

Quantum Chemistry

Seminar 9

Hartree-Fock method

Exercise 1 (Anila)

Simplify the Hartree-Fock equations for the helium atom supposing that $\varphi_1(\vec{r}, \xi) = \varphi(\vec{r})\alpha(\xi)$ and $\varphi_2(\vec{r}, \xi) = \varphi(\vec{r})\beta(\xi)$, where $\alpha(+1/2) = 1$, $\alpha(-1/2) = 0$, $\beta(+1/2) = 0$, and $\beta(-1/2) = 1$.

Exercise 2 (unassigned)

Show that the Slater determinants represent for functions φ_k a $\tilde{\varphi}_k$ (see lesson 9, page 6) physically equivalent wave functions.

Hint: Use formulas known from the linear algebra course:

- $|\det \mathbf{U}| = |\det \mathbf{U}^+| = 1$ ($\Rightarrow \det \mathbf{U} = e^{i\alpha}$) for a complex-valued unitary matrix, or alternatively, $|\det \mathbf{Q}| = |\det \mathbf{Q}^T| = 1$ ($\Rightarrow \det \mathbf{Q} = \pm 1$) for a real-valued orthogonal matrix,
- $\det(\mathbf{A} \cdot \mathbf{B}) = \det \mathbf{A} \det \mathbf{B}$.