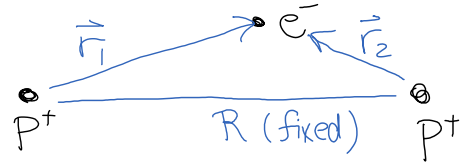


L74-H2+ Ion

Friday, April 1, 2016 07:41

$$H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$



* goal: calculate ground state energy
- bound state if $E_{gs} < E(H_{gs}^0 + H_{gs}^+)$

* Trial wavefunction: linear combination of atomic orbitals (LCAO)

$$\psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad \text{ground state of } H^0 \text{ atom}$$

let $\psi(\vec{r}_1, \vec{r}_2) = A [\psi_0(r_1) + \psi_0(r_2)]$ symmetric under P_{12}
again, must be spin singlet

* normalize $\psi(\vec{r}_1, \vec{r}_2)$:

$$\langle \psi | \psi \rangle = |A|^2 \left[2 \underbrace{\langle \psi_0(r) | \psi_0(r) \rangle}_{r=r_1 \text{ or } r_2} + 2 \underbrace{\langle \psi_0(r_1) | \psi_0(r_2) \rangle}_I \right] = 2|A|^2(1+I) \quad A = (2/(1+I))^{1/2}$$

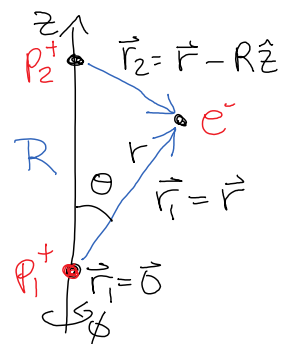
$$I \equiv \langle \psi_0(\vec{r}_1) | \psi_0(\vec{r}_2) \rangle = \frac{1}{\pi a^3} \int d^3\vec{r} e^{-(r_1+r_2)/a} \quad \bullet \text{ choose origin at } r_1=0$$

$$= \frac{1}{\pi a^3} \int_0^\pi \int_0^{2\pi} \int_0^\infty e^{-r/a} e^{-(r^2+R^2-2rR\cos\theta)^{1/2}/a} r^2 dr \sin\theta d\theta d\phi$$

$$\text{let } y = (r^2 + R^2 - 2rR\cos\theta)^{1/2} \quad dy = Rr \sin\theta d\theta / y$$

$$\int_0^\pi e^{-y/a} \sin\theta d\theta = \int_{|R-r|}^{R+r} e^{-y/a} \cdot \frac{y dy}{Rr} = \frac{a^2}{Rr} \int_{|R-r|}^{R+r} z e^{-z/a} dz$$

$$= \frac{-a}{Rr} (y+a) e^{-y/a} \Big|_{|R-r|}^{R+r} = \frac{-a}{Rr} \left[(R+r+a) e^{-\frac{R+r}{a}} - (|R-r|+a) e^{-\frac{|R-r|}{a}} \right]$$



`Integrate[Exp[-Sqrt[r^2 + R^2 - 2 r R Cos[theta]] / a] r^2 Sin[theta], {theta, 0, Pi},
Assumptions -> a > 0 && r > 0 && R > 0]`

$$\frac{ar \left(e^{-\frac{|r-R|}{a}} (a+|r-R|) - e^{-\frac{r+R}{a}} (a+r+R) \right)}{R}$$

$$I = \frac{2\pi}{\pi a^3} \left[\int_0^R \frac{-ar}{R} (R+r+a) e^{-\frac{R+r}{a}} dr + \int_R^\infty \frac{ar}{R} (R-r+a) e^{-\frac{R-r}{a}} dr + \int_R^\infty \frac{ar}{R} (r-R+a) e^{-\frac{R-2r}{a}} dr \right]$$

$$I = \frac{1}{\pi a^3} \left[\int_0^R \frac{1}{R} (R+r+a) e^{-a} dr + \int_R^\infty \frac{1}{R} (R-r+a) e^{-a} dr + \int_R^\infty \frac{1}{R} (r-R+a) e^{-a} dr \right]$$

$$= e^{-R/a} \left[1 + R/a + \frac{1}{3} (R/a)^2 \right] \rightarrow \begin{cases} 1 & \text{as } R \rightarrow 0 \\ 0 & \text{as } R \rightarrow \infty \end{cases} \quad \text{"overlap integral"}$$

`Integrate[Exp[-x/a] I0, {x, 0, Infinity},`
`Assumptions -> a > 0 && R > 0]`

$$\frac{e^{-\frac{R}{a}} (3a^2 + 3aR + R^2)}{3a^2}$$

* Calculate $\langle \mathcal{H} \rangle = \langle \Psi | \mathcal{H} | \Psi \rangle$ note: $\mathcal{H}_0(r_i) \psi_0(r_i) = E_1 \psi_0(r_i)$

$$\mathcal{H}|\Psi\rangle = A \left[\underbrace{-\frac{\hbar^2}{2m} \nabla^2}_{\mathcal{H}_0(r_i)} - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right] [\psi_0(r_1) + \psi_0(r_2)]$$

$$= E_1 \Psi - A \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_2} \psi_0(r_1) + \frac{1}{r_1} \psi_0(r_2) \right]$$

$$\langle \Psi | \mathcal{H} | \Psi \rangle = E_1 - |A|^2 \frac{e^2}{4\pi\epsilon_0} \langle \psi_0(r_1) + \psi_0(r_2) | \frac{1}{r_2} \psi_0(r_1) + \frac{1}{r_1} \psi_0(r_2) \rangle$$

$$= E_1 - |A|^2 \underbrace{\frac{e^2}{4\pi\epsilon_0 a}}_{E_1} 2 (D+X) \quad \text{where}$$

$$D \equiv a \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle = a \langle \psi_0(r_2) | \frac{1}{r_1} | \psi_0(r_2) \rangle = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a}$$

$$X \equiv a \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle = a \langle \psi_0(r_2) | \frac{1}{r_2} | \psi_0(r_1) \rangle = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

$$\langle \mathcal{H} \rangle = E_1 \left(1 + \frac{2(D+X)}{1+1} \right) \rightarrow + V_{pp} = \frac{e^2}{4\pi\epsilon_0 R} = -\frac{2a}{R} E_1 = -E_1 \cdot F(R/a)$$

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - \frac{2}{3}x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + \frac{1}{3}x^2)e^{-x}} \right\}$$

