Quantum Physics, Course KFY/7KVAF

WS 2022/2023

Theme 10: Hartree-Fock method

1. Write down the wavefunction of the ground state of the lithium atom, if electron interaction is neglected. [Hint: Use the Slater determinant.]

2. Derive the charge density in $\vec{r}$ position from the system of N electrons. Show, that in Hartree-Fock approximation $\rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2$, where $\psi_i(\vec{r})$ are one-electron wavefunction as usual in Hatree-Fock approximation. [Hint: Use the wavefunction in Slater determinant form.]

3. Write down Hartree and Hartree-Fock equations for a) the helium atom, and b) the lithium atom. In b), assume both the case of the same spatial parts and opposite spins ("restricted" Hartree-Fock approximation) and the case of different spatial parts corresponding to opposite spins ("unrestricted" Hartree-Fock approximation).

4. Show for the closed shell Hartree-Fock theory, that the first ionization energy of molecule equals negative orbital energy corresponding to the highest occupied molecular orbital (HOMO), i.e., proof the validity of the so-called Koopmans theorem. [Hint: Write down the energy of N-electron system (without details, using one-electron hamiltonian, coulombic, and exchange integrals) and of $(N-1)$-electron system. Make a difference.]