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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:

$$\begin{aligned}
E^{\mathrm{HF}} &= \left\langle \Psi^{\mathrm{HF}} \right| \hat{H} \left| \Psi^{\mathrm{HF}} \right\rangle \qquad (15)\\
&= \frac{1}{2} \left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) - \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) - \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle \qquad (16)\\
&= \frac{1}{2} \Big[\underbrace{\left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right\rangle}_{\text{A}} - \underbrace{\left\langle \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right| \hat{H} \left| \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle}_{\text{B}} \qquad (17)\\
&\quad - \underbrace{\left\langle \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2) \right\rangle}_{\text{C}} + \underbrace{\left\langle \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right| \hat{H} \left| \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) \right\rangle}_{\text{D}} \Big] \qquad (18)
\end{aligned}$$

$$\begin{aligned}
\text{A} &= \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (19)\\
&= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_n(\mathbf{q}_1)\, d\mathbf{q}_1 \underbrace{\int \psi_m^*(\mathbf{q}_2)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_2}_{=1} + \qquad (20)\\
&\qquad \underbrace{\int \psi_n^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\, d\mathbf{q}_1}_{=1} \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_m(\mathbf{q}_2)\, d\mathbf{q}_2 + \qquad (21)\\
&\qquad \int \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (22)\\
&= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_n(\mathbf{q}_1)\, d\mathbf{q}_1 + \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_m(\mathbf{q}_2)\, d\mathbf{q}_2 + \qquad (23)\\
&\qquad \int \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (24)
\end{aligned}$$

$$\begin{aligned}
\text{B} &= \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \left[\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (25)\\
&= \int \psi_n^*(\mathbf{q}_1)\, \hat{h}_1\, \psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 \cancel{\int \psi_m^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2) d\mathbf{q}_2} + \qquad (26)\\
&\qquad \cancel{\int \psi_n^*(\mathbf{q}_1)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1} \int \psi_m^*(\mathbf{q}_2)\, \hat{h}_2\, \psi_n(\mathbf{q}_2) d\mathbf{q}_2 + \qquad (27)\\
&\qquad \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (28)\\
&= \iint \psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2) \frac{1}{r_{12}} \psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1)\, d\mathbf{q}_1 d\mathbf{q}_2 \qquad (29)
\end{aligned}$$

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\begin{aligned}
\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 && (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} + && (31)\\
&\quad \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 + && (32)\\
&\quad \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 && (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 && (34)
\end{aligned}
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\begin{aligned}
\text{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 && (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} + && (36)\\
&\quad \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 + && (37)\\
&\quad \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) && (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 + && (39)\\
&\quad \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) && (40)
\end{aligned}
$$

$$
\begin{aligned}
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] && (41)\\
&\quad + \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 && (42)\\
&\qquad - \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] && (43)\\
&= \sum_{i=1}^{2}\langle\psi_i(\mathbf{q})|\,\hat{h}\,|\psi_i(\mathbf{q})\rangle && (44)\\
&\quad + \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 && (45)\\
&\qquad - \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] && (46)\\
&= \sum_{i=1}^{2}\int \psi_i^*(\mathbf{q})\,\left[-\frac{1}{2}\nabla^2\right]\,\psi_i(\mathbf{q})\,d\mathbf{q} + \sum_{i=1}^{2}\int \rho_i(\mathbf{q})\,v(\mathbf{r})\,d\mathbf{q} && (47)\\
&\quad + \frac{1}{2}\iint \frac{\psi_n^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2)\psi_m(\mathbf{q}_2) + \psi_m^*(\mathbf{q}_1)\psi_m(\mathbf{q}_1)\psi_n^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2)}{r_{12}}\,d\mathbf{q}_1\,d\mathbf{q}_2 && (48)\\
&\qquad - \frac{1}{2}\iint \frac{\psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) + \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)}{r_{12}}\,d\mathbf{q}_1\,d\mathbf{q}_2 && (49)
\end{aligned}
$$

$$E^{\mathrm{HF}} = \sum_{i=1}^{2} \int \psi_i^*(\mathbf{q}) \left[-\frac{1}{2} \nabla^2 \right] \psi_i(\mathbf{q}) \, d\mathbf{q} + \sum_{i=1}^{2} \int \rho_i(\mathbf{q}) \, v(\mathbf{r}) \, d\mathbf{q} \tag{50}$$

$$+ \frac{1}{2} \iint \frac{\rho_n(\mathbf{q}_1)\rho_m(\mathbf{q}_2) + \rho_m(\mathbf{q}_1)\rho_n(\mathbf{q}_2)}{r_{12}} \, d\mathbf{q}_1 \, d\mathbf{q}_2 \tag{51}$$

$$- \frac{1}{2} \iint \frac{\psi_n^*(\mathbf{q}_1)\psi_m^*(\mathbf{q}_2)\psi_n(\mathbf{q}_2)\psi_m(\mathbf{q}_1) + \psi_n^*(\mathbf{q}_2)\psi_m^*(\mathbf{q}_1)\psi_n(\mathbf{q}_1)\psi_m(\mathbf{q}_2)}{r_{12}} \, d\mathbf{q}_1 \, d\mathbf{q}_2 \tag{52}$$