Hydrogen atom energies

$$E_n = -\frac{1}{2}\frac{E_h}{n^2} = -\frac{1}{2}\frac{1}{n^2}\frac{m_e Z^2 e^4}{\hbar^2} = -\frac{13.6}{n^2}eV$$

$$a_0 = \frac{\hbar^2}{m_e Z e^2}$$

Note dependence on 1) me 2) Ze and 3)n

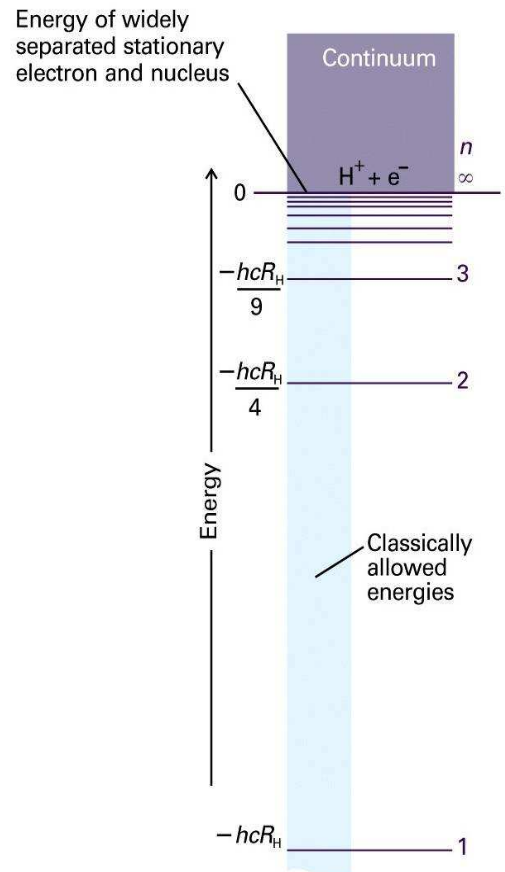

Figure 10-5
Atkins Physical Chemistry, Eighth Edition

Hydrogen atom wavefunctions

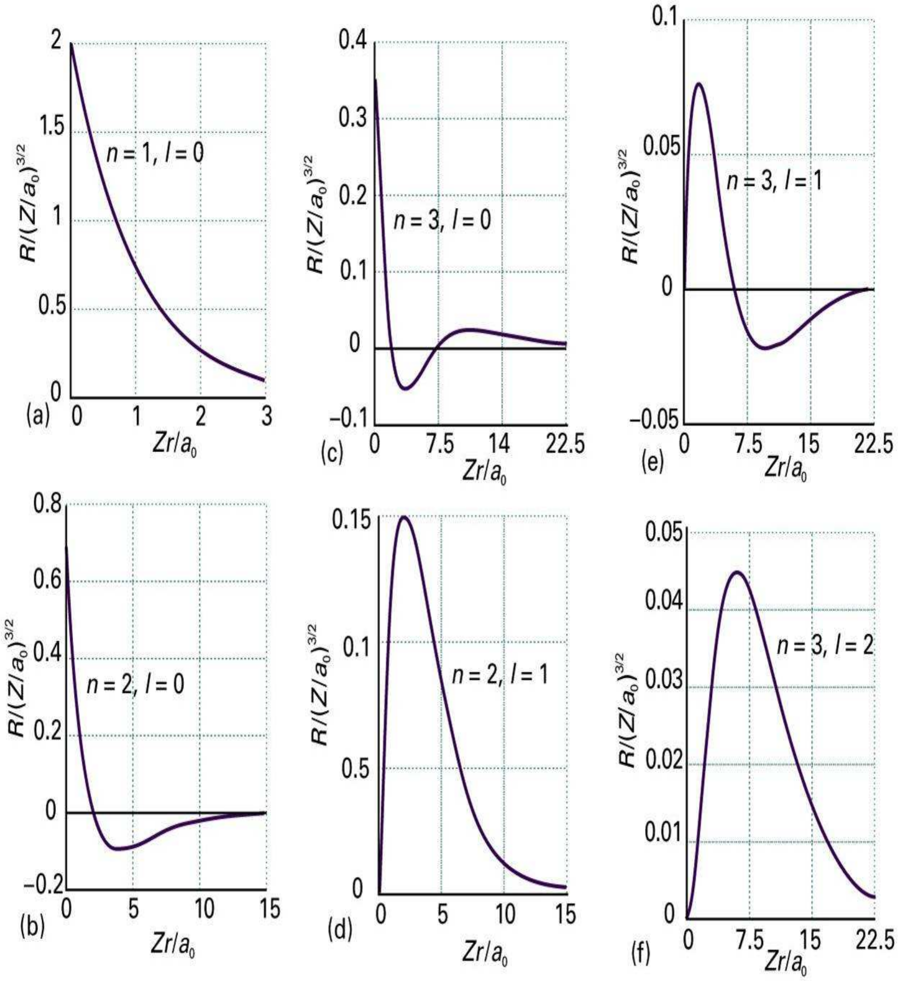

Figure 10-4
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$$ {}_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na_0}\right) \cdot Y_\ell^m(\vartheta,\varphi) $$

$$ L^{2\ell+1}_{n-\ell-1}(x) = \sum_{i=0}^{n-\ell-1} (-1)^i \binom{n+\ell}{(n-\ell-1)-i} \frac{x^i}{i!} $$

$$ \psi_{100} = N_1 \exp\left(-\frac{Zr}{a_0}\right) $$

$$ \psi_{200} = N_2 \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) $$

$$ \psi_{210} = N_2 \left(\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) \cos\vartheta $$

$$ \psi_{300} = N_3 \left[27 - 18\left(\frac{Zr}{a_0}\right) + 2\left(\frac{Zr}{a_0}\right)^2\right] \exp\left(-\frac{Zr}{3a_0}\right) $$

$$ \psi_{322} = N_3 \sqrt{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{Zr}{3a_0}\right) \sin^2\vartheta \exp(i2\varphi) $$

Radial distribution function

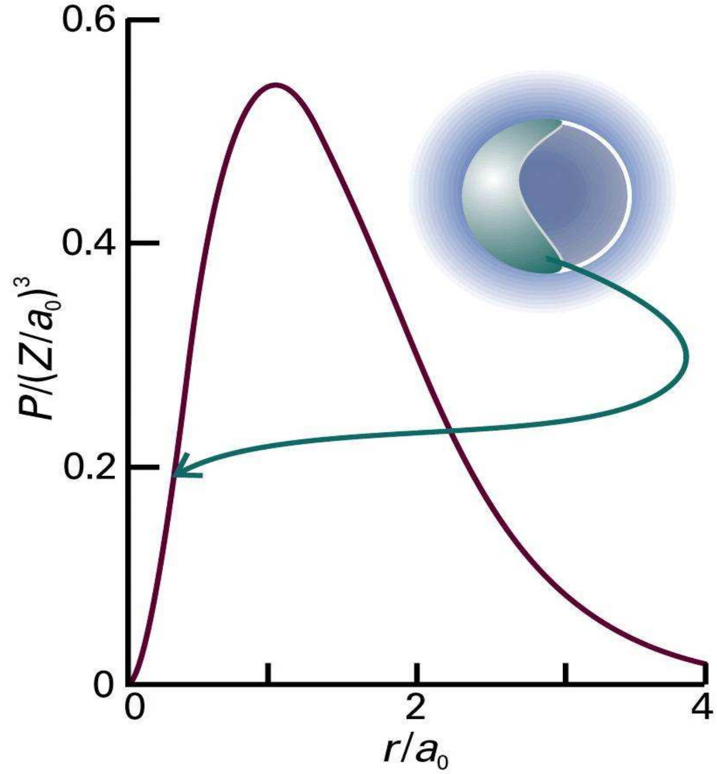

Figure 10-14
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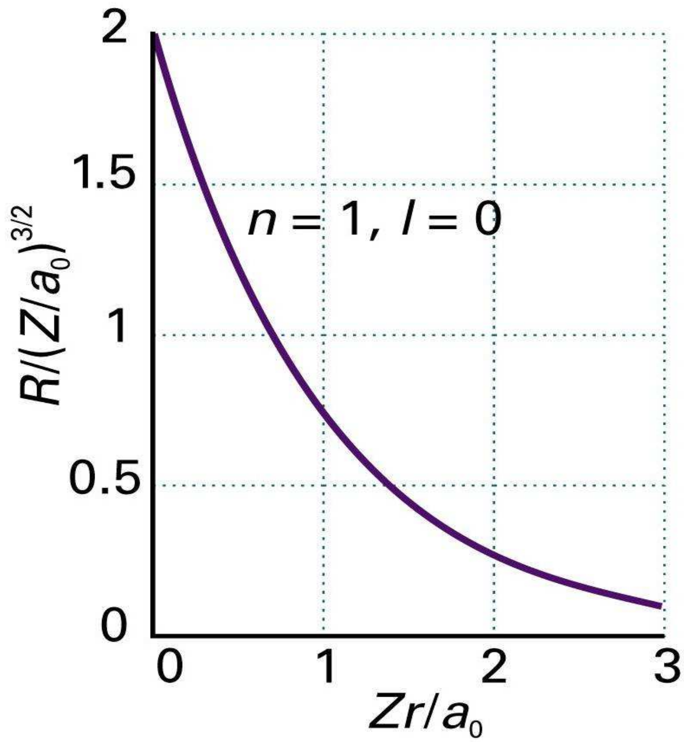

Figure 10-4a
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$$NR_{10}R_{10}r^2 \int Y^*_{lm} Y_{lm} \sin\vartheta d\vartheta d\varphi$$

$$\psi_{100} = N_1 \exp\left(-\frac{Zr}{a_0}\right)$$

$$Nr^2 \exp\left(-\frac{2Zr}{a_0}\right)$$

Particle in boxes (wells)

H.O, RR, H-atom

Helium atom

e_1 r_{12} e_2

$$\hat{\mathcal{H}} = \hat{T}_{1e} + \hat{T}_{2e} + \hat{V}_{1n} + \hat{V}_{2n} + \hat{V}_{12} \quad +2e$$

interelectronic repulsion

$$= \qquad + \frac{e^2}{r_{12}}$$

$$\psi(\vec{r}_1, \vec{r}_2) \neq \psi_1(\vec{r}_1)\, \psi_2(\vec{r}_2)$$

e_1 e_2

Zeroth level approximation

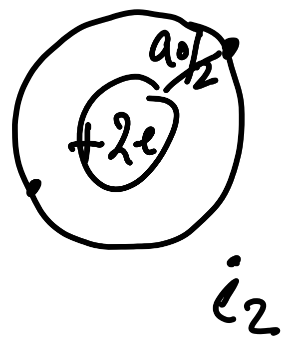
$$V_{12} = 0 \qquad +2e$$

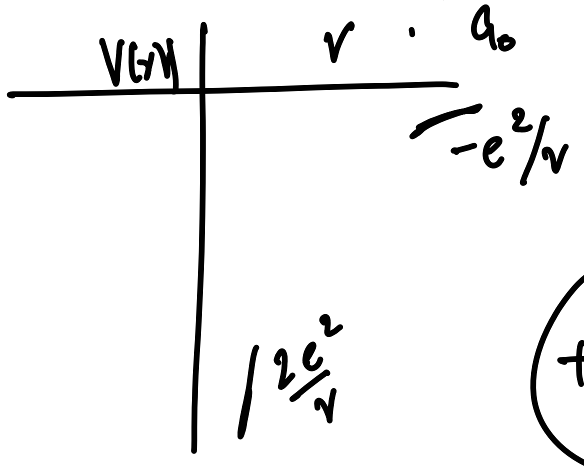
$$E_{gs} = (-13.6) \times \underset{Z^2}{4} \times \underset{2e}{2} = -108.8\,\text{eV}$$

$$E_{expt} = -79\ \text{eV}$$

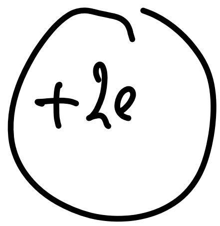
1st level approximation

$$V = \frac{e^2}{r \;\cdot\; a_0} \sim 25\,eV$$





e_1 $\quad V_{eff} = \frac{Z(r)\,e^2}{r}$



$$1 \leq Z \leq 2$$

2nd level approximation

E_{expt} $\quad (13.6)Ze^2$

$Z \sim 1.4$

Variation method

$$\psi_{gs} = \psi_1 \psi_2 \qquad \psi_1(Z)$$

unknown parameter

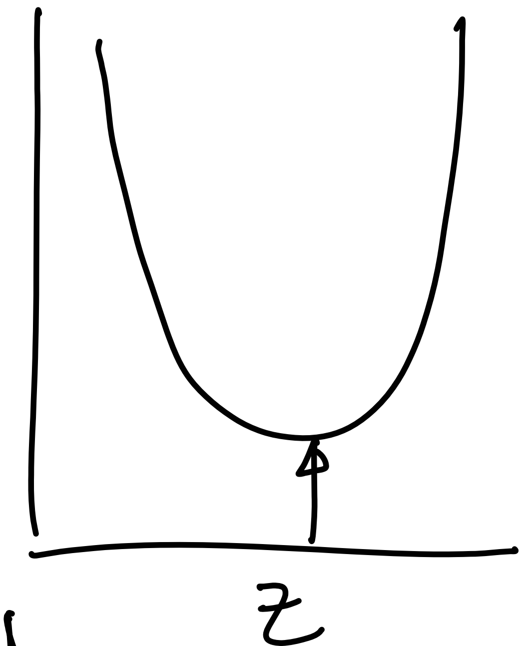
$$\mathcal{H} = \hat{T}_e + \hat{T}_e + \hat{V}_{1e} + \hat{V}_{2e} + V_{12}$$

$$\langle E \rangle = \int \psi_{gs}^* \mathcal{H} \psi_{gs}\, d\tau$$

$$\langle E \rangle (Z)$$

$Z = 1.65$

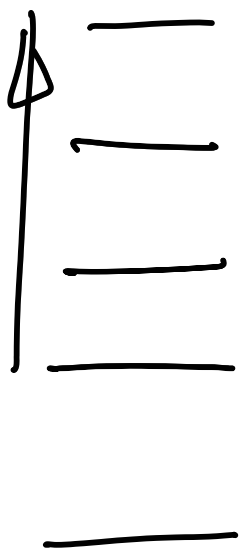
$\langle E \rangle$

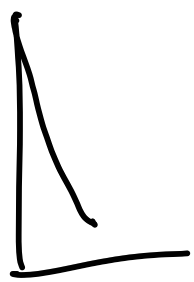


$\psi_{1s}^{H} = e^{-r/a_0}$

$\psi_{1s} = e^{-Zr/a_0}$

unknown

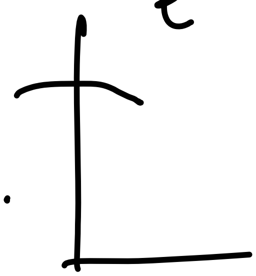




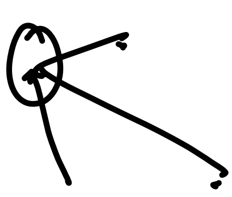
$e^{-(a+br)\, r/a_0}$

unknowns

E_{gs}



Self-Consistent field method



$\psi = \psi_1 \psi_2 \cdots \psi_n$ → atomic orbitals

1) Average potential due to all other electrons
2) Spherically symmetric