Exam in density functional theory (M1 course)

December 2022 – Duration: 30 minutes

We consider the following density-functional partially-interacting N-electron Schrödinger equation,

$$\left(\hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v^\lambda[n](\mathbf{r}_i)\times\right) \Psi^\lambda[n] = \mathcal{E}^\lambda[n] \times \Psi^\lambda[n], \tag{1}$$

where the two-electron repulsion operator $\hat{W}_{\text{ee}}$ is scaled by an arbitrary number λ in the range $0 \leq \lambda \leq 1$. For any λ value, the local potential $v^\lambda[n](\mathbf{r})$ is chosen such that the normalized N-electron ground-state wave function $\Psi^\lambda[n] \equiv \Psi^\lambda[n](\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ reproduces the density n, i.e., $n_{\Psi^\lambda[n]}(\mathbf{r}) = n(\mathbf{r})$.

a) [**2 pts**] Is the potential $v^\lambda[n](\mathbf{r})$ unique? What does it correspond to when $\lambda = 1$ and $\lambda = 0$, respectively? What is interesting about the $\lambda = 0$ case in terms of computational cost?

b) [**2.5 pts**] Let $F^\lambda[n] = \left\langle \Psi^\lambda[n] \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} \middle| \Psi^\lambda[n] \right\rangle$. Is $F^\lambda[n]$ a universal functional of the density? The so-called Hartree-exchange-correlation (Hxc) density-functional energy $E_{\text{Hxc}}[n]$ is central in Kohn-Sham density-functional theory (KS-DFT). Discuss briefly the physical meaning of the Hartree, exchange, and correlation energies, respectively. How is $E_{\text{Hxc}}[n]$ evaluated from $F^{\lambda=1}[n]$ and $F^{\lambda=0}[n]$?

c) [**2 pts**] For simplicity, we use *real algebra* in the following. Consequently, for any contribution $\hat{\mathcal{H}}$ to a Hamiltonian operator, we have $\langle \Psi | \hat{\mathcal{H}} | \chi \rangle + \langle \chi | \hat{\mathcal{H}} | \Psi \rangle = 2 \langle \Psi | \hat{\mathcal{H}} | \chi \rangle$. Deduce from Eq. (1) that

$$\frac{\delta F^\lambda[n]}{\delta n(\mathbf{r})} = 2 \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} \middle| \Psi^\lambda[n] \right\rangle = 2\mathcal{E}^\lambda[n] \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \Psi^\lambda[n] \right\rangle - 2 \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \sum_{i=1}^{N} v^\lambda[n](\mathbf{r}_i)\times \middle| \Psi^\lambda[n] \right\rangle. \tag{2}$$

d) [**0.5 pts**] Deduce from the normalization of $\Psi^\lambda[n]$ that $2 \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \Psi^\lambda[n] \right\rangle = \frac{\delta}{\delta n(\mathbf{r})} \left[\left\langle \Psi^\lambda[n] \middle| \Psi^\lambda[n] \right\rangle \right] = 0$.

e) [**1 pt**] Explain why $2 \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \sum_{i=1}^{N} v^\lambda[n](\mathbf{r}_i)\times \middle| \Psi^\lambda[n] \right\rangle = \frac{\delta}{\delta n(\mathbf{r})} \left[\left\langle \Psi^\lambda[n] \middle| \sum_{i=1}^{N} v^\lambda[\nu](\mathbf{r}_i)\times \middle| \Psi^\lambda[n] \right\rangle \right]\Big|_{\nu=n}$. Deduce that $2 \left\langle \frac{\delta \Psi^\lambda[n]}{\delta n(\mathbf{r})} \middle| \sum_{i=1}^{N} v^\lambda[n](\mathbf{r}_i)\times \middle| \Psi^\lambda[n] \right\rangle = \frac{\delta}{\delta n(\mathbf{r})} \left[\int d\mathbf{r}\, v^\lambda[\nu](\mathbf{r})\, n(\mathbf{r}) \right]\Big|_{\nu=n} = v^\lambda[n](\mathbf{r})$.

f) [**1 pt**] Conclude from Eq. (2) that $v^\lambda[n](\mathbf{r}) = -\frac{\delta F^\lambda[n]}{\delta n(\mathbf{r})}$. Deduce from b) that $v^{\lambda=0}[n](\mathbf{r}) - v^{\lambda=1}[n](\mathbf{r}) = \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})}$. Explain how the self-consistent KS equations can be recovered from the latter relation.

g) [**2 pts**] The exact density-functional exchange energy can be expressed in terms of the (doubly here, for simplicity) occupied KS orbitals as follows, $E_{\text{x}}[n] = - \sum_{i,j=1}^{N/2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\varphi_i(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)\varphi_j(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$, where $n(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \varphi_i^2(\mathbf{r})$. Is $E_{\text{x}}[n]$ an explicit functional of the density? Is it possible to design density-functional approximations to $E_{\text{x}}[n]$? Show that, in the *particular case of two electrons* (i.e., $N = 2$), the exchange functional simply reads $E_{\text{x}}[n] = -\frac{1}{2} E_{\text{H}}[n]$, where $E_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$ is the Hartree functional.