"Modelling 1" M1 course

# Exam: Density functional theory

December 2020 – Duration: 30 minutes

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a) [**2 pts**] Why solving the Kohn–Sham equations of density-functional theory (DFT) is *a priori* much simpler than solving the true Schrödinger equation? What is the most challenging task in DFT?

b) [**1 pt**] Many exchange-correlation (xc) density functionals are available in electronic structure softwares. Does it mean that we cannot, in principle, use the same xc functional for all molecules? Detail your answer.

c) [**2 pts**] In the literature, the acronym "DFT" is often used to refer to Kohn–Sham (KS) DFT. It would be more appropriate to distinguish KS-DFT from DFT. Why? If the exact universal Hohenberg–Kohn functional $F[n]$ were known, would KS-DFT be of any use?

d) **[2 pts]** Let $\Phi^{\mathrm{KS}}[n]$ denote the $N$-electron Kohn–Sham (KS) determinant with density $n(\mathbf{r})$ and $v^{\mathrm{KS}}[n](\mathbf{r})$ the corresponding KS local potential. Explain why, for any trial $N$-electron wave function $\Psi$, we have

$$\left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{T} + \sum_{i=1}^{N} v^{\mathrm{KS}}[n](\mathbf{r}_i)\times \middle| \Phi^{\mathrm{KS}}[n] \right\rangle \leq \left\langle \Psi \middle| \hat{T} + \sum_{i=1}^{N} v^{\mathrm{KS}}[n](\mathbf{r}_i)\times \middle| \Psi \right\rangle, \tag{1}$$

where $\hat{T}$ is the kinetic energy operator. Conclude, by considering only the wave functions $\Psi$ that fulfill the density constraint $n_\Psi(\mathbf{r}) = n(\mathbf{r})$ [the latter condition is often denoted $\Psi \rightarrow n$], that the non-interacting kinetic energy functional reads $T_{\mathrm{s}}[n] = \left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{T} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle = \min\limits_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle$.

e) **[2+2 pts]** In the light of question d), explain why the exact ground-state energy $E_0$ of a given molecule with nuclear potential $v_{\mathrm{ne}}(\mathbf{r})$ can be determined as follows:

$$\begin{aligned}
E_0 &= \min_n \left\{ \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle \right\} + E_{\mathrm{Hxc}}[n] + \int d\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \right\} && (2)\\
&= \min_n \left\{ \min_{\Psi \rightarrow n} \left\{ \left\langle \Psi \middle| \hat{T} + \sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)\times \middle| \Psi \right\rangle + E_{\mathrm{Hxc}}[n_\Psi] \right\} \right\} && (3)\\
&= \min_\Psi \left\{ \left\langle \Psi \middle| \hat{T} + \sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)\times \middle| \Psi \right\rangle + E_{\mathrm{Hxc}}[n_\Psi] \right\}, && (4)
\end{aligned}$$

where $E_{\mathrm{Hxc}}[n]$ is the universal Hartree-exchange-correlation functional. How does Eq. (4) differ from the conventional Rayleigh–Ritz variational principle? What is the minimizing wave function $\Psi$ in Eq. (4)?