7.1.3 Second-Order Energies:

We will use a formula we derived a few pages back:

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

Again, we take the inner product with ψ_n^0 and arrive to:

$$\langle\psi_n^0|H^0\psi_n^2\rangle + \langle\psi_n^0|H'\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle$$

Normalized to 1. Note that E_n^2 is what we want.

Again, we use the hermiticity of the unperturbed H^0 to move it around:

$$\langle\psi_n^0|H^0\psi_n^2\rangle = \langle H^0\psi_n^0|\psi_n^2\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle$$

The first term on each side are equal and they cancel.

We are left with a formula for the quantity we need:

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$$

Moreover, expanding in a complete basis as before:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0$$

Then:

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0$$

Also, we already deduced the wave function first-order correction:

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

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

Putting all together:

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

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$

We use Hermitian

$\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle$

and $\langle g | f \rangle = \langle f | g \rangle^*$

from chapter 3.

Second order perturbation theory widely used. See https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.127.077204

Our derivation of formulas stops here, although in principle we can follow the same steps to any order.

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:

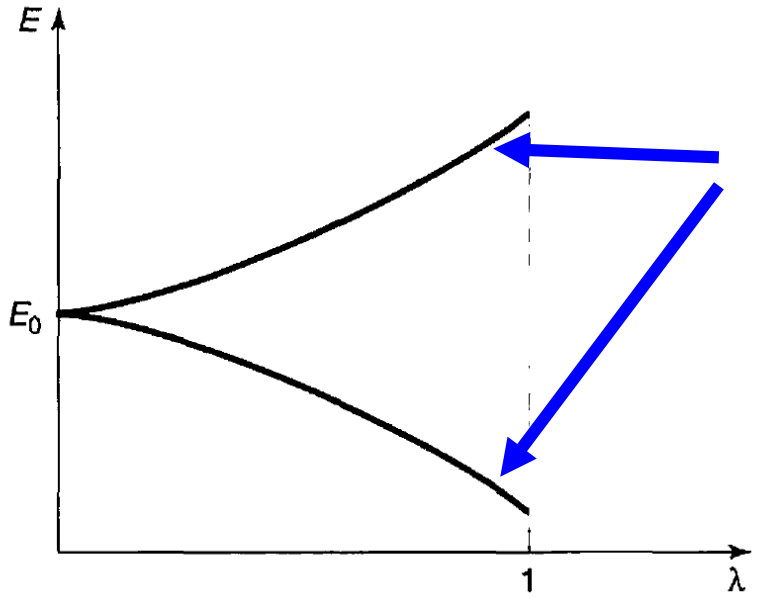
$$H^0\psi_a^0 = E^0\psi_a^0 \qquad H^0\psi_b^0 = E^0\psi_b^0 \qquad \langle\psi_a^0|\psi_b^0\rangle = 0$$

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

Important: any linear combination has the same energy.

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0 \qquad H^0\psi^0 = E^0\psi^0$$

Usually, the perturbation H' will break the degeneracy.



Resulting states -- after perturbation acts -- are special 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 both: 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 out.

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:

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

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

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^1 \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

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:

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

Total energy — 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= $-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

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