TIME-INDEPENDENT PERTURBATION THEORY

Another approximation method is applicable to cases in which the Hamiltonian can be written as a sum of two terms one of which is exactly solvable while the other is in some sense "small".

$$H = H_0 + V \qquad \text{where } H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \text{ is a solved problem, and}$$

V is known as the "perturbation".

To add a degree of analytic control to our approximate solution, we will in fact solve the problem

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

which is the same as above for $\lambda = 1$, and is the exactly solvable problem if $\lambda = 0$. Our solution will present itself as a power series expansion in λ.

To get an idea of how this might work, consider the following two-state system:

$$H = \begin{bmatrix} E_1^{(0)} & \lambda V \\ \lambda V & E_2^{(0)} \end{bmatrix}$$

The <u>exact</u> eigenenergies for this system are easily obtained from $\det(H - E) = 0$

$$\left.\begin{matrix} E_1 \\ E_2 \end{matrix}\right\} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{\left(E_2^{(0)} - E_1^{(0)}\right)^2}{4} + \lambda^2 |V|^2} \, .$$

Now suppose that the pertubation $\lambda|V|$ is much smaller than the energy gap $E_2^{(0)} - E_1^{(0)}$

$\lambda|V| \ll \left|E_2^{(0)} - E_1^{(0)}\right|$, then we can expand the square root

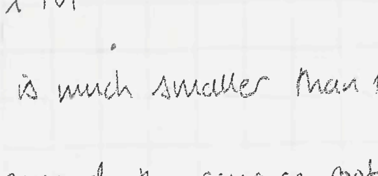
$$\left.\begin{matrix} E_1 \\ E_2 \end{matrix}\right\} \approx \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\left(E_2^{(0)} - E_1^{(0)}\right)\left(1 + \frac{2\lambda^2|V|^2}{\left(E_2^{(0)} - E_1^{(0)}\right)^2} + O(\lambda^4)\right)$$

$$\Rightarrow E_1 \simeq E_1^{(0)} + \lambda^2 \frac{|V|^2}{E_1^{(0)} - E_2^{(0)}} + O(\lambda^4) \quad \xrightarrow{\lambda \to 0} E_1^{(0)} \ \checkmark$$

$$\& \quad E_2 \simeq E_2^{(0)} + \lambda^2 \frac{|V|^2}{E_2^{(0)} - E_1^{(0)}} + O(\lambda^4) \quad \xrightarrow{\lambda \to 0} E_2^{(0)} \ \checkmark$$

In this case we know the exact solution so we can consider the convergence of this series easily: increasing $|\lambda|$ from zero we encounter the branch point of the square root when

$$\lambda|V| = \pm i \frac{1}{2}\left(E_2^{(0)} - E_1^{(0)}\right)$$



$\Rightarrow$ for $\lambda = 1$ we require $|V| < \frac{1}{2}\left|E_2^{(0)} - E_1^{(0)}\right|$ for the series to converge.

In general we'd like $|V| \ll \frac{1}{2}\left|E_2^{(0)} - E_1^{(0)}\right|$ so that just a few terms is a good approximation.

(The Perturbative Expansion in the Non-degenerate Case)

The fact that the power series expansion in the two-state case contained the object $\dfrac{1}{E_2^{(0)} - E_1^{(0)}}$ might suggest to us that degeneracies in the spectrum of H_0 could be a problem. Indeed they are and they require separate treatment, here we will first assume that the spectrum of H_0 is non-degenerate:

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \quad \text{where } \{|n^{(0)}\rangle\} \text{ is a complete set of states: } \mathbb{1} = \sum_n |n^{(0)}\rangle\langle n^{(0)}|$$

We are trying to solve $(H_0 + \lambda V)|n\rangle = E_n |n\rangle$

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

$$\Rightarrow \underline{(E_n^{(0)} - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle} \quad \text{A}$$

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

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

$\Rightarrow$ the state $(\lambda V - \Delta_n)|n\rangle$ has no component in the 'direction' $|n^{(0)}\rangle$.

- consider the operator $\phi_n^{(0)} \equiv 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|$

  with properties $\phi_n^{(0)} |k^{(0)}\rangle = (1 - \delta_{nk})|k^{(0)}\rangle \qquad (\phi_n^{(0)}|n^{(0)}\rangle = 0)$

Clearly $\dfrac{1}{E_n^{(0)} - H_0} \phi_n^{(0)} = \sum_{k \neq n} \dfrac{1}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle\langle k^{(0)}|$ which is finite provided there are no degeneracies.

- notice that $(\lambda V - \Delta_n)|n\rangle = \phi_n^{(0)} (\lambda V - \Delta_n)|n\rangle$

then from A we should be able to write $|n\rangle = \dfrac{1}{E_n^{(0)} - H_0} \phi_n^{(0)} (\lambda V - \Delta_n)|n\rangle$?

but this can't be correct since as $\lambda \to 0$ $\quad \to 0$ when it should $\to |n^{(0)}\rangle$

We haven't written the most general solution which would be

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

which is still a solution of A because $(E_n^{(0)} - H_0)|n^{(0)}\rangle = 0$.

we will deal with proper normalisation later & for now set $c_n(\lambda) = 1$

Also note that $\phi_n^{(0)}$ commutes with the operator $\dfrac{1}{E_n^{(0)} - H_0}$

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

(in the temporary normalisation $\langle n^{(0)}|n\rangle = 1$)

Our approximate solution is to solve these two equations as a power series in λ:

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

Substituting in: $O(\lambda^0)$: $|n^{(0)}\rangle = |n^{(0)}\rangle$

$$O(\lambda^1): \; |n^{(1)}\rangle = \frac{\phi_n^{(0)}}{E_n^{(0)} - H_0}\cdot\left(V - \Delta_n^{(1)}\right)|n^{(0)}\rangle \qquad \& \quad \underline{\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle}$$

$$O(\lambda^2): \; |n^{(2)}\rangle = \frac{\phi_n^{(0)}}{E_n^{(0)} - H_0}(V - \Delta_n^{(1)})|n^{(1)}\rangle + \frac{\phi_n^{(0)}}{E_n^{(0)} - H_0}(-\Delta_n^{(2)})|n^{(0)}\rangle \qquad \& \quad \Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle$$

$\vdots$

$$O(\lambda^N) \qquad \Delta_n^{(N)} = \langle n^{(0)}|V|n^{(N-1)}\rangle$$

$\vdots$

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

(since $\Delta_n^{(1)}$ is just a number)

$$\Rightarrow \Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle = \underline{\langle n^{(0)}|\,V\frac{\phi_n^{(0)}}{E_n^{(0)} - H_0}V\,|n^{(0)}\rangle}$$

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

and we can continue in this manner to an 'order' of perturbation theory:

$$\boxed{\begin{aligned}\Delta_n &\equiv E_n - E_n^{(0)} = \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2\sum_{k\neq n}\frac{|\langle n^{(0)}|V|k^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)\\ |n\rangle &= |n^{(0)}\rangle + \lambda\sum_{k\neq n}\frac{\langle k^{(0)}|V|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}\cdot|k^{(0)}\rangle + \lambda^2\cdot\sum_{k\neq n}\left(\sum_{\ell\neq n}\frac{\langle k^{(0)}|V|\ell^{(0)}\rangle\langle \ell^{(0)}|V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_\ell^{(0)})} - \frac{\langle n^{(0)}|V|n^{(0)}\rangle\langle k^{(0)}|V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})^2}\right)|k^{(0)}\rangle + O(\lambda^3)\end{aligned}}$$

Some basic properties :

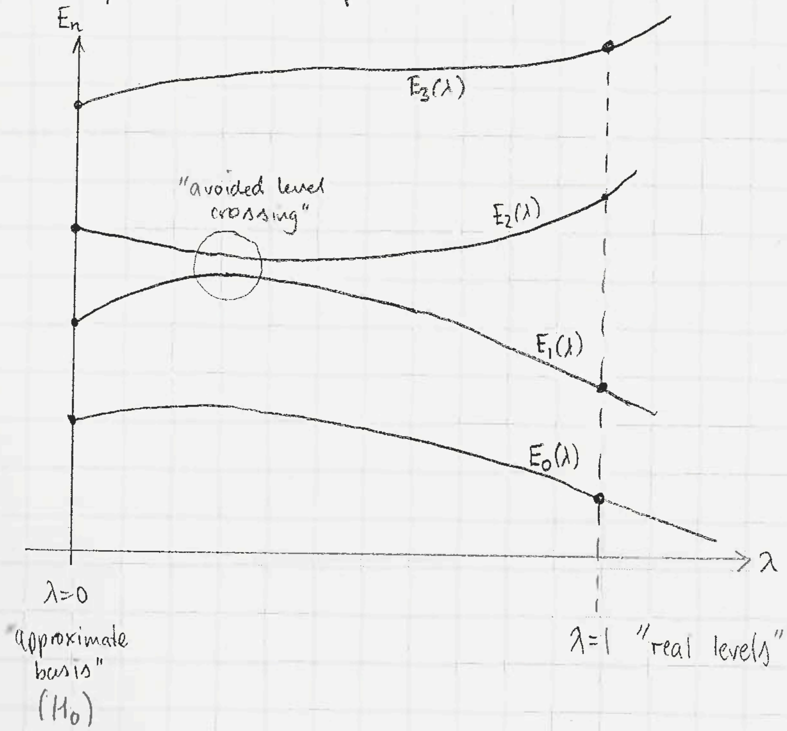
$$* \text{ ground state } \quad \Delta_{n=0} = \underbrace{\lambda \langle 0^{(0)} | V | 0^{(0)} \rangle}_{\text{either } \pm} + \lambda^2 \sum_{k>0} \frac{\overbrace{|\langle 0^{(0)} | V | k^{(0)} \rangle|^2}^{\text{positive or zero}}}{\underbrace{E_0^{(0)} - E_k^{(0)}}_{\text{negative}}} + O(\lambda^3)$$

So the first order correction can either increase or decrease the ground state energy, but the second order correction always reduces it

$$* \; n^{th} \text{ state} \quad \Delta_n^{(2)} = \underbrace{-\sum_{k>n} \frac{|\langle n^{(0)} | V | k^{(0)} \rangle|^2}{E_k^{(0)} - E_n^{(0)}}}_{\substack{\text{levels above } n \\ \text{"push down"}}} + \underbrace{\sum_{k<n} \frac{|\langle n^{(0)} | V | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}}_{\substack{\text{levels below } n \\ \text{"push up"}}}$$

in general, two levels, (n, k) with non-zero matrix element $\langle n^{(0)} | V | k^{(0)} \rangle$ will never cross (energy denominator would diverge!)

Sketch of plausible λ-dependence :



e.g. one dimensional harmonic oscillator in an electric field:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 + q\mathcal{E}x$$

$F = -\frac{dV}{dx} = -q\mathcal{E}$ ⇒ uniform electric field in the -ve x direction

Since we know how to solve the harmonic oscillator problem it makes sense to split the hamiltonian as

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

$$V = q\mathcal{E}x.$$ (we will leave $\lambda = 1$ throughout)

We found that a very easy way to deal with the HO is to use an operator method

$$a = \sqrt{\frac{m\omega}{2\hbar}}\, x - i\frac{1}{\sqrt{2m\hbar\omega}}\, p \quad \Rightarrow \quad H_0 = \hbar\omega(a^\dagger a + \tfrac{1}{2})$$

$$[a, a^\dagger] = 1 \qquad H_0|n\rangle = E_n^{(0)}|n\rangle, \quad E_n^{(0)} = \hbar\omega(n + \tfrac{1}{2})$$

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^\dagger)$$

$$\langle m|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right)$$

FIRST ORDER

$$\Rightarrow \Delta_n^{(1)} = \langle n|V|n\rangle = q\mathcal{E}\langle n|x|n\rangle = \underline{0}$$ no first order energy shift

$$|n^{(1)}\rangle = \sum_{k\neq n}\frac{\langle k^{(0)}|V|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle = q\mathcal{E}\sum_{k\neq n}\sqrt{\frac{\hbar}{2m\omega}}\,\frac{\sqrt{n}\,\delta_{k,n-1} + \sqrt{n+1}\,\delta_{k,n+1}}{\hbar\omega(n-k)}|k^{(0)}\rangle$$

$$|n^{(1)}\rangle = \frac{q\mathcal{E}}{\sqrt{2m\hbar\omega^2}}\left(\sqrt{n}\,|(n-1)^{(0)}\rangle - \sqrt{n+1}\,|(n+1)^{(0)}\rangle\right)$$

neighbouring states are mixed in at first order (for this system)

SECOND ORDER

$$\Delta_n^{(2)} = \sum_{k\neq n}\frac{|\langle n^{(0)}|V|k^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} = q^2\mathcal{E}^2\frac{\cancel{\hbar}}{2m\omega}\frac{1}{\cancel{\hbar}\omega}\sum_{k\neq n}\frac{1}{n-k}\left|\sqrt{n}\,\delta_{k,n-1} + \sqrt{n+1}\,\delta_{k,n+1}\right|^2$$

$$= \frac{q^2\mathcal{E}^2}{2m\omega^2}\sum_k\frac{1}{n-k}\left(n\,\delta_{k,n-1} + (n+1)\,\delta_{k,n+1}\right) = \frac{q^2\mathcal{E}^2}{2m\omega^2}\left(\frac{n}{1} + \frac{n+1}{-1}\right) = \underline{-\frac{q^2\mathcal{E}^2}{2m\omega^2}}$$

energy shift is uniform for all levels in this system.

$$|n^{(2)}\rangle = \sum_{k\neq n}\left(\sum_{\ell\neq n}\frac{\langle k^{(0)}|V|\ell^{(0)}\rangle\langle \ell^{(0)}|V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_\ell^{(0)})} - \frac{\langle n^{(0)}|V|n^{(0)}\rangle\langle k^{(0)}|V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})^2}\right)|k^{(0)}\rangle$$

$$= \sum_{k\neq n}\left(\sum_{\ell\neq n}\frac{q^2\mathcal{E}^2}{(\hbar\omega)^2}\cdot\frac{\hbar}{2m\omega}\cdot\frac{1}{n-k}\,\frac{1}{n-\ell}\left(\sqrt{\ell}\,\delta_{k,\ell-1} + \sqrt{\ell+1}\,\delta_{k,\ell+1}\right)\left(\sqrt{n}\,\delta_{\ell,n-1} + \sqrt{n+1}\,\delta_{\ell,n+1}\right) - 0\right)|k^{(0)}\rangle$$

$$|n^{(2)}\rangle = \frac{q^2\mathcal{E}^2}{2\hbar m\omega^3}\sum_{k\neq n}\sum_{l\neq n}\frac{1}{n-k}\frac{1}{n-l}\left(\sqrt{l}\,\delta_{k,l-1}+\sqrt{l+1}\,\delta_{k,l+1}\right)\left(\sqrt{n}\,\delta_{l,n-1}+\sqrt{n+1}\,\delta_{l,n+1}\right)|k^{(0)}\rangle$$

$$= \frac{q^2\mathcal{E}^2}{2\hbar m\omega^3}\sum_{k\neq n}\Big(\frac{1}{n-k}\frac{1}{1}\left(\sqrt{n-1}\,\delta_{k,n-2}+\sqrt{n}\,\delta_{k,n}\right)\sqrt{n}$$

$$+\frac{1}{n-k}\frac{1}{(-1)}\left(\sqrt{n+1}\,\delta_{k,n}+\sqrt{n+2}\,\delta_{k,n+2}\right)\sqrt{n+1}\Big)|k^{(0)}\rangle$$

$$= \frac{q^2\mathcal{E}^2}{2\hbar m\omega^3}\left(\frac{1}{2}\sqrt{n(n-1)}\,|(n-2)^{(0)}\rangle - \frac{1}{(-2)}\sqrt{(n+1)(n+2)}\,|(n+2)^{(0)}\rangle\right)$$

$$|n^{(2)}\rangle = \frac{q^2\mathcal{E}^2}{4\hbar m\omega^3}\left(\sqrt{n(n-1)}\,|(n-2)^{(0)}\rangle + \sqrt{(n+1)(n+2)}\,|(n+2)^{(0)}\rangle\right)$$

in second order, next-to neighbouring states get mixing in.
(for this system)

In fact this system can be solved exactly:

$$H = \frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2+q\mathcal{E}x = \frac{p^2}{2m}+\frac{1}{2}m\omega^2\left(x+\frac{q\mathcal{E}}{m\omega^2}\right)^2-\frac{q^2\mathcal{E}^2}{2m\omega^2}$$

define $\tilde{x} = x+\frac{q\mathcal{E}}{m\omega^2}$; $\tilde{p}=p$

& $E_n = \hbar\omega(n+\frac{1}{2})-\frac{q^2\mathcal{E}^2}{2m\omega^2}$ $\xrightarrow{\text{expand in powers of } \mathcal{E}}$ $\left.\begin{array}{l}\Delta^{(1)}=0\\ \Delta^{(2)}=-\frac{q^2\mathcal{E}^2}{2m\omega^2}\\ \Delta^{(n>2)}=0\end{array}\right\}$ agrees with our p.t. result.

Consider e.g. the ground state wavefunction $\psi_0(\tilde{x}) = N e^{-\frac{m\omega}{2\hbar}\tilde{x}^2}$

$$\psi_0(x) = N e^{-\frac{m\omega}{2\hbar}\left(x+\frac{q\mathcal{E}}{m\omega^2}\right)^2}$$

expanding in powers of $\mathcal{E}$: $\psi_0(x) = N e^{-\frac{m\omega}{2\hbar}x^2}\cdot\left(e^{-\frac{m\omega}{2\hbar}\frac{q^2\mathcal{E}^2}{m^2\omega^4}}\right)\left(1-\frac{2q\mathcal{E}}{2\hbar\omega}x+\frac{1}{2}\frac{2q^2\mathcal{E}^2}{2\hbar^2\omega^2}x^2+\dots\right)$

$$\psi_0(x)\propto e^{-\frac{m\omega x^2}{2\hbar}}-\frac{q\mathcal{E}}{\hbar\omega}xe^{-\frac{m\omega x^2}{2\hbar}}+\frac{q^2\mathcal{E}^2}{\hbar m\omega^3}\left(\frac{m\omega}{\hbar}x^2-\frac{1}{2}\right)e^{-\frac{m\omega}{2\hbar}x^2}+\dots \quad \text{(A)}$$

compare with the p.t. result:

$$\langle x|0^{(1)}\rangle = \frac{-q\mathcal{E}}{\sqrt{2m\hbar\omega^2}}\langle x|1^{(0)}\rangle = \frac{-q\mathcal{E}}{\sqrt{2m\hbar\omega^2}}\cdot\left(\frac{1}{\sqrt{2}}\cdot e^{-\frac{m\omega}{2\hbar}x^2}\,2\sqrt{\frac{m\omega}{\hbar}}x\right)\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

overall normalisation

$$\frac{\langle x|0^{(1)}\rangle}{\langle x|0^{(0)}\rangle} = -\frac{q\mathcal{E}}{\hbar\omega}x$$ in agreement with (A)

Second order also agrees if we're careful about normalisation.

e.g. gx^4 anharmonic correction to HO:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 + gx^4 \quad \to \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 + gx^4\right)\psi = E\psi$$

make our lives easier (and save ink) by changing to dimensionless variable, z:

$$x = \alpha z \quad \Rightarrow \quad \left(-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{dz^2} + \frac{1}{2}m\omega^2\alpha^2 z^2 + g\alpha^4 z^4\right)\psi = E\psi$$

$$\left(-\frac{d^2}{dz^2} + \frac{m^2\omega^2\alpha^4}{\hbar^2}z^2 + \frac{2mg\alpha^6}{\hbar^2}z^4\right)\psi = \frac{2m\alpha^2}{\hbar^2}E\,\psi$$

choose $\alpha^4 = \frac{\hbar^2}{m^2\omega^2} \Rightarrow \alpha = \frac{\sqrt{\hbar}}{\sqrt{m\omega}}$ & $\boxed{(p_z^2 + z^2 + \bar{g}z^4)\psi = \varepsilon\psi}$

$$\bar{g} = \hbar^3\frac{2mg}{\hbar^2 m^3\omega^3} = \frac{2g}{m^2\omega^3}\hbar$$

$$E = \frac{\hbar^2\varepsilon}{2m\alpha^2} = \hbar\frac{m\omega}{2m}\varepsilon = \frac{1}{2}\hbar\omega\cdot\varepsilon$$

We can approach the solution using the operator method, but for variety let's try using wavefunctions:

$$H_0 = p_z^2 + z^2 \quad ; \quad V = \bar{g}z^4$$

$$\varepsilon_n^{(0)} = 2n+1$$

$$\phi_n^{(0)}(z) = \pi^{-1/4}\frac{1}{\sqrt{2^n n!}}H_n(z)e^{-z^2/2}$$

FIRST ORDER:

$$\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle = \int_{-\infty}^{\infty}dz\ \phi_n^{(0)*}(z)\,\bar{g}z^4\cdot\phi_n^{(0)}(z)$$

e.g. ground state $\langle 0^{(0)}|V|0^{(0)}\rangle = \frac{\bar{g}}{\sqrt{\pi}}\int_{-\infty}^{\infty}dz\ z^4e^{-z^2} = \frac{\bar{g}}{\sqrt{\pi}}\cdot\frac{3}{4}\sqrt{\pi} = \underline{\frac{3}{4}\bar{g}}$

first excited state $\langle 1^{(0)}|V|1^{(0)}\rangle = \frac{\bar{g}}{\sqrt{\pi}}\cdot\frac{1}{2}\int_{-\infty}^{\infty}dz\ z^4\cdot(2z)^2e^{-z^2} = \frac{2\bar{g}}{\sqrt{\pi}}\int_{-\infty}^{\infty}dz\ z^6e^{-z^2} = \underline{\frac{15}{4}\bar{g}}$

⋮

$$|n^{(1)}\rangle = \sum_{k\neq n}\frac{\langle k^{(0)}|V|n^{(0)}\rangle}{\varepsilon_n^{(0)} - \varepsilon_k^{(0)}}|k^{(0)}\rangle \Rightarrow \phi_n^{(1)}(z) = \sum_{k\neq n}\frac{\int_{-\infty}^{\infty}dz\ \phi_k^{(0)*}V\phi_n^{(0)}}{\varepsilon_n^{(0)} - \varepsilon_k^{(0)}}\cdot\phi_k^{(0)}(z)$$

e.g. ground state $\phi_0^{(1)}(z) = \sum_{k\neq 0}\frac{1}{2(0-k)}\phi_k^{(0)}(z)\cdot\frac{\bar{g}}{\sqrt{\pi}}\cdot\frac{1}{\sqrt{2^k k!}}\underbrace{\int_{-\infty}^{\infty}dz\ z^4\cdot H_k(z)e^{-z^2}}_{I_k}$

$I_k = \int_{-\infty}^{\infty}dz\ z^4 H_k(z)e^{-z^2}$? N.B. the Hermite polynomials are orthogonal on the metric e^{-z^2}

$$\int_{-\infty}^{\infty}dz\ H_n(z)H_m(z)e^{-z^2} = \delta_{nm}2^n n!\sqrt{\pi}$$

$\Rightarrow$ expand z^4 as a sum of Hermite polynomials: $z^4 = \sum_m C_m H_m(z)$

This is easily done by inspection: $H_4(z) = 16z^4 - 48z^2 + 12$

$H_2(z) = 4z^2 - 2$

$H_0(z) = 1$

$\left.\begin{array}{l} \\ \\ \end{array}\right\}$ $H_4(z) + 12H_2(z) = 16z^4 - 12$

$\Rightarrow H_4(z) + 12H_2(z) + 12H_0(z) = 16z^4$

$$z^4 = \frac{1}{16} H_4(z) + \frac{3}{4} H_2(z) + \frac{3}{4} H_0(z)$$

then
$$I_k = \frac{1}{16}\int_{-\infty}^{\infty} dz\, H_4(z) H_k(z) e^{-z^2} + \frac{3}{4}\int_{-\infty}^{\infty} dz\, H_2(z) H_k(z) e^{-z^2} + \frac{3}{4}\int_{-\infty}^{\infty} dz\, H_0(z) H_k(z) e^{-z^2}$$

$$= \frac{1}{16}\delta_{k4}\cdot 16\, 4!\sqrt{\pi} + \frac{3}{4}\delta_{k2}\, 4.2!\sqrt{\pi} + \frac{3}{4}\delta_{k0}\sqrt{\pi}$$

$$I_k = \sqrt{\pi}\left(4!\,\delta_{k4} + 3!\,\delta_{k2} + 3/4\,\delta_{k0}\right)$$

$$\Rightarrow \phi_0^{(1)}(z) = \sum_{k\neq 0} \frac{-1}{2k} \phi_k^{(0)}(z) \frac{\bar{g}}{\sqrt{2^k k!}} \cdot \left(4!\,\delta_{k4} + 3!\,\delta_{k2} + \frac{3}{4}\delta_{k0}\right)$$

$$= -\bar{g}\left(\phi_4^{(0)}(z)\frac{\sqrt{4!}}{4.8} + \phi_2^{(0)}(z)\cdot\frac{3!}{4\,2\sqrt{2!}}\right) = -\bar{g}\left(\frac{\sqrt{6}}{16}\phi_4^{(0)}(z) + \frac{3}{4\sqrt{2}}\phi_2^{(0)}(z)\right)$$

$\Rightarrow$ up to first order the ground state wavefunction is approximated by

$$\phi_0(z) \simeq \phi_0^{(0)}(z) - \bar{g}\frac{\sqrt{3}}{4\sqrt{2}}\phi_2^{(0)}(z) - \bar{g}\frac{\sqrt{3}}{8\sqrt{2}}\phi_4^{(0)}(z)$$

SECOND ORDER:

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

e.g. ground state
$$\Delta_0^{(2)} = \sum_{k\neq 0} \frac{1}{2(0-k)} \left|\frac{\bar{g}}{\sqrt{\pi}}\cdot\frac{1}{\sqrt{2^k k!}} I_k\right|^2$$

$$= \sum_{k\neq 0} \frac{-\bar{g}^2}{2k}\left|\frac{\sqrt{4!}}{4}\delta_{k4} + \frac{3!}{2\sqrt{2}}\delta_{k2}\right|^2$$

$$= -\frac{\bar{g}^2}{8}\frac{4!}{16} - \frac{\bar{g}^2}{4}\frac{(3!)^2}{8} = -\frac{21}{16}\bar{g}^2$$

$\Rightarrow$ up to second order $\mathcal{E}_0 = 1 + \frac{3}{4}\bar{g} - \frac{21}{16}\bar{g}^2$

converting back to dimensionful units

$$E_0 = \frac{1}{2}\hbar\omega\cdot\mathcal{E}_0 = \frac{1}{2}\hbar\omega + \frac{3}{8}\hbar\omega\left(\frac{2g\hbar}{m^2\omega^3}\right) - \frac{21}{32}\hbar\omega\left(\frac{2g\hbar}{m^2\omega^3}\right)^2$$

$$= \frac{1}{2}\hbar\omega + \frac{3}{4}\cdot\frac{g\hbar^2}{m^2\omega^2} - \frac{21}{8}\frac{g^2\hbar^3}{m^4\omega^5} + O(g^3)$$

The perturbative expansion with H_0 degenerate

If there are degeneracies in the spectrum of H_0, we clearly cannot safely apply our perturbative formulae, e.g.

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

if any of the states $|k^{(0)}\rangle$ are degenerate with $|n^{(0)}\rangle$ & the matrix element $\langle n^{(0)} | V | k^{(0)} \rangle$ is non-zero, this correction to the energy diverges.

Let's consider a simple system that demonstrates the problem when eigenstates of H_0 are degenerate.

$$\underline{H} = \begin{bmatrix} 0 & g & g \\ g & 0 & g \\ g & g & \varepsilon \end{bmatrix}$$

– this system can be solved exactly by finding the eigenvalues & eigenvectors

$$\det(\underline{H} - E\underline{\underline{I}}) = 0 \quad \longrightarrow \quad E = \begin{cases} -g \\ \frac{1}{2}\left(\varepsilon + g \pm \sqrt{\varepsilon^2 - 2\varepsilon g + 9g^2}\right) \end{cases}$$

now consider the expansion in powers of g that we'd hope to reproduce using perturbation theory:

$$E \simeq \begin{cases} -g \\ +g - \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3) \\ \varepsilon + \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3) \end{cases} \quad \text{(A)}$$

Now split H as follows: $H_0 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \varepsilon \end{bmatrix}$; $V = \begin{bmatrix} 0 & g & g \\ g & 0 & g \\ g & g & 0 \end{bmatrix}$

So the eigenstates of H_0 are

$$|0^{(0)}\rangle \sim \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \text{ with } E_0^{(0)} = 0$$

$$|1^{(0)}\rangle \sim \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \text{ with } E_1^{(0)} = 0$$

$\Big\}$ degenerate

$$|2^{(0)}\rangle \sim \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \text{ with } E_2^{(0)} = \varepsilon$$

at first order in p.t.

$$\Delta_0^{(1)} = \langle 0^{(0)} | V | 0^{(0)} \rangle = V_{11} = 0$$

$$\Delta_1^{(1)} = \langle 1^{(0)} | V | 1^{(0)} \rangle = V_{22} = 0$$

$$\Delta_2^{(1)} = \langle 2^{(0)} | V | 2^{(0)} \rangle = V_{33} = 0$$

but notice in the exact solution (A) that the levels which $\rightarrow E_{0,1}^{(0)} = 0$ have terms linear in g which can only occur in first order p.t. !

Consider the exact eigenvectors expanded in powers of g:

n	E_n	$\|n\rangle$
0	$-g$	$\frac{1}{\sqrt{2}}(\|0^{(0)}\rangle - \|1^{(0)}\rangle)$
1	$+g - \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3)$	$\frac{1}{\sqrt{2}}(\|0^{(0)}\rangle + \|1^{(0)}\rangle) + \mathcal{O}(g)\|2^{(0)}\rangle$
2	$\varepsilon + \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3)$	$\|2^{(0)}\rangle + \mathcal{O}(g)\frac{1}{\sqrt{2}}(\|0^{(0)}\rangle + \|1^{(0)}\rangle)$

& here is the problem. As $g \to 0$, the exact solution $|0\rangle \not\to |0^{(0)}\rangle$, but rather a certain linear combination of the degenerate states, namely $|0^{(0)}\rangle - |1^{(0)}\rangle$. We built our perturbative solution around the fact that $|n\rangle \xrightarrow[\lambda\to 0]{} |n^{(0)}\rangle$ which is violated for degenerate states.

The trick here is to find the linear combination of degenerate states such that $\langle \tilde{n}^{(0)}|V|\tilde{m}^{(0)}\rangle = 0 \;\; \forall\, \tilde{n} \neq \tilde{m}$. Since there will only ever be a finite # of degenerate states we can do this exactly, e.g.

$$\underline{\underline{H}} = \begin{pmatrix} \begin{bmatrix} 0 & g \\ g & 0 \end{bmatrix} & \begin{matrix} g \\ g \end{matrix} \\ \begin{matrix} g & g \end{matrix} & \varepsilon \end{pmatrix}$$

degenerate subspace $\{|0^{(0)}\rangle, |1^{(0)}\rangle\}$

diagonalise this $\Rightarrow$ solve $\underline{h}\,\underline{\psi} = e\,\underline{\psi}$

$\det(\underline{h} - e\underline{1}) = 0 \;\rightarrow$

$$e = \begin{cases} +g & \frac{1}{\sqrt{2}}(|0^{(0)}\rangle + |1^{(0)}\rangle) \equiv |+^{(0)}\rangle \\ -g & \frac{1}{\sqrt{2}}(|0^{(0)}\rangle - |1^{(0)}\rangle) \equiv |-^{(0)}\rangle \end{cases}$$

use the $|+^{(0)}\rangle, |-^{(0)}\rangle, |2^{(0)}\rangle$ basis as our zeroth order states

$$\begin{bmatrix} |+^{(0)}\rangle \\ |-^{(0)}\rangle \\ |2^{(0)}\rangle \end{bmatrix} = \underbrace{\begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{U} \begin{bmatrix} |0^{(0)}\rangle \\ |1^{(0)}\rangle \\ |2^{(0)}\rangle \end{bmatrix}$$

$\Rightarrow$ transform $H' = U^{\dagger} H U$

$$H' = \begin{array}{cc} & \begin{matrix} + & - & 2 \end{matrix} \\ & \begin{bmatrix} g & 0 & \sqrt{2}g \\ 0 & -g & 0 \\ \sqrt{2}g & 0 & \varepsilon \end{bmatrix} \end{array} \begin{matrix} + \\ - \\ 2 \end{matrix}$$

now split H': $H_0 = \begin{bmatrix} g & 0 & 0 \\ 0 & -g & 0 \\ 0 & 0 & \varepsilon \end{bmatrix}$ & $V = \begin{bmatrix} 0 & 0 & \sqrt{2}g \\ 0 & 0 & 0 \\ \sqrt{2}g & 0 & 0 \end{bmatrix}$

& perform standard perturbation theory

e.g. $$E_+ = E_+^{(0)} + \Delta_+^{(1)} + \Delta_+^{(2)} + \ldots = g + \langle +^{(0)}|V|+^{(0)}\rangle + \sum_{k\neq +} \frac{|\langle +^{(0)}|V|k^{(0)}\rangle|^2}{g - E_k^{(0)}} + \ldots$$

$$= g + 0 + \frac{2g^2}{g-\varepsilon} \simeq \underline{g - 2g^2/\varepsilon + \mathcal{O}(g^3)}$$

$$|+\rangle = |+^{(0)}\rangle + \sum_{k\neq +} \frac{\langle k^{(0)}|V|+^{(0)}\rangle}{g - E_k^{(0)}}|k^{(0)}\rangle + \ldots = \underline{\frac{1}{\sqrt{2}}(|0^{(0)}\rangle + |1^{(0)}\rangle) - \sqrt{2}\frac{g}{\varepsilon}|2^{(0)}\rangle + \mathcal{O}(g^2)}$$

Degenerate Pert. Thy - Formal construction

The effect of the perturbation on any non-degenerate level can be computed using the conventional perturbation theory, but the effect on degenerate states must be computed separately.

Suppose we have a Hamiltonian, H_0, whose eigenstates $\{|n^{(0)}\rangle\}$ are non-degenerate, except for a set of states $\{|m^0\rangle\}$ that all have a common energy $E_D^{(0)}$.

We can define an operator $P \equiv \sum_{m \in D} |m^{(0)}\rangle\langle m^{(0)}|$, which projects out only

the degenerate states : $P|n^{(0)}\rangle = 0$ if $n \notin D$
$= |n^{(0)}\rangle$ if $n \in D$

& similarly the complement operator $Q = 1 - P = \sum_{k \notin D} |k^{(0)}\rangle\langle k^{(0)}|$, which project out

only the non-degenerate states : $Q|n^{(0)}\rangle = 0$ if $n \in D$
$= |n^{(0)}\rangle$ if $n \notin D$

It is easy to see that $P^2 = P$, $Q^2 = Q$, $PQ = 0$, $QP = 0$. $\quad \underline{P + Q = 1}$

Consider the system to be solved: $(H_0 + \lambda V)|n\rangle = E_n|n\rangle$

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

$\times P$: $(PH_0P + \lambda PVP + PH_0Q + \lambda PVQ)|n\rangle = E_n P|n\rangle$

but when we expand $|n\rangle$ in eigenstates of H_0 we'll have $PH_0Q|m^{(0)}\rangle$
$= E_m^{(0)} PQ|m^{(0)}\rangle = 0$

$\Rightarrow P(E_n - H_0 - \lambda V)P|n\rangle = \lambda PVQ|n\rangle$

the PVP term is the problem, it mixes states within the degenerate subspace.

Remove it by the following refactoring : $\left.\begin{aligned} \bar{H}_0 &= H_0 + \lambda PVP \\ \lambda\bar{V} &= \lambda V - \lambda PVP \end{aligned}\right\} \bar{H}_0 + \lambda\bar{V} = H_0 + \lambda V$

i.e in the basis diagonalising H_0

$$\underline{\underline{H_0}} = \begin{bmatrix} \begin{bmatrix} E_D^{(0)} & 0 & \cdots \\ 0 & E_D^{(0)} & \\ \vdots & & \ddots \end{bmatrix} & \begin{bmatrix} & 0 & \end{bmatrix} \\ \begin{bmatrix} & 0 & \end{bmatrix} & \begin{bmatrix} E_1^{(0)} & 0 & \cdots \\ 0 & E_2^{(0)} & \\ \vdots & & \ddots \end{bmatrix} \end{bmatrix}$$

but $$\underline{\underline{\bar{H}_0}} = \begin{bmatrix} \begin{bmatrix} E_D^{(0)}\underline{\underline{1}} + \lambda\underline{\underline{V}} \end{bmatrix} & \begin{bmatrix} & 0 & \end{bmatrix} \\ \begin{bmatrix} & 0 & \end{bmatrix} & \begin{bmatrix} E_1^{(0)} & 0 & \cdots \\ 0 & E_2^{(0)} & \\ \vdots & & \ddots \end{bmatrix} \end{bmatrix}$$

& $$\underline{\underline{\bar{V}}} = \begin{bmatrix} \begin{bmatrix} 0 \end{bmatrix} & \begin{bmatrix} V \end{bmatrix} \\ \begin{bmatrix} V \end{bmatrix} & \begin{bmatrix} V \end{bmatrix} \end{bmatrix}$$

So $\bar{H}_0$ within the degenerate subspace contains the full perturbation - we will diagonalise this subspace exactly: $\bar{H}_0 |\bar{n}^{(0)}\rangle = \bar{E}_n^{(0)} |\bar{n}^{(0)}\rangle$

$$(H_0 + \lambda V)|n\rangle = (\bar{H}_0 + \lambda \bar{V})|n\rangle = E_n |n\rangle$$

$$= (\bar{H}_0 + \lambda \bar{V})(P+Q)|n\rangle$$

NB $\begin{cases} P\bar{H}_0 Q = 0 \;;\; Q\bar{H}_0 Q = QH_0Q \\ P\bar{V}P = 0 \;; \quad Q\bar{V}Q = QVQ \\ P\bar{V}Q = PVQ \;; \end{cases}$

$$\times P: \quad \boxed{P(E_n - \bar{H}_0)P|n\rangle = \lambda P\bar{V}Q|n\rangle} \quad (A)$$

$$\times Q: \quad \boxed{Q(E_n - \bar{H}_0 - \lambda\bar{V})Q|n\rangle = \lambda Q\bar{V}P|n\rangle}$$

$|n\rangle$ is a level that as $\lambda \to 0 \quad \to$ state in the degenerate set, $P|n^{(0)}\rangle$
so $Q(E_n - \bar{H}_0 - \lambda\bar{V})Q$ should not be singular &

$$Q|n\rangle = Q\frac{\lambda}{E_n - \bar{H}_0 - \lambda\bar{V}} Q\bar{V}P|n\rangle$$

which we can substitute into (A) $\to P(E_n - \bar{H}_0)P|n\rangle = \lambda^2 P\bar{V}Q\dfrac{1}{E_n - \bar{H}_0 - \lambda\bar{V}}Q\bar{V}P|n\rangle$

now if $E_n = \bar{E}_n^{(0)} + \Delta_n \quad \& \quad V_n \equiv P\bar{V}Q\dfrac{1}{E_n - \bar{H}_0 - \lambda V}Q\bar{V}P$

eigenvalue of $\bar{H}_0$

$$\Rightarrow \boxed{P(\bar{E}_n^{(0)} - \bar{H}_0)P|n\rangle = P(\lambda^2 V_n - \Delta_n)P|n\rangle}$$

multiply from the left by a state $\langle\bar{n}^{(0)}|$ (in the degenerate subspace)

$$\boxed{0 = \langle\bar{n}^{(0)}|P(\lambda^2 V_n - \Delta_n)P|n\rangle} \quad (B)$$

which is analogous to what we had in the non-degenerate case

$$\Rightarrow \underbrace{P|n\rangle} = |\bar{n}^{(0)}\rangle + \frac{\phi_n^{(0)}}{\bar{E}_n^{(0)} - \bar{H}_0} P(\lambda^2 V_n - \Delta_n)P|n\rangle \quad (C)$$

that part of $|n\rangle$ in the degenerate subspace

$$\underbrace{Q|n\rangle} = \lambda Q\frac{1}{E_n - \bar{H}_0 - \lambda\bar{V}} Q\bar{V}\left(|\bar{n}^{(0)}\rangle + \frac{\phi_n^{(0)}}{\bar{E}_n^{(0)} - \bar{H}_0} P(\lambda^2 V_n - \Delta_n)P|n\rangle\right) \quad (D)$$

that part of $|n\rangle$ outside the degenerate subspace

So far this is exact. Now consider an expansion in powers of λ:

$$E_n = \bar{E}_n^{(0)} + \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \dots$$

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

in the degenerate subspace

FIRST ORDER:

eqn B to $O(\lambda)$ $\Rightarrow$ $0 = \langle \bar{n}^{(0)} | (-\Delta_n^{(1)}) | \bar{n}^{(0)} \rangle \Rightarrow \underline{\Delta_n^{(1)} = 0}$

the first order shift in the degenerate subspace has already been included by solving $\bar{H}_0 |\bar{n}^{(0)}\rangle = \bar{E}_n^{(0)} |\bar{n}^{(0)}\rangle$

eqn C to $O(\lambda)$ $\Rightarrow$ $P|n^{(1)}\rangle = \dfrac{\phi_n^{(0)}}{\bar{E}_n^{(0)} - \bar{H}_0} P(-\Delta_n^{(1)}) P |\bar{n}^{(0)}\rangle \underline{= 0}$

eqn D to $O(\lambda)$ $\Rightarrow$ $Q|n^{(1)}\rangle = Q \dfrac{1}{\bar{E}_n^{(0)} + \bar{H}_0} Q \bar{V} |\bar{n}^{(0)}\rangle$

$$= \sum_k Q \frac{1}{\bar{E}_n^{(0)} - \bar{H}_0} |k^{(0)}\rangle \underbrace{\langle k^{(0)}|}_{\text{must be outside the deg subspace}} Q \bar{V} |\bar{n}^{(0)}\rangle$$

$$Q|n^{(1)}\rangle = \sum_{k \notin D} |k^{(0)}\rangle \cdot \frac{\langle k^{(0)} | V | \bar{n}^{(0)} \rangle}{\bar{E}_n^{(0)} - E_k^{(0)}}$$

so at first order states outside the deg. subspace get mixed in.

SECOND ORDER:

eqn B to $O(\lambda^2)$ $\Rightarrow$ $0 = \langle \bar{n}^{(0)} | (\bar{V}_n - \Delta_n^{(2)}) P |\bar{n}^{(0)}\rangle + \cancel{\langle \bar{n}^{(0)} | (-\Delta_n^{(1)}) P | n^{(1)} \rangle} \rightarrow 0$

$$\Rightarrow \Delta_n^{(2)} = \langle \bar{n}^{(0)} | \bar{V}_n | \bar{n}^{(0)} \rangle$$

$$\underline{\Delta_n^{(2)} = \sum_{k \notin D} \frac{|\langle \bar{n}^{(0)} | V | k^{(0)} \rangle|^2}{\bar{E}_n^{(0)} - E_k^{(0)}}}$$

second order shift due to states outside the degenerate subspace.

[EXERCISE: use these formulas to compute the effect of the perturbation in the 3-state system considered earlier.]

* The Stark Effect – an "atom" in a uniform electric field

$$H = \underbrace{\frac{\vec{p}^2}{2\mu} - e^2/r}_{H_0} \underbrace{- e|\vec{E}|z}_{V}$$

e.g. effect on the ground state (1S), $E^{(0)}_{1S} = -\dfrac{e^2}{2a_B}$ (a_B = Bohr radius)
(a non-degenerate level)

$$\Delta^{(1)}_{1S} = \langle 1S|(-e|\vec{E}|z)|1S\rangle = -e|\vec{E}|\langle 1S|z|1S\rangle = 0$$

parity even
parity odd

$$\Delta^{(2)}_{1S} = \sum_{k\neq 1S} \frac{|\langle 1S|(-e|\vec{E}|z)|k\rangle|^2}{E^{(0)}_{1S} - E^{(0)}_{k}} = e^2|\vec{E}|^2 \sum_{k\neq 1S} \frac{|\langle 1S|z|k\rangle|^2}{-\frac{e^2}{2a_B} + \frac{e^2}{2a_B}\cdot\frac{1}{k^2}}$$ + positive energy plane wave contributions

$$= -2|\vec{E}|^2 a_B^3 \sum_{k\neq 1S} \frac{|\langle 1S|z/a_B|k\rangle|^2}{1 - 1/k^2} + (\text{+ve energy})$$

$$\left[\begin{array}{c}\langle 1S|z/a_B|k\rangle = \langle 1S|z/a_B|n\,l\,m_l\rangle \\ = 0 \text{ unless } l = P,\ m_l = 0.\end{array}\right]$$

"quadratic ($|\vec{E}|^2$) Stark effect".

e.g. effect on the degenerate 1st excited states $\left(2S,\ 1P\left[\begin{smallmatrix} m=-1 \\ m=0 \\ m=+1\end{smallmatrix}\right]\right)$, $E^{(0)}_D = -\dfrac{e^2}{2a_B}\cdot\dfrac{1}{4}$

in this subspace

$$\underline{\underline{H}} = \begin{array}{cc} & \begin{array}{cccc} 2S & 1P\ m=0 & m=+1 & m=-1 \end{array} \\ \begin{array}{c} 2S \\ 1P\ m=0 \\ m=+1 \\ m=-1 \end{array} & \begin{bmatrix} E^{(0)}_D & \langle 2S|V|{}^{1P}_{m=0}\rangle & 0 & 0 \\ \langle {}^{1P}_{m=0}|V|2S\rangle & E^{(0)}_D & 0 & 0 \\ 0 & 0 & E^{(0)}_D & 0 \\ 0 & 0 & 0 & E^{(0)}_D \end{bmatrix} \end{array}$$

since $\langle n'S|z|nP, m\neq 0\rangle = 0$.

$$\langle 2S|z|1P, m=0\rangle = \int r^2 dr\, d\phi\, d\cos\theta \cdot (r\cos\theta) \cdot 2\left(\frac{1}{2a_B}\right)^{3/2}\left(1 - \frac{r}{2a_B}\right)e^{-r/2a_B} \cdot Y^{0*}_0(\theta,\phi)$$
$$\cdot \frac{1}{\sqrt{3}}\left(\frac{1}{2a_B}\right)^{3/2} \cdot \frac{r}{a_B}\, e^{-r/2a_B} \cdot Y^0_1(\theta,\phi)$$

$\cos\theta = \sqrt{\frac{4\pi}{3}}\, Y^{0*}_1(\theta,\phi)$

$$= \frac{2}{\sqrt{3}}\frac{1}{(2a_B)^3}\sqrt{\frac{4\pi}{3}}\cdot\frac{1}{\sqrt{4\pi}}a_B \underbrace{\int d\Omega\, Y^0_1(\theta,\phi)Y^{0*}_1(\theta,\phi)}_{1} \int_0^\infty r^2 dr \left(\frac{r}{a_B}\right)^2\left(1 - \frac{r}{2a_B}\right)e^{-r/a_B}$$

$(\rho = r/a_B)$

$$= \frac{1}{12}a_B \int_0^\infty \rho^2 d\rho\, \rho^2(1 - \rho/2)e^{-\rho} = \frac{a_B}{12}\left(I_4 - \tfrac{1}{2}I_5\right) = \underline{-3a_B}$$

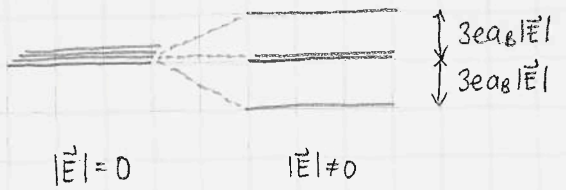
$\left(I_n = \int_0^\infty d\rho\, \rho^n e^{-\rho} = n!\right)$

$$\underline{\langle 2S|V|1P, m=0\rangle = 3ea_B|\vec{E}|}$$

$$\underline{\underline{H}} = \begin{bmatrix} E_D^{(0)} & 3ea_B|\vec{E}| & 0 & 0 \\ 3ea_B|\vec{E}| & E_D^{(0)} & 0 & 0 \\ 0 & 0 & E_D^{(0)} & 0 \\ 0 & 0 & 0 & E_D^{(0)} \end{bmatrix}$$

eigenvalues $E_D^{(0)} \pm 3ea_B|\vec{E}|, \; E_D^{(0)}, \; E_D^{(0)}$

eigenstates $\frac{1}{\sqrt{2}}\left(|2S\rangle \pm |1P, m=0\rangle\right)$ $\quad |1P, m=\pm 1\rangle$



"*linear* Stark effect"
(requires degeneracy)

* The "fine" structure of the hydrogen spectrum – relativistic effects & perturbation theory.

We have considered the hydrogen atom as the bound state of an electron in the Coulomb potential, treating the electron as moving non-relativistically, $K = p^2/2m$.

To have a more accurate description one should in fact consider the effects of relativity – this can be done rather well using the Dirac wave equation, which is beyond the scope of this course. If one considers the expansion of the Dirac equation in powers of $\vec{p}/m$, one obtains a Hamiltonian of the form

$$H = \frac{\vec{p}^2}{2m} - \frac{\vec{p}^4}{8m^3} - e^2/r + \frac{e^2}{2m^2}\frac{\vec{L}\cdot\vec{S}}{r^3} + \ldots \quad \text{(A)}$$

in units where $c = 1$. & $\hbar = 1$

The origin of the $\vec{p}^4$ term is the straightforward expansion of the relativistic kinetic energy:

$$E - mc^2 = \sqrt{m^2c^4 + p^2c^2} - mc^2 = mc^2\left(\sqrt{1 + \frac{p^2}{m^2c^2}} - 1\right) = mc^2\left(\frac{p^2}{2m^2c^2} + \frac{p^4}{8m^4c^4} + \ldots\right)$$

$$= \frac{p^2}{2m} + \frac{p^4}{8m^3c^2} + \ldots \xrightarrow[c=1]{} \frac{p^2}{2m} + p^4/8m^3 + \ldots$$

The $\vec{L}\cdot\vec{S}$ or "spin-orbit" term is due to the interaction of the electron's spin-magnetic moment with the magnetic field seen in its accelerated frame of reference.

From the solution to the Coulomb problem we know that

$$\langle \vec{p}^2 \rangle = 2m\langle H \rangle + 2me^2\left\langle \frac{1}{r} \right\rangle \sim 2mE_N + 2me^2 \cdot \frac{1}{a_B} \sim -\frac{2me^2}{2a_B} + \frac{2me^2}{a_B}$$

$$\sim \frac{me^2}{a_B}$$

so

$$\frac{\langle \vec{p}^4 \rangle}{8m^3} \Big/ \frac{\langle \vec{p}^2 \rangle}{2m} \approx \frac{\langle \vec{p}^2 \rangle}{4m^2} = \frac{e^2}{4ma_B} = \frac{\alpha}{4ma_B}$$

$$\sim \alpha^2/4$$

$$\sim 10^{-5} \quad \Rightarrow \text{kinetic energy correction should be small.}$$

$e^2 = \alpha\hbar c = \alpha$ in $\hbar = 1, c = 1$ units
$a_B = \frac{1}{m\alpha}$ in same units
$ma_B = \frac{1}{\alpha}$

& $\left\langle \frac{1}{r^3} \right\rangle \sim a_B^{-3}$

$$\Rightarrow \frac{\left\langle \frac{e^2}{2m^2}\frac{\vec{L}\cdot\vec{S}}{r^3} \right\rangle}{\langle e^2/r \rangle} \sim \frac{e^2/2m^2a_B^3}{e^2/a_B} \sim \frac{1}{2m^2a_B^2} \sim \alpha^2/2 \sim 10^{-5}$$

$\Rightarrow$ spin-orbit effects should be small

Suggests that a perturbative approach, considering the relativistic effects as perturbations to the Coulomb system, might be fruitful

The presence of the spin operator in Ⓐ forces us to consider the spin state of the electron in the quantum state of the hydrogen atom - a suitable basis would be the direct product state

$$|nlm_l; \tfrac{1}{2} m_s\rangle \equiv |nlm_l\rangle \otimes |\tfrac{1}{2} m_s\rangle$$

with the exception of the spin-orbit term we have $[H, L_z] = [H, L^2] = [H, S_z] = [H, S^2] = 0$

So $n, l, m_l, s=\frac{1}{2}, m_s$ would be good quantum numbers.

On the other hand,

$$[H_{SO}, L^2] = [H_{SO}, S^2] = 0$$

but

$$[H_{SO}, L_z] \neq 0 \qquad [H_{SO}, S_z] \neq 0$$

$$\left[\begin{aligned} &\vec{L}\cdot\vec{S} = L_x S_x + L_y S_y + L_z S_z \\ &\Rightarrow [\vec{L}\cdot\vec{S}, L_z] = S_x [L_x, L_z] + S_y [L_y, L_z] \\ &\qquad = -i\hbar S_x L_y + i\hbar S_y L_x = i\hbar (\vec{L}\times\vec{S})_z \neq 0. \end{aligned} \right.$$

So m_l, m_s are not good quantum numbers with a spin-orbit term.

As such we expect that $\langle \dots m_l' \dots m_s' | \vec{L}\cdot\vec{S} | \dots m_l \dots m_s \rangle \neq 0$

& the perturbation H_{SO} will mix states that are <u>degenerate</u> under H_0. This would appear to require us to use the machinery of degenerate perturbation theory.

Actually we can avoid this by <u>recoupling</u> the $\vec{L}$ & $\vec{S}$ vectors such that the $\vec{L}\cdot\vec{S}$ term is partially diagonalised:

consider coupling $\vec{L}, \vec{S}$ to a total spin, $\vec{J}$: $\vec{J} = \vec{L} + \vec{S}$, then we have a new basis

$$|n, l, s=\tfrac{1}{2}, j, m_j\rangle \longrightarrow \begin{array}{lcccc} \text{eigenvector of :} & L^2 & S^2 & J^2 & J_z \\ \text{with eigenvalue :} & l(l+1)\hbar^2 & s(s+1)\hbar^2 & j(j+1)\hbar^2 & m_j\hbar \end{array}$$

the relation to the old basis is by Clebsch-Gordan coefficients:

$$|n, l, s=\tfrac{1}{2}, j, m_j\rangle = \sum_{m_l m_s} \langle l m_l ; \tfrac{1}{2} m_s | j m_j \rangle \, |nlm_l; \tfrac{1}{2} m_s\rangle \qquad (m_j = m_l + m_s)$$

notice that $J^2 = (\vec{L}+\vec{S})^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S} \Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$

& $|n, l, s=\frac{1}{2}, j, m_j\rangle$ is an eigenstate of $\vec{L}\cdot\vec{S}$ with eigenvalue $\frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - 3/4\right)$

$$\Rightarrow \langle n l' \tfrac{1}{2} j' m_j' | \vec{L}\cdot\vec{S} | n l \tfrac{1}{2} j m_j \rangle = \delta_{ll'} \delta_{jj'} \underbrace{\delta_{m_j m_j'}}_{} \cdot \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - 3/4\right)$$

↳ so degenerate m_j states are <u>not</u> mixed by $\vec{L}\cdot\vec{S}$.

Using this basis we avoid the need for degenerate p.t.

TIME-DEPENDENT POTENTIALS

In the first semester we found it easy to show that for systems where the Hamiltonian does not explicitly contain time-dependence, $H \neq fn(t)$, the time evolution operator is,

$$U(t,t_0) = e^{-iH(t-t_0)/\hbar}$$

When the Hamiltonian is dependent on time (say we're adjusting the strength of an external magnetic field), matters are not so simple.
We can help ourselves by separating the Hamiltonian into two terms, one containing all the time-independent pieces & one contain the time-dependence:

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

We know that in the Schrodinger picture, states will have time-dependence even just from H_0, e.g. the eigenstates of H_0:

$$|n;t\rangle = e^{-iE_nt/\hbar}|n\rangle.$$

Suppose we express an arbitrary state $|\alpha\rangle$ in terms of the eigenstates of H_0:

$$|\alpha\rangle = \sum_n c_n(0)|n\rangle, \text{ then } |\alpha;t\rangle = \sum_n c_n(t)\, e^{-iE_nt/\hbar}|n\rangle.$$

Notice that we have two sources of time-dependence - the $e^{-iE_nt/\hbar}$ which would be there even if $V(t)=0$ & the $c_n(t)$ whose time-dependence is entirely due to $V(t)$. We can show that the $c_n(t)$ satisfy simple differential equations.

We can formalise this separation of H_0 & $V(t)$ in the "interaction" or "Dirac" picture:

define the "interaction picture" state by $|\alpha,t_0;t\rangle_I = e^{+iH_0t/\hbar}|\alpha,t_0;t\rangle_S$

(where the time-dependence of the Schrödinger state in the Hamiltonian $H = H_0 + V(t)$ isn't yet known)

consider observables: ${}_I\langle\beta,t_0;t|A_I|\alpha,t_0;t\rangle_I = {}_S\langle\beta,t_0;t|A_S|\alpha,t_0;t\rangle_S$

$$= {}_S\langle\alpha,t_0;t|e^{-iH_0t/\hbar}A_I\, e^{iH_0t/\hbar}|\alpha,t_0;t\rangle_S$$

$$\Rightarrow A_I = e^{+iH_0t/\hbar}A_S\, e^{-iH_0t/\hbar} \quad \text{\& especially } V_I(t) = e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}$$

N.B. this is not the same as the Heisenberg picture since we are not putting the whole of H into the exponent, just the time-independent piece.

consider $i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I = i\hbar \frac{\partial}{\partial t}\left(e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S\right)$

$$= -H_0 e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S + e^{iH_0 t/\hbar} \left(i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_S\right)$$

Schrödinger eqn
$H|\alpha, t_0, t\rangle_S = (H_0 + V(t))|\alpha, t_0; t\rangle_S$

$$= e^{iH_0 t/\hbar} V(t) |\alpha, t_0; t\rangle_S = e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} |\alpha, t_0; t\rangle_S$$

$$\Rightarrow \boxed{i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I = V_I |\alpha, t_0; t\rangle_I} \quad (A)$$

now consider expanding $|\alpha, t_0; t\rangle_I$ in the eigenkets of H_0 : $H_0|n\rangle = E_n|n\rangle$

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

$\langle n| \times (A) \Rightarrow$ $i\hbar \frac{\partial}{\partial t} \langle n|\alpha, t_0, t\rangle_I = \sum_m \langle n|V_I|m\rangle\langle m|\alpha, t_0; t\rangle_I$ $\quad (t_0 = 0)$

$$\Rightarrow i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_m \langle n| e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} |m\rangle c_m(t)$$

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

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

set of coupled differential equations to be solved for $c_n(t)$

The complication here is that we can't solve these for arbitrary time-dependence in $V_{nm}(t)$. We'll find that the best we can usually do is an approximate perturbative expansion in $V_{nm}(t)$.

However there is one exactly solvable system that it is worth us working out – two states coupled by a sinusoidal potential.

Consider the two-state problem described by the Hamiltonian matrix

$$\underline{\underline{H}} = \begin{bmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & E_2 \end{bmatrix}$$ where $E_2 > E_1$ & γ, ω are real & positive

$$\Rightarrow \underline{\underline{H}}_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \quad \& \quad \underline{\underline{V}}(t) = \begin{bmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{bmatrix}$$

Suppose that initially we are in the eigenstate of $\underline{H}_0$ of energy E_1, $|1\rangle \sim \begin{bmatrix} 1 \\ 0 \end{bmatrix}$,

then $c_1(0)=1$, $c_2(0)=0$. This is the initial condition to be applied to the solution of

$$i\hbar \frac{d}{dt}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 & \gamma e^{i\omega t} e^{i\omega_{12} t} \\ \gamma e^{-i\omega t} e^{i\omega_{21} t} & 0 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$\omega_{12} = (E_1 - E_2)/\hbar$

$\omega_{21} = -\omega_{12} > 0$

$$= \gamma \begin{bmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$\Rightarrow \quad i\hbar \frac{d}{dt} c_1 = \gamma e^{i\Delta\omega t} c_2 \quad \& \quad i\hbar \frac{d}{dt} c_2 = \gamma e^{-i\Delta\omega t} c_1$$

$$i\hbar e^{-i\Delta\omega/2\, t} \frac{d}{dt} c_1 = \gamma e^{i\Delta\omega/2\, t} c_2 \quad \& \quad i\hbar e^{i\Delta\omega/2\, t} \frac{d}{dt} c_2 = \gamma e^{-i\Delta\omega/2\, t} c_1$$

$$i\hbar \frac{d}{dt}\left(e^{-i\Delta\omega/2\, t} c_1\right) = \frac{\hbar\Delta\omega}{2} e^{-i\Delta\omega/2\, t} c_1 + \gamma e^{i\Delta\omega/2\, t} c_2$$

$$i\hbar \frac{d}{dt}\left(e^{i\Delta\omega/2\, t} c_2\right) = -\frac{\hbar\Delta\omega}{2} e^{i\Delta\omega/2\, t} c_2 + \gamma e^{-i\Delta\omega/2\, t} c_1$$

$$\bar{c}_1 \equiv e^{-i\Delta\omega/2\, t} c_1 \quad \& \quad \bar{c}_2 \equiv e^{i\Delta\omega/2\, t} c_2 \quad \Rightarrow \quad \boxed{\begin{aligned} & i\hbar \frac{d}{dt}\bar{c}_1 = \frac{\hbar\Delta\omega}{2}\bar{c}_1 + \gamma \bar{c}_2 \\ \& \; & i\hbar \frac{d}{dt}\bar{c}_2 = -\frac{\hbar\Delta\omega}{2}\bar{c}_2 + \gamma \bar{c}_1 \end{aligned}}$$

$$i\hbar \frac{d}{dt}\bar{c} = \underbrace{\begin{bmatrix} \hbar\Delta\omega/2 & \gamma \\ \gamma & -\hbar\Delta\omega/2 \end{bmatrix}}_{\text{time-independent!}} \bar{c} = \underline{\underline{M}}\,\bar{c}$$

$\Rightarrow$ just need to diagonalise this

$$0 = \begin{vmatrix} \frac{\hbar\Delta\omega}{2} - \lambda & \gamma \\ \gamma & -\frac{\hbar\Delta\omega}{2} - \lambda \end{vmatrix} = -\left(\frac{\hbar\Delta\omega}{2} + \lambda\right)\left(\frac{\hbar\Delta\omega}{2} - \lambda\right) - \gamma^2 \Rightarrow 0 = \left(\frac{\hbar\Delta\omega}{2}\right)^2 - \lambda^2 + \gamma^2 \Rightarrow \underline{\lambda = \pm\sqrt{\frac{\hbar^2\Delta\omega^2}{4} + \gamma^2}}$$

eigenvectors: (λ_+) $\left(\frac{\hbar\Delta\omega}{2} - \lambda_+\right) a - \gamma b = 0 \Rightarrow V_+ = N_+ \begin{bmatrix} \gamma \\ \frac{\hbar\Delta\omega}{2} - \lambda_+ \end{bmatrix}$

(λ_-) $V_- = N_- \begin{bmatrix} \gamma \\ \frac{\hbar\Delta\omega}{2} - \lambda_- \end{bmatrix}$

$$\underline{\underline{M}} = \underline{V}\begin{bmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{bmatrix}\underline{V}^\dagger$$

$$i\hbar \frac{d}{dt}\underline{c} = \underline{\underline{M}}\,\underline{c} = \underline{\underline{V}}\,\underline{\underline{\lambda}}\,\underline{\underline{V}}^{\dagger}\underline{c} \quad \Rightarrow \quad i\hbar\frac{d}{dt}(\underline{\underline{V}}^{\dagger}\underline{c}) = \lambda(\underline{\underline{V}}^{\dagger}\underline{c})$$

$$(\underline{\underline{V}}^{\dagger}\underline{c})_{\pm} = e^{-i\lambda_{\pm}t/\hbar}(\underline{\underline{V}}^{\dagger}\underline{c})_{\pm}(0) \quad \Rightarrow \quad \gamma\,\bar{c}_1(t) + \left(\frac{\hbar\Delta\omega}{2} - \lambda_+\right)\bar{c}_2(t) = e^{-i\lambda_+t/\hbar}\cdot\gamma$$

since $c_1(0)=1$, $c_2(0)=0$.

$$\& \quad \gamma\,\bar{c}_1(t) + \left(\frac{\hbar\Delta\omega}{2} - \lambda_-\right)\bar{c}_2(t) = e^{-i\lambda_-t/\hbar}\cdot\gamma$$

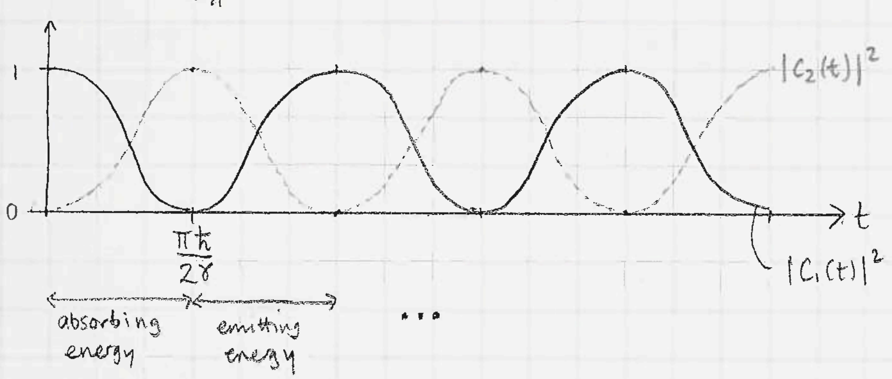
subtracting $(\lambda_- - \lambda_+)\bar{c}_2(t) = \gamma\left(e^{-i\lambda_+t/\hbar} - e^{-i\lambda_-t/\hbar}\right)$

$$\Rightarrow \bar{c}_2(t) = \frac{-\gamma}{2\sqrt{\gamma^2 + \frac{\hbar^2\Delta\omega^2}{4}}}\,2i\sin\left(\sqrt{\gamma^2/\hbar^2 + \Delta\omega^2/4}\;t\right)$$

$$\boxed{|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\left(\gamma^2/\hbar^2 + \frac{(\omega-\omega_{21})^2}{4}\right)}\sin^2\left(\sqrt{\gamma^2/\hbar^2 + \frac{(\omega-\omega_{21})^2}{4}}\;t\right) \quad \& \quad |c_1(t)|^2 = 1 - |c_2(t)|^2}$$

Suppose that the potential is driven at exactly the frequency $\omega_{21} = \frac{E_2 - E_1}{\hbar}$, then

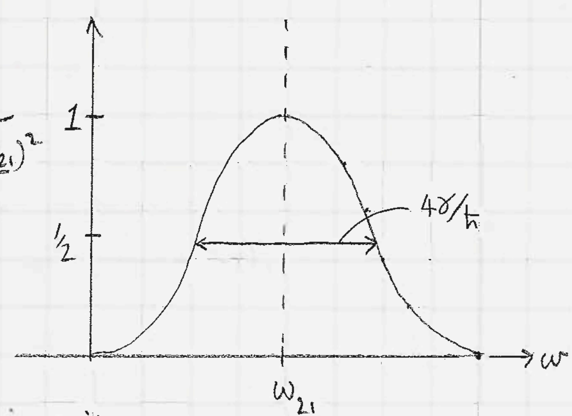
$$|c_2(t)|^2 \xrightarrow[\omega=\omega_{21}]{} \sin^2 \gamma t/\hbar \quad \& \quad |c_1(t)|^2 = \cos^2 \gamma t/\hbar$$



If the potential is driven at other frequencies, the maximal value of $|c_2(t)|^2$ is reduced & the oscillation frequency adjusted

the peak value of $|c_2(t)|^2 = \dfrac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + \frac{(\omega-\omega_{21})^2}{4}}$

"resonant peak"



These results apply to a broad set of physical situations including nuclear magnetic resonance and MASERs.

(perturbative expansion in time-dependent interaction)

In general we cannot solve systems having time-dependent interaction exactly - if the interaction strength is in some sense "small" we can consider a perturbative expansion,

$$c_n(t) = \underbrace{c_n^{(0)}(t)}_{\text{no perturbation}} + \underbrace{c_n^{(1)}(t)}_{\mathcal{O}(V(t))} + \underbrace{c_n^{(2)}(t)}_{\mathcal{O}(V^2(t))} + \dots$$

A useful way to derive this series is to work in terms of the time-evolution operator in the interaction picture, $U_I(t,t_0)$.

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

where it is easy to show that $i\hbar \frac{d}{dt} U_I(t,t_0) = V_I(t)\, U_I(t,t_0)$ Ⓐ

where the solution should obey the boundary condition $U_I(t_0,t_0) = 1$.

a <u>formal</u> solution to Ⓐ can be obtained trivially:

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

unfortunately integral equations of unspecified kernel are not easily solved exactly, and we are forced to approximate. If $V_I(t)$ is "small" then the iterated solution, truncated to some finite order might be reasonable:

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

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

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

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

→ the "Dyson series".

We can choose phases such that $|i, t_0, t\rangle_I = U_I(t,t_0)\,|i\rangle$ where $|i\rangle$ is an eigenstate of H_0 & since we decompose $|i, t_0; t\rangle_I = \sum_n c_n(t)\,|n\rangle$ we have <u>$c_n(t) = \langle n|\, U_I(t,t_0)\,|i\rangle$</u>

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

$$-i/\hbar \int_{t_0}^{t} dt' \langle n|V_I(t')|i\rangle$$

$$+ (-i/\hbar)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \langle n|V_I(t')\,V_I(t'')|i\rangle$$

$$+ \cdots$$

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

$$\Rightarrow \quad c_n^{(0)}(t) = \langle n|i\rangle = \underline{\delta_{ni}}$$

$$c_n^{(1)}(t) = -i/\hbar \int_{t_0}^{t} dt' \langle n|V_I(t')|i\rangle = -i/\hbar \int_{t_0}^{t} dt' \langle n| e^{iH_0 t'/\hbar} V(t) e^{-iH_0 t'/\hbar} |i\rangle$$

$$= -i/\hbar \int_{t_0}^{t} dt' e^{i(E_n - E_i)t'/\hbar} \langle n|V(t')|i\rangle \equiv \underline{-i/\hbar \int_{t_0}^{t} dt' e^{i\omega_{ni}t'} V_{ni}(t')}$$

$$c_n^{(2)}(t) = \left(-i/\hbar\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \langle n|V_I(t')V_I(t'')|i\rangle$$

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

* a "constant" potential :

$$V(t) = \begin{cases} 0 & t<0 \\ V & 0\le t\le T \\ 0 & t>T \end{cases}$$

where V is a operator depending upon dynamical operators such as $\hat{x}, \hat{p}, \hat{S}$ ...
but not time.

With the system in the eigenstate $|i\rangle$ of H_0 at time $t_0=0$, we have

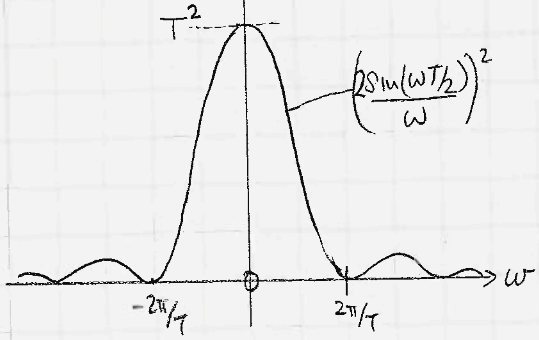
$$c_n^{(0)}(t>T) = \delta_{ni}.$$

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

$$= -\frac{V_{ni}}{E_n - E_i} e^{i\omega_{ni}T/2} \left(e^{i\omega_{ni}T/2} - e^{-i\omega_{ni}T/2}\right) = \left(-ie^{i\omega_{ni}T/2}\right) \cdot \frac{2V_{ni}}{E_n-E_i} \sin\left(\frac{(E_n-E_i)}{2\hbar}T\right)$$

So up to 1st order in p.t. the probability to have a transition from level i to level $n\neq i$ is

$$|c_n^{(1)}|^2 = \frac{4|V_{ni}|^2}{(E_n-E_i)^2} \sin^2\left(\frac{E_n-E_i}{2\hbar}T\right) = \frac{1}{\hbar^2}|V_{ni}|^2 \cdot 4\frac{\sin^2 \omega T/2}{\omega^2}$$



the function $\frac{4\sin^2 \omega T/2}{\omega^2}$ is of height T^2

& width $\sim 4\pi/T$.

for any fixed value of T, the only probable transition are those whose frequency difference $|\omega| \lesssim 2\pi/T$

$\Rightarrow$ for a transition on for Δt, only states within $\Delta E \sim 2\pi\hbar/\Delta t$ will get populated

$\Rightarrow$ $\underline{\Delta E \Delta t \sim \hbar}$ or, in terms of eigenstates of H_0, we can tolerate a degree of energy non-conservation ΔE over a period Δt.

Then in the limit $T\to\infty$ (the potential on for a long time), we'll have exact energy conservation –

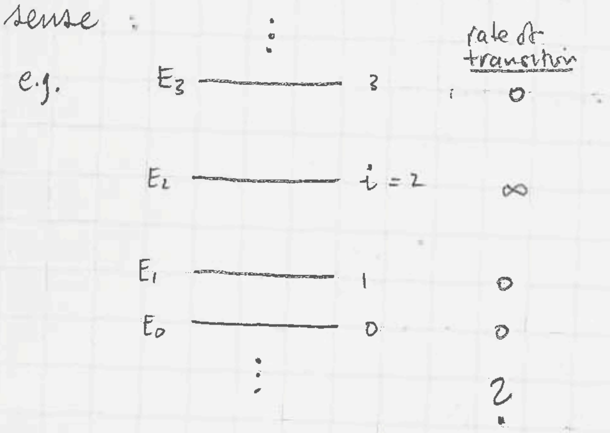
$$\lim_{T\to\infty} \frac{1}{\pi} \frac{\sin^2 \omega T/2}{\omega^2 \cdot T/2} = \delta(\omega) \quad \Rightarrow \lim_{T\to\infty} |c_n^{(1)}|^2 = \frac{4}{\hbar^2}|V_{ni}|^2 \cdot \frac{\pi}{2} T\,\delta(\omega)$$

$$= \frac{2\pi}{\hbar^2}|V_{ni}|^2\, T\hbar\,\delta(E_n - E_i)$$

$$= \frac{2\pi}{\hbar}|V_{ni}|^2 \cdot T \cdot \delta(E_n - E_i)$$

such that the <u>rate</u> of transition, $\frac{d}{dT}|C_n^{(1)}(T)| = \frac{2\pi}{\hbar}|V_{ni}|^2\,\delta(E_n - E_i)$
(with respect to the time the perturbation is on)

For a single, isolated state in a discrete spectrum, this doesnt make much sense:



problem is we're conserving energy!

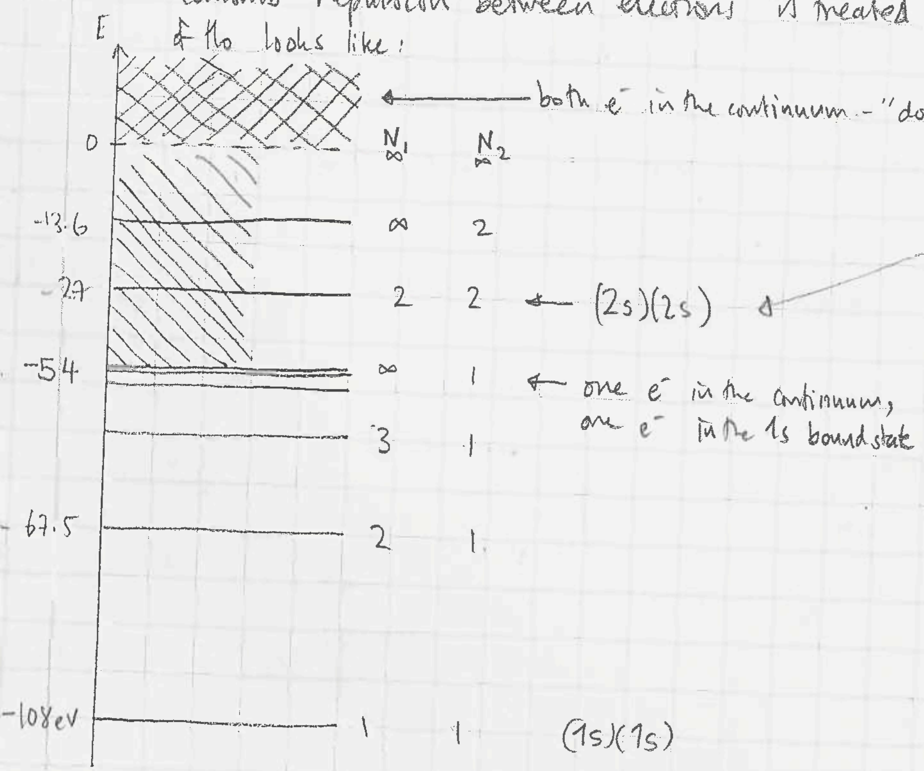
This formula is useful if rather than a single isolated state, there are a set of states with energy very close to E_i.

e.g. autoionization in Helium

consider the following separation of the Hamiltonian: $H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}$

$$V = e^2 / |\vec{r}_1 - \vec{r}_2|$$

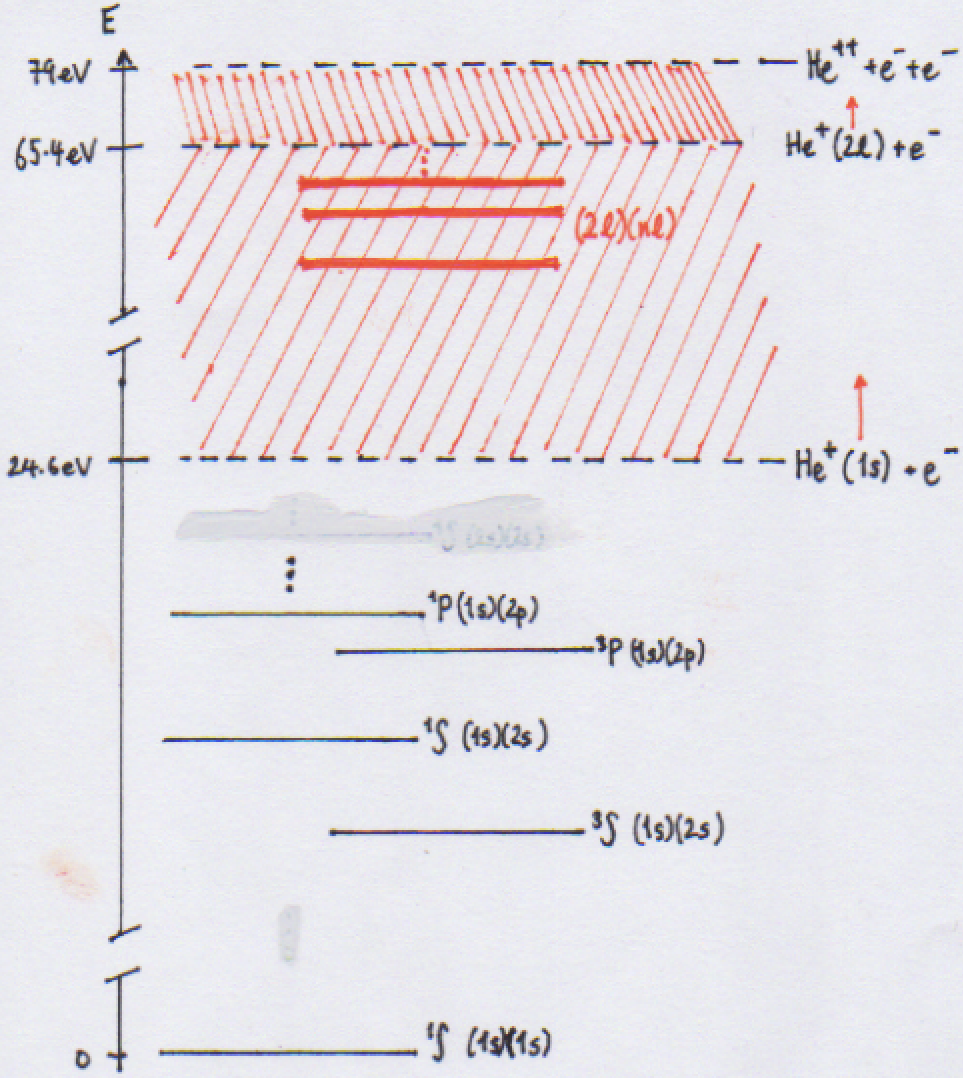
the spectrum of H_0 is trivially related to the hydrogen spectrum while the Coulomb repulsion between electrons is treated as a perturbation. The spectrum of H_0 looks like:



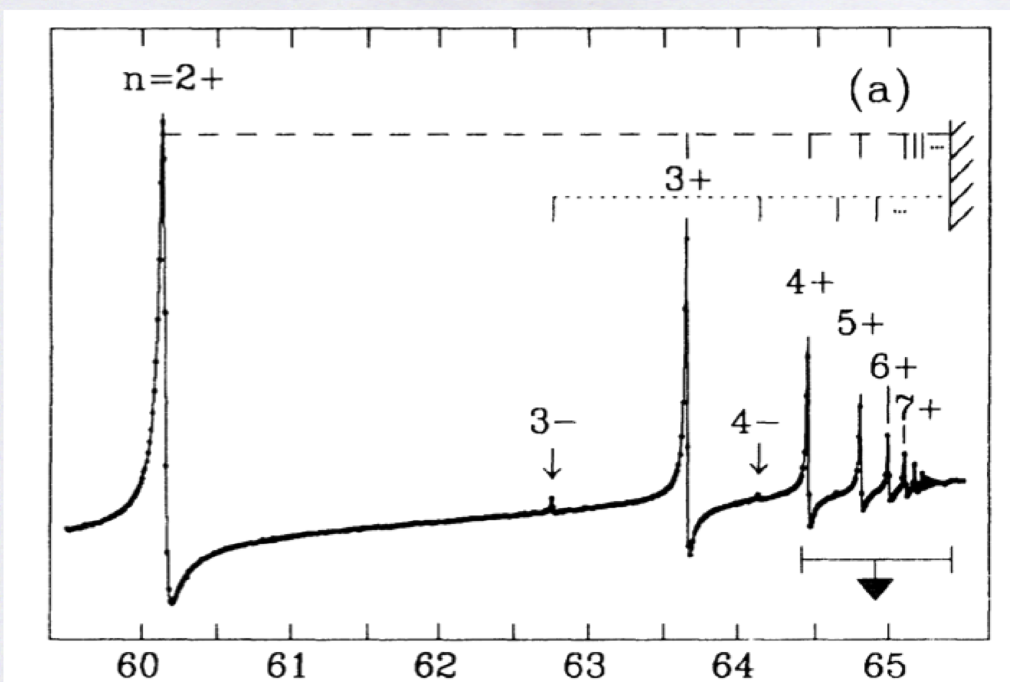
the bound state (2s)(2s) is surrounded by a continuum of levels, (1s)($\vec{k}$)

$\Rightarrow$ can get an approximately energy conserving transition from (2s)(2s) to any of the nearby continuum.

HELIUM



autoionising resonances



Suppose we're interested in the transition rate to any of the neighbouring continuum states, $\frac{d}{dT}\sum_n |C_n^{(1)}(T)|^2$.

In fact we can't really sum since there is a continuous distribution of states (possible values of momentum of the free electron) :

$$\sum_n \longrightarrow \int dn = \int dE \frac{dn}{dE} = \int dE \underbrace{\rho(E)}_{\text{"density of states"}} \quad *$$

then $$W^{(1)}_{i\to[n]} = \frac{d}{dT}\int dn\, |C_n^{(1)}(T)|^2 = \frac{2\pi}{\hbar}\int dE_n\, |V_{ni}|^2 \rho(E_n)\,\delta(E_n - E_i)$$

provided the nearby continuum of states all have approximately the same matrix elements we have

$$W^{(1)}_{i\to[n]} = \frac{2\pi}{\hbar}|\langle n|V|i\rangle|^2 \rho(E_i) \qquad \text{"Fermi's Golden Rule"}$$

at this point we will not attempt to extend this formalism to second order or higher.

---

an aside: we might have wondered if the delta function in (A) on page 51 wasn't somehow caused by the unphysical "switch on" nature of the perturbation.
We can easily test this by using a smoother time-dependence,
e.g. $V(t) = V e^{-t^2/T^2}$.
Then for a system initially $(t\to-\infty)$ in state $|i\rangle$, $C_n^{(1)}(t\to\infty) \to -\frac{i}{\hbar}V_{ni}\int_{-\infty}^{\infty} dt'\, e^{i\omega_{ni}t'} e^{-t'^2/T^2}$

$$C_n^{(1)}(t\to\infty) \to -\frac{i}{\hbar}V_{ni}\, T\int_{-\infty}^{\infty} d\tau\, \exp\left(-\left(\tau - \frac{i\omega_{ni}T}{2}\right)^2\right)\cdot e^{-\omega_{ni}^2T^2/4}$$

$$\to -\frac{i}{\hbar}V_{ni}\, T\cdot\sqrt{\pi}\, e^{-\omega_{ni}^2T^2/4}$$

$$|C_n^{(1)}(t\to\infty)|^2 = \frac{\pi}{\hbar^2}|V_{ni}|^2\, T^2 e^{-\omega_{ni}^2T^2/2}$$

which in the limit $T\to\infty$ $\;\propto T\,\delta(E_n - E_i)$

so the delta function is ubiquitous!

---

* more rigourous: suppose we have a continuum of states labelled by b & normalised as $\langle b|b'\rangle = \delta(b-b')/n(b)$. Then we can project out states in some particular region of b-values (call it B) using $P_B = \int_B db\, |b\rangle\langle b|\, n(b)$.

If the energy is a function of b, $E(b)$ then $P_B = \int_B dE\, |b\rangle\langle b|\,\rho(E)$ where $\rho(E) = n(b)\frac{db}{dE}$.

* a harmonic potential:

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

$$c_n^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt'\, e^{i\omega_{ni}t'} \cdot \left(\mathbb{V}_{ni}\, e^{i\omega t'} + (\mathbb{V}^{\dagger})_{ni}\, e^{-i\omega t'}\right)$$

$$= \frac{-i}{\hbar}\left(\mathbb{V}_{ni}\frac{1}{i(\omega_{ni}+\omega)}\left(e^{i(\omega_{ni}+\omega)t}-1\right) + (\mathbb{V}^{\dagger})_{ni}\frac{1}{i(\omega_{ni}-\omega)}\left(e^{i(\omega_{ni}-\omega)t}-1\right)\right)$$

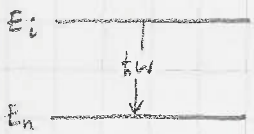
$$= -\frac{i}{\hbar}\left(\mathbb{V}_{ni}\, e^{i(\omega_{ni}+\omega)t/2} \cdot \frac{2i\sin\frac{\omega_{ni}+\omega}{2}t}{\omega_{ni}+\omega} + (\mathbb{V}^{\dagger})_{ni}\, e^{i(\omega_{ni}-\omega)t/2} \cdot \frac{2i\sin\frac{\omega_{ni}-\omega}{2}t}{\omega_{ni}-\omega}\right)$$

this is analagous to the previous case,
as $t \to \infty$,

- the first term will contribute when $\omega_{ni} \simeq -\omega$ $\Rightarrow$ $E_n \simeq E_i - \hbar\omega$
- the second term will contribute when $\omega_{ni} \simeq \omega$ $\Rightarrow$ $E_n \simeq E_i + \hbar\omega$

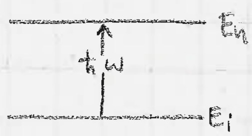
& we have

$$\frac{d}{dt}\left|c_n(t)\right|^2 = \frac{2\pi}{\hbar}\begin{Bmatrix}\left|(\mathbb{V}^{\dagger})_{ni}\right|^2 \\ \left|\mathbb{V}_{ni}\right|^2\end{Bmatrix}\delta\left(E_n - E_i \mp \hbar\omega\right)$$



"stimulated emission"
(gives up energy $\hbar\omega$ to V)

&



"stimulated absorption"
(receives $\hbar\omega$ from V)

let's consider a physical system with a harmonic time-dependence -
electromagnetic transitions in atomic / nuclear systems.

electromagnetic transitions

We're going to consider this in a 'semi-classical' way - that is, while we'll treat the electron (or whatever) in a potential well quantum mechanically, we'll treat the radiation field classically, using Maxwell's equations. The fully quantum treatment requires field-theory which is beyond the scope of this course.

Recall that Maxwell's equations can be written in terms of scalar & vector potentials, $\phi(\vec{x},t)$, $\vec{A}(\vec{x},t)$ - these satisfy "wave" equations:

$$\nabla^2\phi + \frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\cdot\vec{A} = -4\pi\rho \qquad \text{(for charge density } \rho)$$

$$\& \quad \nabla^2\vec{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A} - \vec{\nabla}\left(\vec{\nabla}\cdot\vec{A} + \frac{1}{c}\frac{\partial\phi}{\partial t}\right) = -\frac{4\pi}{c}\vec{j} \qquad \text{(for current density } \vec{j})$$

In the Coulomb gauge, $\vec{\nabla}\cdot\vec{A} = 0$ these equations become

$$\nabla^2\phi = -4\pi\rho$$

$\longrightarrow$ e.g. solution for a point charge, $\rho(\vec{x}) = q\,\delta(\vec{x})$ gives us the Coulomb potential

$$\& \quad \nabla^2\vec{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A} = -\frac{4\pi}{c}\vec{j}$$

so that away from any currents, $\nabla^2\vec{A} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A}$, which is a free-wave equation with solution

$$\vec{A} = A_0\,\vec{\varepsilon}\,e^{\pm i(\vec{k}\cdot\vec{x} - \omega t)}$$

$\omega^2 = k^2c^2$

$\vec{\varepsilon}$ = constant vector "polarisation vector"

A_0 = amplitude (normalise $\vec{\varepsilon}\cdot\vec{\varepsilon} = 1$)

but the Coulomb gauge condition requires

$\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow \vec{k}\cdot\vec{\varepsilon} = 0$ & the vector potential must be <u>transverse</u> to the direction of motion.

As we showed last semester, the Hamiltonian for a charged particle in an e/m field is

$$H = \frac{\vec{p}^2}{2m} - e\phi + \frac{e}{mc}\vec{A}\cdot\vec{p} + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A}. \qquad \text{(in the Coulomb gauge)}$$

treating e as a small quantity (justify later) we can drop the last term & consider the following separation:

$$H_0 = \vec{p}^2/2m - e\phi \quad ; \quad V(t) = \frac{e}{mc}\vec{A}\cdot\vec{p} = \left(\frac{eA_0}{mc}e^{\pm i\vec{k}\cdot\vec{x}}\,\vec{\varepsilon}\cdot\vec{p}\right)e^{\mp i\omega t}$$

e.g. <u>real</u> classical wave solution $A_0\vec{\varepsilon}\cos(\vec{k}\cdot\vec{x} - \omega t)$

$$\Rightarrow V(t) = \frac{eA_0}{2mc}\left(e^{-i\vec{k}\cdot\vec{x}}e^{i\omega t} + e^{i\vec{k}\cdot\vec{x}}e^{-i\omega t}\right)\vec{\varepsilon}\cdot\vec{p} = Ve^{i\omega t} + V^\dagger e^{-i\omega t}$$

a classical e/m wave $\vec{A} = A_0 \vec{\varepsilon} \cos(\vec{k}\cdot\vec{x} - \omega t)$ carries energy (as we require to excite levels in atoms)

the energy flux is given by the Poynting vector $\vec{S} = \frac{c}{4\pi} \vec{E} \times \vec{B}$

$$\left.\begin{aligned} \vec{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} = -\frac{\omega}{c} A_0 \vec{\varepsilon} \sin(\vec{k}\vec{x} - \omega t) \\ \vec{B} &= \vec{\nabla}\times\vec{A} = -\vec{k}\times\vec{\varepsilon} A_0 \sin(\vec{k}\cdot\vec{x} - \omega t) \end{aligned}\right\} \vec{E}\times\vec{B} = A_0^2 \left(\frac{+\omega}{c}\right) \vec{\varepsilon}\times(\vec{k}\times\vec{\varepsilon}) \sin^2(\vec{k}\cdot\vec{x} - \omega t)$$

$$= A_0^2 \frac{\omega}{c} \left(\vec{k}\overset{1}{\cancel{(\vec{\varepsilon}\cdot\vec{\varepsilon})}} - \vec{\varepsilon}\overset{0}{\cancel{(\vec{\varepsilon}\cdot\vec{k})}}\right) \sin^2(\vec{k}\cdot\vec{x} - \omega t)$$

$$\vec{S} = \vec{k} \cdot \frac{\omega}{4\pi} A_0^2 \sin^2(\vec{k}\cdot\vec{x} - \omega t)$$

so as expected, the energy flow is in the direction of wave propagation

the average flux over one period is

$$\vec{S}_{av} = \frac{1}{T}\int_0^T dt\, \vec{S} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} dt\, \vec{k}\frac{\omega}{4\pi} A_0^2 \sin^2(\vec{k}\cdot\vec{x} - \omega t)$$

$z = \vec{k}\cdot\vec{x} - \omega t$

$$= \frac{-1}{2\pi}\frac{\omega}{4\pi} A_0^2 \vec{k} \underbrace{\int_{\vec{k}\cdot\vec{x}}^{\vec{k}\cdot\vec{x} - 2\pi} dz \sin^2 z}_{-\pi} = \frac{\omega}{8\pi} A_0^2 \vec{k} = \frac{A_0^2}{8\pi}\frac{\omega^2}{c}\cdot\hat{n}$$

↖ direction of motion

and this quantity is known as the 'intensity' of the wave, $I(\omega) = \frac{\omega^2}{8\pi c}|A_0|^2$

or $A_0 = \frac{\sqrt{8\pi c}}{\omega}\sqrt{I(\omega)}$, which normalises our wave i.t.o the light intensity.

By comparison with our general harmonic result we have

$$W_{i\to n} = \frac{2\pi}{\hbar}\cdot\left|\langle n| \frac{eA_0}{2mc} e^{\pm i\vec{k}\cdot\vec{x}} \vec{\varepsilon}\cdot\vec{p}\, |i\rangle\right|^2 \cdot \delta(E_n - E_i \mp \hbar\omega)$$

$$= \frac{2\pi}{\hbar}\cdot\frac{e^2}{4m^2c^2}\cdot\frac{8\pi c}{\omega^2} I(\omega) \left|\langle n| e^{\pm i\vec{k}\cdot\vec{x}} \vec{\varepsilon}\cdot\vec{p}|i\rangle\right|^2 \delta(E_n - E_i \mp \hbar\omega)$$

$$= \frac{4\pi^2}{\hbar}\frac{e^2}{m^2 c}\frac{I(\omega)}{\omega^2}\left|\langle n| e^{\pm i\vec{k}\cdot\vec{x}} \vec{\varepsilon}\cdot\vec{p}|i\rangle\right|^2 \delta(E_n - E_i \mp \hbar\omega)$$

the "cross-section" per unit energy is given by $\frac{d\sigma}{dE} = \frac{W_{i\to n}}{I(\omega)}$

$$\underline{\underline{\frac{d\sigma}{dE} = \frac{4\pi^2}{m^2\omega^2}\left(\frac{e^2}{\hbar c}\right)\cdot\left|\langle n| e^{\pm i\vec{k}\cdot\vec{x}} \vec{\varepsilon}\cdot\vec{p}|i\rangle\right|^2 \delta(E_n - E_i \mp \hbar\omega)}}$$

(in our unit system $\frac{e^2}{\hbar c} = \alpha \simeq \frac{1}{137}$)

decay width

Returning to the constant potential, we found that for a state $|i\rangle$ embedded in a (quasi-) continuum, that provided $\langle n|V|i\rangle \neq 0$, states $|n\rangle$ will be populated at a constant rate - to conserve probability there must be a corresponding depletion of the state $|i\rangle$.

We also know from experiments in, for example, nuclear radioactive decay, that systems often decay exponentially with time. Additionally we are looking for a reason why spectral lines observed in atom experiments are not the delta functions predicted by our simple perturbation theory

We can address all these points by pushing our perturbation theory to second order in V.

Let us introduce a new 'regulator' that causes the perturbation to turn on gradually, $V(t) = e^{\eta t} V$, where finally we will take $\eta \to 0$ to get a constant potential.

Suppose we are in state $|i\rangle$ 'before' the perturbation, i.e as $t \to -\infty$. We can easily check that we recover the golden rule for transitions to $|n\rangle$:

$$C^{(0)}_{n\neq i}(t) = 0 \; ; \quad C^{(1)}_{n\neq i}(t) = -\frac{i}{\hbar} V_{ni} \int_{-\infty}^{t} dt' \, e^{i\omega_{ni}t'} e^{\eta t'} = -\frac{i}{\hbar} V_{ni} \frac{1}{i\omega_{ni}+\eta} e^{(i\omega_{ni}+\eta)t}$$

at lowest order then,

$$|c_n(t)|^2 = \frac{|V_{ni}|^2}{\hbar^2} \cdot \frac{e^{2\eta t}}{\eta^2+\omega_{ni}^2} \quad \Rightarrow \quad \frac{d}{dt}|c_n(t)|^2 = \frac{|V_{ni}|^2}{\hbar^2} \cdot \frac{2\eta}{\eta^2+\omega_{ni}^2} e^{2\eta t}$$

$$\lim_{\eta\to 0} \frac{\eta}{\eta^2+\omega_{ni}^2} = \pi\delta(\omega_{ni}) = \pi\hbar\,\delta(E_n - E_i)$$

$$\text{so} \quad w_{i\to n} = \frac{2\pi}{\hbar}|V_{ni}|^2 \delta(E_n - E_i)$$

which reproduces the Golden Rule

Now let's consider what happens to $c_i(t)$, the amplitude to find the system in state $|i\rangle$ at time t:

$$c_i^{(0)}(t) = \delta_{ii} = 1 \quad ; \quad c_i^{(1)}(t) = -\frac{i}{\hbar} V_{ii} \int_{-\infty}^{t} dt' \, e^{\eta t'} = -\frac{i}{\hbar} V_{ii} \cdot \frac{1}{\eta} e^{\eta t}$$

$$c_i^{(2)}(t) = \sum_m \left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \, e^{i\omega_{im}t'} e^{i\omega_{mi}t''} e^{\eta t'} e^{\eta t''} V_{im} V_{mi} = \sum_m \left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{t} dt' \, e^{i\omega_{im}t'} e^{\eta t'} |V_{im}|^2 \frac{e^{i\omega_{mi}t' + \eta t'}}{i\omega_{mi}+\eta}$$

$$= \sum_m \left(\frac{-i}{\hbar}\right)^2 |V_{im}|^2 \frac{1}{i\omega_{mi}+\eta} \int_{-\infty}^{t} dt' \, e^{2\eta t'} = \sum_m \left(\frac{-i}{\hbar}\right)^2 |V_{im}|^2 \frac{1}{2\eta(i\omega_{mi}+\eta)} e^{2\eta t}$$

Separating i out from the sum over m : $C_i^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \cdot |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \sum_{m\neq i} \left(\frac{-i}{\hbar}\right)^2 \frac{|V_{im}|^2}{2\eta} \frac{(-i\hbar) e^{2\eta t}}{E_m - E_i - i\hbar\eta}$

$$C_i^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} - \frac{i}{\hbar} \sum_{m\neq i} \frac{|V_{im}|^2}{E_i - E_m + i\hbar\eta} \frac{e^{2\eta t}}{2\eta}$$

Including all terms up to $\mathcal{O}(V^2)$ we have $c_i(t) = 1 - \frac{i}{\hbar\eta} V_{ii} e^{\eta t} + \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2}$

$$- \frac{i}{\hbar} \sum_{m\neq i} \frac{|V_{im}|^2}{E_i - E_m + i\hbar\eta} \frac{e^{2\eta t}}{2\eta}$$

we can play a mathematical trick to simplify the time-dependence,

$$\frac{d}{dt} c_i(t) = -\frac{i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{1}{\eta} e^{2\eta t} - \frac{i}{\hbar} \sum_{m\neq i} \frac{\cancel{2\eta}}{\cancel{2\eta}} \frac{|V_{im}|^2}{E_i - E_m + i\hbar\eta} e^{2\eta t}$$

$$\Rightarrow \frac{dc_i/dt}{c_i} \simeq \frac{dc_i/dt}{1 - \frac{i}{\hbar\eta} V_{ii} e^{\eta t}} \simeq -\frac{i}{\hbar} V_{ii} - \left(\frac{-i}{\hbar}\right)^2 \frac{|V_{ii}|^2}{\eta} e^{\eta t} + \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{1}{\eta} e^{2\eta t}$$

$$- \frac{i}{\hbar} \sum_{m\neq i} \frac{|V_{im}|^2}{E_i - E_m + i\hbar\eta} e^{2\eta t} + \mathcal{O}(V^3)$$

$$\xrightarrow[\eta \to 0]{} -\frac{i}{\hbar} V_{ii} - \frac{i}{\hbar} \sum_{m\neq i} \frac{|V_{im}|^2}{E_i - E_m + i\hbar\eta} = -\frac{i}{\hbar} \Delta_i$$

independent of time

$$\Rightarrow c_i(t) = e^{-i\Delta_i t/\hbar} c_i(0) = e^{-i\Delta_i t/\hbar}$$

so the Schrödinger picture time dependence

$$|i, -\infty; t\rangle = e^{-i\Delta_i t/\hbar} e^{-iE_i t/\hbar} |i\rangle = e^{-i\tilde{E}_i t/\hbar} |i\rangle$$

$$\tilde{E}_i = E_i + \Delta_i$$

energy shift!

expand $\Delta_i = \underbrace{\Delta_i^{(1)}}_{\mathcal{O}(V)} + \underbrace{\Delta_i^{(2)}}_{\mathcal{O}(V^2)} + \ldots$

$$\Rightarrow \Delta_i^{(1)} = \langle i | V | i \rangle$$

N.B. exactly what time-independent p.t. said it should be.

the second order term requires some care

$$\Delta_i^{(2)} = \lim_{\eta \to 0} \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}$$

→ an aside on Cauchy's Principal Value:

Suppose we have to consider an integral $\int_{-x_0}^{x_1} dx \, \frac{g(x)}{x}$ where $x_0 > 0$, $x_1 > 0$ & $g(x)$ is a smooth function around $x=0$.

This integral diverges because of the $x \to 0$ behaviour. In fact it is only the point $x=0$ that is troublesome. Consider the case $g(x) = 1$ and the following integrals:

$$\int_{-x_0}^{-a} dx \, \frac{1}{x} = \ln a/x_0 \quad ; \quad \int_{a}^{x_1} dx \, \frac{1}{x} = \ln x_1/a$$

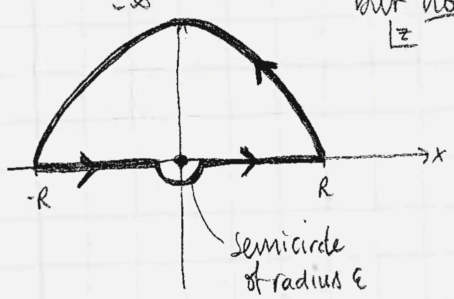
so that $\int_{-x_0}^{-a} dx \frac{1}{x} + \int_{a}^{x_1} dx \frac{1}{x} = \ln \frac{x_1}{x_0}$, which can be perfectly finite, even if we take $a \to 0$.

Thus provided we exclude the point $x=0$, we get finite integrals. This is known as the Cauchy Principal Value

$$\mathbb{P} \int_{-x_0}^{x_1} dx \, f(x) = \lim_{a \to 0} \left(\int_{-x_0}^{a} dx \, f(x) + \int_{-a}^{x_1} dx \, f(x) \right)$$ when $f(0)$ is a singular point.

This object can appear if we consider an integral that we evaluate by a contour

$\int_{-\infty}^{\infty} dx \, \frac{g(x)}{x}$ where $g(x)$ falls as $x \to \pm\infty$ & may have singularities but not at $x=0$.



$$\oint dz \, \frac{g(z)}{z} = 2\pi i \, g(0) + \text{residues due to singularities of } g(z)$$

$$= \int_{-R}^{-\varepsilon} dx \, \frac{g(x)}{x} + \int_{\pi}^{2\pi} i\cancel{\varepsilon} \cancel{e^{i\phi}} \, d\phi \, \frac{g(\varepsilon e^{i\phi})}{\cancel{\varepsilon} \cancel{e^{i\phi}}} + \int_{\varepsilon}^{R} dx \, \frac{g(x)}{x} + \int_{0}^{\pi} i\cancel{R}\cancel{e^{i\phi}} \, d\phi \, \frac{g(Re^{i\phi})}{Re^{i\phi}}$$

in the limit $R \to \infty$, $\varepsilon \to 0$

$$\to \mathbb{P} \int_{-\infty}^{\infty} dx \, \frac{g(x)}{x} + i\pi \, g(0)$$

or residues due to sing of $g(z)$ $= \mathbb{P} \int_{-\infty}^{\infty} dx \, \frac{g(x)}{x} - i\pi \, g(0)$.

An equivalent way to consider this is to shift the pole just off the real axis, then for this to work for all functions $g(x)$ we can write

$$\lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = \mathbb{P} \frac{1}{x} - i\pi \delta(x)$$

$$\Delta_i^{(2)} = \lim_{\eta\to 0} \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta} \Rightarrow Re(\Delta_i^{(2)}) = \mathbb{P}\sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m}$$ (c.f. time-ind. pert thy)

$$\& \; Im(\Delta_i^{(2)}) = -\pi \sum_{m\neq i} |V_{mi}|^2 \delta(E_i - E_m)$$

$$= -\frac{\hbar}{2} \sum_{m\neq i} W_{i\to m} \equiv -\Gamma_i/2$$

so provided there is a (quasi-) continuum of states $|m\rangle$ with energy close to E_i, the energy shift can develop an imaginary part, something we didn't allow for in our study of time-independent perturbation theory.

$|C_i(t)|^2 = e^{-\Gamma_i t/\hbar}$ – exponential decay of a state, Γ_i describes the rate.

N.B. if we expand this to $O(V^2)$ $\rightarrow |C_i(t)|^2 = 1 - \frac{\Gamma_i}{\hbar} t = \left(1 - \sum_{m\neq i} W_{i\to m}\right)$

while $\sum_{m\neq i} |C_m(t)|^2 = \sum_{m\neq i} \int dt \; W_{i\to m} = t \cdot \sum_{m\neq i} W_{i\to m}$

so $|C_i(t)|^2 + \sum_{m\neq i} |C_m(t)|^2 = \underline{1}$ & probability is conserved to this order in perturbation theory

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This possibility of decay will also resolve our problem of delta-functions in the energy dependence of $W_{i\to n}$. A <u>schematic</u> solution to this follows:

recall that $C_n(t)$ satisfies a coupled diffential equation:

$$i\hbar \frac{d}{dt} C_n(t) = \sum_m e^{i\omega_{nm}t} \langle n|V|m\rangle C_m(t)$$

and will will assume that the largest effect on the RHS comes from $m=i$

$$i\hbar \frac{d}{dt} C_n(t) \simeq e^{i\omega_{ni}t} \langle n|V|i\rangle C_i(t)$$

$$\Rightarrow C_n(t) = -\frac{i}{\hbar} \int^t dt' \, e^{i\omega_{ni}t'} \langle n|V|i\rangle c_i(t')$$

$$= -\frac{i}{\hbar} \int^t dt' \, e^{i\omega_{ni}t'} \langle n|V|i\rangle e^{-i\Delta_i t/\hbar}$$

now here we have to be a bit careful – using $t_0 = -\infty$ & $V(t) = Ve^{\eta t}$ means that each state has had infinite time to decay & we might have trouble dealing with the $t_0 \to -\infty$, $\eta \to 0$ limit. Instead let's just switch on V at $t=0$.

$$C_n(t) \simeq -\frac{i}{\hbar} V_{ni} \int_0^t dt' \, e^{i\omega_{ni}t'} e^{-i\Delta_i t'/\hbar}$$

$$\simeq -\frac{i}{\hbar} V_{ni} \frac{1}{i(\omega_{ni} - \Delta_i/\hbar)} \left(e^{i(\omega_{ni} - \Delta_i/\hbar)t} - 1 \right)$$

$$\simeq V_{ni} \frac{\left(1 - e^{i(\omega_{ni} - \Delta_i^R/\hbar)t} e^{-\Gamma_i t/2\hbar}\right)}{(E_n - E_i - \Delta_i^R) + i\Gamma_i/2}$$

$$|c_n(t)|^2 \simeq \frac{|V_{ni}|^2}{\left(E_n - (E_i + \Delta_i^R)\right)^2 + \Gamma_i^2/4} \cdot \left(1 - 2e^{-\Gamma_i t/2\hbar} \cos(\omega_{ni} - \Delta_i^R/\hbar)t + e^{-\Gamma_i t/\hbar} \right)$$

for times $t \gg \hbar/\Gamma$, $|c_n(t \gg \hbar/\Gamma)|^2 \longrightarrow \dfrac{|V_{ni}|^2}{(E_n - \tilde{E}_i)^2 + \Gamma_i^2/4}$

Clearly we won't really get perfectly sharp energy levels if they're able to decay through the effect of the potential, rather the energy will be distributed with a Lorentzian probability

$$p(E)\,dE = \frac{1}{2\pi} \frac{\Gamma}{(E - E_i)^2 + \Gamma^2/4} \, dE \xrightarrow[\Gamma \to 0]{} \delta(E - E_i)\, dE$$

This applies also to spectral lines, which will appear 'broadened' due to decay effects and not as the delta functions we initially predicted.