Exam in density functional theory (M1 course)

December 2021 – Duration: 30 minutes

In Kohn–Sham density-functional theory (KS-DFT), the N-electron ground-state energy E_0 of a molecule with nuclear potential $v_{\rm ne}(\mathbf{r})$ is evaluated, in principle exactly, as follows:

$$E_0 = \left\langle \Phi^{\rm KS} \middle| \hat{T} + \sum_{i=1}^{N} v_{\rm ne}(\mathbf{r}_i)\times \middle| \Phi^{\rm KS} \right\rangle + E_{\rm Hxc}[n_0], \tag{1}$$

or, equivalently, $E_0 = 2\left(\sum_{i=1}^{N/2} -\dfrac{1}{2}\int d\mathbf{r}\; \varphi_i(\mathbf{r})\nabla^2_{\mathbf{r}}\varphi_i(\mathbf{r})\right) + \int d\mathbf{r}\; v_{\rm ne}(\mathbf{r})\, n_0(\mathbf{r}) + E_{\rm Hxc}[n_0]$, where $\Phi^{\rm KS}$ denotes the N-electron KS determinant whose orbitals $\{\varphi_i\}_{1\leq i\leq N/2}$ (we assume that they are all *doubly occupied*, for simplicity) fulfill the KS equations $\left(-\dfrac{1}{2}\nabla^2_{\mathbf{r}} + v^{\rm KS}(\mathbf{r})\times\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$. The density-functional KS potential reads as $v^{\rm KS}(\mathbf{r}) = v_{\rm ne}(\mathbf{r}) + v_{\rm Hxc}[n_0](\mathbf{r})$, where $v_{\rm Hxc}[n](\mathbf{r}) = \delta E_{\rm Hxc}[n]/\delta n(\mathbf{r})$ and $n_0(\mathbf{r}) = 2\sum_{i=1}^{N/2}\varphi_i^2(\mathbf{r})$.

a) [**2 pts**] Which interaction is described by $v_{\rm ne}(\mathbf{r})$? Where does the factor 2 in the expression of $n_0(\mathbf{r})$ come from? Verify that $n_0(\mathbf{r})$ integrates to the number N of electrons. We recall that the KS orbitals are normalized, *i.e.*, $\displaystyle\int d\mathbf{r}\; \varphi_i^2(\mathbf{r}) = 1$. Is the electron density $n_0(\mathbf{r})$ known before the KS-DFT calculation starts? How is it determined from the KS equations?

b) [**3 pts**] Why are the KS equations much simpler to solve than the N-electron Schrödinger equation? How do the exact KS orbitals $\{\varphi_i\}_{1\leq i\leq N/2}$ connect to the true N-electron ground state of the molecule?

c) [**2 pts**] Is the ground-state energy E_0 equal to the sum of the occupied KS orbital energies? **Hint:** Explain why $\varepsilon_i = -\dfrac{1}{2}\int d\mathbf{r}\; \varphi_i(\mathbf{r})\nabla^2_{\mathbf{r}}\varphi_i(\mathbf{r}) + \int d\mathbf{r}\; v^{\rm KS}(\mathbf{r})\varphi_i^2(\mathbf{r})$. Deduce that $2\sum_{i=1}^{N/2}\varepsilon_i = E_0 - E_{\rm Hxc}[n_0] + \int d\mathbf{r}\; v_{\rm Hxc}[n_0](\mathbf{r})\, n_0(\mathbf{r})$, and conclude.

d) [**3 pts**] By analogy with Hartree–Fock theory, the exact density-functional Hartree-exchange (Hx) energy is evaluated as follows, $E_{\rm Hx}[n_0] = \left\langle \Phi^{\rm KS} \middle| \hat{W}_{\rm ee} \middle| \Phi^{\rm KS} \right\rangle$, which leads to the more explicit expression $E_{\rm Hx}[n_0] = 2\sum_{i,j=1}^{N/2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \dfrac{\varphi_i^2(\mathbf{r}_1)\varphi_j^2(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} - \sum_{i,j=1}^{N/2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \dfrac{\varphi_i(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)\varphi_j(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$. Show that the first contribution (with the factor 2) is an explicit functional of the density that corresponds to the Hartree functional $E_{\rm H}[n_0] = \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \frac{n_0(\mathbf{r}_1)n_0(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$. Is the complementary (second contribution) exchange energy an explicit functional of the density? Can it be modelled easily with a density functional? What (successful) strategy is used in the so-called hybrid exchange functionals?

e) [**2 pts**] How would you define the concept of electron correlation? Show that correlation effects systematically lower the energy. **Hint:** Explain why, according to Eq. (1) and question d), the correlation energy $E_{\rm c}[n_0] = E_{\rm Hxc}[n_0] - E_{\rm Hx}[n_0]$ can be written as $E_{\rm c}[n_0] = E_0 - \left\langle \Phi^{\rm KS} \middle| \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v_{\rm ne}(\mathbf{r}_i)\times \middle| \Phi^{\rm KS} \right\rangle < 0$, and conclude.