Estructura Electrónica de Materias: Cálculo desde primeros principios

Guía Práctica N°1

1. **Principio Variacional**:

Siendo $|\psi_n\rangle$ la solución exacta de la ecuación de Schrödinger independiente del tiempo de un sistema de N partículas,

$$\hat{H}\,|\psi_n\rangle = E_n\,|\psi_n\rangle \tag{1}$$

y $|\epsilon\rangle$ un vector que representa un error pequeño. Si el autovalor solución $|\phi\rangle$ que se obtiene del principio variacional difiere de la solución exacta por $|\epsilon\rangle$:

$$\phi = |\psi_n\rangle + |\epsilon\rangle\ , \tag{2}$$

entonces, el error en la energía, $E[\phi] - E_n$, es de segundo orden.

Del principio variacional, se define el funcional de la energía

$$E[\phi] = \frac{\langle\phi|\,\hat{H}\,|\phi\rangle}{\langle\phi|\phi\rangle}\,. \tag{3}$$

Si la autofunción solución puede escribirse como

$$|\phi\rangle = |\psi_n\rangle + |\epsilon\rangle \tag{4}$$

y si $\langle\psi_n|\psi_n\rangle = \langle\phi|\phi\rangle = 1$, entonces, la ecuación (3) puede escribirse como

$$\begin{aligned}
E\,[\phi] &= \langle\psi_n + \epsilon|\,\hat{H}\,|\psi_n + \epsilon\rangle && (5)\\
&= \langle\psi_n|\,\hat{H}\,|\psi_n\rangle + \langle\psi_n|\,\hat{H}\,|\epsilon\rangle + \langle\epsilon|\,\hat{H}\,|\psi_n\rangle + \langle\epsilon|\,\hat{H}\,|\epsilon\rangle && (6)\\
&= E_n \underbrace{\langle\psi_n|\psi_n\rangle}_{=1} + \cancel{\langle\psi_n|\,\hat{H}\,|\epsilon\rangle} + \cancel{\langle\epsilon|\,\hat{H}\,|\psi_n\rangle} + \langle\epsilon|\,\hat{H}\,|\epsilon\rangle && (7)\\
&= E_n + \langle\epsilon|\,\hat{H}\,|\epsilon\rangle && (8)\\
\Rightarrow &\quad E_n - E\,[\phi] = \mathcal{O}^2(\epsilon) && (9)
\end{aligned}$$

2. **Método de Hartree–Fock**:

El Hamiltoniano de dos electrones se escribe como:

$$\begin{aligned}
\hat{H} &= -\frac{1}{2}\sum_{i=1}^{2}\nabla^2_{\mathrm{r}_i} + \sum_{i=1}^{2} v(\mathbf{r}_i) + \sum_{i<j}^{2}\frac{1}{r_{ij}} && (10)\\
&= -\frac{1}{2}\nabla^2_{\mathrm{r}_1} - \frac{1}{2}\nabla^2_{\mathrm{r}_1} + v(\mathbf{r}_1) + v(\mathbf{r}_2) + \frac{1}{r_{12}} && (11)\\
&= \left[-\frac{1}{2}\nabla^2_{\mathrm{r}_1} + v(\mathbf{r}_1)\right] + \left[-\frac{1}{2}\nabla^2_{\mathrm{r}_1} + v(\mathbf{r}_2)\right] + \frac{1}{r_{12}} && (12)\\
&= \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} && (13)
\end{aligned}$$

Asumiendo que la función de onda del sistema está dada por

$$\Psi^{\mathrm{HF}}(\mathbf{q}_1, \mathbf{q}_2) = \frac{1}{\sqrt{2}}\left[\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) - \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\right]\ , \tag{14}$$

donde $\mathbf{q}_i$ representa las coordenadas espaciales y de espín, la energía total de Hartree Fock del sistema resulta:

$$E^{\mathrm{HF}} = \left\langle \Psi^{\mathrm{HF}} \right| \hat{H} \left| \Psi^{\mathrm{HF}} \right\rangle \tag{15}$$

$$= \frac{1}{2} \left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) - \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) - \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle \tag{16}$$

$$= \frac{1}{2} \Big[\underbrace{\left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right\rangle}_{\text{(A)}} - \underbrace{\left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right| \hat{H} \left| \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle}_{\text{(B)}} \tag{17}$$

$$- \underbrace{\left\langle \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right\rangle}_{\text{(C)}} + \underbrace{\left\langle \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle}_{\text{(D)}} \Big] \tag{18}$$

$$\text{(A)} = \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{19}$$

$$= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_n(\mathbf{q}_1)\, d\mathbf{q}_1 \underbrace{\int \psi_m^*(\mathbf{q}_2)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_2}_{=1} \tag{20}$$

$$+ \underbrace{\int \psi_n^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\, d\mathbf{q}_1}_{=1} \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_m(\mathbf{q}_2)\, d\mathbf{q}_2 \tag{21}$$

$$+ \int \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{22}$$

$$= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_n(\mathbf{q}_1)\, d\mathbf{q}_1 + \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_m(\mathbf{q}_2)\, d\mathbf{q}_2 + \tag{23}$$

$$\int \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{24}$$

$$\text{(B)} = \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{25}$$

$$= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 \cancel{\int \psi_m^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2) d\mathbf{q}_2} + \tag{26}$$

$$\cancel{\int \psi_n^*(\mathbf{q}_1)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1} \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_n(\mathbf{q}_2) d\mathbf{q}_2 + \tag{27}$$

$$\iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{28}$$

$$= \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{29}$$

$$\text{(C)} = \iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1) \left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{30}$$

$$= \int \psi_m^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_n(\mathbf{q}_1)\, d\mathbf{q}_1 \cancel{\int \psi_n^*(\mathbf{q}_2)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_2} + \tag{31}$$

$$\cancel{\int \psi_m^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\, d\mathbf{q}_1} \int \psi_n^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_m(\mathbf{q}_2)\, d\mathbf{q}_2 + \tag{32}$$

$$\iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{33}$$

$$= \iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \tag{34}$$

$$\textcircled{D} = \iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1)\left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}\right]\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\,d\mathbf{q}_1 d\mathbf{q}_2 \tag{35}$$

$$= \int \psi_m^*(\mathbf{q}_1)\,\hat{h}_1\,\psi_m(\mathbf{q}_1)\,d\mathbf{q}_1 \underbrace{\int \psi_n^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2)\;d\mathbf{q}_2}_{=1} + \tag{36}$$

$$\underbrace{\int \psi_m^*(\mathbf{q}_1)\psi_m(\mathbf{q}_1)\,d\mathbf{q}_1}_{=1}\int \psi_n^*(\mathbf{q}_2)\,\hat{h}_2\,\psi_n(\mathbf{q}_2)\,d\mathbf{q}_2 + \tag{37}$$

$$\iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1)\frac{1}{r_{12}}\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \tag{38}$$

$$= \int \psi_m^*(\mathbf{q}_1)\,\hat{h}_1\,\psi_m(\mathbf{q}_1)\,d\mathbf{q}_1 + \int \psi_n^*(\mathbf{q}_2)\,\hat{h}_2\,\psi_n(\mathbf{q}_2)\,d\mathbf{q}_2 + \tag{39}$$

$$\iint \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1)\frac{1}{r_{12}}\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \tag{40}$$

$$E^{\mathrm{HF}} = \frac{1}{2}\left[\sum_{i=1}^{2}\langle\psi_i(\mathbf{q}_1)|\,\hat{h}_1\,|\psi_i(\mathbf{q}_1)\rangle + \sum_{i=1}^{2}\langle\psi_i(\mathbf{q}_2)|\,\hat{h}_2\,|\psi_i(\mathbf{q}_2)\rangle\right] \tag{41}$$

$$+ \frac{1}{2}\Bigg[\langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle - \langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle \tag{42}$$

$$- \langle\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle + \langle\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle\Bigg] \tag{43}$$

$$= \sum_{i=1}^{2}\langle\psi_i(\mathbf{q})|\,\hat{h}\,|\psi_i(\mathbf{q})\rangle \tag{44}$$

$$+ \frac{1}{2}\Bigg[\langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle + \langle\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\rangle \tag{45}$$

$$- \langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle - \langle\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle\Bigg] \tag{46}$$

Dado que los electrones son indistinguibles, tenemos

$$E^{\mathrm{HF}} = \sum_{i=1}^{2}\langle\psi_i(\mathbf{q})|\,\hat{h}\,|\psi_i(\mathbf{q})\rangle \tag{47}$$

$$+ \frac{1}{2}\Bigg[\langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle + \langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{21}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle \tag{48}$$

$$- \langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle - \langle\psi_m(\mathbf{q}_2)\psi_n(\mathbf{q}_1)|\,\frac{1}{r_{21}}\,|\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\rangle\Bigg] \tag{49}$$

$$= \underbrace{\sum_{i=1}^{2}\langle\psi_i(\mathbf{q})|-\frac{1}{2}\nabla^2\,|\psi_i(\mathbf{q})\rangle}_{\text{Energia cinetica de particula indep.}} + \underbrace{\sum_{i=1}^{2}\langle\psi_i(\mathbf{q})|\,v(\mathbf{r}_i)\,|\psi_i(\mathbf{q})\rangle}_{\text{Energia debido a potencial externo}} \tag{50}$$

$$+ \underbrace{\langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\rangle}_{\text{Termino directo}} - \underbrace{\langle\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)|\,\frac{1}{r_{12}}\,|\psi_m(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle}_{\text{Termino de intercambio}} \tag{51}$$

En las ecuaciones de Hartree–Fock, el término de la energía directa está dado por la repulsión Coulombiana entre el electrón 1 en el orbital n y el electron 2 en el orbital m. Por otro lado, el término de la energía de intercambio no tiene una explicación física, sino que surge de la condición de indistinguibilidad dada por el determinante de Slater definido en la ecuación (14).

Los términos directo y de intercambio en un sistema de un electrón, en donde $n = m$, resultan

$$J_{n,n} = \langle \psi_n(\mathbf{q}_1)\psi_n(\mathbf{q}_2)| \, \frac{1}{r_{12}} \, |\psi_n(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle \tag{52}$$

$$K_{n,m} = \langle \psi_n(\mathbf{q}_1)\psi_n(\mathbf{q}_2)| \, \frac{1}{r_{12}} \, |\psi_n(\mathbf{q}_1)\psi_n(\mathbf{q}_2)\rangle \tag{53}$$

$$\Rightarrow \quad J_{n,n} = K_{n,n} \tag{54}$$

La función de onda de un electrón se puede descomponer en sus coordenadas espacial y de espín como

$$\psi_n(\mathbf{q}) = \phi_n(\mathbf{r})\chi_n(\omega)\,. \tag{55}$$

El término de la energía de interacción resulta

$$K_{n,m} = \int \frac{\phi_n^*(\mathbf{r}_1)\chi_n^*(\omega_1)\phi_m^*(\mathbf{r}_2)\chi_m^*(\omega_2)\phi_m(\mathbf{r}_1)\chi_m(\omega_1)\phi_n(\mathbf{r}_2)\chi_n(\omega_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\omega_1 \, d\omega_2 \tag{56}$$

$$= \int \frac{\phi_n^*(\mathbf{r}_1)\phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \int \chi_n^*(\omega_1)\chi_m(\omega_1) \, d\omega_1 \int \chi_m^*(\omega_2)\chi_n(\omega_2) \, d\omega_2 \tag{57}$$

$$\tag{58}$$

Cuando los dos electrones tienen igual projección de espín $\chi_n(\omega) = \chi_m(\omega) = \alpha(\omega)$ o $\chi_n(\omega) = \chi_m(\omega) = \beta(\omega)$. Entonces,

$$K_{n,m} = \int \frac{\phi_n^*(\mathbf{r}_1)\phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \underbrace{\int \alpha^*(\omega_1)\alpha(\omega_1) \, d\omega_1}_{=1} \underbrace{\int \alpha^*(\omega_2)\alpha(\omega_2) \, d\omega_2}_{=1} \tag{59}$$

$$= \int \frac{\phi_n^*(\mathbf{r}_1)\phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{60}$$

Cuando los electrones tienen projección de espín opuesta, $\chi_n(\omega) = \alpha(\omega)$ y $\chi_m(\omega) = \beta(\omega)$ o $\chi_n(\omega) = \beta(\omega)$ y $\chi_m(\omega) = \alpha(\omega)$. Entonces,

$$K_{n,m} = \int \frac{\phi_n^*(\mathbf{r}_1)\phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \underbrace{\int \alpha^*(\omega_1)\beta(\omega_1) \, d\omega_1}_{=0} \underbrace{\int \alpha^*(\omega_2)\beta(\omega_2) \, d\omega_2}_{=0} \tag{61}$$

$$= 0 \tag{62}$$