HOMEWORK 3 SOLUTIONS

12) $H_1 = AS_x^2 + BS_z^2$

$$S_x^2 = \frac{\hbar^2}{2}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} = \frac{\hbar^2}{2}\begin{bmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{bmatrix}$$

$$S_z^2 = \hbar^2\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \hbar^2\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

So
$$H_1 = \frac{\hbar^2}{2}\begin{bmatrix} A+2B & 0 & A \\ 0 & 2A & 0 \\ A & 0 & A+2B \end{bmatrix}$$

Note that the basis states for constructing the spin operators are
$$\chi_1^1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \chi_1^0 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \chi_1^{-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$
and if we use these basis states for the perturbation calculation, the matrix we need for the perturbation calculation ($H_{ij} = \langle \phi_i | H_1 | \phi_j \rangle$) is identical to the H_1 matrix above: i.e. $\langle \phi_i | H_1 | \phi_j \rangle$ just gives the i,j element of H_1. So our problem is

$$+\frac{\hbar^2}{2}\begin{bmatrix} A+2B & 0 & A \\ 0 & 2A & 0 \\ A & 0 & A+2B \end{bmatrix}\begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix} = E^{(1)}\begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix}$$

$\Rightarrow$

Let $a = \hbar^2 A \quad b = \hbar^2 B \Rightarrow$ we get

$$\text{DET}\begin{bmatrix} \frac{a}{2}+b-E & 0 & \frac{a}{2} \\ 0 & a-E & 0 \\ \frac{a}{2} & 0 & \frac{a}{2}+b-E \end{bmatrix} = (a-E)\left[\left(\frac{a}{2}+b-E\right)^2 - \left(\frac{a}{2}\right)^2\right] = 0$$

$$(a-E)\left[\cancel{\left(\tfrac{a}{2}\right)^2}+b^2+E^2+ab-2bE-aE-\cancel{\left(\tfrac{a}{2}\right)^2}\right]$$

$$=(a-E)\left[(b-E)(a+b-E)\right]$$

So the roots are

$$\boxed{E = a,\ b,\ a+b = \hbar^2 A,\ \hbar^2 B,\ \hbar^2(A+B)}$$

Eigenvectors: We need

$$\begin{bmatrix} \frac{a}{2}+b & 0 & \frac{a}{2} \\ 0 & a & 0 \\ \frac{a}{2} & 0 & \frac{a}{2}+b \end{bmatrix}\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\end{bmatrix} = \begin{bmatrix} b\alpha_1+\frac{a}{2}(\alpha_1+\alpha_3) \\ a\alpha_2 \\ \frac{a}{2}(\alpha_1+\alpha_3)+b\alpha_3\end{bmatrix} = E\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\end{bmatrix}$$

i) $E=a \Rightarrow$

$$\left.\begin{array}{l} b\alpha_1+\frac{a}{2}\alpha_1+\frac{a}{2}\alpha_3 = a\alpha_1 \\ \frac{a}{2}\alpha_1+\frac{a}{2}\alpha_3+b\alpha_3 = a\alpha_3 \end{array}\right\}\ \text{require } \alpha_1=\alpha_3=0$$

$a\alpha_2=a\alpha_2 \Rightarrow \alpha_2 = \text{anything}$

$$\psi=\begin{bmatrix}0\\1\\0\end{bmatrix}$$

ii) $E=b \Rightarrow$

$$b\alpha_1+\frac{a}{2}\alpha_1+\frac{a}{2}\alpha_3 = b\alpha_1 \Rightarrow \frac{a}{2}(\alpha_1+\alpha_3)=0$$

$$\frac{a}{2}(\alpha_1+\alpha_3)+b\alpha_3 = b\alpha_3 \Rightarrow \quad ''$$

$$a\alpha_2=b\alpha_2 \Rightarrow \alpha_2=0 \qquad \psi=\frac{1}{\sqrt{2}}\begin{bmatrix}1\\0\\-1\end{bmatrix}$$

iii) $E=a+b$

$$b\alpha_1+\frac{a}{2}\alpha_1+\frac{a}{2}\alpha_3=(a+b)\alpha_1 \Rightarrow \frac{a}{2}\alpha_3=\frac{a}{2}\alpha_1$$

$$\frac{a}{2}(\alpha_1+\alpha_3)+b\alpha_3=(a+b)\alpha_3 \Rightarrow \quad ''$$

$$a\alpha_2=(a+b)\alpha_2 \Rightarrow \alpha_2=0 \qquad \psi=\frac{1}{\sqrt{2}}\begin{bmatrix}1\\0\\1\end{bmatrix}$$

13) (a) In a 1-electron system $E=-\frac{mc^2}{2}\alpha^2\left[\frac{Z^2}{n^2}\right]=-13.6\text{eV}\left(\frac{Z}{n}\right)^2$ so the ground state energy is $-13.6\text{eV}\cdot Z^2$. For the 2-electron system we have $(1s)^2$ and so the energy is predicted to be $-2(13.6\text{eV})\cdot Z^2$ + correction for V_{ee}

$$= -2(13.6\,eV)\cdot Z^2 + \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{a_0}$$

The ionization energy is the difference

$$E(2e) + \overset{\text{ionization energy}}{I} = E(1e)$$

$$-2(13.6\,eV)\cdot Z^2 + \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{a_0} + I = -(13.6\,eV)Z^2$$

$\Rightarrow$

$$I = (13.6\,eV)\cdot Z^2 - \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{a_0} = (13.6\,eV)\cdot Z^2 - \frac{5}{8} Z\cdot(27.2\,eV)$$

He	$I = 20.4\,eV$
Li^+	$71.4\,eV$
Be^{++}	$149.6\,eV$
B^{+++}	$255.0\,eV$

(b) It looks like we are always too low by about 4eV.

14) (a) $\boxed{\psi = \left(\frac{2}{L}\right) \sin\frac{\pi}{L}x_1 \sin\frac{\pi}{L}x_2 \left(\frac{1}{\sqrt{2}}\right)\left[\chi_1^+\chi_2^- - \chi_1^-\chi_2^+\right]}$

(b) $\psi_1 = \left(\frac{2}{L}\right)\frac{1}{\sqrt{2}}\left[\sin\frac{\pi}{L}x_1 \sin\frac{2\pi}{L}x_2 + \sin\frac{2\pi}{L}x_1 \sin\frac{\pi}{L}x_1\right]\times\frac{1}{\sqrt{2}}$
$\left[\chi_1^+\chi_2^- - \chi_1^-\chi_2^+\right]$ (Singlet)

$$\psi_2 = \left(\frac{2}{L}\right)\frac{1}{\sqrt{2}}\left[\sin\frac{\pi}{L}x_1 \sin\frac{2\pi}{L}x_2 - \sin\frac{2\pi}{L}x_1 \sin\frac{\pi}{L}x_2\right]\chi_1^+\chi_2^+$$

$$\psi_3 = \left(\frac{2}{L}\right)\frac{1}{\sqrt{2}}\left[\quad '' \quad - \quad '' \quad\right]\chi_1^-\chi_2^-$$

$$\psi_4 = \left(\frac{2}{L}\right)\frac{1}{\sqrt{2}}\left[\quad '' \quad - \quad '' \quad\right]\frac{1}{\sqrt{2}}\left[\chi_1^+\chi_2^- + \chi_1^-\chi_2^+\right]$$

(c) In perturbation theory

$$\Delta E = \langle\psi|H_1|\psi\rangle$$

(we don't need to do degenerate state perturbation

theory here because all the off-diagonal matrix elements $\langle \psi_i | H_1 | \psi_j \rangle$ with $i \neq j$ are zero from the spin functions).
Since H_1 is spin independent

$$\langle \psi_i | H_1 | \psi_i \rangle = \frac{1}{2} \langle \phi_1(x_1)\phi_2(x_2) \pm \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \pm \phi_2(x_1)\phi_1(x_2) \rangle$$

$$= \frac{1}{2}\left\{ \langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \rangle + \langle \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle \right\}$$

$$\pm \frac{1}{2}\left\{ \langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle + \langle \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \rangle \right\}$$

where $+$ is for the singlet state and $-$ for the triplets.
So the energy difference is

$$\Delta E = E^{(1)}_{S=0} - E^{(1)}_{S=1} = \langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle + \langle \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \rangle$$

Now we write

$$H_1 = \frac{1}{2}k(x_1 - x_2)^2 = \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2 - kx_1x_2$$

Then, for example

$$\langle \phi_1(x_1)\phi_2(x_2) | \tfrac{1}{2}kx_1^2 | \phi_2(x_1)\phi_1(x_2) \rangle = \frac{1}{2}k \langle \phi_1(x_1) | x_1^2 | \phi_2(x_1) \rangle \langle \phi_2(x_2) | \phi_1(x_2) \rangle$$
$$= 0$$

Since ϕ_1 and ϕ_2 are orthogonal (both integrands are odd about the center of the well).
Similarly all terms involving $\frac{1}{2}kx_2^2$ will give zero and we have

$$\Delta E = -k \left\{ \langle \phi_1(x_1) | x_1 | \phi_2(x_1) \rangle \langle \phi_2(x_2) | x_2 | \phi_1(x_2) \rangle + \langle \phi_2(x_1) | x_1 | \phi_1(x_1) \rangle \cdot \langle \phi_1(x_2) | x_2 | \phi_2(x_1) \rangle \right\}$$

So really we only have one integral to do

$$I = \langle \phi_1(x_1) | x_1 | \phi_2(x_1) \rangle = \frac{2}{L} \int_0^L x \sin\frac{\pi}{L}x \sin\frac{2\pi}{L}x \, dx$$

First use $\sin x \sin y = \frac{1}{2}\left[\cos(y-x) - \cos(y+x)\right] \Rightarrow$

$$I = \frac{1}{L} \int_0^L \left(x \cos\frac{\pi}{L}x - x\cos\frac{3\pi}{L}x \right) dx$$

$$= \frac{1}{L} \left[\left(\frac{L}{\pi}\right)^2 \cos\frac{\pi}{L}x + x\frac{L}{\pi}\sin\frac{\pi}{L}x - \left(\frac{L}{3\pi}\right)^2 \cos\frac{3\pi}{L}x - x\left(\frac{L}{3\pi}\right)\sin\frac{3\pi}{L}x \right]_0^L$$

$$= \frac{1}{L} \left[\left(\frac{L}{\pi}\right)^2(-1-1) + 0 - \left(\frac{L}{3\pi}\right)^2(-1-1) + 0 \right]$$

$$= -2\left(\frac{L}{\pi^2}\right)\left(1 - \frac{1}{9}\right) = -\frac{16}{9}\frac{L}{\pi^2}$$

So we get

$$\Delta E = -k\left\{ \left(-\frac{16}{9}\frac{L}{\pi^2}\right)^2 + \left(-\frac{16}{9}\frac{L}{\pi^2}\right)^2 \right\}$$

$$\boxed{\Delta E = -2k\left(\frac{16}{9}\frac{L}{\pi^2}\right)^2}$$