

CHM 633 Assignment 1

September 20, 2017

Due on 12th October, 2017.

- Using the commutation relations for matrices for rotation about x , y and z axes show that the components of the angular momentum operator commute according to $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$.
- Find the energy levels and eigenfunctions of the 3-d isotropic harmonic oscillator $V = \frac{1}{2}kr^2$ by solving for the wave function in cartesian coordinates.
 - Show that these are also eigenfunctions of \hat{L}^2 .
 - Find eigenfunctions of \hat{L}_z for each energy level.
- A 2-dimensional harmonic oscillator with a Hamiltonian $\hat{H} = -\nabla^2 + \frac{1}{2}k(x^2 + y^2)$ is perturbed by term $\hat{V} = bx^2y^2$.
 - To first-order in b evaluate the corrections to the ground and the first excited state of the oscillator.
 - Calculate the first-order corrected wavefunctions of the ground and first excited state.
 - By evaluating the matrix elements of the dipole operator $\hat{\mu} = -\hat{r}$ check whether the dipole-selection rules conserved upon perturbation?
 - Evaluate the second-order correction to the energy of the ground and first excited states assuming.

4. Consider a one-dimensional He atom modelled by the proton-electron potential $v(x) = \frac{1}{2}k(x - a_0)^2$ for each electron and inter-electron repulsion $w(x_1, x_2)$ (x_i is the coordinate of the i^{th} electron and a_0 the Bohr radius).
- Write down the IPA hamiltonian for the system and solve for the IPA eigenvalues and eigenfunctions.
 - Taking $w(x_1, x_2) = W_0\delta(x_1 - x_2)$ compute the first-order correction to the eigenvalues.
 - Taking $w(x_1, x_2) = W_0\exp(-\eta(x_1 - x_2)^2)$ compute the first-order correction to the eigenvalues.
5. For He atom the first-order perturbation energy correction is $\langle \frac{1}{r_{12}} \rangle$ calculated over the correct unperturbed (parity symmetry-adapted) wave function. Show that this is $J_{1s2s} \pm K_{1s2s}$. Show that if we evaluate the same integral using the incorrect zeroth-order functions $1s(1)2s(2)$ or $1s(2)2s(1)$ we get J_{1s2s} in each case. What is then the physical origin of the exchange integral?
6. Consider the doubly excited He atom in configuration $2s^2$. Show that in the IPA this configuration is unstable towards formation of He^+ . Determine the first-order correction to the IPA for He $2s^2$ and verify if it is still unstable.
7. Consider the normalised variation function $\phi(x) = \left(\frac{3}{l^3}\right)^{\frac{1}{2}} x$ for $0 \leq x \leq l$ applied to the particle-in-a-1d-box problem. Estimate the ground-state energy. Is the estimate correct? If not what is wrong with it and why?
8. Show that for all normalisable $|\psi\rangle$ that satisfy $\langle \phi_0 | \psi \rangle = 0$, where $|\phi_n\rangle$ satisfy $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$, the following variation theorem is satisfied :

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_1$$

9. Apply the variation function $\phi = \frac{1}{a^2+x^2}$ to the 1-d harmonic oscillator. Chose a to minimise the variation integral and find the percent error in the ground-state energy.

10. A particle on a ring is perturbed when the size of the ring is increased by a small fraction δ . Show that the excitation energies increase linearly with increasing δ up to first order in the perturbation.