7.2 Degenerate Perturbation Theory:

What happens if the state you are correcting by perturbation theory is degenerate? (e.g. 2p - - -)

Consider first degeneracy two (we will drop the index "n" because degenerate states are not generic but special cases). This means:

$$H^0\psi_a^0 = E^0\psi_a^0 \qquad H^0\psi_b^0 = E^0\psi_b^0 \qquad \langle\psi_a^0|\psi_b^0\rangle = 0$$

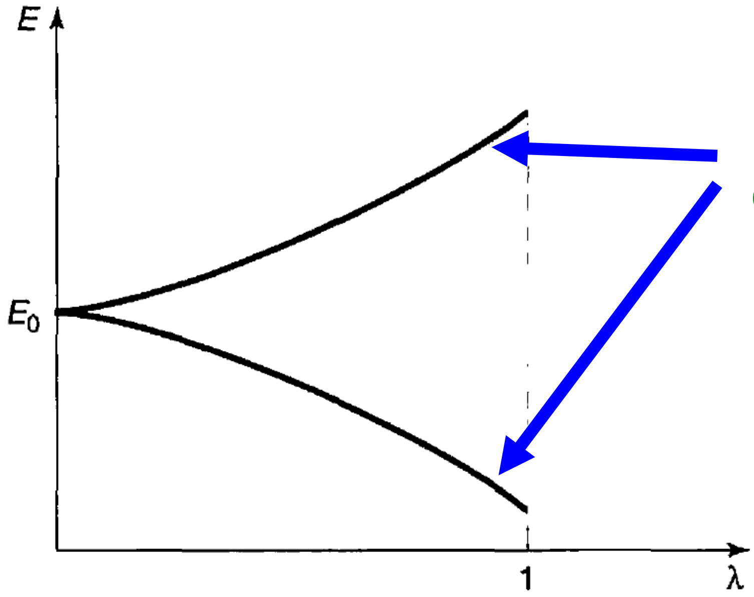
Same energy, like 2p levels in H atom. The most important corrections arise from orbitals with same or similar energy.

Any linear combination has the same energy.

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$$

$$H^0\psi^0 = E^0\psi^0$$

Usually, the perturbation H' will break the degeneracy.



Resulting states are particular linear combination of the two original degenerate states.

We will repeat the same steps as before:

$$H = H^0 + \lambda H'$$

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \cdots$$

$$\psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \cdots$$

To lowest order we arrive to the same equation as before, just without the index n.

$$H^0\psi^1 + H'\psi^0 = E^0\psi^1 + E^1\psi^0$$

Again, follow the same procedure as before, namely take the inner product but using first ψ_a^0 and then ψ_b^0 :

$$\langle\psi_a^0|H^0\psi^1\rangle + \langle\psi_a^0|H'\psi^0\rangle = E^0\langle\psi_a^0|\psi^1\rangle + E^1\langle\psi_a^0|\psi^0\rangle$$

Via Hermiticity of H^0, again these two cancel.

Gives only α

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$$

$$\alpha\langle\psi_a^0|H'|\psi_a^0\rangle + \beta\langle\psi_a^0|H'|\psi_b^0\rangle = \alpha E^1$$

$$\boxed{\alpha W_{aa} + \beta W_{ab} = \alpha E^1}$$

When the "b" degenerate state is used, we find a similar formula:

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1$$

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1$$

$$\begin{bmatrix} Waa & Wab \\ Wba & Wbb \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^1 \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

It is like a 2x2 matrix problem. α and β are the components of the eigenfunction and E^1 the eigenvalue.

$$E^1_{\pm} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right]$$

7.3 The Fine Structure of Hydrogen:

When we studied the hydrogen atom we used what, at first sight, seemed to be the complete Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \qquad \mathbf{p} \to (\hbar/i)\nabla$$

However, small corrections are still missing. The most important is called fine structure and it is made of a relativistic component and a spin-orbit coupling. These are small corrections that are incorporated by perturbation theory (not possible to solve problem exactly anymore).

7.3.1 Relativity first.

The first term of the Hamiltonian above is the quantum version of:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\mathbf{p} \to (\hbar/i)\nabla$$

We will try to improve the kinetic energy including corrections from relativity:

The full "classical" relativistic formula is:

$$T = \underbrace{\frac{mc^2}{\sqrt{1-(v/c)^2}}}_{\text{Total energy}} - \underbrace{mc^2}_{\text{Rest energy}}$$

… and the momentum is:

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}$$

It can be shown (see book) that:

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

Trying to use $\mathbf{p} \rightarrow (\hbar/i)\nabla$ is complicated because of the square root …

$$T = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots - 1\right]$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots$$

$\sqrt{1+x} \sim 1 + x/2 - x^2/8 + x^3/16 + \ldots$

Then our perturbative correction is:

$$H'_r = -\frac{p^4}{8m^3c^2}$$

To lowest order in perturbation theory the energy correction is:

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3c^2}\langle \psi | p^4 \psi \rangle$$

The "sandwich" is with the unperturbed states of Ch. 4 and we are using non-deg perturbation theory.

From the unperturbed Sch Eq we know that:

$$p^2\psi = 2m(E - V)\psi$$

Unperturbed energies of Ch. 4.

Then we arrive to:

$$E_r^1 = -\frac{1}{2mc^2}\langle(E-V)^2\rangle = -\frac{1}{2mc^2}[E^2 - 2E\langle V\rangle + \langle V^2\rangle]$$

Now specifically for the hydrogen atom potential V= $-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$

It can be shown (no need to verify) that:

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

Then, we arrive to the result:

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{(l+1/2)n^3 a^2}\right]$$

Using formulas of Ch. 4 for the Bohr radius *a* and for E_n :

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \qquad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$E_r^1 = -\frac{(E_n)^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$$

Example: for ground state use n=1, l=0, E_1 = -13.6 eV, *m* mass of electron, and *c* speed of light. Result ~ 10^{-3} eV (small!).