

STEFANO
CURTAROLO

HYDROGEN ATOM

H1 - H9

HYDROGEN ATOM

proton + electron around
(and other things)

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

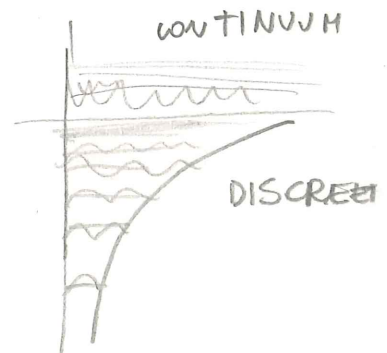
depends only on distance
⇒ suggest change of coordinates

→ New coordinates

POSITION: center of mass + distance

— $m_N \gg m_e$ (~1850 times)
introduce effective mass

μ .



COORDINATES

center of mass

$$R \equiv \frac{m_N r_N + m_e r_e}{m_N + m_e}$$

$$r \equiv r_e - r_N$$

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

$$M \equiv m_N + m_e$$

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

STACK:

ERROR: undefined
OFFENDING COMMAND: E

H1

$\frac{\hat{p}^2}{2M} \Rightarrow$ heavy M , do with C.M.
 $\Rightarrow$ electron fast follows M
 as cloud

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

$$-\frac{Ze^2}{r}$$

central potential

spherically symmetric $\Rightarrow \psi =$

$\Rightarrow$ go in spherical coordinates

SCHRÖDINGER

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases}$$

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

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

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

EQUATION becomes

$$\frac{-\hbar^2}{2\mu r^2} \left[\Theta \phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + R \phi \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + R \Theta \frac{1}{\sin^2 \theta} \frac{d^2 \phi}{d\phi^2} \right] - \frac{Ze^2}{(4\pi\epsilon_0)r} R\Theta\phi = E R\Theta\phi$$

1) isolate ϕ dependence.

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

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} \left(E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\phi} \frac{d^2 \phi}{d\phi^2} = 0$$

- r, θ dependence is mixed

- ϕ is simple, if I rotate around ϕ for symmetry the stuff in r, θ does not change $\Rightarrow$

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

must be real and integer for boundary

ϕ must be normalized

$$\phi = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m \text{ integer, which??}$$

2) equation becomes

$$\underbrace{\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right)}_{\text{all in } R \forall \theta = \beta} + \underbrace{\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta}}_{\text{all in } \theta \forall r = -\beta} = 0$$

all in $R \forall \theta$

$$= \beta$$

all in $\theta \forall r$

$$= -\beta$$

$$\left\{ \begin{aligned} & \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) R = \beta R \end{aligned} \right.$$

$$\left\{ \begin{aligned} & \cancel{\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta}} \quad \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} = -\beta \Theta \end{aligned} \right.$$

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

can be solved (poin)

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 = series $\Rightarrow$ to terminate (no divergences)

$$\Rightarrow \beta = l(l+1) \quad l = \text{integer}$$

d) truncated series = Legendre polynomial $P_l^m(\cos \theta)$

e) Return to original frame:

$$\Theta_{lm}(\theta) = \left[\frac{(2l+1)}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) \quad \begin{matrix} \swarrow \text{associated} \\ \text{Legendre} \\ \text{polynomial} \end{matrix}$$

H4)

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

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

$$P_\ell^{lm}(x) = 0 \quad \text{if } |m| > \ell$$

$$\Rightarrow m = -\ell, -\ell+1, \dots, 0, \dots, \ell$$

4) The R equation (pam).

- E is negative bound state
- plug $\beta = \ell(\ell+1)$ from Θ
- change variables
- Find asymptotic solution for large $r = \text{asymptotic}(r)$
- guess R as product $\text{asymptotic}(r) * \text{unknown}(r)$
express R equation in the unknown solution and
get power series of $\text{unknown}(r)$
- get recursive solution of coefficients of $\text{unknown}(r)$
 $\int R^2 dr = 1 \Rightarrow$ convergence $\Rightarrow$ series must be
truncated at n step (with $n > \ell$)
- series becomes Laguerre polynomials

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

$$H5 \quad \rho = \frac{2Zr}{na_0} \quad a_0 = \frac{\epsilon_0 \hbar^2}{m_e e^2} \sim 0.5 \text{ \AA} \quad \text{H radius}$$

$$L_1'(p) = 1 \quad L_2'(p) = 2p - 4 \quad L_3'(p) = 3p^2 + 18p - 18$$

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

$$E = \frac{-\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6}{n^2} \text{ eV}$$

$$n = \text{integer} = 0, 1, 2, \dots$$

$$l = \text{integer} \quad l < n \Rightarrow l = 0, 1, \dots, n-1$$

$$m = \text{integer} \quad || \leq l \quad m = -l, \dots, 0, \dots, l$$

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

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

Quantum Numbers			Eigenfunctions
n	l	m_l	
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
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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	$\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi}$
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3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos \theta$
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3	2	± 2	$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

$$a_0 = \frac{\epsilon_0 \hbar^2}{m_e e^2}$$

in spherical coordinates

$$\hat{L}_z \psi = m \hbar \psi$$

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

$$L_1'(p) = 1 \quad L_2'(p) = 2p - 4 \quad L_3'(p) = -3p^2 + 18p - 18$$

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

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$$a_0 = \frac{\epsilon_0 \hbar^2}{m_e e^2}$$

in spherical coordinates

$$\hat{L}_z \psi = m \hbar \psi$$

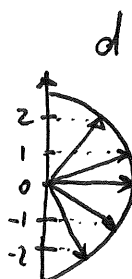
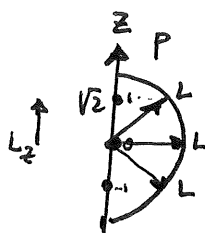
$$\hat{L}^2 \psi = l(l+1) \hbar^2 \psi$$

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

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

draw radius $L =$

s



$\sqrt{6} \hbar + \uparrow$ Same for $\downarrow$

$$\Rightarrow S_z = \pm \frac{1}{2} \hbar$$

$$S^2 = \frac{3}{4} \hbar^2$$

system with 2 electrons and so on

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
	s		s	p	s	p
Number of degenerate eigenfunctions for each n	1	4		9		
	s	s	p	s	p	d

Origin of the periodic table



Hydrogen Wavefunctions

H7c

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H
72

Physical Nature of Orbitals (Ψ^2)

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

$$\text{Radial Probability Density} = R^* R 4\pi r^2 dr$$

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

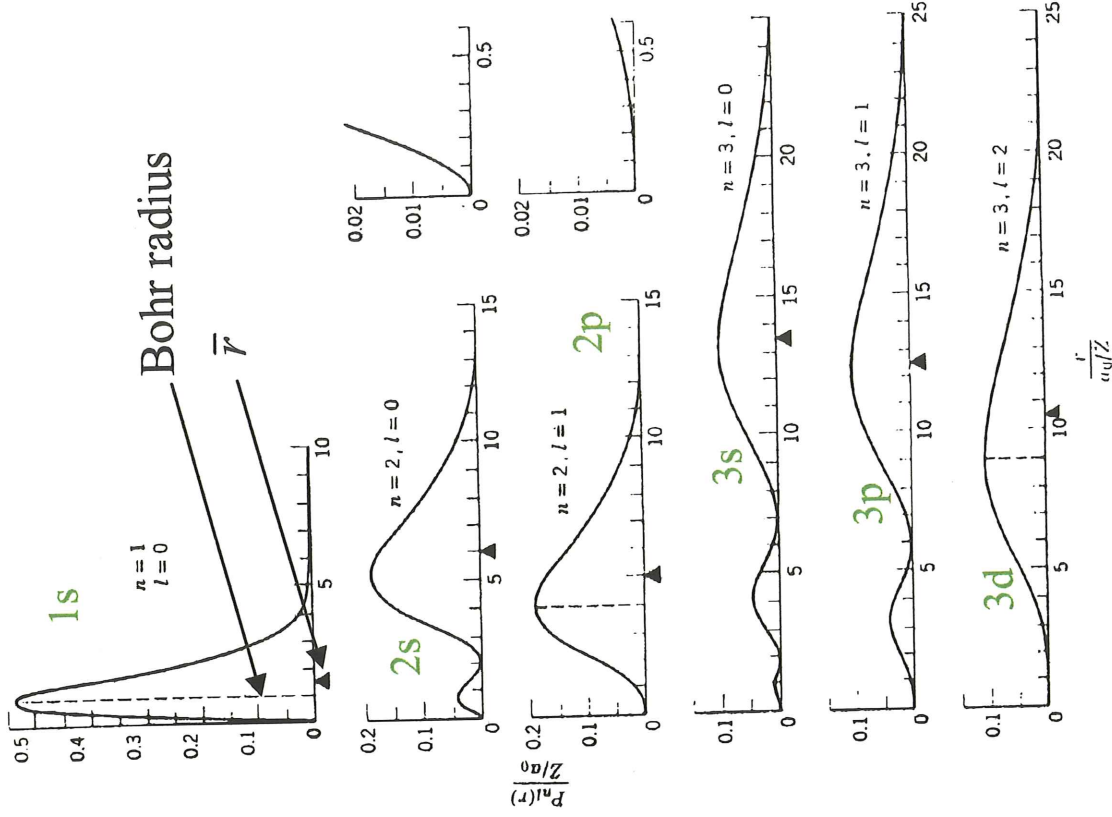
Ψ can be negative; cross over is 0 in Ψ^2

Compare to Bohr

$$\bar{r} = \int_0^{\infty} r P(r, l, m_l) dr = \int_0^{\infty} r R^* R 4\pi r^2 dr$$

$$\bar{r} = \frac{n^2 a_0}{Z} \left[1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right]$$

$$r_{Bohr} = \frac{n^2 a_0}{Z}; \quad a_0 = \frac{\hbar^2}{\mu e^2} = 0.52 \text{ \AA}$$



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

After solving, the energy E is a function of n

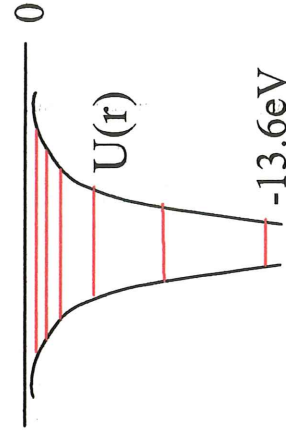
ϕ separation yields m_l
 θ gives ℓ
 r gives n

$$E = \frac{-\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6\text{eV}}{n^2}$$

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:)

- $n=1,2,3,\dots$
- $\ell=0,1,2,\dots,n-1$
- $m_l=-\ell, -\ell+1, \dots, 0, \dots, \ell-1,$
- $(m_s=+\text{ or } - 1/2)$



ive function, and can be
ynomials in front of the
omials (*c'est Laguerre*).

for the 2s wave function

s are also plotted in Fig.
where $\psi = 0$, not count-
function to larger radii
electron increases with

in the 1s state involves
This integration yields
e average kinetic energy
ctron could significantly
ver, that decreased un-
ad to increased momen-
.6 eV = -13.6 eV, and
resent a minimum in the

ie 2p ($n = 2, l = 1$), 3p
electrons and their wave
quantum number n , fol-
he p functions have one
han their corresponding
make up for that with
netic quantum number

(9.16)

$\pi/2$. If we identify the
9.4). The other two 2p

(9.17)

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):

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

$\psi_{2p_y}(r) = A(r/a_0)e^{-r/2a_0} \sin \theta \sin \phi$ (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 $m = 0$:

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

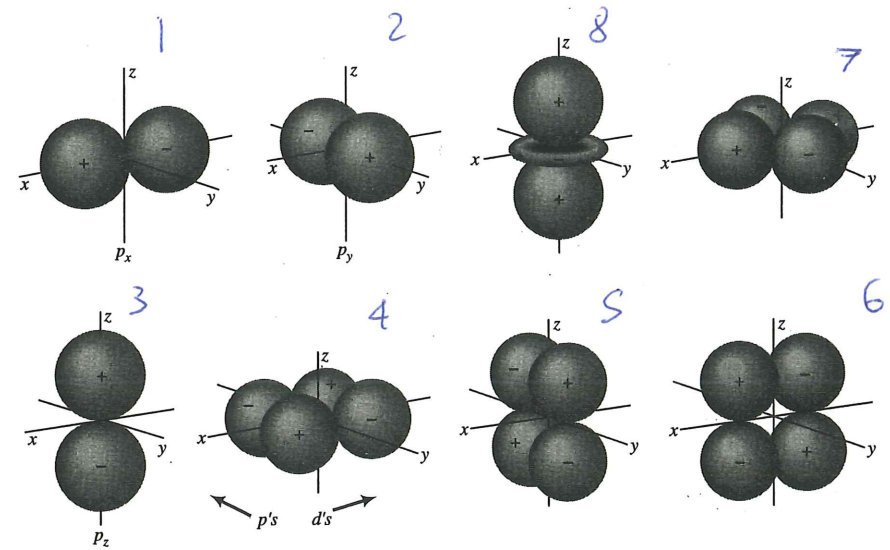


Figure 9.4. Shapes of p and d wave functions.

H 7f

COMMUTATION'S

have seen $[\hat{H}, \hat{L}_z] = 0$ $[\hat{H}, \hat{L}_x] = 0$

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

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

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

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

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

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

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

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

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

$f(t) = \int \psi^*(t) f \psi(t) dV \Rightarrow \int \psi_0^* U^* f U \psi_0 dV = 0 = \int \psi f U^* U \psi_0 dV$

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

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

$f(t) = f(0)$

$\leftarrow = \int \psi(0) f \psi(0) dV = f(0)$

H8

CONSERVATION

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

MULTI-ELECTRONS

- previous wavefunctions ψ_{mem} 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 ~~is~~ modifies to minimize $E \Rightarrow \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \Rightarrow \delta\psi \Rightarrow \min(E)!$