Ch. 10 Radial Bound States

$$\hat{H}_{rad}|R_{n\ell}\rangle = E_n|R_{n\ell}\rangle \quad \Longleftrightarrow$$

$$\boxed{-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right]R(r)+\left[V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]R(r) = E\,R(r)}$$

<u>Looks like 1-d QM</u> <u>but</u>:

(1) $0 \le r < \infty$ (<u>not</u> $-\infty < x < \infty$) (*)

(2) KE different (<u>not</u> $-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$)

(3) norm. of wv. function not same:

$$1 = \int d^3r\,|\psi|^2 = \int_0^\infty r^2dr\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi}d\varphi\,|\psi|^2$$

$$= \left(\int_0^\infty r^2dr\,|R(r)|^2\right)\cdot\left(\underbrace{\int \sin\theta\,d\theta\,d\varphi\,|Y|^2}_{=1}\right)$$

chose

$$\Rightarrow \boxed{1 = \int_0^\infty r^2dr\,|R|^2} \qquad \left(\underline{\text{not}} \int_{-\infty}^{\infty}dx\,|\psi|^2 = 1\right).$$

Make look more alike by defining

$$u(r) \equiv r \cdot R(r)$$

Norm ⇒ $1 = \int_0^\infty dr\, |u|^2$ ← like 1-d

(*) ⇒ ... $$\boxed{\underbrace{-\frac{\hbar^2}{2\mu} u''}_{\text{like 1-d}} + \underbrace{\left(V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right)}_{\text{eff pot'l}} u = E u}$$ (★)

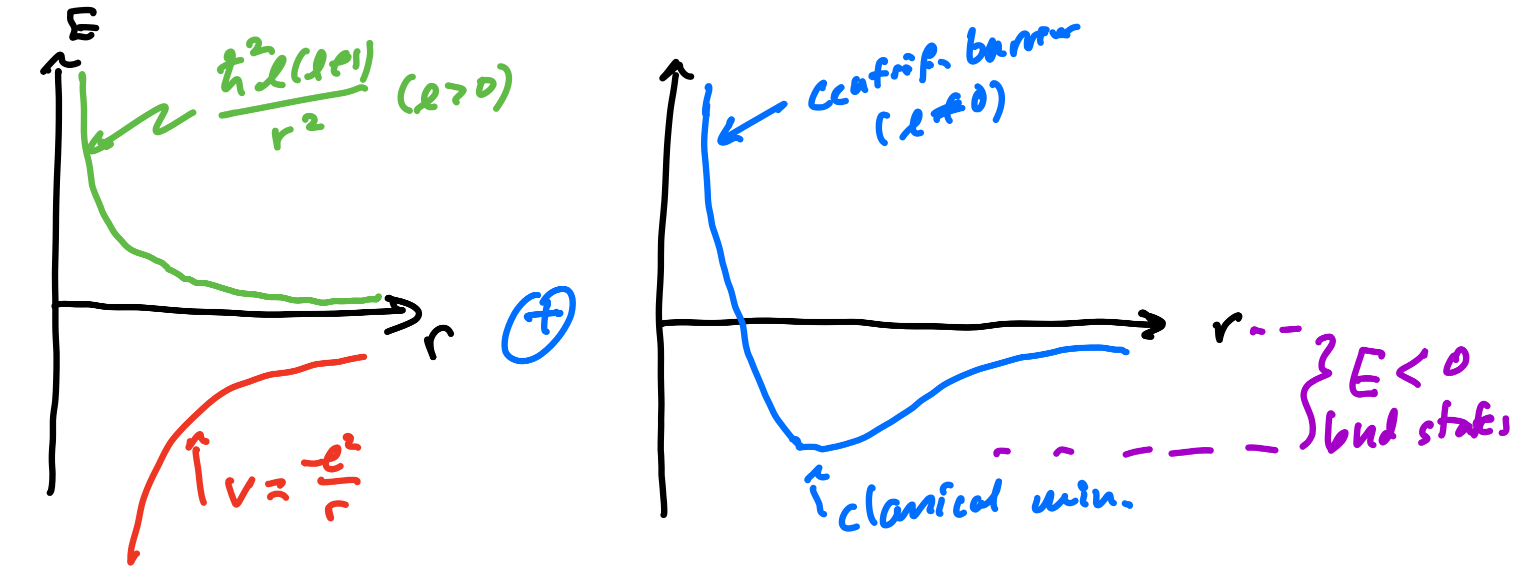
<u>Ex:</u> <u>Spherical well</u> $V(r) = \begin{cases} 0 & r > a \\ -V_0 & r \le a \end{cases}$

... Finite # B.S.; nucleon decay → $V(r) = -V_0 \delta(r-a)$

Limit: <u>Rigid rotor</u> ... model of 2-atom molecule.

<u>3d simple harmonic oscillator</u> ... small oscillations around pot'l minima

<u>Ex:</u> Coulomb pot'l $V = \frac{-e^2}{r}$



$l \gg 1$ → shallower ⇒ $E_{bnd} \to 0^-$

$l = 0$ → $-\infty$ ⇒ $E_{bnd} \to -\infty$??

Back to solving diffeq. (A)

$$\hat{H}_{rad}|R_{n\ell}\rangle = E_n|R_{n\ell}\rangle \rightsquigarrow R_{n\ell}(r) \equiv \frac{1}{r}u_{n\ell}(r)$$

$$\text{w/} \int_0^\infty dr\, |u_{n\ell}|^2 = 1.$$

$$\& \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + V(r)\right] u(r) = E_n u(r)$$

Rewrite as

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{eff}(r)\right] u = E_n u$$

$$\boxed{V_{eff}(r) \doteq \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + V(r)}$$

Or, more simply as

$$\mathcal{D} u = E_n u$$

$$\boxed{\mathcal{D} \doteq -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{eff}(r)}$$

To solve a differential equation, we need boundary conditions:

@ $r=0$ & $r=\infty$

$r=\infty$: To be normalizable $\Rightarrow \lim_{r\to\infty} u(r) = 0$. ✓

$r=0$: ?? Comes from hermiticity of $\hat{H}_{rad} = \hat{H}_{rad}^{\dagger}$:

$$\Rightarrow \langle u_1|\hat{H}_{rad}|u_2\rangle^* = \langle u_2|\hat{H}_{rad}^{\dagger}|u_1\rangle = \langle u_2|\hat{H}_{rad}|u_1\rangle$$

$$\langle u_1|\hat{H}_{rad}|u_2\rangle^* = \left(\int_0^\infty dr\, u_1^* \mathcal{D} u_2\right)^* = \int_0^\infty dr\, (\mathcal{D} u_2^*)\, u_1 = \int_0^\infty dr \left[-\frac{\cancel{\hbar}^2}{2\mu}\frac{d^2 u_2^*}{dr^2} u_1 + \cancel{V_{eff}(r)\, u_2^* u_1}\right]$$

$$\stackrel{?}{=}$$

$$\langle u_2|\hat{H}_{rad}|u_1\rangle = \int_0^\infty dr\, u_2^* \mathcal{D} u_1 = \int_0^\infty dr \left[-\frac{\cancel{\hbar}^2}{2\mu} u_2^* \frac{d^2 u_1}{dr^2} + \cancel{V_{eff}(r)\, u_2^* u_1}\right]$$

$$\Rightarrow \int_0^\infty dr\, (u_2^*)''\, u_1 \stackrel{?}{=} \int_0^\infty dr\, u_2^*\, u_1''$$

$\int$-by-parts l.h.s. $\Rightarrow$
(twice)

$$\int_0^\infty dr\,(u_2^*)''u_1 = -\int_0^\infty dr\,(u_2^*)'u_1' + (u_2^*)'u_1\Big|_0^\infty$$

$$= +\int_0^\infty dr\, u_2^* u_1'' - u_2^* u_1'\Big|_0^\infty + (u_2^*)'u_1\Big|_0^\infty$$

$$\Rightarrow \boxed{\left(\frac{du_2^*}{dr}u_1 - u_2^*\frac{du_1}{dr}\right)\Big|_0^\infty = 0} \quad \forall\, u_1, u_2 \in \text{Hilb. spa.}$$

$u, \frac{du}{dr} \to 0$ as $r\to\infty$ (∞ BC) $\Rightarrow$

$$\therefore \boxed{(u_2^*)'(0)\; u_1(0) = u_2^*(0)\; u_1'(0) \quad \forall\, u_1, u_2 \quad (r=0 \text{ BC}).}$$

$\hookrightarrow$ generally $\exists$ many BC's on $u(0)$
that satisfy this, e.g.

$$\alpha u'(0) = \beta u(0) \qquad \alpha, \beta \in \mathbb{R}$$

$\alpha = 0 \Rightarrow u(0) = 0$ "Dirichlet"
$\beta = 0 \Rightarrow u'(0) = 0$ "Neumann"
$\alpha/\beta \neq 0 \Rightarrow$ "Mixed"

- What is right α/β? (or other? ...)
- Need to look at $\hat{H}_{rad}|u\rangle = E|u\rangle$ eqn:

$$\lim_{r\to 0}\left\{-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu}\frac{u}{r^2} + V(r)u = Eu\right.$$

Assume: $V(r) = \mathcal{O}\left(\frac{1}{r^{2-\varepsilon}}\right)$ w/ $\varepsilon > 0$

$\left(= \frac{\alpha}{r^{2-\varepsilon}} + \text{less singular terms e.g. } \frac{1}{r}, 1, r \ldots \right)$

(True of Coulomb: $V(r) = -\frac{e^2}{r}$ ✓)

Then $V(r)u$ & $E_n u$ terms are less important than other 2 terms:

$$\frac{d^2u}{dr^2} \sim \frac{u}{r^2},$$

so as $r \to 0$, have approximately

$$u'' \approx \frac{\ell(\ell+1)}{r^2} u$$

$\Rightarrow \quad u \propto r^{\alpha}$ with

$$\alpha(\alpha-1) r^{\alpha-2} = \ell(\ell+1) r^{\alpha-2}$$

$$\Rightarrow \quad \alpha^2 - \alpha - \ell(\ell+1) = 0$$

$$\Rightarrow \quad \boxed{\alpha = \begin{cases} \ell+1 \\ \text{or} \\ -\ell \end{cases}}$$

If $l > 0$:

$$u \propto \begin{cases} r^{l+1} + O(r^{l+2}) \\ \text{or} \\ r^{-l} + O(r^{-l+1}) \end{cases}$$

But $u \propto r^{-l}$ not allowed:

$$\int_0^\infty dr\, |u|^2 \sim \int_0 dr \frac{1}{r^{2l}} = \infty \text{ if } l \geq 1/2$$

$\Rightarrow$ not normalizable!

$\therefore$ Must have $u \propto r^{l+1}$ $\Rightarrow$

$u(0) = 0$ (Dirichlet) for $l > 0$.

If $l = 0$:

$$u \propto \begin{cases} r + O(r^2) \to \text{Dirichlet BC} \\ \text{or} \\ 1 + O(r) \to \text{Mixed BC} \end{cases}$$

Both possibilities are allowed! But we need B.C. for whole Hilbert space:

$\therefore$ If $\exists$ any state w/ $l > 0$ $\Rightarrow$ $\boxed{\text{Dirichlet BC}}$

$$\therefore \boxed{r = 0 \text{ BC:} \quad u(0) = 0}.$$

(more precisely: $\lim_{r \to 0} u(r) \propto r^{l+1}$.)

So now have Diff Eq + BC's : can solve for given choice of pot'l $V(r)$:

Hydrogenic Atom :

Nucleus charge Ze & electron charge $-e$

$$V(r) = -\frac{Ze^2}{r}$$

$$(Z=1 \leftrightarrow H,\ Z=2 \leftrightarrow He^+,\ Z=3 \leftrightarrow Li^{++}, \dots)$$

Bnd state energies $E<0$ $\therefore$ $E = -|E|$.

Want to solve

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} - E_n\right) u_{n,\ell} = 0$$

w/ BC $\lim_{r\to 0} u_{n\ell}(r) \propto r^{\ell+1}$

(1) Define dim'len variables

convenient

$$\rho := \sqrt{\frac{8\mu|E_n|}{\hbar^2}} \cdot r \qquad \lambda := \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E_n|}}$$

$$\left(\Rightarrow \frac{d}{dr} = \sqrt{\frac{\hbar^2}{8\mu|E_n|}}\,\frac{d}{d\rho}\right) \quad \cdots\!> \quad (\div\, 4|E_n|)$$

$$\boxed{\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0} \qquad \boxed{\begin{matrix} u(\infty)=0 \\ u(0)=0 \end{matrix}}$$

solve for u & λ.

(2) Try series sol'n $u(\rho) = \rho^{\ell+1}(c_0 + c_1\rho + c_2\rho^2 + \cdots)$

... complicated ...

(3) Look at $\rho \to \infty$ limit $\left(\frac{1}{\rho}, \frac{1}{\rho^2}\right)u \ll \frac{1}{4}u$

$$\Rightarrow \quad u'' \approx \frac{1}{4}u \Rightarrow u \approx Ae^{-\rho/2} + \cancel{Be^{+\rho/2}}$$

$\rho = \infty$ BC

$$\Rightarrow \quad u = \rho^{\ell+1} e^{-\rho/2} F(\rho)$$ & plug in:

$$\Rightarrow \quad F'' + \left(\frac{2\ell+2}{\rho} - 1\right)F' + \left(\frac{\lambda - \ell - 1}{\rho}\right)F = 0$$

(not obviously simpler ...)

(4) Now try series sol'n $F = c_0 + c_1\rho + c_2\rho^2 + \cdots = \sum_{k=0}^{\infty} c_k \rho^k$

Plug in & collect terms in powers of ρ ...

$$0 = \sum_{k=0}^{\infty} \left\{(k+2\ell+2)(k+1)c_{k+1} - (k-\lambda+\ell+1)c_k\right\}\rho^{k-1}$$

$$\Rightarrow \quad \boxed{\frac{c_{k+1}}{c_k} = \frac{k+\ell+1-\lambda}{(k+1)(k+2\ell+2)}} \quad \forall k \quad \xrightarrow[k\to\infty]{} \frac{1}{k}$$

recursion rel'tn : solves F.

$$\therefore \lim_{k\to\infty} c_{k+1} \approx \frac{1}{k!}$$

$$\therefore \lim_{\rho\to\infty} F \approx \sum_k \frac{1}{k!}\rho^k \approx e^{+\rho}$$

$$\therefore \lim_{\rho\to\infty} u \approx e^{-\rho/2} \cdot e^{+\rho} \approx e^{+\rho/2} \to \infty$$ #!?

(5) Sol'n: series must terminate!

If there is a k_{max} such that $C_{k_{max}+1} = 0$

then recursion $\Rightarrow$ $C_n = 0$ $\forall\, n > k_{max}$.

$0 = C_{k_{max}+1} \Rightarrow k_{max} + l + 1 - \lambda = 0$

$$\Rightarrow \boxed{\lambda = k_{max} + l + 1 \equiv n} \in \{1, 2, 3, \ldots\}$$

$l, k_{max} \in \{0, 1, 2, \ldots\} \Rightarrow$

Recall $\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} \Rightarrow$

$$\boxed{E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}} \quad n = 1, 2, 3, \ldots$$

Degeneracy: since $n = k_{max} + l + 1$

& $l, k_{max} \in \{0, 1, 2, \ldots\}$

- for each n, have: $l \in \{0, 1, 2, \ldots, n-1\}$
- & for each l have: $m \in \{-l, -l+1, \ldots, l\} \Rightarrow \# = 2l+1$

$\therefore$ Each E_n have $\sum_{l=0}^{n-1} (2l+1) = n^2$ degenerate states!

H atom $Z = 1 \Rightarrow$

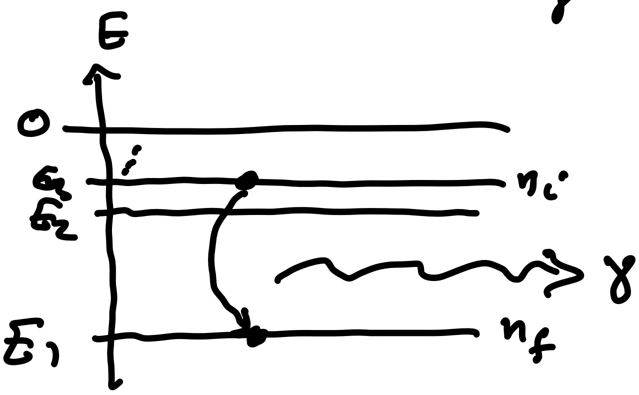
$$E_n = -\frac{\mu c^2 \cdot Z^2 \cdot \alpha^2}{2n^2} \quad \text{where}$$

$$\begin{cases} \mu c^2 \approx m_e c^2 \approx 0.5\ \text{MeV} \\ \alpha^2 \equiv \left(\frac{e^2}{\hbar c}\right)^2 \approx \left(\frac{1}{137}\right)^2 \approx 5\times 10^{-5} \end{cases} \Rightarrow \frac{\mu c^2 \alpha^2}{2} \doteq Ry \approx 13.6\,\text{eV}$$

"Rydberg energy"

So $|E_n| \ll m_e c^2$, so non-relativistic. ✓

Spectral lines: emission of light (photon) when e^- changes energy level



w/ $E_\gamma = E_{n_i} - E_{n_f} = \frac{\mu c^2 \alpha^2}{2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

$\quad ||$

$\hbar\omega = h\nu$

$$\nu = \frac{1}{\lambda c} \quad \Longrightarrow \quad \frac{1}{\lambda} = \underbrace{\frac{\mu c \alpha^2}{2h}}_{\equiv R_H}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$\equiv R_H$ "Rydberg constant"

$\approx 10^7\,\text{m}^{-1}$

Energy eigenfunctions

$$\langle \vec{r} | n\ell m \rangle = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi) = \frac{u_{n\ell}(r)}{r} Y_{\ell m}(\theta,\varphi)$$

$$\rho \equiv \sqrt{\frac{8\mu|E|}{\hbar^2}} \cdot r = \frac{2Z}{n}\frac{r}{a_0} \qquad a_0 \equiv \frac{\hbar}{\mu c\alpha} \approx .5\,\text{Å} \quad \text{"Bohr rad."}$$

Ground state: $n=1 \Rightarrow \ell=0 \Rightarrow m=0$ ← single state

$$u_{1,0}(\rho) = \rho e^{-\rho/2} c_0, \quad \text{Normalize} \Rightarrow$$

$$\begin{cases} R_{1,0}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \\ Y_{0,0}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} \end{cases}$$

$$\text{Prob}\left(e^- @ (r,\theta,\varphi) \pm (dr, d\theta, d\varphi)\right) = \underbrace{r^2 \sin\theta\, dr\, d\theta\, d\varphi}_{r^2 dr\, d\Omega} \cdot |\psi(r,\theta,\varphi)|^2$$

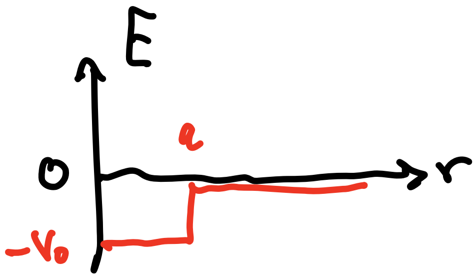
$$\therefore \text{Prob}(e^- @ r \pm dr, \text{ any } \theta,\varphi) = \int d\Omega \;\text{''}$$

$$= r^2 dr\, |R|^2 \overbrace{\int d\Omega\, |Y_{\ell m}|^2}^{1}$$

$$\therefore \langle r^s \rangle = \int_0^\infty r^2 dr \cdot r^s \cdot |R|^2$$

Other central potentials

- ## Finite spherical well



$$V(r) = \begin{cases} 0 & r > a \\ -V_0 & r < a \end{cases}$$

- Good model of deuteron $= p^+ + n$ bound by strong nuclear force.

- Similar to 1d square well, but if $a^2 V_0 < \left(\frac{\pi}{2}\right)^2 \frac{\hbar^2}{2\mu}$

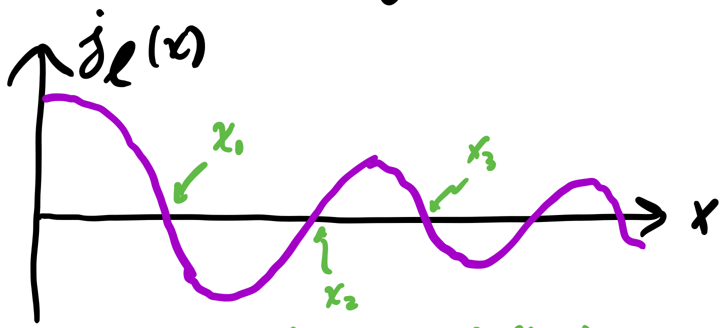
  then no bound states!
  This is unlike the 1d situation where there always existed at least one bound state.

- ## Infinite spherical well

- $V_0 \to \infty$ limit of above.

- Find $R(r) \sim$ "spherical Bessel fncs"

$R_{n\ell}(r) \propto r \cdot j_\ell(kr)$ "spherical Neumann fnc."



$$\begin{cases} j_0(x) = \dfrac{\sin x}{x} \\ j_1(x) = \dfrac{\sin x}{x^2} - \dfrac{\cos x}{x} \\ \vdots \end{cases}$$

$k_1 = \frac{x_1}{a}$ then $j_\ell(k_1 r) = 0$ @ $r = a$, ... $k_n = \frac{x_n}{a}$

- Boundary condition at $r = a$:

$$j_\ell(ka) = 0$$

$\Rightarrow$ determines discrete set of values of $k = \{k_{1,\ell}, k_{2,\ell}, \ldots, k_{n,\ell}, \ldots\}$

& $$E_{n\ell} = \frac{\hbar^2 k_{n\ell}^2}{2\mu}$$

- Unlike H-atom, the degeneracy of the $E_{n\ell}$ level is just $2\ell+1$.

- 3d Spherical Harmonic Oscillator

$$H = \frac{P^2}{2\mu} + \frac{\mu\omega_0^2}{2} r^2 \qquad \left(\begin{array}{l} P^2 = P_x^2 + P_y^2 + P_z^2 \\ r^2 = x^2 + y^2 + z^2 \end{array}\right)$$

- Solve using spherical symmetry:

$$H|nlm\rangle = E_n|nlm\rangle$$
$$L^2|nlm\rangle = \hbar^2 l(l+1)|nlm\rangle$$
$$L_z|nlm\rangle = \hbar m|nlm\rangle$$

so $\langle\vec{r}|nlm\rangle = R_{nl}(r)\,Y_{lm}(\theta,\varphi)$

& get usual radial equation for R_{nl}

& find series solution terminates for

$$E_n = \left(n+\tfrac{3}{2}\right)\hbar\omega_0 \qquad n \in \{0,1,2,3,\ldots\}$$

and all $l \le n$ with $l-n$ even.

- E.g.: $n=0 \Rightarrow l=0 \Rightarrow \#m=1 \Rightarrow$ degeneracy 1

  $n=1 \Rightarrow l=1 \Rightarrow \#m=3 \Rightarrow$ degeneracy 3

  $n=2 \Rightarrow l=2 \Rightarrow \#m=5$ or $l=0 \Rightarrow \#m=1$ $\Rightarrow$ degeneracy 6

  $n=3 \Rightarrow l=3 \Rightarrow \#m=7$ or $l=1 \Rightarrow \#m=3$ $\Rightarrow$ degeneracy 10

  $n=4 \Rightarrow l=4 \Rightarrow \#m=9$ or $l=2 \Rightarrow \#m=5$ or $l=0 \Rightarrow \#m=1$ $\Rightarrow$ degeneracy 15

  $\vdots$

$\Rightarrow$ Degeneracy of level n $= \underbrace{\frac{(n+2)(n+1)}{2}}$

- Alternatively: solve in cartesian coordinates

$$H = \underbrace{\left(\frac{P_x^2}{2\mu} + \frac{\mu\omega_0^2}{2}x^2\right)}_{\overset{\shortparallel}{H_x}} + \underbrace{\left(\frac{P_y^2}{2\mu} + \frac{\mu\omega_0^2}{2}y^2\right)}_{\overset{\shortparallel}{H_y}} + \underbrace{\left(\frac{P_z^2}{2\mu} + \frac{\mu\omega_0^2}{2}z^2\right)}_{\overset{\shortparallel}{H_z}}$$

All commute, so simultaneously diagonalize:

$$H_x |n_x\, n_y\, n_z\rangle = E_x^{(n_x)} |n_x\, n_y\, n_z\rangle$$
$$H_y |n_x\, n_y\, n_z\rangle = E_y^{(n_y)} |n_x\, n_y\, n_z\rangle$$
$$H_z |n_x\, n_y\, n_z\rangle = E_z^{(n_z)} |n_x\, n_y\, n_z\rangle$$

$$\Rightarrow \quad H\, |n_x, n_y, n_z\rangle = E\, |n_x, n_y, n_z\rangle$$

$$\text{w/} \quad E = E_x + E_y + E_z$$

- In position basis, write

$$\langle \vec{r}\, | n_x n_y n_z\rangle \doteq X(x)\, Y(y)\, Z(z) .$$

Then H_x eigenvalue equation becomes

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\frac{\mu\omega_0^2}{2}x^2\right)X(x)\cancel{Y(y)}\cancel{Z(z)}=E_x X(x)\cancel{Y(y)}\cancel{Z(z)}$$

Same as 1d harmonic oscillator!

$$\therefore \quad E_x=(n_x+\tfrac{1}{2})\hbar\omega_0 \qquad n_x\in\{0,1,2,\dots\}$$

- Exactly same for Y, Z, therefore

$$E=E_x+E_y+E_z=(n_x+n_y+n_z+\tfrac{3}{2})\hbar\omega_0$$
$$=(n+\tfrac{3}{2})\hbar\omega_0 \qquad n\in\{0,1,2,\dots\}$$
$$(n\doteq n_x+n_y+n_z)$$

- Degeneracies:

$0=n=n_x+n_y+n_z \Rightarrow (n_x,n_y,n_z)=(0,0,0) \Rightarrow$ degen. $=1$ ✓

$1=n=n_x+n_y+n_z \Rightarrow (n_x,n_y,n_z)=\begin{Bmatrix}(1,0,0)\\(0,1,0)\\(0,0,1)\end{Bmatrix} \Rightarrow$ degen. $=3$ ✓

$2=n=n_x+n_y+n_z \Rightarrow \vec{n}=\begin{Bmatrix}(2,0,0) & (1,1,0)\\(0,2,0) & (1,0,1)\\(0,0,2) & (0,1,1)\end{Bmatrix} \Rightarrow$ degen $=6$ ✓

$3=n=n_x+n_y+n_z \Rightarrow \vec{n}=\begin{Bmatrix}(300) & (210) & (120) & \\(030) & (021) & (012) & (111)\\(003) & (102) & (201) & \end{Bmatrix} \Rightarrow$ degen $=10$ ✓