PH30030: Quantum Mechanics   Problems Sheet 4

This problems sheet covers section 4 of the course, on approximate methods for stationary states.

1. Work carefully through the analysis of non-degenerate perturbation theory in the lecture notes. Make sure that you understand how the first order correction for the energy eigenvalue, $E_{1n} = \langle \phi_{0n} | \hat{H}' | \phi_{0n} \rangle$, is obtained.

2. In the course of the analysis referred to in question 1, we derive the equation: $\left(\hat{H}' - E_{1n}\right)|\phi_{0n}\rangle = \sum_k a_{nk}\left(E_{0n} - E_{0k}\right)|\phi_{0k}\rangle$. By closing both sides of this equation with $\langle \phi_{0m}|$ (where $m \neq n$), show that $a_{nm} = \dfrac{\langle \phi_{0m} | \hat{H}' | \phi_{0n} \rangle}{E_{0n} - E_{0m}}$ for $m \neq n$.

3. Extend the analysis in the lecture notes to show that the second order correction to the energy is $E_{2n} = \sum_{k \neq n} \dfrac{\langle \phi_{0n} | \hat{H}' | \phi_{0k} \rangle \langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle}{E_{0n} - E_{0k}}$.

   Hint: Start by writing $|\phi_{1n}\rangle = \sum_k a_{nk} |\phi_{0k}\rangle$ and $|\phi_{2n}\rangle = \sum_k b_{nk} |\phi_{0k}\rangle$, and substitute these into equation (8) in the lecture notes. You will also need to use the result of question 2.

4. What is the first order correction to the energy of the $1s$ state of the H atom when the atom is situated in an electric field of magnitude ε?

   Hint: if we assume that the electric field is in the z direction, then the potential energy of an electron in this field is $V = e\varepsilon z = e\varepsilon r \cos\theta$.

5. When we solved for the energy eigenvalues and eigenfunctions of the hydrogen atom, we assumed that the nucleus is a point charge. In reality, the nucleus has a finite size. One way to model this is to say that the charge of the nucleus is spread uniformly over a sphere of radius R_N. For the hydrogen atom, this leads to a change of the potential energy (relative to the point charge approximation) of $\delta V(r) = -\dfrac{e^2}{4\pi\epsilon_0}\left(\dfrac{r^2}{2R_N^3} + \dfrac{1}{2R_N} - \dfrac{1}{r}\right)$ for $r \leq R_N$ (you are welcome to derive this if you want to – use Gauss's Law!). Show that the first order correction this causes to the energy of the $1s$ state of hydrogen is $E_1 = \dfrac{e^2}{4\pi\epsilon_0 a_0}\dfrac{14}{15}\left(\dfrac{R_N}{a_0}\right)^2$.

   Estimate the magnitude of this correction in eV.

   Hint: because R_N is very small, you can ignore the variation of the wavefunction over the volume of the nucleus.

6. Work carefully through the analysis of degenerate perturbation theory in the lecture notes for the case of two degenerate levels. Make sure that you understand how to obtain the equation $\begin{pmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{21} & (E_0 + H'_{22}) - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$.

7. In the lecture notes we showed that in the case where $H'_{11} = H'_{22}$ the energy levels of the two originally degenerate states become $E = E_0 + H'_{11} + |H'_{12}|$ and $E = E_0 + H'_{11} - |H'_{12}|$. Before the perturbation is applied, the eigenfunctions of the two degenerate states are $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$. Derive expressions for the eigenfunctions after the perturbation is applied.

   Hint: In the lectures, we noted that H'_{12} and H'_{21} are complex conjugates of each other, ie $H'_{12} = (H'_{21})^*$. To make this question easier, you can assume that H'_{12} and H'_{21} are both real, in which case $H'_{12} = H'_{21}$.

8. Consider an electron in a quantum state that, ignoring spin, is singly degenerate. If spin is included, there are two degenerate states – we can write the spin part of these states as $|\phi_{01}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\phi_{02}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ (i.e., as the eigenstates of $\hat{S}_z$). If a magnetic field $\underline{B}$ is applied to the system (note that $\underline{B}$ is a vector quantity), this can be treated as a perturbation of the form $\hat{H}' = \frac{e}{mc}\underline{B}.\underline{\hat{S}}$, where $\underline{\hat{S}}$ is the spin angular momentum operator with Cartesian components $\underline{\hat{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$. (This expression for $\hat{H}'$ is derived from a calculation of the magnetic moment of the electron – this calculation requires relativistic quantum theory, i.e., Dirac's equation). What happens to the energy levels if a magnetic field is applied in the z direction?

9. Repeat question 8, but for a magnetic field in the x direction.