PH30030: Quantum Mechanics   Problems Sheet 4 Solutions

1. I'll leave this to you.

2. Start with $\left(\hat{H}'-E_{1n}\right)\left|\phi_{0n}\right\rangle=\sum_k a_{nk}\left(E_{0n}-E_{0k}\right)\left|\phi_{0k}\right\rangle$ and close with $\left\langle\phi_{0m}\right|$.

   Because $m\neq n$ the left-hand side gives $\left\langle\phi_{0m}\right|\hat{H}'\left|\phi_{0n}\right\rangle$.

   The right-hand side gives $\sum_k a_{nk}\left(E_{0n}-E_{0k}\right)\delta_{mk}=a_{nm}\left(E_{0n}-E_{0m}\right)$.

   Equating these gives the required result $a_{nm}=\dfrac{\left\langle\phi_{0m}\right|\hat{H}'\left|\phi_{0n}\right\rangle}{E_{0n}-E_{0m}}$ for $m\neq n$.

3. Equation (8) in the lecture notes is $\hat{H}'\left|\phi_{1n}\right\rangle+\hat{H}_0\left|\phi_{2n}\right\rangle=E_{0n}\left|\phi_{2n}\right\rangle+E_{1n}\left|\phi_{1n}\right\rangle+E_{2n}\left|\phi_{0n}\right\rangle$.

   We write $\left|\phi_{1n}\right\rangle=\sum_k a_{nk}\left|\phi_{0k}\right\rangle$ and $\left|\phi_{2n}\right\rangle=\sum_k b_{nk}\left|\phi_{0k}\right\rangle$ and substitute these in to give

   $$\sum_k a_{nk}\hat{H}'\left|\phi_{0k}\right\rangle+\sum_k b_{nk}E_{0k}\left|\phi_{0k}\right\rangle=E_{0n}\sum_k b_{nk}\left|\phi_{0k}\right\rangle+E_{1n}\sum_k a_{nk}\left|\phi_{0k}\right\rangle+E_{2n}\left|\phi_{0n}\right\rangle.$$

   Re-arranging this gives $\sum_k a_{nk}\left(\hat{H}'-E_{1n}\right)\left|\phi_{0k}\right\rangle+\sum_k b_{nk}\left(E_{0k}-E_{0n}\right)\left|\phi_{0k}\right\rangle=E_{2n}\left|\phi_{0n}\right\rangle$.

   We now close with $\left\langle\phi_{0n}\right|$.

   The second sum on the left-hand side gives zero.

   In the first sum, the term with $k=n$ gives zero, because $E_{1n}=\left\langle\phi_{0n}\right|\hat{H}'\left|\phi_{0n}\right\rangle$.

   We therefore get $E_{2n}=\sum_{k\neq n}a_{nk}\left\langle\phi_{0n}\right|\hat{H}'\left|\phi_{0k}\right\rangle$.

   Combining this with the result of question 2 gives the required result

   $$E_{2n}=\sum_{k\neq n}\frac{\left\langle\phi_{0k}\right|\hat{H}'\left|\phi_{0n}\right\rangle\left\langle\phi_{0n}\right|\hat{H}'\left|\phi_{0k}\right\rangle}{E_{0n}-E_{0k}}.$$

4. In general, the first order correction is $E_{1n} = \langle \phi_{0n} | \hat{H}' | \phi_{0n} \rangle$.

   In this case, $|\phi_{0n}\rangle$ is the $1s$ state of the hydrogen atom, i.e., $\phi_{0n} = \sqrt{\frac{1}{\pi a_0^3}} \exp(-r/a_0)$.

   The perturbation is $\hat{H}' = e\varepsilon\, r\cos\theta$ and so we get

$$E_1 = e\varepsilon \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^2 \exp(-2r/a_0)\ r\cos\theta .$$

   The θ integral gives $\int_0^{\pi} d\theta \sin\theta\cos\theta = \frac{1}{2}\int_0^{\pi} d\theta \sin 2\theta = 0$.

   So, the first order correction is zero.

5. Here, $|\phi_{0n}\rangle$ is the same as in question 4, and $\hat{H}'$ is the given $\delta V(r)$.

   Following the hint, we just need the value of the wavefunction at the origin, i.e. $\phi_{0n} = \sqrt{\frac{1}{\pi a_0^3}}$.

   The θ and ϕ integrals give 4π, so the first order correction becomes

$$E_1 = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{\pi a_0^3} \int_0^{R_N} dr\, r^2 \left(\frac{r^2}{2R_N^3} + \frac{1}{2R_N} - \frac{1}{r} \right).$$

   Doing the integrals gives $\left[\frac{r^5}{10R_N^3} + \frac{r^3}{6R_N} - \frac{r^2}{2} \right]_0^{R_N} = -\frac{7}{30} R_N^2$.

   We therefore find $E_1 = \frac{e^2}{4\pi\epsilon_0 a_0} \frac{14}{15} \left(\frac{R_N}{a_0} \right)^2$.

   To estimate the value of this, we note (see problem 4 on problems sheet 3) that the energy of the $1s$ state is given by

$$E_0 = -\frac{\hbar^2}{2\mu} \frac{1}{a_0^2} = -\frac{\hbar^2}{2\mu} \frac{e^2\mu}{4\pi\varepsilon_0\hbar^2} \frac{1}{a_0} = -\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0}$$ since the Bohr radius $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2\mu}$.

   Hence, $\frac{e^2}{4\pi\epsilon_0 a_0}$ is $-2\times$ the energy of the $1s$ state, i.e., $-2 \times (-13.6) = 27.2$ eV.

   $(R_N/a_0)^2$ is of the order of 10^{-10}.

   So, E_1 is of the order of 10^{-9} eV.

6. I'll leave this one to you.

7. When $H'_{11} = H'_{22}$ and $H'_{12} = H'_{21}$, the governing equation becomes
$\begin{pmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{12} & (E_0 + H'_{11}) - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$ and the eigenvalues are $E = E_0 + H'_{11} \pm H'_{12}$.

   If we substitute $E = E_0 + H'_{11} + H'_{12}$ into the governing equation we find $\begin{pmatrix} -H'_{12} & H'_{12} \\ H'_{12} & -H'_{12} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$.

   The normalised eigenvector is therefore $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and the perturbed eigenfunction is
$\frac{1}{\sqrt{2}} |\phi_{01}\rangle + \frac{1}{\sqrt{2}} |\phi_{02}\rangle$.

   If we substitute $E = E_0 + H'_{11} - H'_{12}$ into the governing equation we find $\begin{pmatrix} H'_{12} & H'_{12} \\ H'_{12} & H'_{12} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$.

   The normalised eigenvector is therefore $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ and the perturbed eigenfunction is
$\frac{1}{\sqrt{2}} |\phi_{01}\rangle - \frac{1}{\sqrt{2}} |\phi_{02}\rangle$.

8. For a magnetic field in the z direction, we have $\hat{H}' = \frac{eB}{mc} \hat{S}_z = \frac{e\hbar B}{2mc} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

   Given that $|\phi_{01}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\phi_{02}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, we find $H'_{11} = \frac{e\hbar B}{2mc} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{e\hbar B}{2mc}$.

   Similarly, we find $H'_{22} = \frac{e\hbar B}{2mc} \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{e\hbar B}{2mc}$ and
$H'_{12} = \frac{e\hbar B}{2mc} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$. H'_{21} is also zero.

   We therefore find that $E = E_0 \pm \frac{e\hbar B}{2mc}$, i.e., the energy level splits into two, with a spacing between the two spin states of $\frac{e\hbar B}{mc}$.

9. In this case we have $\hat{H}' = \frac{eB}{mc}\hat{S}_x = \frac{e\hbar B}{2mc}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

We find $H'_{11} = \frac{e\hbar B}{2mc}\begin{pmatrix} 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$, $H'_{22} = \frac{e\hbar B}{2mc}\begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$,
$H'_{12} = \frac{e\hbar B}{2mc}\begin{pmatrix} 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{e\hbar B}{2mc}$, $H'_{21} = \frac{e\hbar B}{2mc}\begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{e\hbar B}{2mc}$.

The energy levels are again given by $E = E_0 \pm \frac{e\hbar B}{2mc}$.