Exercise Sheet 8

Due: 18.06.24 14h00

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General Regulations.

- Please hand in your solutions in groups of up to two people.
- Your solutions to theoretical exercises can be either handwritten notes (scanned), or typeset using LaTeX. In case you hand in handwritten notes, please make sure that they are legible and not too blurred or low resolution.
- For the practical exercises, always provide the (commented) code as well as the output, and don't forget to explain/interpret the latter. Please hand in an exported PDF of your notebook.
- Submit all your files in the Übungsgruppenverwaltung, only once for your group.

1 Paper reading

Starting this week, you will read chunks of two papers which we will discuss in an inverted classroom setting three weeks from now. One of the papers is 70 pages long and has detailed technical sections, so it is important to start studying them now.

This week, please read those sections which should be accessible given what we have covered in the lecture so far:

- KineticNet [1]: Abstract, sections I and IV.
- M-OFDFT [2]: Main text up to eq. 2, appendices A1 and A2.

To check your understanding, write down the differences between the two methods in terms of their representation of the electron density. (5 pts)

2 External energy functional

Consider a system of N electrons in an external potential V_{ext}.

(a) Show that the external energy $E_{\text{ext}} = \langle\psi|V_{\text{ext}}|\psi\rangle$ is a density functional given by

$$E_{\text{ext}}[\rho] = \int \rho(\boldsymbol{r}) V_{\text{ext}}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r},$$

where ρ is the electron density corresponding to the wave function ψ. (4 pts)

(b) Give the external potential V_{ext} of a molecular system. (2 pts)

3 Two-electron kinetic energy functional

For a two-electron restricted system, the "non-interacting" kinetic energy can be written as a functional $T_{\text{S}}[\rho]$ of the electron density $\rho(\boldsymbol{r})$.

(a) Write down the kinetic energy of the two electrons sharing a single spatial orbital $\varphi(\boldsymbol{r})$. (2 pts)

(b) Write down the electron density $\rho(\boldsymbol{r})$ in terms of the spatial orbital $\varphi(\boldsymbol{r})$. Show that $\|\nabla\rho(\boldsymbol{r})\|^2 = 8\rho(\boldsymbol{r})\,\|\nabla\varphi(\boldsymbol{r})\|^2$. (3 pts)

(c) Use the identity $\nabla\cdot(\varphi\nabla\varphi) = \|\nabla\varphi\|^2 + \varphi\nabla^2\varphi$ to derive the kinetic energy functional $T_{\text{S}}[\rho]$.
Hint: Use the divergence theorem to convert one integral into a vanishing surface integral. (4 pts)

References

[1] Roman Remme et al. "KineticNet: Deep learning a transferable kinetic energy functional for orbital-free density functional theory". In: *The Journal of Chemical Physics* 159.14 (Oct. 2023). ISSN: 0021-9606, 1089-7690. URL: https://pubs.aip.org/jcp/article/159/14/144113/2916356/KineticNet-Deep-learning-a-transferable-kinetic.

[2] He Zhang et al. "Overcoming the barrier of orbital-free density functional theory for molecular systems using deep learning". In: *Nature Computational Science* 4.3 (Mar. 2024), pp. 210–223. ISSN: 2662-8457. DOI: 10.1038/s43588-024-00605-8. URL: https://uebungen.physik.uni-heidelberg.de/c/image/d/vorlesung/20241/1883/material/zhang_24_overcoming.pdf.