UNIVERSITY OF REGENSBURG

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http://www.physik.uni-regensburg.de/forschung/evers/courses/2021/comp_nanoscience.phtml

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Computational Nanoscience: Exercise Sheet No. 2

Exercise 2.1: Normalization and antisymmetry of Slater determinants

Use the definition of a Slater determinant

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \tag{1}$$

and the Leibniz formula

$$|A| = \sum_{\sigma \in S_N} \left(\text{sgn}(\sigma) \prod_{i=1}^{N} a_{i,\sigma(i)} \right)$$

to prove $\langle \Psi_{SD} | \Psi_{SD} \rangle = 1$ and $\Psi_{SD}(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots \mathbf{x}_N) = -\Psi_{SD}(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots \mathbf{x}_N)$.

Exercise 2.2: Hartree energy

The electron density can be computed from a many-electron wavefunction as

$$n(\mathbf{r}) = N \int d\sigma \, d^3\mathbf{x}_2 \, d^3\mathbf{x}_3 \, \ldots \, d^3\mathbf{x}_N \, |\Psi(\mathbf{x}, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)|^2 . \tag{2}$$

In case of a Slater determinant from Eq. (1), the electron density is given by

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{3}$$

where $\psi_i(\mathbf{r})$ is the orbital part of the spin orbital $\psi_i(\mathbf{x}) = \psi_i(\mathbf{r}) f_{m_s}(\sigma)$.

(a) Show $\int d^3\mathbf{r} \, n(\mathbf{r}) = N$.

(b) Interpret Eq. (3).

(c) Prove that the Hartree energy as defined in the lecture can be computed as

$$E_H = \frac{e^2}{2} \iint \frac{n(\mathbf{r}) \, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d^3\mathbf{r} \, d^3\mathbf{r}', \tag{4}$$

where $n(\mathbf{r})$ is the electron density of the Hartree-Fock wavefunction.

(d) How can you interpret Eq. (4) using classical electrostatics?

(e) Argue why the factor $\frac{1}{2}$ is appearing. For your reasoning, you can use a system with two point charges of charge $-e$. For this system, the electron density is $n(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_1) + \delta(\mathbf{r} - \mathbf{r}_2)$.

(f) The quantum-mechanical electron-electron interaction energy E_{ee}^{exact} is defined as

$$E_{ee}^{exact} = \langle \Psi | \hat{V}_{ee} | \Psi \rangle \,, \tag{5}$$

where Ψ is the many-electron ground state wavefunction and $\hat{V}_{ee}$ has been defined in the lecture. Is E_H in general identical to the quantum-mechanical electrostatic electron-electron interaction? Prove your answer rigorously by considering a special case.

(g) Is $E_H + E_x$ (E_x: exchange energy) in general identical to the quantum-mechanical electrostatic electron-electron interaction of a many-electron system?

(h) Prove Eq. (3) using Eqs. (1) and (2). (bonus exercise)

Exercise 2.3: Hartree-Fock for bond length and lattice constant

Based on a Hartree-Fock computer program, propose and briefly describe a method to compute

(a) the equilibrium distance between two atoms in a diatomic molecule (e.g. in O_2).

(b) the equilibrium lattice constant of diamond. For your method, you can use the experimentally known crystal structure (except for the lattice constant) and the knowledge that the distance between neighboring atoms is identical. You can also assume that your Hartree-Fock computer program includes periodic boundary conditions such that you can do Hartree-Fock calculations on a unit cell of diamond including periodic boundary conditions.