CHM 652 / PHY 626 Assignment 1

February 11, 2025

Due on 25^{th} Feb, 2025.

1. Consider the H_2 molecule problem under the independent electron approximation (IEA) with $1s$ orbitals $|\phi_1\rangle$ and $|\phi_2\rangle$.

   (a) Employing the linear combination of atomic ($1s$) orbitals (LCAO)approach for representing the molecular orbitals, solve the problem in terms of the overlap integral ($S = \langle\phi_1|\phi_2\rangle$), the resonance integral ($\beta = \left\langle\phi_1|\hat{H}|\phi_2\right\rangle$), and on-site integral ($\alpha = \left\langle\phi_1|\hat{H}|\phi_1\right\rangle$).

   (b) Compute S, α, β in terms of the bond-length R by direct integration.

   (c) Estimate the equilibrium bond length of H_2 in the IEA by minimizing the molecular potential energy function and also determine the ground-state molecular binding energy $E_b = E_{H_2} - 2 \times E_H$ in atomic units (Hartrees). Here, E_H is ground-state energy of the isolated H atom.

2. Consider a heteronuclear diatomic molecule AB where A and B have differing electronegativities.

   (a) Using the zero overlap approximation and an LCAO approach, solve for the electronic energies and eigenstates of the system in the IEA in terms of $\alpha_A, \alpha_B, \beta$ with $\alpha_A > \alpha_B$.

   (b) For (a) 1, (b) 2, and (c) 3 electrons in the system, compute the bond order of the system in its corresponding ground-state.

(c) Compute the charge density on atom A in the bonding and anti-bonding states.

3. Using the orthogonal tight-binding approach and only the p_z orbitals of C atoms in the LCAO basis, compute the molecular orbital energy levels and wavefunctions of the following:

   (a) Allyl radical cation

   (b) Cyclobutadine

   (c) Cyclopropenyl cation

   (d) Benzene

4. A 1-d lattice made of Li atoms is modified to include an extra side-chain X attached to every third lattice site (i.e. for site indices $3 * (j - 1)$ where j runs over all integers). Assuming an LCAO basis of only the $2s$ orbitals of Li, the same resonance integral for all Li-Li bonds, an onsite energy α for all unmodified atoms and α' for the modified atoms, write down the tight-binding Hamiltonian for the lattice assuming zero differential orbital overlap and only nearest-neighbour interactions. Solve the system for eigenvalues and eigenstates.

5. For a semi-infinite 1-d chain of H-atoms, determine the local density of states (LDOS) at the first three atoms closest to the edge. How does this compare with the LDOS obtained for the infinite 1-d lattice? Compare all the cases in the same plot, if possible. (Hint: Use the Green's function approach).