

Notice: quiz III at 5/28, covering ch3, allowing 3 pages A4 formula sheet
final exam 6/10, covering all materials. allowing 4 pages of above

for a particle of mass m in an infinitely deep spherical potential well

$V(r) = \begin{cases} 0, & r < a \\ +\infty, & r \geq a \end{cases}$, find the eigenenergy and eigen-wave function for the bound state, $\boxed{l=0}$ case.

- recap particle dynamics in 3D

introduce 3D coordinate

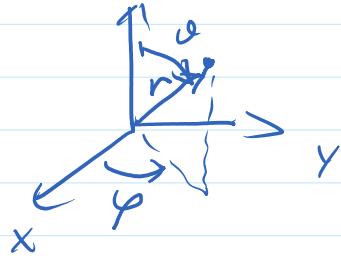
introduce state ket. wavefunctions in 3D
 $\Psi(x, y, z)$

introduce probability distribution. \leftrightarrow 1D case.

introduce degeneracy \star

§ 1. Wavetunction in spherical coordinates.

$$\vec{r} = (x, y, z) \longleftrightarrow (r, \theta, \varphi)$$



H_0 in treespace

$$H = \frac{\vec{P}^2}{2m} = \frac{P_x^2 + P_y^2 + P_z^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

in spherical coordinate

$$\vec{P} = -i\hbar \vec{\nabla} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

scalar $\star \frac{\hbar^2}{2m}$

$$\vec{\nabla} \cdot \vec{f} = \frac{\partial f}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial f}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial f}{\partial \varphi} \hat{\varphi}$$

$$\frac{\vec{P}^2}{2m} = -\frac{\hbar^2}{2m} \vec{\nabla}^2$$

$\rightarrow \vec{\nabla}^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}$

$$\vec{P} = -\hbar \nabla$$

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

$$H = \frac{\vec{P}^2}{2m} = -\frac{\hbar^2}{2m} \vec{\nabla}^2$$

$$H \text{ for spherical } -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) - \frac{1}{2mr^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) \right)$$

angular momentum

$$\vec{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right)$$

$$H_0 = \frac{P_r^2}{2m} + \frac{\vec{L}^2}{2mr^2}$$

radial angular
径向 角向

central potential 中心勢

$$V = V(r)$$

$$+V = \frac{P_r^2}{2m} + \frac{\vec{L}^2}{2mr^2} + V(r).$$

- H depending on
- (1) momentum along radial direction
 - (2) radial "position" \rightarrow
 - (3) angular momentum \vec{L}

because $V = V(r) \neq V(\theta, \phi)$, so there is a symmetry of the Hamiltonian along angular position coordinate.

to see the structure of H, then we calculate commutators with operators:

$[H, \vec{L}^2] = 0 \rightarrow H, \vec{L}^2 \text{ share the same eigenstates.}$

$$[H, L_z] = 0 \quad H, L_z \text{ share } \vee \vee \vee$$

the eigen state $\psi(r, \theta, \varphi) = R(r) \Phi(\theta, \varphi)$
 $\Phi(\theta, \varphi) = Y_l^m(\theta, \varphi)$

let's show this is true that $\psi(r, \theta, \varphi) = R(r) \Phi(\theta, \varphi)$.
 trying solve the eigen equation

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + r^2 (V(r) - E) \psi = \frac{\hbar^2}{2m} \psi$$

if we set $\psi = R(r) \Phi(\theta, \varphi)$
 and devide ψ on both sides

$$-\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + r^2 (V(r) - E) = \frac{\hbar^2}{2m} \frac{\Phi(\theta, \varphi)}{R} = C$$

separation of variable 分離变量

$$\Phi(\theta, \varphi) = Y_l^m(\theta, \varphi) \text{ spherical harmonics}$$

$$\hbar^2 Y_l^m(\theta, \varphi) = \underbrace{\hbar^2 (l(l+1))}_{C} \cdot Y_l^m(\theta, \varphi) \quad \text{填空题}$$

fill-in-the-blanks

$$C = \frac{\hbar^2}{2m} l(l+1)$$

plug it back to radial equation, and we arrive to

$$-\frac{\hbar^2}{2m} \underbrace{\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right)}_{\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right)} + r^2 (V(r) - E) R - \frac{\hbar^2}{2m} l(l+1) R = 0$$

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) = 2r \frac{\partial R}{\partial r} + r^2 \frac{\partial^2 R}{\partial r^2}.$$

introduce a new radial function $U(r)$

$$R(r) = \frac{U(r)}{r}$$

$$\begin{aligned} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) &= \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \left(\frac{U}{r} \right) \right) = \frac{\partial}{\partial r} \left(r^2 \frac{U'}{r} - U \right) \\ &= \cancel{r} \left(rU' - U \right) = \cancel{r}U' + rU'' - \cancel{r}U' = rU'' = r \frac{\partial^2 U}{\partial r^2}. \end{aligned}$$

$$\frac{\partial r}{\partial r} = \frac{\partial r'}{\partial r} (ru' - u) = u' + ru'' - u' = ru'' = r \frac{\partial^2 u}{\partial r^2}$$

$$\Rightarrow -\frac{\hbar^2}{2mr^2} \frac{\partial^2 u}{\partial r^2} + \left[\frac{l(l+1)}{2mr^2} \hbar^2 + V(r) \right] u(r) = E u(r)$$

effective Schrödinger's equation for $u(r)$.

probability around (r, θ, ϕ)

$$|\psi|^2 r^2 dr \sin\theta d\theta d\phi = |R(r)|^2 r^2 dr |\psi_r^m|^2$$

$\psi = R(r)\psi_r^m(\theta, \phi)$

$$R = \frac{u}{r} = \frac{1}{r} u^2 dr |\psi_r^m(\theta, \phi)|^2 \sin\theta d\theta d\phi$$

\Rightarrow $u(r)$ is sufficient to act like a one-dimensional wavefunction along r .

$r \in [0, \infty)$
vs. for normal one-dimensional $x \in (-\infty, \infty)$

effective Schrödinger's - equation

$$H_r = H_{0,r} + V_{eff,r}$$

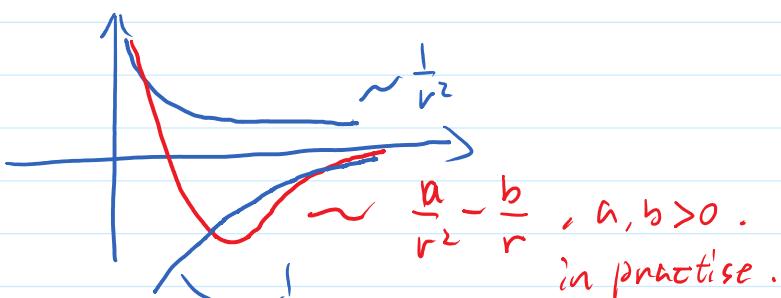
$$= \frac{P_r^2}{2mr^2} + \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] = \frac{P_r^2}{2mr^2} + V_{eff}$$

$\uparrow V_{eff.}$

if we have $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$
Coulomb potential



V_{eff} ? sketch



$\frac{\hbar^2}{2mr^2} (l(l+1)) \rightarrow$ centrifugal potential

离心势.

◦ properties of $u(r)$.

$\psi(r, \theta, \varphi)$ as a wave function.

continuous

finite

square integrable.

single value.

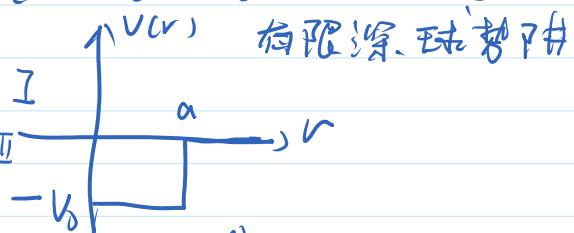
$R(r) = \frac{u(r)}{r}$, R shares the same property as wavefunction

$$\Rightarrow \boxed{\lim_{r \rightarrow 0} u(r) \rightarrow 0}$$

as we show $|R(r)|^2 dr$ represents probability,
we also need $\lim_{r \rightarrow \infty} |u(r)| \rightarrow 0$.

example 1. Spherical square well. (finite case)

$$V(r) = \begin{cases} -V_0, & r < a, \text{ section I} \\ 0, & r > a, \text{ section II} \\ V_0 > 0. \end{cases}$$



Schrödinger's equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left(\frac{\hbar^2(l(l+1)}{2mr^2} + V(r) \right) u(r) = E u(r)$$

solve for the ground state. $l=0$, $E < 0$.

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + V(r) u(r) = E u(r)$$

one dimensional finite depth square well

$$\text{section I: } -\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} - V_0 u(r) = E u(r) \Rightarrow$$

$$\text{section II} \quad -\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} = E u(r).$$

$$\text{section III} \quad \frac{du}{dr} + \frac{2Em}{\hbar^2} (V_0 + E) u = 0.$$

Section I $\frac{\partial^2 u}{\partial r^2} + \frac{2m}{\hbar^2} (V_0 + E) u = 0$.

define $K^2 = \frac{2m}{\hbar^2} (V_0 + E)$, $\begin{cases} -V_0 < E < 0 \\ V_0 + E \text{ positive.} \end{cases}$

$\frac{\partial^2 u}{\partial r^2} + K^2 u = 0$

$u = A \sin kr + C \cos kr$. $\Rightarrow u = A \sin kr$, $r < a$.

we need $\lim_{r \rightarrow 0} u \rightarrow 0$, $C = 0$

Section II $\frac{\partial^2 u}{\partial r^2} + \frac{2m}{\hbar^2} E u = 0$, $E < 0$.

define $\alpha^2 = -\frac{2mE}{\hbar^2}$

$u = B e^{-\alpha r}$, $r > a$

$$\Rightarrow u(r) = \begin{cases} A \sin kr, & r < a \\ B e^{-\alpha r}, & r > a \end{cases}$$

$$\int_0^\infty |u(r)|^2 dr = 1 \Rightarrow \int_0^a A^2 \sin^2 kr dr + \int_a^\infty B^2 e^{-2\alpha r} dr = 1$$

continuous $A \sin ka = B e^{-\alpha a}$

choose A and B , so that

$$u(r) = \begin{cases} N \frac{\sin kr}{\sin ka}, & r < a \\ N e^{-\alpha(r-a)}, & r > a. \end{cases}$$

N : normalization factor, $N = \frac{1}{\sqrt{\int_0^a \frac{\sin^2 kr}{\sin^2 ka} dr + \int_a^\infty e^{-2\alpha(r-a)} dr}}$

for the full eigenstate, we have

$$\psi(r, \theta, \varphi) = \frac{u(r)}{r} Y_l^m(\theta, \varphi)$$

$$\begin{cases} l=0 : & Y_0^0(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{\pi}} \end{cases}$$

final answer: $\begin{cases} \psi(r, \theta, \varphi) = \begin{cases} N \frac{\sin kr}{\sin ka} \cdot \frac{1}{r} - \frac{l}{\sqrt{4\pi}}, & r < a \\ N e^{-\alpha(r-a)} \cdot \frac{1}{r}, & r > a. \end{cases} \end{cases}$

$$\left| \frac{N e^{-\alpha(r-a)}}{r} \cdot \frac{1}{\sqrt{4\pi}}, r \geq a. \right.$$

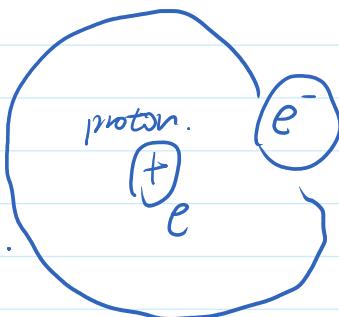
N as above.

$$Y_0^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{1}{\pi}},$$

$$\begin{cases} Y_1^- = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin\theta e^{-i\phi}, & Y_1^+ = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin\theta e^{i\phi}, \\ Y_1^0 = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos\theta. \end{cases}$$

Hydrogen atom.

try to solve for eigen wavefunction
and eigen energy of a H-atom.



We ignore spin for e^- and proton for now.

$$H = \frac{P_{\text{proton}}^2}{2m_{\text{proton}}} + \frac{P_e^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_e - \vec{r}_{\text{proton}}|}$$

apply techniques from classical mechanics.

define $\vec{r} = \vec{r}_e - \vec{r}_p$ ← relative position between e^- and proton.

$$\mu = \frac{m_e m_p}{m_e + m_p} \leftarrow \text{reduced mass}$$

$$\vec{p} = \frac{m_p \vec{P}_e - m_e \vec{P}_p}{m_p + m_e}, \quad \vec{p}_c = \vec{P}_e + \vec{P}_p, \quad M = m_e m_p / \mu.$$

$$\Rightarrow H = \frac{P_c^2}{2M} + \frac{\vec{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\vec{r}|}$$

⇒ in the center of mass frame 质心坐标.

$$H = \frac{\vec{p}^2}{2\mu} - \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}|}}_{V(r)}$$

we can apply the separation between radial and angular to the Hamiltonian.

$$M = \frac{me m_p}{me + m_p} \xrightarrow{m_p \approx 1836 me} M = \frac{me}{1 + \frac{me}{m_p}} \approx me$$

$$\Rightarrow -\frac{\hbar^2}{2\mu} \vec{\nabla}^2 \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E \psi.$$

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi) = \frac{u(r)}{r} Y_l^m(\theta, \phi)$$

we apply effective Schrödinger's equation of $u(r)$

$$\Rightarrow \left(-\frac{\partial^2}{\partial r^2} + \frac{(l(l+1))}{r^2} - \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{r} + \frac{2\mu E}{\hbar^2} \right) u(r) = 0$$

Q: If we need a bound state, what do we need for E ? V_{eff.} effective potential.

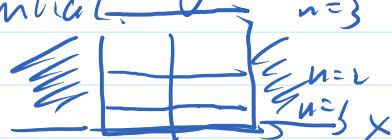
A: $E < 0$.



how is the eigen energy spacing for bound states?

① We have 1-D infinitely deep potential.

$$V = \begin{cases} +\infty, & x > a \text{ or } x < -a \\ 0, & -a < x < a. \end{cases}$$

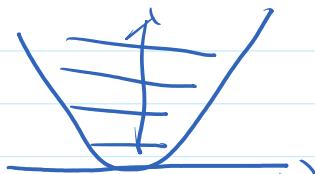


- E_n ~ a.
 - b. E_n ∝ n² ✓
 - c. E_n ∝ n³



② 1-D harmonic oscillator

$$V = \frac{1}{2} m \omega^2 x^2$$



④ 1-D harmonic oscillator

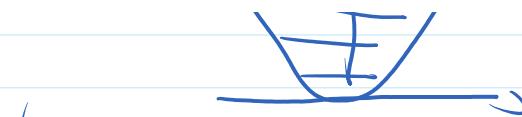
$$V = \frac{1}{2} m\omega^2 x^2$$

a. $E_n \propto n + \frac{1}{2}$

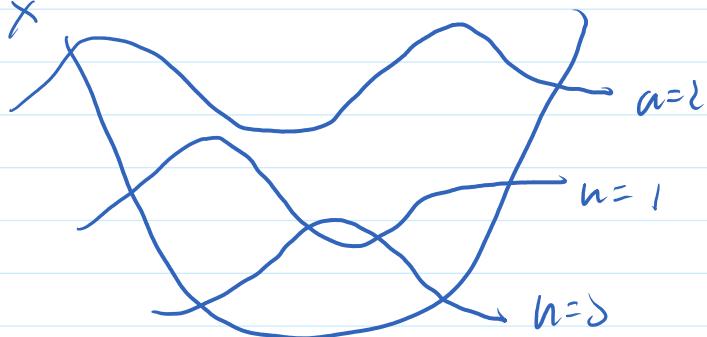
E_n

b.
c.

$$\frac{n^2}{n^3}$$

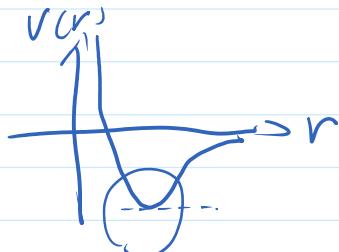


$$E_n = \hbar\omega(n + \frac{1}{2}), n=0,1,2,\dots$$



③ H-atom

$$V_{eff} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2mr^2} (1/r)$$

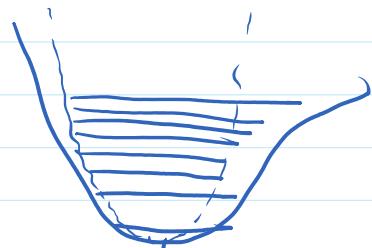


ask, minimum of V_{eff} ?

$$V_{eff} = 0 \Rightarrow r_{min}$$

then expand V_{eff} around r_{min}

$$V_{eff} = V_{min} + \frac{1}{2}kr^2 + \frac{1}{2}\eta r^3 + \dots$$



even more relaxed \Rightarrow the harmonic oscillator,

$$E_n \propto -\frac{1}{n^2}$$

$$\left(-\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} - \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{r} + \frac{2mE}{\hbar^2} \right) u(r) = 0$$

first is to redefine the coordinates

$$\left(\frac{r}{\epsilon} \right)^2 = \frac{2mE}{\hbar^2}, \text{ let } \begin{cases} x = r\epsilon \\ x \text{ is unitless.} \end{cases}$$

$$\Rightarrow \frac{d^2u}{dx^2} + \left[-\frac{1}{4} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{\epsilon x} - \frac{1}{\epsilon^2 x^2} \right] u = 0.$$

$\frac{4\pi\epsilon_0 h^2}{me^2} \sim \text{unit of length. effective Bohr radius.}$

$$a_0 = \frac{4\pi\epsilon_0 h^2}{me^2}, \quad a'_0 = \frac{4\pi\epsilon_0 h^3}{me^2}, \quad \text{let } \boxed{\lambda = \frac{z}{a'_0 E}} \sim \text{unitless}$$

$$\frac{d^2u}{dx^2} + \left[-\frac{1}{4} + \frac{\lambda}{x} - \frac{l(l+1)}{x^2} \right] u = 0.$$

$$\lim_{x \rightarrow 0} u = 0, \quad \lim_{x \rightarrow \infty} u = 0.$$

method: asymptotic

let $x \rightarrow 0$, dominant part is $-\frac{l(l+1)}{x^2}$

$$\frac{d^2u}{dx^2} - \frac{l(l+1)}{x^2} u = 0 \rightarrow u \xrightarrow{x \rightarrow 0} x^{l+1}$$

$x \rightarrow \infty$, dominant part is $-\frac{1}{4}$

$$\frac{d^2u}{dx^2} - \frac{1}{4} u = 0 \rightarrow u \xrightarrow{x \rightarrow \infty} e^{-x/2}$$

$$u = \underbrace{e^{-x/2}}_{\text{asymptotic part}} \underbrace{x^{l+1}}_{\text{stirling}} F(x) \xrightarrow{\text{polynomial}}$$

$$\Rightarrow xF'' + (2l+2-x)F' - (l+l-\lambda)F = 0.$$

define $F = \sum_i c_i x^i \Rightarrow$ formular between different orders of c_i

$$\Rightarrow (i+1)(2l+2+i)c_{i+1} = (l+l-\lambda+i)c_i.$$

\Rightarrow need to truncate at certain i

we have $\lambda = l+l+i \geq l$

$$\lambda = \frac{2}{a'_0 E} = l+l+i = n \text{ as integer}$$

$$\lambda = \frac{1}{a_0} E = l + 1 + \ell = n \text{ as integer}$$

$$\Rightarrow \text{with } \left\{ \begin{array}{l} \left(\frac{E}{2}\right)^2 = \frac{2\mu |E|}{h^2} \\ E = \frac{2}{na_0} \end{array} \right. \Rightarrow |E| = \frac{h^2}{2\mu a_0^2} - \frac{1}{n^2}$$

$E < 0$ for bound state.

we have

$$E_n = -\frac{h^2}{2\mu a_0^2} - \frac{1}{n^2}$$

$$n \geq l+1, \text{ or } l \leq n-1$$

$$l = 0, 1, 2, \dots, n-1 \text{ for H-atom.}$$

n : primary quantum number

choice of l depends on n .

$E_n = -\frac{1}{n^2}$, nothing to do with l , so for each n ,

there are $l=0 \sim n-1$ different states, so it's n -fold degenerate so far.

choice of n, l, m

$$\text{on } n-1 - (l+1)$$

\Rightarrow for a given n , overall degeneracy is

$$\sum_{l=0}^{n-1} \sum_{m=-l}^{l+1} = \sum_{l=0}^{n-1} 2(l+1) = n(n+1) + n = n^2.$$

$$\psi = \frac{u(r)}{r} Y_l^m(\theta, \varphi) \Leftrightarrow u(x) = e^{-x/2} x^{l+1} F(x)$$

$$\psi(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2^n (n+l)!}} e^{-\frac{R}{na_0}} \left(\frac{2R}{na_0}\right)^l F_{nl}(na_0) Y_l^m(\theta, \varphi)$$

$$C_0' = \frac{4\pi \epsilon_0 \hbar^2}{m_e m_p}, \quad \mu = \frac{m_e m_p}{m_e + m_p}.$$

$$G_0' = \frac{4\pi\epsilon_0 t_0^2}{\mu e^2}, \quad \mu = \frac{m_e m_p}{m_e + m_p}.$$

Bohr radius $0.5 \text{ \AA} \sim 5 \times 10^{-11} \text{ m}$

$$E = -\frac{\hbar^2}{2\mu G_0'^2} \cdot \frac{1}{n^2}, \quad \text{quantum number } n, l, m_l.$$