4012 Condensed Matter Theory: Tutorial 1

1. Consider the ground state of the H_2 molecule. Let $|1\rangle$ and $|2\rangle$ be atomic 1s states of the H atoms and assume they form a basis in which to expand the molecular state $|\psi\rangle$.

   Assume the basis state are normalized, but not orthogonal in such a way that:

$$\langle 1|1\rangle = \langle 2|2\rangle = 1$$
$$\langle 1|2\rangle = \langle 2|1\rangle = S$$

   Let the Hamiltonian matrix elements be:

$$\langle 1|H|1\rangle = \langle 2|H|2\rangle = \epsilon_0$$

$$\langle 1|H|2\rangle = \langle 2|H|1\rangle = \gamma$$

   Calculate the energy of the bonding and antibonding states and the normalized wavefunctions to which they correspond. Compare your results with those obtained for the case $S = 0$.

2.(a) Define the charge density operator, $\hat{\rho}$, associated to a quantum mechanical system described by a hermitian Hamiltonian. Demonstrate that $\hat{\rho}^2 = \hat{\rho}$ and that $N = \mathrm{Tr}[\hat{\rho}]$, where N is the total number of particles and "Tr" is the trace (when $\hat{\rho}$ is expanded over a complete orthonormal basis set).

   (b) Consider now a heteronuclear diatomic molecule formed by atoms A and B. Its electronic structure can be described by using only the $1s$

orbitals of A, $|\mathrm{A}\rangle$, and B, $|\mathrm{B}\rangle$, (approximated to be orthonormal). Calculate the associated density matrix expanded over the basis set $|\mathrm{A}\rangle$ and $|\mathrm{B}\rangle$ as a function of the number of electrons for $N = 1, 2, 3, 4$. For this calculation use the nearest neighbour approximation with on-site energies $\epsilon_{\mathrm{A}} = -4$ eV, $\epsilon_{\mathrm{B}} = 4$ eV and hopping parameter $\gamma = -3$ eV.

(c) By using the calculated density matrix evaluate the total energy of the molecule for $N = 1, 2, 3, 4$.