Advanced Materials Modeling
Homework 3 solution

***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

Solution:
(C)
Hartree approximates many-electron wave function as a product of one-particle states. Such a function is not in general antisymmetric with respect to permutation of any two electrons, but the exact electronic wave function should be antisymmetric.
Only one electron can occupy a spin-orbital, according to Pauli exclusion principle.
Static correlation is by definition a consequence of approximating many-body wave function by a single Slater determinant.
Hartree-Fock is not an exact method, although it is self-interaction free.

2. Derive first-order correction to the ground-state wave function within Rayleigh-Schrödinger perturbation theory for systems with non-degenerate ground state
Solution:
Substitute equations

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

and

$$\psi = \sum_m c_m \psi_m^{(0)} \tag{2}$$

into the perturbed Schrödinger equation:

$$(\hat{H}_0 + \hat{V})\psi = E\psi\,, \tag{3}$$

taking into account that

$$c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots \tag{4}$$

and keeping only first-order terms (this can be done, because the Schrödinger equation should be correct in all orders). The results is:

$$\hat{V}\sum_m c_m^{(0)}\psi_m^{(0)} + \hat{H}_0\sum_m c_m^{(1)}\psi_m^{(0)} = E^{(0)}\sum_m c_m^{(1)}\psi_m^{(0)} + E^{(1)}\sum_m c_m^{(0)}\psi_m^{(0)}\,. \tag{5}$$

Remember that $\sum_m c_m^{(0)}\psi_m^{(0)} = \psi_0^{(0)}$ since $c_m^{(0)} = \delta_{m0}$, and that $\hat{H}_0\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}$. Now, multiply both sides of the above equation by $\psi_k^{(0)*}$, $k \neq 0$, and integrate over $\mathbf{r}$:

$$\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle + \sum_m E_m^{(0)}c_m^{(1)}\langle\psi_k^{(0)}|\psi_m^{(0)}\rangle = E^{(0)}\sum_m c_m^{(1)}\langle\psi_k^{(0)}|\psi_m^{(0)}\rangle + E^{(1)}\langle\psi_k^{(0)}|\psi_0^{(0)}\rangle\,. \tag{6}$$

Taking into account that $\langle\psi_k^{(0)}|\psi_m^{(0)}\rangle = \delta_{km}$, we obtain:

$$\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle + E_k^{(0)}c_k^{(1)} = E^{(0)}c_k^{(1)} + 0\,, \tag{7}$$

and

$$c_k^{(1)} = \frac{\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{E^{(0)} - E_k^{(0)}}\,, \tag{8}$$

where $k \neq 0$ and we took into account that the ground state is non-degenerate (i.e., $E^{(0)} - E_k^{(0)} \neq 0$).
We still need to determine $c_0^{(1)}$. To do this, we should remember that perturbed wave function should be normalized:

$$\langle\psi|\psi\rangle = 1\,. \tag{9}$$

To satisfy this condition up to the first order, the following should be true:

$$\langle\psi_0^{(0)} + \sum_m c_m^{(1)}\psi_m^{(0)}|\psi_0^{(0)} + \sum_m c_m^{(1)}\psi_m^{(0)}\rangle = 1\,. \tag{10}$$

Keeping only up to first-order terms, we obtain $2\mathrm{Re}\left(c_0^{(1)}\right) = 0$. We are free to choose $c_0^{(1)} = 0$ to satisfy this condition. Thus, the first-order correction to the wave function is:

$$\psi^{(1)} = \sum_{k\neq 0}\frac{\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{E^{(0)} - E_k^{(0)}}\psi_k^{(0)}\,. \tag{11}$$

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

(A) Hartree-Fock

(B) approximate DFT

(C) Møller-Plesset perturbation theory at order 10

(D) truncated configuration interaction

(E) full configuration interaction

(F) truncated coulped cluster

Solution:
(A), (B), (C), (E), (F)
Møller-Plesset perturbation theory is size-extensive at any order. Truncated CI is not size-extensive at any truncation level except full CI, because it is missing higher excitations needed to describe the combined system. Coupled cluster is size-extensive even when truncated, because it formally contains higher excitations up to a maximum level, just like FCI.