Advanced Materials Modeling
Homework 3

***Notes**: In multiple choice problems explain your answer. Add references if needed. Upload solution as a single file "YourName.pdf" or "YourName.zip".*

1. Mark all correct statements:

(A) Hartree approximation gives electronic wave functions with correct permutational symmetry

(B) Up to two electrons can occupy every state described by a spin-orbital wave function

(C) Static correlation is a consequence of approximating many-electron wave functions by a single determinant

(D) Hartree-Fock approximation describes electron-electron interaction exactly

2. Derive first-order correction to the ground-state wave function within Rayleigh-Schrödinger perturbation theory for systems with non-degenerate ground state
Hint:
Solve perturbed Schrödinger equation $\hat{H}\psi = E\psi$ up to first order by considering the following facts:

$$\hat{H} = \hat{H}_0 + \hat{V}\,, \tag{1}$$

solutions of the unperturbed Schrödinger equation are known:

$$\hat{H}_0\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}\,, \tag{2}$$

$$\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}\,, \tag{3}$$

perturbed wave function can be expressed as

$$\psi = \sum_m c_m\psi_m^{(0)}\,, \tag{4}$$

and the coefficients c_m and perturbed energy E can be expanded in orders of $\hat{V}$:

$$c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots\,, \tag{5}$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots\,, \tag{6}$$

and $c_m^{(0)} = 1$ for $m = 0$ (ground state for which the perturbation is calculated), and $c_m^{(0)} = 0$ for $m \neq 0$.

3. Mark all correct statements:
The following methods are size-extensive

(A) Hartree-Fock

(B) approximate DFT

(C) Moller-Plesset perturbation theory at order 10

(D) truncated configuration interaction

(E) full configuration interaction

(F) truncated coulped cluster