CHM 633 Assignment 2

October 29, 2017

Due on 10th November, 2017.

1. For a system of N interacting electrons let $\hat{H}_0 = \sum_i \hat{h}(i)$ be the independent particle approximated (IPA) Hamiltonian (the electron-electron repulsion is neglected). The eigenfunctions of $\hat{h}$ are given as $\{\phi_n\}$ with non-degenerate eigenvalues $\{\epsilon_n\}$. Let Φ_0 denote the ground state of the IPA Hamiltonian. Singly excited states to this Hamiltonian are obtained by removing one electron from orbital $m < N$ and placing it in orbital $p > N$ and are denoted by Φ_m^p. Similarly, doubly excited states are obtained by removing one electron from $m < N$ and another from $n < N$ and placing them in $p > N$ and $q > N$ and denoted by $\Phi_{m,n}^{p,q}$.

   (a) If $\hat{F} = \sum_i \hat{f}(i)$ is a one-electron operator then derive an expression for the matrix element of this operator between the ground state and a singly excited state; and the ground state and any doubly excited state.

   (b) If $\hat{G} = \frac{1}{2} \sum_{i \neq j} \hat{g}(i,j)$ is a two-electron operator then derive expressions for the above matrix elements for this operator.

   (c) If the many-electron system is perturbed by an electric field $E_0 \hat{z}$ then calculate the change in ground-state energy in the IPA.

   Note : These results are called the Slater-Condon rules.

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2. For the H_2^+ molecule use the LCAO approach (in minimal basis mode) to calculate the overlap, coulomb and resonance integrals as a function of the internuclear separation R. Using these also calculate the energy of the bonding and anti-bonding levels as a function of R. Plot these energies as a function of R and obtain the equilibrium bond-length, energy and frequency (in the harmonic approximation) for the H_2^+ molecule. What is the first vertical excitation energy of the H_2^+ molecule? What would happen upon such an excitation? (**Note**: Please use plotting software to present your results clearly indicating the units used, the points of interest and legends. Hand-drawn plots will not be considered.)

3. For the H_2 molecule write down the various two-electron eigenstates (including spin) of the IPA Hamiltonian in the minimal basis LCAO approach and their corresponding energy eigenvalues along with their appropriate term symbols. Plot the ground-state energy as a function of R and obtain the equilibrium bond-length (R_0), energy and vibration frequency of H_2. Next, treating the electron-electron repulsion as a perturbation compute the first-order correction to the IPA eigenvalues (at R_0). Comment on the origin of the new ordering of energies.

4. Show that atomic orbitals belonging to different irreducible representations of the molecular point group of a homonuclear diatomic molecule will not mix in the LCAO approach to yield a molecular orbital.

5. Show that the molecular orbitals formed by linear combination of atomic orbitals separated by large energy will essentially be localized on either atom and also will not lead to significant stabilization or destabilization.

6. For etheylene, estimate the error in the energies of the π molecular orbitals made by the Hückel method in ignoring the overlap integral.

7. Show that the Fock operator is invariant upon a Unitary transformation of the Hartree-Fock orbitals.

   $\rho(\vec{r}) = \langle \Psi_0 | \hat{\rho}(\vec{r}) | \Psi_0 \rangle$.

8. (a) Use the generalized Hellman-Feynman theorem to calculate $\left\langle \frac{1}{r} \right\rangle$ for the hydrogen-atom bound states. (b) Show that $\left\langle \frac{1}{r^2} \right\rangle = \frac{2Z^2}{(2l+1)n^3} \left(\frac{1}{a_0^2} \right)$.

(See Problem 14.12 in *Quantum Chemistry*, Levine).

9. Let 1 and 2 be two bound stationary states of an atom, with $E_2 > E_1$. For which state is the average electronic kinetic energy larger and why?

10. Exercise 3.32 (pg. 193) in *Modern Quantum Chemistry*, Szabo and Ostlund.