GABARITO LISTA IX

1. Obtenha a energia do estado fundamental do átomo de Hélio utilizando o método variacional utilizando as funções tentativa,

a) $\Psi(\vec{r}_1, \vec{r}_2) = e^{-\alpha(r_1+r_2)}$ $\qquad r_i = |\vec{r}_i|$

A hamiltoniana neste caso é

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left[\frac{1}{r_1} + \frac{1}{r_2}\right] + \underbrace{\frac{e^2}{4\pi\varepsilon_0}}_{\varepsilon^2} \frac{1}{|\vec{r}_1 - \vec{r}_2|^2} .$$

Para determinar a energia do estado fundamental, devemos calcular

$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} .$$

Calculamos primeiro

•) $\langle \Psi | \Psi \rangle = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \, e^{-2\alpha(r_1+r_2)}$

$$= \int d^3\vec{r}_1 \, e^{-2\alpha r_1} \int d^3\vec{r}_2 \, e^{-2\alpha r_2}$$

$$= \int_0^\infty r_1^2 dr_1 \underbrace{d\Omega_1}_{4\pi} e^{-2\alpha r_1} \int_0^\infty 4\pi r_2^2 dr_2 \, e^{-2\alpha r_2}$$

$$= \frac{\pi^2}{\alpha^6} .$$

Agora

$$\circ)\ \langle \Psi | H | \Psi \rangle = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; e^{-\alpha(r_1+r_2)} \left\{ -\frac{\hbar^2}{2m}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} \right] - 2\varepsilon^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\} e^{-\alpha(r_1+r_2)} .$$

Derivando,

$$\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2 \frac{\partial}{\partial r_i}\right) e^{-\alpha(r_1+r_2)} = \frac{\alpha}{r_i}(\alpha r_i - 2)\, e^{-\alpha(r_1+r_2)}, \quad \text{com} \quad i = 1,2 .$$

Portanto,

$$\langle \Psi | H | \Psi \rangle = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; e^{-2\alpha(r_1+r_2)} \left\{ -\frac{\hbar^2}{2m}\left[\frac{\alpha}{r_1}(\alpha r_1 - 2) + \frac{\alpha}{r_2}(\alpha r_2 - 2) \right] - 2\varepsilon^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\}$$

$$= \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; e^{-2\alpha(r_1+r_2)} \left\{ -\frac{\hbar^2}{2m}\left[2\alpha^2 - 2\alpha\left(\frac{1}{r_1}+\frac{1}{r_2}\right) \right] - 2\varepsilon^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\}$$

$$= \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; e^{-2\alpha(r_1+r_2)} \left\{ -\frac{\alpha^2\hbar^2}{m} + \left(\frac{\hbar^2\alpha}{m} - 2\varepsilon^2\right)\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\}$$

$$= -\frac{\alpha^2\hbar^2}{m} \underbrace{\int d^3\vec{r}_1 \int d^3\vec{r}_2 \, e^{-2\alpha(r_1+r_2)}}_{\frac{\pi^2}{\alpha^6}} + \left(\frac{\hbar^2\alpha}{m} - 2\varepsilon^2\right) \underbrace{\int d^3\vec{r}_1 \int d^3\vec{r}_2 \left(\frac{1}{r_1}+\frac{1}{r_2}\right) e^{-2\alpha(r_1+r_2)}}_{I_1}$$

$$+\ \varepsilon^2 \underbrace{\int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{1}{|\vec{r}_1-\vec{r}_2|^2} e^{-2\alpha(r_1+r_2)}}_{I_2}.$$

fazemos as integrais,

∘)

$$I_1 = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \left(\frac{1}{r_1}+\frac{1}{r_2}\right) e^{-2\alpha(r_1+r_2)}$$

$$= \int d^3\vec{r}_1 \frac{e^{-2\alpha r_1}}{r_1} \int d^3\vec{r}_2 e^{-2\alpha r_2} + \int d^3\vec{r}_1 e^{-2\alpha r_1} \int d^3\vec{r}_2 \frac{1}{r_2} e^{-2\alpha r_2}.$$

É facil ver que

$$\int d^3\vec{r}_a e^{-2\alpha r_a} \int d^3\vec{r}_b \frac{1}{r_b} e^{-2\alpha r_b} = 16\pi^2 \int_0^\infty r_a^2 e^{-2\alpha r_a} dr_a \int_0^\infty r_b e^{-2\alpha r_b} dr_b$$

$$= 16\pi^2 \cdot \frac{1}{4\alpha^3} \cdot \frac{1}{4\alpha^2}$$

$$= \frac{\pi^2}{\alpha^5},$$

portanto

$$I_1 = \frac{2\pi^2}{\alpha^5}.$$

∘)

$$I_2 = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{1}{|\vec{r}_1-\vec{r}_2|^2} e^{-2\alpha(r_1+r_2)}$$

$$= \int r_1^2 dr_1 \int r_2^2 dr_2\ e^{-2\alpha(r_1+r_2)} \int d\Omega_1\, d\Omega_2 \frac{1}{|\vec{r}_1-\vec{r}_2|^2}$$

Para fazer a integral ângular, usamos a expansão multipolar

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \begin{cases} \dfrac{1}{r_2} \displaystyle\sum_{l=0}^{\infty} \left(\frac{r_1}{r_2}\right)^l \left(\frac{4\pi}{2l+1}\right) \sum_{m=-l}^{l} Y_{lm}(\theta_1, \phi_1)\, Y^*_{lm}(\theta_2, \phi_2) & r_1 < r_2 \\ \dfrac{1}{r_2} \displaystyle\sum_{l=0}^{\infty} \left(\frac{r_2}{r_1}\right)^l \left(\frac{4\pi}{2l+1}\right) \sum Y_{lm}(\theta_1, \phi_1)\, Y^*_{lm}(\theta_2, \phi_2), & \end{cases}$$

Portanto

$$\int d\Omega_1 \int d\Omega_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \begin{cases} \dfrac{16\pi^2}{r_2} & r_1 < r_2 \\ \dfrac{16\pi^2}{r_1} & r_1 > r_2 \end{cases}$$

onde usamos que

$$\int d\Omega\, Y_{lm}(\theta, \phi) = \sqrt{4\pi}\, \delta_{l0}\delta_{m0}.$$

Portanto,

$$I_2 = \int_0^\infty r_1^2 dr_1\, e^{-2\alpha r_1} \left[\frac{1}{r_1} \int_0^{r_1} dr_2\, r_2^2 e^{-2\alpha r_2} + \int_{r_1}^{\infty} dr_2\, r_2\, e^{-2\alpha r_2} \right] 16\pi^2$$

$$= 16\pi^2 \int_0^\infty dr_1\, r_1\, e^{-2\alpha r_1} \int_0^{r_1} dr_2\, r_2^2 e^{-2\alpha r_2} + 16\pi^2 \int_0^\infty dr_1\, r_1^2 e^{-2\alpha r_1} \int_{r_1}^{\infty} dr_2\, r_2\, e^{-2\alpha r_2}$$

$$= \frac{5\pi^2}{16\alpha^5} + \frac{5\pi^2}{16\alpha^5} = \frac{5\pi^2}{8\alpha^5}.$$

Juntando os resultados,

$$\langle\Psi|H|\Psi\rangle = -\frac{\pi^2\hbar^2}{m\alpha^4} + \left(\frac{\hbar^2\alpha}{m} - 2\varepsilon^2\right)\frac{2\pi^2}{\alpha^5} + \varepsilon^2\,\frac{5\pi^2}{8\alpha^5}$$

$$= -\frac{\pi^2\hbar^2}{m\alpha^4} + \frac{2\pi^2\hbar^2\alpha}{m\alpha^{\cancel{5}4}} - 4\,\frac{\varepsilon^2\pi^2}{\alpha^5} + \varepsilon^2\,\frac{5\pi^2}{8\alpha^5}$$

$$= \frac{\pi^2\hbar^2}{m\alpha^4} - \frac{27}{8}\,\frac{\varepsilon^2\pi^2}{\alpha^5}.$$

O valor esperado da energia fica

$$\langle E\rangle = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\alpha^{\cancel{5}2}}{\cancel{\pi^2}}\left(\frac{\cancel{\pi^2}\hbar^2}{m\alpha^4} - \frac{27}{8}\,\frac{\varepsilon^2\cancel{\pi^2}}{\alpha^{\cancel{5}}}\right)$$

$$= \frac{\hbar^2\alpha^2}{m} - \frac{27}{8}\varepsilon^2\alpha,$$

minimizando

$$\frac{\partial\langle E\rangle}{\partial\alpha} = \frac{2\hbar^2\alpha}{m} - \frac{27}{8}\varepsilon^2 = 0 \implies \alpha = \frac{m}{2\hbar^2}\,\frac{27}{8}\varepsilon^2,$$

substituindo em $\langle E\rangle$

$$\langle E\rangle = \frac{\cancel{\hbar^2}}{\cancel{m}}\left(\frac{m}{\hbar^2}\right)^{\cancel{2}}\left(\frac{27}{16}\right)^2\varepsilon^4 - \frac{27}{8}\left(\frac{27}{16}\right)\frac{m}{\hbar^2}\varepsilon^4\cdot\frac{2}{2}$$

$$\langle E\rangle = -\frac{m\varepsilon^4}{\hbar^2}\left(\frac{27}{16}\right)^2.$$

b) $f(r_1+r_2)$

Definamos o funcional $\mathcal{E}$ como

$$\mathcal{E} = \langle f|H|f\rangle - \lambda(\langle f|f\rangle - 1),$$

sendo λ um multiplicador de Lagrange. Explicitamente,

$$\mathcal{E} = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; f^*(r_1+r_2)\left\{-\frac{\hbar^2}{2m}\left[\nabla_{r_1}^2 + \nabla_{r_2}^2\right] - 2\varepsilon^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|}\right\} f(r_1+r_2)$$

$$-\lambda\left\{\int d^3\vec{r}_1 \int d^3\vec{r}_2 \; f^*(r_1+r_2) f(r_1+r_2) - 1\right\}$$

$$\mathcal{E} = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; f^*(r_1+r_2)\left\{-\frac{\hbar^2}{2m}\left[\nabla_{r_1}^2 + \nabla_{r_2}^2\right] - 2\varepsilon^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \varepsilon^2 \frac{1}{|\vec{r}_1-\vec{r}_2|} - \lambda\right\} f(r_1+r_2)$$

$$+\lambda$$

Usando que

$$\int d^3\vec{r}\; \psi^*\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi = \int d^3\vec{r}\left[\nabla\left(\psi^*\left(-\frac{\hbar^2}{2m}\right)\nabla\psi\right) + \frac{\hbar^2}{2m}\nabla\psi^*\nabla\psi\right]$$

$$= \cancelto{0}{\psi^*\left(-\frac{\hbar^2}{2m}\nabla\psi\right)\Big|_{-\infty}^{\infty}} + \int d^3\vec{r}\;\frac{\hbar^2}{2m}\nabla\psi^*\nabla\psi$$

Devemos então minimizar o funcional $\mathcal{E}$ para obter a energia do estado fundamental.

$$\delta \mathcal{E} = 0,$$

ou seja

$$\delta \mathcal{E} = \int 4\pi r_1^2 dr_1 \, 4\pi r_2^2 dr_2 \left\{ \frac{\partial F}{\partial f} \delta f + \frac{\partial F}{\partial f^*} \delta f^* + \frac{\partial F}{\partial (\partial_i f)} \delta (\partial_i f) \right.$$
$$\left. + \frac{\partial F}{\partial (\partial_i f^*)} \delta (\partial_i f) \right\} = 0,$$

onde introduzimos a notação $\partial_i f = \dfrac{\partial f}{\partial r_i}$, $i = 1, 2$, e os índices repetidos indicam soma. Simplificando,

∘) $$\frac{\partial F}{\partial (\partial_i f)} \delta (\partial_i f) = \partial_i \left(\frac{\partial F}{\partial (\partial_i f)} \delta f \right) - \partial_i \left(\frac{\partial F}{\partial (\partial_i f)} \right) \delta f,$$

∘) $$\frac{\partial F}{\partial (\partial_i f^*)} \delta (\partial_i f^*) = \partial_i \left(\frac{\partial F}{\partial (\partial_i f^*)} \delta f^* \right) - \partial_i \left(\frac{\partial F}{\partial (\partial_i f^*)} \right) \delta f^*.$$

Dado que supomos que δf, δf^* são zero no infinito, a variação do funcional fica

$$\delta \mathcal{E} = \int 4\pi r_1^2 dr_1 \, 4\pi r_2^2 dr_2 \left\{ \left[\frac{\partial F}{\partial f} - \partial_i \left(\frac{\partial F}{\partial (\partial_i f)} \right) \right] \delta f \right.$$
$$\left. + \left[\frac{\partial F}{\partial f^*} - \partial_i \left(\frac{\partial F}{\partial (\partial_i f^*)} \right) \right] \delta f^* \right] = 0.$$

onde usamos que a função de onda tende a zero no infinito. O funcional fica

$$\mathcal{E} = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \left[\frac{\hbar^2}{2m} \left\{ \nabla_{r_1} f^* \nabla_{r_1} f + \nabla_{r_2} f^* \nabla_{r_2} f \right\} - \left[2\mathcal{E}^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) - \mathcal{E}^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \lambda \right] f^* f \right\} + \lambda$$

Dado que $f(r_1 + r_2)$ não depende do ângulo entre $\vec{r}_1$ e $\vec{r}_2$, podemos integrar em $d\Omega_1$, $d\Omega_2$, usando que

$$\int d\Omega_1 \int d\Omega_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} = 16\pi^2 \left\{ \theta(r_2 - r_1) \frac{1}{r_2} + \theta(r_1 - r_2) \frac{1}{r_1} \right\}.$$

Portanto

$$\mathcal{E} = 16\pi^2 \int dr_1\, dr_2\, r_1^2 r_2^2 \left[\frac{\hbar^2}{2m} \left\{ \nabla_{r_1} f^* \nabla_{r_1} f + \nabla_{r_2} f^* \nabla_{r_2} f \right\} - \tilde{V}(r_1, r_2) f^* f - \lambda f^* f \right\} + \lambda,$$

sendo

$$\tilde{V}(r_1, r_2) = -2\mathcal{E}^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) - \mathcal{E}^2 \left\{ \theta(r_2 - r_1) \frac{1}{r_2} + \theta(r_1 - r_2) \frac{1}{r_1} \right\}.$$

Definindo

$$F\left(f, f^*, \frac{\partial f}{\partial r_1}, \frac{\partial f}{\partial r_2}, r_1, r_2\right) = \frac{\hbar^2}{2m} \left\{ \frac{\partial f^*}{\partial r_1} \frac{\partial f}{\partial r_1} + \frac{\partial f^*}{\partial r_2} \frac{\partial f}{\partial r_2} \right\} - \tilde{V}(r_1, r_2) f^* f - \lambda f^* f,$$

temos que

$$\mathcal{E} = 16\pi^2 \int dr_1\, r_1^2\, dr_2\, r_2^2\; F\left(f, f^*, \frac{\partial f^*}{\partial r_1}, \frac{\partial f^*}{\partial r_2}, \frac{\partial f}{\partial r_1}, \frac{\partial f}{\partial r_2}, r_1, r_2\right) + \lambda$$

Portanto, o funcional deve obedecer

$$\frac{\partial F}{\partial f} - \partial_i \left(\frac{\partial F}{\partial(\partial_i f)}\right) = 0,$$

$$\frac{\partial F}{\partial f^*} - \partial_i \left(\frac{\partial F}{\partial(\partial_i f^*)}\right) = 0.$$

Para o caso específico que estamos considerando,

•) $\dfrac{\partial F}{\partial f^*} = \tilde{V}(r_1, r_2) f - \lambda f$

•) $\dfrac{\partial F}{\partial(\partial_i f^*)} = \dfrac{\hbar^2}{2m} \partial_i f$,

Portanto

$$\tilde{V}(r_1, r_2) f - \lambda f - \partial_i \left(\frac{\hbar^2}{2m} \partial_i f\right) = 0,$$

$$-\frac{\hbar^2}{2m} \left\{ \frac{\partial^2 f}{\partial r_2^2} + \frac{\partial^2 f}{\partial r_1^2} \right\} - \tilde{V}(r_1, r_2) f = \lambda f.$$

que é a equação de Schrödinger para o potencial $\tilde{V}(r_1, r_2)$. O λ vai corresponder a energia do estado fundamental. O problema então vai corresponder a solucionar esta equação.

3.) Calcule o efeito Zeeman quadrático para o estado fundamental do átomo de Hidrogênio devido ao termo

$$\frac{e^2}{2mc^2}|\vec{A}|^2.$$

Escreva o desvio como

$$\Delta = -\frac{1}{2}\chi|\vec{B}|^2,$$

e obtenha uma expressão para a suscetibilidade magnética χ.

Supomos que o campo magnético esta em direção z, portanto podemos escolher um potencial vetor da forma,

$$\vec{A} = -\frac{1}{2}B(y\hat{x} - x\hat{y}),$$

que ao tomar o rotacional,

$$\vec{\nabla}\times\vec{A} = B\hat{z}.$$

A correção a primeira ordem é

$$\Delta^{(1)} = \langle 1\,0\,0|\frac{+e^2B^2}{8mc^2}(x^2+y^2)|1\,0\,0\rangle$$

$$= +\frac{e^2B^2}{8mc^2}\langle 1\,0\,0|x^2+y^2|1\,0\,0\rangle$$

$$\Delta^{(1)} = \frac{e^2B^2}{8mc^2} \langle 1\,0\,0 | r^2 - z^2 | 1\,0\,0 \rangle$$

$$= \frac{e^2B^2}{8mc^2} \int d^3\vec{r}\, \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} \left(r^2 - r^2\cos^2\theta\right) \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

$$= \frac{e^2B^2}{\underset{4}{\cancel{8}}mc^2} \frac{1}{\cancel{\pi} a_0^3} \int r^2 dr\, \cancel{2\pi}\, d(\cos\theta)\, e^{-\frac{2r}{a_0}} r^2 \left(1 - \cos^2\theta\right)$$

$$= \frac{e^2B^2}{4mc^2a_0^3} \cdot \underbrace{\int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr}_{\frac{3a_0^5}{\cancel{4}}} \underbrace{\int_{-1}^{1} dx\, (1 - x^2)}_{\cancel{\frac{4}{3}}}$$

$$\Delta^{(1)} = \frac{e^2B^2a_0^2}{4mc^2},$$

a suscetibilidade é

$$\chi = -\frac{2\Delta^{(1)}}{B^2} = -\frac{e^2a_0^2}{2mc^2}.$$