Phys 5870: Modern Computational Methods in Solids
Homework 4

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Hartree-Fock solution of the HeH^+ molecule

We will use a basis of Hydrogen-like atomic wave-functions for each atom:

$$\phi_1(r) = \sqrt{\frac{r^3}{\pi}} \exp\left(-\alpha_1(r - R_1)\right)$$
$$\phi_2(r) = \sqrt{\frac{r^3}{\pi}} \exp\left(-\alpha_2(r - R_2)\right)$$

where R_1 and R_2 are the positions of the two nuclei. We take the distance between them as $R = 1.4632$ in atomic units, and we use the optimal values $\alpha_1 = 2.0925$ for He and $\alpha_2 = 1.24$ for H.

We propose a solution for the orbital part of the form

$$\phi(r) = C_1\phi_1(r) + C_2\phi_2(r)$$

where C_1 and C_2 are constants to be determined.

With these numbers we obtain the following overlap matrix

$$S = \begin{pmatrix} 1.0 & 0.4508 \\ 0.4508 & 1.0 \end{pmatrix}, \tag{1}$$

and kinetic energy

$$T = \begin{pmatrix} 2.1643 & 0.1670 \\ 0.1670 & 0.76 \end{pmatrix}. \tag{2}$$

The electrostatic interaction with nuclei 1 and 2 are given by:

$$V_1 = \begin{pmatrix} -4.1398 & -1.1029 \\ -1.1029 & -1.2652 \end{pmatrix}, \tag{3}$$

and

$$V_2 = \begin{pmatrix} -0.6772 & -0.4313 \\ -0.4313 & -1.2266 \end{pmatrix}, \tag{4}$$

The next step is to calculate the integrals

$$\langle \phi_p \phi_q | \frac{1}{r_{12}} | \phi_r \phi_s \rangle$$

with $p, q, r, s = 1, 2$. These give 16 possibilities. However, of these, there are only six unique integrals

$$\begin{aligned}
\langle \phi_1 \phi_1 | \frac{1}{r_{12}} | \phi_1 \phi_1 \rangle &= 1.3072 \\
\langle \phi_2 \phi_1 | \frac{1}{r_{12}} | \phi_1 \phi_1 \rangle &= 0.4373 \\
\langle \phi_2 \phi_1 | \frac{1}{r_{12}} | \phi_2 \phi_1 \rangle &= 0.1773 \\
\langle \phi_2 \phi_2 | \frac{1}{r_{12}} | \phi_1 \phi_1 \rangle &= 0.6057 \\
\langle \phi_2 \phi_2 | \frac{1}{r_{12}} | \phi_2 \phi_1 \rangle &= 0.3118 \\
\langle \phi_2 \phi_2 | \frac{1}{r_{12}} | \phi_2 \phi_2 \rangle &= 0.7746
\end{aligned} \tag{5}$$

Using all this information calculate:

a) The Fock matrix "F" for this problem. To do this, pick as the initial condition $C_1 = C_2 = 1/\sqrt{2}$.

b) Solve "by hand" (it is a two by two determinant) the first iteration H-F/Roothaan equations

$$FC = \epsilon SC$$

and obtain the energies, and the ground-state.