Exercise Sheet 2

Due: 07.05.24 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 both the notebook (`.ipynb`), as well as an exported pdf.
- Submit all your files in the Übungsgruppenverwaltung, only once for your group.

1 Hartree vs. Hartree-Fock

Consider the two-electron system with the electronic Hamiltonian,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} - \frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} + \frac{1}{r_{12}}.$$

Compute the energy difference between the Hartree product and the Slater determinant ansatz for the wave function. (4 pts)

2 Slater determinant

The Slater determinant for a two-electron is given by

$$\Phi_{\mathrm{SD}}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{C} \det \begin{pmatrix} \phi_1(\boldsymbol{x}_1) & \phi_2(\boldsymbol{x}_1) \\ \phi_1(\boldsymbol{x}_2) & \phi_2(\boldsymbol{x}_2) \end{pmatrix}.$$

(a) Why can we assume that the single-particle wave functions ϕ_i are orthonormal? Hint: Check what changes when the functions ϕ_i are orthonormalized. (2 pts)

(b) Determine the normalization constant C for the Slater determinant of a two-electron system. (2 pts)

(c) Write down the electron density generated by the two-electron Slater determinant. (2 pts)

3 Coulomb and exchange terms

Consider a two-electron system. The Coulomb and the exchange term are given by

$$J_{ij} = \int \frac{\phi_i^*(\boldsymbol{x}_1)\phi_j^*(\boldsymbol{x}_2)\phi_i(\boldsymbol{x}_1)\phi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \,\mathrm{d}\boldsymbol{x}_1 \,\mathrm{d}\boldsymbol{x}_2,$$

$$K_{ij} = \int \frac{\phi_i^*(\boldsymbol{x}_1)\phi_j^*(\boldsymbol{x}_2)\phi_j(\boldsymbol{x}_1)\phi_i(\boldsymbol{x}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \,\mathrm{d}\boldsymbol{x}_1 \,\mathrm{d}\boldsymbol{x}_2,$$

where $\boldsymbol{x} = (\boldsymbol{r}, w)$ is the tuple of spatial and spin coordinates.

(a) Show that J_{ij} and K_{ij} are real. (3 pts)

(b) Prove that J and K are symmetric, $J_{ij} = J_{ji}$ and $K_{ij} = K_{ji}$. (2 pts)

(c) Show that $J_{ii} = K_{ii}$. What does this mean physically? Hint: Recall the sign in the total energy. (2 pts)

(d) Which integrals vanish because of spin? (3 pts)