Química Cuántica de Sólidos
Tarea 02: Método de Hartree-Fock

Dr. Omar De la Peña Seaman

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Nombre del Estudiante: ______________________________

Problema 1 *Koopmans' theorem*

Demonstrate the Koopman's theorem,

$$
\begin{aligned}
E_{HF}(N-1) - E_{HF}(N) &\approx -\epsilon_n, \\
E_{HF}(N+1) - E_{HF}(N) &\approx \epsilon_m,
\end{aligned}
$$

where we have assumed that an electron of the nth orbital has been removed, and that an extra electron has been added to the mth orbital. $E_{HF}(M)$ is the total electronic energy for the M-electron system.

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Problema 2 *Hartree-Fock-Roothaan method*

Consider a system with four electrons. These four electrons occupy pairwise two orbitals but have different spin dependence, thus the Slater determinant is,

$$
\begin{aligned}
\Phi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4) &= \frac{1}{\sqrt{4!}} \begin{bmatrix} \phi_1(\mathbf{r}_1)\alpha(1) & \phi_1(\mathbf{r}_1)\beta(1) & \phi_2(\mathbf{r}_1)\alpha(1) & \phi_2(\mathbf{r}_1)\beta(1) \\ \phi_1(\mathbf{r}_2)\alpha(2) & \phi_1(\mathbf{r}_2)\beta(2) & \phi_2(\mathbf{r}_2)\alpha(2) & \phi_2(\mathbf{r}_2)\beta(2) \\ \phi_1(\mathbf{r}_3)\alpha(3) & \phi_1(\mathbf{r}_3)\beta(3) & \phi_2(\mathbf{r}_3)\alpha(3) & \phi_2(\mathbf{r}_3)\beta(3) \\ \phi_1(\mathbf{r}_4)\alpha(4) & \phi_1(\mathbf{r}_4)\beta(4) & \phi_2(\mathbf{r}_4)\alpha(4) & \phi_2(\mathbf{r}_4)\beta(4) \end{bmatrix}, \\
&\equiv |\phi_1\alpha, \phi_1\beta, \phi_2\alpha, \phi_2\beta| \, .
\end{aligned}
$$

Applying the Roothaan approximation and the H−F−R restricted method, the orbitals $\phi_1\alpha$, $\phi_1\beta$, $\phi_2\alpha$, and $\phi_2\beta$ can be expanded in the following four basis functions $\chi_1\alpha$, $\chi_1\beta$, $\chi_2\alpha$, and $\chi_2\beta$, then $N_b = 2$ and:

$$
\begin{aligned}
\phi_1(\mathbf{r}) &= c_{11}\chi_1(\mathbf{r}) + c_{12}\chi_2(\mathbf{r}), \\
\phi_2(\mathbf{r}) &= c_{21}\chi_1(\mathbf{r}) + c_{22}\chi_2(\mathbf{r}).
\end{aligned}
$$

where the precise form of χ_p is unimportant right now.

We denote the matrix elements as following,

$$\langle \chi_p | \chi_n \rangle \equiv o_{pn},$$
$$\langle \chi_p | \hat{h}_1 | \chi_n \rangle \equiv h_{1,pn},$$
$$\langle \chi_p \chi_q | \hat{h}_2 | \chi_n \chi_r \rangle \equiv h_{2,pqnr},$$

with the corresponding values given on the tables,

p	n	o_{pn}	$h_{1,pn}$
1	1	1.0	-3.0
1	2	-0.5	-2.0
2	2	1.1875	-5.0

p	q	n	r	$h_{2,pqnr}$
1	1	1	1	0.5
1	1	1	2	0.3
1	1	2	2	0.2
1	2	2	1	0.2
1	2	1	2	0.4
1	2	2	2	0.3
2	2	2	2	0.5

and the matrix elements obey the following,

$$o_{pn} = o^*_{np},$$
$$h_{1,pn} = h^*_{1,np},$$
$$h_{2,pqnr} = h_{2,qprn} = h^*_{2,nrpq} = h^*_{2,rnqp}.$$

Assuming the following orbitals as an initial guess,

$$\phi_1 = a_1 \left(0.2\chi_1 + 0.8\chi_2\right),$$
$$\phi_2 = a_2 \left(1.0\chi_1 + \frac{4}{17}\chi_2\right),$$

obtain a new full set of orbitals ϕ_1 and ϕ_2 after two iteration steps, and compare the eigenvalues ϵ_l and the coefficients c_{pl} between the different steps and the initial guess. *Hint*: Do not forget to apply the normalization condition to the $\{\phi_l\}$ orbital set.

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