Exo 2

⇒ ~~Sans interaction électronique.~~

$$\psi(\vec r_1,\vec r_2) = \psi_1(\vec r_1)\cdot\psi_2(\vec r_2)$$

1). l'éq aux valeurs propres du Hamiltonien:

$$H\psi = E\psi$$

$$E_T = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(r_1) + V(r_2) + V(r_1,r_2)$$

avec: $V(r_1) = -\frac{2q^2}{r_1}$, $V(r_2) = \frac{-2q^2}{r_2}$, $V(r) = \frac{q^2}{r}$

et $\vec r = \vec r_2 - \vec r_1$, $q^2 = \frac{e^2}{4\pi\varepsilon_0}$

Donc:

$$H = \frac{-\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{2q^2}{r_1} - \frac{2q^2}{r_2} + \frac{q^2}{r}$$

⇒ Sans interaction électronique ($\frac{q^2}{r}=0$).

$$H = \underbrace{\frac{-\hbar^2}{2m}\Delta_1 - \frac{2q^2}{r_1}}_{H_1}\underbrace{-\frac{\hbar^2\Delta_2}{2m} - \frac{2q^2}{r_2}}_{H_2} = H_1 + H_2$$

on pose: $\psi = \psi_1\cdot\psi_2$

$$\Rightarrow \begin{cases} H_1\psi_1 = E_1\psi_1 \\ H_2\psi_2 = E_2\psi_2 \end{cases} \quad \text{avec } E = E_1 + E_2$$

où $\left(-\frac{\hbar^2\Delta_1}{2m} - \frac{2q^2}{r_1}\right)\psi_1 = E_1\psi_1$

$$\Rightarrow \left[\Delta_1 + \frac{2m}{\hbar^2}\left(E_1 + \frac{2q^2}{r_1}\right)\right]\psi_1 = 0$$

on a: $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, $r^2 = x^2+y^2+z^2$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\cdot\frac{\partial r}{\partial x} = \frac{x}{r}\cdot\frac{\partial f}{\partial r}$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{x}{r}\cdot\frac{\partial f}{\partial r}\right) = \frac{\partial}{\partial x}\left(\frac{x}{r}\right)\cdot\frac{\partial f}{\partial r} + \left(\frac{x}{r}\right)^2\frac{\partial^2 f}{\partial r^2}$$

$\left(\frac{1}{r} + x\frac{\partial}{\partial x}\left(\frac{1}{r}\right)\right)\frac{\partial f}{\partial r}$

de m̂ pour $\frac{\partial^2 f}{\partial y^2}$, $\frac{\partial^2 f}{\partial z^2}$.

Finalement, on aura:

$$\Delta f = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}$$

$$\Rightarrow \frac{\partial^2\psi_{1,2}}{\partial r_{1,2}^2} + \frac{2}{r_{1,2}}\frac{\partial\psi_{1,2}}{\partial r_{1,2}} + \frac{2m}{\hbar^2}\left(E_{1,2} + \frac{2q^2}{r_{1,2}}\right)\psi_{1,2} = 0$$

b). Lorsque: $\psi(\vec r_1,\vec r_2) = A\,e^{-\frac{2}{a}(r_1+r_2)}$.

C.à.d. $\psi_1(r_1) = A_1 e^{-\frac{2r_1}{a}}$, $\psi_2(r_2) = A_2 e^{-\frac{2r_2}{a}}$, A=

$$\left(\frac{4}{a^2} + \frac{2mE_{1,2}}{\hbar^2}\right) + \left(\frac{-4}{a} + \frac{4mq^2}{\hbar^2}\right)\frac{1}{r_{1,2}} = 0.$$

$$\Rightarrow \begin{cases} \frac{4}{a^2} + \frac{2mE_{1,2}}{\hbar^2} = 0 \\ \frac{-4}{a} + \frac{4mq^2}{\hbar^2} = 0 \end{cases} \Rightarrow \cancel{E_{1,2} = -4m}$$

$$\Rightarrow \boxed{a = \frac{\hbar^2}{mq^2}}, \quad \boxed{E_{1,2} = -\frac{2mq^4}{\hbar^2}}$$

$$\Rightarrow E = E_1 + E_2 = -\frac{4mq^4}{\hbar^2} = -108{,}8\ \text{eV}$$

$E_{exp} = -79$ eV

⇒ Avec l'interaction électronique.

a) $E = E_1 + E_2 + E_3 + E_4 + E_5$.

avec: $E_1 = \frac{-\hbar^2}{2m}\int_{V_1}\int_{V_2}\psi^*\Delta_1\psi\,d\tau_1 d\tau_2$

$E_2 = \frac{-\hbar^2}{2m}\int_{V_1}\int_{V_2}\psi^*\Delta_2\psi\,d\tau_1 d\tau_2$

$E_3 = -2q^2\int_{V_1}\int_{V_2}\psi^*\frac{1}{r_1}\psi\,d\tau_1 d\tau_2$

$E_4 = -2q^2\int_{V_1}\int_{V_2}\psi^*\frac{1}{r_2}\psi\,d\tau_1 d\tau_2$

$E_5 = q^2\int_{V_1}\int_{V_2}\psi^*\frac{1}{r}\psi\,d\tau_1 d\tau_2$.

b) on a: $E_1 = \frac{-\hbar^2}{2m}A\int_{V_2}\psi_2^*\psi_2\,d\tau_2\cdot\int_{V_1}\psi_1^*\Delta_1\psi_1\,d\tau_1$

d'où: $\frac{\partial\psi_1}{\partial r} = -\frac{2}{a}\psi_1$, $\frac{\partial^2\psi_1}{\partial r^2} = \frac{4}{a^2}\psi_1$

$$\Rightarrow \int\psi_1^*\Delta_1\psi_1\,d\tau_1 = \int_{V_1}\left(\frac{4}{a^2} - \frac{4}{ar_1}\right)\psi_1^*\psi_1\,d\tau_1$$

Donc.

$$E_1 = \frac{-\hbar^2 A}{2m}\Big\{\frac{4}{a^2}\int_{V_1}\psi_1^*\psi_1\,d\tau_1\int_{V_2}\psi_2^*\psi_2\,d\tau_2$$

$$-\frac{4}{a}\int\psi^*\psi\,d\tau_2\int\psi^*\frac{1}{\ }\psi\,d\tau\Big\}$$