$$i\hbar \frac{\partial \psi(t,\vec{x})}{\partial t} = \hat{H}\psi(t,\vec{x}) \quad , \quad \hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\vec{x})$$

$$\psi(t,\vec{x}) = e^{-iEt/\hbar}\phi(\vec{x})$$

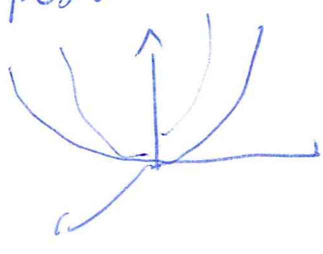
$$i\hbar\left(-\frac{iE}{\hbar}\right)\phi(\vec{x})e^{-iEt/\hbar} = e^{-iEt/\hbar}\hat{H}\psi(\vec{x})$$

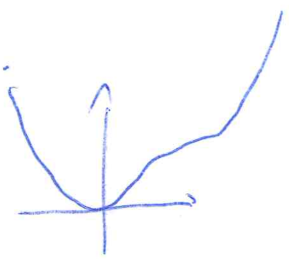
$$\hat{H}\phi(\vec{x}) = E\phi(\vec{x})$$

This is an eigenvalue equation for the operator $\hat{H}$. $\psi(x)$ is the eigenfunction with energy E.

The spectrum depends on the problem under study.

For "binding" potentials one "usually" has a discrete spectrum:





$\phi_n(\vec{x})$ with $n = 0, 1, 2, \ldots$

$\{\phi_n(\vec{x})\}$ is a "basis". If one determines $\phi_n(\vec{x})$ one has 'solved' the associated QM problem.

At $t=0$ I have: $\psi(0,\vec{x})$.

In general, I can write $\psi(0,\vec{x})$ as:

$$\psi(0,\vec{x}) = \sum_{n=0}^{\infty} c_n \phi_n(\vec{x})$$

But then, I immediately know the full solution at each t:

$$\psi(t,\vec{x}) = \sum_{n=0}^{\infty} c_n e^{-iE_n t/\hbar} \phi_n(\vec{x})$$

Namely:

$$i\hbar \frac{\partial \psi}{\partial t} = \sum_{n=0}^{\infty} c_n E_n e^{-iE_n t/\hbar} \phi_n = \sum_n c_n H\left(e^{-iE_n t/\hbar} \phi_n\right)$$

$$= H \sum_n c_n e^{-iE_n t/\hbar} \phi_n$$

$$= H\psi$$

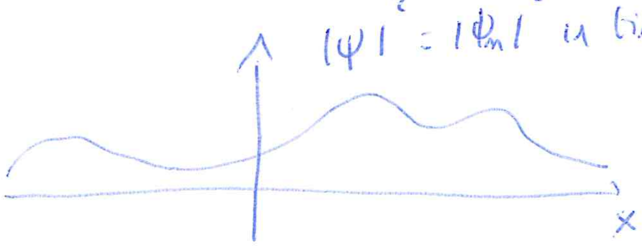
$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = H\psi \qquad \forall t.}$$

PROPERTY OF STATIONARY STATES:

- $\psi(t,\vec{x}) = e^{-iE_n t/\hbar}\,\phi_n(\vec{x})$

$\rho(t,\vec{x}) = |\psi(t,\vec{x})|^2 = |\phi_n(\vec{x})|^2$ indip. on t! $(= \rho(\vec{x})$ only!)

$|\psi|^2 = |\phi_n|^2$ is time-independent.



- $\hat{A}$ observable:

$$\langle \hat{A} \rangle_{\psi(t,\vec{x})} = \int d^3x\, \psi^*(t,\vec{x})\, \hat{A}\, \psi(t,\vec{x})$$

$$= \int d^3x\, \phi_n(\vec{x})\, \hat{A}\, \phi_n(\vec{x}) = \langle \hat{A} \rangle_{\phi_n(\vec{x})}$$

is also time-independent.

- $\int d^3x\, \rho(\vec{x}) = 1 \mapsto \psi(|\vec{x}| \to \infty) = 0$

- $\phi(\vec{x})$ is everywhere cont.
- $\partial_{x_i}\phi(\vec{x})$ is almost everywhere continuous.

One-dimensional-problem

$\vec{x} \mapsto x$

$$\psi(t,x) = e^{-iEt/\hbar}\,\phi(x)$$

$$\boxed{\begin{gathered} H\phi = E\phi \\ \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\phi(x) = E\,\phi(x) \end{gathered}}$$

$\phi \equiv \phi_n(x)$ for a binding problem.

General properties:

1) if $\{\phi_n(x)\}$ is discrete $\mapsto$ no energy degenerecy

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\phi(x) = E\,\phi(x)$$

ϕ_1, ϕ_2 solution.

$$W = \phi_1\frac{d\phi_2}{dx} - \phi_2\frac{d\phi_1}{dx} = C \quad (=0 \text{ for } x \mapsto \pm\infty).$$

$$\frac{\frac{d\phi_2}{dx}}{\phi_2} = \frac{\frac{d\phi_1}{dx}}{\phi_1} \rightarrow \phi_2 = K\phi_1.$$

Intuitively, it is obvious... "n" determines the solution, there is no other quantity which can do that...

Proof:

$$-\frac{\hbar^2}{2m}\phi_1'' + V\phi_1 = E\phi_1$$

$$-\frac{\hbar^2}{2m}\phi_2'' + V\phi_2 = E\phi_2$$

$$\psi_2\psi_1'' - \psi_1\psi_2'' = 0$$

Ergo: $\psi_2\psi_1' - \psi_1\psi_2' = \text{const} = 0\,!$

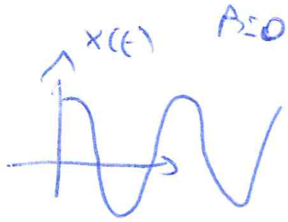
- $\phi_n(x)$ can be chosen as real

(time invariance of QM, also a bad beast....)

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

$$m\ddot{x} = -\omega^2 x \qquad \ddot{x} + \omega^2 x = 0$$

$$x(t) = a\cos(\omega t + \beta) \qquad a \in \mathbb{R}$$



$$\langle x \rangle = 0 \;,\; \langle x^2 \rangle = \frac{a^2}{2}$$

$$E = \frac{1}{2} m \omega^2 a^2 = \text{const.}$$

All values between 0 and ∞ are allowed.

All energies are permitted.

Harmonic oscillators → QM

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

$H\psi = E\,\psi(x)$ $\quad \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\psi = E\psi$

→ ansatz that $\psi(x \pm \infty) = 0$

$$(*) \quad \psi_n = N_n \, e^{-\frac{1}{2}(\alpha x)^2} \, H_n(\alpha x)$$

$$\alpha = \sqrt{\frac{m\omega}{\hbar}}$$

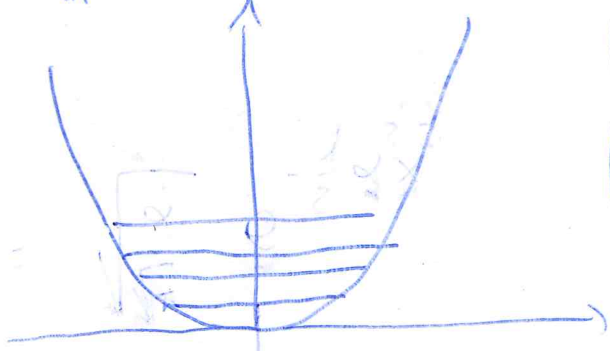
→ Hermite polinomal

If you plug $(*)$ into the stationary eq. you find:

$$H'' - 2(\alpha x) H' + (\varepsilon - 1) H = 0$$

⇒ $H_n(\alpha x)$ are the so-called Hermite polinomals.

⇒



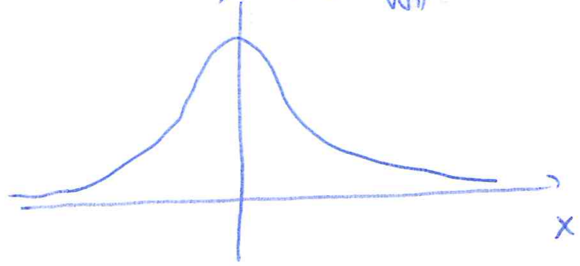
$E = 0$ is not possible.

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega}$$

$n = 0, 1, 2, \ldots$

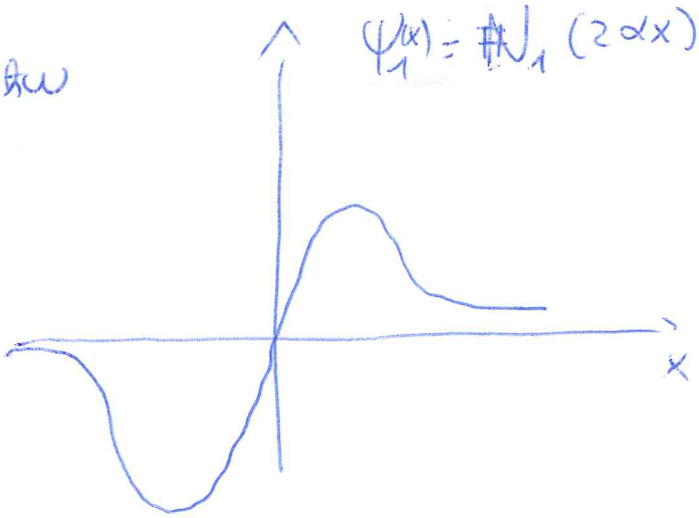
Only some values are allowed. Discrete spectrum.

$E_0 = \frac{1}{2}\hbar\omega$ $\quad \psi_0 = \sqrt{\frac{\alpha}{\sqrt{\pi}}}\, e^{-\frac{1}{2}\alpha^2 x^2}$ $\quad \int_{-\infty} |\psi_0|^2 dx = 1$



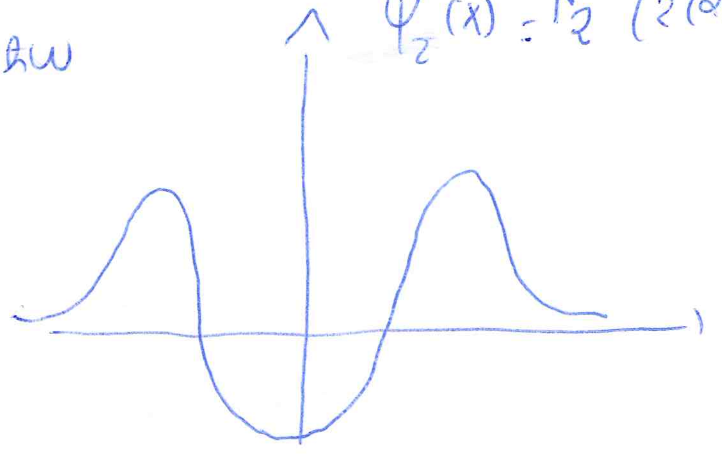
even
$\psi_0(-x) = \psi_0(x)$

$E_1 = \frac{3}{2}\hbar\omega$ $\quad \psi_1(x) = N_1 (2\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$ $\quad N_1 \wedge \int_{-\infty}^{\infty} |\psi_1(x)|^2 dx = 1$



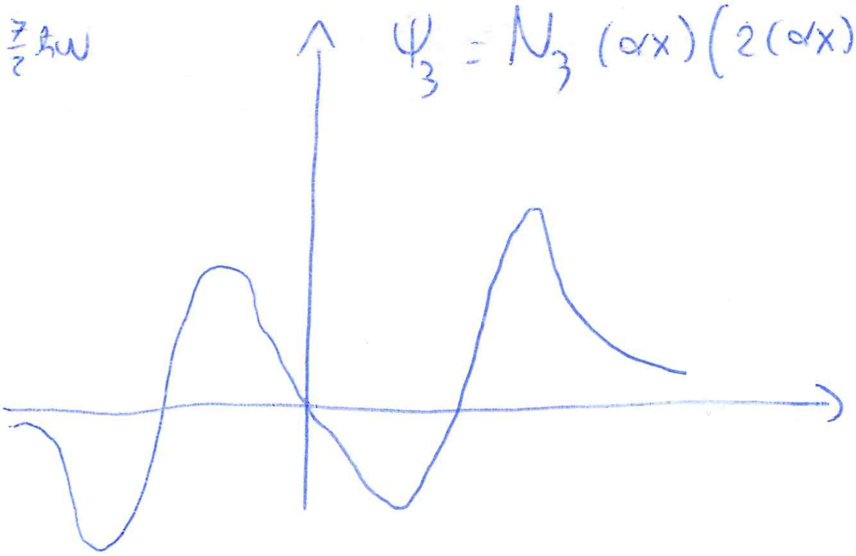
odd

$E_2 = \frac{5}{2}\hbar\omega$ $\quad \psi_2(x) = N_2 \left(2(\alpha x)^2 - 1\right) e^{-\frac{1}{2}\alpha^2 x^2}$



even
$\psi_2(-x) = \psi_2(x)$

$E_3 = \frac{7}{2}\hbar\omega$ $\quad \psi_3 = N_3 (\alpha x)\left(2(\alpha x)^2 - 3\right) e^{-\frac{1}{2}\alpha^2 x^2}$

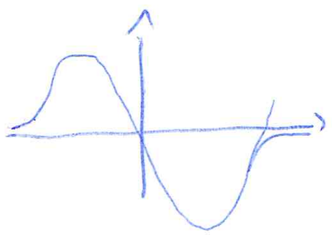


odd

- $\psi_0(x)$ is the ground state. It is the minimal energy but is not zero energy...

[$E_0 = 0$ is not possible. Namely, one would have $\Delta x < \infty$, $\Delta p = 0$ $\to$ one would violate the uncertainty relation]

- quantized spectrum: photon absorption and emission.

- 

$\psi_1(x)$ $\to$ contrary to intuition, it is not in the middle...

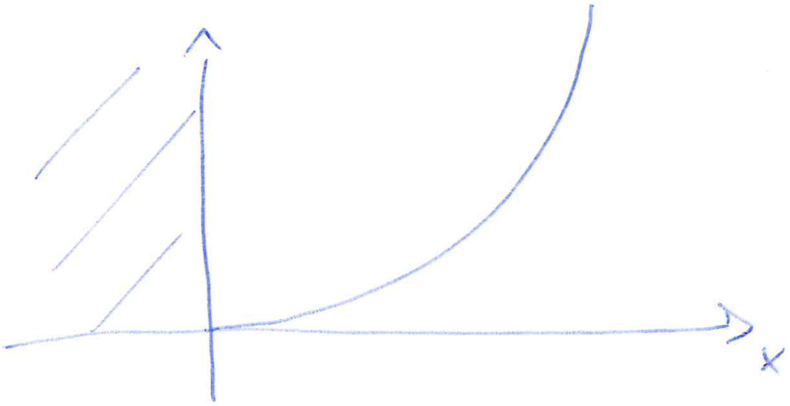
- $\begin{cases} \psi_0, \psi_2, \psi_4, \ldots \to \text{even} \\ \psi_1, \psi_3, \psi_5, \ldots \to \text{odd} \end{cases}$

This is general for every binding potential with $V(x) = V(-x)$.

- "$\hbar\omega$" very small for macroscopic oscillators. It looks as it were continuous!!!

exercise without solving

$$V(x) = \begin{cases} \frac{1}{2} m\omega^2 x^2 & x \geq 0 \\ \infty & x < 0 \end{cases}$$



$\psi(0) = 0$

Ergo, only the odd part of the spectrum survives.

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 1, 3, 5$$

$$\boxed{E_k = \left(2k + 1 + \frac{1}{2}\right)\hbar\omega} \qquad k = 0, 1, 2, \ldots$$

From 1 dim to 3 dim : a special simple case.

$$V(\vec{x}) = V_1(x) + V_2(y) + V_3(z)$$

$$H = -\frac{\hbar^2}{2m}\left(\partial_x^2 + \partial_y^2 + \partial_z^2\right) + V(\vec{x}) = H_1(x) + H_2(y) + H_3(z)$$

$$H_1 \phi_1(x) = E_1 \phi_1(x) \qquad \phi_{1,n}(x)$$

$$H_2 \phi_2(y) = E_2 \phi_2(y) \qquad \phi_{2,k}(y)$$

$$H_3 \phi_3(z) = E_3 \phi_3(z) \qquad \phi_{3,r}(z)$$

$$\boxed{\psi_{nkr}(x,y,z) = \phi_{1,n}(x)\, \phi_{2,k}(y)\, \phi_{3,r}(z)}$$

is a solution of the whole Schr. eq $H\psi = E\psi$

with energy

$$\boxed{E_{nkr} = E_{1,n} + E_{2,k} + E_{3,r}}$$

If we have:

$$V(x,y,z) = \frac{1}{2} m\omega_1^2 x^2 + \frac{1}{2} m\omega_2^2 y^2 + \frac{1}{2} m\omega_3^2 z^2$$

The spectrum is given by

$$E_{nkr} = \hbar\omega_1 \left(n + \frac{1}{2}\right) + \hbar\omega_2 \left(k + \frac{1}{2}\right) + \hbar\omega_3 \left(r + \frac{1}{2}\right)$$

The ground state is given by

$$E_0 = E_{000} = \frac{1}{2}\left(\hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3\right)$$

$\rightarrow$ INTUITIVE

(The wf is the product of 3 wfs).

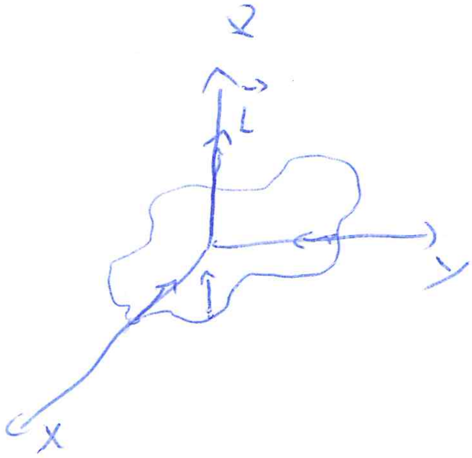
(Quantum field theory:
$E_0 = \infty$, infinity of oscillators with all possible frequencies)

$$E = \frac{m}{2}(\dot x^2 + \dot y^2 + \dot z^2) + V(r)$$

$$\vec L = \vec r \times \vec p = \text{const.}$$

let us choose $z = 0$, x and $y \neq 0$.

$$\begin{cases} x = r\cos\theta \\ y = r\sin\theta \end{cases}$$ Polar coordinates



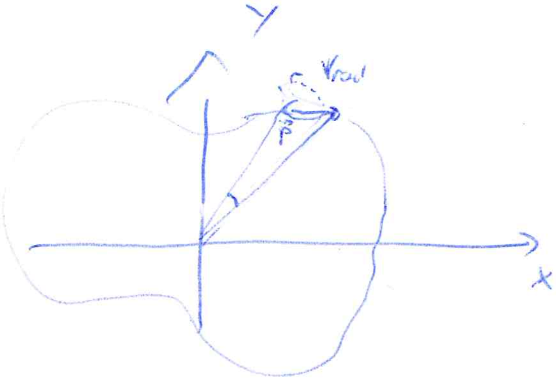
$$|\vec L| = r m v \sin\varphi_{\vec r, \vec v} = \text{const.}$$

$$\dot x = \dot r\cos\theta - r\sin\theta \cdot \dot\theta$$
$$\dot y = \dot r\sin\theta + r\cos\theta\,\dot\theta$$

$$\dot x^2 + \dot y^2 = \dot r^2 c^2 + r^2 s^2 \dot\theta^2 + \dot r^2 s^2 + r^2 c^2 \dot\theta^2 = \dot r^2 + r^2\dot\theta^2$$

Ergo, the Energy is:

$$E = \frac{1}{2} m(\dot{r}^2 + r^2\dot{\theta}^2) + V(r) \quad (= \text{const.})$$



But:

$$|\vec{L}| = |\vec{r} \times \vec{p}| = m\, r \cdot v_{rad} =$$

$$= m r \dot{\theta} r = m r^2 \dot{\theta} = L$$

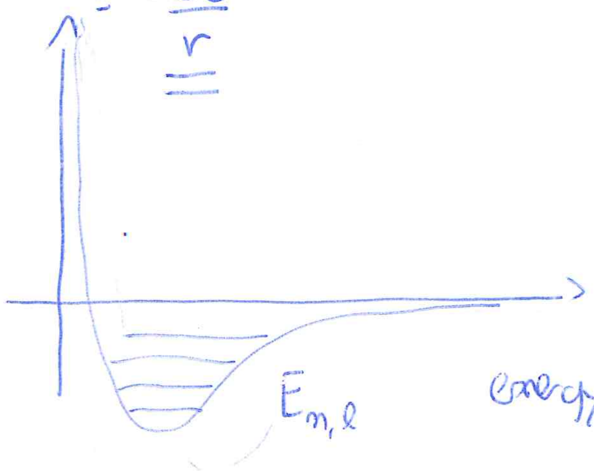
Ergo:

$$E = \frac{1}{2} m \dot{r}^2 + \frac{1}{2} \cancel{m} \cancel{r^2} \cdot \frac{L^2}{m^{\cancel{2}} r^{\cancel{4} 2}} + V(r)$$

$$= \frac{1}{2} m \dot{r}^2 + V_{eff}(r)$$

$$\boxed{V_{eff}(r) = V(r) + \frac{L^2}{2mr^2}} \xrightarrow{QM} \boxed{V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}} = V_{eff}$$

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



energy level.

n is the radial quan number.

$E \mapsto H$

$$\psi(r,\vartheta,\varphi) = \frac{\chi_{nl}(r)}{r} Y_{lm}(\vartheta,\varphi) \qquad H\psi = E\psi$$

reduces to an eq. for $\chi_{n,l}(r)$ only.

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right]\chi_{nl}(r) = E_{nl}\chi_{nl}(r)$$

$$\int_0^\infty |\chi_{nl}|^2 dr = 1$$

$$\int d^3r\, |\psi|^2 = 1 = \int_0^\infty r^2 \frac{|\chi_{nl}|^2}{r^2} \underbrace{\int \sin\vartheta\, d\vartheta\, d\varphi\, |Y_{lm}|^2}_{1} = \int_0^\infty |\chi_{nl}(r)|^2 dr = 1!!$$

$$\psi_{nlm} = \frac{1}{r}\chi_{nl}(r)\, Y_{lm}(\vartheta, \varphi)$$

$$\chi_{nl}(r) = N_{nl}\, \eta^{l+1} L^{2l+1}_{n-l-1}(\eta)\, e^{-\frac{1}{2}\eta} \qquad \eta = 2\sqrt{\frac{-2mE}{\hbar}} \cdot r$$

Examples:

$$\boxed{a_0 = \frac{\hbar^2}{me^2}}$$

$$\chi_{10} = \sqrt{\frac{Z}{a_0}}\, \frac{2r}{a_0}\, e^{-\frac{Zr}{a_0}}$$

$$\chi_{20} = \sqrt{\frac{Z}{8a_0}}\, \frac{Zr}{a_0}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$$

$n = 1, 2, \ldots$ přirozené čísla na

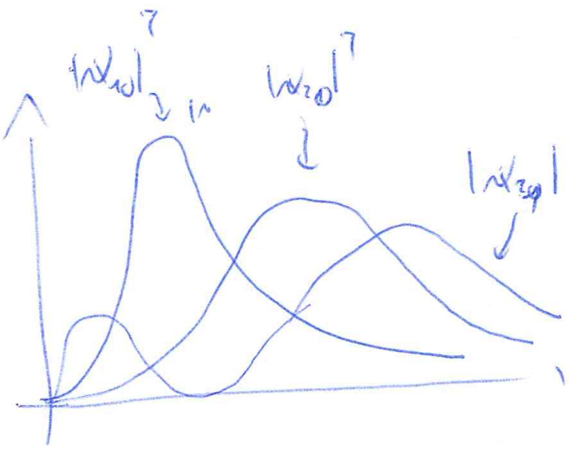
$l = 0, \ldots, n-1$

$$\chi_{21} = \sqrt{\frac{Z}{24 a_0}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{2a_0}}$$

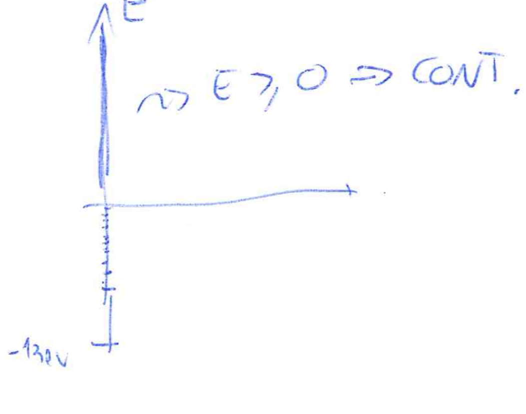
$n = 1,\ l = 0$

$n = 2 \to l = 0$

$\quad\;\; \to l = 1$



$$E_n = -\frac{Z^2 e^2}{2a_0}\frac{1}{n^2}$$



Spectrum is [illegible] of n'

$$E_{n'l} = -\frac{Z^2 e^2}{2a_0} \frac{1}{(n'+l+1)^2}$$

$n = 0, 1, 2, \dots$

$l = 0, 1, \dots$

n' is the nr of zero of $u_{n'l}(r)$ .....