12.5 3D square well example (cont)

so the non-trivial solution (i.e. $\alpha, \beta, \gamma \neq 0$) is when the determinant of the matrix is zero

$$(1-w)\begin{vmatrix} 1-w & \kappa \\ \kappa & 1-w \end{vmatrix} - 0\begin{vmatrix} 0 & \kappa \\ 0 & 1-w \end{vmatrix} + 0 = 0$$

$$(1-w)[(1-w)^2 - \kappa^2] = 0$$

so the roots are $1-w=0$ i.e. $w=1$ and $(1-w)^2 = \kappa^2$ i.e. $1-w = \pm\kappa$ so $4E_1/V_0 = 1$ and $4E_1/V_0 = 1 \mp \kappa$ so $E_1 = V_0/4,\ V_0/4 - 16/(9\pi^2)$ and $V_0/4 + 16/(9\pi^2)$.

sub each value of w back into the matrix - first w=1

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

so $\kappa\gamma = 0$ and $\kappa\beta = 0$ and the only one left is α so the eigenvector for $w=1$ is just $|1>= \psi_{112}$

similarly for $w = 1-\kappa$ we have

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

so $\kappa\alpha = 0$ and $\kappa\beta + \kappa\gamma = 0$ so $\gamma = -\beta$ so $\sqrt{1/2}(|2> - |3>) = \sqrt{1/2}(\psi_{121} - \psi_{211})$

and for $w = 1+\kappa$ is $\sqrt{1/2}(\psi_{121} + \psi_{211})$

so if we had started with these in the first place we would have been OK to use non-degenerate perturbation theory - you can check that with these wavefunctions all off diagonal terms $W_{ij} = 0$ for $j \neq i$

$a >= 1 >$, $b >= \frac{1}{\sqrt{2}}(2 > -3 >)$, $c >= \frac{1}{\sqrt{2}}(2 > -3 >)$

$W_{aa} = W_{11} = V_0/4$

$W_{ab} =< a|H'b >= \frac{1}{\sqrt{2}}(< 1|H'2 > - < 1|H'3 >) = 0$

$W_{ac} =< a|H'c >= \frac{1}{\sqrt{2}}(< 1|H'2 > + < 1|H'3 >) = 0$

$W_{bb} =< b|H'b >= \frac{1}{\sqrt{2}}(< b|H'2 > - < b|H'3 >) = 1/2(< 2|H'2 > - < 3|H'2 > - < 2|H'3 > + < 3|H'3 >) = 1/2(2V_0/4 - 2\kappa V_0/4) = (1-\kappa)V_0/4$

$W_{bc} =< b|H'c >= \frac{1}{\sqrt{2}}(< b|H'2 > + < b|H'3 >) = 1/2(< 2|H'2 > - < 3|H'2 > + < 2|H'3 > - < 3|H'3 >) = 0$

$W_{cc} =< c|H'c >= \frac{1}{\sqrt{2}}(< c|H'2 > + < c|H'3 >) = 1/2(< 2|H'2 > + < 3|H'2 > + < 2|H'3 > + < 3|H'3 >) = V_0/4(1+\kappa)$

Hence the matrix is

$$\begin{pmatrix} V_0/4 - E^1 & 0 & 0 \\ 0 & (1-\kappa)V_0/4 - E^1 & 0 \\ 0 & 0 & (1+\kappa)V_0/4 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = 0$$

so we have $E^1 = V_0/4, (1-\kappa)V_0/4, (1+\kappa)V_0/4$. Had we chosen $a > b >$ and $c >$ at the start we could have used non-degenerate perturbation theory with $E^1_a =< a|H'a >$ etc

13 Application to Hydrogen

we saw that each level n in Hydrogen was n^2 degenerate (without spin) or $2n^2$ degenerate once we count spin as well, bringing in an additional quantum number $m_s = \pm 1/2$. So now lets do it!!!

13.1 Spin-orbit coupling

The perturbation to the potential from the magnetic dipole moment generated by electron spin, μ_s, is $H' = -\underline{\mu}_s.\underline{B}$ where B is the external magnetic field.

we already know $\underline{\mu_s} = -g_s \frac{e}{2m_e}\underline{S}$ (see lecture 14). And g_s, the spin factor of an electron, is OBSERVED to be ~ 2 (as can be calculated from relativistic quantum theory). so $\underline{\mu}_s = -\frac{e}{m_e}\underline{S}$.

now all we need is $\underline{B}$. For orbitals which have angular momentum (i.e. everything except $l = 0$), then in a classical picture, the electron is orbiting the nucleus. but from the electrons point of view its the +ve nucleus which orbits around it! This sets up a magnetic field from the current loop $B = \mu_0 I/2r$ from the effective current $I = e/P$ where P is the period of the orbit $P = 2\pi r/v$. But orbital angular momentum is

$$L = rmv = rm2\pi r/P = 2\pi mr^2/P = \frac{2\pi mr^2 I}{e} = \frac{2\pi mr^2 2rB}{\mu_0 e}$$

this was just about magnitute, but B and L are both vectors, and they point in the same direction as they are from the same effect! so

$$\underline{L} = \frac{2\pi mr^2 2r\underline{B}}{\mu_0 e} = \frac{4\pi\epsilon_0 c^2 mr^3}{e}\underline{B}$$

as $\epsilon_0\mu_0 = 1/c^2$. Turn this around and get

$$\underline{B} == \frac{e}{4\pi\epsilon_0 c^2 mr^3}\underline{L}$$

hence

$$H' = -\underline{\mu}_s.\underline{B} = \frac{e}{m}\underline{S}.\frac{e}{4\pi\epsilon_0 c^2 m r^3}\underline{L} = \frac{e^2}{4\pi\epsilon_0 c^2 m^2 r^3}\underline{S}.\underline{L}$$

However, this ignored the acceleration of the electron - putting this in approximately results in an answer which is approximately half. so there is an additional (small) potential from spin-orbit coupling which gives a perturbation

$$H'_{so} = \frac{e^2}{8\pi\epsilon_0 c^2 m^2 r^3}\underline{S}.\underline{L}$$

so our hamiltonian has an extra term from $\underline{S}.\underline{L} = S_x L_x + S_y L_y + S_z L_z$. so we know that if the perturbation commutes with H^0 then we can use the $E_i^1 =< \psi_i^0 | H' \psi_i^0 >$ even on degenerate levels!

so we might want to use ψ_{nlmm_s} i.e. use the joint eigenfunctions of H^0, L^2, L_z, S^2, S_z labeled by our standard quantum numbers n, m, l, m_s where $m_s = \pm 1/2$ becasue $s = 1/2$ BUT these do not commute with the perturbation $\underline{S}.\underline{L}$. $\underline{S}.\underline{L}$ will contain terms with L_x and L_y which will not commute with L_z and terms S_x, S_y which will not commute with S_z. ... so we'd have to use full degenerate perturbation theory which is a *real* pain.

But if we make a total angular momentum $\underline{J} = \underline{L} + \underline{S}$, then this total J does commute with all our original operators AND with the perturbation!