

## Chapter 6 - Time Independent Perturbation Theory

This is the first of several chapters about how the Schrödinger eq. is solved in practice. The most powerful method (computational) will be used in many spots. Some basic computer skills will be assumed.

Perturbation theory allows for the approximate solution in powers of a small effect. For the time independent solution of the Sch. eq. the perturbation series is often not convergent!

I will slightly change the notation from that in the book.

Want the solution  $H|\psi_n\rangle = |\psi_n\rangle E_n$  but the  $H, \psi, E$  are too complicated.

But!!  $H \approx H^{(0)}$  which we know how to solve.

The eigenstates and vectors are known

$$H^{(0)}|\psi_n^{(0)}\rangle = |\psi_n^{(0)}\rangle E_n^{(0)} \quad \text{with} \quad \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}$$

For now we will assume the eigenvalues are non-degenerate  
 $E_1^{(0)} < E_2^{(0)} < E_3^{(0)} \dots$

Since  $H \approx H^{(0)}$ , you might expect the eigenvalues and vectors  $E_n, |\psi_n\rangle$  are close to  $E_n^{(0)}, |\psi_n^{(0)}\rangle$ . Sometimes it's true.  
When is small actually small??

Make an ansatz for the Hamiltonian, energies, and wave functions

$$H = H^{(0)} + H^{(1)} \quad , \quad E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \quad , \quad |\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \dots$$

Why does  $H$  stop at 1? Why doesn't  $E, |\psi\rangle$ ? Is this a well defined procedure???

As usual, solve by substituting into the Sch. eq.

$$[H^{(0)} + H^{(1)}] [|\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \dots] = [|\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \dots] [E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots]$$

There are  $\infty$  more unknowns than equations! How to get same number of equations and unknowns?

Prescription:  $E_n^{(m)}, |\psi_n^{(m)}\rangle$  should have  $m$  powers of  $H^{(1)}$ . In practice, set equations so sum of superscript is  $m$ .

0:  $H^{(0)} |\psi_n^{(0)}\rangle = |\psi_n^{(0)}\rangle E_n^{(0)}$  automatically satisfied (Eq. 6.1)

1:  $H^{(0)} |\psi_n^{(1)}\rangle + H^{(1)} |\psi_n^{(0)}\rangle = |\psi_n^{(1)}\rangle E_n^{(0)} + |\psi_n^{(0)}\rangle E_n^{(1)}$  Eq. 6.7

2:  $H^{(0)} |\psi_n^{(2)}\rangle + H^{(1)} |\psi_n^{(1)}\rangle = |\psi_n^{(2)}\rangle E_n^{(0)} + |\psi_n^{(1)}\rangle E_n^{(1)} + |\psi_n^{(0)}\rangle E_n^{(2)}$  Eq. 6.8

etc. Looks straightforward, but is very tricky to apply. Even to just these equations.

First order perturbation theory is when you stop at 1. The energy can be unambiguously obtained by dotting the  $\langle \psi_n^{(0)} |$

$$\langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle E_n^{(0)} + E_n^{(1)}$$

$$\cancel{E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle} + \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \cancel{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle E_n^{(0)}} + E_n^{(1)}$$

cancels each other

The 1<sup>st</sup> order energy shift  $E_n^{(1)} = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$  is the expectation value of the perturbation!

But these steps also point to a problem. The amount of  $|\psi_n^{(0)}\rangle$  in the  $|\psi_n^{(1)}\rangle$  can not be determined by the equation. Go to the original equation. Add any finite amount of  $|\psi_n^{(0)}\rangle$  to  $|\psi_n^{(1)}\rangle \rightarrow |\psi_n^{(1)}\rangle + |\psi_n^{(0)}\rangle \alpha$  will still be a solution. Common feature of linear inhomogeneous equations. Can add any finite amount of the homogeneous solution.

Define  $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$  The correction to the wave function is orthogonal to the original  $|\psi_n^{(0)}\rangle$ . This is a sensible choice because any amount of  $|\psi_n^{(0)}\rangle$  in  $|\psi_n^{(1)}\rangle$  can be sucked into the  $|\psi_n^{(0)}\rangle$  term of  $|\psi_n\rangle$ .

There are two ways that I've solved for  $|\psi_n^{(1)}\rangle$ .

1) Solve by superposing solutions of  $H^{(0)}$

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} |\psi_m^{(0)}\rangle C_{m,n}^{(1)} \quad (\text{note change of notation})$$

Dot  $\langle \psi_m^{(0)} |$  into the 1<sup>st</sup> order equation

$$\langle \psi_m^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle E_n^{(0)} + \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle E_n^{(1)}$$

$$E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle E_n^{(0)}$$

$$E_m^{(0)} C_{m,n}^{(1)} + \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = E_n^{(0)} C_{m,n}^{(1)}$$

$$C_{m,n}^{(1)} = \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \Rightarrow |\psi_n^{(1)}\rangle = \sum_{m \neq n} |\psi_m^{(0)}\rangle \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \text{Eq [6.13]}$$

This gives an idea of what is meant by "small". Small is when  $|\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle| \ll |E_n^{(0)} - E_m^{(0)}| \Rightarrow$  the perturbation is between  $n$  states is much smaller than the energy difference.

2) Directly solve the differential equation (Dalgarno-Lewis method)

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n^{(1)}(\vec{r}) + V(\vec{r}) \psi_n^{(1)}(\vec{r}) = E_n^{(0)} \psi_n^{(1)}(\vec{r}) + \underbrace{(E_n^{(1)} - H^{(1)}) \psi_n^{(0)}(\vec{r})}_{\text{inhomogeneous term}}$$

Can sometimes be tricky to enforce  $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$

## 2<sup>nd</sup> order perturbation

To get the energy  $E_n^{(2)}$ , project  $\langle \psi_n^{(0)} |$  onto order 2 equation

$$\langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle E_n^{(0)} + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle E_n^{(1)} + \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle E_n^{(2)}$$

$E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle \leftarrow \text{cancels} \rightarrow$

$$\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(1)} \rangle = E_n^{(2)} \quad \text{Substitute expression for } |\psi_n^{(1)}\rangle$$

$$E_n^{(2)} = \sum_m \frac{\langle \psi_n^{(0)} | H^{(1)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \text{Eg [6.15]}$$

To get the 2<sup>nd</sup> order correction to the wave function, project  $\langle \psi_{m'}^{(0)} |$  onto order 2 equation

$$\begin{aligned} \langle \psi_{m'}^{(0)} | \psi_n^{(2)} \rangle &= \frac{1}{E_n^{(0)} - E_{m'}^{(0)}} \left[ \langle \psi_{m'}^{(0)} | H^{(1)} | \psi_n^{(1)} \rangle - \langle \psi_{m'}^{(0)} | \psi_n^{(1)} \rangle E_n^{(1)} \right] \\ &= \frac{1}{E_n^{(0)} - E_{m'}^{(0)}} \left[ \sum_{m \neq n} \frac{\langle \psi_{m'}^{(0)} | H^{(1)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} - \frac{\langle \psi_{m'}^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{m'}^{(0)}} \right] \end{aligned}$$

Problem: A particle of mass  $M$  is in an infinite square well from 0 to  $a$  plus a potential  $V(x) = V_0 \cos(\pi x/a)$ . Find the energies through  $V_0^2$  and the wave functions through  $V_0$ .

Identify  $H^{(0)}$ ,  $E_n^{(0)}$ ,  $|\psi_n^{(0)}\rangle \rightarrow H^{(0)} = \frac{p^2}{2m}$ ,  $\langle X | \psi_n^{(0)} \rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ ,  
 $E_n^{(0)} = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2} n^2 = E_1^{(0)} \cdot n^2$

Identify  $H^{(1)}$  and calculate  $\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$

$$H^{(1)} = V_0 \cos\left(\frac{\pi x}{a}\right)$$

$$\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = V_0 \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{V_0}{2} \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \sqrt{\frac{2}{a}} \left[ \sin\left(\frac{(n+1)\pi x}{a}\right) + \sin\left(\frac{(n-1)\pi x}{a}\right) \right] dx$$

$\cos a \sin b = \frac{1}{2} [\sin(b+a) + \sin(b-a)]$

$$= \frac{V_0}{2} \left[ \delta_{m, n+1} + \delta_{m, n-1} \right]$$

Compute  $E_n^{(1)} = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \frac{V_0}{2} [\delta_{n,n+1} + \delta_{n,n-1}] = 0$

Compute  $|\psi_n^{(1)}\rangle = \sum_{m \neq n} |\psi_m^{(0)}\rangle \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$

$= |\psi_{n+1}^{(0)}\rangle \frac{V_0/2}{E_1^{(0)} [n^2 - (n+1)^2]} + |\psi_{n-1}^{(0)}\rangle \frac{V_0/2}{E_1^{(0)} [n^2 - (n-1)^2]}$  ↙ except  $n=1$  because no  $|\psi_0^{(0)}\rangle$

$= \frac{V_0/2}{E_1^{(0)}} \left[ -\frac{1}{2n+1} |\psi_{n+1}^{(0)}\rangle + \frac{1 - \delta_{n,1}}{2n-1} |\psi_{n-1}^{(0)}\rangle \right]$

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

$= \frac{(V_0/2)^2}{E_1^{(0)}} \left[ \frac{1}{n^2 - (n+1)^2} + \frac{1}{n^2 - (n-1)^2} \right]$  ↙ except  $n=1$

$= \frac{(V_0/2)^2}{E_1^{(0)}} \left[ \frac{1 - \delta_{n,1}}{2n-1} - \frac{1}{2n+1} \right]$

Note that the ground state is pushed down in energy. Typical. If  $\langle \psi_{g.s.}^{(0)} | H^{(1)} | \psi_{g.s.}^{(0)} \rangle = 0$ , then perturbation pushes energy down.

Degenerate perturbation theory - what to do if  $E_n^{(0)} = E_m^{(0)}$ ?

Two strategies: 1) find other operator that commutes with  $H$  that give eigenstates where  $\langle \psi_n^{(0)} | H^{(1)} | \psi_m^{(0)} \rangle = 0$  when  $E_n^{(0)} = E_m^{(0)}$   $m \neq n$

OR 2) Diagonalize within the degenerate space.

For Sch. Eg. in 1D, all discrete eigenstates (that sample the same region of space) are non degenerate.

For 1) see the Theorem on pgs 259-260

Example: 2D  $\infty$  square well  $0 \leq x \leq a$  and  $0 \leq y \leq a$

$$\psi_{m,n}^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi y}{a}\right)$$

There are degenerate pairs  $E_{m,n}^{(0)} = E_{n,m}^{(0)}$

Suppose  $H^{(1)} = V(x) + V(y)$ . There is no problem in this case because the off diagonal elements are 0 for degenerate states.

$$\langle \Psi_{mn}^{(0)} | H^{(1)} | \Psi_{m'n'}^{(0)} \rangle = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) V(x) \sqrt{\frac{2}{a}} \sin\left(\frac{m'\pi x}{a}\right) dx + \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{m'\pi x}{a}\right) dx + \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi y}{a}\right) V(y) \sqrt{\frac{2}{a}} \sin\left(\frac{m'\pi y}{a}\right) dy + \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi y}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{m'\pi y}{a}\right) dy$$

$$= V_{mm'} \delta_{nn'} + \delta_{mm'} V_{nn'}$$

Show this is 0 for all the degenerate pairs.

Harder Case: Suppose  $H^{(1)} = V(x, y) = V(y, x)$

Now the Hamiltonian commutes with the  $x \leftrightarrow y$  operator

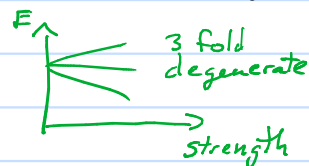
Choose states that are eigenstates of this operator

$$\Psi_{m,n,\pm}^{(0)} \equiv \frac{1}{\sqrt{2(1+\delta_{mn})}} \left[ \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi y}{a}\right) \pm \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi y}{a}\right) \right]$$

The perturbation can't mix the + states with - states.

If this isn't possible, then you need the 2<sup>nd</sup> method which almost always means numerical diagonalization.

(Note Fig 6.4 can't be correct. Must change linearly)



How to do degenerate perturbation theory:

1) Find all of the different sets of states

2) For each set, construct the Hamiltonian matrix

$$H_{mn} = \langle \Psi_m^{(0)} | H^{(0)} + H^{(1)} | \Psi_n^{(0)} \rangle$$

3) Diagonalize the matrix  $\sum_n H_{mn} U_{n,\mu} = U_{m,\mu} E_\mu$

4) Use the  $|\Psi_\mu\rangle = \sum_m |\Psi_m^{(0)}\rangle U_{m,\mu}$  and  $E_\mu$  in the place of  $|\Psi_m^{(0)}\rangle$  and  $E_m^{(0)}$

For the case a double degeneracy, you need to diagonalize

$$\begin{pmatrix} H_{aa}^{(1)} & H_{ab}^{(1)} \\ H_{ba}^{(1)} & H_{bb}^{(1)} \end{pmatrix}$$

$$\text{The two energies are } E_{\pm}^{(1)} = \frac{H_{aa}^{(1)} + H_{bb}^{(1)}}{2} \pm \frac{1}{2} \sqrt{(H_{aa}^{(1)} - H_{bb}^{(1)})^2 + 4 H_{ab}^{(1)} H_{ba}^{(1)}}$$

Problem: An isotropic, 3D, harmonic oscillator is perturbed by the point interaction  $H^{(1)} = \alpha \delta(x-L) \delta(y-L)$ . Get the lowest 4 energies accurate to order  $\alpha$

$$\Psi_{n\ell m}^{(0)}(x, y, z) = \Psi_n(x) \Psi_\ell(y) \Psi_m(z)$$

The ground state is nondegenerate. So can just do

$$E_{000}^{(1)} = \langle \Psi_{000}^{(0)} | H^{(1)} | \Psi_{000}^{(0)} \rangle = \alpha \Psi_0^2(L) \Psi_0^2(L)$$

The next 3 states are degenerate.

Use method 1.  $H^{(1)}$  commutes with operator  $x \leftrightarrow y$ . The 3 states

$$\Psi_a^{(0)} = \frac{1}{\sqrt{2}} (\Psi_{100} + \Psi_{010}), \quad \Psi_b^{(0)} = \frac{1}{\sqrt{2}} (\Psi_{100} - \Psi_{010}), \quad \Psi_c^{(0)} = \Psi_{001}$$

commutes with this operator, which means  $H^{(1)}$  is diagonal

$$E_a^{(1)} = \frac{\alpha}{2} (\Psi_1(L) \Psi_0(L) + \Psi_0(L) \Psi_1(L))^2 = 2\alpha \Psi_1^2(L) \Psi_0^2(L)$$

$$E_b^{(1)} = \frac{\alpha}{2} (\Psi_1(L) \Psi_0(L) - \Psi_0(L) \Psi_1(L))^2 = 0$$

$$E_c^{(1)} = \alpha \Psi_0^2(L) \Psi_0^2(L)$$

Use method 2. Order the states  $\Psi_{100}, \Psi_{010}, \Psi_{001}$

$$H^{(1)} = \alpha \begin{pmatrix} \Psi_1^2(L) \Psi_0^2(L) & \Psi_1(L) \Psi_0(L) \Psi_1(L) \Psi_0(L) & 0 \\ \Psi_0(L) \Psi_1(L) \Psi_0(L) \Psi_1(L) & \Psi_0^2(L) \Psi_1^2(L) & 0 \\ 0 & 0 & \Psi_0^2(L) \Psi_0^2(L) \end{pmatrix}$$

This is a  $2 \times 2$  and a  $1 \times 1$

$$\alpha \Psi_1^2(L) \Psi_0^2(L) \begin{pmatrix} 1 & \\ & 1 \end{pmatrix} \quad \alpha \Psi_0^2(L) \Psi_0^2(L)$$

The eigenvalues of  $\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$  are 2 (+state) and 0 (-state)

$$E_a^{(1)} = 2\alpha \Psi_1^2(L) \Psi_0^2(L) \quad \Psi_a = \frac{1}{\sqrt{2}} (\Psi_{100} + \Psi_{010})$$

$$E_b^{(1)} = 0 \quad \Psi_b = \frac{1}{\sqrt{2}} (\Psi_{100} - \Psi_{010})$$

$$E_c^{(1)} = \alpha \Psi_0^2(L) \Psi_0^2(L) \quad \Psi_c = \Psi_{001}$$

Same answer, as it should be

Example find energies for same Hamiltonian but now for states with 2 quanta.

$$\Psi_{200}, \Psi_{020}, \Psi_{002}, \Psi_{110}, \Psi_{010}, \Psi_{001} \rightarrow \frac{1}{\sqrt{2}} (\Psi_{200} \pm \Psi_{020}), \Psi_{002}, \Psi_{110}, \frac{1}{\sqrt{2}} (\Psi_{010} \pm \Psi_{001})$$

only two of the symmetrized states are not diagonal (Hint: integral over  $z$ )

Hydrogen is a ripe system for doing perturbation theory because the energies and wave functions are analytically known and the effects beyond the non-relativistic Hamiltonian are small.

$$H^{(0)} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

(should use reduced mass, but complicates the following discussion)

The first effect to look at is correction due to relativity

$$\begin{aligned} KE_{rel} &= \sqrt{m^2 c^4 + p^2 c^2} - mc^2 = mc^2 \left[ 1 + \frac{p^2}{m^2 c^2} \right]^{1/2} - mc^2 \\ &= mc^2 \left( 1 + \frac{p^2}{2m^2 c^2} - \frac{p^4}{8m^4 c^4} \dots \right) - mc^2 \\ &\approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} \end{aligned}$$

The  $H^{(1)}$  is the change from  $H^{(0)}$  to  $H = \Rightarrow H^{(1)} = -\frac{p^4}{8m^3 c^2}$

Before doing math, roughly how big is the correction? is it increasing or decreasing with  $n$  at fixed  $l$ ? with  $l$  at fixed  $n$ ?

Do we need to worry about degenerate states?

$$\begin{aligned} E_{nlm}^{(1)} &= \langle \psi_{nlm} | H^{(1)} | \psi_{nlm} \rangle = -\frac{1}{2mc^2} \langle \psi_{nlm} | \frac{p^2}{2m} \frac{p^2}{2m} | \psi_{nlm} \rangle \quad \text{sign?} \\ &= -\frac{1}{2mc^2} \langle \psi_{nlm} | (E_{nl} + \frac{e^2}{4\pi\epsilon_0 r})^2 | \psi_{nlm} \rangle \quad \leftarrow \text{why?} \quad \text{footnote 9 + prob 6.15 are wrong! see erratum 2} \\ &= -\frac{1}{2mc^2} \left[ E_{nl}^2 + 2E_{nl} \frac{e^2}{4\pi\epsilon_0 r} \langle \psi_{nlm} | \frac{1}{r} | \psi_{nlm} \rangle + \left( \frac{e^2}{4\pi\epsilon_0 r} \right)^2 \langle \psi_{nlm} | \frac{1}{r^2} | \psi_{nlm} \rangle \right] \end{aligned}$$

See book for bunch of math steps

$$E_{nlm}^{(1)} = -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l+1/2} - 3 \right] \quad \text{Trends? } n? l?$$

This result is often rewritten using a different notation.

$$\frac{E_n^2}{2mc^2} = -E_n \frac{-E_n}{2mc^2} = -E_n \frac{m^2}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \frac{1}{2mc^2} = -\frac{E_n}{4n^2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 = -\alpha^2 \frac{E_n}{4n^2}$$

$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137.036}$  is a dimensionless constant fine structure constant



Rewrite the energy correction  $E_{n\ell m}^{(1)} = E_n \alpha^2 \left[ \frac{1}{n(l+1/2)} - \frac{3}{4n^2} \right]$   
Remember  $E_n < 0$ !!

The spin-orbit interaction arises from the magnetic dipole moment of the electron interacting with the effective magnetic field from the "proton circling" (or from E-field from proton and effective electric dipole moment from moving electron).

$$H^{(1)} = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

The states now also have the spin  $m_s$

$\psi_{n,\ell,m,\ell}^{(0)}$  are the unperturbed states.

The interaction does not change  $\ell$ , but can mix all states with the same  $m+m_s$ . Why this restriction??  $S_z + L_z$ ??

So you have to use degenerate perturbation theory.

Fortunately, we can find another operator that commutes with  $H$ .

$\vec{J} = \vec{L} + \vec{S}$  is the total angular momentum of the electron

Use the trick:  $\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{L} - \vec{S} \cdot \vec{S})$

The allowed values of  $j$  are  $j = \ell - 1/2$  ( $\ell \geq 1$ ) and  $j = \ell + 1/2$  (all  $\ell$ )

The transformation from the states  $n, \ell, m, m_s$  to  $n, \ell, j, m_j$  are done with Clebsch-Gordan coefficients

$$\psi_{n,\ell,j,m_j}^{(0)} = \sum_{m,m_s} \psi_{n,\ell,m,m_s}^{(0)} \langle \ell, m, s, m_s | j, m_j \rangle \quad \text{only nonzero for } m+m_s = m_j$$

With these quantum numbers, all of the off diagonal matrix elements are 0.

$$(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) |j,\ell\rangle = \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)] |j,\ell\rangle$$

We can now combine all of these factors to get the energy

$$E_{n,l,s}^{(1)} = \frac{e^2}{16\pi\epsilon_0} \frac{\hbar^2}{m^2 c^2} \langle \psi_{nl} | \frac{1}{r^3} | \psi_{nl} \rangle [j(j+1) - l(l+1) - s(s+1)]$$

$$\langle \psi_{nl} | \frac{1}{r^3} | \psi_{nl} \rangle = \frac{1}{2(l+\frac{1}{2})(l+1)n^3 a_0^3} \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2}$$

$$E_{n,l,s}^{(1)} = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 E_{nl} \frac{j(j+1) - l(l+1) - s(s+1)}{2(l+\frac{1}{2})(l+1)n} = -E_{nl} \frac{\alpha^2}{2} \frac{j(j+1) - l(l+1) - s(s+1)}{2(l+\frac{1}{2})(l+1)n}$$

Combining these two corrections, give (after a fair amount of algebra)

$$E_{n,l,s}^{(1)} = E_n \alpha^2 \left[ \frac{1}{n(j+\frac{1}{2})} - \frac{3}{4n^2} \right]$$

The total energy at this level is

$$E_{n,l,s} = E_n \left( 1 + \frac{\alpha^2}{n} \left[ \frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right] \right)$$

Let's see how good this expression is!

$$E_n = E_1 / n^2 = -\frac{1}{2} m c^2 \alpha^2 / n^2$$

Look at the calculation from hydrogen-energy.cpp

The results are very good, fractional errors  $< \sim 10^{-6}$

However, the  $l=0$  are  $\sim 100\times$  worse than the  $l>0$ . Why?

The actual energy is higher than our estimate  $\Rightarrow$  some perturbation with positive energy.

Prob 6.19 gives "exact" formula including relativistic effects.

Numerically can see this isn't the problem.

The nucleus has a finite size  $R \sim 1 \text{ fm}$ . The actual potential inside the nucleus is larger than if using  $1/r$  for  $r < R$ . Could this shift be the problem?  $l=0$  wave function is non-zero as  $r \rightarrow 0$  but  $l>0$  goes to 0!! Let's estimate!

The most extreme case: all of the proton charge is on a shell of radius  $R$ . What is the PE in this case?

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad r > R$$

$$= -\frac{e^2}{4\pi\epsilon_0 R} \quad r < R$$

What is  $H_0$ ? What is  $H_1$ ?

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$H_1 = -\frac{e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 r} \quad r < R$$

$$= 0 \quad r > R$$

Compute the change in the  $1s$  energy!

$$E_{1s}^{(1)} = \langle \psi_{1s} | H^{(1)} | \psi_{1s} \rangle = \iiint H_1(r) |\psi_{1s}(r)|^2 d\phi d(\cos\theta) r^2 dr$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$E_{1s}^{(1)} = \frac{4}{a_0^3} \int_0^R e^{-2r/a_0} \left( \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 R} \right) r^2 dr$$

$$\approx \frac{4}{a_0^3} \int_0^R \left( \frac{e^2}{4\pi\epsilon_0} r - \frac{e^2}{4\pi\epsilon_0 R} r^2 \right) dr = \frac{4}{a_0^3} \left( \frac{e^2}{4\pi\epsilon_0} \frac{R^2}{2} - \frac{e^2}{4\pi\epsilon_0} \frac{R^3}{3} \right)$$

$$= \frac{4}{6} \frac{e^2}{4\pi\epsilon_0 a_0} \left( \frac{R}{a_0} \right)^2 \approx \frac{2}{3} \cdot 27.21 \text{ eV} \cdot \left( \frac{10^{-15}}{0.53 \times 10^{-10}} \right)^2 \approx 6.5 \times 10^{-9} \text{ eV}$$

This correction is too small by  $\sim 4$  orders of magnitude. (This effect is measurable and gives an estimate for the size of the proton. The same shift for muonic H is much bigger because  $a$  is smaller.)

What is causing the shift ??? The error in the  $1s$  state is  $3.37 \times 10^{-5} \text{ eV} = 5.39 \times 10^{-24} \text{ J} = 8.14 \text{ GHz } h$ . The error in the  $2s$  state is  $4.32 \times 10^{-6} \text{ eV} = 6.91 \times 10^{-25} \text{ J} = 1.04 \text{ GHz } h$

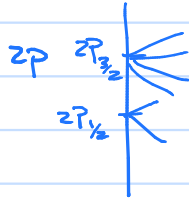
Notice: Dirac  $\Rightarrow 2S_{1/2}$  and  $2P_{1/2}$  have same energy. But the experiment has a "large" shift for  $2S_{1/2}$

Measured using microwaves  $\Delta E = 1057.845(3) \text{ MHz}$

QED effects; the full Maxwell eq. is needed for the  $\gamma$ - $e$  interaction

See Sec 6.4 for how the energy levels are split by a B-field at this level (fine structure)

## Zeeman Effect



$M_T = \text{conserved}$   
 $M_T = 3/2, -3/2$  good eigenstates  
 $M_T = 1/2$  2 states that can mix  
 $M_T = -1/2$  2 states that can mix

Hyperfine effect: There is an effective interaction between the electron and the proton with the form

$$H_{\text{HF}} = C \vec{S}_p \cdot \vec{S}_e \quad \text{What are the units of } C?$$

We can find the eigen energies and states using the trick  
 $\vec{J} = \vec{S}_p + \vec{S}_e$

This gives

$$H_{\text{HF}} = \frac{C}{2} (J^2 - S_p^2 - S_e^2)$$

There are 3 states with  $j=1$  and 1 state with  $j=0$

$$\begin{aligned} |j, m_j\rangle & \\ |1, 1\rangle &= |1/2\rangle_e |1/2\rangle_p \\ |1, 0\rangle &= \frac{1}{\sqrt{2}} (|1/2\rangle_e |-1/2\rangle_p + |-1/2\rangle_e |1/2\rangle_p) \\ |1, -1\rangle &= |-1/2\rangle_e |1/2\rangle_p \\ |0, 0\rangle &= \frac{1}{\sqrt{2}} (|1/2\rangle_e |-1/2\rangle_p - |-1/2\rangle_e |1/2\rangle_p) \end{aligned}$$

The energies are  $E_{j, m_j} = \frac{\hbar^2 C}{2} [j(j+1) - \frac{1}{2} \frac{3}{2} - \frac{1}{2} \frac{3}{2}]$

The splitting between the  $j=0$  and  $j=1$  states is known very accurately  $E_{j=1} - E_{j=0} = 1420.4057517667(10) \text{ MHz} \cdot h$

Photons emitted with this frequency have a wave length of  $\lambda = c/f = 2.998 \times 10^{10} \text{ cm/s} / 1420 \times 10^6 \text{ Hz} = 21.1 \text{ cm}$  (The famous 21 cm line in astrophysics. Remember most of the matter between the stars is H in it's ground state.)

Use the relation to figure out C

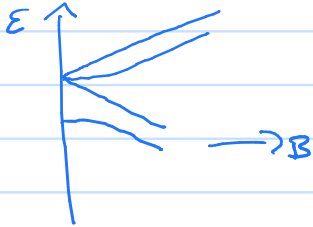
$$E_{j=1} - E_{j=0} = \hbar^2 C \equiv \Delta E_{\text{HF}} \Rightarrow C = \Delta E_{\text{HF}} / \hbar^2$$

What is the Hamiltonian if there's a magnetic field

$$H = H_{HF} + \mu_p \frac{2}{\hbar} S_{p,z} B - \mu_e \frac{2}{\hbar} S_{e,z} B$$

The  $\mu_e = 928.4764620(57) \times 10^{-26} \text{ J/T}$ ,  $\mu_p = 1.4106067873(47) \times 10^{-26} \text{ J/T}$  are the magnitudes of the magnetic moment of the electron and proton.

What does the energies vs.  $B$  have to look like?



For small  $B$   $H^{(0)} = H_{HF}$   $H^{(1)} = (\mu_p S_{p,z} - \mu_e S_{e,z}) \frac{2}{\hbar} B$

First order correction

$$E_{j, m_j}^{(1)} = \langle j, m_j | H^{(1)} | j, m_j \rangle$$

$$E_{1,1}^{(1)} = (\mu_p - \mu_e) B = -(\mu_e - \mu_p) B$$

$$E_{1,0}^{(1)} = \frac{1}{2} \frac{2}{\hbar} B (\langle \frac{1}{2}, -\frac{1}{2} | + \langle -\frac{1}{2}, \frac{1}{2} |) (\mu_p S_{p,z} - \mu_e S_{e,z}) (\frac{1}{2}, -\frac{1}{2} \rangle + | -\frac{1}{2}, \frac{1}{2} \rangle)$$

= 0 go through all 8 terms to show add to 0

$$E_{1,-1}^{(1)} = (\mu_e - \mu_p) B = -E_{1,1}^{(1)}$$

$$E_{0,0}^{(1)} = 0$$

Second order correction

$H^{(1)}$  commutes with  $J_z \Rightarrow$  the only nonzero terms are between the  $m_j=0$  states

$$\begin{aligned} \langle j=1, m_j=0 | H^{(1)} | j=0, m_j=0 \rangle &= \frac{1}{2} \frac{2}{\hbar} B (\langle \frac{1}{2}, -\frac{1}{2} | + \langle -\frac{1}{2}, \frac{1}{2} |) (\mu_e S_{e,z} - \mu_p S_{p,z}) (\frac{1}{2}, -\frac{1}{2} \rangle - | -\frac{1}{2}, \frac{1}{2} \rangle) \\ &= -\frac{B}{\hbar} [\mu_e \frac{\hbar}{2} - -\mu_e \frac{\hbar}{2} - \mu_p \frac{\hbar}{2} - -\mu_p \frac{\hbar}{2}] \\ &= -B(\mu_e - \mu_p) \end{aligned}$$

$$E_{j=1, m=0}^{(2)} = \frac{[-B(\mu_e - \mu_p)]^2}{\Delta E_{HF}}$$

$$E_{j=0, m=0}^{(2)} = \frac{[-B(\mu_e - \mu_p)]^2}{-\Delta E_{HF}}$$

} Note the change in energy is quadratic in  $B$

What should you do if the B-field is large??  
The hyperfine interaction becomes the perturbation.

$$H^{(0)} = (\mu_p S_{p,z} - \mu_e S_{e,z}) \frac{2}{\hbar} B$$

$$H^{(1)} = H_{\text{HF}}$$

The 4 eigenstates of  $H^{(0)}$  are  $|\frac{1}{2}, \frac{1}{2}\rangle$ ,  $|\frac{-1}{2}, \frac{-1}{2}\rangle$ ,  $|\frac{1}{2}, \frac{-1}{2}\rangle$ ,  $|\frac{-1}{2}, \frac{1}{2}\rangle$

The hyperfine interaction gives nonzero first order shift for all of the states. The 2<sup>nd</sup> order energy shift only affects the last two states  $M_e + M_p = 0$ .