

Perturbation Theory

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1 Stationary state perturbation theory

1.1 Nondegenerate Formalism

We have a Hamiltonian

$$H = H_0 + V$$

and we suppose that we have determined the complete set of solutions to H_0 with ket $|n_0\rangle$ so that $H_0|n_0\rangle = E_n^0|n_0\rangle$. And we suppose that there is no degeneracy. The eigenkets of H satisfy

$$H|n\rangle = E_n|n\rangle \rightarrow (H_0 + V)|n\rangle = (E_n^0 + \Delta_n)|n\rangle \quad (1)$$

$$(E_n^0 - H_0)|n\rangle = (V - \Delta_n)|n\rangle \quad (2)$$

where $E_n = E_n^0 + \Delta_n$. We multiply the perturbative term by a real parameter λ and insist that Δ_n is analytic in λ as λ goes from 0 to 1. Then Equation ?? becomes

$$(E_n^0 - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle \quad (3)$$

The perturbation is small if the energy shift is small compared to the spacing of the unperturbed levels that might be connected by the perturbation. That last equation is our Schrodinger equation and we could invert it like so

$$|n\rangle = \frac{1}{E_n^0 - H_0}(\lambda V - \Delta_n)|n\rangle$$

To make sure we don't do something crazy like divide by zero we project out the $|n_0\rangle$ ket by introducing a projection operator

$$\phi = \sum_{k \neq n} |k^0\rangle \langle k^0|$$

Then we make the equation safe from nan.

$$|n\rangle = \frac{\phi}{E_n^0 - H_0} (\lambda V - \Delta_n) |n\rangle$$

We are not losing anything here since Equation ?? says that

$$\langle n_0 | \lambda V - \Delta_n | n \rangle = 0 \tag{4}$$

Finally, so we have something sensible as $\lambda \rightarrow 0$ we add the solution to the unperturbed part and write

$$|n\rangle = |n_0\rangle + \frac{\phi}{E_n^0 - H_0} (\lambda V - \Delta_n) |n\rangle$$

One last thing to note. Normalization. It seems that $\langle n | n_0 \rangle = 1$. We will use this fact. $|n\rangle$ is not normalized by itself. Now Equation ?? says that

$$\Delta_n = \lambda \langle n_0 | V | n \rangle$$

Now we suppose that

$$|n\rangle = |n_0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots$$

and

$$\Delta_n = \lambda \Delta_n^1 + \lambda^2 \Delta_n^2 + \dots$$

Then equation powers of λ . Our energy equation becomes

$$\lambda \Delta_n^1 + \lambda^2 \Delta_n^2 + \dots = \lambda \langle n_0 | V (|n_0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots)$$

So

$$\begin{aligned} \Delta_n^1 &= \langle n_0 | V | n_0 \rangle \\ \Delta_n^2 &= \langle n_0 | V | n^1 \rangle \\ \Delta_n^3 &= \langle n_0 | V | n^2 \rangle \end{aligned}$$

And for the wave function

$$|n_0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots = |n_0\rangle + \frac{\phi}{E_n^0 - H_0}(\lambda V - (\lambda\Delta_n^1 - \lambda^2\Delta_n^2 + \dots))|n_0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots$$

Equating stuff linear in λ we get

$$|n^1\rangle = \frac{\phi}{E_n^0 - H_0} V |n_0\rangle \quad (5)$$

Next everything quadratic in λ gives

$$|n^2\rangle = \frac{\phi}{E_n^0 - H_0} (V|n^1\rangle - \Delta_n^1|n^1\rangle)$$

$$|n^2\rangle = \frac{\phi}{E_n^0 - H_0} \left(V \frac{\phi}{E_n^0 - H_0} V |n_0\rangle - \langle n_0 | V | n_0 \rangle \frac{\phi}{E_n^0 - H_0} V |n_0\rangle \right)$$

And we can use our solution for $|n^1\rangle$ to see that

$$\Delta_n^2 = \langle n_0 | V \frac{\phi}{E_n^0 - H_0} V |n_0\rangle = \sum_{k \neq n} \frac{|\langle n_0 | V | k_0 \rangle|^2}{E_n^0 - E_k^0}$$

It is evident that degeneracy could get us in trouble.

1.2 Examples

1.2.1 Helium

To first approximation, the energy of the ground state of helium is

$$2Z^2 E_0 = -2Z^2 \left(\frac{e^2}{2a} \right) = 2(4)(-13.6 \text{ eV}) = -108.8 \text{ eV}$$

The next approximation would be to include the interaction of the electrons as a perturbation.

$$V = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The unperturbed wave function is taken to be

$$\psi(r_1, r_2) = \psi_0(r_1)\psi_0(r_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

where

$$a = \frac{\hbar c}{\alpha m c^2}$$

Set the polar axis along \mathbf{r}_1 and

$$E^1 = e^2 \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} r_1^2 d\Omega_1 r_2^2 d\Omega_2 = e^2 \frac{5}{4a}$$

Then the total energy is

$$E = 2(4) \left(\frac{-e^2}{2a} \right) + \frac{5e^2}{4a} = -\frac{11e^2}{4a} = -\frac{11}{2}(13.6\text{ev}) = -74.8\text{ev}$$

1.2.2 Stark effect for rigid rotator

The hamilonian for the rigid rotator is

$$H = \frac{L^2}{2I}$$

where I is the moment of inertia and the vibrational levels are assumed infinitely far apart as compared to the spacing of the rotational levels. Then the energy eigenstates and eigenvalues are $|\psi\rangle = |l, m\rangle$ and $E_l = \frac{\hbar^2 l(l+1)}{2I}$. In the presence of a uniform electric field in the z direction we introduce

$$V = -e\mathbf{z}\mathcal{E} = -er\mathcal{E} \cos \theta$$

We suppose that $e\langle r \rangle = d$ is the electric dipole moment of the rotator. (All states have the same radial wave function). We can write

$$V = T_0^1 = -d\mathcal{E} \sqrt{\frac{4\pi}{3}} Y_{1,0}(\theta)$$

We need to evaluate

$$\langle l_2, m_2 | T_0^1 | l_1, m_1 \rangle$$

The matrix element is non zero if $m_1 = m_2$ and $(|l_2 - l_1| \leq 1, \text{Wigner Eckart}), l_1 \neq l_2, \text{(parity)}$. Then the non zero matrix element can be written

$$\langle l \pm 1, m | T_0^1 | l, m \rangle = -d\mathcal{E} \sqrt{\frac{4\pi}{3}} \int Y_{l \pm 1, m}^* Y_{1,0} Y_{l, m} d\Omega$$

$$\begin{aligned}
&= -d\mathcal{E} \sqrt{\frac{4\pi}{3}} \sqrt{\frac{(2(1)+1)(2l+1)}{4\pi(2(l\pm 1)+1)}} \langle 1, 0, l, m | l \pm 1, m \rangle \langle 1, 0, l, 0 | l \pm 1, 0 \rangle \\
&= -d\mathcal{E} \sqrt{\frac{(2l+1)}{(2(l\pm 1)+1)}} \langle 1, 0, l, m | l \pm 1, m \rangle \langle 1, 0, l, 0 | l \pm 1, 0 \rangle \\
&= -d\mathcal{E} \sqrt{\frac{l^2 - m^2}{4l^2 - 1}}
\end{aligned}$$

The unperturbed levels are all degenerate. But since H_0 and V both commute with L_z , there is no mixing, and non degenerate theory is OK. In each of the m subspaces, the spectrum is non degenerate. The first order correction is zero, by the rules above, $\langle l, m | T_0^1 | l, m \rangle = 0$. The second order correction reduces to the two terms corresponding to $l = \pm 1$. Finally

$$\epsilon_2^{lm} = \left(\frac{d\mathcal{E}}{E_l^0} \right)^2 \frac{l(l+1) - 3m^2}{2(2l-1)(2l+3)}$$

The degeneracy is only partly removed, since it depends on m^2 . Some symmetry remains. We could compute the electric dipole moment.

$$\mu \sim e \langle n | \mathbf{z} | n \rangle$$

We have that

$$|n\rangle \sim |n_0\rangle + \sum_{k \neq n} \frac{\langle k_0 | T_0^1 | n_0 \rangle}{E_n^0 - E_k^0} |k_0\rangle$$

Then

$$\mu \sim \sum_{k \neq n} \frac{\langle n_0 | z | k_0 \rangle \langle k_0 | T_0^1 | n_0 \rangle}{(E_n^0 - E_k^0)} = \frac{1}{\mathcal{E}} \sum_{k \neq n} \frac{\langle n_0 | T_0^1 | k_0 \rangle \langle k_0 | T_0^1 | n_0 \rangle}{(E_n^0 - E_k^0)}$$

1.2.3 Stark effect in hydrogen

As in the case of the rigid rotator, the perturbation commutes with L_z so there is no mixing of states with different m and we use non degenerate perturbation theory. Also, since all of the eigenstates with definite angular momentum have definite parity, there is no first order correction. Another way to see this is to note that although the perturbed Hamiltonian does not commute with L^2 , it does commute with L_z . So there is no change to the z-component and therefore no mixing of states with

$m \neq m'$. Parity eigenstates have zero electric dipole moment. The electric dipole moment is

$$d = \langle \alpha, l, m | \mathbf{x} | \alpha, l, m \rangle = \int \mathbf{x} |\psi(\mathbf{x})|^2 d^3\mathbf{x} = 0$$

since \mathbf{x} has odd parity. An electric dipole emerges in second order since the first order correction to the wave function includes contributions of opposite parity. That also means that the electric dipole moment scales with the applied electric field. The energy shift is quadratic in E

The polarizability is α where

$$\Delta = -\frac{1}{2}\alpha|\mathbf{E}|^2$$

The energy shift is second order

$$\Delta^2 = e^2 \mathcal{E}^2 \sum_{k \neq 0} \frac{|\langle k^0 | z | 1, 0, 0 \rangle|^2}{(E_0^0 - E_k^0)}$$

We approximate the sum by assuming that the denominator is constant, (this will give us an upper limit on the energy shift) and noting that

$$\sum_{k \neq 0} |\langle k^0 | z | 1, 0, 0 \rangle|^2 = \sum_{all\ k} |\langle k^0 | z | 1, 0, 0 \rangle|^2$$

since $\langle 1, 0, 0 | z | 1, 0, 0 \rangle = 0$. The sum over all k becomes

$$\sum_{all\ k} |\langle k^0 | z | 1, 0, 0 \rangle|^2 = \langle 1, 0, 0 | z^2 | 1, 0, 0 \rangle = \frac{1}{3} \langle r^2 \rangle = a_0^2$$

Therefore,

$$\Delta^2 \leq e^2 \mathcal{E}^2 \frac{a_0^2}{(E_0^0 - E_k^0)} = \Delta^2 \leq e^2 \mathcal{E}^2 \frac{a_0^2}{(-e^2/2a_0 - \frac{-1}{4}e^2/2a_0)} = -\mathcal{E}^2 \frac{8a_0^3}{3}$$

2 Degenerate perturbation theory

Our formalism falls apart if there are degeneracies. But actually, it is OK as long as the perturbation does not couple the degenerate states. If it does couple degenerate states we are in trouble since then we have finite numerator and an energy denominator that is zero in Equation ???. The strategy is to find a new basis for the degenerate states in which none of the states in that basis are coupled by the perturbation.

2.1 Formalism

So here's what we do. Suppose that there is a degenerate set of states and we are interested in the effect on the perturbation of states at that energy. The states are $|i\rangle$, $i = 1, 2, 3$ for example. Now if $\langle i | V | j \rangle = |V|\delta_{ij}$ then we do not have a problem. Business as usual. If there are off-diagonal terms, then we need to find a different linear combination of the degenerate states for which the perturbation matrix is diagonal. That is we diagonalize

$$V = \begin{pmatrix} \langle 1 | V | 1 \rangle & \langle 1 | V | 2 \rangle & \langle 1 | V | 3 \rangle \\ \langle 2 | V | 1 \rangle & \langle 2 | V | 2 \rangle & \langle 2 | V | 3 \rangle \\ \langle 3 | V | 1 \rangle & \langle 3 | V | 2 \rangle & \langle 3 | V | 3 \rangle \end{pmatrix} \rightarrow \begin{pmatrix} \langle I | V | I \rangle & 0 & 0 \\ 0 & \langle II | V | II \rangle & 0 \\ 0 & 0 & \langle III | V | III \rangle \end{pmatrix}$$

The new basis is related to the old by a unitary transformation.

$$|I\rangle = a|1\rangle + b|2\rangle + c|3\rangle$$

The states $|I\rangle, |II\rangle, |III\rangle$ are the eigenkets of the perturbation matrix and the diagonal elements of the perturbation matrix in the new basis are the eigenvalues. In fact we see that the eigenvalues are the first order energy shift. The first order shift in the state vector is given as before by

$$|n^1\rangle = \sum_{k \neq D} \frac{\langle k^0 | V | n^0 \rangle}{(E_n^0 - E_k^0)} |k^0\rangle$$

The states in the degenerate subspace do not contribute because all of the off diagonal matrix elements are zero. Likewise for the second order correction to the energy.

2.1.1 Projection operators

We could more formally use the projection operator approach. We go back to the Schrodinger equation

$$\begin{aligned} 0 &= (E - H_0 - \lambda V)|l\rangle \\ &= (E - E_D - \lambda V)P_0|l\rangle + (E - H_0 - \lambda V)P_1|l\rangle \end{aligned}$$

Projecting from the left by P_0 and P_1 we get

$$\begin{aligned} &P_0((E - E_D - \lambda V)P_0|l\rangle + (E - H_0 - \lambda V)P_1|l\rangle) \\ &= (E - E_D - \lambda P_0 V P_0|l\rangle - \lambda P_0 V P_1|l\rangle) \end{aligned} \tag{6}$$

$$\begin{aligned} &P_1((E - E_D - \lambda V)P_0|l\rangle + (E - H_0 - \lambda V)P_1|l\rangle) \\ &= -\lambda P_1 V P_0|l\rangle + (E - H_0 - \lambda P_1 V P_1)|l\rangle \end{aligned} \tag{7}$$

We solve Equation ?? for $|l\rangle$ and then project out the states not part of the degenerate subspace and then the denominator is safe

$$\begin{aligned} P_1|l\rangle &= P_1 \frac{1}{E - H_0 - \lambda P_1 V P_1} \lambda P_1 V P_0 |l\rangle \\ &\sim P_1|l^1\rangle \sim \sum_{k \neq D} |k^0\rangle \frac{\langle k^0 | V | l^0\rangle}{E_D^0 - E_k^0} \end{aligned} \quad (8)$$

Then substitute Equation ?? into Equation ?? for $P_1|l\rangle$ multiply by P_0 and we have

$$\begin{aligned} &(E - E_D - \lambda P_0 V P_0 - \lambda P_0 V P_1 \frac{1}{E - H_0 - \lambda P_1 V P_1} \lambda P_1 V) P_0 |l\rangle \\ &\sim (E - E_D - \lambda P_0 V P_0) |l\rangle = 0 \end{aligned}$$

The energies are the eigenvalues of the perturbation matrix. In summary we divide the space into the subspace of degenerate states, and the all the rest. The exact state vector is a linear combination of all $|l^0\rangle$ kets.

$$|l\rangle = \sum a_i |l_i\rangle$$

Then the Schrodinger equation including the perturbation is

$$(E_l^0 - H_0) |l\rangle = (\lambda V - \Delta_n) |l\rangle \quad (9)$$

Substitute the expansion for Δ_l and

$$|l\rangle = |l_0\rangle + \lambda |l^1\rangle + \lambda^2 |l^2\rangle + \dots$$

Here

$$|l_0\rangle = \sum_{i=D} a_i |i\rangle$$

$|l_0\rangle$ is a normalized linear combination of the degenerate states in the basis in which the perturbation matrix is diagonalized. Multiply by $\langle m_0 |$ from the left

$$\langle m_0 | E_n^0 - H_0 |l\rangle = \lambda \langle m_0 | V |l\rangle - \Delta_l \langle m_0 |l\rangle$$

and keep the first order in λ , when $m_0 = l_D$ and we get that

$$0 = \langle l_D | V |l_0\rangle - \Delta_l^1 \langle l_D |l\rangle \rightarrow \langle l_D | V \rangle l_D = \Delta_l^i$$

When $m_0 \neq l_D$

$$(E_n^0 - E_m^0) \langle m_0 |l\rangle = \lambda \langle m_0 | V |l\rangle - \Delta_l \langle m_0 |l\rangle$$

To first order in λ we have

$$(E_n^0 - E_m^0) \langle m_0 | l^1 \rangle = \langle m_0 | V | l_0 \rangle$$

and

$$\langle m_0 | l^1 \rangle \sim \frac{\langle m_0 | V | l_0 \rangle}{E_l^0 - E_m^0}$$

and

$$| l^1 \rangle = \sum_{l \neq D} \frac{\langle m_0 | V | l_0 \rangle}{E_n^0 - E_m^0} | m_0 \rangle$$

Note that we can always add states with eigenvalue E_l^0 . The above gives no information about them. We define $| l^1 \rangle$ and all higher order contributions to include no $| l^0 \rangle$ or for that matter any of the $| l_D \rangle$ degenerate states. Then the exact solution is

$$| l \rangle = \sum_{i=D} a_i | i \rangle + | l^1 \rangle + | l^2 \rangle + \dots$$

and

$$| l_0 \rangle = \sum_{i=D} a_i | i \rangle$$

$\langle l_0 | l^j \rangle = 0$, for $j \neq 0$. We suppose that the a_i are chosen so that $| l_0 \rangle$ is normalized. We see that in this way $| l \rangle$ is a solution to Equation ?? independent of the coefficients a_i . And the second order energy shift

$$\Delta_l^2 = \langle l_0 | V | n^1 \rangle =$$

2.1.2 Second order degenerate perturbation theory

Another strategy¹ for getting second order correction of degenerate states is to write the true state

$$| a \rangle = \sum_{\alpha} c_{\alpha} | \alpha \rangle + \sum_{\mu} d_{\mu} | \mu \rangle$$

where the sum over α includes the degenerate states and the sum over μ is all the others. We know that

$$(H - E_a) | a \rangle = (H_0 + \lambda H_1 - E_a) | a \rangle = 0$$

¹Gottfried and Yan

Then

$$\begin{aligned}
0 &= \sum_{\alpha} c_{\alpha} (H - E_a) | \alpha \rangle + \sum_{\mu} d_{\mu} (H - E_a) | \mu \rangle \\
0 &= \sum_{\alpha} c_{\alpha} (E_{\alpha} - E_a + \lambda H_1) | \alpha \rangle + \sum_{\mu} d_{\mu} (E_{\mu} - E_a + \lambda H_1) | \mu \rangle
\end{aligned}$$

Then multiply from the left first by $\langle \beta |$ which is an element of the degenerate space and then by $\langle \nu |$ which is outside of the degenerate space.

$$0 = c_{\beta} (E_{\beta} - E_a) + \lambda \sum_{\alpha} c_{\alpha} \langle \beta | H_1 | \alpha \rangle + \lambda \sum_{\mu} d_{\mu} \langle \beta | H_1 | \mu \rangle \quad (10)$$

$$0 = \sum_{\alpha} c_{\alpha} \lambda \langle \nu | H_1 | \alpha \rangle + d_{\nu} (E_{\nu} - E_a) + \lambda \sum_{\mu} d_{\mu} \langle \nu | H_1 | \mu \rangle \quad (11)$$

Drop the last term in Equation ?? as it is higher order in λ . Justification for this step is that the state $| a \rangle$ is mostly a linear combination of the states in the degenerate space. The coefficients d_{μ} would all be zero in the $\lambda \rightarrow 0$ limit so they are at most first order in λ . Then that last term is second order in λ . You might then argue that we should drop the last term in Equation ??, but probably $\langle \beta | H_1 | \mu \rangle$ is more important than $\langle \nu | H_1 | \mu \rangle$ since it connects to the relevant states. Finally, we could keep the last term in Equation ??, solve for d_{ν} , substitute into Equation ?? and then drop the highest order term. That would be equivalent to solving for

$$d_{\nu} = -\lambda \frac{\sum_{\alpha} c_{\alpha} \langle \nu | H_1 | \alpha \rangle}{(E_{\nu} - E_D)} \quad (12)$$

Substitution into ?? gives

$$0 = c_{\beta} (E_{\beta} - E_a) + \sum_{\alpha} c_{\alpha} \left(\lambda \langle \beta | H_1 | \alpha \rangle + \lambda^2 \sum_{\mu} \frac{\langle \mu | H_1 | \alpha \rangle \langle \beta | H_1 | \mu \rangle}{E_{\mu} - E_D} \right) \quad (13)$$

which is the eigenvalue problem in the subspace \mathcal{D} for the effective Hamiltonian H_{eff}

$$\langle \beta | H_{eff} | \alpha \rangle = \lambda \langle \beta | H_1 | \alpha \rangle + \lambda^2 \sum_{\mu} \frac{\langle \beta | H_1 | \mu \rangle \langle \mu | H_1 | \alpha \rangle}{E_D - E_{\mu}}.$$

So we diagonalize $\langle \beta | H_1 | \alpha \rangle$.

Define P to be the projection operator onto the degenerate subspace \mathcal{D} , $P = \sum_{\alpha} | \alpha \rangle \langle \alpha |$. Then we can write

$$H_{eff} = \lambda P H_1 P + \lambda^2 P H_1 \frac{1 - P}{E - H_0} H_1 P$$

2.1.3 Example

Suppose we have a system with 3 states. The first two are degenerate. The third is at energy Δ above the two.

$$H_1 = \begin{pmatrix} 0 & 0 & \lambda M \\ 0 & 0 & \lambda M \\ \lambda M & \lambda M & \Delta \end{pmatrix}$$

The

$$H_{eff} = -\frac{(\lambda M)^2}{\Delta} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

The energies and eigenstates are

$$E_S = -2\frac{(\lambda M)^2}{\Delta}, \quad |E_S\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

and

$$E_A = 0, \quad |E_S\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

That's what happens if $\Delta \gg \lambda M$. On the other hand, if $\Delta \sim \lambda M$, then we treat all three states as though they were degenerate. Assume the unperturbed energies are all the same. Then the shift in the energy of each of the three states is given by the eigenvalues of H_1 which are, $E_0 = 0$, $E_{\pm} = \frac{1}{2}(\Delta \pm \sqrt{\Delta^2 + 8(\lambda M)^2})$. The eigenvectors are

$$|0\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle), \quad |\pm\rangle = \frac{(|1\rangle + |2\rangle + \frac{E_{\pm}}{\lambda M}|3\rangle)}{\sqrt{2 + E_{\pm}^2/\lambda^2 M^2}}$$

What if we went back to the weak perturbation case where $M \ll \Delta$, but we had started with states $|S\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ and $|A\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$ and $|III\rangle = |3\rangle$. Then

$$V = \begin{pmatrix} 0 & 0 & \sqrt{2}M \\ 0 & 0 & 0 \\ \sqrt{2}M & 0 & \Delta \end{pmatrix}$$

Now

$$H_{eff} = \begin{pmatrix} -2M^2/\Delta & 0 \\ 0 & 0 \end{pmatrix}$$

2.2 Fine Structure

2.2.1 Spin orbit coupling

The magnetic field at the electron due to its motion through the E field of the nucleus is

$$\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c}$$

The electric field is radial so $\mathbf{E} = \frac{|\mathbf{E}|}{r}\mathbf{r}$ and $\mathbf{p} = m\mathbf{v}$ and then

$$\mathbf{B} = \frac{\mathbf{r} \times \mathbf{p}}{mc} \frac{|\mathbf{E}|}{r} = \frac{\mathbf{L}}{mc} \frac{|\mathbf{E}|}{r}$$

Next, note that $\mathbf{E} = \frac{1}{e}\nabla V = \frac{1}{e}\frac{\partial V}{\partial r}$ and we get that

$$\mathbf{B} = \frac{\mathbf{L}}{mec} \frac{1}{r} \frac{\partial V}{\partial r}$$

The magnetic moment of the electron is

$$\mu_{\mathbf{e}} = -\frac{e}{mc}\mathbf{S}$$

Finally

$$\Delta H = -\mu \cdot \mathbf{B} = \frac{1}{m^2 c^2 r} \frac{\partial V}{\partial r} \mathbf{L} \cdot \mathbf{S}$$

and if $V = e/r$ then

$$\Delta H = \frac{e^2 \mathbf{L} \cdot \mathbf{S}}{m^2 c^2 r^3} \rightarrow \frac{e^2 \mathbf{L} \cdot \mathbf{S}}{2m^2 c^2 r^3}$$

Then a factor of $\frac{1}{2}$ for the Thomas Precession. The best way to do this is to take the nonrelativistic limit of the Dirac equation with a vector potential.

Or we could use the Biot Savart Law which states that

$$\mathbf{B} = \int \frac{(\mathbf{J}dV) \times \mathbf{r}}{c|r|^3}$$

For a current loop, we find the magnetic field at the center is

$$\mathbf{B} = \frac{I}{cr^3} \int e\lambda dl \mathbf{v} \times \mathbf{r} = -\frac{e\mathbf{r} \times \mathbf{p}}{cmr^3}$$

The unperturbed states have orbital angular momentum and spin. We can use $|l, m_l\rangle |s, m_s\rangle$ as base kets with eigenvalues $l, m, s,$ and $m_s,$ or we can take the linear

combinations that would be eigenkets of j, j_z, l, s . Since $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2)$, it is clear that it will be more convenient to use the latter. Then

$$\begin{aligned} E_n^1 &= \frac{e^2 \hbar^2}{4m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \left(j(j+1) - l(l+1) - \frac{3}{4} \right) \\ E_{SO} &= \frac{\hbar^2 e^2}{4m^2 c^2} \frac{1}{n^3 a_0^3} \left\{ \frac{[j(j+1) - l(l+1) - 3/4]}{l(l + \frac{1}{2})(l+1)} \right\} \end{aligned}$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 a_0^3 l(l + \frac{1}{2})(l+1)}$$

For $j = l \pm \frac{1}{2}$

$$\begin{aligned} E_{SO} &= \frac{\hbar^2 e^2}{4m^2 c^2} \frac{1}{a_0^3 n^3} \left\{ \frac{\begin{matrix} l \\ -(l+1) \end{matrix}}{l(l + \frac{1}{2})(l+1)} \right\} \\ &= \frac{mc^2 \alpha^4}{4} \left\{ \frac{\begin{matrix} l \\ -(l+1) \end{matrix}}{n^3 l(l + \frac{1}{2})(l+1)} \right\} \end{aligned}$$

We remember that

$$E_0 = -\frac{1}{2} \alpha^2 mc^2 = -\frac{e^2}{2a_0} \rightarrow a_0 = \frac{e^2}{\alpha^2 mc^2} = \frac{\hbar^2}{me^2}$$

Substitution into the above gives

$$E_n^1 \sim \frac{e^2 \hbar^2 (\alpha^2 mc^2)^3}{2m^2 c^2 e^6} = \frac{\hbar^2 c^2 (\alpha^2 mc^2)^3}{2e^4 (mc^2)^2} = \frac{1}{2} \alpha^2 mc^2 (\alpha^2) \left(j(j+1) - l(l+1) - \frac{3}{4} \right)$$

No dependence on m_l . No mixing of levels. No need for degenerate formalism. Each level is split into $j = l \pm \frac{1}{2}$.

2.2.2 Relativistic correction

Really

$$K = \sqrt{(mc^2)^2 + (pc)^2} - mc^2 \sim \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}$$

And

$$\begin{aligned}\left\langle \psi \left| \left(\frac{p^4}{2m} \right) \right| \psi \right\rangle &= \left\langle \frac{p^2}{2m} \psi \left| \frac{p^2}{2m} \psi \right\rangle = \langle (E_0 - V)\psi \mid (E_0 - V)\psi \rangle \\ &= \langle \psi \mid (E_0^2 - 2E_0V + V^2 \mid \psi \rangle\end{aligned}$$

We use the fact that p^2 is Hermitian in the first step.

$$\begin{aligned}\Delta E_0^1 &\sim -\frac{(2m)^2}{8m^3c^2} \langle (E_n - V(r))^2 \rangle \sim \frac{4m^2}{8m^3c^2} \left(E_n^2 - 2E_n \langle \frac{-e^2}{r} \rangle + \langle \frac{e^4}{r^2} \rangle \right) \\ &\sim -\frac{4m^2}{8m^3c^2} \left(E_n^2 - 2E_n \frac{-e^2}{n^2a_0} + \frac{e^4}{(l + \frac{1}{2})n^3a_0^3} \right) \\ &\sim -\frac{4m^2}{8m^3c^2} E_n^2 \left(1 - 4 + \frac{4n}{(l + \frac{1}{2})} \right) \\ &\sim -\frac{1}{2mc^2} E_n^2 \left(-3 + \frac{4n}{(l + \frac{1}{2})} \right) \\ &\sim -\frac{1}{2} \frac{mc^2\alpha^4}{4n^4} \left(-3 + \frac{4n}{(l + \frac{1}{2})} \right) \\ &\sim -\frac{5}{2mc^2} E_0 \left(\frac{1}{2} \alpha^2 mc^2 \right) = \frac{5}{4} E_0 \alpha^2\end{aligned}$$

(Note that $\langle 1, 0, 0 \mid \frac{1}{r} \mid 1, 0, 0 \rangle = \frac{1}{a_0}$ and $\langle 1, 0, 0 \mid \frac{1}{r^2} \mid 1, 0, 0 \rangle = \frac{2}{a_0^2}$.) Depends on n, l , not on j . Again there is no mixing of degenerate levels. In general

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2a_0}, \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2})n^3a_0^2}$$

2.2.3 Darwin term

The particle cannot be localized to better than its Compton wavelength \hbar/mc . The potential that is relevant is not $V(\mathbf{r})$ but some smeared average about the point \mathbf{r} .

$$\begin{aligned}\overline{V(\mathbf{r})} &= V(\mathbf{r}) + \sum_i \overline{\frac{\partial V}{\partial r_i} \delta r_i} + \frac{1}{2!} \sum_i \sum_j \overline{\frac{\partial^2 V}{\partial r_i \partial r_j} \delta r_i \delta r_j} + \mathcal{O}(\delta r^3) \\ &= V(\mathbf{r}) + \frac{1}{6} (\delta r)^2 \nabla^2 V + \mathcal{O}(\delta r^3)\end{aligned}$$

If $\delta r \sim \hbar/mc$ then

$$H_D \sim \frac{2}{3}\pi \frac{e^2 \hbar^2}{m^2 c^2} \delta^3(\mathbf{r})$$

Note that according to Merzbacher (p. 206 and 208)

$$\psi_{n,l,m}(0) = \sqrt{\frac{1}{(na)^3} \frac{n!}{2n(n-1)!}} = \frac{1}{\sqrt{2(na_0)^3}}$$

Then

$$\langle n00 | H_D | n00 \rangle = \frac{2}{3}\pi \frac{e^2 \hbar^2}{m^2 c^2} \frac{1}{2(na_0)^3} = \frac{2\pi}{3} \frac{e^2 \hbar^2}{m^2 c^2} \frac{1}{2n^3} \frac{m^3 e^6}{\hbar^6} = \frac{2\pi}{3} \frac{1}{2n^3} m c^2 \alpha^4$$

and it exactly compensates for the $l = 0$ term that we got from the spin orbit term. Or it would if we did it properly using the Dirac equation.

2.2.4 Fine Structure

Combining all order α^2 corrections we have

$$E_{SO} = \frac{E_n^2}{m c^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l + \frac{1}{2})(l+1)} \right\}$$

The relativistic correction is

$$E_r^1 = -\frac{E_n^2}{2m c^2} \left[\frac{4n}{l + \frac{1}{2}} - 3 \right]$$

The total α^2 correction is

$$-\frac{E_1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]$$

2.3 Stark effect

To determine the effect of an external uniform electric field on a set of degenerate levels we need to exercise a bit more care. Consider $n = 2$ in hydrogen. There are $2l+1 = 3$ levels with $l = 1$ and 1 level with $l = 0$. Spin is not relevant. The candidate

set of base states are the orbital angular momentum kets. The perturbation matrix elements $\langle i | V | j \rangle$, where $V = -ez|\mathbf{E}|$ are

$$V = \begin{pmatrix} 0 & \langle 2, 0, 0 | V | 2, 1, 0 \rangle & 0 & 0 \\ \langle 2, 1, 0 | V | 2, 0, 0 \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Only the upper left is relevant. All of the other states are not coupled. The eigenvectors of the upper left 2X2 matrix are

$$\Delta_{\pm}^1 = -\pm e|\mathbf{E}| \langle 2, 0 | r | 2, 1 \rangle \langle 2, 0, 0 | \cos \theta | 2, 1, 0 \rangle = \pm 3ea_0|\mathbf{E}|$$

The eigenvectors are

$$| \pm \rangle = \frac{1}{\sqrt{2}}(| 2, 0, 0 \rangle \pm | 2, 1, 0 \rangle)$$

These two states are shifted positively and negatively with an electric field. The other 2 states are not effected by the E-field.

2.4 Zeeman effect

$$H = \frac{p^2}{2m} + V_c(r) - \frac{e}{2mc}|\mathbf{B}|L_z + \frac{e^2}{8mc^2}|\mathbf{B}|^2(x^2 + y^2)$$

We have

$$H_Z = -\frac{e}{2mc}|\mathbf{B}|(L_z + 2S_z)$$

and then

$$H_{spin} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\frac{e}{mc}\mathbf{S} \cdot \mathbf{B} = -\frac{e}{mc}|\mathbf{B}|S_z$$

and

$$H_{spin-orbit} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{L} \cdot \mathbf{S}$$

Assuming B is very weak so that the spin-orbit piece dominates, we need to evaluate $\langle j, m, l, s | L_z + 2S_z | j, m, l, s \rangle = \langle j, m, l, s | J_z + S_z | j, m, l, s \rangle$ Since

$$| l \pm \frac{1}{2}, m \rangle = \pm \sqrt{\frac{l \pm m + \frac{1}{2}}{2l + 1}} | l, m - \frac{1}{2} \rangle | \frac{1}{2}, \frac{1}{2} \rangle + \sqrt{\frac{l \mp m + \frac{1}{2}}{2l + 1}} | l, m + \frac{1}{2} \rangle | \frac{1}{2}, -\frac{1}{2} \rangle$$

we can compute

$$\left\langle l \pm \frac{1}{2}, m | S_z | l \pm \frac{1}{2}, m \right\rangle = \pm \frac{m\hbar}{2l + 1}$$

Meanwhile $\langle l \pm \frac{1}{2}, m | J_z | l \pm \frac{1}{2}, m \rangle = \hbar m$. Then

$$\Delta_B^1 = -\frac{e\hbar B}{2mc} m \left(1 \pm \frac{1}{2l+1} \right)$$

2.4.1 Paschen-Back limit

If the magnetic field is very strong, then total angular momentum is not conserved. (There is an external torque). But the L_z and S_z are fixed. So now it is better to use the basis $|l, m_l\rangle |s, m_s\rangle$. It is easy to evaluate $\langle L_z + 2S_z \rangle$ but not quite as simple to compute $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ for the spin orbit coupling. But if we write

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \langle L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+) \rangle$$

and note that $\langle L_{\pm} \rangle = \langle S_{\pm} \rangle = 0$ then we get that

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \hbar^2 m_l m_s$$

2.4.2 Intermediate field

Let's examine the effect of an external magnetic field on the $n = 2$ states of hydrogen. And we suppose that $\langle H_{spin-orbit} \rangle \approx \langle H_z \rangle$. Now we have to exercise some care in computing energy shifts. There are 8 degenerate states. We can choose as a basis eigenstates of j, j_z, l, s , ($l = 1, j = \pm 3/2, \pm 1/2$, or $l = 0, j = \pm 1/2$ or eigenstates of l, m_l, s, m_s , ($l = 1, m_l = \pm 1, 0, m_s = \pm 1/2$, $l = 0, m_s = \pm 1/2$). We have to construct the perturbation matrix elements $\langle i | V | j \rangle$ in whatever basis we have chosen and

$$V = -\frac{e}{2mc} B(L_z + 2S_z) + \frac{e^2}{2m^2 c^2} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S}$$

Let's pick the basis of eigenstates of j, j_z, l, s . Then the $\mathbf{L} \cdot \mathbf{S}$ term only contributes along the diagonal. So let's look at the effect of the external field. We had better label the states.

$$\begin{aligned} |1\rangle &= \left| \frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2} \right\rangle = |0, 0\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ |2\rangle &= \left| \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2} \right\rangle = |0, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\ |3\rangle &= \left| \frac{1}{2}, -\frac{1}{2}, 1, \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle \end{aligned}$$

$$\begin{aligned}
|4\rangle &= \left| \frac{1}{2}, \frac{1}{2}, 1, \frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
|5\rangle &= \left| \frac{3}{2}, -\frac{1}{2}, 1, \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
|6\rangle &= \left| \frac{3}{2}, \frac{1}{2}, 1, \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
|7\rangle &= \left| \frac{3}{2}, -\frac{3}{2}, 1, \frac{1}{2} \right\rangle = |1, -1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
|8\rangle &= \left| \frac{3}{2}, \frac{3}{2}, 1, \frac{1}{2} \right\rangle = |1, 1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle
\end{aligned}$$

Now we can compute the matrix elements

$$\left(\begin{array}{cccccccc}
\alpha_0 - b & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \alpha_0 + b & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \alpha_1 - b\sqrt{1/3} & 0 & -b\sqrt{2}/3 & 0 & 0 & 0 \\
0 & 0 & 0 & \alpha_1 + b(\sqrt{1/3}) & 0 & -b\sqrt{2}/3 & 0 & 0 \\
0 & 0 & -b(\sqrt{2}/3) & 0 & \alpha_1 - b(\sqrt{2/3}) & 0 & 0 & 0 \\
0 & 0 & 0 & -b(\sqrt{2}/3(1)) & 0 & \alpha_1 + b(\sqrt{2/3}) & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \alpha_1 + b(-2) & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \alpha_1 + b(2)
\end{array} \right)$$

Next we find the eigenvalues Δ_i . The energy of the state $|i\rangle$ shifts by Δ_i .

3 Variational method

3.1 Formalism

Let's think about that helium calculation again. We approximated the wave function for the Helium atom with two electrons as the product of the wave functions of two singly ionized atoms. Then we included the interaction of the two electrons as a perturbation.

The total hamiltonian is

$$H = \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

with $Z = 2$. The approximate wave function is

$$|\psi_1\rangle|\psi_2\rangle = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_1/a_0} e^{-Zr_2/a_0}$$

Then we calculated

$$E_{approx} = E_1^0 + E_2^0 + \Delta = \langle \psi_1\psi_2 | H | \psi_1\psi_2 \rangle = \langle \psi_1\psi_2 | H_0 | \psi_1\psi_2 \rangle + \langle \psi_1\psi_2 | H_H | \psi_1\psi_2 \rangle$$

Now it is possible to write our trial wave function as a linear combination of the complete set of exact eigenkets.

$$|\psi_1\psi_2\rangle = \sum_n a_n |n\rangle, \quad H|n\rangle = E_n|n\rangle$$

Then

$$E_{approx} = \sum_n |a_n|^2 E_n \geq E_0 \sum_n |a_n|^2$$

So we know for sure that $E_{approx} \geq E_0$ and in fact that will be true for any trial wave function that we choose. It's expectation value will always overestimate the ground state energy. So why not try to come up with a better approximation. One adjustment that we might make is to account for the shielding effect of one electron on the other. That is, each electron does not really see the full coulomb attraction because it is shielded by the other. The effective Z is a little less than 2. We can incorporate this approximation in our wave function by writing

$$|\psi_1\rangle|\psi_2\rangle = \left(\frac{Z'^3}{\pi a_0^3}\right)^{1/2} \left(\frac{Z'^3}{\pi a_0^3}\right)^{1/2} e^{-Z'r_1/a_0} e^{-Z'r_2/a_0} = \left(\frac{Z'}{\pi a_0}\right)^3 e^{-Z'(r_1+r_2)/a_0}$$

Or define $a'_0 = a_0/Z'$ and we get that

$$\psi_1\psi_2 = \left(\frac{1}{\pi a'^3}\right)^{1/2} e^{-r/a'} \left(\frac{1}{\pi a'^3}\right)^{1/2} e^{-r/a'}$$

Note that our new wave function is normalized. This is very important. Now we compute

$$\langle \psi_1\psi_2 | H | \psi_1\psi_2 \rangle = \left\langle \psi_1\psi_2 \left| \frac{p^2}{2m} \right| \psi_1\psi_2 \right\rangle + \left\langle \psi_1\psi_2 \left| \frac{-Ze^2}{r_1} + \frac{-Ze^2}{r_2} \right| \psi_1\psi_2 \right\rangle + \left\langle \psi_1\psi_2 \left| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_1\psi_2 \right\rangle$$

Note that ψ_1 and ψ_2 just look like the hydrogen ground state. Therefore

$$\left\langle \psi_1 \psi_2 \left| \frac{p^2}{2m} \right| \psi_1 \psi_2 \right\rangle = 2 \left(\frac{Z' e^2}{2a'} \right) = \frac{Z'^2 e^2}{a_0}$$

The second term

$$\left\langle \psi_1 \psi_2 \left| \frac{-Ze^2}{r_1} + \frac{-Ze^2}{r_2} \right| \psi_1 \psi_2 \right\rangle = -2Z \left(\frac{e^2}{a'} \right) = -2 \frac{Z' Z e^2}{a_0}$$

The third term we calculated before

$$E^1 = e^2 \left(\frac{Z'^3}{\pi a^3} \right)^2 \int \frac{e^{-2Z'(r_1+r_2)/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} r_1^2 d\Omega_1 r_2^2 d\Omega_2 = e^2 \frac{5}{8a'} = Z' \frac{5}{8} \frac{e^2}{a_0}$$

Therefore

$$\langle \psi_1 \psi_2 | H | \psi_1 \psi_2 \rangle = (Z'^2 - 2Z'Z + Z' \frac{5}{8}) \frac{e^2}{a_0}$$

It will be a function of the parameter Z' . Next, we minimize the expectation value with respect to Z' . This is OK because no matter what we choose for Z' , we know that we are overestimating the energy. Set

$$\frac{d\langle H \rangle}{dZ'} = (2Z' - 2Z + \frac{5}{8}) = 0 \rightarrow Z' = Z - \frac{5}{16} = \frac{27}{16}$$

And

$$\langle H \rangle = -2.85 \frac{e^2}{a_0} = -77.5 \text{ eV}$$

3.2 Examples

4 Time dependent perturbation theory

4.1 Formalism

Now we want to consider time dependent perturbations. The Hamiltonian is written in the form

$$H = H_0 + V(t)$$

We suppose that we know the complete set of eigenkets of H_0 , namely $|n\rangle$ and as usual $H_0|n\rangle = E_n|n\rangle$. We note that for a time dependent hamiltonian, the time evolution operator is not simply $e^{-iHt/\hbar}$. Typically the time dependent part of the hamiltonian is something that turns on and then off so it is reasonable to ask about the probability of

finding the system in one of the unperturbed states. An arbitrary state at $t = 0$ can be written

$$|\alpha\rangle = \sum_n c_n(0) |n\rangle$$

We want

$$|\alpha, t_0 = 0; t\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

We work in the interaction picture, which is somewhere between the Schrodinger picture, in which operators have no time dependence, but the states evolve in time, and the Heisenberg picture in which the states are fixed and the operators evolve. In the interaction picture, we take the time dependence associated with the unperturbed Hamiltonian from states and attach it to operators. And we attach the time dependence from the perturbation to the states. So in the interaction picture

$$|\alpha, t_0; t\rangle_I = e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S$$

Observables are

$$A_I = e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar}$$

According to the Schrodinger equation

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_S &= (H_0 + V) |\alpha, t_0; t\rangle_S \\ i\hbar \frac{\partial}{\partial t} (e^{-iH_0 t/\hbar} |\alpha, t_0; t\rangle_I) &= (H_0 + V) e^{-iH_0 t/\hbar} |\alpha, t_0; t\rangle_I \\ i\hbar e^{-iH_0 t/\hbar} \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I &= e^{iH_0 t} V e^{-iH_0 t} |\alpha, t_0; t\rangle_I \\ i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I &= V_I |\alpha, t_0; t\rangle_I \end{aligned} \quad (14)$$

Then we can also write that

$$|\alpha, t_0; t\rangle = \sum_n c_n(t) |n\rangle \quad (15)$$

Substitute that last into Equation ?? and multiply from the left by $\langle n |$ and we have

$$i\hbar \frac{\partial}{\partial t} \langle n | \alpha, t_0; t\rangle = \sum_m \langle n | V_I | m\rangle \langle m | \alpha, t_0; t\rangle_I \quad (16)$$

Also from Equation ?? we see that $c_n = \langle n | \alpha, t_0; t\rangle$. Then

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m V_{nm} e^{i\omega_{nm} t} c_m(t)$$

where

$$\omega_{mn} = \frac{E_n - E_m}{\hbar}$$

and we used

$$\langle n | e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} | m \rangle = V_{nm}(t) e^{i(E_n - E_m)t/\hbar}$$

We expand the time evolution operator

$$\begin{aligned} | \alpha, t_0; t \rangle_I &= U_I(t, t_0) | \alpha, t_0; t_0 \rangle_I \\ i\hbar \frac{d}{dt} U_I(t, t_0) &= V_I(t) U_I(t, t_0) \end{aligned}$$

The initial condition is

$$U(t, t_0)|_{t=t_0} = 1$$

and we integrate to get

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V_I(t') U_I(t', t_0) dt'$$

We get an approximate solution by iteration:

$$\begin{aligned} U_I(t, t_0) &= 1 - \frac{i}{\hbar} \int_{t_0}^t V_I(t') \left[1 - \frac{i}{\hbar} \int_{t_0}^{t'} V_I(t'') U_I(t'', t_0) dt'' \right] dt' \\ &= 1 - \frac{i}{\hbar} \int_{t_0}^t V_I(t') + \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' V_I(t') V_I(t'') \\ &= + \dots \end{aligned}$$

4.1.1 Transition

Suppose we have a system in an eigenket $| i \rangle$. Then

$$| i, t_0; t \rangle = U_I(t, t_0) | i \rangle = \sum_n | n \rangle \langle n | U_I(t, t_0) | i \rangle = \sum_n c_n(t)$$

We see that $\langle n | U_I | i \rangle$ is the amplitude that a system initial in state $| i \rangle$ will be in state $| n \rangle$ as a function of time. We note that

$$\begin{aligned} | i \rangle_I &= e^{iH_0 t/\hbar} | \alpha, t_0; t \rangle_S \\ | i \rangle_I &= e^{iH_0 t/\hbar} U(t, t_0) | \alpha, t_0; t_0 \rangle_S \\ | i \rangle_I &= e^{iH_0 t/\hbar} U(t, t_0) e^{-iH_0 t_0/\hbar} | \alpha, t_0; t_0 \rangle_I \end{aligned}$$

$$\rightarrow U_I(t, t_0) = e^{iH_0 t/\hbar} U_S e^{-iH_0 t_0/\hbar}$$

Therefore

$$\langle n | U_I | i \rangle = e^{i(E_n t - E_i t_0)/\hbar} \langle n | U | i \rangle$$

Then as long as $|i\rangle$ and $|n\rangle$ are eigenkets of H_0 ,

$$|\langle n | U_I | i \rangle| = |\langle n | U | i \rangle|$$

So

$$\begin{aligned} c_n^0(t) &= \delta_{ni} \\ c_n^1(t) &= -\frac{i}{\hbar} \int_{t_0}^t \langle n | V_I(t') | i \rangle dt' \\ c_n^1(t) &= -\frac{i}{\hbar} \int_{t_0}^t \langle n | V(t') | i \rangle e^{i(E_n - E_i)t'/\hbar} dt' \\ c_n^2(t) &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \langle n | V_I(t') | m \rangle \langle m | V_I(t'') | i \rangle \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' V_{nm}(t') e^{i\omega_{nm}t'} V_{mi}(t'') e^{i\omega_{mi}t''} \end{aligned}$$

4.1.2 Constant perturbation

We turn on a constant perturbation at t_0 . Then the amplitude to make a transition from state i to n to first order is

$$c_n(t) = -\frac{i}{\hbar} \int_{t_0}^t V_{ni} e^{i\omega_{ni}t} = \frac{-i}{\hbar} \frac{V_{ni}}{i\omega_{ni}} (e^{i\omega_{ni}t} - 1)$$

Then

$$|c_n(t)|^2 = 4 \frac{|V_{ni}|^2}{\hbar^2 \omega_{ni}^2} \sin^2(\omega_{ni}t/2) = 4 \frac{|V_{ni}|^2}{(E_n - E_i)^2} \sin^2(\omega_{ni}t/2) = 4 \frac{|V_{ni}|^2}{(E_n - E_i)^2} \sin^2((E_n - E_i)t/2\hbar)$$

If $E_n = E_i$, then $|c_n(t)|^2 = \frac{1}{\hbar^2} |V_{ni}|^2 t^2$. If there is a finite number of final states close to $|n\rangle$ then the total transition probability is

$$\sum_{n, E_n = E_i} |c_n|^2.$$

and if there are many final states, more or less nearby we replace

$$\sum |c_n|^2 \rightarrow \int dE \rho(E) |c_n|^2 = 4 \int \sin^2 \left[\frac{(E_n - E_i)t}{2\hbar} \right] \frac{|V_{ni}^2}{|E_n - E_i|^2} \rho(E) dE$$

Next we see that

$$\lim_{t \rightarrow \infty} \sin^2 \left[\frac{(E_n - E_i)t}{2\hbar} \right] \frac{|V_{ni}|^2}{|E_n - E_i|^2} \rho(E) = \frac{\pi t}{2\hbar} \delta(E_n - E_i)$$

Finally

$$|c_n(t)|^2 = \int \rho(E) dE |c_n(t)|^2 = \left(\frac{2\pi}{\hbar}\right) \overline{|V_{ni}|^2} \rho(E_n) t$$

The rate is

$$w_{i \rightarrow n} = \left(\frac{2\pi}{\hbar}\right) |V_{ni}|^2 \rho(E_n)$$

or

$$w_{i \rightarrow n} = \left(\frac{2\pi}{\hbar}\right) |V_{ni}|^2 \delta(E_n - E_i)$$

where integration over final states is implied.

4.1.3 Second order perturbation

We found earlier that

$$c_n^2(t) = -\frac{1}{\hbar^2} \sum_m \int_0^t dt' \int_0^{t'} dt'' V_{nm}(t') e^{i\omega_{nm}t'} V_{mi}(t'') e^{i\omega_{mi}t''}$$

If $V(t)$ is constant in time then

$$\begin{aligned} c_n^2(t) &= -\frac{1}{\hbar^2} \sum_m \int_0^t dt' V_{nm} e^{i\omega_{nm}t'} V_{mi} \left(\frac{e^{i\omega_{mi}t'} - 1}{i\omega_{mi}} \right) \\ &= -\frac{1}{\hbar^2} \sum_m \int_0^t dt' V_{nm} (e^{i\omega_{ni}t'} - e^{i\omega_{mn}t'}) V_{mi} \left(\frac{1}{i\omega_{mi}} \right) \\ &= \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t (e^{i\omega_{ni}t'} - e^{i\omega_{mn}t'}) dt' \\ &\sim \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t (e^{i\omega_{ni}t'}) dt' \end{aligned}$$

Now it looks just like the first order term with

$$\frac{-i}{\hbar} V_{ni} \rightarrow \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{ni}}{E_m - E_i}$$

So to second order

$$w_{i \rightarrow n} = \frac{2\pi}{\hbar} \overline{\left| V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_i - E_m} \right|^2} \rho(E_n) \rightarrow \frac{2\pi}{\hbar} \int dE_n \overline{\left| V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_i - E_m} \right|^2} \rho(E_n) \delta(E_n - E_i)$$

The average is over all final states n with energy $E_n \sim E_i$.

4.1.4 Scattering

Scattering from a fixed potential is a fine example of a perturbation that turns on, stays on for awhile and then turns off. In our study of time dependent perturbation theory we determined the the transition probability from initial state ψ_a to final state ψ_b is given by the absolute square of the amplitude

$$c_b(t) = -\frac{i}{\hbar} \int_{-t/2}^{t/2} \langle \psi_b | H(t') | \psi_a \rangle e^{i\omega_{ab}t'} dt'$$

where $\omega_{ab} = \frac{E_a - E_b}{\hbar}$. To apply the theory to a scattering process we imagine that the perturbation $H(t')$ turns on at $-t/2$ and off at $t/2$ and while it is turned on it has constant value H . Then we can integrate and we get

$$c_b(t) = -\frac{i}{\hbar} \frac{1}{i\omega_{ab}} \left[e^{i\omega_{ab}t/2} - e^{-i\omega_{ab}t/2} \right] H_{ab} = -\frac{H_{ab}}{\hbar} \frac{2i \sin \omega_{ab}t/2}{\omega_{ab}}$$

and the transition probability is

$$|c_b|^2 = \frac{1}{\hbar^2} |H_{ab}|^2 \frac{4 \sin^2 \omega_{ab}t/2}{\omega_{ab}^2} = \frac{1}{\hbar^2} |H_{ab}|^2 \left(\frac{\sin \omega_{ab}t/2}{\omega_{ab}t/2} \right)^2 t^2$$

Let's examine the ω_{ab} dependent piece

$$f(\omega) \equiv \left(\frac{\sin \omega t/2}{\omega t/2} \right)^2 t^2$$

The first zero of $f(\omega)$ occurs when $\omega = 2\pi/t$. Its maximum value (at $\omega = 0$) is t^2 . In the limit of large t , $f(\omega) \rightarrow 2\pi t \delta(\omega)$. To check that assertion we integrate over all ω

$$\int_{-\infty}^{\infty} f(\omega) d\omega = \int \frac{\sin^2 x}{x^2} dx \frac{2}{t} t^2 = 2\pi t = \int 2\pi t \delta(\omega) d\omega$$

In terms of the energies of initial and final states,

$$2\pi t \delta(\omega) \rightarrow 2\pi t \hbar \delta(E_b - E_a)$$

and we can write

$$|c_b|^2 = \frac{1}{\hbar^2} |H_{ab}|^2 2\pi t \delta(E_b - E_a)$$

The transition rate is

$$R = \frac{2\pi}{\hbar} |H_{ab}|^2 \delta(E_b - E_a)$$

In scattering experiments, the detector always has some finite acceptance. And what we measure is a sum over all final states consistent with that acceptance.

$$R = \frac{2\pi}{\hbar} \int |H_{ab}|^2 \delta(E_b - E_a) \rho(E_b) dE_b$$

$\rho(E_b)$ is the density of final states, the number of final states per unit energy. Well, we have figured this out before. The number of states between k and $k + dk$ is

$$dN = \frac{V k^2 dk d\Omega}{8\pi^3} = \frac{V p^2 dp d\Omega}{(2\pi\hbar)^3}$$

Using $E = p^2/2m$ and $2pdp/2m = dE$ we have

$$dN = \frac{V p m dE d\Omega}{(2\pi\hbar)^3}$$

$$\frac{dN}{dE} = \rho(E) = \frac{V p m}{(2\pi\hbar)^3} d\Omega$$

so

$$R = \frac{2\pi}{\hbar} \frac{1}{(2\pi\hbar)^3} V p m |H_{ab}|^2 d\Omega$$

Now how do we connect to the cross section? The incoming particle is represented by a plane wave

$$\psi_a = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_a \cdot \mathbf{r}}$$

and the outgoing wave by

$$\psi_b = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_b \cdot \mathbf{r}}$$

The \sqrt{V} in the denominator is so that the wave function is normalized. The particle density in the incoming wave is $|\psi_a|^2 = 1/V$ and the flux of incoming particles is $\frac{v}{V} = \frac{p/m}{V}$. And

$$(d\sigma)\text{Flux} = dN = R$$

$$d\sigma = \frac{R}{\text{Flux}} = \frac{V^2 m^2}{(2\pi\hbar^2)^2} |\langle \psi_b | H | \psi_a \rangle|^2 d\Omega$$

$$\frac{d\sigma}{d\Omega} = \left(\frac{Vm}{2\pi\hbar^2} \right)^2 |H_{ab}|^2$$

That means that

$$f(\theta) = -\frac{mV}{2\pi\hbar^2} \langle \psi_b | H | \psi_a \rangle$$

The negative sign is a convention. Suppose that $H = V(\vec{r})$. Then

$$\begin{aligned} f(\theta) &= -\frac{mV}{2\pi\hbar^2} \int \frac{1}{\sqrt{V}} e^{-i\vec{k}_b \cdot \vec{r}} V(\vec{r}) \frac{1}{\sqrt{V}} e^{i\vec{k}_a \cdot \vec{r}} d^3r \\ &= -\frac{m}{2\pi\hbar^2} \int e^{i(\vec{k}_a - \vec{k}_b) \cdot \vec{r}} V(\vec{r}) d^3r \end{aligned}$$

The result is equivalent to that of the Green's function analysis in the first Born approximation. (See Griffiths p. 368)

4.2 Harmonic perturbation

Now suppose that the perturbation is

$$V(t) = Ve^{i\omega t} + V^\dagger e^{-i\omega t}$$

We will get that

$$\begin{aligned} c_n(t) &= -\frac{i}{\hbar} \int_0^t \left(V_{ni} e^{i(\omega_{ni} + \omega)t} + V_{ni}^\dagger e^{i(\omega_{ni} - \omega)t} \right) \\ &= -\frac{i}{\hbar} \left(V_{ni} \frac{e^{i(\omega_{ni} + \omega)t} - 1}{i(\omega_{ni} + \omega)} + V_{ni}^\dagger \frac{e^{i(\omega_{ni} - \omega)t} - 1}{i(\omega_{ni} - \omega)} \right) \end{aligned}$$

If $\omega_{ni} \sim \omega$ then the second term is the significant one. $E_n > E_i$ and there is absorption. If $E_f < E_i$ then $\omega_{ni} < 0$ and the first term counts. Then

$$|c_n(t)|^2 = \frac{4}{\hbar^2} |V_{ni}|^2 \frac{\sin^2(\omega_{ni} \pm \omega)t/2}{(\omega_{ni} \pm \omega)^2} = \lim_{t \rightarrow \infty} \rightarrow \frac{4\pi}{\hbar^2} |V_{ni}|^2 \delta(\omega_{ni} \pm \omega)t/2$$

and just like for the constant perturbation

$$w_{i \rightarrow n} = \frac{\pi 2}{\hbar^2} |V_{ni}|^2 \pi \delta(\omega_{ni} \pm \omega) = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i \pm \hbar\omega) \quad E_n = E_i \pm \hbar\omega$$

4.2.1 Interactions with radiation field

Let

$$V(t) = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p}$$

legit as long as $\nabla \cdot \mathbf{A} = 0$ which is true for a plane wave in empty space. For that very same plane wave

$$\mathbf{A} = 2A_0 \epsilon \cos(\omega t - \mathbf{k} \cdot \mathbf{x}) = A_0 \epsilon \left(e^{i(\omega t - \mathbf{k} \cdot \mathbf{x})} + e^{-i(\omega t - \mathbf{k} \cdot \mathbf{x})} \right)$$

Consider absorption. Then we take the second term. We can expand the exponential for small k . Then

$$\mathbf{A} \sim 2A_0 \epsilon (1 + i\mathbf{k} \cdot \mathbf{x} + \dots)$$

In the long wavelength limit, $xk \rightarrow 2\pi x/\lambda$ is small. Small that is compared to the size of the wave function which is perhaps the size of an atom. The typical transition energy for an atom is

$$E < \frac{Z^2 e^2}{2a_0}$$

The corresponding wavelength is

$$\lambda \sim \frac{\hbar c}{E} = \frac{2a_0 \hbar c}{Z^2 e^2} = \frac{2a_0}{Z^2 \alpha} \gg a_0$$

The transition rate in the dipole approximation is

$$w_{i \rightarrow n} = \frac{2\pi}{\hbar} \left| \frac{e}{mc} A_0 \langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} | i \rangle \right|^2 \delta(E_n - E_i \pm \hbar\omega)$$

The energy density of the radiation field is $U = \frac{1}{2} \left(\frac{E_{max}^2}{8\pi} + \frac{B_{max}^2}{8\pi} \right) = \frac{1}{2\pi} \frac{\omega^2}{c^2} |A_0|^2$. Substitution gives us

$$\begin{aligned} w_{i \rightarrow n} &= \frac{(2\pi)^2}{\hbar} U \left| \frac{e}{m\omega} \langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} | i \rangle \right|^2 \delta(E_n - E_i \pm \hbar\omega) \\ \rightarrow &= \frac{(2\pi)^2}{\hbar} \rho(\omega) d\omega \left| \frac{e}{m\omega} \langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} | i \rangle \right|^2 \delta(E_n - E_i \pm \hbar\omega) \\ &= \frac{(2\pi)^2}{\hbar^2} \rho(\omega) \left| \frac{e}{m\omega} \langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} | i \rangle \right|^2 \\ &= \frac{(2\pi)^2}{\hbar^2} \rho(\omega) \left| \frac{e}{m\omega} \boldsymbol{\epsilon} \cdot \langle n | \mathbf{p} | i \rangle \right|^2 \\ &= \frac{(2\pi)^2}{\hbar^2} \rho(\omega) \left| \frac{e}{m\omega} \frac{m}{\hbar} \boldsymbol{\epsilon} \cdot \langle n | [H, \mathbf{x}] | i \rangle \right|^2 \\ &= \frac{(2\pi e)^2}{\hbar^2} \rho(\omega) \left| \boldsymbol{\epsilon} \cdot \langle n | \mathbf{x} | i \rangle \right|^2 \end{aligned}$$

In the last step we use

$$\langle n | [H, x] | i \rangle = \frac{-\hbar}{m} \langle n | p | i \rangle = \hbar\omega_{ni} \langle n | x | i \rangle$$

4.2.2 Absorption vs emission

The rate that we just computed for absorption from a radiation field with energy density $\rho(\omega)$ is identically the rate we would find for the emission in that same radiation field. In the event of spontaneous emission, we can replace ρ with an expression for the density of final states available to the photon.

4.2.3 Spontaneous emission

An alternative strategy for determining the spontaneous emission rate is to begin with the expression for the stimulated rate, and then substitute the ground state radiation density of the vacuum.

Let's try to come up with a more systematic development.

The rate

$$w_{i \rightarrow n} = \frac{2\pi}{\hbar} \left(\frac{e}{mc} A_0 \right)^2 |\langle n | \epsilon \cdot \mathbf{p} e^{i\mathbf{k} \cdot \mathbf{r}} | i \rangle|^2 \delta(E_n - E_i \pm \hbar\omega)$$

We want to replace vector potential with energy density. We use

$$U = \frac{1}{2\pi} \frac{\omega^2}{c^2} |A_0|^2$$

Then

$$w_{i \rightarrow n} = \frac{2\pi}{\hbar} \left(\frac{2\pi c^2}{\omega^2} U \right) \left(\frac{e}{mc} \right)^2 |\langle n | \epsilon \cdot \mathbf{p} e^{i\mathbf{k} \cdot \mathbf{r}} | i \rangle|^2 \delta(E_n - E_i \pm \hbar\omega)$$

U has some frequency dependence. The total energy density is

$$\int \rho(\omega) d\omega = U$$

We replace U with $\rho(\omega)d\omega$ and integrate with the δ function. We get

$$w_{i \rightarrow n} = \frac{2\pi}{\hbar^2} \left(\frac{2\pi c^2}{\omega^2} \rho(\omega_{ni}) \right) \left(\frac{e}{mc} \right)^2 |\langle n | \epsilon \cdot \mathbf{p} e^{i\mathbf{k} \cdot \mathbf{r}} | i \rangle|^2$$

What do we mean by $\rho(\omega)$? It is the energy density per unity volume per unit frequency. The density at the frequency corresponding to the transition energy is the only part that counts. The transition rate from $n \rightarrow i$ or in the other direction is exactly the same, in one case it is absorption and in the other it is stimulated emission. How do we get from here to spontaneous emission?

It must be that there is some vacuum fluctuation or vacuum radiation density. We need second quantization for a mathematically complete theory. But we can develop an expression for spontaneous emission based on a heuristic argument. We simply replace the expression for the radiation density with the energy density of available photon states. The total number of states with energy $E < \hbar kc$, where $k_x = \pi n_x/L$, etc. is

$$\begin{aligned} N &= \frac{1}{8} \frac{4}{3} \pi (n_x^2 + n_y^2 + n_z^2)^{3/2} \\ &= \frac{1}{8} \frac{4}{3} \pi \left(\frac{L}{\pi} \right)^3 (k^2)^{3/2} \\ &= \frac{\pi}{6} \left(\frac{L}{\pi} \right)^3 \left(\frac{\omega}{c} \right)^3 \\ \frac{1}{V} \frac{dN}{d\omega} &= \frac{1}{2\pi^2} \frac{\omega^2}{c^3} \text{ number of states per unit volume per unit frequency} \end{aligned}$$

Finally to get the energy density we multiply by two to include the two polarization states and multiply by $\hbar\omega$, the energy of the photon in the state and we end up with

$$\rho(\omega) = \frac{\hbar}{\pi^2} \frac{\omega^3}{c^3}$$

The spontaneous transition rate becomes

$$\begin{aligned} w_{i \rightarrow n} &= \frac{4\pi}{\hbar^2} \left(\frac{2\pi c^2}{\omega^2} \frac{\hbar}{2\pi^2} \frac{\omega^3}{c^3} \right) \left(\frac{e}{mc} \right)^2 |\langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} | i \rangle|^2 \\ &= 4 \left(\frac{\omega}{\hbar c} \right) \left(\frac{e}{mc} \right)^2 |\langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} | i \rangle|^2 \\ &= 4(\omega) \frac{\alpha}{mc^2} \frac{1}{m} |\langle n | \boldsymbol{\epsilon} \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} | i \rangle|^2 \end{aligned}$$

which sure enough is a rate. In the dipole approximation we get

$$\begin{aligned} w_{i \rightarrow n} &= 4(\omega) \frac{\alpha}{mc^2} \frac{1}{m} |m\omega \langle n | \boldsymbol{\epsilon} \cdot \mathbf{x} | i \rangle|^2 \\ &= 4(\omega^3) \frac{\alpha}{c^2} |\langle n | \boldsymbol{\epsilon} \cdot \mathbf{x} | i \rangle|^2 \end{aligned}$$

4.2.4 Average over polarization and angle

To get the total spontaneous emission rate we average that last over all directions k for the outgoing photon and all polarizations $\boldsymbol{\epsilon}$. Suppose that \mathbf{x} is along the z-direction and the outgoing photon is at an angle $\theta, \phi = 0$. First note that if $\theta = 0$, then $\boldsymbol{\epsilon} \cdot \mathbf{x} = 0$. So project onto the x-axis. Then the polarization is in the y-z plane and the average of $\langle \boldsymbol{\epsilon} \cdot \hat{\mathbf{z}} \rangle^2 = \frac{1}{4\pi} \int \sin^2 \theta d\theta \int \cos^2 \alpha d\alpha = \frac{1}{4\pi} \left(\frac{4}{3}\right)\pi = \frac{1}{3}$. The total spontaneous decay rate into all angles and polarizations is

$$w_{i \rightarrow n} = \frac{4}{3} (\omega^3) \frac{\alpha}{c^2} |\langle n | \mathbf{x} | i \rangle|^2$$

4.2.5 Angular distribution

Suppose we know that the transition is $E1$ and $\Delta m = 1$. Since it is $E1$ that means that $\Delta l = \pm 1$ by Wigner Eckart. Then

$$\langle f | \mathbf{x} | i \rangle = \langle l \pm 1, m \pm 1 | \mathbf{x} | lm \rangle$$

will be a vector in the x-y plane. No z-component. That means that if the photon is headed in the z-direction $\epsilon \cdot \mathbf{x} = 1$ for all polarizations. If it is headed in the x-direction then we need to average. The angle θ is that of the polarization with respect to the y-axis.

$$\frac{1}{2\pi} \int \cos^2 \theta d\theta = \frac{1}{2}$$

For a photon headed in the θ direction with respect to the z-axis, it has a component $\cos \theta$ in the z-direction and component $\sin \theta$ in the x-direction. We get all of the z-direction piece and half of the x-direction piece so the probability to go into the angle θ is

$$P(\theta) = \cos^2 \theta + \frac{1}{2} \sin^2 \theta = \frac{1}{2}(1 + \cos^2 \theta)$$

which happens to be the same

$$|d_{1,1}^1|^2 + |d_{1,-1}^1|^2 = \left(\frac{1}{2}(1 + \cos \theta)\right)^2 + \left(\frac{1}{2}(1 - \cos \theta)\right)^2 = \frac{1}{2}(1 + \cos^2 \theta)$$

4.2.6 Absorption cross section

Or instead of writing the rate in terms of the energy density of the incident radiation, we could define the cross section. Then the rate is the incoming flux times the cross section. The incoming energy flux is the energy density times the velocity. The flux of photons is the energy flux/photon energy. So

$$\text{Rate} = \sigma \text{Flux} \quad \text{and} \quad \text{Flux} = cU/\hbar\omega$$

Then

$$\sigma_{abs} = \frac{w_{i \rightarrow n} \hbar\omega}{cU} = \frac{(2\pi)^2}{c} \frac{e^2}{m^2\omega} |\langle n | \epsilon \cdot \mathbf{p} | i \rangle|^2 \delta(E_n - E_i \pm \hbar\omega)$$

Again we replace $\langle p \rangle$ with $m/\hbar \langle [H, x] \rangle$ and get that

$$\sigma_{abs} = \frac{(2\pi)^2}{c} \frac{\omega e^2}{\hbar^2} |\langle n | \epsilon \cdot \mathbf{x} | i \rangle|^2 \delta(E_n - E_i \pm \hbar\omega) = \frac{(2\pi)^2}{c} \frac{\omega e^2}{\hbar} |\langle n | \epsilon \cdot \mathbf{x} | i \rangle|^2 \delta(\omega_{ni} - \omega)$$

If we suppose the polarization is in the x direction then The total absorption cross section is

$$\int \sigma(\omega) d\omega = \sum_n 4\pi^2 \omega_{ni} \alpha |\langle n | x | i \rangle|^2$$

4.3 Photo electric effect

Imagine a hydrogen atom at rest at the origin. Electromagnetic radiation in the form of a plane wave is propagating in the $+z$ direction ($\mathbf{k} = |\mathbf{k}| \hat{z}$) with E-field polarized along the x-direction. The radiation field interacts with the atom and frees the electron. The electron flies off in the (θ, ϕ) direction with momentum $\mathbf{p} = \hbar \mathbf{k}_f$

4.3.1 Golden rule

The transition rate is given by the golden rule

$$R = \frac{|\langle f | H' | i \rangle|^2}{\hbar} 2\pi\delta(E_f - E_i - \hbar\omega)$$

The initial state is the ground state of hydrogen

$$\langle \vec{x} | i \rangle = \frac{2}{\sqrt{4\pi a^3}} e^{-r/a}$$

The final state is a free electron

$$\langle \vec{x} | f \rangle = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

which we represent as a plane wave. We imagine the plane wave in a box with sides of length L so that it is normalized over the volume. We assume that the energy of the electron is so high that we can neglect the effect of the coulomb attraction of the hydrogen nucleus in the final state.

4.3.2 Interaction Hamiltonian

The interaction hamiltonian is

$$H' = \frac{q}{mc} \mathbf{A} \cdot \mathbf{p}$$

We write the vector potential as a plane wave,

$$\mathbf{A} = 2A_0\epsilon \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (17)$$

$$= A_0\epsilon \left(e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \right) \quad (18)$$

where ϵ is the unit vector that gives the polarization of \mathbf{A} and $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$. After application of the energy conserving δ -function we are left with

$$\mathbf{A} = A_0\epsilon e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$$

Then

$$H' = \frac{-i\hbar q}{mc} A_0 e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon \cdot \nabla$$

4.3.3 Density of states

The free electron in the final state is traveling at angle θ, ϕ into solid angle $d\Omega$. In order to determine the total rate for the transition we need to integrate over all possible final state electrons that are directed into the solid angle. The electrons are free particles confined to a box with side L . The electron wave function at the boundaries vanishes so

$$k_x = \frac{2n_x\pi}{L}, \quad k_y = \frac{2n_y\pi}{L}, \quad k_z = \frac{2n_z\pi}{L}$$

and

$$k_f^2 = \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

Imagine a sphere of radius $\sqrt{n_x^2 + n_y^2 + n_z^2}$. The total number of states with $|k| < |k_f|$ is the volume of the sphere,

$$N = \frac{4}{3}\pi(n_x^2 + n_y^2 + n_z^2)^{3/2} = \frac{4}{3}\pi \left(\left(\frac{L}{2\pi} k \right)^2 \right)^{3/2}$$

The number of states per unit k into solid angle $d\Omega$ are

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

The number of states per unit energy into solid angle $d\Omega$ are

$$\frac{dN}{dE} = \left(\frac{L}{2\pi} \right)^3 k^2 \frac{dk}{dE} \frac{d\Omega}{4\pi} \quad (19)$$

$$= \left(\frac{L}{2\pi} \right)^3 \frac{km}{\hbar^2} d\Omega \quad (20)$$

where we have use $E = \frac{\hbar^2 k^2}{2m}$.

4.3.4 Transition rate

The total transition rate is

$$R = \frac{|\langle f | H' | i \rangle|^2}{\hbar} 2\pi \int \delta(E_f - E_i - \hbar\omega) \frac{dN}{dE} \quad (21)$$

$$= \frac{|\langle f | H' | i \rangle|^2}{\hbar} 2\pi \left(\frac{L}{2\pi} \right)^3 \frac{km}{\hbar^2} d\Omega \quad (22)$$

$$= \hbar \left(\frac{qA_0}{mc} \right)^2 |\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle|^2 2\pi \left(\frac{L}{2\pi} \right)^3 \frac{km}{\hbar^2} d\Omega \quad (23)$$

4.3.5 Absorption cross section

We define a differential cross section

$$\frac{d\sigma}{d\Omega} = \frac{\text{Rate for photoelectrons}}{\text{Flux of incident photons}}$$

The energy flux for the incoming plane wave is

$$cu = \frac{c}{8\pi} E_{max}^2 = \frac{1}{2\pi} \frac{\omega^2}{c} A_0^2$$

and since each photon has energy $\hbar\omega$, the photon flux is

$$\text{Flux} = \frac{1}{2\pi\hbar\omega c} \omega^2 A_0^2 = \frac{1}{2\pi\hbar c} \omega A_0^2$$

Then

$$\frac{d\sigma}{d\Omega} = \frac{\hbar \frac{q^2 A_0^2}{(mc)^2} |\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle|^2 2\pi \left(\frac{L}{2\pi}\right)^3 \frac{km}{\hbar^2}}{(\omega A_0^2 / 2\pi\hbar c)} \quad (24)$$

$$= \frac{2\pi (q\hbar)^2 |\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle|^2 2\pi \left(\frac{L}{2\pi}\right)^3 \frac{km}{\hbar^2}}{m^2 c \omega} \quad (25)$$

$$= \frac{q^2 |\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle|^2 L^3 k}{2\pi m c \omega} \quad (26)$$

4.3.6 Expectation value

All that remains is to compute the expectation value. Note that it is not appropriate to work in the electric dipole limit. We are assuming that the energy of the final state electron is big compared to the binding energy. Therefore it is not safe to assume that $\mathbf{k} \cdot \mathbf{r} \ll 1$ and we will attempt to do the integral exactly.

We have that

$$\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle = \frac{1}{L^{3/2}} \frac{1}{\pi^{1/2} a^{3/2}} I$$

where

$$I = \int e^{-i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla e^{-r/a} r^2 dr d\Omega$$

Integrating by parts we get that

$$I = \boldsymbol{\epsilon} \cdot \int \nabla \left(e^{-i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-r/a} \right) r^2 dr d\Omega \quad (27)$$

$$= \boldsymbol{\epsilon} \cdot \int \nabla \left(e^{-i\mathbf{k}\cdot\mathbf{r}} \right) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-r/a} r^2 dr d\Omega \quad (28)$$

$$= \boldsymbol{\epsilon} \cdot \int e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla \left(e^{i\mathbf{k}\cdot\mathbf{r}} \right) e^{-r/a} r^2 dr d\Omega \quad (29)$$

Equation 11 can be written as a surface integral over a volume that we can take to infinity. The wave function falls off exponentially so Equation ?? is zero. On taking the gradient Equation ?? and pulling \mathbf{k} outside of the integral, we get

$$i\epsilon \cdot \mathbf{k} \int e^{-i\mathbf{k}_f \cdot \mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} e^{-r/a} r^2 dr d\Omega = 0$$

since polarization ϵ and propagation vector \mathbf{k} are orthogonal. Finally

$$I = \epsilon \cdot \int \nabla \left(e^{i\mathbf{k}_f \cdot \mathbf{r}} \right) e^{i\mathbf{k} \cdot \mathbf{r}} e^{-r/a} r^2 dr d\Omega \quad (30)$$

$$= -i\epsilon \cdot \mathbf{k}_f \int e^{-i\mathbf{k}_f \cdot \mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} e^{-r/a} r^2 dr d\Omega \quad (31)$$

$$= -i\epsilon \cdot \mathbf{k}_f \int e^{-i(\mathbf{k}_f - \mathbf{k}) \cdot \mathbf{r}} e^{-r/a} r^2 dr d\Omega \quad (32)$$

$$= -i\epsilon \cdot \mathbf{k}_f \int e^{-i\mathbf{q} \cdot \mathbf{r}} e^{-r/a} r^2 dr d\Omega \quad (33)$$

$$= -i\epsilon \cdot \mathbf{k}_f \int e^{-iq \cos \theta r} e^{-r/a} r^2 dr \sin \theta d\phi \quad (34)$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}$. First we do the angular integral

$$I = i2\pi\epsilon \cdot \mathbf{k}_f \int \frac{(e^{-iqr} - e^{iqr})}{iqr} e^{-r/a} r^2 dr \quad (35)$$

Then integrate over r .

$$I = 2\pi\epsilon \cdot \mathbf{k}_f \int \frac{(e^{-iqr-r/a} - e^{iqr-r/a})}{iq} r dr \quad (36)$$

$$= 2\pi\epsilon \cdot \mathbf{k}_f \left(\frac{1}{q(-iq - 1/a)^2} - \frac{1}{q(iq - 1/a)^2} \right) \quad (37)$$

$$= 2\pi\epsilon \cdot \mathbf{k}_f \left(\frac{1}{q(-q^2 + 1/a^2 - 2iq/a)} - \frac{1}{q(-q^2 + 1/a^2 + 2iq/a)} \right) \quad (38)$$

$$= 2\pi\epsilon \cdot \mathbf{k}_f \left(\frac{-4iq/a}{q((-q^2 + 1/a^2)^2 + 4(q/a)^2)} \right) \quad (39)$$

$$= 2\pi\epsilon \cdot \mathbf{k}_f \frac{-4i}{a(q^2 + (1/a)^2)} \quad (40)$$

Finally

$$\langle f | e^{i\mathbf{k} \cdot \mathbf{r}} \epsilon \cdot \nabla | i \rangle = \frac{1}{L^{3/2}} \frac{1}{\pi^{1/2} a^{3/2}} 2\pi\epsilon \cdot \mathbf{k}_f \frac{-4i}{a(q^2 + (1/a)^2)^2} \quad (41)$$

$$= \frac{-8i\pi^{1/2}\epsilon \cdot \mathbf{k}_f}{L^{3/2} a^{3/2} a(q^2 + (1/a)^2)^2} \quad (42)$$

$$(43)$$

and

$$\frac{d\sigma}{d\Omega} = \frac{\alpha\hbar L^3 k_f}{2\pi m\omega} \left(\frac{8\pi^{1/2} \epsilon \cdot \mathbf{k}_f}{L^{3/2} a^{5/2} (q^2 + (1/a)^2)^2} \right)^2 \quad (44)$$

$$= \frac{32\alpha\hbar k_f}{m\omega} \frac{(\epsilon \cdot \mathbf{k}_f)^2}{a^5 (q^2 + (1/a)^2)^4} \quad (45)$$

4.3.7 Angular distribution

The E-field vector \mathbf{k} is in the z-direction and the electron in the final state has \mathbf{k}_f in the θ, ϕ direction. Then $q^2 = k_f^2 + k^2 - 2k_f k \cos \theta$. And the polarization is in the x-direction so that $\epsilon \cdot \mathbf{k}_f = k_f \sin \theta \cos \phi$ and

$$\frac{d\sigma}{d\Omega} = \frac{32\alpha\hbar k_f}{m\omega} \frac{(k_f \sin \theta \cos \phi)^2}{a^5 (k_f^2 + k^2 - 2k_f k \cos \theta + (1/a)^2)^4}$$

The differential cross section is peaked for the outgoing electron in the $\theta = \pi/2, \phi = 0$ direction, namely parallel to the polarization of the field.