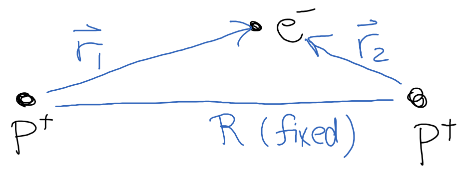
L74-H2+ Ion

Friday, April 1, 2016 07:41

$$\mathcal{H} = \frac{-\hbar^2}{2m}\nabla - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$



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

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

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

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

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

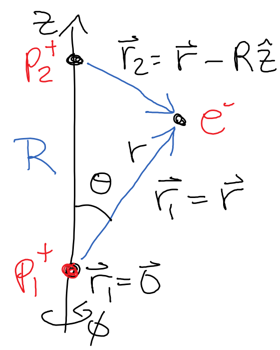
$$\langle\psi|\psi\rangle = |A|^2\Big[2\underbrace{\langle\psi_0(r)|\psi_0(r)\rangle}_{r=r_1 \text{ or } r_2} + 2\underbrace{\langle\psi_0(r_1)|\psi_0(r_2)\rangle}_{I \quad \text{let } \vec{r}=\vec{r}_1}\Big] = 2|A|^2(1+I)$$

$$A = \left(2/1+I\right)^{1/2}$$

$$I \equiv \langle\psi_0(\vec{r}_1)|\psi_0(\vec{r}_2)\rangle = \frac{1}{\pi a^3}\int d^3\vec{r}\, e^{-(r_1+r_2)/a}$$

• choose origin at $r_1 = 0$

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



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

$$\int_{\theta=0}^{\pi} e^{-y/a}\sin\theta\, d\theta = \int_{|R-r|}^{R+r} e^{-y/a}\cdot\frac{y\,dy}{Rr} = \frac{a^2}{Rr}\underbrace{\int z e^{-z} dz}_{-(z+1)e^{-z}}$$

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

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Integrate[Exp[-Sqrt[r^2 + R^2 - 2 r R Cos[θ]] / a] r^2 Sin[θ], {θ, 0, Pi},
 Assumptions → a > 0 && r > 0 && R > 0]
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$$\frac{a\,r\left(e^{-\frac{|r-R|}{a}}(a+|r-R|) - e^{-\frac{r+R}{a}}(a+r+R)\right)}{R}$$

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

$$I = \frac{2\pi}{\pi a^3}\Big[\int_0 \frac{\pi r}{R}(R+r+a)e^{-r/a} + \int_0 \frac{\pi r}{R}(R-r+a)e^{-r/a}\,dr + \int_R \frac{\pi r}{R}(r-R+a)e^{-r/a}\,dr$$

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

"overlap integral"

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Irθ = 1 / (Pi a^3) * 2 Pi Integrate[Exp[-r / a] Iθ, {r, 0, Infinity},
   Assumptions → a > 0 && R > 0]
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$$\frac{e^{-\frac{R}{a}}\left(3a^2 + 3aR + R^2\right)}{3a^2}$$

* Calculate $\langle \mathcal{H} \rangle = \langle \psi | \mathcal{H} | \psi \rangle$ note: $\mathcal{H}_0(r_1)\psi_0(r_1) = E_1 \psi_0(r_1)$

$$\mathcal{H}|\psi\rangle = A\Big[\underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\Big(\frac{1}{r_1}}_{H_0(r_1)} + \frac{1}{r_2}\Big)\Big]\left[\psi_0(r_1) + \psi_0(r_2)\right]$$

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

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

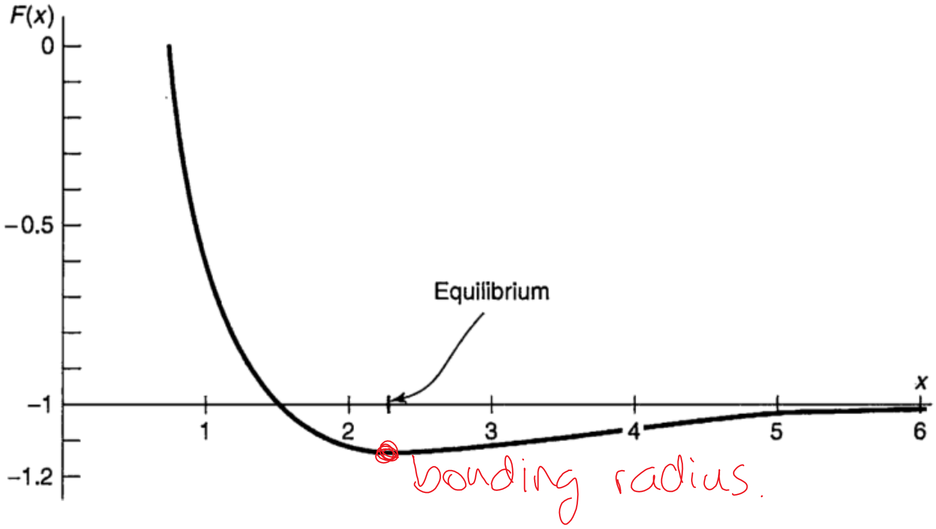
$$= E_1 - |A|^2 \underbrace{\frac{e^2}{4\pi\epsilon_0 a}}_{E_1}\cdot 2\,(D+X) \qquad \text{where}$$

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

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

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

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



F(x)
0
−0.5
−1
−1.2
Equilibrium
x
1
2
3
4
5
6
bonding radius.