Estado fundamental do átomo de Hélio

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- Função tentativa:

$$\tilde{\Phi}(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\pi}\left(\frac{\xi}{a_0}\right)^3 e^{-\xi\frac{r_1}{a_0}} e^{-\xi\frac{r_2}{a_0}} \tag{1}$$

- O Hamiltoniano é

$$H = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \tag{2}$$

- Reescrevendo:

$$H = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze^2}{r_1} + \left(\frac{\xi e^2}{r_1} - \frac{\xi e^2}{r_1}\right) - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_2} + \left(\frac{\xi e^2}{r_2} - \frac{\xi e^2}{r_2}\right) + \frac{e^2}{r_{12}}$$

$$H = \overbrace{\left[-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\xi e^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{\xi e^2}{r_2}\right]}^{H_0} + \overbrace{(\xi - Z)\frac{e^2}{r_1} + (\xi - Z)\frac{e^2}{r_2} + \frac{e^2}{r_{12}}}^{V} \tag{3}$$

- H_0: como se fosse “2 átomos de H independentes” com carga ξ
- Com $H_0 \left|\tilde{\Phi}\right\rangle = E^{(0)} \left|\tilde{\Phi}\right\rangle$

$$E^{(0)} = 2\left(-\frac{\xi^2 e^2}{2a_0}\right) = -\frac{\xi^2 e^2}{a_0} \tag{4}$$

- Vamos verificar se $\left|\tilde{\Phi}\right\rangle$ é normalizado. Com a Eq. (1):

$$\left\langle\tilde{\Phi}\middle|\tilde{\Phi}\right\rangle = \int d^3 r_1 \int d^3 r_2 \left(\frac{1}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6 e^{-\frac{2\xi r_1}{a_0}} e^{-\frac{2\xi r_2}{a_0}}$$

$$\begin{aligned}\left\langle\tilde{\Phi}\middle|\tilde{\Phi}\right\rangle = \left(\frac{1}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6 &\overbrace{\int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \sin\theta_1}^{4\pi} \int_0^{+\infty} dr_1 r_1^2 e^{-\frac{2\xi r_1}{a_0}} \times \\ &\times \overbrace{\int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_2 \sin\theta_2}^{4\pi} \int_0^{+\infty} dr_2 r_2^2 e^{-\frac{2\xi r_2}{a_0}}\end{aligned} \tag{5}$$

- Temos que

$$\int_0^{+\infty} r^n e^{-qr} dr = \frac{n!}{q^{n+1}} \tag{6}$$

- Com (6) aplicado em (5), temos

$$\boxed{\langle\tilde{\Phi}|\tilde{\Phi}\rangle = \left(\frac{1}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6 (4\pi)\frac{2!}{\left(\frac{2\xi}{a_0}\right)^3} (4\pi)\frac{2!}{\left(\frac{2\xi}{a_0}\right)^3} = 1} \tag{7}$$

- Calculemos o seguinte elemento de matriz, com (6)

$$\begin{aligned}\langle\tilde{\Phi}|\frac{1}{r_1}|\tilde{\Phi}\rangle = \left(\frac{1}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6 &\overbrace{\int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_2 \sin\theta_2}^{4\pi} \overbrace{\int_0^{+\infty} dr_2 r_2^2 e^{-\frac{2\xi r_2}{a_0}}}^{2!/(2\xi/a_0)^3} \times \\ &\times \overbrace{\int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \sin\theta_1}^{4\pi} \overbrace{\int_0^{+\infty} dr_1 \frac{r_1^2}{r_1} e^{-\frac{2\xi r_1}{a_0}}}^{1!/(2\xi/a_0)^2}\end{aligned} \tag{8}$$

- Da Eq. (8)

$$\boxed{\left\langle\tilde{\Phi}\right|\frac{(\xi-Z)e^2}{r_1}\left|\tilde{\Phi}\right\rangle = \left(\frac{1}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6 (4\pi)^2 \frac{2e^2(\xi-Z)}{\left(\frac{2\xi}{a_0}\right)^3\left(\frac{2\xi}{a_0}\right)^2} = (\xi-Z)\frac{\xi e^2}{a_0}} \quad (9)$$

- Semelhantemente

$$\boxed{\left\langle\tilde{\Phi}\right|\frac{(\xi-Z)e^2}{r_2}\left|\tilde{\Phi}\right\rangle = (\xi-Z)\frac{\xi e^2}{a_0}} \quad (10)$$

- Agora, consideremos o seguinte elemento de matriz:

$$\left\langle\tilde{\Phi}\right|\frac{e^2}{r_{12}}\left|\tilde{\Phi}\right\rangle = \int d^3r_1 \int d^3r_2 \left[\tilde{\Phi}(\mathbf{r_1},\mathbf{r_2})\right]^2 \frac{e^2}{r_{12}} \quad (11)$$

- Expressando $1/r_{12}$ em harmônicos esféricos (Apêndice):

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{+\infty}\sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1}\frac{r_<^{\ell}}{r_>^{\ell+1}}\left[Y_\ell^m(\theta_1,\phi_1)\right]^* Y_\ell^m(\theta_2,\phi_2) \quad (12)$$

- Com as Eqs. (1) e (12) na Eq. (11), temos

$$\begin{aligned}\left\langle\tilde{\Phi}\right|\frac{e^2}{r_{12}}\left|\tilde{\Phi}\right\rangle = &\left(\frac{e^2}{\pi^2}\right)\left(\frac{\xi}{a_0}\right)^6\sum_{\ell=0}^{+\infty}\sum_{m=-\ell}^{+\ell}\frac{4\pi}{2\ell+1}\times\\ &\times\int dr_1\int dr_2 r_1^2 r_2^2\frac{r_<^{\ell}}{r_>^{\ell+1}}e^{-\frac{2\xi r_1}{a_0}}e^{-\frac{2\xi r_2}{a_0}}\times\\ &\times\int_0^{2\pi}d\phi_1\int_0^{\pi}d\theta_1\left[Y_\ell^m(\theta_1,\phi_1)\right]^*\sin\theta_1\times\\ &\times\int_0^{2\pi}d\phi_2\int_0^{\pi}d\theta_2 Y_\ell^m(\theta_2,\phi_2)\sin\theta_2\end{aligned} \tag{13}$$

- Como

$$Y_0^0(\theta_1,\phi_1)\left[Y_0^0(\theta_2,\phi_2)\right]^* = \frac{1}{4\pi}$$

- Ou ainda

$$1 = 4\pi Y_0^0(\theta_1,\phi_1)\left[Y_0^0(\theta_2,\phi_2)\right]^* \tag{14}$$

- Lembremos que

$$\int_0^{2\pi} d\phi_i \int_0^{\pi} d\theta_i Y_\ell^m(\theta_i,\phi_i)\left[Y_{\ell'}^{m'}(\theta_i,\phi_i)\right]^* \sin\theta_i = \delta_{\ell\ell'}\delta_{mm'} \tag{15}$$

- Com as Eqs. (14) e (15) na Eq. (13), obtemos

$$\left\langle\tilde{\Phi}\right|\frac{e^2}{r_{12}}\left|\tilde{\Phi}\right\rangle = \left(\frac{e}{\pi}\right)^2\left(\frac{\xi}{a_0}\right)^6 \sum_{\ell=0}^{+\infty}\sum_{m=-\ell}^{+\ell}\frac{(4\pi)^2}{2\ell+1}\times$$

$$\times\int dr_1\int dr_2 r_1^2 r_2^2 \frac{r_<^\ell}{r_>^{\ell+1}} e^{-\frac{2\xi r_1}{a_0}} e^{-\frac{2\xi r_2}{a_0}}\times$$

$$\times\overbrace{\int_0^{2\pi} d\phi_1\int_0^{\pi} d\theta_1 Y_0^0(\theta_1,\phi_1)\left[Y_\ell^m(\theta_1,\phi_1)\right]^*\sin\theta_1}^{\delta_{\ell 0}\delta_{m0}}\times$$

$$\times\overbrace{\int_0^{2\pi} d\phi_2\int_0^{\pi} d\theta_2 Y_\ell^m(\theta_2,\phi_2)\left[Y_0^0(\theta_2,\phi_2)\right]^*\sin\theta_2}^{\delta_{0\ell'}\delta_{0m'}}$$

- Rearranjando

$$\left\langle\tilde{\Phi}\middle|\frac{e^2}{r_{12}}\middle|\tilde{\Phi}\right\rangle = 16e^2\left(\frac{\xi}{a_0}\right)^6\int_0^{+\infty} dr_1\int_0^{+\infty} dr_2\frac{1}{r_>}r_1^2r_2^2e^{-\frac{2\xi r_1}{a_0}}e^{-\frac{2\xi r_2}{a_0}} \tag{16}$$

- Para $r < r_2$, $r_> = r_2$ e para $r > r_2$, $r_> = r_1$
- Com isso, a Eq. (16) fica

$$\left\langle\tilde{\Phi}\middle|\frac{e^2}{r_{12}}\middle|\tilde{\Phi}\right\rangle = 16e^2\left(\frac{\xi}{a_0}\right)^6\int_0^{+\infty} dr_2e^{-\frac{2\xi r_2}{a_0}}r_2^2\left(\overbrace{\int_0^{r_2} dr_1\frac{r_1^2}{r_2}e^{-\frac{2\xi r_1}{a_0}}}^{I} + \right.$$
$$\left. + \overbrace{\int_0^{r_2} dr_1\frac{r_1^2}{r_1}e^{-\frac{2\xi r_1}{a_0}}}^{J}\right) \tag{17}$$

- Da Eq. (17), temos

$$I = \frac{1}{r_2}\int_0^{r_2} dr_1 r_1^2 e^{-\frac{2\xi r_1}{a_0}} \tag{18}$$

- E

$$J = \int_{r_2}^{+\infty} dr_1 r_1 e^{-\frac{2\xi r_1}{a_0}} \tag{19}$$

- Temos que

$$\int re^{br}dr = \left(\frac{r}{b} - \frac{1}{b^2}\right)e^{br} + C \tag{20}$$

- E

$$\int r^2 e^{br}dr = \left(\frac{r^2}{b} - \frac{2r}{b} + \frac{2}{b^3}\right)e^{br} + C \tag{21}$$

- Da Eq. (21), a integral (18) fica

$$I = \frac{1}{r_2}e^{-\frac{2\xi r_2}{a_0}}\left[-\left(\frac{a_0}{2\xi}\right)r_2^2 - 2\left(\frac{a_0}{2\xi}\right)^2 r_2 - 2\left(\frac{a_0}{2\xi}\right)^3\right] + \frac{2}{r_2}\left(\frac{a_0}{2\xi}\right)^3 \tag{22}$$

- Da Eq. (20), a integral (19) fica

$$J = \left[\left(\frac{a_0}{2\xi}\right) r_2 + \left(\frac{a_0}{2\xi}\right)^2\right] e^{-\frac{2\xi r_2}{a_0}} \tag{23}$$

- Definindo

$$\alpha = 16e^2\left(\frac{\xi}{a_0}\right)^6 \qquad \beta = \frac{2\xi}{a_0} \tag{24}$$

- Com as Eqs. (22), (23) e (24) na Eq. (17), temos

$$\left\langle\tilde{\Phi}\right|\frac{e^2}{r_{12}}\left|\tilde{\Phi}\right\rangle = \alpha\int_0^{+\infty} dr_2 e^{-\beta r_2} r_2^2 \left\{\frac{1}{r_2} e^{-\beta r_2}\left[-\left(\frac{1}{\beta}\right) r_2^2 - 2\left(\frac{1}{\beta}\right)^2 r_2 - 2\left(\frac{1}{\beta}\right)^3\right] + \right.$$
$$\left. + \frac{2}{r_2}\left(\frac{1}{\beta}\right)^3 + \left[\left(\frac{1}{\beta}\right) r_2 + \left(\frac{1}{\beta}\right)^2\right] e^{-\beta r_2}\right\}$$

- Após manipulações e integrações com ajuda da Eq. (6), obtemos

$$\boxed{\left\langle\tilde{\Phi}\right|\frac{e^2}{r_{12}}\left|\tilde{\Phi}\right\rangle = \frac{5}{8}\left(\frac{\xi}{a_0}\right) e^2} \tag{25}$$

- Com as Eqs. (4), (7), (9), (10) e (25), encontramos

$$\tilde{E} = \frac{\langle \tilde{\Phi} | H | \tilde{\Phi} \rangle}{\langle \tilde{\Phi} | \tilde{\Phi} \rangle} = -\frac{\xi^2 e^2}{a_0} + 2(\xi - Z)\frac{\xi e^2}{a_0} + \frac{5}{8}\left(\frac{\xi}{a_0}\right) e^2$$

- Após manipulações, obtemos

$$\boxed{\tilde{E} = \left(\xi^2 - 2Z\xi + \frac{5}{8}\xi\right)\frac{e^2}{a_0}} \qquad (26)$$

- Com a Eq. (26) ($Z = 2$)

$$\frac{d\tilde{E}}{d\xi} = 0 = 2\xi - 2Z + \frac{5}{8} \Rightarrow \boxed{\xi = Z - \frac{5}{16} = 1,6825} \qquad (27)$$

- Com a Eq. (27) na Eq. (26), temos

$$\boxed{\tilde{E} \approx -77,5 \text{ eV}} \qquad (28)$$

- A energia experimental é

$$\boxed{E_{exp} \approx -79,0 \text{ eV}} \qquad (29)$$

ON THE GROUND STATE OF THE HELIUM ATOM

By EGIL A. HYLLERAAS in Göttingen
With 2 illustrations. (Received 16 March 1928.)

ABSTRACT

The goal of this work is a calculation of the ionisation potential of the helium atom which is as precise as possible. To this end a method for the solution of the Schrödinger equation is used, which resembles the method of *Ritz*[1] for the solution of the variational problem. The calculations are extended through eleventh order, and the ground term obtained in this way differs from the one obtained by experiment by only 1.5 prom. By contrast, the ionisation potential differs by 4.8 prom. since the subtraction of the known energy of the helium ion leads to an increase in the relative error.

$$\boxed{\tilde{\Phi}(\mathbf{r_1}, \mathbf{r_2}) = N e^{-\xi \frac{r_1}{a_0}} e^{-\xi \frac{r_2}{a_0}} (1 + b r_{12})}$$

$$\xi = 1,849 \qquad b = \frac{0,364}{a_0} \Rightarrow \boxed{\tilde{E} \approx -78,7 \text{ eV}}$$

E. A. Hylleraas, Z. Phys. 48, 469 (1929).

Referência

- Ira N. Levine, Quantum Chemistry. Upper Saddle River, N.J: Prentice Hall (2000).

Obrigado pela atenção!

Apêndice