Universidade Estadual de Campinas

Estados excitados do átomo de Hélio

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FI002 – Mecânica Quântica

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Determinantes de Slater

$$a)\Psi_0(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\begin{vmatrix} \phi_{1s}(\mathbf{x_1})\alpha(1) & \phi_{1s}(\mathbf{x_1})\beta(1) \\ \phi_{1s}(\mathbf{x_2})\alpha(2) & \phi_{1s}(\mathbf{x_2})\beta(2) \end{vmatrix}$$

$$\Psi_0(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\alpha(1)\,\phi_{1s}(\mathbf{x_2})\beta(2) - \phi_{1s}(\mathbf{x_2})\alpha(2)\,\phi_{1s}(\mathbf{x_1})\beta(1)\right]$$

$$\Psi_0(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})\right]\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

$$2^{-1/2}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \Rightarrow \chi_{\text{singleto}}$$

$$\Psi_0(\mathbf{x_1},\mathbf{x_2}) = \left[\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})\right]\chi_{\text{singleto}}$$

Integrais direta e troca

$a) E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$

$$\langle \Psi_0 | H | \Psi_0 \rangle = \int dx_1 \int dx_2 \; \Big\{ [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})]^* \left(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1} \right) [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})]$$

$$+ [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})]^* \left(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2} \right) [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})]$$

$$+ [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})]^* \left(\frac{e^2}{r_{12}} \right) [\phi_{1s}(\mathbf{x_1})\,\phi_{1s}(\mathbf{x_2})] \Big\}$$

$$= \int dx_2 \; \phi_{1s}(\mathbf{x_2})^* \phi_{1s}(\mathbf{x_2}) \int dx_1 \; \phi_{1s}(\mathbf{x_1})^* \left(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1} \right) \phi_{1s}(\mathbf{x_1})$$

$$+ \int dx_1 \; \phi_{1s}(\mathbf{x_1})^* \phi_{1s}(\mathbf{x_1}) \int dx_2 \; \phi_{1s}(\mathbf{x_2})^* \left(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2} \right) \phi_{1s}(\mathbf{x_2})$$

$$+ \int dx_1 \int dx_2 \; \phi_{1s}(\mathbf{x_1})^* \phi_{1s}(\mathbf{x_1}) \left(\frac{e^2}{r_{12}} \right) \phi_{1s}(\mathbf{x_2})^* \phi_{1s}(\mathbf{x_2})$$

$$= h_{11} + h_{11} + J_{11} = 2 \cdot h_{11} + J_{11}$$

Determinantes de Slater

$$b)\Psi_1(\mathbf{x_1},\mathbf{x_2}) = \frac{\begin{vmatrix} \phi_{1s}(\mathbf{x_1})\alpha(1) & \phi_{2s}(\mathbf{x_1})\beta(1) \\ \phi_{1s}(\mathbf{x_2})\alpha(2) & \phi_{2s}(\mathbf{x_2})\beta(2) \end{vmatrix} - \begin{vmatrix} \phi_{1s}(\mathbf{x_1})\beta(1) & \phi_{2s}(\mathbf{x_1})\alpha(1) \\ \phi_{1s}(\mathbf{x_2})\beta(2) & \phi_{2s}(\mathbf{x_2})\alpha(2) \end{vmatrix}}{2}$$

$$\Psi_1(\mathbf{x_1},\mathbf{x_2}) = [\phi_{1s}(\mathbf{x_1})\alpha(1)\,\phi_{2s}(\mathbf{x_2})\beta(2) - \phi_{1s}(\mathbf{x_2})\alpha(2)\,\phi_{2s}(\mathbf{x_1})\beta(1)$$
$$- \phi_{1s}(\mathbf{x_1})\beta(1)\,\phi_{2s}(\mathbf{x_2})\alpha(2) + \phi_{1s}(\mathbf{x_2})\beta(2)\,\phi_{2s}(\mathbf{x_1})\alpha(1)]\,/\,2$$

$$\Psi_1(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]\,2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \Rightarrow \chi_{singleto}$$

$$\Psi_1(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]\,\chi_{singleto}$$

Integrais direta e troca

$b)\Delta_1 = \langle\Psi_1|H|\Psi_1\rangle - E_0$

$$\langle\Psi_1|H|\Psi_1\rangle = \frac{1}{2}\int dx_1 \int dx_2$$

$$\Big\{[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]^*\Big(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1}\Big)[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]$$

$$+[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]^*\Big(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2}\Big)[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]$$

$$+[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]^*\Big(\frac{e^2}{r_{12}}\Big)[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) + \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]\Big\}$$

$$=\frac{1}{2}\Big\{\int dx_2\;\phi_{2s}(\mathbf{x_2})^*\phi_{2s}(\mathbf{x_2})\int dx_1\;\phi_{1s}(\mathbf{x_1})^*\Big(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1}\Big)\phi_{1s}(\mathbf{x_1})$$

$$+\int dx_2\;\phi_{1s}(\mathbf{x_2})^*\phi_{1s}(\mathbf{x_2})\int dx_1\;\phi_{2s}(\mathbf{x_1})^*\Big(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1}\Big)\phi_{2s}(\mathbf{x_1})$$

$$+\int dx_1\;\phi_{2s}(\mathbf{x_1})^*\phi_{2s}(\mathbf{x_1})\int dx_2\;\phi_{1s}(\mathbf{x_2})^*\Big(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2}\Big)\phi_{1s}(\mathbf{x_2})$$

$$+\int dx_1\;\phi_{1s}(\mathbf{x_1})^*\phi_{1s}(\mathbf{x_1})\int dx_2\;\phi_{2s}(\mathbf{x_2})^*\Big(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2}\Big)\phi_{2s}(\mathbf{x_2})$$

Já desconsiderei os termos de integrais

$$\int dx_2\varphi_1^*\varphi_2$$

$$\int dx_2\varphi_2^*\varphi_1$$

e também p/ dx_1

Integrais direta e troca

$$+\int dx_1 \int dx_2 \; \phi_{1s}(\mathbf{x_1})^* \phi_{1s}(\mathbf{x_1}) \left(\frac{e^2}{r_{12}} \right) \phi_{2s}(\mathbf{x_2})^* \phi_{2s}(\mathbf{x_2})$$

$$+\int dx_1 \int dx_2 \; \phi_{1s}(\mathbf{x_1})^* \phi_{2s}(\mathbf{x_2})^* \left(\frac{e^2}{r_{12}} \right) \phi_{1s}(\mathbf{x_2}) \; \phi_{2s}(\mathbf{x_1})$$

$$+\int dx_1 \int dx_2 \; \phi_{1s}(\mathbf{x_2})^* \phi_{2s}(\mathbf{x_1})^* \left(\frac{e^2}{r_{12}} \right) \phi_{1s}(\mathbf{x_1}) \; \phi_{2s}(\mathbf{x_2})$$

$$+\int dx_1 \int dx_2 \; \phi_{1s}(\mathbf{x_2})^* \phi_{1s}(\mathbf{x_2}) \left(\frac{e^2}{r_{12}} \right) \phi_{2s}(\mathbf{x_1})^* \phi_{2s}(\mathbf{x_1}) \}$$

$$= 1/2 \cdot (h_{11} + h_{22} + h_{11} + h_{22} + J_{12} + K_{12} + J_{12} + K_{12})$$

$$= h_{11} + h_{22} + J_{12} + K_{12}$$

$$\Delta_1 = \langle \Psi_1 | H | \Psi_1 \rangle - E_0$$

$$= h_{11} + h_{22} + J_{12} + K_{12} - 2 \cdot h_{11} - J_{11} = -h_{11} + h_{22} + J_{12} + K_{12} - J_{11}$$

Determinantes de Slater

$$c)\Psi_2(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\begin{vmatrix} \phi_{1s}(\mathbf{x_1})\alpha(1) & \phi_{2s}(\mathbf{x_1})\alpha(1) \\ \phi_{1s}(\mathbf{x_2})\alpha(2) & \phi_{2s}(\mathbf{x_2})\alpha(2) \end{vmatrix}$$

$$\Psi_2(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\,\phi_{2s}(\mathbf{x_1})\right]\left[\alpha(1)\,\alpha(2)\right]$$

$$\left[\alpha(1)\,\alpha(2)\right] \Rightarrow \chi_{\text{tripleto}}$$

$$\Psi_2(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\,\phi_{2s}(\mathbf{x_1})\right]\chi_{\text{tripleto}}$$

Integrais direta e troca

$$c)\Delta_2 = \langle\Psi_2|H|\Psi_2\rangle - E_0$$

$$\langle\Psi_2|H|\Psi_2\rangle = \frac{1}{2}\Big\{ \int dx_2\ \phi_{2s}(\mathbf{x_2})^*\phi_{2s}(\mathbf{x_2}) \int dx_1\ \phi_{1s}(\mathbf{x_1})^* \left(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1} \right) \phi_{1s}(\mathbf{x_1})$$

$$+ \int dx_2\ \phi_{1s}(\mathbf{x_2})^*\phi_{1s}(\mathbf{x_2}) \int dx_1\ \phi_{2s}(\mathbf{x_1})^* \left(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1} \right) \phi_{2s}(\mathbf{x_1})$$

$$+ \int dx_1\ \phi_{2s}(\mathbf{x_1})^*\phi_{2s}(\mathbf{x_1}) \int dx_2\ \phi_{1s}(\mathbf{x_2})^* \left(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2} \right) \phi_{1s}(\mathbf{x_2})$$

$$+ \int dx_1\ \phi_{1s}(\mathbf{x_1})^*\phi_{1s}(\mathbf{x_1}) \int dx_2\ \phi_{2s}(\mathbf{x_2})^* \left(\frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_2} \right) \phi_{2s}(\mathbf{x_2})$$

$$+ \int dx_1 \int dx_2\ \phi_{1s}(\mathbf{x_1})^*\phi_{1s}(\mathbf{x_1}) \left(\frac{e^2}{r_{12}} \right) \phi_{2s}(\mathbf{x_2})^*\phi_{2s}(\mathbf{x_2})$$

$$- \int dx_1 \int dx_2\ \phi_{1s}(\mathbf{x_1})^*\phi_{2s}(\mathbf{x_2})^* \left(\frac{e^2}{r_{12}} \right) \phi_{1s}(\mathbf{x_2})\ \phi_{2s}(\mathbf{x_1})$$

$$- \int dx_1 \int dx_2\ \phi_{1s}(\mathbf{x_2})^*\phi_{2s}(\mathbf{x_1})^* \left(\frac{e^2}{r_{12}} \right) \phi_{1s}(\mathbf{x_1})\ \phi_{2s}(\mathbf{x_2})$$

$$+ \int dx_1 \int dx_2\ \phi_{1s}(\mathbf{x_2})^*\phi_{1s}(\mathbf{x_2}) \left(\frac{e^2}{r_{12}} \right) \phi_{2s}(\mathbf{x_1})^*\phi_{2s}(\mathbf{x_1}) \Big\}$$

Integrais direta e troca

$$\langle \Psi_2 | H | \Psi_2 \rangle$$

$$= 1/2 \cdot (h_{11} + h_{22} + h_{11} + h_{22} + J_{12} - K_{12} + J_{12} - K_{12})$$

$$= h_{11} + h_{22} + J_{12} - K_{12}$$

$$\Delta_2 = \langle \Psi_2 | H | \Psi_2 \rangle - E_0$$

$$= h_{11} + h_{22} + J_{12} - K_{12} - 2 \cdot h_{11} - J_{11} = -h_{11} + h_{22} + J_{12} - K_{12} - J_{11}$$

$J_{12} \Rightarrow I$ *(integral direta)*

$K_{12} \Rightarrow J$ *(integral de troca)*

Observar o sinal negativo para tripleto e positivo para singleto na integral de troca e comparar com o gráfico do formulário 2

Determinantes de Slater e Integrais direta e troca

$$d)\Psi_3(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\begin{vmatrix} \phi_{1s}(\mathbf{x_1})\beta(1) & \phi_{2s}(\mathbf{x_1})\beta(1) \\ \phi_{1s}(\mathbf{x_2})\beta(2) & \phi_{2s}(\mathbf{x_2})\beta(2) \end{vmatrix}$$

$$\Psi_3(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})\right]\ \left[\beta(1)\,\beta(2)\right]$$

$$\left[\beta(1)\,\beta(2)\right] \Longrightarrow \chi_{\text{tripleto}}$$

$$\Psi_3(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}\left[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})\right]\chi_{\text{tripleto}}$$

$$\langle\Psi_3|H|\Psi_3\rangle$$

$$= 1/2 \cdot (h_{11} + h_{22} + h_{11} + h_{22} + J_{12} - K_{12} + J_{12} - K_{12})$$

$$= h_{11} + h_{22} + J_{12} - K_{12}$$

$$\Delta_3 = \langle\Psi_3|H|\Psi_3\rangle - E_0$$

$$= h_{11} + h_{22} + J_{12} - K_{12} - 2\cdot h_{11} - J_{11} = -h_{11} + h_{22} + J_{12} - K_{12} - J_{11}$$

Determinantes de Slater e Integrais direta e troca

$$e)\Psi_4(\mathbf{x_1},\mathbf{x_2}) = \frac{\begin{vmatrix} \phi_{1s}(\mathbf{x_1})\alpha(1) & \phi_{2s}(\mathbf{x_1})\beta(1) \\ \phi_{1s}(\mathbf{x_2})\alpha(2) & \phi_{2s}(\mathbf{x_2})\beta(2) \end{vmatrix} + \begin{vmatrix} \phi_{1s}(\mathbf{x_1})\beta(1) & \phi_{2s}(\mathbf{x_1})\alpha(1) \\ \phi_{1s}(\mathbf{x_2})\beta(2) & \phi_{2s}(\mathbf{x_2})\alpha(2) \end{vmatrix}}{2}$$

$$\Psi_4(\mathbf{x_1},\mathbf{x_2}) = [\phi_{1s}(\mathbf{x_1})\alpha(1)\,\phi_{2s}(\mathbf{x_2})\beta(2) - \phi_{1s}(\mathbf{x_2})\alpha(2)\,\phi_{2s}(\mathbf{x_1})\beta(1)$$
$$+\phi_{1s}(\mathbf{x_1})\beta(1)\,\phi_{2s}(\mathbf{x_2})\alpha(2) - \phi_{1s}(\mathbf{x_2})\beta(2)\,\phi_{2s}(\mathbf{x_1})\alpha(1)]\,/\,2$$

$$\Psi_4(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]\;2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \Rightarrow \chi\text{tripleto}$$

$$\Psi_4(\mathbf{x_1},\mathbf{x_2}) = 2^{-1/2}[\phi_{1s}(\mathbf{x_1})\,\phi_{2s}(\mathbf{x_2}) - \phi_{1s}(\mathbf{x_2})\phi_{2s}(\mathbf{x_1})]\;\chi\text{tripleto}$$

$$\langle\Psi_4|H|\Psi_4\rangle$$
$$= 1/2 \cdot (h_{11} + h_{22} + h_{11} + h_{22} + J_{12} - K_{12} + J_{12} - K_{12})$$
$$= h_{11} + h_{22} + J_{12} - K_{12}$$

$$\Delta_4 = \langle\Psi_4|H|\Psi_4\rangle - E_0$$
$$= h_{11} + h_{22} + J_{12} - K_{12} - 2 \cdot h_{11} - J_{11} = -h_{11} + h_{22} + J_{12} - K_{12} - J_{11}$$

Formulário I

A Hamiltoniana básica do problema é dada por

$$H = \frac{\mathbf{p_1^2}}{2m} + \frac{\mathbf{p_2^2}}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

onde $r_1 = |\mathbf{x_1}|; r_2 = |\mathbf{x_2}|; r_{12} = |\mathbf{x_1} - \mathbf{x_2}|$

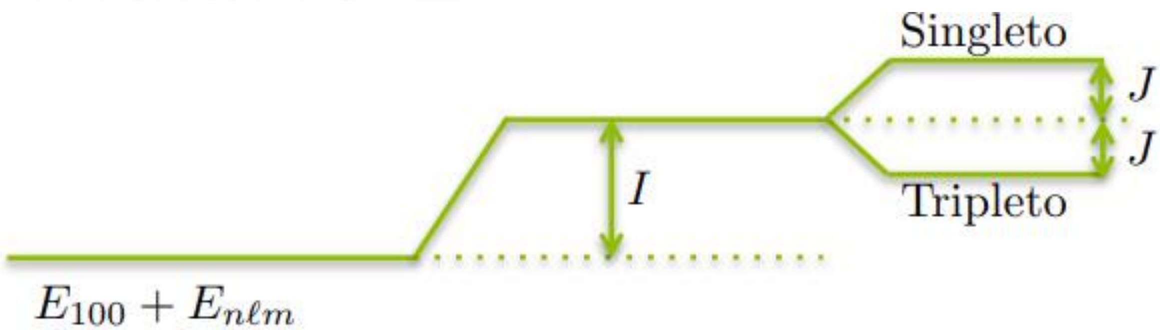
Integrais conhecidas:

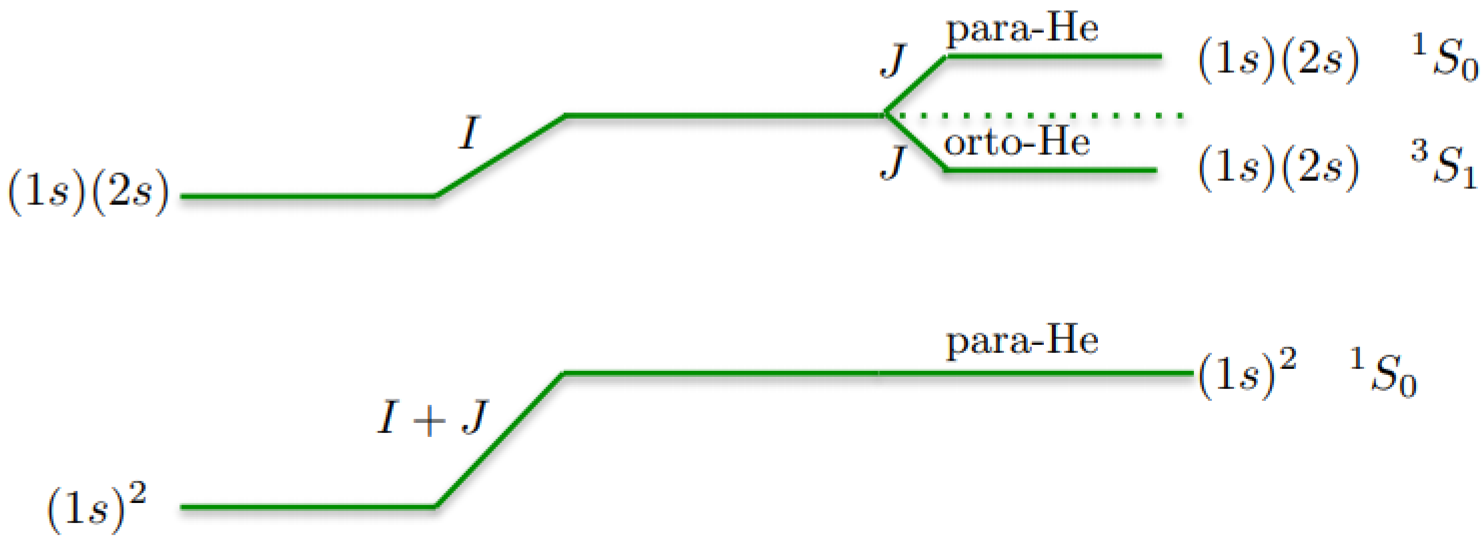
$$\int d^3x_1 \psi_i^*(\mathbf{x_1})(\frac{\mathbf{p_1^2}}{2m} - \frac{2e^2}{r_1})\psi_j(\mathbf{x_1}) \equiv h_{ij}$$

$$\int d^3x_1 \int d^3x_2 |\psi_i(\mathbf{x_1})|^2 \frac{e^2}{r_{12}} |\psi_j(\mathbf{x_2})|^2 \equiv < ij|ij >= J_{ij}$$

$$\int d^3x_1 \int d^3x_2 \psi_i^*(\mathbf{x_1})\psi_j^*(\mathbf{x_2}) \frac{e^2}{r_{12}} \psi_j(\mathbf{x_1})\psi_i(\mathbf{x_2}) \equiv < ij|ji >= K_{ij}$$

Formulário 2





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