Quantentheorie II

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Blatt 7

1. Helium atom: Hartree Fock approach

The Hamiltonian for two electrons that move in the Coulomb potential generated by a nucleus of charge $Z = 2$ is $H = H_0 + H_1$ with

$$H_0 = -\frac{\hbar^2}{2\mu}(\triangle_1 + \triangle_2) - Ze^2\left(\frac{1}{|\vec{r}_1|} + \frac{1}{|\vec{r}_2|}\right)$$

and

$$H_1 = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\,.$$

The Hamiltonian H_0 is the sum of two single particle contributions, one for each of the two electrons. The single particle Hamiltonian is diagonalized by the set of eigenfunctions

$$\langle\sigma|\,\langle\vec{r}|\;|nlm\rangle\,|m_s\rangle \equiv \psi_{nlmm_s}(r,\theta,\phi,\sigma) = R_{nl}(r)Y_l^m(\theta,\phi)\delta_{\sigma m_s},$$

where R_{nl} can be expressed in terms of Laguerre polinomials, Y_l^m are the spherical harmonics and $\delta_{\sigma m_s}$ is the Kronecker delta. Moreover (r,θ,ϕ) are the orbital coordinates in polar representation while $\sigma =\uparrow,\downarrow$ represents the spin coordinate of the electron. The associated single particle energy is ε_{nl}.

a) • Let us only consider now the orbitals ψ_{100m_s} and ψ_{200m_s}. How many fermionic (antisymmetric) two electron states can you construct with them? Write explicitly the eigenstates and the associated eigenenergies for the the two electron Hamiltonian H_0. Express the energies in Rydberg. *Hint*: Remember that the wave functions should be antisymmetric with respect to the simultaneous exchange of the orbital *and* spin coordinates.

(2 Points)

b) • Classify all the states calculated in the previous point according to their energy, their total spin and the projection of the total spin along the z direction.

(3 Points)

Let us now consider the interaction between the two electrons at the Hartree-Fock (HF) level. We take as an Ansatz for the two single particle HF states

$$|\varphi_1^{\mathrm{HF}}\rangle = a\,|100\rangle\,|\uparrow\rangle + b\,|100\rangle\,|\downarrow\rangle + c\,|200\rangle\,|\uparrow\rangle + d\,|200\rangle\,|\downarrow\rangle$$

and

$$|\varphi_2^{\mathrm{HF}}\rangle = e\,|100\rangle\,|\uparrow\rangle + f\,|100\rangle\,|\downarrow\rangle + g\,|200\rangle\,|\uparrow\rangle + h\,|200\rangle\,|\downarrow\rangle,$$

where a, b, c, d, e, f, g, h are coefficients to be determined from the Hartree-Fock equations.

c) • Prove that the HF two particle state can be written in the form:

$$\begin{aligned}|\Psi^{\mathrm{HF}}\rangle =&(af-be)\Big(|1\uparrow\rangle\,|1\downarrow\rangle - |1\downarrow\rangle\,|1\uparrow\rangle\Big) + (ag-ce)\Big(|1\uparrow\rangle\,|2\uparrow\rangle - |2\uparrow\rangle\,|1\uparrow\rangle\Big)+\\ &(ah-de)\Big(|1\uparrow\rangle\,|2\downarrow\rangle - |2\downarrow\rangle\,|1\uparrow\rangle\Big) + (bg-cf)\Big(|1\downarrow\rangle\,|2\uparrow\rangle - |2\uparrow\rangle\,|1\downarrow\rangle\Big)+\\ &(bh-df)\Big(|1\downarrow\rangle\,|2\downarrow\rangle - |2\downarrow\rangle\,|1\downarrow\rangle\Big) + (ch-dg)\Big(|2\uparrow\rangle\,|2\downarrow\rangle - |2\downarrow\rangle\,|2\uparrow\rangle\Big),\end{aligned}$$

where we have used the short notation $|i\, m_s\rangle$ instead of $|i00\rangle\,|m_s\rangle$. Write the square of the norm of the single particle HF states $|\varphi_1^{\rm HF}\rangle$ and $|\varphi_1^{\rm HF}\rangle$ in terms of the coefficients $a,\dots,h$.

(2 Points)

d) • Calculate the expectation value of the energy, *i.e.* of the total Hamiltonian H, on the HF state.

Hint: You may use the following relations:

$$\begin{aligned}
\langle 1\sigma_2|\,\langle 1\sigma_1|\,H_1\,|1\sigma_1'\rangle\,|1\sigma_2'\rangle &= U_{11}\delta_{\sigma_1\sigma_1'}\delta_{\sigma_2\sigma_2'}\,,\\
\langle 1\sigma_2|\,\langle 2\sigma_1|\,H_1\,|2\sigma_1'\rangle\,|1\sigma_2'\rangle &= U_{12}\delta_{\sigma_1\sigma_1'}\delta_{\sigma_2\sigma_2'}\,,\\
\langle 2\sigma_2|\,\langle 2\sigma_1|\,H_1\,|2\sigma_1'\rangle\,|2\sigma_2'\rangle &= U_{22}\delta_{\sigma_1\sigma_1'}\delta_{\sigma_2\sigma_2'}\,,\\
\langle 1\sigma_2|\,\langle 2\sigma_1|\,H_1\,|1\sigma_1'\rangle\,|2\sigma_2'\rangle &= J\delta_{\sigma_1\sigma_1'}\delta_{\sigma_2\sigma_2'}\,.
\end{aligned}$$

(3 Points)

e) Derive the HF equations for the coefficients $a,\dots,h$ by differentiation of the functional:

$$\langle\tilde{H}\rangle = \langle\Psi^{\rm HF}|\,H\,|\Psi^{\rm HF}\rangle - \sum_{n=1}^{2}\varepsilon_n\Big(|\langle\varphi_n^{\rm HF}|\varphi_n^{\rm HF}\rangle|^2 - 1\Big)$$

with respect of the coefficients $a,\dots,h$.

f) Compare the equations obtained at point e) with those obtained by minimization of the functional $\langle\tilde{H}\rangle$ with respect to the functions $(\varphi_i^{\rm HF})^*(\vec{r},\sigma)$ $(i=1,2)$:

$$\left(-\frac{\hbar^2}{2\mu}\triangle_1 - \frac{Ze^2}{|\vec{r_1}|}\right)\varphi_i^{\rm HF}(\vec{r_1},\sigma_1) + \sum_{\sigma_2}\int d\vec{r}_2\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$
$$\times\sum_{j=1}^{2}\varphi_j^{\rm HF\,*}(\vec{r}_2,\sigma_2)\Big[\varphi_j^{\rm HF}(\vec{r}_2,\sigma_2)\varphi_i^{\rm HF}(\vec{r}_1,\sigma_1) - \varphi_j^{\rm HF}(\vec{r}_1,\sigma_1)\varphi_i^{\rm HF}(\vec{r}_2,\sigma_2)\Big] = \varepsilon_i\varphi_i^{\rm HF}(\vec{r}_1,\sigma_1)$$

Hint: Notice that the two equations written here should be integrated (in space and spin) over the functions

$$\psi^*_{100\uparrow}(\vec{r}_1,\sigma_1)\,,\ \psi^*_{100\downarrow}(\vec{r}_1,\sigma_1)\,,\ \psi^*_{200\uparrow}(\vec{r}_1,\sigma_1)\,,\ \psi^*_{200\downarrow}(\vec{r}_1,\sigma_1)\,,$$

in order to derive the equations for the coefficients $a,\dots,h$ obtained at point e).

Frohes Schaffen!

Return the solution of the exercises marked with • by Monday 1st of December at 10:00.