Quantum Mechanics of Atoms and Molecules (PC 3602)
Exercise 3

1. Let $\{|n\rangle, n = 0, 1, 2, \cdots\}$ be the eigenstates of an harmonic oscillator of mass m and frequency ω and let a perturbation potential be given by

$$\hat{V} = Ax^3$$

where A is a small constant.
(a) Prove

$$\hat{V}|n\rangle = \alpha_1 |n-3\rangle + \alpha_2 |n-1\rangle + \alpha_3 |n+1\rangle + \alpha_4 |n+3\rangle$$

and determine the constants $\alpha_1, \alpha_2, \alpha_3$ and α_4.
(b) Calculate the 2nd-order energy correction

$$E_n^{(2)} = \sum_{n' \neq n} \frac{V_{nn'} V_{n'n}}{e_n - e_{n'}}$$

where $V_{n'n} = \langle n'| \hat{V} |n\rangle$ and $e_n = \hbar\omega (n + 1/2)$.

2. The spin interaction energy of positronium in a magnetic field can be written as a (4×4) matrix Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ with

$$\hat{H}_0 = \begin{pmatrix} \varepsilon_1 & 0 & 0 & 0 \\ 0 & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \varepsilon_3 & 0 \\ 0 & 0 & 0 & \varepsilon_4 \end{pmatrix}, \quad \hat{V} = \begin{pmatrix} 0 & v & 0 & 0 \\ v & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

Apply perturbation theory to obtain corrections to the first and second energies ε_1 and ε_2 up to second order and the corresponding states up to first order, treating $\hat{V}$ as perturbation.

3. Consider the LS-coupling for the electron in a hydrogen atom. The perturbation potential is given by

$$\hat{V}_{LS} = A(r)\, \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad A(r) = \frac{1}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0 r^3}.$$

Prove the 1st-order energy correction is given by

$$E_{nlsj}^{(1)} = \frac{|e_n|}{n} \alpha^2 \left(\frac{1}{l + 1/2} - \frac{1}{j + 1/2} \right), \quad j = l \pm \frac{1}{2}, \quad l \neq 0$$

where

$$e_n = -\frac{e^2}{8\pi\epsilon_0 a_0}\frac{1}{n^2}$$

is the energy values of hydrogen (without the perturbation) and $\alpha = \hbar/mca_0$ is a constant. Hint: for hydrogen orbital $R_{nl}(r)$, we have the following integral

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \int_0^\infty r^2 dr R_{nl}^2 \frac{1}{r^3} = \frac{2}{a_0^3 n^3 l (l+1)(2l+1)}, \quad l \neq 0 .$$

4. As we have discussed in class, the one-dimensional harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

has the ground-state energy $E_0 = \hbar\omega/2$ and the ground-state wavefunction

$$\phi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) .$$

If we choose a trial wavefunction in the form

$$\phi_t = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\alpha x^2/2\right)$$

proof that the variational method with α as the variational parameter will give the exact result of $\alpha = m\omega/\hbar$ and $E_0 = \hbar\omega/2$.

5. Use a Gaussian function to estimate the ground-state energy of hydrogen atom. Compare your result with the exact one.

6. A one-dimensional harmonic oscillator of mass m and angular frequency ω in its ground state is subject to a small constant force F acting for a time interval τ. What value of τ gives the greatest chance that the oscillator will be found in its first excited state thereafter?