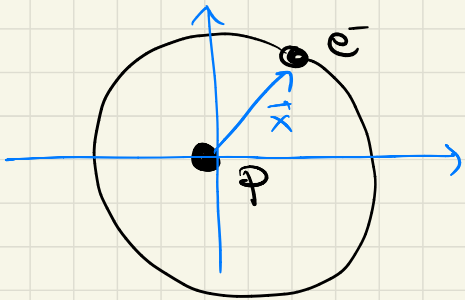
Lecture 6

Hydrogen atom

Step 1 - Construction of the Hamiltonian

Classical model $(d=3)$



- e^-, p are pointwise particles
- $m_p \gg m_e \Rightarrow$ we consider the proton fixed, at the origin of the reference frame

$$H_e^{class} = \frac{p^2}{2\mu} - \frac{e^2}{|x|}$$ ← Coulomb potential

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

Quantum Hamiltonian: $$H_e = \overbrace{-\frac{\hbar^2}{2\mu}\Delta}^{H_0} + V_e \quad \text{in } L^2(\mathbb{R}^3)$$

<u>Prop.</u> V_e is a small perturbation w.r.t. H_0, namely there exist $a \in (0,1)$ and $b > 0$ s.t. $\forall \phi \in D(H_0)$

$$(*) \quad \| V_e \phi \| \le a \| H_0 \phi \| + b \| \phi \|$$

$\Rightarrow$ By Kato-Rellich thm. $H_e, D(H_0)$ is s.a.

<u>Proof of $(*)$</u> Write $V_e = \underbrace{V_e \chi_R}_{V_1} + \underbrace{V_e (1-\chi_R)}_{V_2}$

where $\| V_1 \|^2 \le \int_{B_R} \frac{c \, d^3x}{|x|^2} \le C$, $\| V_2 \|_\infty \le \sup_{|x|>R} \frac{c}{|x|} \le C$

$$\| V_e \phi \| \le \| V_1 \phi \| + \| V_2 \phi \| \le \| V_1 \| \, \| \phi \|_\infty + \| V_2 \|_\infty \| \phi \|_2$$

$\eta > 0$

$$|\phi(x)| \le C \int d^3k \, \frac{|\hat{\phi}(k)|}{(k^2+\eta^2)} (k^2+\eta^2) \le \left[\int d^3k \, |\hat{\phi}(k)|^2 (k^2+\eta^2)^2 \right]^{1/2} \Big[\underbrace{\int \frac{d^3k}{(k^2+\eta^2)^2}}_{\eta^{-1}} \Big]^{1/2}$$

$$\le C \eta^{-1/2} \| H_0 \phi + \eta^2 \phi \| \le C \eta^{-1} \| H_0 \phi \| + C \eta^{3/2} \| \phi \|$$

For η suff. large $C\eta^{-1} < 1$ ∎

RK$_1$ In the proof of s.a. we used $V = V_1 + V_2$

$\|V_1\|_2 < \infty$, $\|V_2\|_\infty \leq \infty$

$\mathcal{H} = -\Delta + V$ $\mathcal{H}, D(\mathcal{H}_0)$ is s.a.

RK$_2$ $\mathcal{H}_e, D(\mathcal{H}_0)$ s.a. $\Rightarrow$ $e^{-i\frac{t}{\hbar}\mathcal{H}_e}$ is well defined

$\forall t$ $\Leftrightarrow$ the sol. to the Schr. eq. is well defined

Differently, in the classical case, for zero angular momentum, one can chose initial conditions s.t. the sol. of Newtons eq. $\exists$ only for a finite time (fall in the center).

Step 2 (Qualitative) Analysis of the spectrum

Prop. The spectrum of $\mathcal{H}_e$ is bounded from below

$\exists\ \lambda_0 > 0$ s.t. $\inf \sigma(\mathcal{H}_e) \geq -\lambda_0$ (stability of 1^{st} kind)

Proof. We want to show that for λ_0 large enough $(\mathcal{H}_e + \lambda_0)^{-1} = R_e(-\lambda_0)$ is bounded.

$$\| V_e\, R_0(-\lambda_0)\,\phi \| \leq a\, \| \mathcal{H}_0\, R_0(-\lambda_0)\phi \| + b\, \| R_0(-\lambda_0)\,\phi \|$$
$$\leq \left(a + \frac{b}{\lambda_0}\right) \|\phi\|$$

$\Rightarrow$ for λ_0 suff. large the op. $V_e R_0(-\lambda)$ has norm less than one.

LS

the Neumann series $\displaystyle\sum_{n=0}^{+\infty} (-1)^n \left[V_e R_0(-\lambda) \right]^n$

converges in norm to the bounded operator

$$\left[\mathbb{1} + V_e R_0(-\lambda) \right]^{-1}$$

Hence

$$(H_e + \lambda)^{-1} = \underbrace{R_0(-\lambda)}_{\substack{\text{bouded} \\ \text{since } \sigma(H_0) = [0,\infty)}} \underbrace{\left[\mathbb{1} + V_e R_0(-\lambda) \right]^{-1}}_{\substack{\text{bouded} \\ \text{for } \lambda \text{ suff} \\ \text{large}}}$$

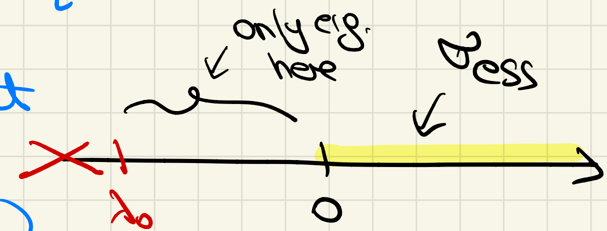
<u>Prop</u>. (Weyl's theorem) Let $A, D(A)$ and $B, D(B)$ be s.a operators in $\mathcal{H}$ and $R_A(z) = (A-z)^{-1}$, $R_B(z) = (B-z)^{-1}$.
If there exist $z \in \rho(A) \cap \rho(B)$ s.t. $R_A(z) - R_B(z)$ is a compact operator, then

$$\sigma_{ess}(A) = \sigma_{ess}(B)$$

<u>Show</u> If λ suff. large and $V_e = \underset{L^2}{\underset{\cap}{V_1}} + \underset{L^\infty}{\underset{\cap}{V_2}}$

$(H_e + \lambda)^{-1} - (H_0 + \lambda)^{-1}$ compact

$\Longrightarrow$ $\sigma_{ess}(H_e) = \sigma_{ess}(H_0) = [0, \infty)$



Proof We use the resolvent identity: for $\lambda \in \rho(H_0) \cap \rho(H_0+V_e)$

$$(H_0+V_e+\lambda)^{-1} = (H_0+\lambda)^{-1} + (H_0+V_e+\lambda)^{-1} V_e (H_0+\lambda)^{-1}$$

$$\Rightarrow \quad R_e(-\lambda)^{-1} - R_0(-\lambda)^{-1} = \underline{R_0(-\lambda)}\,(\mathbb{1} + \underline{V_e R_0(-\lambda)})^{-1}\, V_e R_0(-\lambda)$$

compact

$\Rightarrow$ $R_e(-\lambda)^{-1} - R_0(-\lambda)^{-1}$ is compact if $V_e R_0(-\lambda)$ is compact

To show compactness of $V_e R_0(-\lambda)$ we write

$$V_e = \underbrace{V_e \chi_n}_{V_n} + \underbrace{V_e (1-\chi_n)}_{W_n}$$

$V_n \in L^2(\mathbb{R}^3)$

$W_n \in L^\infty(\mathbb{R}^3)$

$\lim_n \|W_n\|_\infty = 0$

Consider first $V_n R_0(-\lambda)$ is an integral operator with kernel

$$V_n(x) \frac{2\mu}{\hbar^2} \frac{e^{-\sqrt{\frac{2\mu\lambda}{\hbar}}\,|x-y|}}{4\pi|x-y|}$$

$R_0(-\lambda)$ can be comp. explicit.

$\forall n$

$$\int dx\,dy\, |V_n(x)|^2 \frac{e^{-c|x-y|}}{|x-y|^2} \le c \int dx\, |V_n(x)|^2 \int_0^{+\infty} \frac{e^{-cr}}{\cancel{r^2}}\, dr\, \cancel{r^2} < \infty$$

$\Rightarrow$ $V_n R_0(-\lambda)$ is an Hilbert-Schmit op $\Rightarrow$ compact

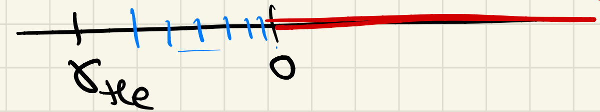
Moreover

$$\|V_e R_0(-\lambda) - V_n R_0(-\lambda)\| = \|W_n R_0(-\lambda)\| \le \|W_n\|_\infty \|R_0(-\lambda)\| \xrightarrow[n\to+\infty]{} 0$$

$\Rightarrow$ $V_e R_0(-\lambda)$ is the limit in norm of a sequence of compact operators and therefore is compact.

Absence of positive eigenvalues

$\sigma_{ess}(H_e) = \sigma_c$



Tool Consider the following strongly cont. group of unitary operators in $L^2(\mathbb{R}^3)$ (DILATION GROUP)

$$(D_s f)(x) = e^{\frac{3}{2}s} f(e^s x), \quad s \in \mathbb{R}$$

Properties $\|D_s f\|^2 = \|f\|^2$ $\quad f \in D(H_0) \Rightarrow D_s f \in D(H_0)$

from $\Delta(D_{-s}f)$

$$(D_s H_0 D_{-s} f)(x) = e^{-2s}(H_0 f)(x)$$

$$(D_s \overset{\frac{1}{|x|}}{V_e} D_{-s} f)(x) = e^{-s}(V_e f)(x)$$

$D_s \frac{1}{|x|}(D_{-s}f)(x)$

<u>Prop.</u> let E is an eigenvalue of $\mathcal{H}_e$, $D(\mathcal{H}_0)$ and $\psi \in D(\mathcal{H}_0)$, $\|\psi\| = 1$ is the corresp. eigenv. then (Virial theorem)

$$E = -\langle \psi, \mathcal{H}_0 \psi \rangle = \frac{1}{2} \langle \psi, V_e \psi \rangle < 0$$

<u>Proof.</u> Assume $(\mathcal{H}_e - E)\psi = 0$ then

$$0 = \langle D_{-s}\psi, (\mathcal{H}_e - E)\psi \rangle = \langle \psi, D_s(\mathcal{H}_e D_s^{-1} D_s - E)\psi \rangle$$

$$= \langle \psi, ((D_s \mathcal{H}_e D_s^{-1}) - E) D_s \psi \rangle = \langle \psi, \underbrace{(e^{-2s}\mathcal{H}_0 + e^{-s} V_e - E) D_s\psi}\rangle$$

Also

$$0 = \langle (\mathcal{H}_e - E)\psi, D_s\psi \rangle -$$

$$\Rightarrow 0 = \lim_{s \to 0} \left\langle \left(\frac{1 - e^{-2s}}{s} \mathcal{H}_0 + \frac{1 - e^{-s}}{s} V_e \right)\psi, D_s \psi \right\rangle$$

$$= \langle 2\mathcal{H}_0 \psi + V_e \psi, \psi \rangle$$

$$\Rightarrow -\langle \psi, \mathcal{H}_0 \psi \rangle = \langle \psi, (\mathcal{H}_0 + V_e)\psi \rangle = E \quad \#$$

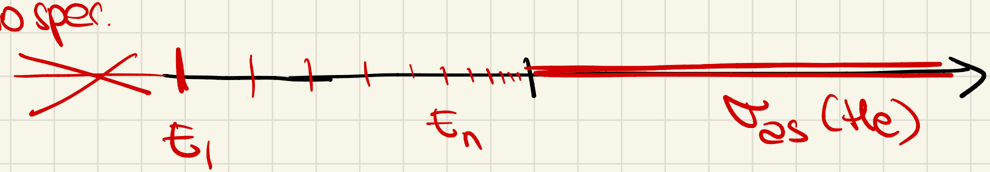
Remark While the proof of Virial theorem is based on the fact that $(D_s V e D_{-s} f)(x) = e^{-s}(V_e f)(x)$ and $(D_s H_0 D_{-s} f)(x) = e^{-2s}(H_0 f)(x)$ and cannot be generalized to arbitrary potentials, the absence of positive eigenvalues can be proved for a large class of Hamiltonians $H_0 + V$ with $\lim_{|x|\to+\infty} V(x) = 0$ following different methods.

(See Reed-Simon IV, Chapter XIII, Sect. 13)

Existence of negative eigenvalues

Prop the point spectrum $\sigma_p(\mathcal{H}_e)$ consists of an ∞ sequence $\{E_n\}$ of negative eigenvalues with finite multiplicity where

$$E_n < E_{n+1}, \qquad E_1 = \inf \sigma(\mathcal{H}_e), \qquad \lim_n E_n = 0$$



$\sigma_{sc}(\mathcal{H}_e) = \emptyset$

Proof For $\psi \in D(\mathcal{H}_0)$

$$\langle D_{-s}\psi, \mathcal{H}_e D_{-s}\psi\rangle = e^{-2s}\langle \psi, \mathcal{H}_0\psi\rangle + e^{-s}\underbrace{\langle \psi, V_e \psi\rangle}_{\text{negative}} < 0$$

for s large enough

then $\gamma_\sigma = \inf \sigma(\mathcal{H}_e) \underset{\text{s.a. op.}}{\equiv} \inf_{\|\phi\|=1} \langle \phi, \mathcal{H}_e \phi\rangle < 0$

<u>Next step</u> Show $\mathrm{Ran}\, E_{H_e}((-\infty,0)) = \mathrm{Ran}\, E_{H_e}([\sigma,0))$ <u>is infinite</u> $\to$ $\exists$ infinite sequence of negative eigenvalue

We show that $\exists$ ∞ set. of linearly indep. vectors $\{\varphi_n\}$ $\varphi_n \in \mathrm{Ran}\, E_{H_e}((-\infty,0))$.

Consider $f_n = (D_{-s_n} f)(x) = 3^{-\frac{3}{2}n} f(3^{-n}x)$ $\quad s_n = n \log 3$

with $f \in C_0^\infty(\mathbb{R}^3)$, $\|f\|=1$ $\quad \mathrm{supp}\, f \subset \{x \in \mathbb{R}^3 : 1 \le |x| \le 2\}$

$\Rightarrow$ $\mathrm{supp}\, f_n \cap \mathrm{supp}\, f_m = \emptyset$ $\quad n \neq m$ $\quad \{f_n\}$ orth.

Moreover $\exists\, n_0 \in \mathbb{N}$ s.t. $n, m > n_0$

$\langle f_n, H_e f_m \rangle = 0$ if $n \neq m$ & $\langle f_n, H_e f_n \rangle < 0$ $\quad n = m$

let X be the subspace generated by $\{f_n\}_{n=0,\dots}$

$$g \in X \iff g = \sum_{j=1}^{+\infty} \langle f_j, g \rangle f_j$$

Prop. $g \in X : E_{H_e}(-\infty,0)g = 0 \implies g = 0$

$$\langle g, H_e g \rangle = \int_{\sigma(H_e)} \lambda \, d\langle E_{H_e}(\lambda) g, g \rangle \overset{E_{H_e}(-\infty,0)g=0}{=} \int_{[0,\infty)} \lambda \, d\langle E_{H_e}(\lambda) g, g \rangle \geq 0$$

$$\langle g, H_e g \rangle \overset{(*)}{=} \sum_{j,e=1}^{+\infty} \overline{\langle f_j, g \rangle} \langle f_e, g \rangle \langle f_j, H_e f_e \rangle$$

$$= \sum_{j=1}^{+\infty} |\langle f_j, g \rangle|^2 \langle f_j, H_e f_j \rangle \underline{\leq} 0$$

$\implies g = 0$ $\square$

let $\varphi_j = E_{H_e}(-\infty,0) f_j \in \operatorname{Ran} E_{H_e}(-\infty,0)$

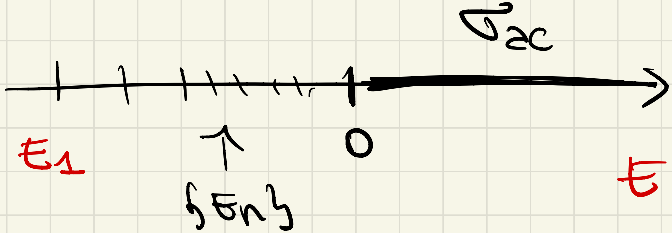
$$0 = \sum_{j=1}^{\infty} c_j \varphi_j = E_{H_e}((-\infty,0)) \underbrace{\sum_{j=1}^{\infty} c_j f_j}_{g} \Rightarrow \sum_{j=1}^{\infty} c_j f_j = 0$$

$$\Rightarrow c_j = 0 \ \forall j$$

$\Rightarrow$ $\{\varphi_j\}$ are linearly indep.

$\Rightarrow$ $\operatorname{Ran} E_{H_e}(-\infty,0)$ is ∞ dim.

Summary



$E_1 = -\frac{2\mu e^4}{\hbar^2}$

ESTIMATE on E_1

lower bound $\langle \psi, H_e \psi \rangle = \frac{\hbar^2}{2\mu} \int |\nabla \psi(x)|^2 dx - e^2 \int \frac{|\psi(x)|^2}{|x|} dx$

Hardy ineq.

$$\int dx\, |\nabla \psi(x)|^2 \geq \int dx\, \frac{|\psi(x)|^2}{4x^2}$$

$$\geq \int \left(\frac{\hbar^2}{8\mu x^2} - \frac{e^2}{|x|} \right) |\psi(x)|^2 dx$$

$$\geq \underbrace{\inf_{r \geq 0} \left(\frac{\hbar^2}{8\mu r^2} - \frac{e^2}{r} \right)}_{-\frac{2\mu e^4}{\hbar^2}} \|\psi\|^2$$

Upper bound $\phi_\alpha(x) = A e^{-\alpha |x|}$

$$E_1 \leq \frac{\langle \phi_\alpha, H_e \phi_\alpha \rangle}{\|\phi_\alpha\|^2} = -\frac{2\mu e^4}{\hbar^2}$$

Explicit solution of the eigenvalue problem

Obs $\mathcal{H}_e = -\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{|x|}$ is covariant under rotations

this suggests to use spherical coordinates, ie to study the problem

$$\mathcal{H}_S = L^2((0,\infty), r^2 dr) \otimes L^2(S^2)$$

$$\|f\|^2_{L^2(\mathcal{H}_S)} = \int_0^\infty r^2 dr \int_{S^2} d\Omega \; |f(r,\theta,\varphi)|^2$$

$$U_S : L^2(\mathbb{R}^3) \longrightarrow \mathcal{H}_S$$

$$f(x_1,x_2,x_3) \longrightarrow (U_S f)(r,\theta,\varphi) = f(r\sin\theta\cos\varphi, r\sin\theta\sin\varphi, r\cos\theta)$$

L18

$$\hat{H}_e = U_s H_e U_s^{-1} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2\mu r^2}L^2 - \frac{e^2}{r}$$

$$L^2 = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}L_3^2$$

Angular momentum operator

$$L_3 = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

z- component of the angular momentum

where $L^2 = L_1^2 + L_2^2 + L_3^2$ with

$$L_1 = U_s\,\frac{\hbar}{i}\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)U_s^{-1}$$

$$L_2 = U_s\,\frac{\hbar}{i}\left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)U_s^{-1}$$

$$L_3 = U_s\,\frac{\hbar}{i}\left(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1}\right)U_s^{-1} = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

Key fact $\hat{H}_e$, L^2, L_3 **commute** $\Rightarrow$ we can determine a common basis of eigenvalues

Strategy We first consider L_3 and L^2 in $L^2(S^2, d\Omega) = D_L$

Goal: find $F_{\lambda m} \in D_L$, $\|F_{\lambda m}\| = 1$

$$L_3 F_{\lambda m} = \hbar m F_{\lambda m} \qquad (*)$$
$$L^2 F_{\lambda m} = \hbar \lambda F_{\lambda m}$$

The eigenvalue problem for L_3 is trivial:

$$\frac{\hbar}{i} \frac{\partial}{\partial \varphi} F_{\lambda m}(\theta, \varphi) = \hbar m F_{\lambda m}(\theta, \varphi)$$

$$\Rightarrow \quad F_{\lambda m}(\theta, \varphi) = e^{im\varphi} G(\theta)$$

To solve the eigenvalue problem for L^2 one uses a method similar to the one for the harmonic oscillator, with suitable creation and annihilation operators. One can show that:

Prop Let $F_{\lambda m}$ be solution of (*). Then we have

$$\lambda = \ell(\ell+1) \qquad \ell = 0, 1, 2, \dots \qquad (\hbar\lambda \text{ eigenv. of } L^2)$$

$$-\ell \le m \le \ell \qquad (\hbar m \text{ eigenv. of } L_3)$$

and the corresponding eigenfunctions are given by the spherical harmonics $Y_{\ell m}(\theta, \varphi)$ which form a complete and orthonormal basis in $L^2(S^2, d\Omega)$.

$\Rightarrow$ L^2 and L_3 are self-adjoint operators in $L^2(S^2, d\Omega)$

RADIAL PROBLEM. Since h_e, L^2, L_3 commute any $\psi \in \mathcal{H}_s$ can be written as

$$\psi(r,\theta,\varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} f_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

where to determine $f_{n\ell}(r)$ is sufficient to solve an ODE. Let

value of L^2 on the subspace with eigenv. $\hbar^2\ell(\ell+1)$

$$h_\ell = -\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{e^2}{r}$$

then we have to solve

$$h_\ell f_{n\ell} = E_n f_{n\ell}, \quad f_{n\ell} \in D(h_\ell)$$

$$\text{with} \quad \|f_{n\ell}\|^2 = \int r^2 |f_{n\ell}(r)|^2 dr = 1$$

<u>Prop</u>. the negative eigenvalues of $\hat{H}_e$ are

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2} \qquad n = 1, 2, \dots$$

Bohr energy levels!

and the corresponding eigenvectors for n fixed are combination of the states

$$\psi_{n\ell m} = f_{n\ell}(r)\, Y_{\ell m}(\theta, \varphi) \qquad \begin{array}{l} \ell = 0, 1, \dots n-1 \\ m = -\ell, \dots, \ell \end{array}$$

<u>RK</u> If $n=1$, E_1 is non degenerate and the corresponding eigenfunction $\psi_{100}(r, \theta, \varphi)$ is called the ground state.

the eigenfunctions corresponding to $n>1$ are called excited states.

The GROUND STATE of the hydrogen atom is

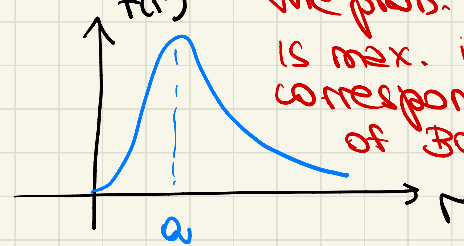
$$\psi_{100}(r) = \frac{1}{\sqrt{\pi}\, a^{3/2}} e^{-r/a} \qquad a = \frac{\hbar^2}{\mu e^2} \quad \text{Bohr's radius}$$

Hence the probability to find the electron at distance $[r_1, r_2]$ when it is in the ground state is given by:

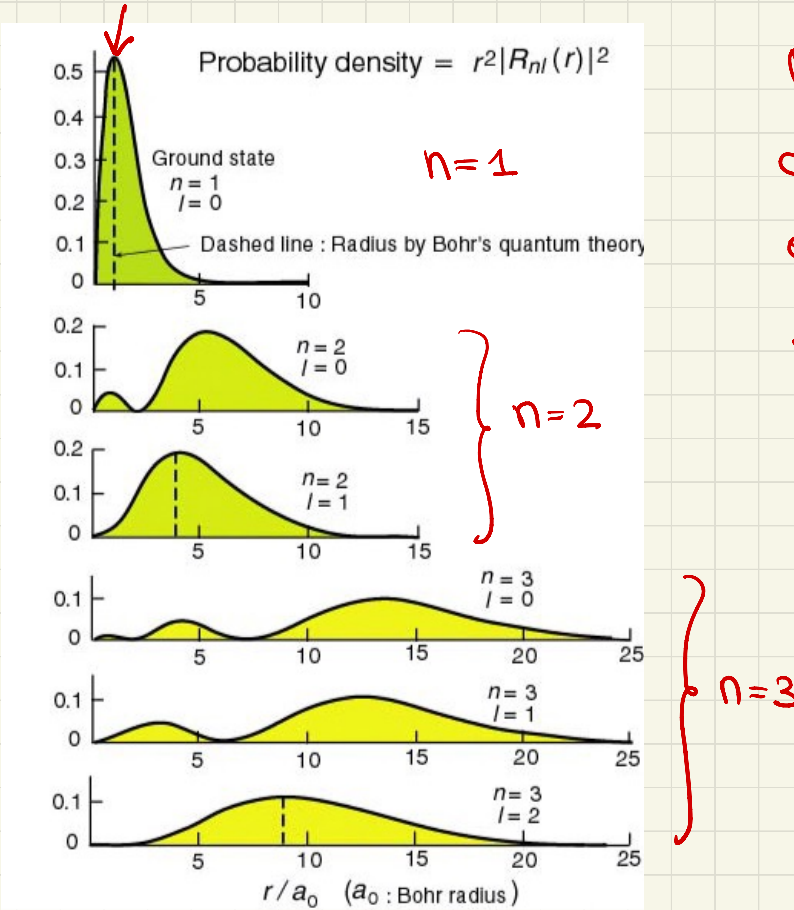
$$\int_{r_1}^{r_2} dr\, r^2 \int_{S^2} d\Omega\, |\psi_{100}(r)|^2 = 4\pi \int_{r_1}^{r_2} \frac{dr\, r^2}{\pi a^3} e^{-2r/a}$$

$$= \int_{r_1}^{r_2} dr \underbrace{\frac{4 r^2}{a^3} e^{-2r/a}}_{}$$

$f(r)$ = probability density of an electron in the ground state of hydrogen atom



the prob. density is max. in correspondence of Bohr's radius



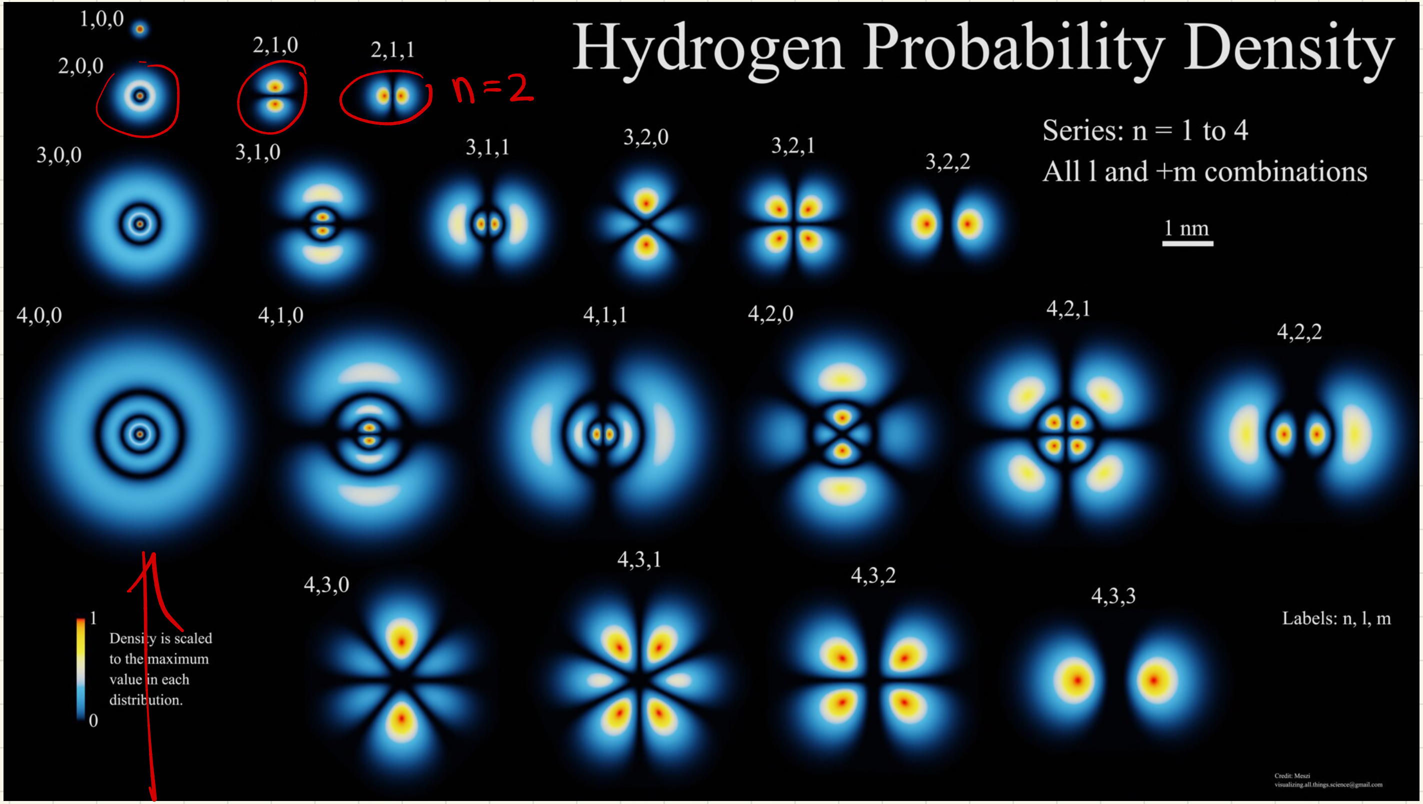
Radial probability densities for different energy level (values of n) and values of the angular momentum

RK the distance at which the prob. density is maximum becomes larger as n increases

http://ne.phys.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm

Rk If $n=2$ we have $\ell=0,1$ and if $\ell=1$, $m=0,\pm 1$ $\rightarrow$ 4 orbitals

L25



$n=2$

- the orbitals corresponding to $\ell=0$ are spherically symm. and called s-orbitals

- the orbitals corresponding to $\ell=1$ are called p-orbitals

RR So far we studied ONE PARTICLE PROBLEMS.

A N-particle system in quantum mechanics is described by

$$\psi(x_1, \dots, x_n) \in \bigotimes_{j=1}^{n} L^2(\mathbb{R}^d) \cong L^2(\mathbb{R}^{nd})$$

$$\neq \text{ in general } \prod_{j=1}^{N} \varphi_j(x_j)$$

$\leftarrow$ having a product of one-particle wave function is a very special case

$\rightarrow$ the many-particle problem is much richer than the one-particle one, as we are going to see in the next two weeks!

References

Chapter 9 Teta's book

→ 9.1 – 9.6 qualitative analysis

→ 9.7 – 9.10 Eigenvalue problem for $-\Delta + V_e$

(only main ideas of the strategy in this class)