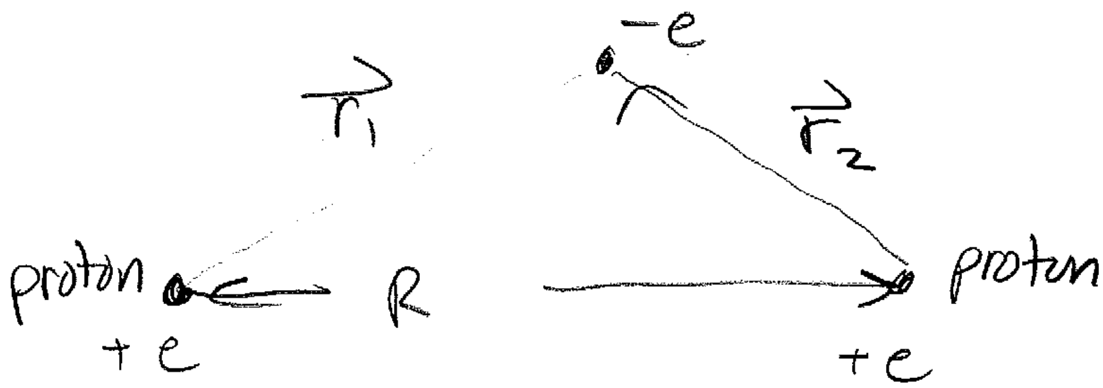
# Hydrogen Molecular Ion

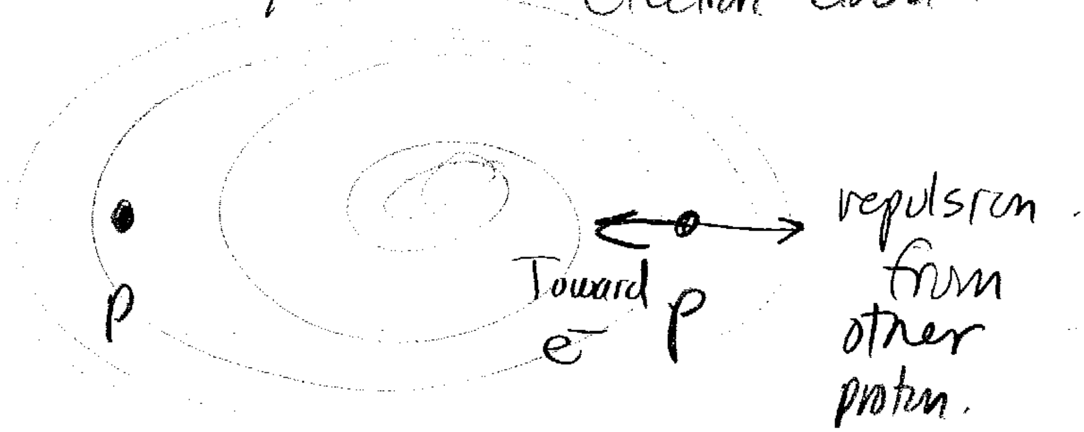



Classically, any stable state?

$\Rightarrow$ $-e$ would stick to a $p$, other proton sees neutral

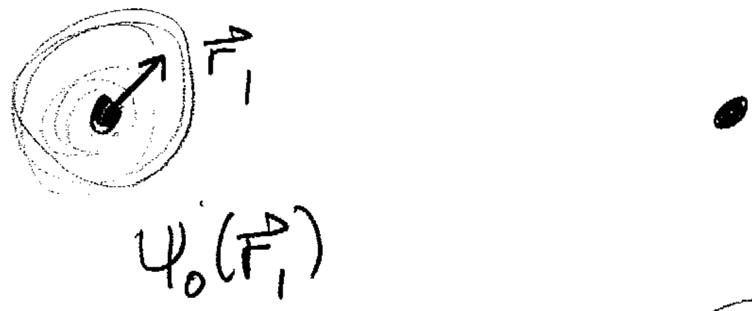
$\Rightarrow$ actually, $-e$, with $m_e \ll m_p$, cannot be localized ... kinetic energy skyrockets.

$\Rightarrow$ Qualitatively ... electron cloud.



Let $\psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

#1




#2


Trial Wave Function . . .

$$\psi_{\pm} = A\left[\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2)\right]$$

should be an eigenstate of Exchange $\vec{r}_1$ + $\vec{r}_2$ - - -

$\vec{r}_1 \leftrightarrow \vec{r}_2$ $\quad$ + . . . +1

− . . . −1

$\psi_- \to 0$ half way in between

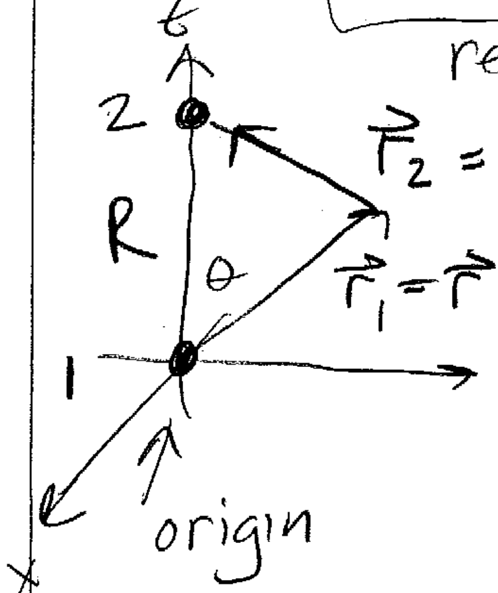
"LCAO"

## NORMALIZATION

$$1 = \int d^3r \, |\psi_{\pm}(\vec{r})|^2$$

$$= |A|^2 \Big[ \overbrace{\int |\psi_0(\vec r_1)|^2 d^3\vec r}^{1} + \overbrace{\int |\psi_0(\vec r_2)|^2 d^3 \vec r}^{1}$$

$$\pm 2 \underbrace{\int \psi_0(\vec r_1)\,\psi_0(\vec r_2)\, d^3 r}_{\text{real work!}} \Big] \quad \equiv I$$




$$\vec r_2 = R\hat z - \vec r_1$$

$$|\vec r_2|^2 = R^2 + r_1^2 - 2R\,\underbrace{\hat z\cdot\vec r_1}_{r_1\cos\theta}$$

$$|\vec r| = |\vec r_1|$$

$$r_2 = \sqrt{R^2+r^2-2Rr\cos\theta}$$

$$I = \frac{1}{\pi a^3}\int d\phi\, \sin\theta\, d\theta\, r^2 dr\, e^{-\frac{r}{a}}\, e^{-\frac{1}{a}\sqrt{R^2+r^2-2Rr\cos\theta}}$$

- Do $d\phi$ integral $\rightarrow 2\pi$
- $d\theta$ integral

$$y^2 \equiv R^2+r^2-2Rr\cos\theta$$

limits: $\cos\underset{0}{\theta} = 1$, $y^2 = R^2+r^2-2Rr = (R-r)^2$

$\cos\underset{\pi}{\theta} = -1$, $y^2 = (R+r)^2$

$$d(y^2) = \underbrace{2Rr\sin\theta\, d\theta}\quad \text{nice!}$$

$$\int_0^{\pi} e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a} \underbrace{\sin\theta\, d\theta}$$

$$e^{-y/a} \qquad \frac{1}{2Rr}\, d(y^2) = \frac{1}{2Rr} 2y\,dy$$

$$= \frac{1}{rR} \int_{|R-r|}^{(R+r)} e^{-y/a}\, y\, dy \qquad \xi = y/a$$

$$= \frac{a^2}{rR} \underbrace{\int_{|R-r|/a}^{(R+r)/a} e^{-\xi} \xi\, d\xi} = -\xi e^{-\xi}\Big|_{\frac{|R-r|}{a}}^{\frac{(R+r)}{a}} + \int_{\frac{R-r}{a}}^{\frac{R+r}{a}} e^{-\xi} d\xi$$

parts
$du = e^{-\xi} d\xi \quad v = \xi$
$u = -e^{-\xi} \quad dv = 1$

$$\frac{a^2}{rR}\left[ = \left[ -\frac{(R+r)}{a} e^{-\frac{(R+r)}{a}} + \frac{|R-r|}{a} e^{-\frac{|R-r|}{a}} - e^{-\frac{(R+r)}{a}} + e^{-\frac{|R-r|}{a}} \right] \right.$$

$$= \frac{a}{rR}\left[ e^{-\frac{|R-r|}{a}} \underset{\#2}{(|R-r|+a)} - e^{-\frac{(R+r)}{a}} \underset{\#1}{((R+r)+a)} \right]$$

now do integral over $r^2 dr$...

$\underline{\#1 : \text{ easy}}$

#2 : break into : $r<R: |R-r| = R-r$

$r>R: |R-r| = r-R$

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

$$+ \int_R^\infty dr\, r\, e^{-\frac{r}{a}} e^{+\frac{R}{a}} e^{-\frac{r}{a}} (r - R + a)$$

$$\left. - \int_0^\infty dr\, r\, e^{-\frac{r}{a}} e^{-\frac{R}{a}} e^{-\frac{r}{a}} (R + r + a)\right]$$

just exponential integrals . .

$$I = e^{-R/a}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]$$

$R \to 0 \quad I \to 1$

$R \to \infty, \; I \to 0$

$$1 = |A|^2 (2 \pm 2I)$$

$$\boxed{|A_\pm|^2 = \frac{1}{2(1 \pm I)}}$$

$R \to 0$,
$I \to 1$,
what happens?

ALL THAT JUST FOR NORMALIZATION!

Need expectation value

$$|A|^2 \langle (\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2)) | H | (\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2)) \rangle$$

$$+ \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R}$$ ⇐ 2 protons! "semiclassical"

$$\| $$

$$-2\underbrace{\left(\frac{-e^2}{8\pi\varepsilon_0 a}\right)}_{E_1\text{, ground state of H p. 307}}\left(\frac{a}{R}\right) = -\frac{2a}{R} E_1$$

$$H(\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2))$$

$$= \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2}\right)(\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2))$$

$$= \underbrace{E_1(\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2))}_{4\text{ of }6\text{ terms}} \underbrace{- \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_2}\psi_0(\vec{r}_1) \pm \frac{1}{r_1}\psi_0(\vec{r}_2)\right)}_{\text{remaining 2! Ack!}}$$

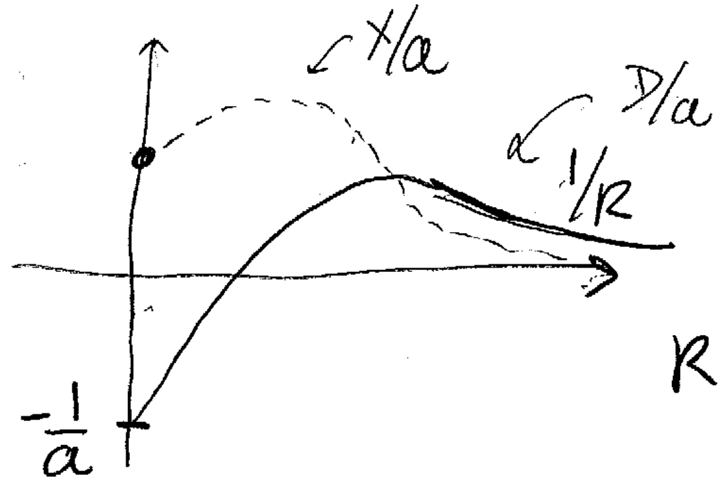
e.v.

$$= E_1 - 2|A|^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left[\langle \psi_0(\vec{r}_1) | \frac{1}{r_2} | \psi_0(\vec{r}_1) \rangle \pm \langle \psi_0(\vec{r}_1) | \frac{1}{r_1} | \psi_0(\vec{r}_2) \rangle\right]$$

"direct" integral

$$\frac{D}{a} \equiv \langle \varphi_0(\vec{r}_1) | \frac{1}{r_2} | \varphi_0(\vec{r}_1) \rangle$$

$$= \frac{1}{R} - \left(\frac{1}{a} + \frac{1}{R}\right) e^{-2R/a}$$




$$\frac{X}{a} = \langle \varphi_0(\vec{r}_1) | \frac{1}{r_1} | \varphi_0(\vec{r}_2) \rangle$$

$$= \frac{1}{a}\left(1 + \frac{R}{a}\right) e^{-R/a}$$

Add up all terms

$$= E_1 - 2|A|^2 \left(\frac{e^2}{4\pi\varepsilon_0 a}\right) \left[ D \pm X \right] - 2\frac{a}{R} E_1$$

$|A|^2 = \frac{1}{2(1 \pm I)}$, $\quad \frac{e^2}{4\pi\varepsilon_0 a} = -2E_1$, $\quad$ p-p $\rightarrow -2\frac{a}{R}E_1$

$$= -E_1 \left[ -1 - \frac{2(D \pm X)}{(1 \pm I)} + 2\frac{a}{R} \right]$$

Let $x \equiv \frac{R}{a}$

$$I = e^{-x}\left[1 + x + \frac{1}{3}x^2\right]$$

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

$$X = (1 + x)e^{-x}$$

$$D \pm X = \frac{1}{x} - \left(1 + \frac{1}{x}\right)e^{-2x} \pm (1 + x)e^{-x}$$

$$\frac{\text{Energy}}{E_1} = -1 - \frac{2\left(\frac{1}{x} - (1 + \frac{1}{x})e^{-2x} \pm (1 + x)e^{-x}\right)}{1 \pm e^{-x}\left[1 + x + \frac{1}{3}x^2\right]}$$

$$+ \frac{2}{x}\left[\frac{\left(1 \pm e^{-x}\left[1 + x + \frac{1}{3}x^2\right]\right)}{1 \pm e^{-x}\left[1 + x + \frac{1}{3}x^2\right]}\right]$$

$$= -1 + \frac{2}{x}\left\{\frac{\cancel{-1} + (x+1)e^{-2x} \mp (x + x^2)e^{-x} + \cancel{1} \pm (x + 1 + \frac{1}{3}x^2)e^{-x}}{1 \pm e^{-x}\left[1 + x + \frac{1}{3}x^2\right]}\right\}$$

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

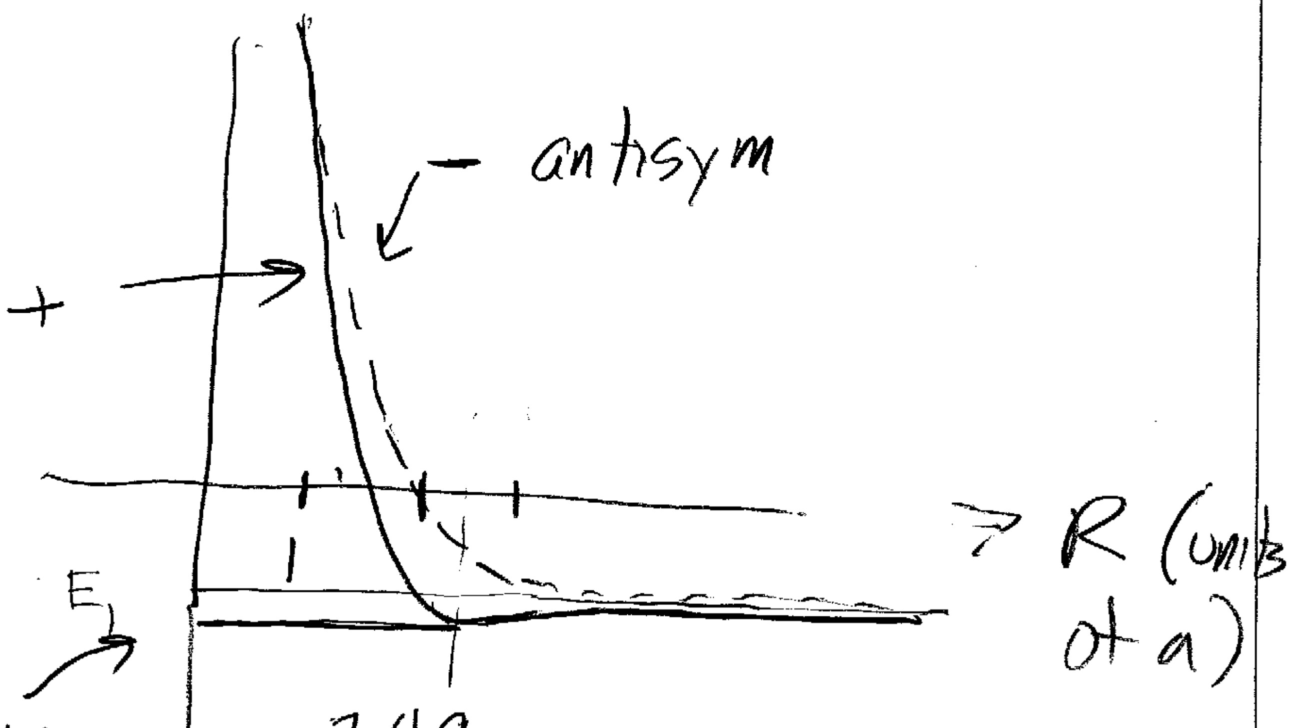
$x \to 0 \quad (R \to 0)$

$$\overset{+}{\to} -1 + \frac{2}{x}, \quad \overset{-}{-1} + \frac{2}{x}\left\{\frac{\overbrace{-1 + \frac{2}{3}x^2 + x - \frac{1}{2}x^2 + 1 - x + 0x^2}^{+\frac{1}{6}x^2}}{1 - 1 - \frac{1}{3}x^2 - \frac{1}{2}x^2 + x^2}\right\}$$

$+\frac{1}{6}x^2$

both $\rightarrow -1 + \frac{2}{x}$

<u>But</u>:




$-1.129 E_1$ $\qquad \underbrace{2.49\,a}$

$\downarrow$

Binding energy... $\simeq 0.129 E_1$ $\sim 1.8\,eV$ $\qquad$ (Bohr Radius) $\times 2.5$

Most interesting ---
replace $e^-$ with $\mu^-$

then $R_{eq} \simeq \frac{1}{200} \cdot 2.5\,a \simeq 7 \cdot 10^{-12}\,cm$

$\simeq 70 \times r_{proton}$ CAN FUSE!