STEFANO
CURTAROLO

HYDROGEN ATOM

H1 - H9

HYDROGEN ATOM

proton + electron around
(and other things)

$$\hat{H} = \frac{\hat{P}_N^2}{2m_N} + \frac{\hat{P}_e^2}{2m_e} + \underbrace{V_{ep}(r_e - r_N)}$$

depends only on distance
$\Rightarrow$ suggest change of coordinates

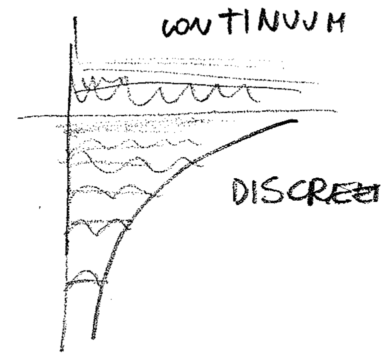
$\nearrow$ New coordinates

POSITION: center of mass + distance

— $m_N >> m_e$ (~1850 times)

introduce effective mass

μ.



COORDINATES

center of mass $\quad R \equiv \dfrac{m_N r_N + m_e r_e}{m_N + m_e}$

$$r \equiv r_e - r_N$$

$$\frac{1}{\mu} \equiv \frac{1}{m_N} + \frac{1}{m_e} \qquad M \equiv m_N + m_e$$

$$\Rightarrow \quad \hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V(r)$$

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H1

$$\frac{\hat{P}^2}{2M} \Rightarrow \text{heavy } M, \text{ do with C.M.}$$

$\Rightarrow$ electron fast follows M as cloud

$$\Rightarrow \quad \hat{H} = \frac{\hat{p}^2}{2\mu} + V(r) \qquad V(r) = \text{COULOMB} \quad -\frac{Ze^2}{r}$$

central potential

spherically simmetric $\Rightarrow \psi =$

$\Rightarrow$ go in spherical coordinates

SCHRÖDINGER

$$\hat{H}\psi(r,\vartheta,\phi) = E\psi(r,\vartheta,\phi) \qquad \begin{cases} x = r\sin\vartheta\cos\phi \\ y = r\sin\vartheta\sin\phi \\ z = r\cos\vartheta \end{cases}$$

$$\psi(r,\theta,\phi) = R(r)\underbrace{\Theta(\theta)\,\Phi(\phi)}_{\varphi(\vartheta,\phi)}$$

$$\nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\boxed{\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2\psi}{\partial\phi^2}}$$

EQUATION becomes

$$\frac{-\hbar^2}{2\mu r^2}\left[\Theta\phi\frac{d}{dr}\left(r^2\frac{dR^2}{dr}\right)+R\phi\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\right.$$

$$\left.+R\Theta\frac{1}{\sin^2\theta}\frac{d^2\phi}{d\phi^2}\right]-\frac{Ze^2}{(4\pi\varepsilon_0)r}R\Theta\phi=ER\Theta\phi$$

1) isolate ϕ dependence.

multiply * $\left(-\frac{2\mu r^2\sin^2\theta}{\hbar^2}\right)R\Theta\phi$ and rearranging

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\phi}\frac{d^2\phi}{d\phi^2}=0$$

- r,θ dependence is mixed
- ϕ is simple, i.e. I rotate around ϕ for symmetry the stuff in r,θ does not change $\Rightarrow$

$$\phi(\phi+m2\pi)=\phi(\phi)$$

$$\Rightarrow\quad \underbrace{\text{constant}}_{+m^2}+\frac{1}{\phi}\frac{d^2\phi}{d\phi^2}=0\quad\Rightarrow\quad \frac{d^2\phi}{d\phi^2}=-m^2\phi$$

↳ real or imaginary?

must be real and integer for boundary

ϕ must be normalized

$$\phi=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

m integer, which??

H3

2) equation becomes

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)}_{\text{all in } R\ \forall\theta\ =\ \beta}+\underbrace{\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2}{\sin^2\theta}}_{\text{all in }\theta\ \forall r\ =\ -\beta}=0$$

$$\begin{cases}\dfrac{d}{dr}\left(r^2\dfrac{dR}{dr}\right)+\dfrac{2\mu r^2}{\hbar^2}\left(E+\dfrac{Ze^2}{(4\pi\varepsilon_0)r}\right)R=\beta R\\[2ex] \cancel{\dfrac{1}{\sin\theta}\dfrac{d}{d\theta}}\quad \dfrac{1}{\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)-\dfrac{m^2\Theta}{\sin^2\theta}=-\beta\Theta\end{cases}$$

3) the $\Theta(\theta)$ equation

can be solved (pain)

a) change variables

b) express solution in power series and get recursive solution $\Rightarrow$ ~~series~~

c) keep only square-summable solutions. ($\int\Theta^2=1$

d Solution = serie $\Rightarrow$ to terminate (no divergences)

$\Rightarrow\ \beta=\ell(\ell+1)\qquad \ell=$ integer

d) truncated serie = Legendre polynomial $P_\ell^m(\cos\theta)$

e) Return to angular frame:

$$\Theta_{\ell m}(\theta)=\left[\frac{(2\ell+1)}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2}P_\ell^{|m|}(\cos\theta)$$

associated Legendre polynomial

H 4)

$P_0(x)=1 \quad P_1(x)=x \quad P_2(x)=\frac{1}{2}(3x^2-1) \quad \ldots\ldots$

$P_1^1(x)=(1-x^2)^{1/2} \quad P_2^1(x)=3(1-x^2)^{1/2}x \quad \ldots\ldots$

$P_e^{|m|}(x)=0$ if $|m|>e$

$\Rightarrow \quad m=-e, -e+1 \ldots\ldots 0 \ldots\ldots e$

4) The R equation (pain).

a) E is negative banded state

b) plug $\beta = e(e+1)$ from Θ

c) change variables

d) Find asyntotic solution for large r = asyntotic(r)

e) guess R as product asyntotic(r) * unknown(r)
express R equation in the unknown solution and get power serie of unknown(r)

f) get recursive solution of coefficients of unknown(r)
$\int R^2 dr = 1 \Rightarrow$ convergence $\Rightarrow$ serie must be truncated at $\underline{\underline{n}}$ step (with $n>e$)

g) serie becomes Laguerre polynomials

$$R_{ne}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-e-1)!}{2n[(n+e)!]^3}\right]^{1/2} \exp(-\rho/2)\, \rho^e L_{n+e}^{2e+1}(\rho)$$

HS $\quad \rho = \frac{2Zr}{na_0} \quad a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} \sim 0.5\,\text{Å}$ H radius

$L_1^1(\rho) = 1 \qquad L_2^1(\rho) = 2\rho - 4 \qquad L_3^1(\rho) = -3\rho^2 + 18\rho - 18$

. . . . .

plot / get $\psi = R(r)\,\Theta(\vartheta)\,\Phi(\varphi)$

$$E = \frac{-\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = \frac{-13.6}{n^2}\ \text{eV}$$

n = integer = 0, 1, 2 . . .

l = integer $l < n \Rightarrow l = 0, 1, \dots n-1$

m = integer $|\,| \le l$ / $m = -l, \dots 0, \dots l$

$(m_z = \pm\frac{1}{2})$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2}$$

in spherical coordinates

$\hat{L}_z \psi_{n,l,m} = m\hbar\psi_{n,l,m}$

$\hat{L}^2 \psi = l(l+1)\hbar^2 \psi$

TABLE 7-2. Some Eigenfunctions for the One-Electron Atom

Quantum Numbers n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$
2	1	±1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\theta$
3	1	±1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\theta e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	±1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\theta\cos\theta e^{\pm i\varphi}$
3	2	±2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\theta e^{\pm 2i\varphi}$

H6.

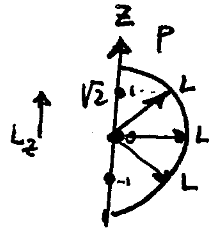
		L_z	L^2	#e	shape
s orbital	$\ell = 0$	$m = 0$	$\ell(\ell+1) = 0$	2	spherical
p orbitals	$\ell = 1$	$m = \underbrace{-1, 0, 1}_{3}$	$\ell(\ell+1) = 2$	6	
d orbitals	$\ell = 2$	$m = \underbrace{-2 \ldots 2}_{5}$	$\ell(\ell+1) = 6$	10	
f orbitals	$\ell = 3$	$m = \underbrace{-3 \ldots 3}_{7}$	$\ell(\ell+1) = 12$	14	

$\Rightarrow L = 0, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar$

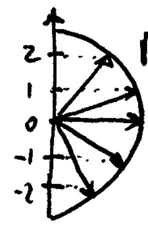
draw radius $L =$

S

p



d



$\sqrt{6}\hbar$ + ↓↑ Same for s

$\Rightarrow S_z = \pm \underbrace{\tfrac{1}{2}}_{s} \hbar$

$\hat{S}^2 = \underbrace{s(s+1)}_{\frac{3}{4}\hbar^2} \hbar$

system with 2e... and so on ...

H7

H7b

Relationship between Quantum Numbers

TABLE 7-1. Possible Values of l and m_l for $n = 1, 2, 3$

n	1	2		3		
l	0	0	1	0	1	2
m_l	0	0	−1, 0, +1	0	−1, 0, +1	−2, −1, 0, +1, +2
Number of degenerate eigenfunctions for each l	1	1	3	1	3	5
Number of degenerate eigenfunctions for each n	1	4		9		
	s	s	p	s	p	d

Origin of the periodic table

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H7c

Hydrogen Wavefunctions

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H7d

Physical Nature of Orbitals (Ψ^2)

$\psi^2 = \psi^* \psi = P(r, l, m_l)$ Probability density

Radial Probability Density = $R^*R4\pi r^2 dr$

Look at only probability of finding electron in a shell of thickness dr at r from the nucleus

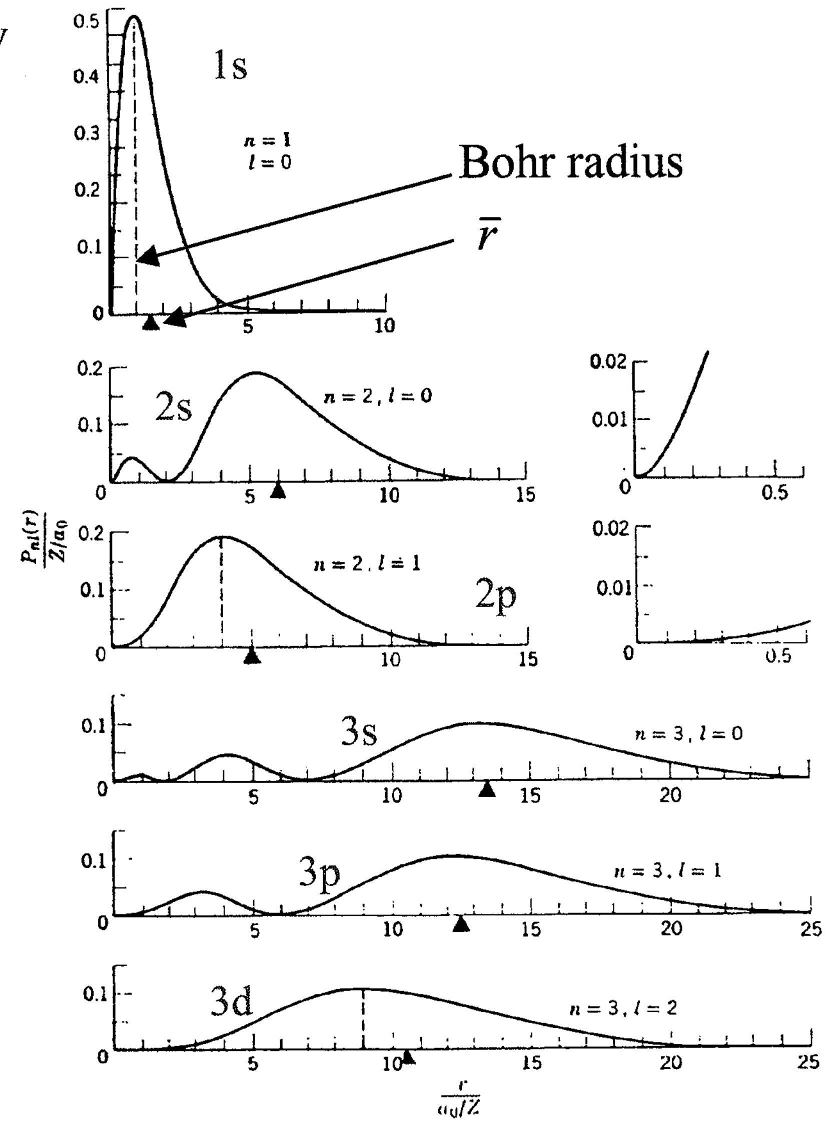
Ψ can be negative; cross over is 0 in Ψ^2

Compare to Bohr

$$\bar{r} = \int_0^\infty rP(r,l,m_l)dr = \int_0^\infty rR^* R4\pi r^2 dr$$

$$\bar{r} = \frac{n^2 a_o}{Z}\left[1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right]$$

$$r_{Bohr} = \frac{n^2 a_o}{Z};\ a_o = \frac{\hbar^2}{\mu e^2} = 0.52\,A$$



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H7e

Review of H atom

$$\psi = R(r)\Theta(\theta)\Phi(\phi)$$

$$H\psi = E\psi$$

Do separation of variables; each variable gives a separation constant

ϕ separation yields m_l
θ gives ℓ
r gives n

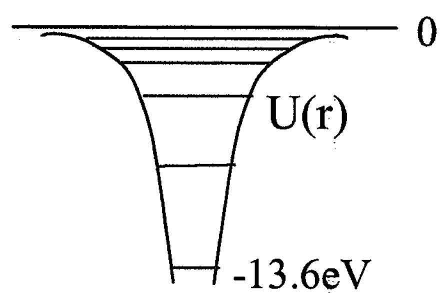
After solving, the energy E is a function of n

$$E = \frac{-\mu Z^2 e^4}{(4\pi\varepsilon_o)^2 2\hbar^2 n^2} = \frac{-13.6eV}{n^2}$$

m_l and ℓ in Φ and Θ give Ψ the shape
(i.e. orbital shape)

The relationship between the separation constants (and therefore the quantum numbers are:)

n=1,2,3,…
ℓ=0,1,2,…,n-1
m_l=-ℓ, -ℓ+1,…,0,…, ℓ-1,
(m_s=+ or - 1/2)



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The sum and difference of these two solutions can be formed if we wish them to represent p_x and p_y specifically (Fig. 9.4):

$$\psi_{2p_x}(r) = A(r/a_0)e^{-r/2a_0} \sin\theta \cos\phi \tag{9.18}$$

$$\psi_{2p_y}(r) = A(r/a_0)e^{-r/2a_0} \sin\theta \sin\phi \tag{9.19}$$

The angular dependence of d functions (Fig. 9.4) includes an additional node. The simplest to represent mathematically is the $3d$ wave function for $m = 0$:

$$\psi_{3d,m=0}(r) = A(r/a_0)^2 e^{-r/3a_0}(3\cos^2\theta - 1) \tag{9.20}$$

The nodes for this function are two cones with $\theta = \cos^{-1}(\pm 1/\sqrt{3})$.

As with the box and the harmonic oscillator, confining a matter wave in the hydrogen atom leads to quantized energy levels and a series of corresponding wave functions that develop more nodes with increasing energy. The three-dimensionality of the problem leads to three quantum numbers (plus the spin quantum number). Although the s, p, d, and f functions all have very different shapes, *the energy, as given in (9.10), depends only on the principal quantum number n.* Thus, in addition to the twofold spin degeneracy of each solution, there is additional degeneracy in the hydrogen atom: the $2s$ and $2p$ levels are degenerate, the $3s$, $3p$, and $3d$ levels are degenerate, and so on. This degeneracy is related to the spherical symmetry of the potential energy function (9.3). We shall see later that some of this degeneracy is removed in multielectron atoms and in molecules.

Although quantum mechanics and the solutions of Schrödinger's equation tell us that Bohr's model of particle-like electrons traveling in orbits around the nucleus was naïve, we retain the name *orbital* for electron wave functions like those in

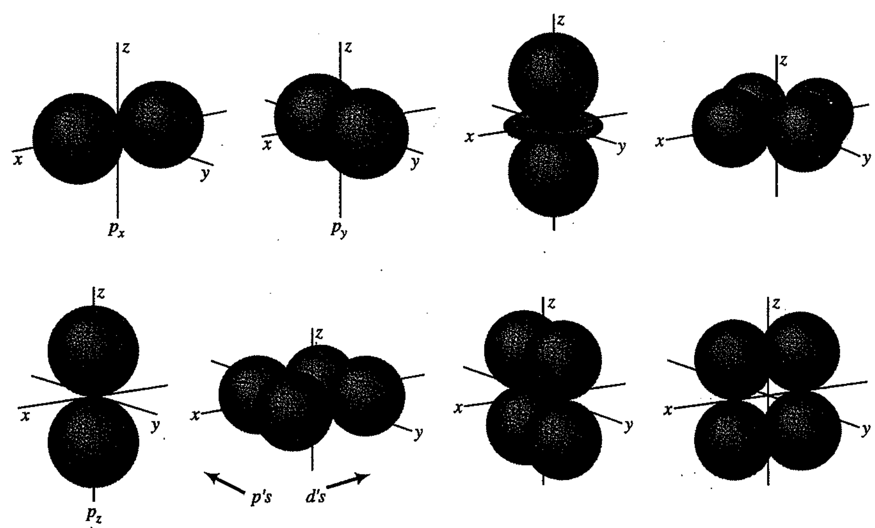

Figure 9.4. Shapes of p and d wave functions.

H 7F

COMMUTATIONS

have seen $[\hat{H}, \hat{L}_z] = 0$ $\quad [\hat{H}, \hat{L}^2] = 0$

and $\hat{H}, \hat{L}_z, \hat{L}^2$ share a common base of eigenvectors:

ed: $H\psi(t) = i\hbar \frac{\partial}{\partial t}\psi(t)$

formally $\psi(t) = \left(e^{\frac{Ht}{i\hbar}}\right)\psi(0)$ solution

$\hat{U}(t) = e^{\frac{\hat{H}t}{i\hbar}}$ time evolution operator

$U^*(t) = U(-t)$ $\quad$ H is called generator of infinitesimal time evolution

$\psi(t) = \hat{U}(t-t_0)\psi(t_0)$ $\quad U(t-t_0) = e^{\hat{H}(t-t_0)/i\hbar}$

$U^*(t) = U(-t)$

$U(\delta t) = 1 + \frac{H\delta t}{i\hbar} \Rightarrow \psi(t) = \psi(0) + \left(\frac{\delta t}{i\hbar}\right)\hat{H}\psi(0)$

if $[H, f] = 0 \Leftrightarrow [e^{\hat{H}t/i\hbar}, f] = 0 \ \forall t = [U, f] = 0$

$f(t) \equiv \int \psi^*(t) f \psi(t)\, dV = \int \psi_0 U^* \underbrace{f U}_{fU = Uf} \psi_0\, dV = 0 = \int \psi f U^* U \psi_0\, dV$

$\psi_0 \to U\psi_0 = \psi(t)$

$U^*(t)\psi(t) = U(-t)\psi(t) = \psi(0)$

$\underline{f(t) = f(0)} \Longleftarrow = \int \psi(0) f \psi(0)\, dV$

CONSERVATION OF MOTION $\Leftrightarrow [f, H] = 0$

H8

MULTI-ELECTRONS

- previous wavefunctions $\psi_{n\ell m}$ where single electron
- 2 electrons? repulsion $\Rightarrow$ screening : how?
- $E = -\frac{13.6 Z^2}{n^2}$ does not work well $\Rightarrow Z_{eff}$
- Technique SCF (self consistent field): starts from a guessed $\psi(r_1, r_2) \Rightarrow \rho = \psi\psi$ and ~~so~~ modifies to minimize $E \Rightarrow \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \Rightarrow \delta\psi \Rightarrow \min(E)$!