.

(Use \( p = 1-\nu^2 \)) Then the value of \( Z' \) which minimizes \( E \) is

\[ Z' = \frac{16 Z - 4 p - p^2 + 16 Z p^3 - 5 p^3}{f(2 - p + p^4)} \]

which gives

\[ E = -\frac{(16 Z - 4 p - p^2 + 16 Z p^3 - 5 p^3)^2}{128 (1 + p^3) (2 - p + p^4)} \text{ Ry} \]

which can now be minimized with respect to \( p \).
For \( z = 2 \) we obtain
\[
Z' = 1.69 \quad \text{and} \quad \nu = 0.30.
\]
The effective nuclear changes are
\[
Z'(1-\nu) = 1.183
\]
\[
Z'(1+\nu) = 2.197
\]

Thus the nucleus is pulling on one electron while pushing the other into a higher orbit.

\[ E = -78.24 \text{ eV} \]

\( \approx -78.62 \text{ eV} \)

\[ 24.587387 \]

\[ 13.60579193 \text{ eV} \]
How does one form the first excited state. Since the hydrogenic states are degenerate for a given \( n \) one can form the following states:

\[
\psi_{1s}^{(1)} \psi_{2s}^{(2)}; \quad \psi_{1s}^{(1)} \psi_{2p}^{(2)}
\]

The proper symmetrized states are

\[
\psi_{1s2s}^{S=0} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}^{(1)} \psi_{2s}^{(2)} + \psi_{1s}^{(2)} \psi_{2s}^{(1)} \right] \chi_{S=0}^{m_S=0}
\]

\[
\psi_{1s2s}^{S=1 m_S} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}^{(1)} \psi_{2s}^{(2)} - \psi_{1s}^{(2)} \psi_{2s}^{(1)} \right] \chi_{S=1}^{m_S} \quad \text{3 state:} \ (m_S).
\]

\[
\psi_{1s2p}^{S=0} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}^{(1)} \psi_{2p}^{(2)} + \psi_{1s}^{(2)} \psi_{2p}^{(1)} \right] \chi_{S=0}^{m_S=0}
\]

\[
\psi_{1s2p}^{S=1 m_S} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}^{(1)} \psi_{2p}^{(2)} - \psi_{1s}^{(2)} \psi_{2p}^{(1)} \right] \chi_{S=1}^{m_S} \quad \text{9 state:} \ (m_S).
\]

All have energy

\[
E_{1s2s} = -\frac{Z^2}{2} \frac{13.6}{1^2} \quad E_{1s2p} = -\frac{Z^2}{2} \frac{13.6}{2^2}
\]

\[
= -68.0 \text{ eV}
\]
Consider now the effect of the electronic repulsion. \( (\frac{e^2}{4\pi \varepsilon_0 r_{12}}) \).

\[
\Delta E_{1523} = \langle \phi_{15,2}^{s=0,1} \mid \frac{e^2}{4\pi \varepsilon_0 r_{12}} \mid \phi_{15,2}^{s=0,1} \rangle \\
= \left( \frac{1}{2} \right) \frac{e^2}{4\pi \varepsilon_0} \left\{ \langle \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \mid \frac{1}{r_{12}} \mid \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \rangle + \right. \\
 \left. \langle \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \mid \frac{1}{r_{12}} \mid \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \rangle \pm \langle \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \mid \frac{1}{r_{12}} \mid \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \rangle \right\} \\
\]

The first two terms are clearly equal to each other. \(( r_1, r_2 \) are dummy indices). Similarly, the 3rd and 4th terms are equal.) Therefore we can write,

\[
\Delta E_{1523}^\pm = K_{15,23}^\pm J_{15,23}^\pm \quad \text{where} \\
K_{15,23} = \langle \phi_{15}^{s=0,1} \phi_{23}^{s=0,1} \mid \frac{1}{r_{12}} \mid \phi_{15}^{s=0,1} \phi_{25}^{s=0,1} \rangle \quad \text{DIRECT} \\
J_{15,23} = \langle \phi_{15}^{s=0,1} \phi_{23}^{s=0,1} \mid \frac{1}{r_{12}} \mid \phi_{25}^{s=0,1} \phi_{15}^{s=0,1} \rangle \quad \text{EXCHANGE.} \\
\]

Similarly one can define,

\[
\Delta E_{152p}^\pm = K_{15,2p}^\pm J_{15,2p}^\pm 
\]
Evaluating the integrals one has

\[ K_{1s2s} \approx 9.1 \text{eV} \]

\[ K_{1s2p} \approx 10.0 \text{eV} \]

One might have expected this difference from the different radial dependences of \( |rR_\text{nl}|^2 \). The 2p electron spends more time near to the 1s electron than a 2s electron.

![Graphs of radial probability density \( (rR_\text{nl})^2 \) for six quantum states of hydrogen as a function of \( r \) in Bohr radii.](image)

*Fig. 14.3* The radial probability density \( \varrho(r) = r^l R_n^2 \) for six quantum states of hydrogen as a function of \( r \) in Bohr radii. (The curve for the 2p orbital is drawn twice for comparison.)
\[ J_{1s, 2s} \approx 0.4 \text{ eV} \]

\[ J_{1s, 2p} \approx 0.1 \text{ eV} \]

Figure 10-1 Schematic diagram of the lowest states of helium. The spin-orbit interaction has been neglected since it is only \( \sim 10^{-4} \text{ eV} \). Degeneracies of levels are given in parentheses.
Molecular Physics.

If the velocity of the electrons is large compared to the nuclear velocity then the nuclear motion can be ignored and the nucleus can be taken as being fixed in space.

Adiabatic Approximation

Complete Hamiltonian is given by

\[
\left[ \mathcal{T}_R + \mathcal{T}_n + \mathcal{V}(\mathbf{r}, \mathbf{R}) \right] \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R})
\]

\[
\sum_k -\frac{\hbar^2}{2m} \nabla_k^2 + \sum_n -\frac{\hbar^2}{2m} \nabla_n^2 \quad \text{all electron coordinates}
\]

\[
\sum \quad \text{all nuclear coordinates}
\]

Now consider a simpler Hamiltonian \( \mathcal{H}_0 = \mathcal{T}_n + \mathcal{V}(\mathbf{r}, \mathbf{R}) \) when \( \mathbf{R} \)'s are fixed!

This Hamiltonian can be solved to obtain eigenfunctions \( U_n(\mathbf{r}, \mathbf{R}) \) with eigenvalues \( E_n(\mathbf{R}) \). The energies depend on the \( \mathbf{R} \) since it appears as a parameter in \( \mathcal{H}_0 \).

Then \( \Psi(\mathbf{r}, \mathbf{R}) \) should be expanded in terms of the \( U_n(\mathbf{r}, \mathbf{R}) \)

\[
\Psi(\mathbf{r}, \mathbf{R}) = \sum \chi_m(\mathbf{R}) U_m(\mathbf{r}, \mathbf{R})
\]

where we use both a sum and integral to denote all discrete and continuous states.
Substituting:

\[
\left[ T_R + T_\gamma + \sqrt{v(n, R)} \right] \mathcal{F}(n, R) = E \sum_{m} \phi_m(R) U_m(n, R).
\]

Or

\[
T_R \sum_{m} \phi_m(R) U_m(n, R) + \sum_{m} E_m(R) \phi_m(R) U_m(n, R) = E \sum_{m} \phi_m(R) U_m(n, R).
\]

Expanding \( T_R = -\frac{\hbar^2}{2m} \nabla_R^2 \):

\[
-\frac{\hbar^2}{2m} \sum_{m} \nabla_R^2 \left\{ \phi_m(R) U_m(n, R) \right\} = \]

\[
= -\frac{\hbar^2}{2m} \sum_{m} \nabla_R \cdot \left\{ \phi_m(R) \nabla_R U_m(n, R) + \nabla_R \phi_m(R) U_m(n, R) \right\}
\]

\[
= -\frac{\hbar^2}{2m} \sum_{m} \left\{ \phi_m(R) \nabla_R^2 U_m(n, R) + U_m(n, R) \nabla_R^2 \phi_m(R) \right\}
\]

\[
+ 2 \left( \nabla_R \phi_m(R) \cdot \nabla_R U_m(n, R) \right).
\]

\[
\text{If terms } 2 \text{ and } 3 \text{ can be ignored then we have:}
\]

\[
\sum_{m} \left\{ -\frac{\hbar^2}{2m} \left( \nabla_R^2 \phi_m(R) \right) U_m(n, R) + E_m(R) \phi_m(R) U_m(n, R) \right\} =
\]

\[
E \sum_{m} \phi_m(R) U_m(n, R)
\]

Using the orthogonality of the \( U_m \)'s we have

\[
-\frac{\hbar^2}{2m} \nabla_R^2 \phi_m(R) + E_m(R) \phi_m(R) = E \phi_m(R).
\]
We can interpret this equation as describing the nuclear motion moving within an “effective potential” $E_m(R)$. Since the effective potential depends upon the electronic wavefunction index $m$, the effective potential will depend upon the particular electronic configuration of interest.

Given the electronic configuration then the above equation can be solved for eigenfunctions $\Phi_m, \psi(R)$ and energies $E_m, \omega$ where the second index described the particular nuclear state for a given $m$ state configuration of the electron.

Interesting results can be shown for systems in which $E_m(R)$ has a minimum with respect to $R$, at $R_0$. (We shall assume $E_m(R)$ is spherically symmetric, i.e. $E_m(R) = E(R)$)

Expanding $E(R)$ about $R_0$ we have:

$$E_m(R) = E_m(R_0) + \frac{1}{2} \left[ \frac{\partial^2 E(R)}{\partial R^2} \right]_{R=R_0} (R-R_0)^2$$

Writing $\Phi_m(R) = \Phi_m(R, \Omega, \Gamma)$, we can rewrite $\Phi_m(R)$ in terms of the spherical harmonics since $E(R)$ is spherically symmetric.

$$\Phi_m(R) = \frac{G(R)}{R} Y^m_l (\Omega, \Gamma)$$

where

$$-\frac{\hbar^2}{2M} \frac{\partial^2 G(R)}{\partial R^2} + \left[ \frac{1}{2} K (R-R_0)^2 + \frac{L(L+1)k^2}{2M} \right] G(R) = (E-E_0) G(R).$$

$K = \left[ \frac{\partial^2 E(R)}{\partial R^2} \right]_{R=R_0}$.
Thus the "effective potential" for the molecular indicates that the nuclear motion can be thought of as harmonic oscillations about the equilibrium position as well as rotations. This would correspond to the vibrational and rotational modes seen in the spectra of molecules.

Note: the potential term of the harmonic oscillator is determined by the binding energy of the electronic system.
Hydrogen Molecule.

To simplify our work a bit we will consider only the ionized molecule, ie only with one electron.

\[
\text{H}_2^+ \rightarrow r_C^+ + r_A^+ + r_l^+ = \frac{e^2}{\sqrt{\pi} a_0 r_A} - \frac{e^2}{\sqrt{\pi} a_0 r_B} + \frac{e^2}{\sqrt{\pi} a_0 |R_A - R_B|}
\]

\[
\begin{align*}
&\quad r_A = r - R_A \\
&\quad r_B = r - R_B
\end{align*}
\]

From our previous analysis we attack this problem by first assuming the protons are fixed in space and solve the resulting electron Hamiltonian with the distance between the protons as a parameter.

\[
\hat{H}_e = -\frac{\hbar^2}{2m} \nabla^2 r - \left( \frac{e^2}{\sqrt{\pi} a_0 r_A} + \frac{e^2}{\sqrt{\pi} a_0 r_B} \right)
\]

Now if the two protons were widely separated one could find a solution of \( \hat{H}_e \) where the electron is only localized about one of the protons.

\[
\begin{align*}
&\quad \bullet_a \quad \text{Described by } \psi_a(r) \\
&\quad \bullet_b \quad \text{or} \\
&\quad \bullet_b \quad \text{Described by } \psi_b(r).
\end{align*}
\]

But \( \hat{H}_e \) is symmetric under the interchange of the labels \( a \) and \( b \). Thus if we invent an operator (call it \( \hat{X}_{ab} \)) which exchanges the labels \( a \) and \( b \) the \( \hat{H}_e \) commutes with \( \hat{X}_{ab} \). \( [\hat{H}_e, \hat{X}_{ab}] = 0 \). Consequently the eigenstates of \( \hat{H}_e \) can be chosen to be eigenstates of \( \hat{X}_{ab} \). [Note: Since \( \hat{X}_{ab} \hat{X}_{ab} = 1 \) the eigenvalues of \( \hat{X}_{ab} \) are just \( \pm 1 \)]. The appropriate eigenstates of \( \hat{H}_e \) are then linear combinations of \( \psi_a(r) \) and \( \psi_b(r) \):

\[
\psi_{\pm}(r) = \left[ \psi_a(r) \pm \psi_b(r) \right] \sqrt{\frac{1}{2}}
\]
Using these two states as our initial wavefunction we can calculate the expectation values of \( \hat{H} \). [See Park Chap 16]

\[
\langle \psi_\pm | \hat{H} | \psi_\pm \rangle = \frac{1}{i} \int \left( \psi_a(n) \pm \psi_b(n) \right) \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{E^2}{4\pi\varepsilon_0} \left( \frac{1}{r_a} + \frac{1}{r_b} \right) \right] \left( \psi_a \pm \psi_b \right) dV
\]

\[
W_\pm = \left( -1 + \frac{\Delta \pm \varepsilon}{1 \pm \Delta} \right) E_{R_g}
\]

where
\[
\Delta = \left( 1 + \frac{R/a_o}{a_o} + \frac{1}{3} \left( \frac{R/a_o}{a_o} \right)^2 \right) e^{-R/a_o}
\]
\[
\varepsilon = -2 \left( 1 + \frac{R/a_o}{a_o} \right) e^{-R/a_o}
\]

The total energy of the system becomes:

\[
E_\pm = W_\pm + \frac{\varepsilon^2}{4\pi\varepsilon_0 R}
\]

\[
E_\pm = \left[ -1 + \frac{2a_o}{R} \right] \left\{ \begin{array}{l}
\pm \left( 1 - \frac{2}{3} \left( \frac{R/a_o}{a_o} \right)^2 \right) e^{-R/a_o} + \left( 1 + \frac{R/a_o}{a_o} \right) e^{-2R/a_o} \\
1 \pm \left( 1 + \frac{R/a_o}{a_o} + \frac{1}{3} \left( \frac{R/a_o}{a_o} \right)^2 \right) e^{-R/a_o}
\end{array} \right\}
\]

\[\frac{E}{R_g}\]

\[\frac{E}{R_g}\]

\[\frac{E}{R_g}\]

\[\frac{E}{R_g}\]

\[\frac{E}{R_g}\]
The interpretation of these curves is rather straightforward.

The anti-bonding orbital (or $4_-$) has a small probability of find the electron between the two protons

$$4_-(r) = \frac{1}{\sqrt{2}} \left[ \psi_a(r) - \psi_b(r) \right] = \frac{1}{\sqrt{2}} \left\{ \psi_{1s}(r-R_a) - \psi_{1s}(r-R_b) \right\}$$

Hydrogenic 1S wave function evaluated at displaced origins.

So for $r \approx 0$ (directly in between protons), the two functions cancel each other. Without the screening provided by the electron, the electrostatic potential between the two protons is too large to permit binding.

The $4_+$ state does have a finite probability density for the electron between the two protons and so the potential energy is smaller. However, once the two protons come closer than $a$, then the electron will start to orbit about both of them (in the limit as $R \rightarrow 0$, the system begins to look like "He+"). Once again, the potential energy increases rapidly as $1/r$ because of the repulsion of the two protons.
Another simple example is the bound state of the finite potential well.

\[
\begin{array}{c}
  \text{The eigenvalues of the bound states are given by the transcendental equation:} \\
  \tan \left[ 2a \sqrt{\frac{2m}{\hbar^2} \left( \frac{1}{V_0} - |E| \right)} \right] = \frac{2 \sqrt{|E| (|V_0| - |E|)}}{|V_0| - 2|E|}
\end{array}
\]

For large \( |V_0| \) we can expand the above equation to estimate the ground state energy as

\[
E = -|V_0| + \frac{k^2 \pi^2}{2m (2a)^2} \left( 1 - \frac{4\pi^2}{\left[ \frac{2m |V_0| (2a)^2}{\hbar^2} \right]^2} \right)
\]

Note: In the limit \( |V_0| \to \infty \) we obtain the standard result for the infinite potential well, \( E = \frac{k^2 \pi^2 n^2}{2m (2a)^2} \).

For two isolated wells, \( \hat{H}_a + \hat{H}_b \)

\[
\begin{array}{c}
  \text{we can approximate the true solutions by using the eigenstates of the single well.}
\end{array}
\]
In this limit (R large) both wave functions are degenerate in energy.

\[ E_+ = -|V_0| + \frac{k^2 \pi^2}{2m(2a)^2} - \frac{4\pi^2}{\left( \frac{2m}{k^2} |V_0| (2a)^2 \right)^{1/2}} \]

When \( R \) becomes smaller, the two wavefunctions \( \psi_+ \) and \( \psi_- \) will begin to overlap. In fact, for \( R \to 0 \) \( \psi_+ \) will begin to look like the ground state of the double well (of width \( 4a \)) whereas \( \psi_- \) begins to look like the 1st excited state of the double well.

\[ E_+ = -|V_0| + \frac{k^2 \pi^2}{2m(4a)^2} - \frac{4\pi^2}{\left( \frac{2m}{k^2} |V_0| (2a)^2 \right)^{1/2}} \]

\[ E_- = -|V_0| + \frac{\left( \frac{1}{2} \right) k^2 \pi^2}{2m(4a)^2} - \frac{\left( \frac{1}{2} \right) 4\pi^2}{\left( \frac{2m}{k^2} |V_0| (2a)^2 \right)^{1/2}} \]

Using the results for a single well of width \( 4a \), we expect the energies \( E_+ \) to approach.

Here we see the effect of the kinetic energy on each wavefunction $\psi_+$ having a smaller curvature than the small kinetic energy and therefore the lower total energy.

To produce a minimum in the energy diagram, as in the case of the hydrogen molecule, we could add a repulsive potential proportional to $1/R$. In this case we would get the same qualitative picture.
An interesting feature of the above problem is that from the single ground state of each well, 2 states were generated in the final configuration. This is a general feature of such problems. In fact if we had N wells one would expect N new states to appear.

What happens in a system, where N is large. An example of such a system might be the atoms in a lattice. For a periodic array of atoms, the potential seen by an electron might look like

\[ \begin{array}{cccccccc}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\end{array} \]

To make the 1D example truly periodic let us assume there are N sites and that points \( x + Nd \) are identified with \( x \).

In this system \( V(x) = V(x + d) \), periodic function with period \( d \)

Define a displacement operator \( \mathcal{D} \) such that

\[ \mathcal{D} f(x) = f(x + d) \].

Clearly the Hamiltonian for the electron commutes with \( \mathcal{D} \)

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \]
Therefore eigenfunctions of $\mathcal{H}$ can be chosen to be eigenfunctions of $D$. is

$$D(d) \psi(x) = \lambda(d) \psi(x)$$

where the eigenvalue $\lambda$ could depend on the value of $d$.

**Determination of $\lambda$:**

1. $D(d) \psi(x) = \psi(x+d) = \lambda(d) \psi(x)$

Therefore,

$$\frac{\partial \psi(x+d)}{\partial d} = \frac{\partial \lambda(d)}{\partial d} \psi(x)$$

but

$$\frac{\partial \psi(x+d)}{\partial d} = \frac{\partial \psi}{\partial x} \bigg|_{x+d} = \frac{\psi(x+d+\epsilon) - \psi(x+\epsilon)}{\epsilon}$$

$$= \frac{\lambda(d)}{\epsilon} \left( \psi(x+\epsilon) - \psi(x) \right) = \lambda(d) \frac{\partial \psi(x)}{\partial x}$$

and so

$$\frac{\partial \lambda(d)}{\partial d} \psi(x) = \lambda(d) \frac{\partial}{\partial x}$$

$$\frac{1}{\lambda(d)} \frac{\partial \lambda(d)}{\partial d} = \frac{1}{\psi(x)} \frac{\partial}{\partial x} = \text{constant} - i k.$$}

$$\frac{\partial \lambda(d)}{\lambda(d)} = i k d \quad \text{or} \quad \ln \lambda = i k d \quad \lambda = e^{i k d}.$$
\[ \frac{\mathcal{D}}{d} \psi(x) = \psi(x + d) = \lambda(d) \psi(x) \]

\[ \mathcal{D} \mathcal{D} \psi(x) = \psi(x + 2d) = \lambda(2d) \psi(x) = \lambda^2(d) \psi(x) \]

and so \( \lambda(2d) = \lambda^2(d) \) clearly is satisfied by \( e^{ikd} = \lambda(d) \)

Note: Previously we showed \( \mathcal{D} = e^{ipd} = e^{d \frac{\partial}{\partial x}} \).

Therefore solutions of \( \mathcal{H} \) have the property of:

\[ \psi(x + d) = e^{ikd} \psi(x) \]

If the wavefunctions are periodic modulo a complex factor with modulus 1. (This makes the electron density \( \psi^* \psi \) periodic in \( d \)!

Alternatively one can express \( \psi(x) = e^{ikx} \mathcal{U}(x) \) subehbning

\[ \psi(x + d) = e^{ikd} e^{ikx} \mathcal{U}(x + d) = e^{ikd} e^{ikx} \mathcal{U}(x). = e^{ikd} \psi(x) \]

which shows \( \psi(x) = e^{ikx} \mathcal{U}(x) \) is a solution if \( \mathcal{U}(x) \) is periodic \( \mathcal{U}(x + d) = \mathcal{U}(x) \)

This formalism is called Bloch's Theorem.

Note: Since \( \mathcal{H} \) does not commute with \( \mathcal{P} \) the momentum is not conserved in the crystal. (Hence the crystal momentum of the electron and electron momentum together are conserved.)
Our initial constraint of periodic boundary conditions imposes a restriction on the values of k. In particular, since the point $x + N \delta$ is indistinguishable from the point $x$ we have that
\[ \psi(x + N \delta) = \psi(x) \] 
but
\[ \psi(x + N \delta) = e^{ikN\delta} \psi(x) = \psi(x) \]
or
\[ e^{ikN\delta} = 1. \]

Therefore $kN\delta = n2\pi$ where $n$ is any integer ranging from 0 to $\pm(N-1)$. The allowed $k$ values then are

\[ k_n = \frac{n(2\pi)}{N\delta} = n\left(\frac{2\pi}{L}\right) \]

where $L$ is the total length of the system.
Can we determine some general features of a periodic potential without specifying the exact details of the potential.

For simplicity consider a single section of the periodic potential isolated from all the others.

We shall also take for convenience a symmetric potential i.e.

\[ V(x) = V(-x) \]

Take electrons to be incident from the left with energy \( E = \frac{k^2}{2m} \). For \( |x| > \frac{a}{2} \) the potential is zero and we can write \( \psi(x) \) as:

\[
\begin{align*}
  x < -\frac{a}{2} & \quad \psi_e(x) = e^{iKx} + e^{-iKx} \\
  x > \frac{a}{2} & \quad \psi_e(x) = t e^{iKx}
\end{align*}
\]

Note: \( \psi_e \) represents the wave function for electrons incident from the left and can be written explicitly in the regions shown above.
The coefficients $r$ and $t$ represent the amplitudes for reflection and transmission respectively.

Similarly if the electrons are incident from the right we can write down the wave function as follows.

$$x > -\frac{a}{2} \quad \psi_r(x) = e^{-ikx} + re^{ikx}$$
$$x \leq -\frac{a}{2} \quad = te^{-ikx}.$$

Note: since $\psi(x) = \psi(-x)$ we know that the amplitudes $r$ and $t$ are equal for each case. (since $\psi_e(x) = \psi_r(-x)$).

Since $\psi_e$ and $\psi_r$ are linearly independent solutions of the Schrödinger equation for the same energy $E = \frac{k^2}{2m}$, then any other solution of the same energy can be written as a linear combination of them $\psi = A\psi_e + B\psi_r$.

In particular, since the Hamiltonian for the periodic potential is the same for our problem in the region $-\frac{a}{2} \leq x \leq \frac{a}{2}$, the solution for the periodic potential with energy $E$ must be a linear combination of $\psi_e$ and $\psi_r$ in that region.

$$\psi(x) = A\psi_e(x) + B\psi_r(x) \quad -\frac{a}{2} \leq x \leq \frac{a}{2}$$
From Block's theorem, \( \psi(x + a) = e^{ika} \psi(x) \)

Similarly for differentiation
\[
\frac{d\psi}{dx}(x + a) = e^{ika} \frac{d\psi}{dx}(x).
\]

Apply these to our problem. At \( x = -a/2 \)

\[
\psi(-a/2 + a) = e^{ika} \psi(-a/2)
\]

but

\[
\psi(a/2) = A \psi_{e} (a/2) + B \psi_{r} (a/2)
\]

\[
= A t e^{ikx/2} + B (e^{-ikx/2} + re^{ikx/2})
\]

and

\[
\psi(-a/2) = A \psi_{e} (-a/2) + B \psi_{r} (-a/2)
\]

\[
= A (e^{-ikx/2} + re^{ikx/2}) + B t e^{ikx/2}
\]

and finally

\[
A t e^{ikx/2} + B (e^{-ikx/2} + re^{ikx/2}) = e^{ika} A (e^{-ikx/2} + re^{ikx/2}) + Be^{ika} + ikA + k \]

\[
\begin{array}{l}
1 \rightarrow \quad A \left[ (t - re^{ika}) e^{ika/2} - e^{ika} e^{-ika/2} \right] \\
+ B \left[ e^{-ika/2} + (1 - e^{ika}) e^{ika/2} \right] = 0
\end{array}
\]

Repeating the above for the derivative relation we obtain

\[
2 \rightarrow \quad A \left[ (t + re^{ika}) e^{ika/2} - e^{ika} e^{-ika/2} \right] \\
+ B \left[ -e^{-ika/2} + (1 + te^{ika}) e^{ika/2} \right] = 0
\]
Substituting in for B from the first relation 1 and 2 we find that

\[
A \left\{ \left( t + re^{ika} \right) e^{ika} + r e^{iKa} \right\} \left( e^{iKa} + (r - e^{ika}) e^{ika} \right) \\
- \left( e^{-ika} + (r + te^{ika}) e^{ika} \right) \left( \left( t - re^{ika} \right) e^{ika} + e^{ika} \right) = 0.
\]

In which case either A = 0 (which is not unlikely) or the bracket vanishes. Expanding and multiplying we have

\[
\left\{ \left( t + re^{ika} \right) e^{ika} + r e^{iKa} \right\} - e^{ika} + e^{ika} \left( r - e^{ika} \right) + \left( t - re^{ika} \right) - e^{ika} + e^{ika} (r + te^{ika}) \right\} = 0
\]

\[
2t - 2 e^{ika} + e^{ika} \left[ t - r e^{ika} + r e^{ika} - r e^{ika} \right] - e^{ika} (r + te^{ika}) - e^{ika} \left[ r t - r e^{ika} + t e^{ika} - r e^{ika} \right] + e^{ika} + te^{ika} = 0
\]

\[
2t - 2 e^{ika} + e^{ika} \left[ r e^{ika} - t e^{ika} \right] = 1
\]

\[
2t \left( 1 + e^{2ika} \right) - 2 e^{ika} + 2 e^{ika} \left( r^2 - t^2 \right) = 0
\]

\[
2t \left( e^{ika} + e^{-ika} \right) - 2 e^{ika} + 2 e^{ika} \left( r^2 - t^2 \right) = 0
\]

\[
4t \cos ka - 2 e^{-ika} + 2 e^{ika} \left( r^2 - t^2 \right) = 0
\]
\[ \cos k \alpha = \frac{t^2 - r^2}{2t} e^{i \alpha k} + \frac{e^{-i \alpha k}}{2t} \]

To simplify these expressions we need to prove relationships between \( r \) and \( t \). From conservation of flux we know

\[ 1 = |k|^2 + |r|^2 \]

Consider the Schrödinger wave equation for \( \psi_e \) and \( \psi_r^* \) (since \( V(x) \)

so read \( \psi_r^* \) is also a solution).

1. \[ -\frac{k^2}{2m} \frac{\partial^2}{\partial x^2} \psi_e + V(x) \psi_e = E \psi_e \]

2. \[ -\frac{k^2}{2m} \frac{\partial^2}{\partial x^2} \psi_r^* + V(x) \psi_r^* = E \psi_r^* \]

Multiplying \( \psi_r \) by \( \psi_r^* \) and \( \frac{\partial}{\partial x} \) by \( \psi_e \) and subbing into we have.

\[ \psi_r^* \frac{\partial^2}{\partial x^2} \psi_e - \psi_e \frac{\partial^2}{\partial x^2} \psi_r^* = 0 \quad \mathfrak{e} \]

\[ -\frac{\partial}{\partial x} \left[ \psi_r^* \frac{\partial}{\partial x} \psi_e - \psi_e \frac{\partial}{\partial x} \psi_r^* \right] = 0 \quad \mathfrak{e} \]

\[ \psi_r^*(x) \frac{\partial}{\partial x} \psi_e(x) - \psi_e(x) \frac{\partial}{\partial x} \psi_r^*(x) = \text{constant} \quad (\text{independent of } x) \]

Evaluating the above at \( x \gg \frac{a}{2} \)

\[ (e^{ikx} + r^* e^{-ikx})(t x e^{ikx}) = te^{ikx} (i k x e^{-ikx} - i k x e^{ikx}) \]

\[ 2ik tr^* = \text{const} \]
at \( x \leq -\frac{q}{2} \)

\[
(t^* e^{ikx})(ik e^{ikx} - ixe^{-ikx}) = (e^{ikx} + e^{-ikx})(i e^{ikx})
\]

\[-2i \kappa t^* = \text{const.}\]

Since the constant is independent of \( x \)

\[-2i \kappa t^* = 2i \kappa r^* t\]

or

\[r^* t = -r^* t = -(r^* t)^*\]

Therefore \( r^* t \) must be pure imaginary.

If we represent \( t = |t| e^{i\delta} \) then

\[r^* t = \pm |r| e^{i\delta} \]

or

\[r = \pm |t| r |e^{i\delta}\]

Consequently

\[
\frac{t^2 - r^2}{2t} = \frac{|t|^2 e^{2i\delta} - (i)^2 |r|^2 e^{2i\delta}}{2 |t| e^{i\delta}}
\]

\[= \frac{|t|^2 + 1r^2 |e^{i\delta} = \frac{e^{i\delta}}{2 |t|}}{2 |t|}\]

and so

\[\cos \kappa a = \frac{t^2 - r^2}{2t} e^{i\kappa a} + \frac{e^{-i\kappa a}}{2t}\]

become
\[
\cos ka = \frac{e^{i(\kappa a + \delta)}}{2|t|} + \frac{e^{-i(\kappa a + \delta)}}{2|t|}
\]

\[
\cos ka = \cos \left( \frac{\kappa a + \delta}{|t|} \right)
\]

\[
\varepsilon = \frac{k^2}{2m}
\]

Now, \(|t| \ll 1\) for all values of \(\varepsilon\), but will approach 1 as \(\varepsilon\) increases. (i.e. the potential barrier becomes ineffective at high energies).

Consequently, \(\cos \left( \frac{\kappa a + \delta}{|t|} \right)\) can be greater than 1. In these regions no solution exists for \(ka\) since \(|\cos ka| \ll 1\). Graphically,

The interpretation is that for some energy regions, such as \(E_3 \leq E \leq E_4\), solutions exist whereas for other regions no solutions exist, \(E_4 \leq E \leq E_5\).
Consider a single region of allowed

\[ \cos\left(\frac{2\alpha + \delta}{1t}\right) \]

large number of k values.

From the \( \cos\left(\frac{2\alpha + \delta}{1t}\right) \) curve we see that for a given \( k_d \) value there will be many (infinite) solutions with different energies.

\[ \text{Band Gaps} \]
Physical significance of $E(k)$

We can take a semi-classical approach and make a wave packet to represent a single electron in the system:

$$\psi(x) = \int_{k_0 - \Delta k}^{k_0 + \Delta k} dx' \psi_{k'}(x)$$

so that $\psi(x)$ is localized.

As we showed earlier, this wave packet travels with a velocity given by $V_{\text{group}} = \frac{\partial E}{\partial p} = \frac{\partial E(k)}{\partial k}$. If $k = k_0$

If we put an electric field on the system the electron will experience a force $-eE$. We would expect the wave packet to accelerate. How does this happen? If the original Hamiltonian is given by $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

$[\hat{D}, \phi_k] = 0$ and $k$ is a good quantum number.

$\hat{D} \phi_k = e i k a \phi_k$. 

If we add this new force \(-e|E|\) we add a potential of the form \(+e|E|\times\) to \(H_0\). Now \(\mathcal{O}\) no longer commutes with \(H = H_0 + e|E|\times\) and in fact,

\[
[H, \mathcal{O}] = [e|E|\times, \mathcal{O}] 
\]

\[
[e|E|\times, \mathcal{O}] \psi(x) = e|E|\times \mathcal{O} \psi(x) - \mathcal{O} e|E|\times \psi(x) 
\]

\[
= e|E|\times \mathcal{O} \psi(x) - e|E| (x+a) \psi(x+a) 
\]

\[
= -e|E| a \psi(x+a) = -e|E| a \mathcal{O} \psi(x). 
\]

and so

\[
\frac{d}{dt} \langle \mathcal{O} \rangle = \frac{i}{\hbar} \langle [H, \mathcal{O}] \rangle = -\frac{i}{\hbar} e|E| a \langle \mathcal{O} \rangle 
\]

The rate of change of \(\langle \mathcal{O} \rangle\) can be related to the time rate of change of \(k_0\), the mean value of the \(k\)-values of the wave packet, to give

\[
\frac{d}{dt} k_0 = -e|E| 
\]

i.e., the value of \(k_0\) increases/decreases at a steady rate.
Consider what happens to a wavepacket with \( k_0 \) in the center of the band \( k_0 \rightarrow 0 \).

(Use \( E = -\hbar^2 k^2 / 2m \).)

As \( k_0 \) increases from zero the velocity of the wave packet increases and the particle accelerates. But as \( k_0 \) approaches \( \pi / d \) the velocity starts to decrease and eventually becomes zero!

If we continue to increase \( k_0 \) we find that \( v_{\text{group}} \) again increases but now in the opposite direction.

If we ask what is the acceleration, we find

\[
a = \frac{d v_{\text{group}}}{dt} = \frac{d}{dt} \frac{dE(k)}{dk} \bigg|_{k_0} = \frac{1}{k} \frac{d^2 E(k)}{dk^2} \bigg|_{k_0}
\]

\[
a = \frac{1}{k^2} \frac{d^2 E(k)}{dk^2} \cdot (-\epsilon |E|).
\]

Which looks like \( F = ma \) if we identify \( \frac{1}{m^*} = \frac{1}{k^2} \frac{d^2 E(k)}{dk^2} \) with the inverse of an effective mass.

It is reasonable that the curvature of the \( E(k) \) curve be related to the mass.
If I have a simple free particle of mass \( m \) then
\[
E = \frac{p^2}{2m}
\]
and so
\[
\frac{1}{E} \frac{\partial E}{\partial k} = \frac{1}{m}
\]

\[\begin{align*}
\text{small } m. & \quad \text{large mass:} \\
\text{ harder to increase energy} & \quad \text{ for a given increase in momentum.}
\end{align*}\]

So for near \( k = 0 \) the wavepacket behaves normally

\[\begin{align*}
\text{but near } k_0 \approx \pi & \quad \text{the curvature is negative!} & \quad \text{Typically people}
\end{align*}\]
define the effective mass as positive definite
\[
m^* = \left[ \frac{1}{k^2} \frac{\partial^2 E}{\partial k^2} \right]^{-1}
\]
and change the sign of the change to compensate. The fact that the wavepacket slows down then is consistent with the particle having the opposite change!

In particular at \( k_0 \approx \pi \) we can expand \( E(k) \) as
\[
E(k) = E(k_0 = \pi) + \left( \frac{\partial E}{\partial k} \right)_{k_0} (k-k_0) + \frac{1}{2!} \left( \frac{\partial^2 E}{\partial k^2} \right)_{k_0} (k-k_0)^2
\]
\[
= E\left( \frac{\pi}{d} \right) + \frac{1}{2} \frac{k^2 (k-k_0)^2}{m^*}
\]