Chapter Five: Approximation Methods:

Time-Independent Perturbation Theory: Nondegenerate Case.

Time-independent Hamiltonian H

$$H = H_0 + \underset{\nwarrow\ \text{perturbation}}{V}$$

We assume that the $V = 0$ has been solved.

i.e. we know that $|n^{(0)}\rangle$ satisfy

$$H_0 |n^{(0)}\rangle = E^{(0)} |n^{(0)}\rangle$$

We want to solve the full problem:

$$(H_0 + V)|n\rangle = E_n |n\rangle$$

We will approach this by considering

$$(H_0 + \lambda V)|n\rangle = E_n |n\rangle$$

where λ is a real continuous parameter which can be used to turn on and off the perturbation as $0 \leq \lambda \rightarrow 1$. We will, for instance, calculate corrections order by order in λ ← we are assuming the analyticity of the energy eigenvalues and eigenkets in the complex λ plane.

A test case - the two-state problem

$$H = \begin{pmatrix} E_1^{(0)} & \lambda V \\ \lambda V & E_2^{(0)} \end{pmatrix} \qquad V \text{ is real.}$$

Now $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ are clearly known as are the unperturbed energy eigenvalues. We can also solve this problem exactly.

$$E_{1,2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\left(\frac{E_1^{(0)} - E_2^{(0)}}{2}\right)^2 + \lambda^2 V^2}$$

Now, if we take λV to be small i.e.

$$|\lambda V| \ll \left|\frac{E_1^{(0)} - E_2^{(0)}}{2}\right|$$

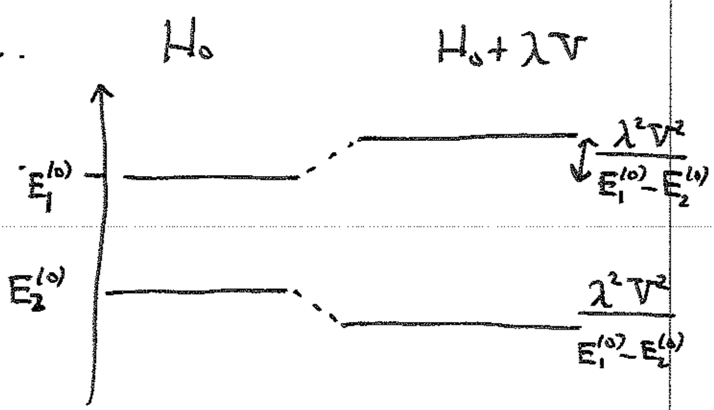
Then

$$E_{1,2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \frac{|E_1^{(0)} - E_2^{(0)}|}{2}\left[1 + \frac{4\lambda^2 V^2}{(E_1^{(0)} - E_2^{(0)})^2}\right]^{1/2}$$

say $E_1^{(0)} > E_2^{(0)}$ to be definite.

$$E_1 = E_1^{(0)} + \frac{\lambda^2 V^2}{E_1^{(0)} - E_2^{(0)}} + \cdots$$

$$E_2 = E_2^{(0)} - \frac{\lambda^2 V^2}{E_1^{(0)} - E_2^{(0)}} + \cdots$$



Notice that we encounter branch points in the λ-plane at

$\lambda = \pm i\,(E_1^{(0)} - E_2^{(0)})/2V$

Note too that the convergence of our expansion above requires that

$|\lambda V| < |E_1^{(0)} - E_2^{(0)}|/2$

We will come back to the issue of convergence later on.

Formal Development of the Theory

$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$ ← We have solved this problem.

The set $\{|n^{(0)}\rangle\}$ is complete.

We *assume* that the energy spectrum $E_n^{(0)}$ is nondegenerate.

We want to solve the problem: $(H_0 + \lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda$

continuous functions of the parameter λ.

As λ is increased from 0 $E_n^{(\lambda)}$ becomes different from $E_n^{(0)}$. Define the shift in the energy level as

$$\Delta_n^{(\lambda)} = E_n^{(\lambda)} - E_n^{(0)}$$

Then: $(\star)$ $(E_n^{(0)} - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle$ {since

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

We need to solve $(\star)$ for $|n\rangle$ and Δ_n. Thus, we need to invert the operator $(E_n^{(0)} - H_0) \Rightarrow$ "resolvent" operator.

Is $\dfrac{1}{E_n^{(0)} - H_0}$ well-defined? As long as it does not act on $|n^{(0)}\rangle$, we are fine. Note that $(\lambda V - \Delta_n)|n\rangle$ has no projection along $|n^{(0)}\rangle$. To see this note that

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

Define the complementary projection operator

$$\phi_n = 1 - |n^0\rangle\langle n^0| = \sum_k |k^{(0)}\rangle\langle k^{(0)}|$$

so that we can define the inverse operator $\dfrac{1}{E_n^{(0)} - H_0}$ when acting to the left of ϕ_n:

$$\frac{1}{E_n^{(0)} - H_0}\phi_n = \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle\langle k^{(0)}|$$

Note also that $(\lambda V - \Delta_n)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle$

So we can write

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

The part of $|n\rangle$ along $|n^{(0)}\rangle$. This part is annihilated when $(E_n^{(0)} - H_0)$ acts on $|n\rangle$.

In fact, we know that, in the limit $\lambda \to 0$, $|n\rangle \to |n^{(0)}\rangle$ so we know that $\lim_{\lambda \to 0} C_n(\lambda) = 1$.

$\langle n^{(0)}|n\rangle = C_n(\lambda)$ (Because of the ϕ_n operator)

It is convenient and traditional to set $C_n(\lambda) = 1$ for $\lambda \neq 0$ and mess up the overall normalization of the ket $|n\rangle$. We can always fix that later. More on this below.

It is also useful to write $\frac{1}{E_n^{(0)} - H_0}\phi_n$ as $\frac{\phi_n}{E_n^{(0)} - H_0}$ so that we can write

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

We also note from $\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = 0$ that the energy

Shift of the perturbed levels is given by

$$\Delta_n = \lambda \langle n^{(0)} | V | n \rangle \quad \text{(since we have chosen } \langle n^0 | n \rangle = 1\text{)}$$

We now have two equations that need to be solved simultaneously:

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

$$\Delta_n = \lambda \langle n^{(0)} | V | n \rangle$$

for $|n\rangle$ and Δ_n.

The fundamental approach is to assume an expansion of the form:

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots$$

$$\Delta_n = \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \cdots$$

and solve order-by-order simply from equating coefficients of λ.

To order λ^1: $\Delta_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle$

λ^2: $\Delta_n^{(2)} = \langle n^{(0)} | V | n^{(1)} \rangle$

λ^N: $\Delta_n^{(N)} = \langle n^{(0)} | V | n^{(N-1)} \rangle$

$\Rightarrow$ To get Δ_n to order N we need the ket to order $(N-1)$.

Now, look at the first of our pair of equations

$$|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \cdots$$

$$= |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0} \left(\lambda V - \lambda \Delta_n^{(1)} - \lambda^2 \Delta_n^{(2)} - \lambda^3 \Delta_n^{(3)} - \cdots \right) \left\{ |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \right\}$$

To order λ^0 $\quad |n^{(0)}\rangle = |n^{(0)}\rangle$ nothing new!

$$\mathcal{O}(\lambda^1) \; : \quad |n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \Delta_n^{(1)} |n^{(0)}\rangle$$

$\uparrow$

But $\phi_n |n^{(0)}\rangle = 0$ so

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

$$\left(\text{So} \quad \Delta_n^{(2)} = \langle n^{(0)} | V \frac{\phi_n}{E_n^{(0)} - H_0} V | n^{(0)} \rangle \right)$$

$\mathcal{O}(\lambda^2)$:

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

$$|n^{(2)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n V}{E_n^{(0)} - H_0} |n^{(0)}\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \langle n^{(0)} | V | n^{(0)} \rangle \cdot$$

$$\cdot \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle$$

Let's write this out in terms of the sums over the unperturbed energy eigenstates - in other words we have to recall our definitions

$$\Delta_n = \lambda \langle n^{(0)} | V | n^{(0)} \rangle + \lambda^2 \langle n^{(0)} | V \sum_{k \neq n} \frac{|k^{(0)}\rangle\langle k^{(0)}|}{E_n^{(0)} - E_k^{(0)}} V | n^{(0)} \rangle$$

$$\Delta_n = \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{\langle n^{(0)} | V | k^{(0)} \rangle \langle k^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

$\uparrow$

refers to the unperturbed states.

More compactly, we can write the energy shift to second order as

$$\Delta_n = \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^3)$$

all matrix elements are taken with respect to the <u>unperturbed</u> states.

Doing the same for the kets:

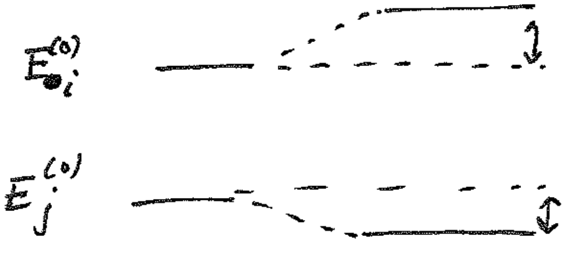
$$|n\rangle = |n^{0}\rangle + \lambda \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle +$$

$$+ \lambda^2 \left(\sum_{\substack{k \neq n \\ \ell \neq n}} |k^{(0)}\rangle \frac{\langle k^{(0)}|V|\ell^{(0)}\rangle\langle \ell^{(0)}|V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_\ell^{(0)})} - \sum_{k \neq n} |k^{(0)}\rangle \frac{V_{nn} V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} \right)$$

$$+ \mathcal{O}(\lambda^3)$$

The n^{th} level now has contributions coming from all the other levels. The amount of this mixing is determined by how the perturbation connects the various <u>unperturbed</u> states.

Two energy levels i and j get shifted away from each other if connected by V_{ij} say $V_{ii} = V_{jj} = 0$ then



$$\frac{|V_{ij}|^2}{E_i^{(0)} - E_j^{(0)}}$$ level repulsion

$$- \frac{|V_{ij}|^2}{E_i^{(0)} - E_j^{(0)}}$$

More generally, a pair of levels cannot cross as λ is varied.
connected by V

Also for the ground state

$$\Delta_0 = \lambda V_{00} + \lambda^2 \sum_{k\neq 0} \frac{|V_{0k}|^2}{\underbrace{E_0^{(0)} - E_k^{(0)}}_{\uparrow\ \text{negative}}}$$

⟺ Lowest states energy tends to decrease due to mixing.

Wave-function Renormalization:

Now let's fix the normalization of the perturbed ket. Defi

$|n\rangle_N = Z_n^{1/2}|n\rangle$, where the constant Z_n ensures that

${}_N\langle n|n\rangle_N = 1$. We can calculate Z_n from

$Z_n^{1/2} = \langle n^{(0)}|n\rangle_N$. $Z_n^{1/2}$ = probability amplitude for the perturbed ket to be found in the unperturbed energy eigenstate.

$$\frac{1}{Z_n} = \langle n|n\rangle = \left(\langle n^{(0)}| + \lambda\langle n^{(1)}| + \lambda^2\langle n^{(2)}| + \cdots\right)\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\right)$$

$$Z_n^{-1} = 1 + \lambda\left(\langle n^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n^{(1)}\rangle\right) + \lambda^2\left(\langle n^{(1)}|n^{(1)}\rangle + \langle n^{(0)}|n^{(2)}\rangle + \langle n^{(2)}|n^{(0)}\rangle\right) + \cdots$$

But recall $|n^{(1)}\rangle \propto \sum_{k\neq n}|k\rangle$ so many of the above terms are zero.

$$|n^{(2)}\rangle \propto \sum_{k\neq n}|k\rangle$$

♡ XOXO ♡

In fact

$$Z_n^{-1} = 1 + \lambda^2 \langle n^{(1)} | n^{(1)} \rangle + \mathcal{O}(\lambda^3)$$

$$= 1 + \lambda^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{\left[E_n^{(0)} - E_k^{(0)}\right]^2} + \mathcal{O}(\lambda^3)$$

so to this order

$$Z_n \cong 1 - \underbrace{\lambda^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{\left[E_n^{(0)} - E_k^{(0)}\right]^2}}_{\text{Probability for leakage to the other states.}}$$

Note that from

$$E_n = E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$Z_n = \frac{\partial E_n}{\partial E_n^{(0)}}$$ ↖ holding V_{ij} fixed.

at least to $\mathcal{O}(\lambda^2)$. Actually this result is more general.

A simple example

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 \qquad V = \frac{1}{2} \varepsilon m \omega^2 x^2, \quad \varepsilon \ll 1$$

Note that all we have done is $\omega \to \omega\sqrt{1+\varepsilon}$ so we actually have an exact solution for the energies and stationary states of $H = H_0 + V$.

But let's apply our perturbation analysis anyway...

Shift in the ground state $|0\rangle$ and energy E_0.

$$|0\rangle = |0^{(0)}\rangle + \sum_{k\neq 0} |k^{(0)}\rangle \frac{V_{k0}}{E_0^{(0)} - E_k^{(0)}} + \cdots$$

$$\Delta_0 = V_{00} + \sum_{k\neq 0} \frac{|V_{k0}|^2}{E_0^{(0)} - E_k^{(0)}} + \cdots$$

$$V_{00} = \frac{\varepsilon m\omega^2}{2}\langle 0^{(0)}|x^2|0^{(0)}\rangle = \frac{\varepsilon\hbar\omega}{4}$$

$$V_{20} = \frac{\varepsilon m\omega^2}{2}\langle 2^{(0)}|x^2|0^{(0)}\rangle = \frac{\varepsilon\hbar\omega}{2\sqrt{2}}$$

$$\Rightarrow \quad |0\rangle = |0^{(0)}\rangle + \frac{\varepsilon\hbar\omega}{2\sqrt{2}}|2^{(0)}\rangle \frac{1}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega}$$

$$|0\rangle = |0^{(0)}\rangle - \frac{\varepsilon}{4\sqrt{2}}|2^{(0)}\rangle + \mathcal{O}(\varepsilon^2)$$

and $$\Delta_0 = E_0 - E_0^{(0)} = \hbar\omega\left[\frac{\varepsilon}{4} - \frac{\varepsilon^2}{16} + \mathcal{O}(\varepsilon^3)\right]$$

$$\uparrow$$

from $$\frac{\varepsilon^2(\hbar\omega)^2}{8}\,\frac{1}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega} = -\frac{\hbar\omega\,\varepsilon^2}{16}$$

checks!

<u>Now is this correct?</u>

Ground state Energy (Exactly) $\frac{\hbar\omega}{2}\sqrt{1+\varepsilon} \cong \frac{\hbar\omega}{2}\left[1 + \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8}\right] + \mathcal{O}(\varepsilon^3)$

What about the shift in the wavefunction

$$\langle x|0^{(0)}\rangle = \pi^{-1/4}x_0^{-1/2}e^{-\frac{x^2}{2x_0^2}} \qquad x_0 = \sqrt{\frac{\hbar}{m\omega}}$$

so $x_0 \longrightarrow x_0(1+\varepsilon)^{-1/4}$ Expand and collect terms.

$$\langle x|0^{(0)}\rangle \to \pi^{-1/4}\frac{1}{x_0^{1/2}}(1+\varepsilon)^{1/8}e^{-\frac{x^2}{2x_0^2}(1+\varepsilon)^{1/2}}$$

$$\cong \frac{\pi^{-1/4}}{x_0^{1/2}}\left(1+\frac{1}{8}\varepsilon\right)e^{-\frac{x^2}{2x_0^2}}\left(1-\frac{x^2}{2x_0^2}\cdot\frac{1}{2}\varepsilon\right)$$

$$= \langle x|0^{(0)}\rangle + \varepsilon\left\{\frac{1}{8}\pi^{-1/4}x_0^{-1/2}e^{-x^2/2x_0^2} - \frac{1}{4}\frac{x^2}{x_0^2}e^{-x^2/2x_0^2}\pi^{-1/4}x_0^{-1/2}\right\}$$

$$= \langle x|0^{(0)}\rangle + \frac{\varepsilon}{8}\underbrace{\left(1-2x^2/x_0^2\right)}_{-\frac{1}{2}H_2(x/x_0)}\pi^{-1/4}x_0^{-1/2}e^{-x^2/2x_0^2}$$

↖ Hermite polynomial $H_2(x) = 4x^2 - 2$

$$\langle x|2^{(0)}\rangle = \frac{1}{\sqrt{8}}\pi^{-1/4}x_0^{-1/2}e^{-\frac{x^2}{2x_0^2}}H_2(x/x_0)$$

$$= \langle x|0^{(0)}\rangle - \frac{\varepsilon}{4\sqrt{2}}\langle x|2^{(0)}\rangle \qquad \text{checks!}$$

$$\frac{1}{8}\frac{\sqrt{8}}{2}\langle x|2^{(0)}\rangle = \frac{1}{4\sqrt{2}}\langle x|2^{(0)}\rangle$$

Time-independent perturbation thry: The degenerate case.

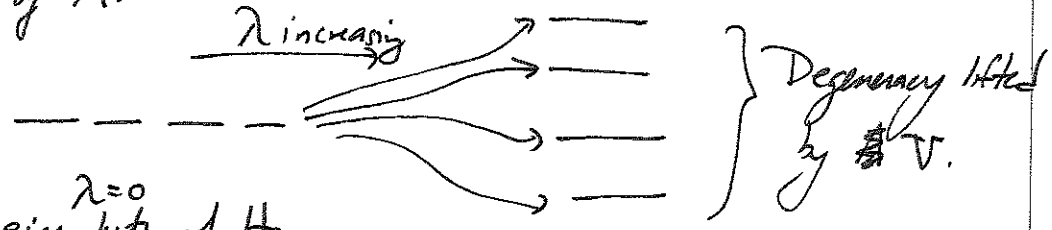
We have a problem when the energy levels are degenerate. Then the denominators $\frac{1}{E_n^{(0)}-E_k^{(0)}}$ vanish so the individual terms in the perturbation series blow-up.

With degenerate states we need to label the kets by their eigenvalues wrt H_0 and another observable A.

$$H_0\,|k^{(0)},a\rangle = E_k\,|k^{(0)},a\rangle$$

$$A\,|k^{(0)},a\rangle = a\,|k^{(0)},a\rangle$$

if $[H,A]\neq 0$ i.e. $[V,A]\neq 0$ then the eigenkets of H are *not* eigenkets of A.



n-fold degenerate eigenkets of H_0

We can choose the unperturbed kets to be given by any linear combination of the n-fold degenerate states.

$$|l^{(0)}\rangle = \sum_{m=1}^{n} \underbrace{|k^{(0)}, a_m\rangle}_{\text{label this by a collective index } |m^{(0)}\rangle} \overbrace{\langle k^{(0)}, a_m | l^{(0)}\rangle}^{\text{NOT specified yet!}}$$

A new set of spanning kets.

sum over the kets spanning the degenerate subspace.

The Schrödinger equation obeyed by the perturbed kets $|l^{(0)}\rangle$ is

$$(E^{(0)} - H_0)|l\rangle = (\lambda V - \Delta_l)|l\rangle$$

energy of *all* the states in the degenerate subspace of the unperturbed Hamiltonian

Expand: $|l\rangle = |l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \lambda^3|l^{(3)}\rangle + \cdots$

$\mathcal{O}(\lambda^0)$ $\quad (E^{(0)} - H_0)|l^{(0)}\rangle = 0$ as expected.

$\mathcal{O}(\lambda^1)$ $\quad (E^{(0)} - H_0)|l^{(1)}\rangle = (V - \Delta_l^{(1)})|l^{(0)}\rangle$

$$= (V - \Delta_l^{(1)}) \sum_{m=1}^{n} |m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle$$

Multiply on the left by $\langle \tilde{m}^{(0)}|$.

$\uparrow$ another of the kets in the degenerate subspace.

$\Longrightarrow$

$$\underbrace{\langle \tilde{m}^{(0)}|(E^{(0)}-H_0)|\ell^{(1)}\rangle}_{\overset{\shortparallel}{0}} = 0 = \sum_m \langle \tilde{m}^{(0)}|V|m^{(0)}\rangle \times \langle m^{(0)}|\ell^{(0)}\rangle - \Delta_\ell^{(1)} \langle \tilde{m}^{(0)}|\ell^{(1)}\rangle$$

or

$$\sum_m \langle \tilde{m}^{(0)}|V|m^{(0)}\rangle\langle m^{(0)}|\ell^{(1)}\rangle = \Delta_\ell^{(1)}\langle \tilde{m}^{(0)}|\ell^{(0)}\rangle$$

This is an eigenvector equation for the vector $\langle m^{(0)}|\ell^{(1)}\rangle$ with eigenvalue $\Delta_\ell^{(1)}$.

$$\underbrace{V_{\tilde{m}m}\,\ell_m = \Delta_\ell^{(1)}\,\ell_{\tilde{m}}}_{\text{in usual vector notation}} \Rightarrow \det\big(\overset{\leftrightarrow}{V} - \mathbb{1}\,\Delta_\ell^{(1)}\big) = 0$$

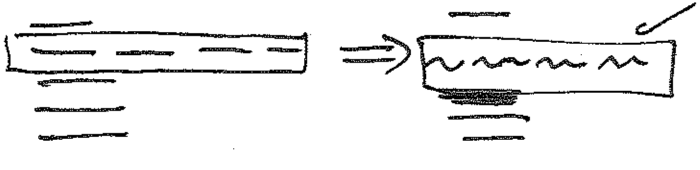
$\uparrow$ Roots of the secular equation determine the eigenvalues $\Delta_\ell^{(1)}$ ← the energy shifts!

Note there are n solutions – one for each ket spanning the degenerate subspace.

The eigenvectors $\ell_m = \langle m^{(0)}|\ell^{(0)}\rangle$ are the linear combinations of the $|m^{(0)}\rangle$'s that diagonalize V $\Rightarrow$

$$\Delta_\ell^{(1)} = \langle \ell^{(0)}|V|\ell^{(0)}\rangle$$ ← diagonal elements are just the 1st order energy shifts.

Basically we have mixed up the states spanning the degenerate subspace of H_0 so that V is diagonal when acting on that part of the Hilbert space.



new linear combinations!

Now looking at the ket equation to 1st order

$$(E^{(0)} - H_0)|l^{(1)}\rangle = (V - \Delta_l^{(1)})|l^{(0)}\rangle$$

Define the complimentary projection operator ϕ_D

$$\phi_D = 1 - \sum_{m=1}^{n} |m^{(0)}\rangle\langle m^{(0)}| = \sum_{\substack{k \notin D \\ \uparrow \\ \text{degenerate subspace}}} |k^{(0)}\rangle\langle k^{(0)}|$$

We can already see that $\langle m^{(0)}|[V - \Delta_l^{(1)}]|l^{(0)}\rangle = 0$ since $\langle m^{(0)}|(E^{(0)} - H_0)|l^{(1)}\rangle = 0$, so:

$$\phi_D (V - \Delta_l^{(1)}) \underset{\substack{\uparrow \\ \text{in the degenerate subspace.}}}{|l^{(0)}\rangle} = \phi_D V |l^{(0)}\rangle$$

Now $\frac{1}{E^{(0)} - H_0}$ is *not* singular when acting on $\phi_D V|l^{(0)}\rangle$ so

$$|l^{(1)}\rangle = \frac{\phi_D}{E^{(0)} - H_0} V |l^{(0)}\rangle$$

$$\boxed{|l^{(1)}\rangle = \sum_{k \notin D} \frac{|k^{(0)}\rangle \overset{\langle k^{(0)}|V|l^{(0)}\rangle}{\overbrace{V_{kl}}}}{\underset{\substack{\uparrow \\ \text{Energy of the degenerate subspace}}}{E_D^{(0)}} - \underset{\substack{\uparrow \\ \text{Energy levels not part of the degenerate subspace.}}}{E_k^{(0)}}}}$$

We have now avoided any singularities associated w/ the energy degeneracy.

By convention we normalize by

$$\langle \ell^{(0)} | \ell \rangle = 1.$$

From $(E^{(0)} - H_0) | \ell \rangle = (\lambda V - \Delta_\ell) | \ell \rangle$

$$\Rightarrow \lambda \langle \ell^{(0)} | V | \ell \rangle = \Delta_\ell \langle \ell^{(0)} | \ell \rangle = \Delta_\ell$$

Expanding $| \ell \rangle$ in powers of λ we find

$$\lambda \langle \ell^{(0)} | V | \left\{ | \ell^{(0)} \rangle + \lambda | \ell^{(1)} \rangle + \lambda^2 | \ell^{(2)} \rangle + \cdots \right\} = \lambda \Delta_\ell^{(1)} + \lambda^2 \Delta_\ell^{(2)} + \cdots$$

$\mathcal{O}(\lambda^1)$: $\langle \ell^{(0)} | V | \lambda^{(0)} \rangle = \Delta_\ell^{(1)}$ ← we already knew that..

$\mathcal{O}(\lambda^2)$: $\langle \ell^{(0)} | V | \ell^{(1)} \rangle = \langle \ell^{(0)} | V \dfrac{\phi_D}{E^{(0)} - H_0} V | \ell^{(0)} \rangle = \Delta_\ell^{(2)}$

so

$$\boxed{\Delta_\ell^{(2)} = \sum_{k \notin D} \frac{| V_{k\ell} |^2}{E^{(0)} - E_k^{(0)}}}$$

↑ Eng of the degenerate subspace kets.

Variational Methods:

There are times when we don't know a sufficient close Hamiltonian H_0 that is solvable (i.e. for which we have exact solutions). In such cases we can use a variational approach to estimate the ground state energy.

Define: $\bar{H} = \dfrac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$ where $| \tilde{0} \rangle$ is an ansatz for the ground state ket.

Thm: $\overline{H}_0 > E_0 \leftarrow$ exact ground state energy.

Pf: Since the exact eigenkets of H are complete

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle ; \quad H|k\rangle = E_k|k\rangle$$

$$\left.\begin{aligned} \langle\tilde{0}|\tilde{0}\rangle &= \sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2 \\ \langle\tilde{0}|H|\tilde{0}\rangle &= \sum_{k=0}^{\infty} E_k|\langle k|\tilde{0}\rangle|^2 \end{aligned}\right\} \overline{H} = \frac{\sum_{k=0}^{\infty} E_k |\langle k|\tilde{0}\rangle|^2}{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2}$$

Write $E_k = \underbrace{(E_k - E_0)}_{\text{positive since } E_0 = \text{ground state energy.}} + E_0$

$$\Rightarrow \quad \overline{H} = E_0 + \sum_{k=1}^{\infty}(E_k - E_0)|\langle k|\tilde{0}\rangle|^2 \Big/ \sum_{k=0}^{\infty}|\langle k|\tilde{0}\rangle|^2 \geqslant E_0$$

Thus our ansatz will always be an upper bound to the energy. The guess may be very good even if the ket isn't! Why?

Consider $\langle k|\tilde{0}\rangle \sim \mathcal{O}(\varepsilon)$ for some ket $|k\rangle$, $k \neq 0$.

i.e. not the ground state.

Then $\overline{H} - E_0 \sim \varepsilon^2$

Ideally we write a trial ket that is parameterised by some adjustable variables. $|\tilde{0}; \lambda_1, \lambda_2, \dots, \lambda_N\rangle$ and then minimize $\overline{H}$ wrt λ_n $n = 1, \dots, N \Leftrightarrow$ i.e. $\dfrac{\partial \overline{H}}{\partial \lambda_p} = 0$ all p.

A simple example of the variational method.

H-atom $H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{-e^2}{4\pi\varepsilon_0 r}$

Try

$\langle \vec{x} | \tilde{0} \rangle = N e^{-r/a}$ to normalize this we take $N = \frac{1}{\sqrt{\pi a^3}}$

$$4\pi |N|^2 \int_0^\infty r^2 e^{-2r/a} dr = \pi a^3 |N|^2 = 1$$

$$\langle \tilde{0} | -\nabla^2 | \tilde{0} \rangle = -|N|^2 4\pi \int_0^\infty r^2 dr \, \frac{1}{r^2} \, \partial_r \left(r^2 \partial_r \left(e^{-r/a} \right) \right) e^{-r/a}$$

$$= \frac{1}{\pi a^3} 4\pi \frac{a}{4} = 1/a^2$$

$$\langle \tilde{0} | \frac{1}{r} | \tilde{0} \rangle = 4\pi |N|^2 \int_0^\infty dr \, r \, e^{-2r/a} = \frac{4}{a^3}\frac{a^2}{4} = 1/a$$

so $\bar{H} = \frac{\hbar^2}{2m}\frac{1}{a^2} - \frac{e^2}{4\pi\varepsilon_0 a}$

$$\frac{\partial \bar{H}}{\partial a} = 0 = -2\frac{\hbar^2}{2m} a^{-3} + \frac{e^2}{4\pi\varepsilon_0 a^2} = 0$$

$$\frac{\hbar^2}{m} a^{-3} = \frac{e^2}{4\pi\varepsilon_0} a^{-2} \Rightarrow a = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m}$$

so the minimum eny ocurs for the width of the wavefunction is the Bohr radius $a = a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} = \frac{\hbar}{mc}\frac{1}{\alpha}$

↑ fine structure constant.

So, we took a pretty good guess!

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \cong \frac{1}{137}$$

Time-Dependent Potentials: The Interaction Picture

$$H = H_0 + V(t) \;; \qquad H_0|n\rangle = E_n|n\rangle \quad \text{known.}$$

When $V(t) \neq 0$ $|n\rangle$ are not stationary states any more! They do not evolve in time as $e^{-iHt/\hbar}$, because H itself is now time-dependent.

Generally, we will find that as time evolves there will be transitions from one of the states $|n\rangle$ to another state $|n'\rangle$

At $t=0$ $\quad |\alpha\rangle = \sum_n c_n(0)|n\rangle$ ← the physical ket

i.e. our initial condition.

We want to predict the future, i.e. to find

$$|\alpha, t\rangle = \sum_n \underbrace{c_n(t)\, e^{-iE_nt/\hbar}} |n\rangle$$

$$c_n(t=0) = c_n(0)$$

Separation into the old "boring" time-dependence $e^{-iE_nt/\hbar}$ and some extra stuff due to $V(t)$: $c_n(t)$.

How to effect this separation: the interaction picture.

Define $\quad |\alpha; t_0, t\rangle_I = e^{iH_0t/\hbar}|\alpha; t_0, t\rangle_S$

↑ interaction rep ket $\qquad$ ↑ Schrödinger rep ket.

observables in the interaction representation

$$A_I = e^{iH_0t/\hbar} A_S e^{-iH_0t/\hbar}$$

↖ Schrödinger operator (w/o time-dependence →

go back and look at the discussion of the Heisenberg representation!

What is the time evolution of a ket in the I-picture?

$$i\hbar\,\partial_t|\alpha;t_0,t\rangle_I = i\hbar\,\partial_t\left(e^{iH_0t/\hbar}|\alpha;t_0,t\rangle_S\right)$$

$$= -H_0e^{iH_0t/\hbar}|\alpha;t_0,t\rangle_S + e^{iH_0t/\hbar}(H_0+V)|\alpha;t_0,t\rangle_S$$

$$= \underbrace{e^{iH_0t/\hbar}\,V\,e^{-iH_0t/\hbar}}_{V_I(t)}\;\underbrace{e^{iH_0t/\hbar}|\alpha;t_0,t\rangle_S}_{|\alpha;t_0,t\rangle_I}$$

So

$$(\star)\quad \boxed{i\hbar\,\partial_t|\alpha;t_0,t\rangle_I = V_I(t)\,|\alpha;t_0,t\rangle_I}$$

A Schrödinger-like Eq w/ V_I replacing H!

So in the I-picture:

operators have a time-dependence determined by H_0

kets have a time-dependence determined by V_I

Half-way between the S and H-pictures!

Thus: $|\alpha,t_0;t\rangle_I = \sum_n c_n(t)|n\rangle$ and (set $t_0=0$)

$$i\hbar\,\partial_t|\alpha,t\rangle_I = \sum_n c_n(t)\,V_I|n\rangle \quad\text{and}\quad |\alpha,0\rangle_I = \sum_n c_n(0)|n\rangle$$

or

~~$i\hbar\,\partial_t\langle n|\alpha,t\rangle_I = \sum_n c_n(t)\,\langle m|V_I|n\rangle$~~

~~But $c_n(0) = \langle n|\alpha,0\rangle_I$~~

From $(\star)$ $\quad i\hbar\,\langle m|\alpha;t_0,t\rangle_I = \sum_n \langle m|V_I|n\rangle\langle n|\alpha,t_0,t\rangle_I$

Note $\quad \langle m|V_I|n\rangle = \langle m|e^{iH_0t/\hbar}V|e^{-iH_0t/\hbar}|n\rangle$

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

And $\langle n|\alpha, t_0, t\rangle_I = c_n(t)$ so

$$i\hbar \frac{\partial}{\partial t} c_m(t) = \sum_n V_{mn}(t)\, e^{i\omega_{mn} t} c_n(t)$$

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

so we have a set of n ordinary differential equations for $c_n(t)$

$$i\hbar \dot{\vec{c}} = \overleftrightarrow{V} \cdot \vec{c}$$

Looking at a simple example: A two-level system.

$$H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| \quad (E_2 > E_1)$$

$$V(t) = \gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1|$$ ω, γ are real and positive

Look for a solution w/ initial conditions $c_1(0) = 1$
$c_2(0) = 0$

$$i\hbar \dot{c}_1 = \gamma e^{+i\omega t} e^{-i\omega_{21} t} c_2$$

$$i\hbar \dot{c}_2 = \gamma e^{-i\omega t} e^{i\omega_{21} t} c_1$$

or

$$\frac{d}{dt}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \frac{\gamma}{i\hbar}\begin{pmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$ let $\frac{\gamma}{i\hbar} = -i\bar{\gamma}$

So $$\ddot{c}_1 = -i\bar{\gamma} e^{i(\omega-\omega_{12})t} \dot{c}_2 + i(\omega-\omega_{21}) e^{i(\omega-\omega_{21})t} c_2 (-i\bar{\gamma})$$

define $\omega - \omega_{12} = \nu$

$$\ddot{c}_1 = -\bar{\gamma}^2 c_1 + i\nu \dot{c}_1 \Rightarrow \ddot{c}_1 - i\nu \dot{c}_1 + \bar{\gamma}^2 c_1 = 0$$

or $\dot{c}_2 = -\bar{\gamma} i e^{-i\nu t}\dot{c}_1 - i\bar{\gamma}(-i\nu)c_1 e^{-i\nu t}$

$$\ddot{c}_2 = (-i\bar{\gamma})^2 c_2 - i\nu\dot{c}_2$$

$$\ddot{c}_2 + 2i\nu c_2 + \bar{\gamma}^2 c_2 = 0$$

$c_2 \sim e^{\alpha t} \Rightarrow \quad \alpha^2 + i\nu\alpha + \bar{\gamma}^2 = 0$

$$\alpha = \frac{-i\nu}{2} \pm \frac{1}{2}\sqrt{-\nu^2 - 4\bar{\gamma}^2}$$

$$c_2 = Ae^{-\frac{i\nu}{2}t}e^{i\sqrt{\frac{\nu^2}{4}+\bar{\gamma}^2}\,t} + Be^{-\frac{i\nu}{2}t}e^{i\sqrt{\frac{\nu^2}{4}+\bar{\gamma}^2}\,t}$$

$c_2(0) = 0 \Rightarrow \quad A + B = 0$ fixed 1-25-10

$$\boxed{c_2(t) = Ae^{-\frac{i\nu}{2}t}\,2i\sin\left[\sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{12})^2}{4}}\,t\right]} ; \quad \nu = \omega - \omega_{12}$$

and

$$\dot{c}_1 = -i\bar{\gamma}\,e^{i\nu t}Ae^{-\frac{i\nu}{2}t}\,2i\sin\left[\sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{12})^2}{4}}\,t\right]$$

$\Rightarrow$

$$c_1(t) = \underset{\substack{\shortparallel \\ c_1(0)}}{1}\,\overset{*}{\cancel{c_1(0)}} + 2A\int_0^t dt\, e^{\frac{i\nu}{2}t}\sin\left[\bar{\omega}t\right]$$

$$c_1(t) = 1 + \frac{2A}{\nu^2 - \left(\frac{4\gamma^2}{\hbar^2} + \nu^2\right)}\left[-4\sqrt{\ } + 2e^{i\nu t/2}\left(2\sqrt{\ }\cos(\sqrt{\ }t) - i\nu\sin(\sqrt{\ }t)\right)\right]$$

when $t = 0$ $\quad c_1(0) = 1 = 1 + \frac{2A}{-\frac{4\gamma^2}{\hbar^2}}\left[-4\sqrt{\ } + 4\sqrt{\ }\right] = 1$ ✓

whoops!

or

or try this the other way...

$$c_1(t) = \frac{i\hbar}{\gamma} e^{+i\nu t} \dot{c}_2(t)$$

$$\dot{c}_2 = 2iA\, e^{-i\nu t/2}\left(\sqrt{\quad}\cos(\sqrt{\quad}\,t) - \frac{i\nu}{2}\sin(\sqrt{\quad}\,t)\right)$$

$$c_1(t) = -\frac{2A\hbar}{\gamma} e^{i\nu t/2}\left(\sqrt{\quad}\cos(\sqrt{\quad}\,t) - \frac{i\nu}{2}\sin(\sqrt{\quad}\,t)\right)$$

$$c_1(0)=1 \Rightarrow \qquad A = -\frac{\gamma}{2\hbar}\frac{1}{\sqrt{\quad}}$$

$$\Rightarrow \boxed{\begin{aligned} c_2(t) &= \frac{-i\gamma}{\hbar}\frac{1}{\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}}\, e^{-i(\omega-\omega_{12})t/2} \sin\left[\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}\,t\right] \\ c_1(t) &= e^{i(\omega-\omega_{12})t/2}\left(\cos\left(\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}\,t\right) - \frac{i(\omega-\omega_{12})\sin}{2\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}}\left[\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}\,t\right]\right) \end{aligned}}$$

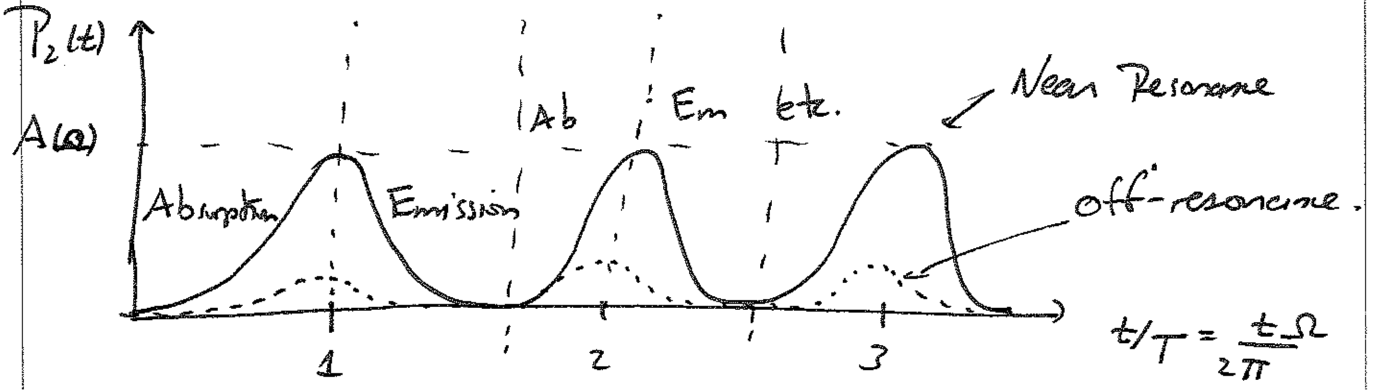
Rabi's Formula   I. I. Rabi

$$P_2(t) = \frac{\gamma^2}{\hbar^2}\frac{1}{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}\sin^2\left(\sqrt{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{12})^2}{4}}\,t\right) \longleftarrow \text{Probability to find the system in state 2}$$

and $P_1(t) = 1 - P_2(t)$ ⟵ Probability to find the system in state 1.

5.23

Rabi : Nobel prize in physics 1944 – Columbia phys. department from 1929 to 1988!!

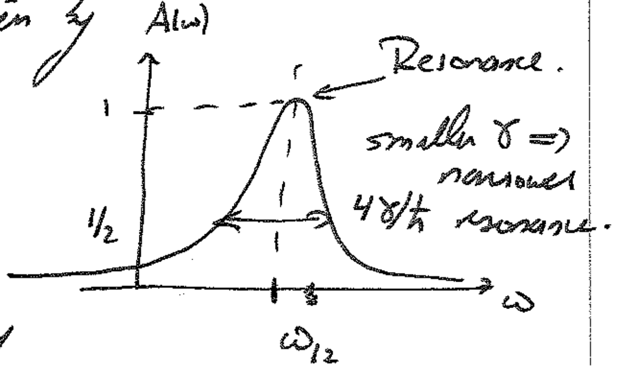


$\sin^2(\omega t)$ ~~has~~ max at $\omega t = \pi/2$ $\omega t = 3\pi/2$ or

$T = \frac{\pi}{\omega}$. In this case the occupation of state 2 is oscillatory with period $\frac{\pi}{\sqrt{\frac{\gamma^2}{\hbar^2} + (\omega-\omega_{12})^2/4}} = T = \frac{2\pi}{\Omega}$

The amplitude of oscillation is given by

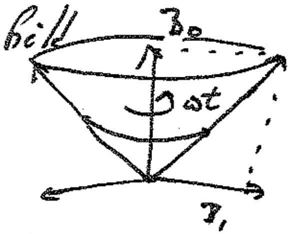
$$\frac{\gamma^2}{\hbar^2}\,\frac{1}{\frac{\gamma^2}{\hbar^2} + (\omega-\omega_{12})^2/4} = A(\omega)$$



Probability of a transition becomes very large when $\omega = \omega_{12} = (E_2 - E_1)/\hbar$ Resonance condition.

A physical application: Spin Magnetic Resonance.

Consider a spin-1/2 system in a rotating B-field



$$\vec{B} = B_0\hat{z} + B_1(\hat{x}\cos\omega t + \hat{y}\sin\omega t)$$

magnetic moment $\vec{\mu} = \frac{e}{mc}\vec{S}$ $H_0 = -\vec{\mu}\cdot\vec{B}_0$ $V(t) = -\vec{\mu}\cdot\vec{B}_1$.

$$H_0 = \frac{-e\hbar B_0}{2mc}\Big[|+\rangle\langle+| - |-\rangle\langle-|\Big];\quad V(t) = -\frac{e\hbar B_1}{2mc}\Big[\cos(\omega t)\big(|+\rangle\langle-| + |-\rangle\langle+|\big)$$
$$i\sin(\omega t)\big(-|+\rangle\langle-| + |-\rangle\langle+|\big)\Big]$$

We just put in S_x, S_y.

Clearly the upper state is $|+\rangle$ and the lower is $|-\rangle$.

$$\omega_{21} = \frac{|e|B}{mc} \leftarrow \text{ spin precession frequency for } B_0,\ B_1 = 0$$

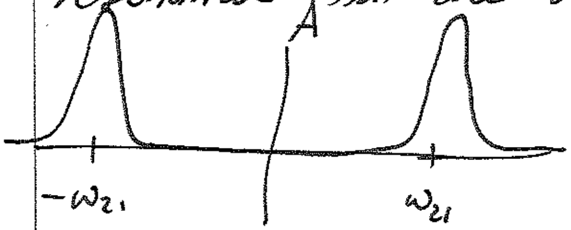
Note that
$$V(t) = -\frac{e\hbar B_1}{2mc}\Big[\big(\cos(\omega t) - i\sin(\omega t)\big)|+\rangle\langle-| + \big(\cos(\omega t) + i\sin(\omega t)\big)|-\rangle\langle+|\Big] = \frac{-e\hbar B_1}{2mc}\Big[e^{-i\omega t}|+\rangle\langle-| + e^{i\omega t}|-\rangle\langle+|\Big]$$

so $\gamma = \dfrac{-e\hbar B_1}{2mc}$ and $\omega = \omega$ in our Rabi's solution.

<u>Side Note:</u> In practice a rotating magnetic field is not used — rather a oscillating one

$$B_1\hat{x}\cos(\omega t) = \underbrace{\tfrac{1}{2}B_1\big[\hat{x}\cos(\omega t) + \hat{y}\sin(\omega t)\big]}_{\text{counter clockwise rotation } \hat{z}\odot\circlearrowleft} + \underbrace{\tfrac{1}{2}B_1\big[\hat{x}\cos(\omega t) - \hat{y}\sin(\omega t)\big]}_{\text{clockwise rotation } \odot\circlearrowright}$$

If the lines are narrow $\dfrac{B_1}{B_0} \ll 1 \Rightarrow \dfrac{\gamma}{\hbar} \ll \omega_{21}$ then the resonance line at ω_{21} is well-separated from the one at $-\omega_{21}$ so really everything we said before is the same — just two resonances that are well-separated instead of 1.



Say something about NMR.

Time-dependent perturbation thry

Looking for approximate solutions to the differential equation for $c_n(t)$

We should be able to find an expansion of the form:

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots$$

where $H = H_0 + \lambda V(t)$

small parameter.

We will obtain a perturbation expansion for $U_I(t,t_0)$ – the time-development operator in the interaction picture.

$$|\alpha, t_0; t\rangle_I = U_I(t,t_0)|\alpha, t_0; t\rangle$$

$$i\hbar\partial_t|\alpha, t_0, t\rangle_I = V_I\,|\alpha, t_0; t\rangle_I \Rightarrow$$

$$i\hbar\partial_t U_I(t,t_0) = V_I\, U_I(t,t_0)$$ with the initial condition $U_I(t_0,t_0) = 1$.

Integrating both sides.

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

Now iterate:

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt'\, V_I(t') \int_{t_0}^{t'} dt''\, V_I(t'')\, U_I(t'',t_0)$$

Continuing, we get:

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt'\, V_I(t') \int_{t_0}^{t'} dt''\, V_I(t'') + \cdots + \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''$$

Transition Probability

state at $t=0$

$$|i,t\rangle_I = U_I(t,0)|i\rangle$$

state in the future.

$$|i,t\rangle_I = \sum_n |n\rangle\underbrace{\langle n|U_I(t,0)|i\rangle}_{c_n(t)}$$

← This was our earlier name for it.

The connection between $U(t,0)$ and $U_I(t,0)$

Schrödinger picture.

$$|\alpha,t_0;t\rangle_I = e^{iH_0t/\hbar}|\alpha,t_0;t\rangle_S = e^{iH_0t/\hbar}U(t,t_0)|\alpha,t_0;t_0\rangle_S$$

so $$|\alpha,t_0,t\rangle_I = \underbrace{e^{iH_0t/\hbar}\,U(t,t_0)\,e^{-iH_0t_0/\hbar}}\,|\alpha,t_0;t_0\rangle_S$$

This must be $U_I(t,t_0)$ – see the first line on this page.

So
$$\langle n|U_I(t,t_0)|i\rangle = e^{i(E_nt-E_it_0)/\hbar}\underbrace{\langle n|U(t,t_0)|i\rangle}$$

This is the transition amplitude that we defined in Chapter 2.

so
$$|\langle n|U_I(t,t_0)|i\rangle|^2 = |\langle n|U(t,t_0)|i\rangle|^2$$

The transition probabilities are equal as long as $|n\rangle, |i\rangle$ are energy eigenkets.

(5.27) II

How do we use the Dyson Expansion?

At $t=t_0$ we have the system in state $|i\rangle$. In the S-picture

$$|i,t_0;t\rangle_S = \underset{\nwarrow \text{ unknown phase}}{e^{i\varphi}}|i\rangle \text{ at } t=t_0.$$

It is convenient to pick this phase to be: $e^{-iE_it_0/\hbar}$ so that

$$|i,t_0;t_0\rangle_S = e^{-iE_it_0/\hbar}|i\rangle \Longrightarrow$$

$$|i,t_0;t_0\rangle_I = |i\rangle$$

Now, we let the system evolve forward in time:

$$|i,t_0;t\rangle_I = U_I(t,t_0)|i\rangle$$ Expanding in kets $|n\rangle$

$$|i,t_0;t\rangle_I = \sum_n |n\rangle \underbrace{\langle n|U_I(t,t_0)|i\rangle}_{c_n(t)}$$

Now, plug in our expansion for U_I:

Note: It the interaction picture

$$c_n^{(0)}(t) = \delta_{ni}$$

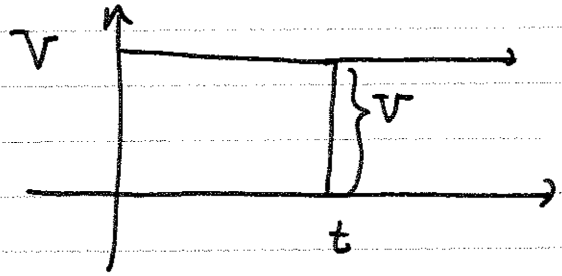
$$c_n^{(1)}(t) = \frac{-i}{\hbar}\int_{t_0}^{t}\langle n|V_I(t')|i\rangle\,dt' = \frac{-i}{\hbar}\int_{t_0}^{t}V_{ni}(t')\,dt'$$

$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}dt'\sum_m\int_{t_0}^{t'}dt''\,e^{i\omega_{nm}t'}V_{nm}(t')\,e^{i\omega_{mi}t''}V_{mi}(t'')$$

Where $\omega_{ab} = \frac{E_a - E_b}{\hbar}$

Some Examples

A. Constant Perturbation



$$V(t) = \begin{cases} 0, & t < 0 \\ V, & t \geq 0 \end{cases}$$

Taking $t_0 = 0$.

$$c_n^{(0)} = \delta_{in}$$

$$c_n^{(1)} = \frac{-i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni} t'} dt' = \frac{-i}{\hbar} \frac{1}{i\omega_{ni}} \left(e^{i\omega_{ni} t} - 1\right)$$

$$= \frac{1}{E_n - E_i} \left(1 - e^{+i\omega_{ni} t}\right)$$

so the 1st order result for the transition probability $n \neq i$

$$|c_n^{(1)}(t)|^2 = \frac{|V_{ni}|^2}{(E_n - E_i)^2} \left[2 - 2\cos(\omega_{ni} t)\right]$$

Recall the half-angle formula: $\sin^2(x/2) + \cos^2(x/2) = 1$ or

$$2\sin^2(x/2) = 1 - \cos^2(x/2) + \sin^2(x/2) = 1 - \left[\cos^2(x/2) - \sin^2(x/2)\right]$$

$$2\sin^2(x/2) = 1 - \cos(2\tfrac{x}{2}) = 1 - \cos(x)$$

$$\Rightarrow \boxed{|c_n^{(1)}(t)|^2 = \frac{4|V_{ni}|^2}{(E_n - E_i)^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right]}$$

5.29 II

Say $|V_{ni}| \neq 0$, what does $|c_n^{(1)}(t)|^2$ look like as a function of the energy of the state n at a <u>fixed time</u>?

$$P_n(t) = \frac{4\,|V_{ni}|^2}{\hbar^2}\,\frac{1}{\omega^2}\sin^2\left[\frac{\omega t}{2}\right]$$

↑ transition probability

Limits $\omega \to \pm\infty$ $P \to 0$

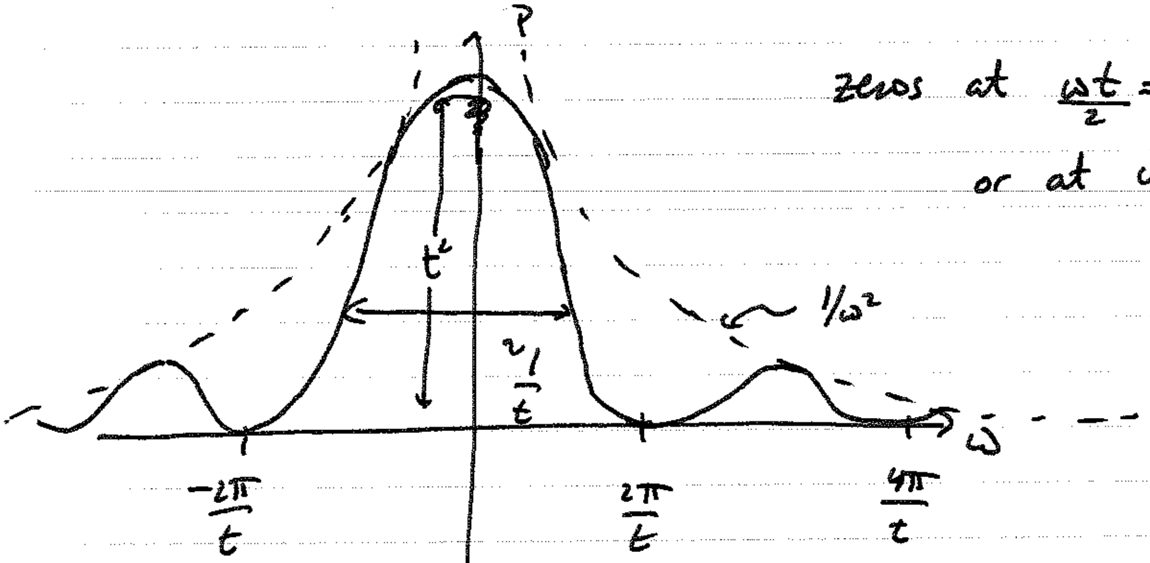
$\omega \to 0$ $P \to c\,\frac{\omega^2 t^2}{\omega^2\, 4} \sim t^2$

↑ height of peak.

and call $E_n - E_i = \hbar\omega$

zeros at $\frac{\omega t}{2} = \pm\pi, \pm 2\pi, \ldots$

or at $\omega = \pm\frac{2\pi}{t}$, $\omega = \pm\frac{4\pi}{t}$



Another statement of the time-energy uncertainty relation!

for fixed $\underline{\omega}$ need $t < \frac{2\pi}{|\omega|}$ for a significant probability of a transition! What does that mean?

$$\underset{\substack{\uparrow\\ \text{observation}\\ \text{time}}}{\Delta t} < \frac{2\pi}{|\omega|} = \frac{2\pi\hbar}{\underbrace{|E_n - E_i|}_{\Delta E}} \Rightarrow \boxed{\Delta E\,\Delta t \lesssim h}$$

Energy nonconservation is ok. as long as it doesn't last too long!

So, at long times we expect $E_n = E_i$?! What happens then

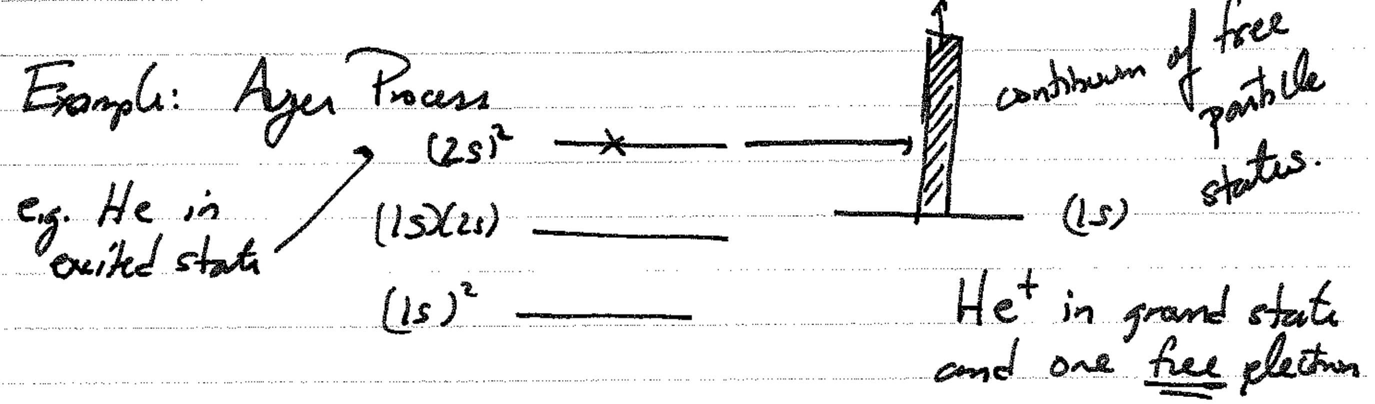
if $E_n = E_i$ then $P_n(t) = \frac{4|V_{ni}|^2}{\hbar^2}\frac{t^2}{4} = \frac{|V_{ni}|^2 t^2}{\cancel{4}\hbar^2}$

The $P_n \propto t^2$ seems odd. After all, there should be some fixed rate of transitions from i → n so $P \propto t$.

To interpret this odd result it helps to think about states arbitrarily close to E_i in energy.

introduce: $dE\,\rho(E)$ = density of state = # states w/ energy between E and E+dE.

Example: Auger Process



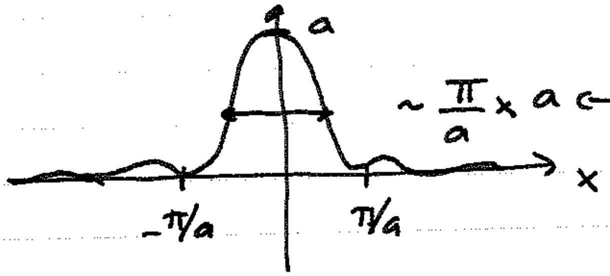
At long times we need to consider the sum of probabilities to all states w/ energy nearly equal to the excited atom.

$$\int dE_n\,\rho(E_n)\,|C_n^{(1)}(t)|^2 = 4\int dE_n\,\rho(E_n)\frac{|V_{ni}|^2}{|E_n-E_i|^2}\sin^2\left[\frac{(E_n-E_i)}{2\hbar}t\right]$$

This integral becomes easy in the large t limit!

$$\lim_{\alpha\to\infty}\frac{1}{\pi}\frac{\sin^2(x\alpha)}{\alpha x^2} = \delta(x)$$ Why?

Plot: $\frac{\sin^2(ax)}{ax^2}$



$\sim \frac{\pi}{a} \times a \leftarrow$ area under the curve $\sim \pi$

$$\text{so} \lim_{t\to\infty} \frac{1}{(E_n-E_i)^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right] = \lim_{t\to\infty} \frac{t}{2\hbar}\,\frac{2\hbar}{(E_n-E_i)^2 t}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]$$

$$\left[\text{so } a = \frac{t}{2\hbar},\ x = |E_n - E_i|\right] \qquad = \frac{\pi t}{2\hbar}\,\delta(E_n - E_i)$$

$$\text{so} \lim_{t\to\infty}\int dE_n\,\rho(E_n)\,|c_n^{(1)}(t)|^2 = \frac{2\pi}{\hbar}\,\overline{|V_{ni}|^2}\,\rho(E_i)\,t\,\Big|_{E_n=E_i}$$

averaged over all states w/ energy $E_n = E_i$

Now, we have a <u>linear</u> time dependence so we have a constant <u>transition rate</u> at long times.

$$W_{i\to[n]} = \frac{2\pi}{\hbar}\,|V_{ni}|^2\rho(E_n)\Big|_{E_n=E_i}$$

transition rate from $|i\rangle$ to $|n\rangle$. This is typically written as:

This expression must be integrated over $\rho(E)\,dE$.

$$\boxed{W_{i\to n} = \frac{2\pi}{\hbar}\,|V_{ni}|^2\,\delta(E_n - E_i) \qquad \text{Fermi's Golden Rule.}}$$

(5.33) II

The time derivative hits $e^{i(E_i-E_n-\hbar\omega)t/\hbar}$ and $e^{2\eta t}$.

Define $\overline{W}_{i\to n}(t) = \dfrac{4 W_{i\to n}}{2\eta}\,\dfrac{e^{-2\eta t}}{|V_{ni}|^2}$ Actual transition rate

transition rate without all the prefactors.

Then
$$\overline{W}_{i\to n} = \frac{1}{x^2+\delta^2} + \frac{1}{y^2+\delta^2} + 2\,\mathrm{Re}\left\{\frac{e^{-2i\omega t}}{(x+i\delta)(y-i\delta)}\right\} +$$
$$+ \frac{2}{\eta}\,\mathrm{Re}\left\{\frac{-i\omega e^{-2i\omega t}}{(x+i\delta)(y-i\delta)}\right\} \quad \text{where} \quad \begin{matrix} x = \Delta E + \hbar\omega \\ y = \Delta E - \hbar\omega \end{matrix} \quad \delta = \eta\hbar$$

Note: The first three terms come from the derivative of $e^{2\eta t} \longrightarrow 2\eta\, e^{2\eta t}|\{\ \ \}|^2$. the last term comes from the derivative of $e^{i(E_n-E_i-\omega\hbar)t/\hbar}\, e^{-i(E_n-E_i+\hbar\omega)t/\hbar} = e^{-2i\omega t}$

So: $$\overline{W}_{i\to n} = \frac{1}{x^2+\delta^2} + \frac{1}{y^2+\delta^2} + 2X$$

where $$X = \mathrm{Re}\left\{\frac{(1-i\omega/\eta)\,e^{-2i\omega t}}{(x+i\delta)(y-i\delta)}\right\}$$

from the cross term in the $|\{\ \}|^2$. The basic question is: what is the effect of the interference between the $e^{i\omega t}$ and $e^{-i\omega t}$ parts of the perturbation?

(5.34) II

$$X = \mathrm{Re}\left\{\frac{(1-i\omega/2)e^{-2i\omega t}}{xy+\delta^2-i\delta(x-y)}\right\} = \mathrm{Re}\left\{\frac{(1-i\omega/2)e^{-2i\omega t}[xy+\delta^2+i\delta(x-y)]}{(xy+\delta^2)^2+\delta^2(x-y)^2}\right\}$$

Now: $(xy+\delta^2)^2+\delta^2(x-y)^2 = x^2y^2+2xy\delta^2+\delta^4+\delta^2(x^2+y^2-2xy)$

$$= x^2y^2+\delta^4+\delta^2(x^2+y^2)$$

$$= (x^2+\delta^2)(y^2+\delta^2)$$

So:

$$X = \frac{1}{(x^2+\delta^2)(y^2+\delta^2)}\mathrm{Re}\{[\cos(2\omega t)-i\sin(2\omega t)][1-i\omega/2][(xy+\delta^2)+$$

$$i\delta(x-y)]\}$$ or

$$X = \frac{[\mathcal{C}\cos(2\omega t)+\mathcal{S}\sin(2\omega t)]}{(x^2+\delta^2)(y^2+\delta^2)}$$ where $\mathcal{C} = xy+\delta^2+\frac{\omega}{2}\delta(x-y)$

So $\mathcal{C} = (\Delta E)^2-(\hbar\omega)^2+(2\hbar)^2+\hbar\omega(2\hbar\omega) = (\Delta E)^2+(\hbar\omega)^2+(2\hbar)^2$

or $\mathcal{C} = \frac{1}{2}(x^2+y^2)+\delta^2 \Longrightarrow$

$$\boxed{\frac{\mathcal{C}}{(x^2+\delta^2)(y^2+\delta^2)} = \frac{1}{2}\left[\frac{1}{x^2+\delta^2}+\frac{1}{y^2+\delta^2}\right]}$$

$$\mathcal{S} = \frac{-\omega}{2}(xy+\delta^2)+\delta(x-y)$$

Now we can write

$$\frac{S}{(x^2+\delta^2)(y^2+\delta^2)} = -\frac{1}{\hbar\eta}\,\frac{(\Delta E)^2-\hbar^3\omega^3-\hbar^3\omega\eta^2}{(x^2+\delta^2)(y^2+\delta^2)}$$

This can be written as:

$$\left(\frac{x}{x^2+\delta^2}-\frac{y}{y^2+\delta^2}\right)A \quad \text{where } A=\frac{1}{2\hbar\eta}$$

and you can see this by putting everything over a common denominator

Now, finally (!!) we can construct the transition probability:

$$W_{i\to n}(t)= \frac{e^{2\eta t}|V_{ni}|^2}{2}\left\{\left[\frac{\eta}{(\Delta E+\hbar\omega)^2+\eta^2\hbar^2}+\frac{\eta}{(\Delta E-\hbar\omega)^2+(\eta\hbar)^2}\right]\cdot\right.$$

$$\left.\cdot\,\big(1+\cos(2\omega t)\big) + 2\sin(2\omega t)\left[\frac{\Delta E/\hbar+\omega}{(\Delta E+\hbar\omega)^2+(\eta\hbar)^2}-\frac{(\Delta E/\hbar-\omega)}{(\Delta E-\hbar\omega)^2+(\eta\hbar)^2}\right]\right\}$$

Part from $e^{\pm i\omega t}$ separately

Interference terms.

To see that the interference terms don't matter, let's average this over time. Set $e^{2\eta t}=1$ but keep η in the denominators. ~~we have~~

$$\cancel{\int\frac{\eta}{x^2+\eta^2}}$$

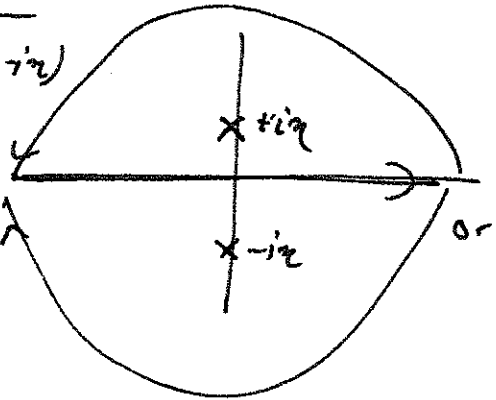
First $\overline{\cos(2\omega t)} = 0$

$\overline{\sin(2\omega t)} = 0$

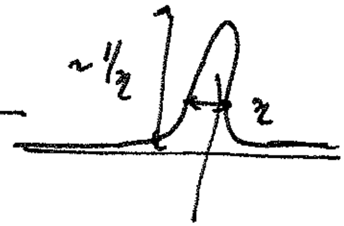
Now we need to consider integrals of the form $\int^{\infty}\frac{\eta}{x^2+\eta^2}\,dx$ in the limit $\eta\to 0$. $\Leftarrow$ ~~Potent~~ Perturbation on a long time!

First note $\int_{-\infty}^{\infty} \frac{\eta}{x^2+\eta^2}\,dx = \int_{-\infty}^{\infty} \frac{\eta}{(x+i\eta)(x-i\eta)}$

$$= 2\pi i\,\eta\,\frac{1}{2i\eta} = \pi$$



But $f_\eta(x) = \frac{\eta}{x^2+\eta^2}$



Another representation of the δ-function! $\Longrightarrow$

$$\boxed{\overline{W_{i\to n}} = \frac{|V_{ni}|^2\pi}{2\hbar}\left[\delta(E_n-E_i-\hbar\omega)+\delta(E_n-E_i+\hbar\omega)\right]}$$

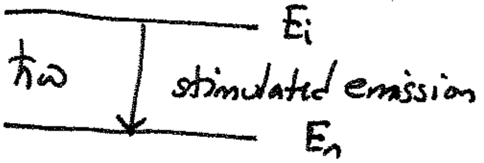
averaged over a period

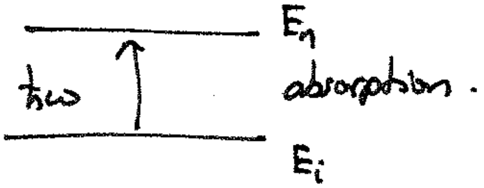
from the $(\hbar\eta)^2$ in the denominators!

So each part of the potential (perturbation) acts independently. on average. The interference between $e^{+i\omega t}$ and $e^{-i\omega t}$ parts cancel.

At long times ($t\to\infty$) we get transitions only if

$$\omega_{ni} = \pm\omega \Longrightarrow E_n = E_i \pm \hbar\omega$$





If we had worried about the difference between V_{ni} and $V_{ni}^{\dagger}$ it wouldn't have mattered since $|V_{ni}|^2 = |V_{ni}^{\dagger}|^2$

We have just derived the principle of detailed balance:

Emission: $$W^{E}_{i\to n} = \frac{2\pi}{\hbar}|V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i - \hbar\omega}$$

Absorption: $$W^{A}_{i\to n} = \frac{2\pi}{\hbar}|V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i + \hbar\omega}$$

$$\Longrightarrow \boxed{\frac{W^{E}_{i\to n}}{W_{i\to n}} = \frac{\rho(E_n)\big|_{E_n = E_i - \hbar\omega}}{\rho(E_n)\big|_{E_n = E_i + \hbar\omega}}}$$

Detailed Balance.

Harmonic Perturbations

$$V(t) = \left(\frac{V}{2} e^{i\omega t} + \frac{V^\dagger}{2} e^{-i\omega t} \right) e^{\eta t} \qquad \eta > 0$$

turn it on slowly in the distant past.

$$\Rightarrow \quad c_n(t) = \frac{-i}{\hbar} \int_{-\infty}^{t} dt' \left\{ e^{i(\omega + \omega_{ni} - i\eta)t'} \frac{V_{ni}}{2} + e^{i(-\omega + \omega_{ni} - i\eta)t'} \frac{V^\dagger_{ni}}{2} \right\}$$

Note: $V^\dagger_{ni} = \langle n | V^\dagger | i \rangle$.

Doing the integral: $\displaystyle\int_{-\infty}^{t} e^{i(x - i\eta)t'} dt' = \frac{1}{i(x - i\eta)} \left(e^{i(x-i\eta)t} - \cancelto{0}{e^{-\infty\eta}} \right)$

if η is small enough (i.e. slow enough turn on...)

$$c_n(t) = \frac{-i}{2\hbar} \left\{ V_{ni} \frac{e^{i(\omega + \omega_{ni})t}}{i(\omega + \omega_{ni} - i\eta)} + \frac{V^\dagger_{ni}\, e^{i(\omega_{ni} - \omega)t}}{(\omega_{ni} - \omega - i\eta)i} \right\}$$

or we can write this out as:

$$c_n^{(1)}(t) = \frac{e^{\eta t}}{2} \left\{ \frac{e^{i(E_n - E_i + \hbar\omega)t/\hbar}}{E_i - E_n - \hbar\omega + i\hbar\eta} + \frac{e^{i(E_n - E_i - \hbar\omega)t/\hbar}}{E_i - E_n + \hbar\omega + i\hbar\eta} \right\} \underset{\uparrow}{V_{ni}}$$

say that V is Hermitian.

We want to compute: $\frac{d}{dt} |c_n^{(1)}(t)|^2 \leftarrow$ A Big Mess!

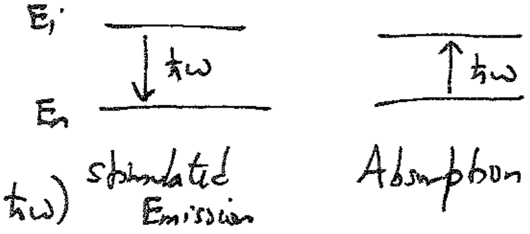
Let's be careful and work this out:

First we'll compute $|\{\ \}|^2 \Rightarrow$ why?

As $t\to\infty$ we get transitions only if:

$$\omega_{ni}+\omega=0 \quad \text{or} \quad \omega_{ni}-\omega=0 \Rightarrow$$

$$E_n = E_i \pm \hbar\omega$$ and



$$W_{i\to[n]} = \frac{2\pi}{\hbar}\begin{pmatrix}|V_{ni}|^2\\ \text{or}\\ |V_{ni}^{+}|^2\end{pmatrix}\delta(E_n-E_i\pm\hbar\omega)$$

these are equal.

Note: $$W_{i\to[n]} = \frac{2\pi}{\hbar}|V_{ni}|^2\rho(E_n)\Big|_{E_n=E_i-\hbar\omega} \quad \text{Emission}$$

$$W_{i\to[n]} = \frac{2\pi}{\hbar}|V_{ni}|^2\rho(E_n)\Big|_{E_n=E_i+\hbar\omega} \quad \text{Absorption}$$

$$\Rightarrow \frac{W^{EM}_{i\to[n]}}{W^{Ab}_{i\to[n]}} = \frac{\rho(E_n)\big|_{E_n=E_i-\hbar\omega}}{\rho(E_n)\big|_{E_n+\hbar\omega}}$$

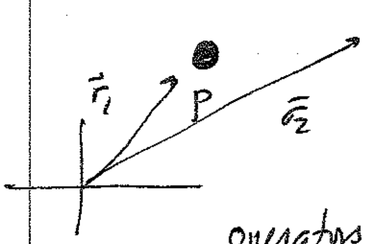
Ratio of the rates = ratio of the density of final states

Principle of Detailed Balance.

Some Applications of Perturbation theory.

To have some interesting problems to look at, we are going to review some features of simple atomic structure.

The Hydrogen Atom:



$\cdot e^-$ A two particle system

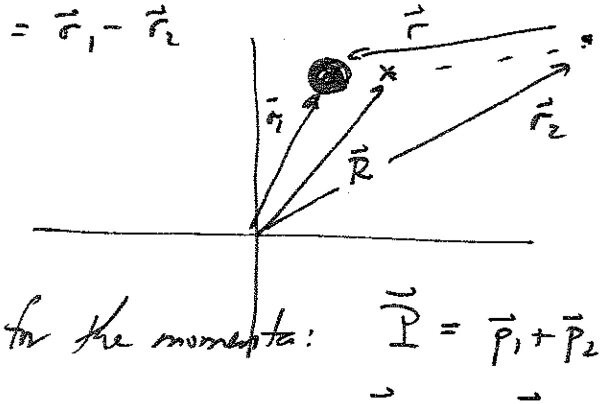
$$\psi(\vec{r}_1,\vec{r}_2,t) = \langle \vec{r}_1,\vec{r}_2|\psi\rangle$$

operators $\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2$ $\quad [\vec{r}_1,\vec{p}_2]=[\vec{r}_2,\vec{p}_1]=0$.

These particles interact via a potential $V(\vec{r}_1-\vec{r}_2$

$$H = \frac{P_1^2}{2m_1}+\frac{P_2^2}{2m_2}+V(\vec{r}_1-\vec{r}_2)$$

Working in terms of center of mass $\vec R = \frac{m_1\vec r_1 + m_2\vec r_2}{m_1+m_2}$ and relative coordinates $\vec r = \vec r_1 - \vec r_2$



Define: $M = m_1+m_2$ total mass of the atom.

and similarly for the momenta: $\vec P = \vec p_1 + \vec p_2$

$\vec p = \frac{m_2\vec p_1 - m_1\vec p_2}{m_1+m_2}$ relative momentum.

Then

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = ?$$

$$\vec p_1 = \vec P - \vec p_2 = P - \frac{m_2}{m_1}\vec p_1 - \frac{M}{m_1}\vec p \Rightarrow \vec p_1\left(\frac{m_1+m_2}{m_1}\right) = \vec P - \frac{M}{m_1}\vec p$$

$M\vec p = m_2\vec p_1 - m_1\vec p_2$ or

$m_1\vec p_2 = m_2\vec p_1 - M\vec p$

$\vec p_1 = \frac{m_1}{M}\vec P - \vec p$

and $\vec p_2 = \frac{m_2}{m_1}\vec p_1 - \frac{M}{m_1}\vec p$

$\vec p_2 = \frac{m_2}{M}\vec P - \frac{m_2}{m_1}\vec p - \vec p\frac{M}{m_1}$

$\vec p_2 = \frac{m_2}{M}\vec P - \frac{M}{m_1}\vec p$

$\vec p_1 = \vec P - \vec p_2$ and

$M\vec p = m_2\vec p_1 - m_1\vec p_2$ or $\vec p_2 m_1 = m_2\vec p_1 - M\vec p$

$\vec p_2 = \frac{m_2}{m_1}\vec p_1 - \frac{M}{m_1}\vec p$

$\vec p_1 = P - \frac{m_2}{m_1}p_1 + \frac{M}{m_1}\vec p \Rightarrow \frac{M}{m_1}\vec p_1 = P + \frac{M}{m_1}p$

$\vec p_1 = \frac{m_1}{M}\vec P + \vec p$ and

$\vec p_2 = \frac{m_2}{M}P + \frac{m_2}{m_1}\vec p - \frac{M}{m_1}\vec p = \frac{m_2\vec P}{M} - \vec p$

So: $$\boxed{\begin{array}{l}\vec p_1 = \frac{m_1}{M}\vec P + \vec p \\ \vec p_2 = \frac{m_2}{M}P - \vec p\end{array}}$$

$$\frac{p_1^2}{2m_1}+\frac{p_2^2}{2m_2}=\left(\frac{m_1^2}{M^2}P^2+2\frac{m_1}{M}\vec{P}\cdot\vec{p}+p^2\right)\frac{1}{2m_1}+\frac{1}{2m_2}\left(\frac{m_2^2}{M^2}P^2-2\frac{m_2}{M}\vec{p}\cdot\vec{P}+p^2\right)$$

$$=\frac{1}{2M^2}(m_1+m_2)P^2+\frac{1}{M}\vec{P}\cdot\vec{p}-\frac{1}{M}\vec{P}\cdot\vec{p}+\left(\frac{1}{2m_1}+\frac{1}{2m_2}\right)p^2$$

$$=\frac{P^2}{2M}+\frac{1}{2}\underset{\uparrow}{\left(\frac{m_1+m_2}{m_1 m_2}\right)}p^2=\frac{P^2}{2M}+\frac{1}{2m}p^2$$

Define reduced mass $m=\dfrac{m_1 m_2}{m_1+m_2}\approx m_e$ ← For us, we will find,

↑ ⟹ since $m_p \approx 2\times10^3 m_e$

In the position representation:

$\vec{P}=-i\hbar\vec{\nabla}_R$ and $\vec{p}=-i\hbar\vec{\nabla}_r$

check one of these: $\vec{r}=\vec{r}_1-\vec{r}_2 \quad \vec{R}=\dfrac{m_1\vec{r}_1+m_2\vec{r}_2}{m_1+m_2}$

$\Longrightarrow \quad \vec{r}_1=\frac{m_2}{M}\vec{r}+\vec{R} \qquad \vec{r}_2=\vec{R}-\frac{m_1}{M}\vec{r}$

$$\partial_r=\left.\frac{\partial r_1}{\partial r}\right|_R\frac{\partial}{\partial r_1}+\left.\frac{\partial r_2}{\partial r}\right|_R\frac{\partial}{\partial r_2}\Rightarrow$$

$$\partial_r=\frac{m_2}{M}\partial_{r_1}-\frac{m_1}{M}\partial_{r_2} \quad \text{so} \quad \underset{\substack{\uparrow\\ \text{in } x\text{-basis}}}{\vec{p}_{op}}=\left(\frac{m_2}{M}\partial_{r_1}-\frac{m_1}{M}\partial_{r_2}\right)(-i\hbar)$$

$$=-i\hbar\,\partial_r \text{ as expected.}$$

so, in the coordinate system of $\vec{r},\vec{R}$ we have a Schrödinger Equation

$$\left[\frac{-\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2m}\nabla_r^2+V(r)\right]\varphi(\vec{r},\vec{R},t)=i\hbar\,\partial_t\,\varphi(\vec{r},\vec{R},t)$$

This is clearly separable: $\varphi(\vec{r},\vec{R},t)=\varphi_r(\vec{r},t)\,\varphi_R(\vec{R},t)$

This is the only nontrivial part of the problem. ↗ (to φ_r)

↑ Just a free particle wavefunction. (for φ_R)

The potential for the relative coordinate is $V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$

$\psi(\vec{r},t) = \underset{\substack{\uparrow \\ \text{Spherically symmetric potential.}}}{Y_{lm}(\theta,\varphi)}R(r)$ ← where $R(r)$ obeys:

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right)R(r)r = E\,r\,R(r)$$

for each l there are an infinite set of solutions labeled by n, the principal quantum number $n \geq l+1$

$$R_{nl}(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2r[(n+l)!]^3}}\; e^{-r/na_0}\left(\frac{2r}{na_0}\right)^l L^{2l+1}_{n+l}\left(\frac{2r}{na_0}\right)$$

where $L^{2l+1}_{n+l}(x) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1}[(n+l)!]^2 x^k}{(n-l-1-k)!\,(2l+1+k)!}$ Associated Laguerre polynomials.

$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ ← Bohr radius.

The energy eigenvalues are $E_n = \underbrace{\frac{-e^2}{2a_0}}_{= 13.6\,eV}\frac{1}{n^2}$ Lyman formula.

So

$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$ are the wavefunctions of the stationary states w/ Energies $E_n = -E_0\frac{1}{n^2}$

A few low lying states

$R_{10} = \frac{2}{a_0^{3/2}}e^{-r/a_0}$ ← Ground state

$R_{20} = \frac{1}{(2a_0)^{3/2}}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$; $R_{21} = \frac{1}{(2a_0)^{3/2}}\frac{r}{\sqrt{3}a_0}e^{-r/2a_0}$

R's of different n but same l are orthogonal.

- For each n we have states w/ $l = 0, 1, 2, \dots, n-1$
- Each of these states has a $(2l+1)$-fold degeneracy due to the azimuthal quantum number m.

$\Rightarrow$ For each energy E_n there are

$$\sum_{l=0}^{n-1} (2l+1) \text{ degenerate states !!}$$

Note: $$\sum_{l=0}^{n-1} l = 0 + 1 + 2 + 3 + \cdots + n-1$$

$$= (n-1)\frac{n}{2}$$

Note if $n-1 =$ even

$$, (n-2)(n-1) + \frac{n-1}{2}$$

$$n^2 - 3n + 2$$

$$\underbrace{0 + \underbrace{1 + 2 + 3}_{} + 4}_{} = 2 \times 4 + 2$$

$$\frac{(n-1)}{2} \times$$

$$4\left(\frac{5}{2}\right)$$

if $n-1 =$ odd

$$\underbrace{0 + \underbrace{1 + 2}_{} + 3}_{}$$

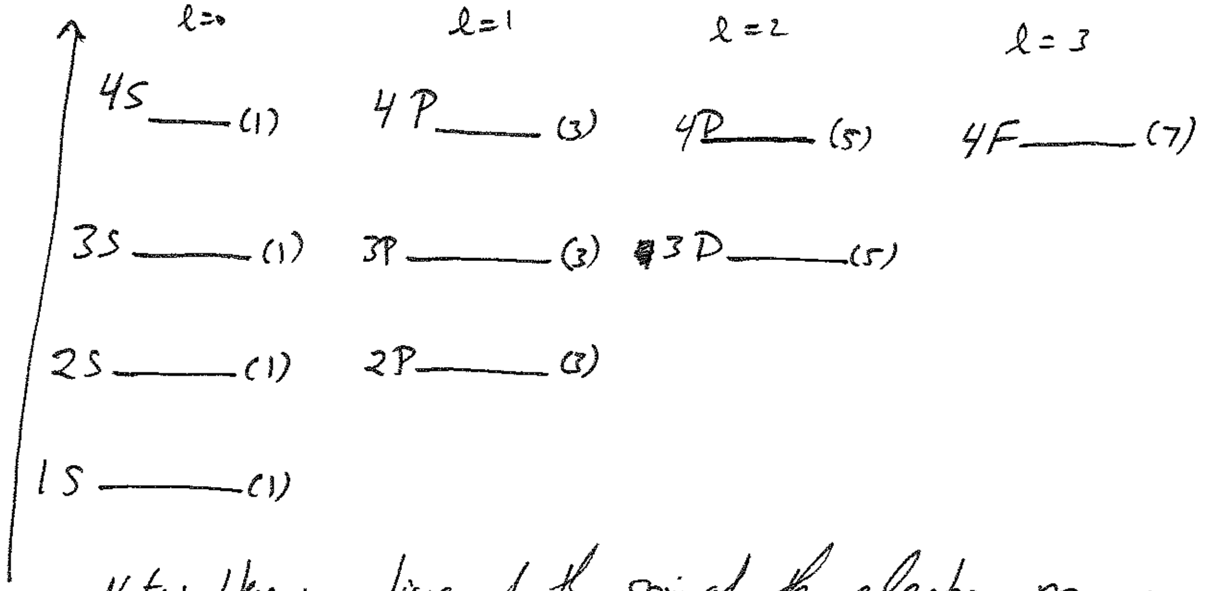
$$(n-1)\frac{n}{2} = 3 \times \frac{4}{2} = 6.$$

So:

$$\sum_{l=0}^{n-1} = (n-1)(n) + n$$

$$= n^2$$

$\Rightarrow$ n^2 degenerate states.



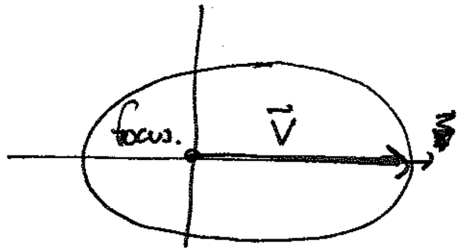
Note: Here we disregard the spin of the electron. More on that later.

Why are the l-levels for the same n degenerate: Symmetries of the Kepler Problem

Lenz's Vector is a constant of the motion:

$\vec{V} = \frac{1}{m}\vec{p}\times\vec{L} - \frac{e^2}{4\pi\epsilon_0 r}\hat{r}$; the Hermitian operator corresponding to this is:

$$\vec{V} = \frac{1}{2m}\left[\vec{p}\times\vec{L} - \vec{L}\times\vec{p}\right] - \frac{e^2}{4\pi\epsilon_0 r}\hat{r}$$



You can check that $[\vec{V}, H] = 0$

$\vec{V}\cdot\vec{L} = 0$ and ~~$V^2 = \frac{1}{m^2}(\vec{p}\times\vec{L})^2 - \frac{2e^2}{4\pi\epsilon_0 r}\hat{r}\cdot\frac{(\vec{p}\times\vec{L})}{m} + \left(\frac{e^2}{4\pi\epsilon_0 r}\right)^2$~~

$V^2 = \frac{e^4}{(4\pi\epsilon_0)^2} + \frac{2H(L^2+\hbar^2)}{m}$ ← This is for you to check this

$\vec{V}$ is a vector ⇒ $[V_i, L_j] = i\hbar\,\epsilon_{ijk}V_k$ and

$[V_i, V_j] = i\hbar\left(\frac{-2H}{m}\right)\epsilon_{ijk}L_k$ ← You should be able to check this as well.

Define $\vec{K} = \sqrt{\frac{-m}{2H}}\,\vec{V}$

so $[K_i, K_j] = i\hbar\,\epsilon_{ijk}L_k$ $[K_i, L_j] = i\hbar\,\epsilon_{ijk}K_k$ and

$[L_i, L_j] = i\hbar\,\epsilon_{ijk}L_k$.

Note also that $-\frac{2H}{m}K^2 = \frac{e^4}{(4\pi\epsilon_0)^2} + \frac{2H}{m}(L^2+\hbar^2)$ or

$H = \frac{-e^4 m}{2(4\pi\epsilon_0)^2}\frac{1}{K^2+L^2+\hbar^2}$ We will now compute the energies and their degeneracies using the commutation relations above.

Define: $\vec{M} = \dfrac{\vec{L}+\vec{K}}{2}$ $\vec{N} = \dfrac{\vec{L}-\vec{K}}{2}$

Then $[M_i, M_j] = \frac{1}{4}\left\{ [L_i, L_j] + [L_i, K_j] + [K_i, L_j] + [K_i, K_j] \right\}$

$$[M_i, M_j] = \frac{1}{4}\left\{ i\hbar\varepsilon_{ijk}L_k + i\hbar(-1)\varepsilon_{jik}K_k + i\hbar\varepsilon_{ijk}K_k + i\hbar\varepsilon_{ijk}L_k \right\}$$

$$= \frac{1}{2} i\hbar\varepsilon_{ijk}(L_k + K_k) = i\hbar\varepsilon_{ijk}M_k$$

Similarly, $[N_i, N_j] = i\hbar\varepsilon_{ijk}N_k$ and $[M_i, N_j] = 0$

$\left\{\begin{matrix}\vec{M}\\ \vec{N}\end{matrix}\right\}$ acts like an angular momentum. These two "angular momenta" commute with each other.

$$H = \frac{-me^4}{(4\pi\varepsilon_0)^2 \cdot 2}\left[\frac{1}{2M^2+2N^2+\hbar^2}\right]$$ since $(\vec{L}+\vec{K})^2 + (\vec{L}-\vec{K})^2 = 2(L^2+K^2)$

We can find simultaneous eigenkets of N^2, M^2, N_z, M_z: $|\mathcal{M}, \mathcal{N}, m_M, m_N\rangle$

$M^2|\mathcal{M}, \mathcal{N}, m_M, m_N\rangle = (\mathcal{M}+1)(\mathcal{M})\hbar^2|\cdots\rangle$ etc.

$M_z|\mathcal{M}, \mathcal{N}, m_M, m_N\rangle = \hbar m_M|\cdots\rangle$ $\mathcal{M}$ can take on values $0, 1/2, 1, 3/2, \ldots$ and

$m_M = -\mathcal{M}, \ldots, \mathcal{M}$

$m_N = -\mathcal{N}, \ldots, \mathcal{N}$

Since $\vec{V}\cdot\vec{L} = 0$ $\vec{K}\cdot\vec{L} = 0 \Rightarrow$

$M^2 = N^2 \Rightarrow$ Bound states of the H-atom correspond to $\mathcal{M} = \mathcal{N}$. $|\mathcal{M}=\mathcal{N}, m_M, m_N\rangle$ so

$$H|\mathcal{M}, m_M, m_N\rangle = \frac{-me^4}{(4\pi\varepsilon_0)^2 2}\frac{1}{[4\mathcal{M}(\mathcal{M}+1)+1]\hbar^2}|\mathcal{M}, m_M, m_N\rangle$$

$$= \frac{-me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{(2\mathcal{M}+1)^2}|\mathcal{M}, m_M, m_N\rangle$$

So the energy eigenvalues are

$$E = -\frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2}\,\frac{1}{(2M+1)^2} \qquad M = 0, \tfrac{1}{2}, 1, \ldots \quad (2M+1)^2 = 1, 4, 9, \ldots$$

What is the degeneracy of the energy levels?

$2M+1$ values of m_M and m_N for each energy level.

$$\Rightarrow \quad E_n = -\frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2}\,\frac{1}{n^2} \qquad \text{degeneracy } \underline{\underline{n}}^2$$

$n=1$ 1 1S = 1

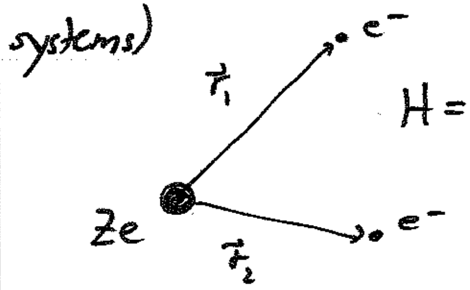
$n=2$ 4 2S $2P^3$ = 4 checks!

$n=3$ 9 3S $3P^3$ $3D^5$ = 9

A Simple look at the Periodic Table

Two-electron atoms He, Li^+, H^-, and Be^{++}

Fixed nucleus (Bethe and Jackiw consider nuclear motion in such systems)



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

Here we set $4\pi\varepsilon_0 = 1$ and $\hbar = 1$.

There are two principal complications:

1) Coulomb interaction between electrons

2) Spin-orbit interaction between electron spins and the electric fields in the atom.

First we look at the effect of the Coulomb interaction between the two electrons:

The grand state of a two-electron atom

We will treat the electron-electron interaction as a perturbation

$\psi_0(\vec r_1,\vec r_2) = \psi_{1s}(\vec r_1)\,\psi_{1s}(\vec r_2)$ ← Consider the spin singlet state.

$\psi_{1s}(\vec x) = N e^{-Zr/a_0}$ $N = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}$ Note that the nuclear charge Z just linearly rescales the Bohr orbit radius.

$$E_0^{(0)} = -\frac{\overset{2}{Z} e^2}{a_0} = -\frac{Z^2 e^2}{2a_0} \times \underset{\text{Two non-interacting electrons.}}{2}$$

← one from $eZ\cdot e$

one from $a_0 \to a_0/Z$

1st order perturbation theory: Note we are setting $\underline{\underline{4\pi\epsilon_0 = 1}}$

$$\Delta E = \left\langle \psi^{(0)} \right| \frac{e^2}{|\vec r_1 - \vec r_2|} \left| \psi^{(0)} \right\rangle$$ ← Just have to work out the integral!

$$\Delta E = \int d^3\vec r_1\, d^3\vec r_2\, |N|^2 e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \frac{e^2}{|\vec r_1 - \vec r_2|} \quad \text{or}$$

remember to square!

$$\Delta E = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^{6} a_0^{6} \int d\vec x_1\, d\vec x_2\, e^{-Z(x_1+x_2)} \frac{e^2}{a_0}\frac{1}{|\vec x_1 - \vec x_2|} \quad \text{or}$$

$$\Delta E = \frac{1}{\pi}\frac{Z^6 e^2}{a_0}\,\bar E\,; \quad \bar E = \int d\vec x_1\, d\vec x_2\, e^{-2(x_1+x_2)Z} \frac{1}{|\vec x_1 - \vec x_2|}$$

Note: $$\frac{1}{|\vec x_1 - \vec x_2|} = \int \frac{d^3\bar k}{(2\pi)^3} e^{i(\vec x_1 - \vec x_2)\cdot \bar k} \frac{4\pi}{k^2}$$ since

$$\frac{1}{|\vec A|} = \int \frac{d^3k}{(2\pi)^3}\frac{4\pi}{k^2} e^{i\vec k\cdot\vec A} = \frac{2\pi}{2\pi^2}\int_{-1}^{+1} d(\cos\theta)\int_0^\infty dk\, e^{ikA\cos\theta}$$

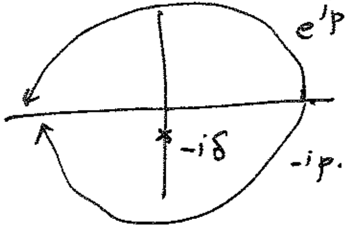
$$= \frac{1}{\pi}\int_0^\infty dk\,\frac{1}{ikA}\left(e^{ikA} - e^{-ikA}\right) = \frac{2}{\pi}\int_0^\infty dk\,\frac{\sin(kA)}{kA}$$

so we have: $\frac{2}{|\vec{A}|\pi}\int_0^\infty dp\,\frac{\sin p}{p}$ ← sine integral $= \pi/2$

$$= \frac{1}{|\vec{A}|}$$

wrong way

$$\frac{1}{2}\lim_{\delta\to 0}\int_{-\infty}^{\infty} dp\,\frac{e^{ip}}{p+i\delta} = \frac{1}{2}(-2\pi i)\,\frac{e^{-i(-i\delta)}}{-2i} \xrightarrow[\delta\to 0]{} \frac{\pi}{2}$$



$= \pi/2$

So

$$\Delta E = \frac{Z^6 e^2}{\pi a_0}\,\bar{E}\,;$$

$$\bar{E} = \int d^3\vec{x}_1\, d^3\vec{x}_2\, e^{-2Z(x_1+x_2)} \int \frac{d^3k}{(2\pi)^3}\, e^{i\vec{k}\cdot(\vec{x}_1-\vec{x}_2)}\,\frac{4\pi}{k^2}$$

$$\bar{E} = \int\frac{d^3k}{(2\pi)^3}\int d^3\vec{x}_1\, e^{-2Zx_1 + i\vec{k}\cdot\vec{x}_1}\int d^3\vec{x}_2\, e^{-Zx_2 - i\vec{k}\cdot\vec{x}_2}\,\frac{4\pi}{k^2} \text{ or}$$

$$\bar{E} = \int\frac{d^3\vec{k}}{(2\pi)^3}\,\frac{4\pi}{k^2}\left|\int d^3\vec{x}\, e^{-2Zx + i\vec{k}\cdot\vec{x}}\right|^2$$

Now $\int d^3\vec{x}\, e^{-Zx}\, e^{i\vec{k}\cdot\vec{x}} = 2\pi\int_0^\infty dx\, x^2 e^{-2Zx}\int_{-1}^{+1} d(\cos\theta)\, e^{ikx\cos\theta} =$

$$2\pi\int_0^\infty dx\, x^2 e^{-2Zx}\,\frac{1}{ikx}\left(e^{ikx} - e^{-ikx}\right) = 4\pi\int_0^\infty dx\, x^2 e^{-2Zx}\,\frac{\sin(kx)}{kx}$$

$$= \frac{4\pi}{k^3}\int_0^\infty dy\, e^{-2(Z/k)y}\, y\,\sin y = \frac{4\pi}{k^2}\,\mathrm{Im}\int_0^\infty dy\, e^{-2(Z/k)y + iy}\, y$$

$$= \frac{4\pi}{k^3}\,\mathrm{Im}\,\frac{-\partial}{\partial(Z/k)}\int_0^\infty dy\, e^{-\frac{Z}{k}y + iy} = \frac{-\partial}{\partial(Z/k)}\frac{4\pi}{k^3}\,\mathrm{Im}\left[\frac{1}{\frac{Z}{k} - i}\right]$$

$$= \frac{-\partial}{\partial(Z/k)}\,\frac{4\pi}{k^3}\,\frac{1}{\frac{Z^2}{k^2}+1} = -4\pi k\,\frac{\partial}{\partial Z}\,\frac{1}{Z^2+k^2}$$

$$= \frac{2Z\cdot 4\pi k}{(Z^2+k^2)^2} = \frac{16\pi Zk}{(Z^2+k^2)^2} = \frac{16\pi Zk}{(4Z^2+k^2)^2}$$

$$\bar{E} = 4\pi \frac{16^2\pi^2 Z^2}{(2\pi)^3}\int_0^\infty \frac{dk\,\cancel{k^2}\,4\pi}{\cancel{k^2}}\,\frac{1}{(4Z^2+k^2)^4} \qquad p = k/2Z$$

$$\bar{E} = \frac{(4\pi)^2 16^2\pi^2}{8\pi^3} Z^2 \int_0^\infty dp\,\frac{2Z}{(2Z)^8(1+p^2)^4}$$

$$\bar{E} = \frac{\pi\, 4}{Z^5}\int_0^\infty dp\,\frac{1}{(1+p^2)^4} = \frac{4\pi}{Z^5}\,\frac{5}{32} = \frac{5}{8}\pi Z^{-5}$$

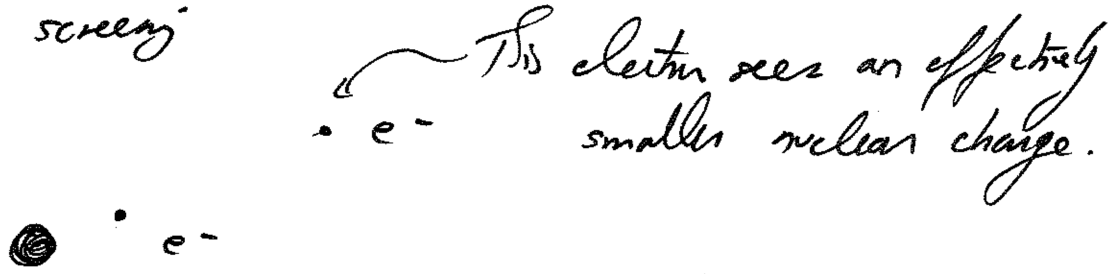
$$\Rightarrow \Delta E = \frac{5}{8}\frac{e^2}{a_0} Z \quad \text{and} \quad E^{(1)} = -\frac{Z e^2}{a_0}\left(Z - 5/8\right)$$

This must be an upper bound on the ground state energy.

In practice, this result is about 5% too high. Not too bad!

What is the principal physical reason for this error?

Electron screening



Suggests that a variational calculation might be in order:

Trial function: $\psi_{1s}(\vec{r}) = \pi^{-1/2}\left(\frac{Z'}{a_0}\right)^{3/2} e^{-Z' r/a_0}$ i.e. vary the effective nuclear charge.

Here the electron-electron part gives:

$$\frac{5}{8}\frac{Z' e^2}{a_0}$$

We have already calculated the kinetic energy before - see our previous attempt at a variational calculation

KE = $\frac{Z'^2 e^2}{2a_0}$. The potential energy expectation value is

PE = $-\frac{ZZ'e^2}{a_0} \Longleftrightarrow \left\langle -\frac{Z'e^2}{r} \right\rangle \frac{Z}{Z'}$ ← no screening   due to the nuclear Coulomb potential

$$E_0(Z') = \frac{5}{8}\frac{Z'e^2}{a_0} + 2\left(\frac{Z'^2 e^2}{2a_0} - \frac{ZZ'e^2}{a_0}\right) = \frac{e^2}{a_0}\left[Z'^2 - 2ZZ' + \frac{5Z'}{8}\right]$$

Ground state energy

Two electrons remember

Find the minimum: $\frac{dE_0}{dZ'} = 0 \Rightarrow 0 = 2Z' - 2Z + 5/8$

$Z' = Z - 5/16$ so

$E_0 = -(Z - 5/16)^2 \frac{e^2}{a_0}$ ← Now, down to about 1% error!!

To summarize: We have $E_0^{(0)} = -\frac{Z^2 e^2}{a_0}$

$$E_0^{(1)} = -\left(Z - \frac{5}{8}\right)\frac{Ze^2}{a_0}$$

$$E_0^{(var)} = -\left(Z - 5/16\right)^2 \frac{e^2}{a_0}$$

The story is not over, however. If we put in $Z = 1$ we get E_{ground} of H^- is higher than a free electron and one H atom. This is not true! H^- is energetically stable.

Thinking about very big atoms: The Hartree Approximation

Side Bar

← this electron see an essentially spherically symmetric average field. We need to determine that average field and the single particle wavefunctions – in a self-consistent approach.

Assume that the wave function is a product of one electron wave functions

$$\psi(\vec r_1,\ldots,\vec r_N) = \varphi_1(\vec r_1)\cdots\varphi_N(\vec r_N)$$ ← Note: This is not antisymmetrized! More on this later, but for now let's just assume that all φ_j are mutually orthogonal to each other. This doesn't fix the problem completely. We will have to learn about many particle states to really think about this.

What is the average potential?

The average charge density at $\vec r'$ due to the jth electron: $e|\varphi_j(\vec r')|^2$

$$\Rightarrow \underbrace{\int d^3\vec r' \frac{e^2}{|\vec r-\vec r'|}|\varphi_j(\vec r')|^2}$$

an electron at $\vec r$ will have the potential energy.

⇒ The ith electron sees an average potential:

$$V_i(\vec r) = \underbrace{\int d^3\vec r' \frac{e^2}{|\vec r-\vec r'|}\sum_{j\neq i}|\varphi_j(\vec r')|^2}_{\text{other electrons}} - \underbrace{\frac{Ze^2}{r}}_{\text{nucleus.}}$$

Then $\varphi_i(\vec r)$ is determined by: $\left[-\frac{\nabla^2}{2m} + V_i(r)\right]\varphi_i = \varepsilon_i\varphi_i$

We now have a set of coupled equations to solve:

$$V_i(\vec r) = \int d^3\vec r' \frac{e^2}{|\vec r - \vec r'|} \sum_{j\neq i} |\varphi_j(\vec r')|^2 - \frac{Ze}{r}$$

$$\left[-\frac{\nabla^2}{2m} + V_i(\vec r)\right]\varphi_i = \varepsilon_i \varphi_i$$

~~Th~~ Can show that energy of the state is

$$E = \sum_i \varepsilon_i - \frac{1}{2} \int \sum_{i\neq j} \int d^3\vec r\, d^3\vec r' \frac{e^2}{|\vec r - \vec r'|} |\varphi_i(\vec r)|^2 |\varphi_j(\vec r')|^2$$

The Fermi-Thomas Approximation

We can get the general features of the self-consistent potential from a semiclassical approach.

For a large atom the potential of the i^{th} electron is approximately equal to the potential seen by a test charge.

$$V_i(\vec r) = V(\vec r) = \int d^3\vec r' \frac{e^2}{|\vec r - \vec r'|} \sum_j |\varphi_j(\vec r')|^2 - \frac{Ze^2}{r}$$

leaving in the self interaction!

and

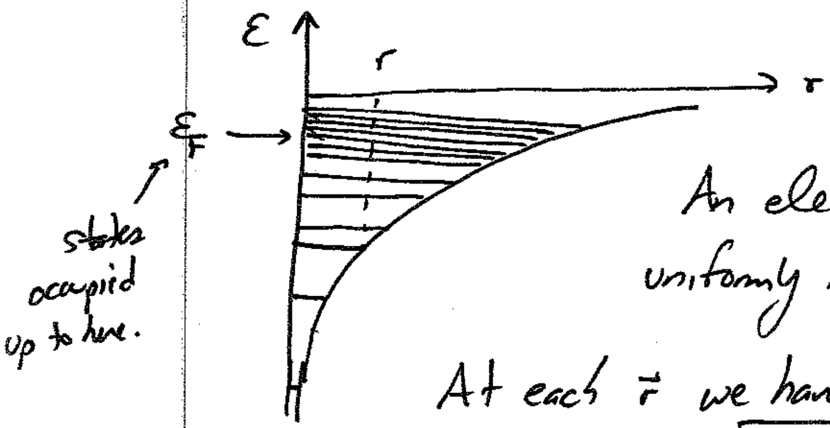
$$\sum_j |\varphi_j(\vec r)|^2 = n(\vec r)$$

charge density (e) at $\vec r$.

We need to find out how the density depends on the potential.

Observation: In a large atom most electrons have a large kinetic energy so $V(r)$ varies slowly compared to the oscillations in $\varphi(\vec r)$. $\Rightarrow$ Treat the wavefunctions as plane-waves

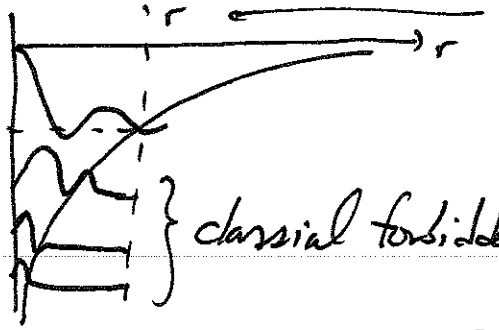
$$\varphi_i(\vec r) \sim e^{i\vec p_i(\vec r)\cdot\vec r} \quad \text{where} \quad \varepsilon_i = \frac{p_i^2(\vec r)}{2m} + V(\vec r)$$



An electron in state φ_i will be spread out uniformly in the classically allowed region:

At each $\vec{r}$ we have electrons w/ momentum ranging from 0 to $P_f(\vec{r}) = \sqrt{2m[\varepsilon_f - V(\vec{r})]}$

Only electrons w/ $\varepsilon_i > V(r)$ have a reasonable chance of being at at $\vec{r}$.



then

$$n(r) = \frac{P_f^3}{3\pi^2} \qquad \text{why?} \qquad \int_0^{P_f} p^2 dp \, \frac{4\pi}{(2\pi)^3} = \frac{1}{2\pi^2} \, \frac{1}{3} P_f^3 \times 2$$

↑ Spin states.

Combining these two results:

$$n(r) = \frac{\left(2m[\varepsilon_f - V(r)]\right)^{3/2}}{3\pi^2}$$

To solve for $V(r)$ write $\nabla^2 V = -4\pi e^2 n(r)$ Poisson's Eq. assuming $V(r)$ is spherically symmetric

$$r^{-2}\partial_r\left(r^2 \partial_r V\right) = -\frac{4\pi e^2}{3\pi^2}\left[2m(\varepsilon_f - V(r))\right]^{3/2}$$

w/ boundary conditions 1) $r \to 0$ $V \to -\frac{Ze^2}{r}$ ← Just see the nuclear charge.

2) Outer radius of the atom

$\varepsilon_f - V(R) = 0$ $n \to 0$

5.47

For a neutral atom $V(R)=0$.

If we change both the dependent and independent variables.

$$\underset{\varepsilon_F}{V(r)} = -\frac{Ze^2}{r}\Phi(x) \qquad r=\frac{bx}{Z^{1/3}} \;; \qquad \Phi(0)=1$$

Note: Shift the zero of energy.

$$V''+\frac{2}{r}V' + \frac{4e^2}{3\pi}(2m)^{3/2}\left[\varepsilon_F - V(r)\right]^{3/2} = 0$$

$$V' = -\frac{Ze^2}{r}\Phi'(x)\frac{Z^{1/3}}{b} + \frac{Ze^2}{r^2}\Phi(x)$$

$$V'' = -\frac{Ze^2}{r}\Phi''(x)\frac{Z^{2/3}}{b^2} + \frac{2Ze^2}{r^2}\Phi'(x)\frac{Z^{1/3}}{b} - \frac{2Ze^2}{r^3}\Phi(x)$$

$$V''+\frac{2}{r}V' = -\frac{Z^{5/3}e^2}{b^2 r}\Phi''(x) = -\frac{Z^{5/3}e^2 Z^{1/3}}{b^2\, bx}\Phi''(x)$$

$$\varepsilon_F - V(r) = \left[\cancel{\varepsilon_F}\ \frac{Ze^2}{r}\Phi(x)\right]$$

$$\Rightarrow -\frac{\cancel{Z^{6/3}}\cancel{e^2}\,\Phi''(x)}{b^3 x} = -\frac{4\cancel{e^2}}{3\pi}(2m)^{3/2}\frac{\cancel{Z^{3/2}}e^3\cancel{Z^{1/2}}}{b^{3/2}x^{3/2}}\Phi^{3/2}(x)$$

or
$$\Phi''(x)\,x^{1/2} = \frac{4}{3\pi}\frac{(2m)^{3/2}e^3}{b^{3/2}}\Phi^{3/2}(x)$$

take $b=\left(\frac{3\pi}{4}\right)^{2/3}\frac{1}{2}a_0$ and we get

$$\boxed{x^{1/2}\,\Phi''(x) = \Phi^{3/2}(x)}$$

Numerical solutions show that
$$\Phi(x) = \begin{cases} 1-1.59x\,, & x\to 0 \\ \dfrac{144}{x^3} & x\to\infty \end{cases}$$

Note that $\Phi = 0$ only at $r \to \infty$ so $V \to 0$ there as well. This means that the electron distribution also extends to ∞

At small r we find (converting back to ~~dimensional~~ dimensionfull units)

$$V(r) = \underset{\substack{\uparrow \\ \text{nucleon} \\ \text{potential}}}{-\frac{Ze^2}{r}} + \underbrace{1.80\,\frac{Z^{4/3}e^2}{a_0}}_{\nwarrow \text{ potential due to the electrons at } \vec{r}=\vec{0}.}$$

Predictions of the Thomas-Fermi Model:

1) $\Phi(x)$ is independent of any atomic parameters $\Rightarrow$ shape of the effective potential is <u>the same</u> for all large atoms.

2) From $r = \frac{bx}{Z^{1/3}} \Rightarrow$ the length scale of the atom $\propto Z^{-1/3}$

so that as Z grows, the atom's size <u>decreases</u>

3) The potential is $\Phi \propto Z^{4/3}$ so $n(r) \sim [\varepsilon_F - V]^{3/2} \Rightarrow$

$$\underset{\substack{\uparrow \\ \text{electron density}}}{n(r)} \propto (Z^{4/3})^{3/2} \sim Z^2 \leftarrow \text{electron density scales as } Z^2$$

4) Consider finite angular momentum eigenstates:

Then $V_{eff}(r) = V(r) + \frac{l(l+1)}{mr^2}$ must have a minimum below 0 energy for bound states to exist:

$\underset{\text{S States}}{Z \le 4 \Rightarrow \text{only } l=0}$; $\underset{\text{S,P states}}{4 < Z < 19 \text{ only } l=0,1}$; $\underset{\text{S,P,D states}}{19 < Z \le 53 \; l=0,1,2}$

Ground state:

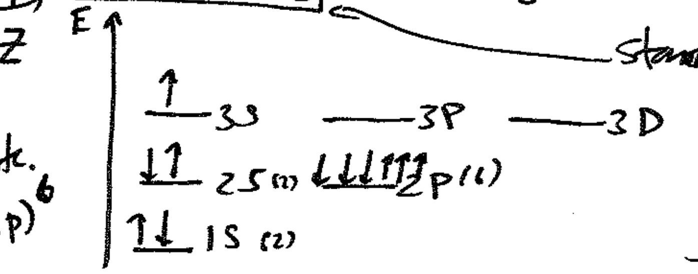
One more example of time-independent perturbation theory: Spin-orbit interaction and Fine Structure.

Consider an alkali atom: e.g. Na ← Ground State

$\boxed{Na^{11}_{\,Z}\,()\,3s \quad {}^2S_{1/2}} \leftarrow {}^{2S+1}L_J \Rightarrow J = \tfrac{1}{2}\hbar \quad S = \tfrac{1}{2}\hbar,\ L = 0$

← Standard Notation

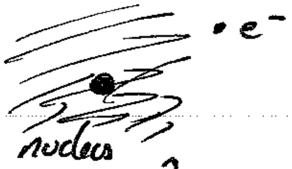
means closed shells below this state. ⇒ i.e. $(1s)^2(2s)^2(2p)^6$



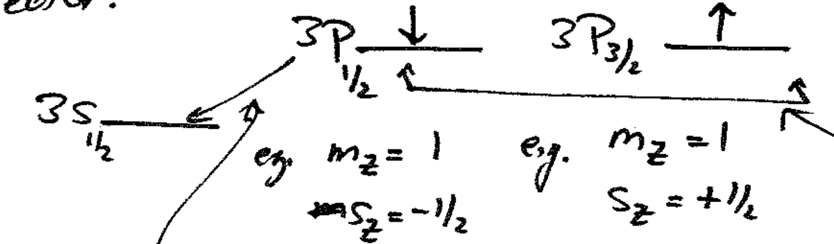
} 1 valence electron outside a closed shell.

Unperturbed (Hydrogenic) States.

Now, what are the excited states?



Note: Central Potential cannot be simply $\sim 1/r \Rightarrow$ 3S and 3P levels are split since we have removed the degeneracy associated with the Lenz vector.



$\vec{J} = \vec{L} + \vec{S}$

These two levels are not quite equal!?!

$\lambda = 5896\,\text{Å}$ But the transition from the $3P_{3/2} \rightarrow 3S_{1/2}$ states is $\lambda = 5890\,\text{Å}$ ← slightly higher energy!

This produces the so-called "Sodium Doublet" or D-lines

Note $E = \dfrac{hc}{\lambda}$ so $\dfrac{\Delta E}{E} = \dfrac{\cancel{hc}}{\cancel{hc}}\left(\dfrac{1}{5890} - \dfrac{1}{5896}\right)(5890) =$

So $\frac{\Delta E}{E} \sim 0.1\%$ ← This is clearly very small! Why should we care about this tiny difference between experiment and theory?

We can understand why the 3S and 3P levels are split, but we have every reason to believe that the various spin states and m_z states within the 3P levels should be identical!

We must be missing a part of the interaction of the electron in an atom. ⇐ We are missing "Fine Structure" due to the spin-orbit interaction

Rough outline of the missing forces:

1) electron sees an electric field $\vec{E} = -\frac{1}{e}\vec{\nabla}\overset{\substack{\text{Coulomb potential}\\ \downarrow}}{V_c}(r)$

2) Since the electron is also moving at ~~some~~ velocity $\vec{v}$ it is subject to a magnetic field $\vec{B}_{eff} = -\frac{\vec{v}}{c}\times\vec{E}$

3) Recall, the electron has a spin magnetic moment:

$\vec{\mu} = \frac{e\vec{S}}{m_e c}$, which interacts w/ the B-field

via:

$$\underset{\substack{\uparrow\\ \text{spin-orbit}}}{H_{so}} \cong -\vec{\mu}\cdot\vec{B}_{eff} \cong \frac{1}{\underset{\uparrow}{2}\, m_e^2 c^2}\frac{1}{r}\frac{dV_c}{dr}\left(\vec{L}\cdot\vec{S}\right)$$

Can't get this factor of two right with this heuristic argument: see Thomas Precession for more details.

Let's consider $H_{SO} = \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV_c}{dr}(\vec{L}\cdot\vec{S})$ as a perturbation to the Hamilitonian of a hydrogenic atom:

$H = \frac{P^2}{2m} + V_c(r)$ ← This way we can study the effect of spin-orbit coupling without worrying about the electron-electron interaction at the same time!

Recall from chapter three: $\vec{L}\cdot\vec{S} = \frac{J^2 - L^2 - S^2}{2}$

since $J^2 = (\vec{L}+\vec{S})^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$

$\Rightarrow$ We should work in $L^2, \underset{S^2}{}J^2, J_z$ eigenket basis!

$|n\,l\,m\,s\rangle \rightarrow |n, l, J, J_z\rangle$ $\quad J = l \pm 1/2$ from addition of angular momenta!

$L^2, L_z^2, S^2, S_z^2 \rightarrow L^2, S^2, J^2, J_z$

1st order energy shifts:

$$\Delta_{nlj} = \left\{\frac{1}{2m_e^2c^2}\int d\vec{r}^3 \frac{1}{r}\frac{dV_c}{dr} R_{nl}(r) R_{nl}(r)\right\}\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - 3/4\right]$$

if $j = l + 1/2$: $[\quad] = (l+3/2)(l+1/2) - l(l+1) - 3/4$

$$= l^2 + 2l + 3/4 - l^2 - l - 3/4$$

$$= l$$

if $j = l - 1/2$ $\quad [\quad] = (l - 1/2)(l+1/2) - l^2 - l - 3/4$

Note $j=3/2$ above $j=1/2$!

$$= l^2 - 1/4 - l^2 - l - 3/4 = -l - 1$$

So:

$$\Delta_{nlj} = \frac{1}{2m_e^2c^2}\left\langle\frac{1}{r}\frac{dV_c}{dr}\right\rangle\frac{\hbar^2}{2}\begin{cases} l, & j = l + 1/2 \\ -(l+1), & j = l - 1/2\end{cases}$$

KNOWN as: Landé's interval rule.

The expectation value of this operator in the R_{nl} state

Let's try to understand the magnitude of the effect:

By dimensional analysis $\left\langle \frac{1}{r}\frac{dV_c}{dr}\right\rangle \sim \frac{e^2}{a_0^3}$ since $V\sim 1/r$

$\Rightarrow \Delta \sim \frac{\hbar^2}{m^2c^2}\frac{e^2}{a_0^3}$ compared to the gaps in the 1S→2S levels.

(Balmer splittings) $\sim \frac{e^2}{a_0}$

Fine structure constant.
(units where $4\pi\epsilon_0=1$)

helpful to know that $\frac{e^2}{\hbar c}\cong\frac{1}{137}$ and:

1) Compton wavelength of an electron $\lambda_c=\frac{\hbar}{mc}$

wavelength of a photon w/ energy equal to the electron rest mass

2) "Classical" Electron radius: $\frac{e^2}{m_ec^2}$ (in units where $4\pi\epsilon_0=1$)

from $E=\frac{\cancel{3}}{\cancel{5}}\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}=\frac{1}{2}mc^2$

sphere of constant charge density

3) Bohr radius:

$$a_0=\frac{\hbar^2}{m_ee^2} \quad (4\pi\epsilon_0=1)$$

---

classical electron radius

$\Rightarrow$ ~~Compton λ~~ $=\dfrac{\frac{e^2}{m_ec^2}}{\frac{\hbar}{m_ec}}=\frac{1}{137}$ and $\dfrac{\frac{\hbar}{m_ec}}{a_0}=\frac{1}{137}$

Compton wavelength of an electron.

Bohr radius

$$\frac{\Delta E}{E} \sim \frac{\frac{e^2}{a_0^3}\frac{\hbar^2}{m_e^2c^2}}{\frac{e^2}{a_0}} = \frac{\hbar^2/m_e^2c^2}{a_0^2} = \left(\frac{\hbar/m_ec}{a_0}\right)^2 \sim \left(\frac{1}{137}\right)^2 \sim 10^{-4}$$

about the right order of magnitude.

There are other effects at this level of precision: we need to drop the nonrelativistic Schrödinger Eq. For example the energy of the electron is really

$$\sqrt{m^2c^4+p^2c^2} - mc^2 \cong \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

But, at least we can understand why in principal the $3P_{1/2}$ and $3P_{3/2}$ levels are split.

Time-dependent Perturbation Theory: Interacting with a classical radiation field $\longleftarrow$ This approach misses the effect of spontaneous emission. for that we have to quantize the radiation field.

$$H = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 + V(r)$$

working in the Coulomb gauge $\vec{\nabla}\cdot\vec{A} = 0$ with no scalar potential $\varphi = 0$ and dropping the $|A|^2$ term

Then $$H = \frac{1}{2m}p^2 - \frac{e}{m_e c}\underbrace{\vec{A}\cdot\vec{p}}$$

note we moved $\vec{p}$ past $\vec{A}$ using $\vec{\nabla}\cdot\vec{A} = 0$.

From Maxwell's Eqns:

$$\vec{B} = \vec{\nabla}\times\vec{A} \quad \text{and} \quad \vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$$

We consider a monochromatic plane wave of light:

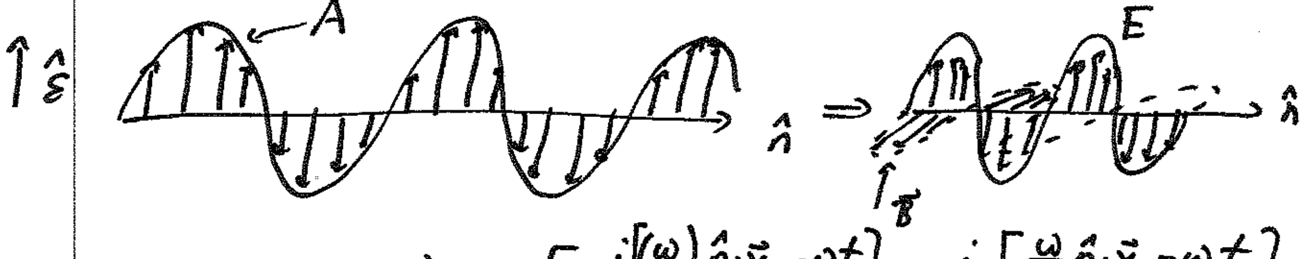
$$\vec{A} = 2A_0\,\hat{\varepsilon}\cos\left(\frac{\omega}{c}\hat{n}\cdot\vec{x} - \omega t\right)$$

Amplitude

polarization state

wavevector $\vec{k} = \frac{\omega}{c}\hat{n}$

$\hat{\varepsilon}\cdot\hat{n} = 0$ (Transverse wave)



$$\cos\left(\frac{\omega}{c}\hat{n}\cdot\vec{x} - \omega t\right) = \frac{1}{2}\left[e^{i\left[\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x} - \omega t\right]} + e^{-i\left[\frac{\omega}{c}\hat{n}\cdot\vec{x} - \omega t\right]}\right]$$

We can now try to understand induced emission and absorption.

Comparing to our earlier result, we see that the $e^{-i\omega t}$ generates absorption and the $e^{+i\omega t}$ gives stimulated emission

$$-\frac{e}{mc}\vec{A}\cdot\vec{p} = -\frac{e}{mc}A_0\,\hat{\varepsilon}\cdot\vec{p}\left[e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}}e^{-i\omega t} + e^{-i\frac{\omega}{c}\hat{n}\cdot\vec{x}}e^{+i\omega t}\right]$$

<u>Absorption</u>: $V_{ni}^{\dagger} = -\frac{e}{mc}A_0\langle n|e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle$

so

$$W_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}|A_0|^2\left|\langle n|e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle\right|^2\delta(E_n-E_i-\hbar\omega)$$

if we have a discrete energy level $|n\rangle$ as the final state we need to interpret the delta function as follows:

$$\delta(\omega-\omega_{ni}) = \lim_{\gamma\to 0}\frac{\gamma}{2\pi}\frac{1}{(\omega-\omega_{ni})^2+\gamma^2/4}$$ — Recall our slow turn-on approach.

we can use this result w/ a finite γ due to the finite lifetime of the excited state.

Absorption Cross Section: $$\sigma_{ab} = \frac{\overset{E/T}{\downarrow}\ \text{Energy absorbed per unit time }(i\to n)}{\text{Energy flux of the radiation field}}$$

$\nearrow$

$$\frac{E}{L^2\cdot T}$$

$[\sigma] = L^2 \leftarrow$ cross section is an <u>area</u>.

$$\mathcal{U} = \frac{1}{2}\cdot\frac{1}{8\pi}\left(E_{max}^2+B_{max}^2\right) \Longrightarrow \mathcal{U} = \frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2$$

$\uparrow$
energy density in the radiation field

See for example Jackson. Chapter 6.

Energy flux: $c\,\mathcal{U}$

$$\Longrightarrow \quad \sigma_{abs} = \frac{\overset{\text{energy absorbed}}{\hbar\omega}\ \overbrace{\frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}|A_0|^2|\langle n|e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle|^2\,\delta(E_n-E_i-\hbar\omega)}^{\text{Transition rate}}}{\frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2}$$

$$\sigma_{abs} = \underbrace{\frac{4\pi^2\hbar}{m^2\omega}}_{\frac{E\cdot T}{M^2T^{-1}}}\overset{\nwarrow\ \alpha\cong\frac{1}{137}\ \text{dimensionless.}}{\left(\frac{e^2}{\hbar c}\right)}\underset{\uparrow\ \frac{M^2L^2}{T^2}}{|\langle n|e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle|^2}\ \underbrace{\delta(E_n-E_i-\hbar\omega)}_{\frac{1}{\hbar}\delta(\omega_{ni}-\omega)\ =\ \frac{T}{E\cdot T}}$$

$$[\sigma] = \frac{T^2}{M^2}\cdot\frac{M^2L^2}{T^2} = L^2 \quad \text{checks.}$$

Electric Dipole Approximation: (E1 approximation)

$$e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}} = 1 + i\frac{\omega}{c}\hat{n}\cdot\vec{x} + \cdots$$

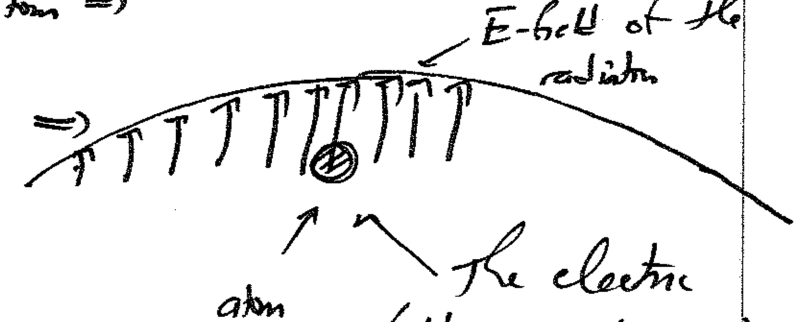
$$\hbar\omega \sim \frac{Z^2e^2}{a_0} \quad \text{and then} \quad \left(\frac{\omega}{c}\right)^{-1} = ƛ = \frac{\lambda}{2\pi} \sim \frac{c\hbar a_0}{Z^2e^2} \quad \text{or}$$

$\uparrow$ atomic level spacing

$$ƛ \sim \frac{c}{\omega} \sim \frac{c\hbar(a_0/Z)}{Ze^2} \approx \left(\frac{1}{137}\right)^{-1}\frac{1}{Z}\overset{a_0/Z}{R_{atom}}$$

so $ƛ \sim 137\, Z^{-1} R_{atom} \Longrightarrow$

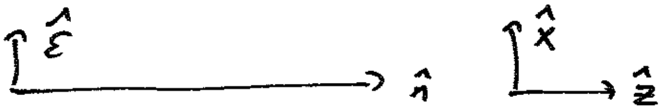
$$\frac{ƛ}{R_{atom}} \sim \frac{137}{Z} \gg 1 \Longrightarrow$$



the electric field is nearly constant across the atom!

$$\Rightarrow \quad \langle n| e^{\frac{i\omega}{c}\hat{n}\cdot\vec{x}}\,\hat{\varepsilon}\cdot\vec{p}\,|i\rangle = \hat{\varepsilon}\cdot\langle n|\vec{p}\,|i\rangle$$

put $\hat{\varepsilon} \parallel \hat{x}$ and $\hat{z} \parallel \hat{n}$



Then we need to know $\langle n|p_x|i\rangle$ since $[x, H_0] = \frac{i\hbar p_x}{m}$

$$\langle n|p_x|i\rangle = \frac{m}{i\hbar}\langle n|[x,H_0]|i\rangle = \frac{m}{i\hbar}\langle n|x|i\rangle\{E_i - E_n\} \text{ or}$$

using $\frac{E_i - E_n}{\hbar} = -\omega_{ni}$ we get:

$$\langle n|p_x|i\rangle = i m\,\omega_{ni}\,\underbrace{\langle n|x|i\rangle}_{\text{dipole matrix element.}}$$

$$\sigma_{ab} = 4\pi^2\alpha\,\omega_{ni}\,|\langle n|x|i\rangle|^2\,\delta(\omega-\omega_{ni})$$

$$\int_0^\infty \sigma_{ab}(\omega)\,d\omega = \sum_n 4\pi^2\alpha\,\omega_{ni}\,|\langle n|x|i\rangle|^2 = \sum_n f_{ni}\,\frac{\hbar}{2m}\,\alpha\, 4\pi^2$$

↑

Define: $f_{ni} = \frac{2\omega_{ni}}{\hbar} m\,|\langle n|x|i\rangle|^2$ oscillat strength.

take $|i\rangle$ to be the ground state

Note: $\sum_n f_{ni} = 1.$

$$[x,[x,H_0]] = \frac{i\hbar}{m}[x,p_x] = -\frac{\hbar^2}{m}$$

5.58

Prove the Thomas Reiche-Kuhn sum rule:

$$\langle n|[x,[H,x]]|n\rangle = \sum_i \{\langle n|xH-Hx|i\rangle\langle i|x|n\rangle +$$

$$+\langle n|x|i\rangle\langle i|Hx-xH|n\rangle\}$$

$$= \sum_i \{\langle n|x|i\rangle\langle i|x|n\rangle (E_i-E_n) +$$

$$+\langle n|x|i\rangle\langle i|x|n\rangle (E_i-E_n)\} = 2\sum_i |\langle n|x|i\rangle|^2 (E_i-E_n)$$

swap n and i to make this look like the text book:

$$\frac{1}{2}\langle i|[x,[H,x]]|i\rangle = \sum_n |\langle i|x|n\rangle|^2 (E_n-E_i)$$

But $$[x,[H,x]] = \left[x,\left[\frac{p^2}{2m}+V(x),x\right]\right]$$

$$= \left[x,\frac{-i\hbar}{2m}p\right] = \frac{\hbar^2}{2m}$$ so

$$\frac{\hbar^2}{2m} = \sum_n |\langle i|x|n\rangle|^2 (E_n-E_i)$$ or

$$1 = \sum_n |\langle i|x|n\rangle|^2 \left(\frac{E_n-E_i}{\hbar}\right)\frac{2m}{\hbar} \Longleftrightarrow 1 = \sum_n f_{ni}$$

Sum of all oscillator strengths is one.