Introduction to Density Functional Theory (SS 2008)

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Problem set No. 4

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1. The "action" functional

Consider the so-called "action" functional:

$$I[\varphi] = \int dt \int d^3r \ \mathcal{L} \ \left(\varphi(\vec{r},t), \nabla\varphi(\vec{r},t)\right) \tag{1}$$

with the Lagrangian density:

$$\mathcal{L} = \varphi^* \left(i\hbar\frac{\partial}{\partial t}\right)\varphi + \frac{\hbar^2}{2m}(\nabla\varphi^*)\cdot(\nabla\varphi) - v(\vec{r},t)\ |\varphi|^2 \tag{2}$$

(φ stands for $\varphi(\vec{r},t)$).
Prove that the stationarity condition:

$$\frac{\delta I}{\delta\varphi^*(\vec{r},t)} = 0 \tag{3}$$

yields the time-dependent Schrödinger equation (TDSE). (4 points)

2. The Hartree-Fock equations

Consider the many-electron Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{N} v(\vec{r}_i)\,. \tag{4}$$

If the exact N-particle wavefunction is approximated by a Slater determinant

$$\phi = \frac{1}{\sqrt{N!}}\ det\left(\varphi_k(\vec{r}_i)\right)\ , \tag{5}$$

the expectation value of H can be written as [1] :

$$\langle\phi|\ H\ |\phi\rangle = 2\sum_{k=1}^{N/2}\int \mathrm{d}^3r\ \varphi_k^*(\vec{r})(-\frac{\hbar^2}{2m}\nabla^2)\varphi_k(\vec{r})+ \qquad \text{(Kinetic energy)}$$

$$+\int \mathrm{d}^3r\ \rho(\vec{r})v(\vec{r})+ \qquad \text{(External potential term)}$$

$$+\frac{e^2}{2}\int \mathrm{d}^3r\int \mathrm{d}^3r'\ \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}- \qquad \text{(Hartree energy)}$$

$$-\frac{1}{2}\sum_{k,k'=1}^{N/2}\int \mathrm{d}^3r\int \mathrm{d}^3r'\ \frac{\varphi_k^*(\vec{r})\varphi_k(\vec{r}')\varphi_{k'}^*(\vec{r}')\varphi_{k'}(\vec{r})}{|\vec{r}-\vec{r}'|}, \qquad \text{(Exchange energy)}$$

where the particle density is given by:

$$\rho(\vec{r}) = 2\sum_{k=1}^{N/2}|\varphi_k(\vec{r})|^2\,. \tag{6}$$

Show that imposing the stationarity conditions:

$$\frac{\delta\left[\langle\phi|\ H\ |\phi\rangle - \sum_{k=1}^{N/2}\epsilon_k\int \mathrm{d}^3r'\varphi_k^*(\vec{r}')\varphi_k(\vec{r}')\right]}{\delta\varphi_j^*(\vec{r})} = 0 \ \ (j = 1\ldots N/2) \tag{7}$$

yields the *Hartree-Fock* equations [2]. (6 points)

[1] We consider a spin-compensated system, i.e. with 2 electrons per orbital.

[2] The Lagrangian multipliers ϵ_k in Eq. 7 arise from the constraint that the single-particle orbitals φ_k be normalized.