First Principle 2017-Fall Homework 2 Solution

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1. We start with Hartree-Fock hamiltonian for N electrons:

$$\hat{H}_{HF} = \sum_{n=1}^{N} \hat{h}_n + \sum_{n=1}^{N} \sum_{m=1}^{N} \frac{1}{|r_n - r_m|}$$

Consider the many-electrons wave function $\Psi(x_1, x_2...)$ which can be represented as slater determinant:

$$\Psi(x_1, x_2, ...) = \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) & ... \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) & ... \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) & ... \\ ... & ... & ... & ... \end{vmatrix}$$

To derive the Koopermans' theorem, we first remove one electron from orbital with wave vector k:

$$\hat{H}^k_{N-1} = \sum_{n=1, n\neq k}^{N-1} \hat{h}_n + \sum_{n=1}^{N-1} \sum_{m=1}^{N-1} \frac{1}{|r_n - r_m|}$$

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