Prof. Andreas Wipf, MSc. Marc Steinhauser November 3, 2019

Problem sheet „Advanced Quantum Mechanics"

winter term 2019/20

Sheet 3

Problem 5: 2-particle operator 2 points

Given is a 2-particle operator

$$A = \frac{1}{2}\sum_{i\neq j} A(i,j)$$

and a product state for three particles

$$\Psi = \Psi_1(1)\Psi_2(2)\Psi_3(3)\,.$$

Calculate $(\Psi, A\Psi)$ explicitly for the symmetrized and antisymmetrized product states.

Problem 6: Hartree-Fock approximation for Beryllium-atom 1+4+2 = 7 points

Beryllium has been discovered in 1797 by Vauquelin. The nucleus has charge $Z = 4$ and the atom has 4 shell electrons. Let us assume, that the $1s$ and $2s$ orbitals are filled in the ground state.

1. What is the Slater determinant for the atom in its ground state? Denote, for example, the $1s$ state of the 'first electron' with spin up by $\psi_{100}(\boldsymbol{x}_1)\chi_{1\uparrow}$.
2. Find the expression for the (approximate) expectation value of the ground state energy, expressed via the so far unknown one-particle wave functions ψ_{100} und ψ_{200}.
3. Derive now the self-consistent Hartree-Fock equation for the one-particle wave functions. In an iterative solution one typically starts with the wave function of the Hydrogen atom (with the correct Z). Determine the ground state energy for the Slater determinant with the wave function of the Hydrogen atom. How close are you to the exact value $-14.57\,e^2/a$?

Hints: The Slater-determinant depends on the four one-particle wave functions $\psi_{n00}(\boldsymbol{x}_a)\chi_{a,s}$. Here $n \in \{1,2\}$ is the principal quantum number, $s \in \{\uparrow,\downarrow\}$ the 3-component of the spins and $a \in \{1,2,3,4\}$ enumerates the electrons. Use (for example) the notation $\psi_{100}(\boldsymbol{x}_3)\chi_{3,\uparrow}$ for the 'third electron' with principal quantum number 1 and spin up.

For the last part of the exercise you will need the following integrals to calculate the mean kinetic energy and nucleus-electron interaction for Hydrogen-wave functions:

$$\int \mathrm{d}^3x\, |\nabla\psi_{100}(\boldsymbol{x})|^2 = \frac{Z^2}{a^2} \quad , \quad \int \mathrm{d}^3x\, |\nabla\psi_{200}(\boldsymbol{x})|^2 = \frac{1}{4}\frac{Z^2}{a^2}$$
$$\int \mathrm{d}^3x\, \frac{|\psi_{100}(\boldsymbol{x})|^2}{|\boldsymbol{x}|} = \frac{Z}{a} \quad , \quad \int \mathrm{d}^3x\, \frac{|\psi_{200}(\boldsymbol{x})|^2}{|\boldsymbol{x}|} = \frac{1}{4}\frac{Z}{a}\,,$$

and the following integrals to calculate the Hartree-Fock-term (direct and exchange term)

$$\int \mathrm{d}^3x \int \mathrm{d}^3y \, \frac{|\psi_{100}(\boldsymbol{x})|^2 |\psi_{100}(\boldsymbol{y})|^2}{|\boldsymbol{x}-\boldsymbol{y}|} = \frac{5}{8}\frac{Z}{a}$$
$$\int \mathrm{d}^3x \int \mathrm{d}^3y \, \frac{|\psi_{200}(\boldsymbol{x})|^2 |\psi_{200}(\boldsymbol{y})|^2}{|\boldsymbol{x}-\boldsymbol{y}|} = \frac{77}{512}\frac{Z}{a}$$
$$\int \mathrm{d}^3x \int \mathrm{d}^3y \, \frac{|\psi_{100}(\boldsymbol{x})|^2 |\psi_{200}(\boldsymbol{y})|^2}{|\boldsymbol{x}-\boldsymbol{y}|} = \frac{17}{81}\frac{Z}{a}$$
$$\int \mathrm{d}^3x \int \mathrm{d}^3y \, \frac{\psi_{100}^*(\boldsymbol{x})\psi_{100}^*(\boldsymbol{y})\psi_{200}(\boldsymbol{x})\psi_{200}(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} = \frac{16}{729}\frac{Z}{a}\,.$$

Recall that $\hbar^2/m = ae^2$.

Supplementary material: The integrals above can be calculated with the help of a Fourier transformation. Let

$$\mathcal{F}(f)(\boldsymbol{k}) = \hat{f}(\boldsymbol{k}) = \int_{\mathbb{R}^3} f(\boldsymbol{x}) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \mathrm{d}^3x$$

be the Fourer transform of f. Then we have

$$\int \mathrm{d}^3x \int \mathrm{d}^3y \, \frac{f^*(\boldsymbol{x})g(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} = \frac{1}{2\pi^2}\int \mathrm{d}^3k \, \frac{\hat{f}^*(\boldsymbol{k})\hat{g}(\boldsymbol{k})}{|\boldsymbol{k}|^2}\,.$$

For example, for $f = \psi_{100}^*\psi_{100}$ and $g = \psi_{200}^*\psi_{200}$ one uses

$$\mathcal{F}(\psi_{100}^*\psi_{100})(\boldsymbol{k}) = \frac{16Z^4}{(2Z^2+|\boldsymbol{k}|^2)^2}$$

together with the Fourier transform of $\psi_{200}^*\psi_{200}$ to calculate an integral, which is needed to evaluate the Hartree-Fock-term.

Submission date: Thursday, 07.11.2019, before the lecture