Last Time

① Wrote down the Schrödinger Equation in 3D

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

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

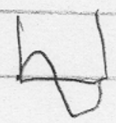
$$= \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2} \right]$$

Try Separation of variables

$$\psi_{n\ell m} = R_{n\ell}(r)\, \Theta_{\ell m}(\theta)\, \Phi_m(\varphi)$$

① $n-1$ = total number of excitations angular or radial $= 0, 1, 2, 3 \ldots$

0 excitations



1 excitation

② ℓ = total number of angular excitations $= 0, 1, \ldots n-1$

angular momentum

$\leftarrow \quad \overline{L^2} = \ell(\ell+1)\hbar^2 \qquad L_x^2 + L_y^2 + L_z^2$

(3) $(n-1)-l$ = total number radial excitations

(4) $m = 0, \pm 1, \pm 2 \ldots l$

$\overline{L}_z$ = angular momentum around z-axis $= m\hbar$

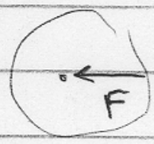
$|m|$ = total number of azimuthal excitations

$+$ = counter clockwise

$-$ = clockwise

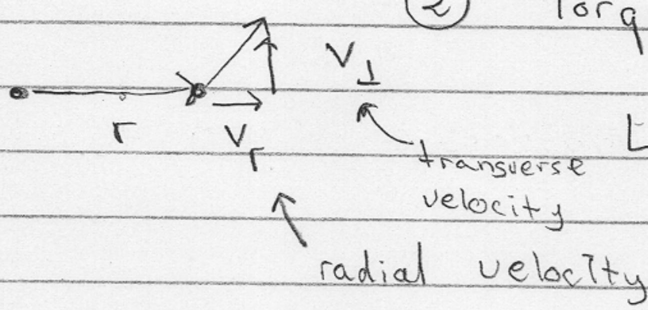
Lets Study Classical Orbits:

① Energy is Constant



$$KE + PE = E$$

② Torque $\vec{F} \times \vec{r} = 0$



$$L = m v_\perp r = \text{constant}$$

So

$$KE = \frac{1}{2} m v_r^2 + \frac{1}{2} m v_\perp^2$$

$$= \frac{1}{2} m v_r^2 + \frac{1}{2} \frac{(m v_\perp r)^2}{m r^2}$$

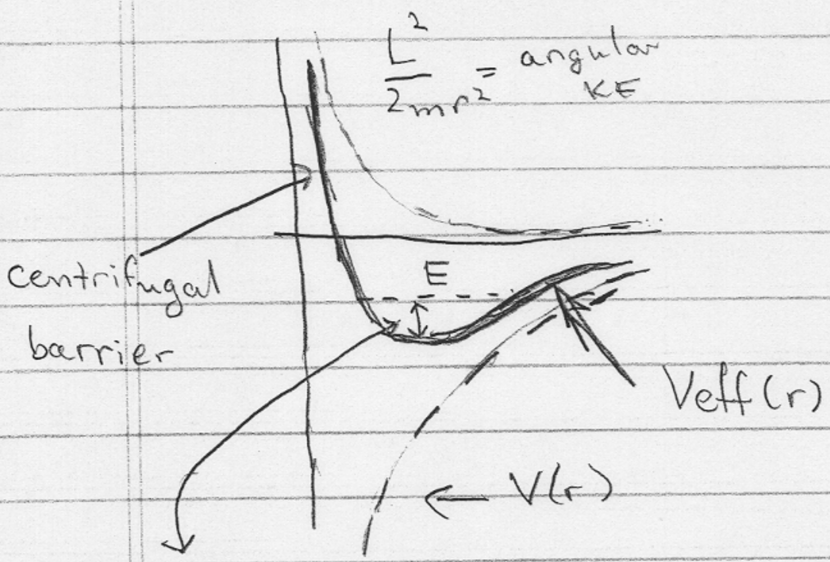
$$= \frac{1}{2} m v_r^2 + \frac{L^2}{2 m r^2}$$

Thus we see that

$$\frac{1}{2} m v_r^2 + \underbrace{\frac{L^2}{2 m r^2} + V(r)}_{\equiv V_{eff}(r)} = E$$

$\equiv V_{eff}(r)$ effective potential

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$



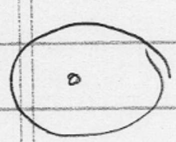
$$\text{radial KE} = \frac{1}{2} m v_r^2 = E - V_{eff}(r)$$

Note the minimum happens

$$\frac{\partial V_{eff}}{\partial r} = -\frac{L^2}{mr^3} + \frac{\partial V}{\partial r} = 0$$

$$\frac{L^2}{mr^3} = \frac{\partial V}{\partial r}$$

$$\frac{m v_\perp r^2}{r^3} = |\vec{F}|$$



$$m\frac{v^2}{r} = |\vec{F}|$$

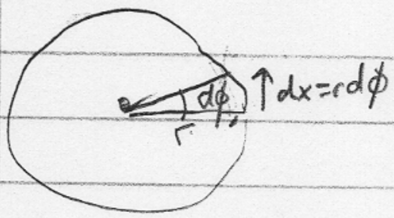
Condition for circular orbit

Now return to quantum Mechanics

$$(KE + PE)\psi = E\psi$$

KE = radial KE + angular KE ← how to define

(1)



$$L_z = r\,p$$

$$= r\left(-i\hbar \frac{d}{dx}\right)$$

$$= \cancel{r}\left(\frac{-i\hbar}{\cancel{r}} \frac{d}{d\phi}\right)$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$ ← angular momentum is an agular derivatives

(2)

$$\vec{L} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \vec{r} \times \vec{p} \qquad p_x = -i\hbar \frac{\partial}{\partial x}$$

After a considerable amount of algebra (See Appendix M)

Find

$$\mathbb{L}^2 = L_x^2 + L_y^2 + L_z^2$$

$$\mathbb{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial}{\partial\phi^2} \right]$$

Cool:

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

$$= \underbrace{-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right)}_{\text{radial KE}} + \underbrace{\frac{\mathbb{L}^2}{2mr^2}}_{\text{angular KE}}$$

Then the Schrödinger Equation becomes

$$\frac{1}{\psi} (KE + PE) \psi = E \psi$$

$$(**) \quad \frac{1}{\psi} \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\mathbb{L}^2}{2mr^2} + V(r) \right] \psi = E$$

Now try separation of Variables

$$* \quad \psi = R \underbrace{\Theta \, \Phi}_{\equiv Y(\theta, \varphi)}$$

known as a Spherical harmonic

Subsituting (*) into the Schrödinger Equation (**) and going through the usual separation of variables (Hmwrk)

radial Schrödin

$$\left[\left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \underbrace{\mathcal{E}_{\Omega}}_{\text{angular KE}} + V(r) \right] R = E R$$

radial wave fcn

$$\underbrace{\left(\frac{\mathbb{L}^2}{2mr^2} \right)}_{\substack{\text{angular} \\ \text{KE}}} \underbrace{Y(\theta, \varphi)}_{\substack{\text{angular} \\ \text{wave - fcn}}} = \mathcal{E}_{\Omega} \, Y(\theta, \varphi)$$

lives on sphere!

Very much like particle in box $\mathcal{E}_{\Omega}$ (the angular KE) must be adjusted so that the wave fcn $Y(\theta, \varphi)$ fits an integral number of wavelengths on the sphere

Find $\mathcal{E}_\Omega$ (angular KE) is discrete

$$\mathcal{E}_\Omega = \frac{l(l+1)\hbar^2}{2mr^2} \qquad \text{compare} \qquad PIB = \frac{\hbar^2\pi^2}{2mL^2} n^2$$

$$= \frac{\overline{L^2}}{2mr} \qquad \overline{L^2} = l(l+1)\hbar^2$$

where $l = 0, 1, \ldots, n-1$

So we have

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \underbrace{\frac{l(l+1)\hbar^2}{2mr^2} + V(r)}_{V^l_{eff}(r)}\right] R_{nl} = E_{nl} R_{nl}$$

Finally motivated by $= \mathcal{P}(r) = 4\pi r^2 |R|^2$ define

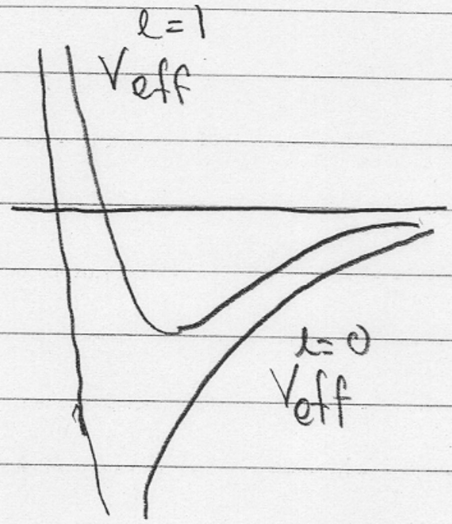
$u_{nl} \equiv \sqrt{4\pi}\, r R_{nl}$ so $\mathcal{P}(r) = |u_{nl}|^2$, find

that (Hmwrk)

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V^l_{eff}(r)\right] u_{nl}(r) = E_{nl} u_{nl}$$

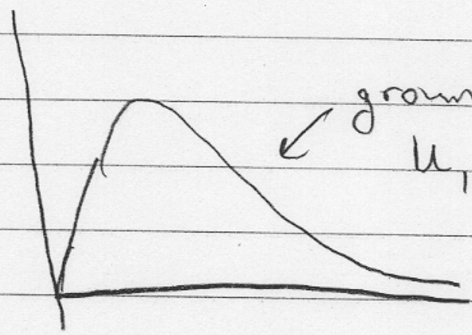
Effective one 1-d Schrödinger Equation

Picture $\quad V_{eff}^{l} = \frac{l(l+1)\hbar^2}{2mr^2} + V(r)$



Now (see slides)

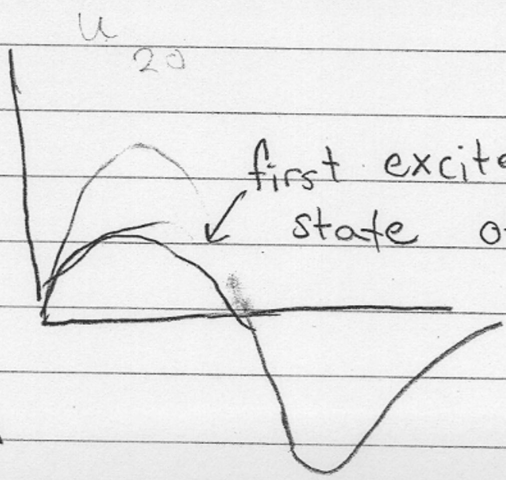
u_{10}



ground state of $l=0$ potential

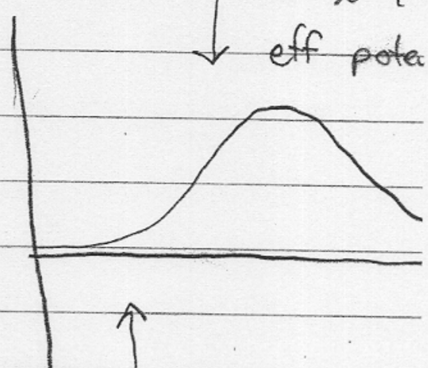
u_{10}

u_{20}



first excited state of $l=0$ pot.

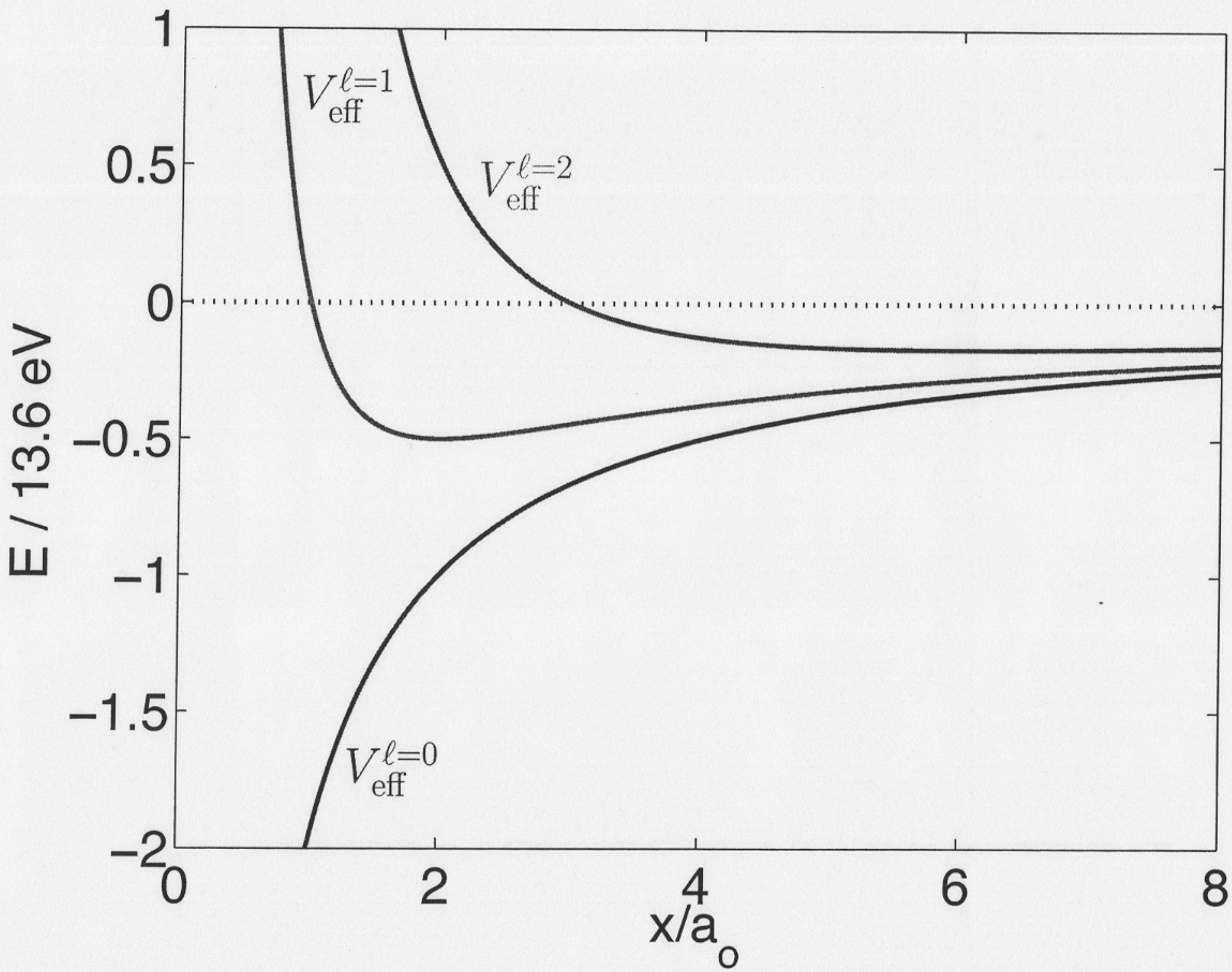
ground state of $l=1$ eff pote



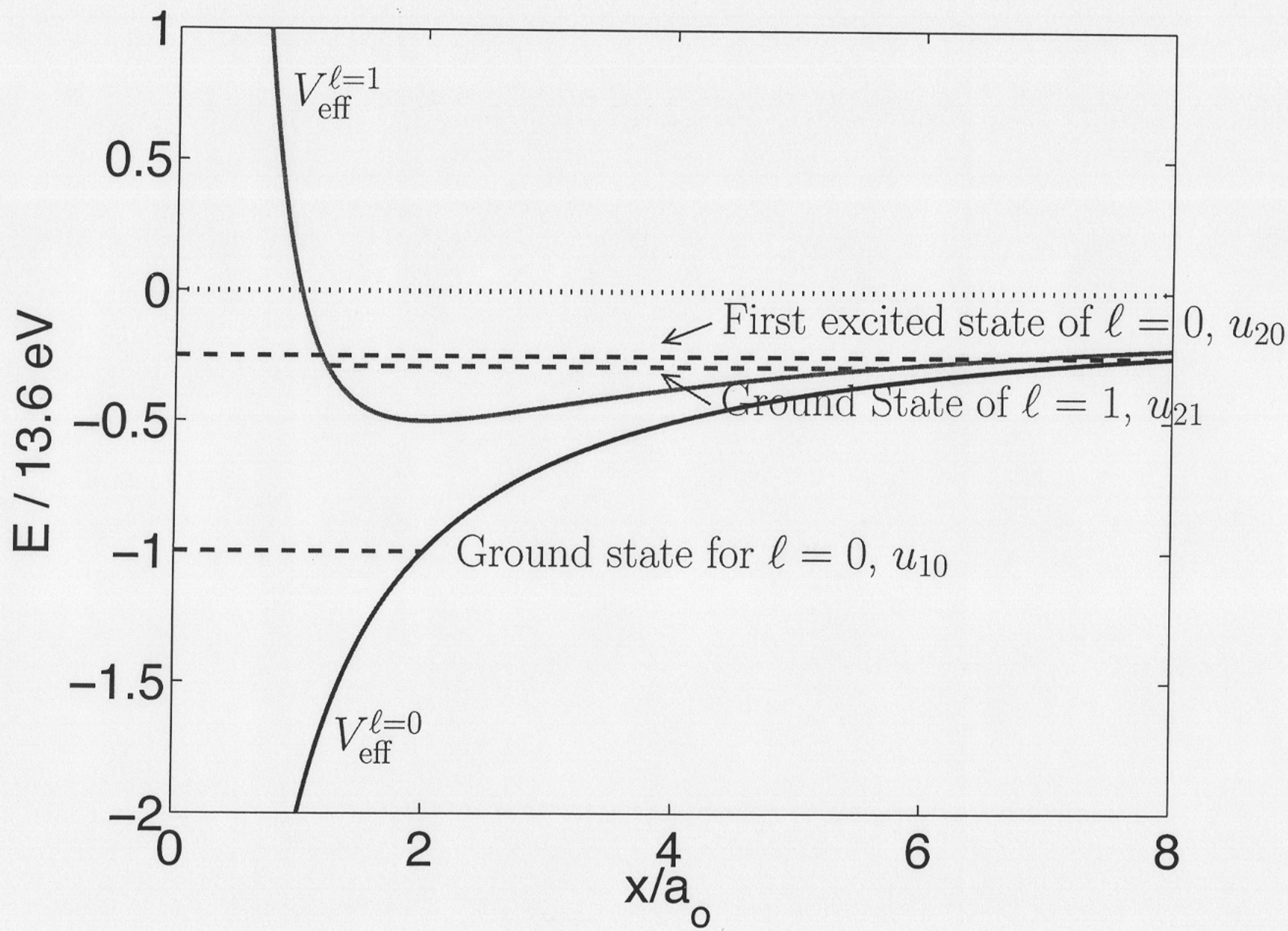
one radial excitation, no angular

one agular ex but no radial

The effective potential for various l



The $(n = 1, \ell = 0)$ and the $(n = 2, \ell = 0)$ and $(n = 2, \ell = 1)$ states



The $(n = 1, \ell = 0)$, the $(n = 2, \ell = 1)$ and the $(n = 3, \ell = 2)$ states

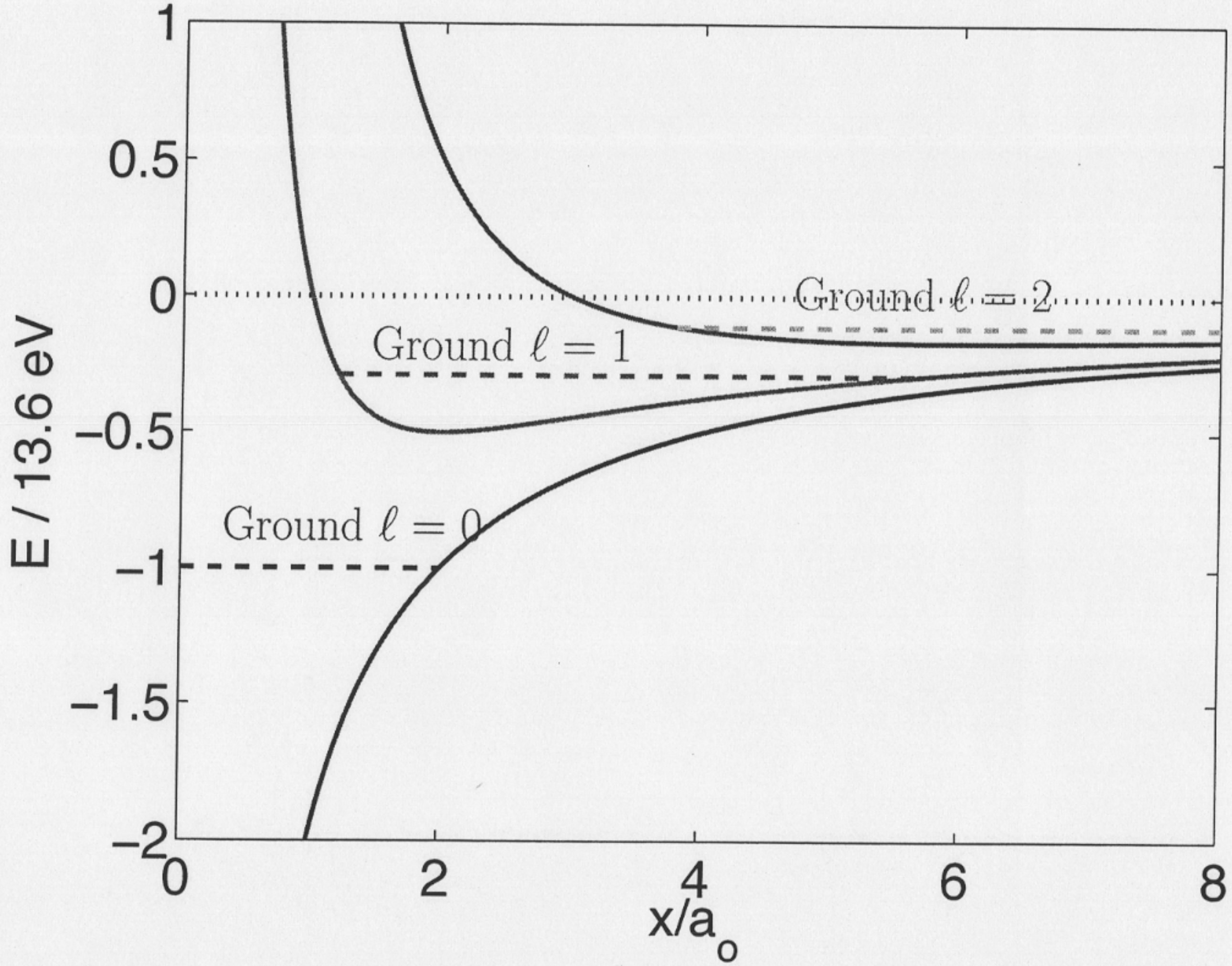
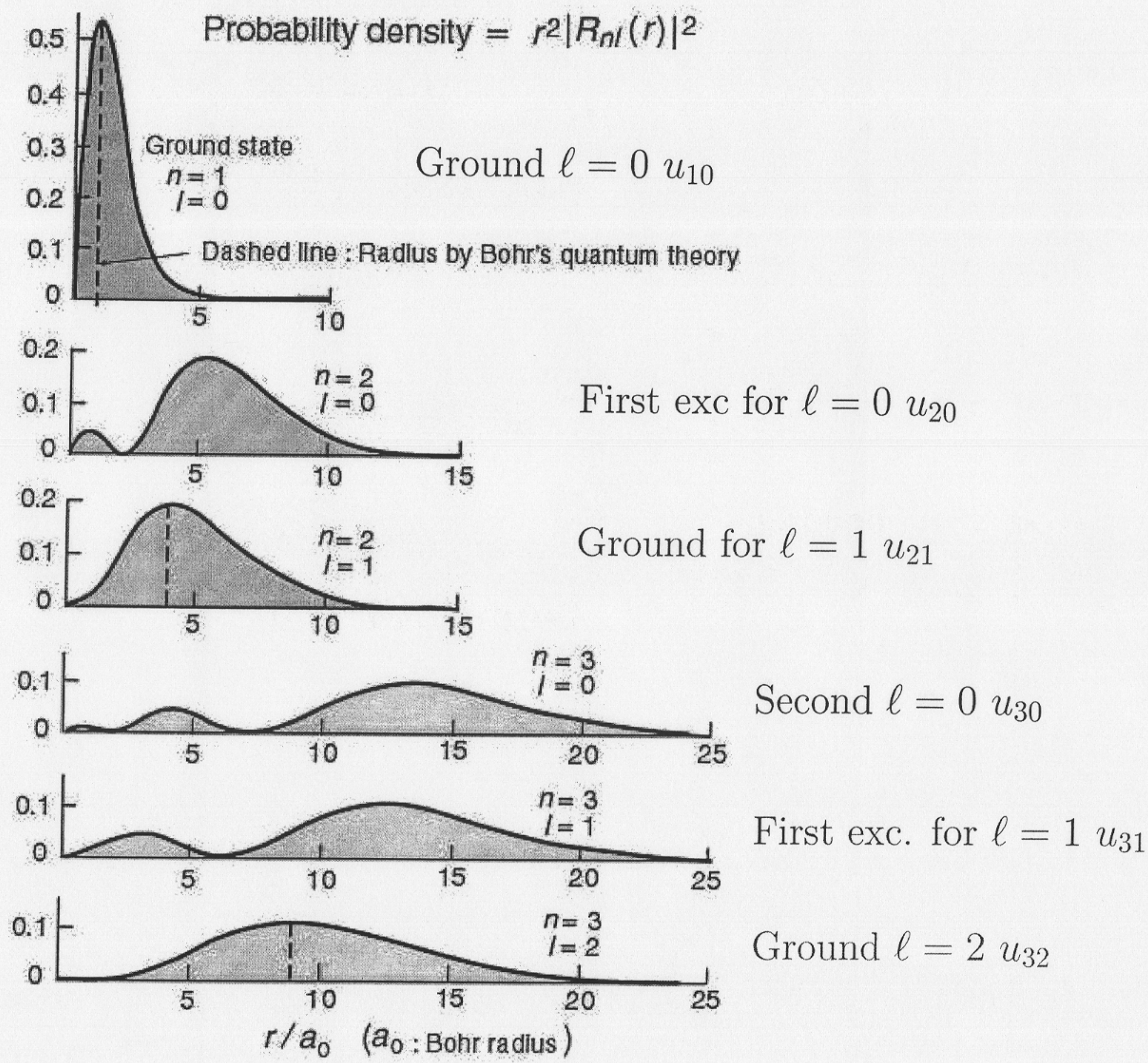


Fig. (C)


Probability density = $r^2|R_{nl}(r)|^2$
Ground state
$n = 1$
$l = 0$
Dashed line : Radius by Bohr's quantum theory
Ground $\ell = 0$ u_{10}
$n = 2$
$l = 0$
First exc for $\ell = 0$ u_{20}
$n = 2$
$l = 1$
Ground for $\ell = 1$ u_{21}
$n = 3$
$l = 0$
Second $\ell = 0$ u_{30}
$n = 3$
$l = 1$
First exc. for $\ell = 1$ u_{31}
$n = 3$
$l = 2$
Ground $\ell = 2$ u_{32}
r/a_0 (a_0 : Bohr radius)