Lecture 16

Tuesday, November 12, 2024 11:27

6.6 The Bound-State Hydrogen Atom

Wave-functions

Last time: recursion relation

$$a_{j+1} = \frac{2Z}{na} \frac{j+l+1-n}{(j+1)(j+2l+2)} a_j$$

$$M(r) = \sum_j a_j r^j$$

Highest power of r is

$k = n - l - 1$

$$\boxed{R_{nl}(r) = r^l e^{-Zr/na} \sum_{j=0}^{n-l-1} a_j r^j}$$

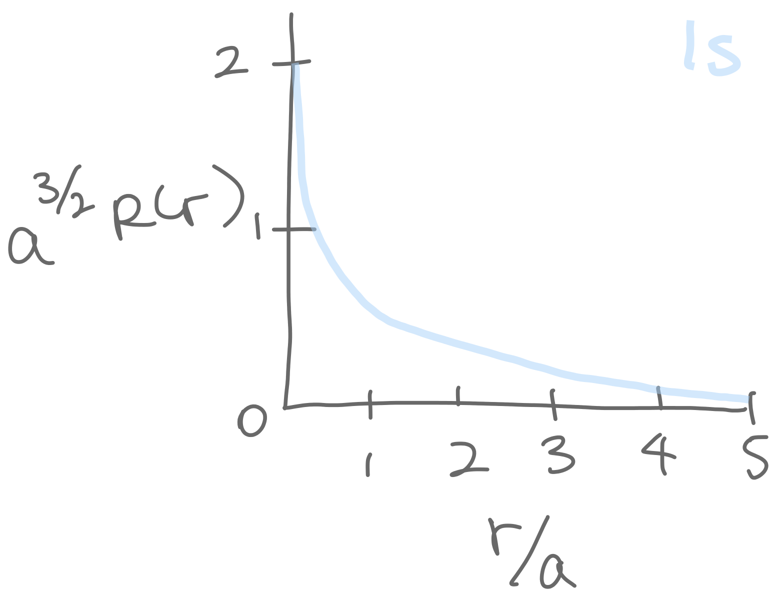
$$\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi)$$

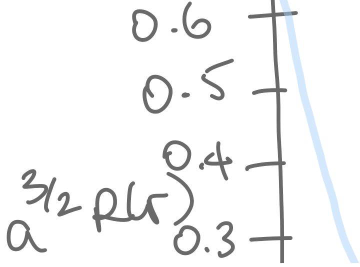
$$\boxed{\psi_{n\ell m} = R_{n\ell}(r)\, S_{\ell m}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}}$$

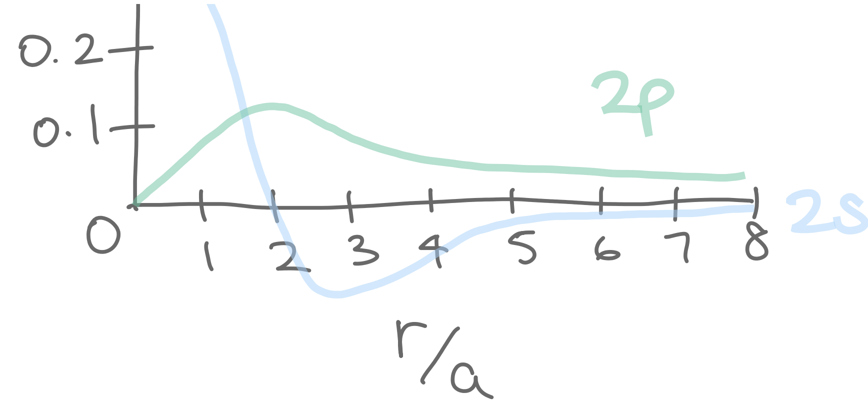
How many nodes does $R(r)$ have?

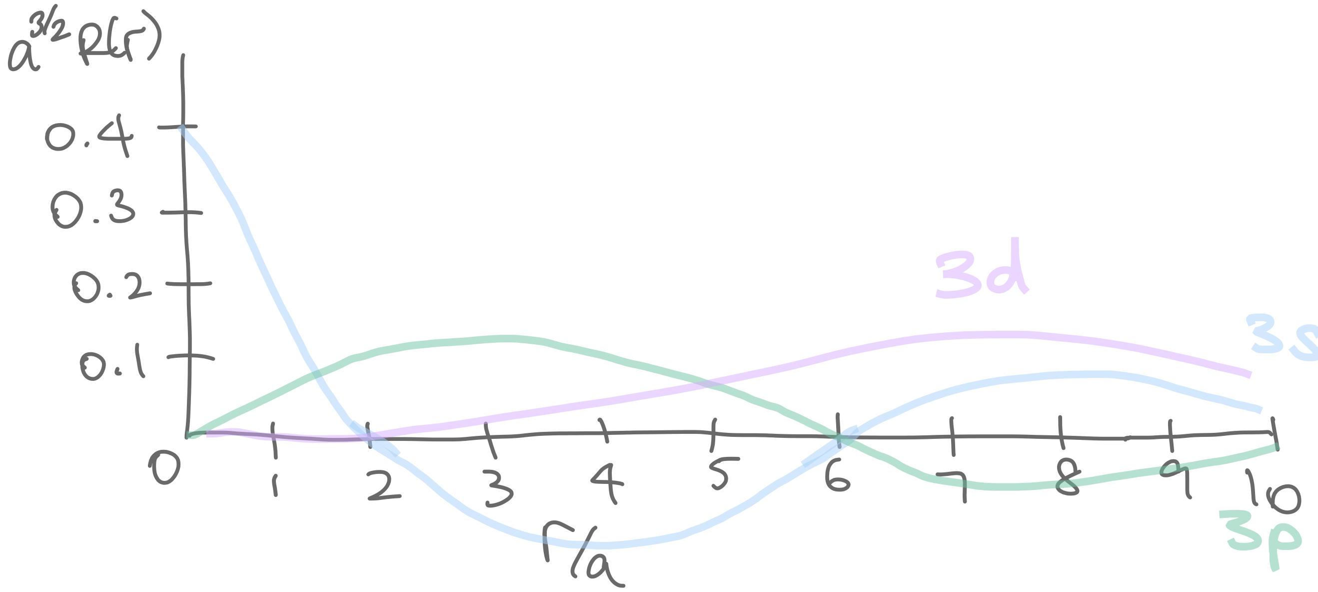
$R(r) = 0$ at $r = \infty$, $r = 0$ for $\ell \neq 0$, and other values of r that make $M(r)$ vanish.

$M(r)$ is a polynomial of degree $n - \ell - 1$, with real, positive roots.









Ground State of the Hydrogenlike Atom

$n=1,\ \ell=0,\ m=0$

$$R_{10}(r) = a_0 e^{-Zr/a}$$

Need to determine a_0 via normalization.

$$|a_0|^2 \int_0^\infty e^{-2Zr/a} r^2 dr = 1$$

Integral Table

$$\int_0^\infty x^n e^{-qx}\,dx = \frac{n!}{q^{n+1}}, \quad n>-1,\ q>0$$

$$|a_0|^2 \frac{2!}{(2Z/a)^3} = 1$$

$$|a_0|^2 \frac{2a^3}{8Z^3} = 1$$

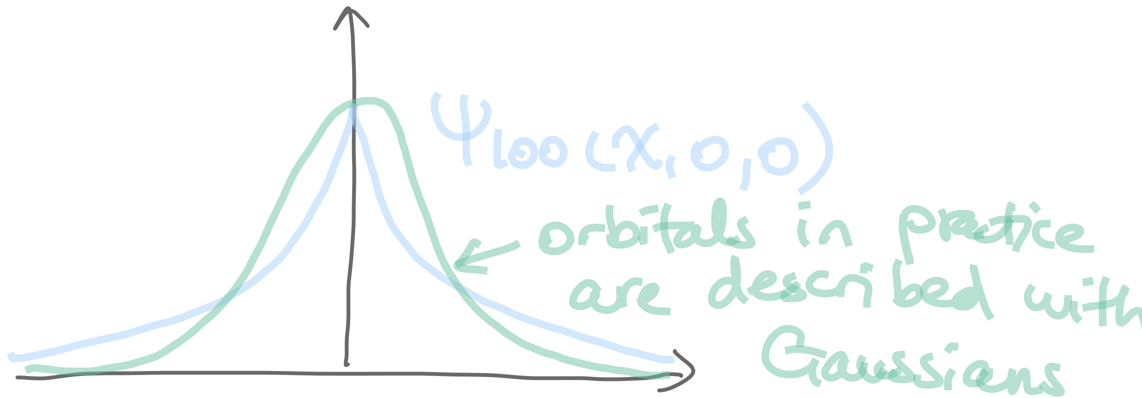
$$|a_0|^2 = \frac{4Z^3}{a^3}$$

$$|a_0| = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}}$$

$$\boxed{R_{10}(r) = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-Zr/a}}$$

$$Y_0^0 = \frac{1}{(4\pi)^{\frac{1}{2}}}$$

$$\boxed{\psi_{100} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}}$$



$\frac{\partial \psi}{\partial x}$ is discontinuous at the origin.

$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$ becomes infinite at the origin.

$\psi_{100} = \psi_{1s}$

Letter notation for l :

Letter	s	p	d	f	g	h	i	k	...
l	0	1	2	3	4	5	6	7	...

s : sharp ; p : principal ; d : diffuse ;
f : fundamental

Wavefunctions for $n=2$:

$n=2: \psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$

$\psi_{2s} \quad \underbrace{\psi_{2p_0} \quad \psi_{2p_1} \quad \psi_{2p_{-1}}}$

all have the same radial factor

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right)e^{-Zr/2a}$$

$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a}$$

Chapter 7: Theorems of Quantum Mechanic

The Schrödinger equation for the one-electron atom is exactly solvable. However, because of the interelectronic repulsion terms in the Hamiltonian, the Schrödinger equation for many-electron atoms and molecules cannot be solved exactly.

Need approximate methods.

- variational method
- perturbation theory.

Bra-ket notation (from "bracket")

Hermitian Operators

QM operators that represent physical quantities must be linear and Hermitian.

expected value of A

$$\langle A \rangle = \int \psi^* \hat{A} \psi \, d\tau$$

now, impose additional constraint that $\langle A \rangle = \langle A \rangle^*$

because the average value of a physical quantity must be a real numb

$$\int \psi^* \hat{A} \psi \, d\tau = \left(\int \psi^* \hat{A} \psi \, d\tau \right)^*$$

$$= \int (\psi^*)^* (\hat{A}\psi)^* d\tau$$

$$\boxed{\int \psi^* \hat{A} \psi \, d\tau = \int \psi (\hat{A}\psi)^* d\tau}$$

Hermitian operator: linear; satisfies the above for all well-behaved functions. Named after Charles Hermite, a French mathematician.

$$\int f^* \hat{A} g \, d\tau = \int g (\hat{A} f)^* d\tau$$

bra-ket notation

$$\int f_m^* \hat{A} f_n \, d\tau \equiv \langle f_m | \hat{A} | f_n \rangle$$

complex conjugate

$$\equiv \langle m | \hat{A} | n \rangle$$

complex conjugate

$$\int f_m^* \hat{A} f_n \, d\tau \equiv A_{mn}$$

complex conjugate

$$\int f_m^* f_n \, d\tau \equiv \langle f_m | f_n \rangle$$
$$\equiv \langle m | n \rangle$$
$$\equiv (f_m, f_n)$$

The definite integral $\langle m | \hat{A} | n \rangle$ is called a <u>matrix element</u> of the operator $\hat{A}$.

Note that

$$\langle f | \hat{B} | g \rangle = \langle f | \hat{B} g \rangle$$

where f and g are functions.

$$\text{Since } \left[\int f_m^* f_n \, d\tau \right]^* = \int f_m f_n^* \, d\tau$$
$$= \int f_n^* f_m \, d\tau$$

$$\langle m | n \rangle^* = \langle n | m \rangle$$

$$\langle c f | \hat{B} | g \rangle = c^* \langle f | \hat{B} | g \rangle$$

$$\langle f|\hat{B}|cg\rangle = c\langle f|B|g\rangle$$

where $\hat{B}$ is a linear operator and c is a constant.

Proof of the more strict requirement

$$\int f^*\hat{A}g\,d\tau = \int g(\hat{A}f)^*\,d\tau$$ from

$$\int \psi^*\hat{A}\psi\,d\tau = \int \psi(\hat{A}\psi)^*\,d\tau$$

Let $\boxed{\psi = f + cg}$

$$\int (f+cg)^*\hat{A}(f+cg)\,d\tau = \int (f+cg)[\hat{A}(f+cg)]^*\,d\tau$$

$$\int (f^*+c^*g^*)\hat{A}f\,d\tau + \int (f^*+c^*g^*)\hat{A}cg\,d\tau$$

$$= \int (f+cg)(\hat{A}f)^*\,d\tau + \int (f+cg)(\hat{A}cg)^*\,d\tau$$

$$\boxed{\int f^*\hat{A}f\,d\tau} + c^*\int g^*\hat{A}f\,d\tau$$

$$+c\int f^*\hat{A}g\,d\tau + \boxed{c^*c\int g^*\hat{A}g\,d\tau}$$

$$= \boxed{\int f(\hat{A}f)^*d\tau} + c\int g(\hat{A}f)^*d\tau$$

$$+c^*\int f(\hat{A}g)^*d\tau + \boxed{cc^*\int g(\hat{A}g)^*d\tau}$$

$$c^*\int g^*\hat{A}f\,d\tau + c\int f^*\hat{A}g\,d\tau$$

$$= c\int g(\hat{A}f)^*d\tau + c^*\int f(\hat{A}g)^*d\tau$$

Set $c=1$

$$\cancel{\int g^*\hat{A}f\,d\tau} + \int f^*\hat{A}g\,d\tau = \int g(\hat{A}f)^*d\tau + \cancel{\int f(\hat{A}g)^*d\tau}$$

set $c=i$, then divide by i add

$$\cancel{-\int g^*\hat{A}f\,d\tau} + \int f^*\hat{A}g\,d\tau = \int g(\hat{A}f)^*d\tau \cancel{-\int f(\hat{A}g)^*d\tau}$$

$$\cancel{2}\int f^*\hat{A}g\,d\tau = \cancel{2}\int g(\hat{A}f)^*d\tau$$

$$\boxed{\int f^* \hat{A} g \, d\tau = \int g (\hat{A} f)^* d\tau}$$

$$\langle f_m | \hat{A} | f_n \rangle = \langle f_n | \hat{A} | f_m \rangle^*$$

$$\langle m | \hat{A} | n \rangle = \langle n | \hat{A} | m \rangle^*$$

$$A_{mn} = (A_{nm})^*$$