11.2 first order correction to the wavefunction

This can be calculated from $\psi_n^1 = \sum_{n\neq l} c_{nl}\psi_l^0$ where

$$c_{nl} = -\frac{<\psi_l^0|H'\psi_n^0>}{(E_l^0 - E_n^0)} = \frac{<\psi_l^0|H'\psi_n^0>}{(E_n^0 - E_l^0)}$$

so $\psi_n(x) \approx \psi_n^0 + \psi_n^1$

while perturbation theory often yields surprisingly accurate first order corrections to the energies, E_n^1, the first order wavefunction corrections, ψ_n^1, are notoriously poor

11.3 second order correction to energy

The second order correction done straightforwardly from our estimate for ψ_n^1

$$E_n^2 =<\psi_n^0|H'\psi_n^1>$$

or we can expand this out into the full sum

$$E_n^2 =<\psi_n^0|H'\sum_{m\neq n} c_{nm}\psi_m^0>=\sum_{m\neq n} c_{nm}<\psi_n^0|H'\psi_m^0>$$

$$=\sum_{m\neq n}\frac{<\psi_m^0|H'\psi_n^0>}{E_n^0 - E_m^0}<\psi_n^0|H'\psi_m^0>$$

But H' is also hermitian (gives us a energy which is always real!) so

$$<\psi_n^0|H'\psi_m^0>=<H'\psi_n^0|\psi_m^0>=<\psi_m^0|H'\psi_n^0>^*$$

so then we have

$< \psi_m^0 | H' \psi_n^0 >< \psi_n^0 | H' \psi_m^0 > = < \psi_m^0 | H' \psi_n^0 >< \psi_m^0 | H' \psi_n^0 >^* = | < \psi_m^0 | H' \psi_n^0 > |^2$

and finally

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

so $E_n \approx E_n^0 + E_n^1 + E_n^2 + \ldots$

12 Degenerate perturbation theory

all that depended on $E_n - E_m \neq 0$. but we had a lot of degenerate levels in hydrogen! so we really need to know how to treat degenerate levels.

12.1 two fold degeneracy

suppose we have a level where there are exactly 2 states ψ_a^0 and ψ_b^0 which give the same energy E^0, so any linear combination $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$ also gives the same energy E^0 e.g. in hydrogen for $l = 0, m = 0, m_s = \pm 1/2$.

typically the perturbation H' breaks the degeneracy, so that E^0 splits into two, with the difference in energy increasing as λ goes from $0 \to 1$. when we turn off the pertubation, the upper states goes back to a unique α, β while the lower states goes back to another unique α, β. we want to find these 'good' unperturbed states!!

we have the same first order correction expression

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

but now we multiply by ONE of our states ψ_a^{0*} and integrate

$$< \psi_a^0|H^0\psi^1 > + < \psi_a^0|H'\psi^0 >=< \psi_a^0|E^0\psi^1 > + < \psi_a^0|E^1\psi^0 >$$

$$< (H^0\psi_a^0|\psi^1 > + < \psi_a^0|H'\psi^0 >=< \psi_a^0|E^0\psi^1 >< \psi_a^{0*}|E^1\psi^0 >$$

$$E^0 < \psi_a^0|\psi^1 > + < \psi_a^0|H'\psi^0 >= E^0 < \psi_a^0|\psi^1 > +E^1 < \psi_a^0|\psi^0 >$$

$$< \psi_a^{0*}|H'\psi^0 >= E^1 < \psi_a^0|\psi^0 >$$

$$< \psi_a^0|H'(\alpha\psi_a^0 + \beta\psi_b^0) >= E^1 < \psi_a^0|(\alpha\psi_a^0 + \beta\psi_b^0) >$$

$$\alpha < \psi_a^0|H'\psi_a^0 > +\beta < \psi_a^0|H'\psi_b^0 >= E^1\alpha < \psi_a^0|\psi_a^0 > +E^1\beta < \psi_a^0|\psi_b^0 >$$

$$\alpha < \psi_a^0|H'\psi_a^0 > +\beta < \psi_a^0|H'\psi_b^0 >= E^1\alpha$$

we can write this more compactly as

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad \text{where } W_{ij} =< \psi_i^0|H'\psi_j^0 >= \int \psi_i^{0*}H'\psi_j^0 dx$$

and i, j is one of a, b. We could have multiplied by ψ_b^{0*} instead in which case we would get

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

this is a matrix equation where

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

we can solve this by subtracting

$$\begin{pmatrix} W_{aa}-E^1 & W_{ab} \\ W_{ba} & W_{bb}-E^1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

so the only non-trivial solutions are where the determinant of the 2x2 matrix is zero so it can't be inverted! so

$$(W_{aa}-E^1)(W_{bb}-E^1) - W_{ab}W_{ba} = 0$$

but $W_{ab} + W_{ba}^*$ so

$$W_{aa}W_{bb} - (W_{aa}+W_{bb})E^1 + (E^1)^2 - |W_{ab}|^2 = 0$$

this is just a quadratic and so it has 2 solutions

$$E_{\pm}^1 = \frac{1}{2}[W_{aa} + W_{bb} \pm \sqrt{(W_{aa}+W_{bb})^2 - 4(W_{aa}W_{bb} - |W_{ab}|^2)} = 0$$

$$E_{\pm}^1 = \frac{1}{2}[W_{aa} + W_{bb} \pm \sqrt{(W_{aa}-W_{bb})^2 + 4|W_{ab}|^2)} = 0$$

12.1.1 example

Two states, ψ_a and ψ_b are degenerate, both having energy E^0, so any linear combination $\psi = \alpha\psi_a + \beta\psi_b$ also has energy E^0. A small perturbation, H', causes a small change in energy, and the first order approximation for this, E^1, is given by the solution of a matrix equation.

suppose the H' is such that $< \psi_a^0|H'\psi_b^0 >=< \psi_b^0|H'\psi_a^0 >= \kappa$ (i.e. κ is real) while $< \psi_a^0|H'\psi_a^0 >=< \psi_b^0|H'\psi_b^0 >= 1$

the matrix equation for E^1 such that

$$\begin{pmatrix} 1 & \kappa \\ \kappa & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\begin{pmatrix} 1 & \kappa \\ \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\begin{pmatrix} 1 - E^1 & \kappa \\ \kappa & 1 - E^1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

only non-trivial solution when the determinant is zero. $(1 - E^1)^2 - \kappa^2 = 0$ so $1 - E^1_\pm = \pm\kappa$ or $E^1_\pm = 1 \pm \kappa$.

so we can draw a graph of the energies splitting as we turn up the perturbation $\lambda H'$ by turning up λ from 0 to 1 - energies go from both being E^0 to splitting into $E^0 + E^1_+$ and $E^0 + E^1_-$

what are the corresponding wavefunctions which 'follow' the perturbation? we can solve separately for $E^1_\pm$ by substituting into our matrix, so $E^1_+ = 1 + \kappa$ gives

$$\begin{pmatrix} 1 - (1 + \kappa) & \kappa \\ \kappa & 1 - (1 + \kappa) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

$$\begin{pmatrix} -\kappa & \kappa \\ \kappa & -\kappa \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

so $-\kappa\alpha + \kappa\beta = 0$ so $\alpha = \beta$. and we need the standard normalisation conditions of $\alpha^2 + \beta^2 = 1$ so $\psi_+ = 1/\sqrt{2}(\psi^0_a + \psi^0_b)$.

similarly for $E^1_- = 1 - \kappa$ we get

$$\begin{pmatrix} \kappa & \kappa \\ \kappa & \kappa \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

i.e. $\kappa\alpha + \kappa\beta = 0$ or $\alpha = -\beta$ so $\psi_- = 1/\sqrt{2}(\psi^0_a - \psi^0_b)$.

these wavefunctions are special combinations of our original wavefunctions in that they are wavefunctions that follow the perturbation. If we had chosen these to start with then the matrix elements would have been

$$W_{++} =< \psi_+^0 | H' \psi_+^0 >= 1/2 < \psi_a^0 + \psi_b^0 | H' (\psi_a^0 + \psi_b^0 >$$
$$= 1/2(< \psi_a^0 | H' \psi_a^0 > + < \psi_a^0 | H' \psi_b^0 > + < \psi_b^0 | H' \psi_a^0 > + < \psi_b^0 | H' \psi_b^0 >)$$
$$= 1/2(1 + \kappa + \kappa + 1) = 1 + \kappa$$
$$W_{+-} = W_{-+}^* =< \psi_+^0 | H' \psi_-^0 >= 1/2(< \psi_a^0 + \psi_b^0 | H' (\psi_a^0 - \psi_b^0 >$$
$$= 1/2(< \psi_a^0 | H' \psi_a^0 > - < \psi_a^0 | H' \psi_b^0 > + < \psi_b^0 | H' \psi_a^0 > - < \psi_b^0 | H' \psi_b^0 >) = 1/2(1 - \kappa + \kappa - 1) = 0$$
$$W_{--} =< \psi_-^0 | H' \psi_-^0 >= 1/2(< \psi_a^0 - \psi_b^0 | e H' (\psi_a^0 - \psi_b^0 >$$
$$= 1/2(< \psi_a^0 | H' \psi_a^0 > - < \psi_a^0 | H' \psi_b^0 > - < \psi_b^0 | H' \psi_a^0 > + < \psi_b^0 | H' \psi_b^0 >)$$
$$= 1/2(1 - \kappa - \kappa + 1) = 1 - \kappa$$