PHYS5111 Advanced Quantum Mechanics I Fall 2015 Assignment 5

Due date is Monday 7 December, 2015. Some problems are taken from Introductory Quantum Mechanics (2nd edition or 4th edition), Richard Liboff.

1. Excited states of Helium. Assume the one electron is in the 1S, the other is in the 2S state, with the spatial part being $\psi_\pm = \frac{1}{\sqrt{2}}\left(\psi_{1S}^Z(1)\,\psi_{2S}^Z(2) \pm \psi_{2S}^Z(1)\,\psi_{1S}^Z(2)\right)$. The $+$ and $-$ corresponds to parahelium and orthohelium, respectively. $\psi_{1S}^Z(r) = \frac{Z^{3/2}}{\pi^{1/2}a^{3/2}}\exp\left(-\frac{Zr}{a}\right)$ and $\psi_{2S}^Z(r) = \frac{Z^{3/2}}{\pi^{1/2}8^{1/2}a^{3/2}}\left(1-\frac{Zr}{2a}\right)\exp\left(-\frac{Zr}{2a}\right)$, where for Helium $Z = 2$. For the repulsive term, $Hee = \frac{e^2}{4\pi\epsilon_0}\frac{1}{\left|\vec{r_1}-\vec{r_2}\right|}$, $\langle H_{ee}\rangle = J \pm K$, $J = \frac{17}{81}ZE_h$, $K = \frac{16}{729}ZE_h$, $E_h = 27.211358eV$

   (A) Calculate the approximate excited state energy, $\langle\psi_\pm\left|H\right|\psi_\pm\rangle = \langle H\rangle_\pm$, where the Hamiltonian is $H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{\left|\vec{r_1}-\vec{r_2}\right|}$.Compare your answer to Figure 12.14 of Liboff 2nd edition Textbook (Figure 12.15 of 4th edition), as well as experimental data that found the orthi- para-helium energy difference of $\left(\langle H\rangle_+ - \langle H\rangle_+\right)_{\exp} \sim 0.8eV$.

   (B) For the ground state 1S-1S calculation the results was improved by introducting the shielded nuclear electric charge $Z_v e$, where Z_v is a variational parameter. Perform the variational calculation for the 1S-2S state, by replacing $Z = 2$ in part a, by Z_v, and then minimize the energy to obtain $\langle H\rangle_\pm^{\min}$. Compare your answer with that obtained in part a. Briefly explain why you **do not expect** the minimized energy $\langle H\rangle_\pm^{\min}$ to be **more accurate** than the answer of part a, $\langle H\rangle_\pm$.

2. Tight Binding LCAO of linear diatomic molecule, with $+$ ion centers at $x = x_1$ and $x = x_2$. This follows the development of section 8.7, page 331-336, of 4th edition of Liboff textbook. This begins with the LCAO state $c_1\phi_1 + c_2\phi_2$, with $\phi_1 = \phi(x - x_1)$ tightly bound to the center at $x = x_1$, and $\phi_2 = \phi(x - x_2)$ tightly bound to the center at $x = x_2$. This gives the "eigenvalue" matrix:

$$\begin{pmatrix} H_{11} - \langle H\rangle & \frac{H_{12}+H_{21}}{2} - \langle H\rangle S \\ \frac{H_{12}+H_{21}}{2} - \langle H\rangle S & H_{22} - \langle H\rangle \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

   where H is the Hamiltonian of the system, $H_{ij} = \langle\phi_i\left|H\right|\phi_j\rangle, ij = 1, 2$, $S = \langle\phi_i \mid \phi_j\rangle$ is the overlap integral.

   (A) Show that by solving the eigenvalue problem, we obtain the energy eigenvalues,

$$\langle H\rangle_\pm = \frac{1}{2(1-s^2)}\left[\begin{array}{c} H_{11} + H_{22} - (H_{12} + H_{21})\,S \\ \pm\sqrt{\left(S\,(H_{11} + H_{22}) - (H_{12} + H_{21})\right)^2 + (1 - S^2)\,(H_{11} - H_{22})^2} \end{array}\right]$$

   (B) For a homonuclear diatomic molecule (H_2, D_2, N_2...), show that $\langle H\rangle_\pm = \frac{H_{11}\pm H_{12}}{1\pm S}$. Verify that the corresponding eigenvectors are $c_1 = 1, c_2 = 1$ and $c_1 = 1, c_2 = -1$.

(C) A broad frequency of photons is incident on a gas of homonuclear diatomic molecule. Only photons of frequency $\nu = 0.75 \times 10^{15} Hz$ are absorbed. From a LCAO 1D model it is found that $|H_{11}| = 10eV$, and $|H_{12}| = 3eV$. Find the value of the overlap integral S in unit of eV.

3. LCAO of H_2^+ and He_2^{3+}. Application of LCAO to H_2^+, produces the energy state $\langle H\rangle_\pm = E_1 - \frac{J\pm K}{1\pm S}$, $S = \left\langle \psi^Z_{1S,A}(-R/2) \mid \psi^Z_{1S,B}(R/2)\right\rangle$, where $\psi^Z_{1S,A}(-R/2) = \psi^Z_{1S}(x + R/2, y, z)$ is ψ_{100} centered at $x = -R/2$, and $\psi^Z_{1S,B}(R/2) = \psi^Z_{1S}(x - R/2, y, z)$ is ψ_{100} centered at $x = R/2$. ψ^Z_{1S} is given in problem 1, with $Z = 1$. $J = \left\langle \psi^Z_{1S,A}(-R/2) \left| \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_B} \right| \psi^Z_{1S,A}(-R/2) \right\rangle = \left\langle \psi^Z_{1S,B}(R/2) \left| \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_A} \right| \psi^Z_{1S,B}(R/2) \right\rangle$, where $r_B = \sqrt{(x + R/2)^2 + y^2 + z^2}$ and $r_B = \sqrt{(x - R/2)^2 + y^2}$
$K = \left\langle \psi^Z_{1S,A}(-R/2) \left| \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_B} \right| \psi^Z_{1S,B}(R/2) \right\rangle = \left\langle \psi^Z_{1S,B}(R/2) \left| \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_A} \right| \psi^Z_{1S,A}(-R/2) \right\rangle$.

(A) Clearly $\langle H\rangle_\pm$ is a function of the separation distance between the protons, R. The functional form is given in Griffith's. Calculate the energy of the bonding $(+)$ and anti-bonding $(-)$ state at the equilibrium bond length. $R = 2.5a$. Find the total energy $E_\pm^{H_2^+} = \langle H\rangle_\pm + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}$. Based on your answer, is the H_2^+ moleculae stable at this R. Why?

(B) Modify the calculation for He_2^{3+}, with two nucleus of charge $+Ze$ at $x = -R/2$, and $+Ze$ at $x = R/2$, where $Z = 2$, bonded by a single electron. Use $\psi^Z_{1S}(r)$ given in problem 1. Calculate $E_\pm^{He_2^{3+}} = \langle H\rangle_\pm + \frac{Z^2e^2}{4\pi\epsilon_0}\frac{1}{R}$at the equilibrium bond length. $R = 2.5a$. Based on your answer, is the He_2^{3+} moleculae stable at this R. Why?

4. These questions are based on section 12.7 page 532 to 539 of the 2nd edition Liboff Textbook, and section 12.7 page 623 to 630 of the 4th edition.

(A) In what manner are the following two phenomena related? 1) The triplet states of He have lower energy than the singlet state. 2) H_2 is bound in the singlet electronic state.

(B) What is the radial probability distribution of either H_2 or D_2 in the ${}^1S_0$? Where are the electrons with respect to this distribution?

(C) What is the intensities of spectral lines due to transitions between even rotational states, compare with that between odd rotational states? How does this compare to the ratio for heavy hydrogen molecules D_2?

(D) In part C, why do rotational transitions only occur between even-even and odd-odd states?

5. This question is based on section 11.12 page 553 to 558 of 4th edition of Liboff.

(A) Integrate **Heisenberg's equation** (11.139a) for a **free particle** to obtain $\widehat{q}(t)$ and $\widehat{p}(t)$, as functions of $\widehat{q}(0)$ and $\widehat{p}(0)$, respectively.

(B) Find $[\widehat{q}(t), \widehat{q}(0)]$. Combine this result with the generalized uncertainty principle (see Griffith's) to find the uncertainty relation $\Delta\widehat{q}(t)\,\Delta\widehat{q}(0)$. Discuss the consequence of this on a localized wave packet (also see Griffith's).

6. Problem 13.44 of 2nd edition of Liboff, which is the same question as 13.44 of the 4th edition

7. A 1D harmonic oscillator is in the ground state for $t < 0$. For $t \geq 0$ it is subjected to a time-dependent force (NOT POTENTIAL!) in the x direction, $F(t) = F_0 \exp\left(-\frac{t}{\tau}\right)$

   (a) Using time-dependent perturbation to the first order, obtain the probability of finding the oscillator in the first excited state for $t > 0$. Show that as $t \to \infty$ (τ finite) the expression becomes independent of time. Is this results reasonable or surprising?

   (b) What is the probability of finding the oscillator in higher excited states.

8. **Spin-Spin Interaction Energy**. Consider two **distinguishable** spin 1/2 particles, $\overrightarrow{S}_1 (s_1 = 1/2)$ and $\overrightarrow{S}_2 (s_2 = 1/2)$, where for $t \leq 0$, $H = 0$, and the system is random. Fot $t > 0$ the Hamiltonian is $H = a\left(\overrightarrow{S}_1 \cdot \overrightarrow{S}_2\right)$.

   (a) If for $t \leq 0$, the system is in the state $|\uparrow\downarrow\rangle$, use the method of sudden perturbation to find the probabilty that the system will be in states $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\downarrow\rangle$.

   (b) Use first-order time-dependent perturbation theory to find the probability of the $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\downarrow\rangle$ states at $t > 0$. Under what condition is the results of part b correct?