

Lecture #21: Hydrogen Atom II

Last time:

TISE For H atom: final exactly solved problem

\hat{H} in spherical polar coordinates

Separation: $\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)Y_\ell^m(\theta, \phi)$

$Y_\ell^m(\theta, \phi)$ is universal — what is the difference between H atom and rigid rotor?

$R_{n\ell}(r)$ is unique for each atom. Worthwhile to develop intuitive interpretation: semi-classical

Experimental evidence for an unexpected internal degree of freedom: electron spin

Why does $[L^2, f(r)] = [L_z, f(r)] = 0$?

different coordinates: ϕ, θ vs. r

Today:

1. Patterns in spectrum of H atom
2. Semi-classical interpretation of $R_{n\ell}(r)$
3. Rydberg states
4. Get ready for many-electron atoms.

H Atom

Separation of variables in TISE gives

$$\Psi_{n\ell m_\ell}(r, \theta, \phi) = \underbrace{R_{n\ell}(r)}_{\text{unique}} \underbrace{Y_\ell^m(\theta, \phi)}_{\text{universal}}$$

all central force problems

separation of r from θ, ϕ gives radial TISE

$$\left[\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} r^2 \frac{d}{dr} + V_\ell(r) - E \right] R_{n\ell}(r) = 0$$

Effective potential

$$V_\ell(r) = + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{(4\pi\epsilon_0)r}$$

centrifugal barrier Coulomb attraction

$$\mu = \frac{m_e m_{\text{ion}}}{m_e + m_{\text{ion}}}$$

$$E_{n\ell m_\ell} = -\frac{hcRZ^2}{n^2} \quad n = 1, 2, 3, \dots$$

degeneracy: $\ell=0, 1, \dots, n-1$

$$m_\ell = -\ell, -\ell+1, \dots, \ell$$

total degeneracy: g_n, g_ℓ

	s	p	d
g_ℓ	1	3	5

$$n = 1 \quad g_n = 1$$

$$n = 2 \quad g_n = 1 + 3 = 4$$

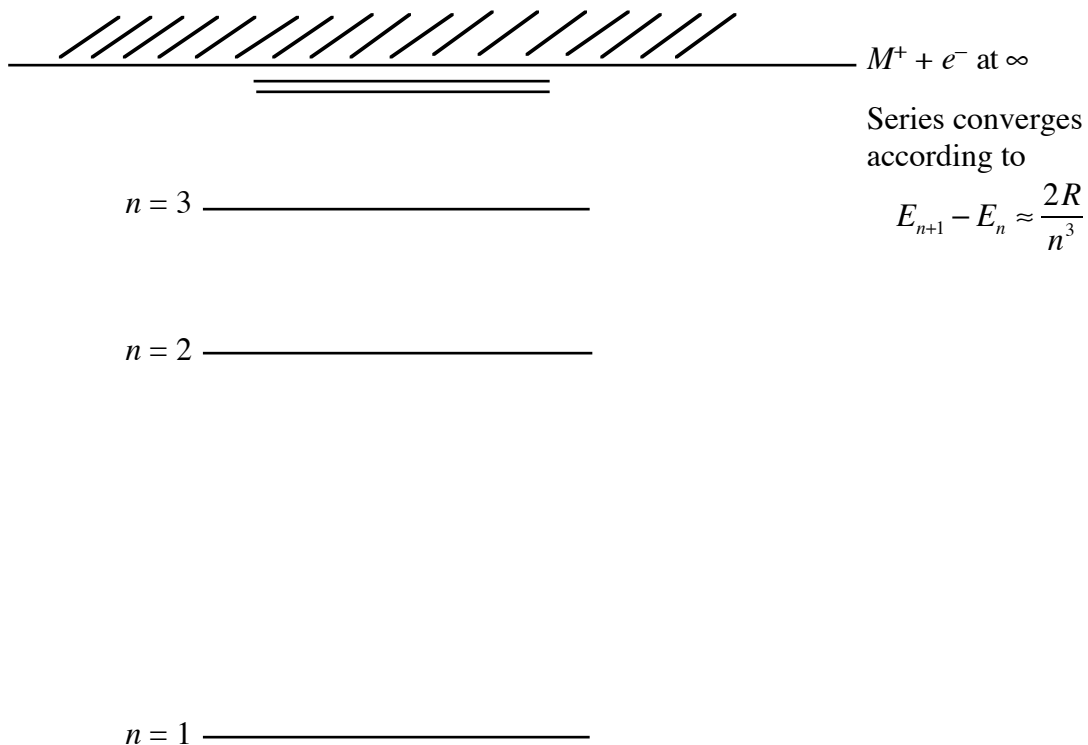
$$n = 3 \quad g_n = 1 + 3 + 5 = 9$$

$$g_n = n^2$$

Number of nodes:

radial	angular	total for $n\ell$ state
$n - \ell - 1$	ℓ	$n - 1$

We want to understand $R_{n\ell}(r)$ for H atom and then extend the cartoon to all many- e^- atoms and even to molecules



Absorption spectrum is simple and easy to assign because all population starts in $n = 1$ (1s) and all ℓ for the same value of n are degenerate (concealing the $\Delta\ell = \pm 1$ selection rule).

In a discharge, see many-line emission spectrum. Many overlapping convergent series.

$$\frac{\Delta E_{n,n'}}{hc} = \mathfrak{R} \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] \quad n' > n$$

Each value of n is associated with a convergent series in n' .

Easy to recognize

$$\frac{\Delta E_{n,n'}}{hc} = \frac{-E_n}{hc} + \frac{\mathfrak{R}Z^2}{n'^2}$$

each series converges at $n' \rightarrow \infty$ Ionization Energy, thus each series reveals the value of E_n .

“Structure”

Most electronic properties scale as the expectation value of an integer power of r . Each such expectation value or matrix element scales as a specific power of n and ℓ .

It is possible to empirically measure n (both for H atom and any other atom or molecule) by using the Rydberg Formula relationship between the ionization energy out of the n -orbital.

$$I_n = \frac{hcRZ}{n^2}$$

Ionization energy:

$$n = \left[\frac{hcRZ}{I_n} \right]^{1/2}$$

Measure $I_n \rightarrow$ empirically determine n (or n^* , the effective principal quantum number, for non-H systems)


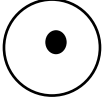
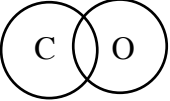
$I_n \rightarrow n \rightarrow$ all n, ℓ dependent properties!

McQuarrie, page 333: expectation values of r^k

k	$\langle r^k \rangle_{nlm_\ell}$
2	$\frac{a_0^2 n^4}{Z^2} \left\{ 1 + \frac{3}{2} \left[1 - \frac{\ell(\ell+1) - 1/3}{n^2} \right] \right\}$
1	$\frac{a_0 n^2}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{\ell(\ell+1)}{n^2} \right] \right\}$ (basis for intuition about orbital size)
0	n^0
-1	$\frac{Z}{a_n n^2}$
-2	$\frac{Z^2}{a_0^2 n^3} (\ell + 1/2)$
-3	$\frac{Z^3}{a_0^3 n^3 \ell \left(\ell + \frac{1}{2} \right) (\ell + 1)}$

a_0 is the Bohr radius $a_0 = 0.529 \text{ \AA}$. Note that $\langle r^k \rangle$ scales as $(a_0/Z)^k$. Most importantly, for all $k \leq -2$, $\langle r^k \rangle \propto n^{-3}$. This reflects the amplitude in the innermost lobe of the radial wavefunction. I will show you that the amplitude in this first lobe of $\chi_{n\ell}(r) \propto n^{-3/2}$.

Generalization from the $1e^-$ atom or ion to many- e^- atoms and molecules.

 H^+ a point	 Na^+ spherical charge surrounding + 11 charge on the nucleus	 a not-round charge distribution shielding C^{+6} and O^{+8} nuclei
$\frac{E_n}{hc} = -\frac{\mathfrak{R}_H}{n^2}$ n integer	$\frac{E_{n\ell}}{hc} = -\frac{\mathfrak{R}_{Na}}{n_\ell^*}$	$\frac{E_{n\ell\lambda}}{hc} = -\frac{\mathfrak{R}_{CO}}{n_{\ell\lambda}^*}$
	$n_\ell^* = n - \delta_\ell$	$n_{\ell\lambda}^* = n - \delta_{\ell\lambda}$
	δ_ℓ is “quantum defect”	λ is projection of \vec{l} on bond axis

Semiclassical theory for $R_{n\ell}(r)$

- * almost everything scales as the amplitude of the innermost lobe of $\chi_{n\ell}(r)$
- * inner lobe (first node) lined up for all n of given ℓ .

We need to go to the $R_{n\ell}(r) = \frac{1}{r} \chi_{n\ell}(r)$ picture.

The 3-D spherical polar volume element is $r^2 \sin\theta dr d\theta d\phi$.

$$\begin{aligned} \langle R_{n\ell} | r^k | R_{n'\ell} \rangle &= \int_0^\infty r^k r^2 R_{n\ell} R_{n'\ell} dr \\ &= \int_0^\infty r^k \chi_{n\ell}(r) \chi_{n'\ell}(r) dr \end{aligned}$$

$\chi(r)$ gets rid of all of the extra factors of r in the radial Schrödinger equation and in all integrals involving $R_{n\ell}(r)$.

The radial TISE and all integrals now look like the ordinary 1-D $V(x)$ problems we have studied.

One more special point: The $r = 0$ boundary condition. $R_{ns}(0) \neq 0$ (surprise!)
 $\chi_{ns}(0) = 0$

Why is $R_{ns}(0) \neq 0$?

The centrifugal barrier term is absent.

$$V_{\ell=0}(r=0) = -\infty$$

The radial wavefunction is pulled in toward the nucleus. There is no barrier that prevents $R_{ns}(0)$ from being non-zero. But this is a forgivable singularity.

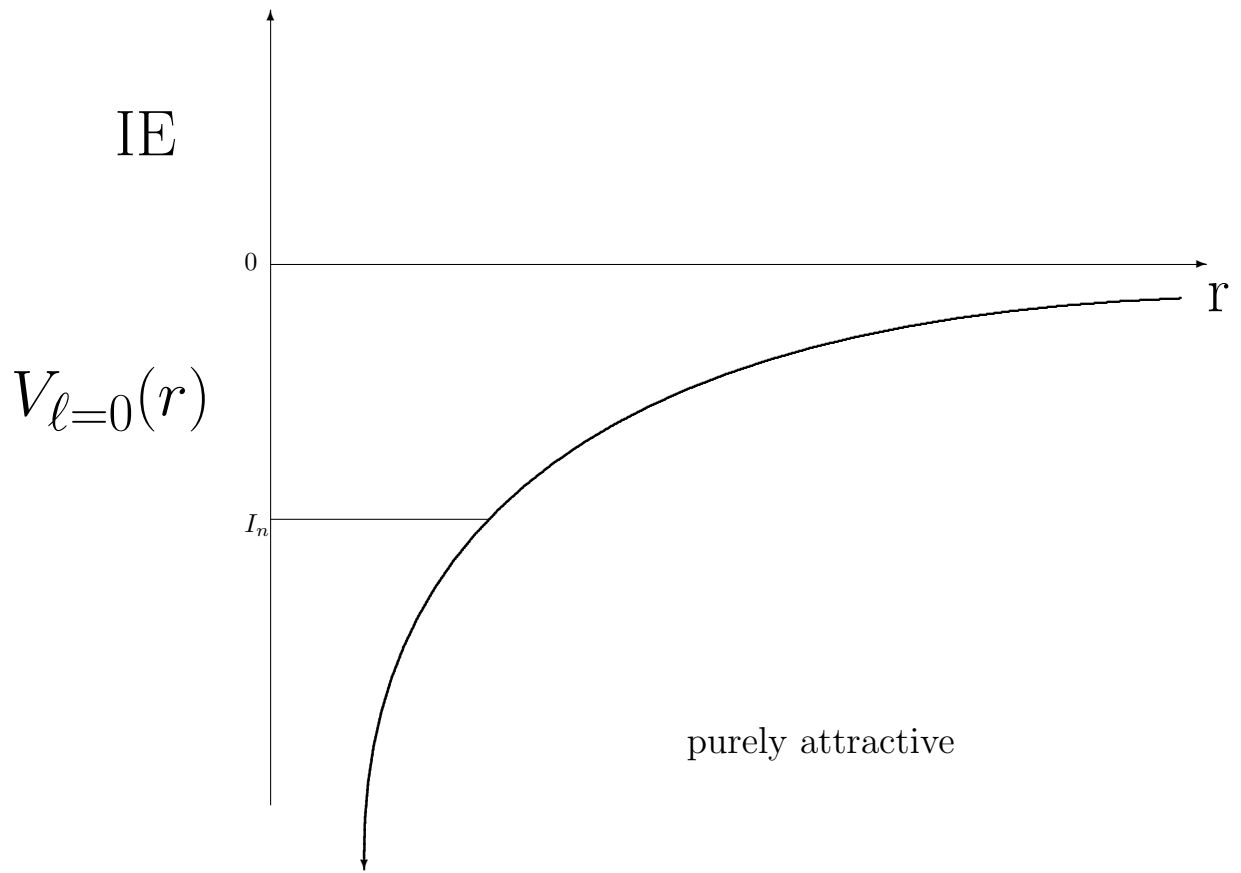
$$\lim_{r \rightarrow 0} r^2 R_{ns}^*(r) R_{ns}(r) \rightarrow 0$$

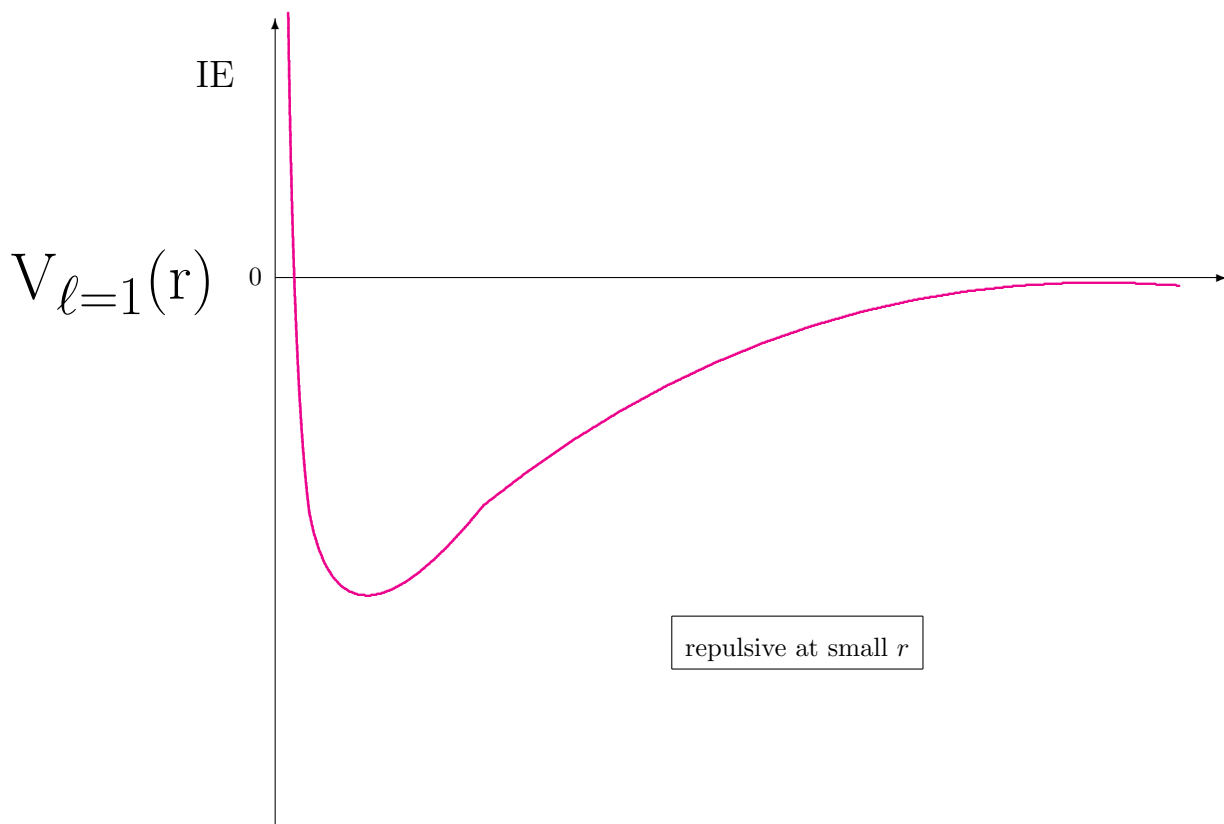
because of the r^2 in the volume element!

There is one extremely important consequence of $R_{ns}(0) \neq 0$. The electron actually comes into *contact* with the nucleus. If there is a non-zero nuclear spin, I , there is “*Fermi Contact*” hyperfine interaction. This gives rise to a very small splitting in the energy levels whenever there is a *half-filled* orbital with ns character. Hyperfine measures $R_{ns}(0)$! Hyperfine is very important in NMR.

Set up a framework for semi-classical analysis

$$V_{\ell}(r) = \underbrace{-\frac{Ze^2}{4\pi\epsilon_0}}_{\text{attractive}} \frac{1}{r} + \underbrace{\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{\text{repulsive}}$$





Turning points: where $E_{n\ell} = V_{\ell}(r_{\pm})$

$$E_{n\ell} = -\frac{hc^2 R}{n^2}$$

Solve for $r_{\pm}(n, \ell)$

$$r_{\pm}(n, \ell) = a_0 n^2 \left(1 \pm \left[1 - \frac{\ell(\ell+1)}{n^2} \right]^{1/2} \right)$$

Note that $r_{+}(n, 1) = a_0 n^2 \left[1 + \left(1 - \frac{2}{n^2} \right)^{1/2} \right] < r_{+}(n, 0)$ a little bit surprising

$$r_{+}(n, 0) = a_0 n^2 (2)$$

Classical mechanical radial momentum

$$p_{n\ell}(r) = [2\mu(E_{n\ell} - V_\ell(r))]^{1/2}$$

$$\lambda_{n\ell}(r) = \frac{h}{p_{n\ell}(r)} \begin{cases} \text{hard inner wall} \\ \text{soft outer wall} \end{cases}$$

We want to know where are the nodes and what is the probability for the e^- between each pair of nodes.

Classical oscillation period at E_n

$$\tau_n = \frac{h}{E_{n+1/2} - E_{n-1/2}} = \frac{h}{hc\mathfrak{R}(2/n^3)} \propto n^{+3}$$

Node to next-node probability

$$\frac{\delta t_{\text{node to node}}}{\Delta t_{\text{turning point to turning point}}} = \frac{\lambda(r_{\text{center of lobe}})/2}{p(r_{\text{center of lobe}})/\mu}$$

$$\Delta t_{\text{turning point to turning point}} = \tau_n/2$$

We will find:

Because inner **wall** of $V_\ell(r)$ is nearly vertical for $n \gtrsim 6$, innermost radial nodes line up at nearly the same value of r (for $n > 6$)

Because $p_{n>6}(r_- + \delta r) \approx p_{n=6}(r_- + \delta r)$, λ is approximately independent of n near inner turning point.

Thus we get an n -dependent amplitude of the corresponding inner lobes that scales as

$$\mathbf{n}^{-3/2}! \quad (\text{from } \tau_n \propto n^{+3})$$

If the system we are interested in is not H, we consider shielding of the nucleus by core electrons, Z -shielding = Z^{eff} .

Z^{eff} goes from Z (charge on the bare nucleus) at $r = 0$ to $+1$ at $r \approx$ radius of core. The degree of penetration of Rydberg e^- into core region is ℓ -dependent.

$$n \rightarrow n_\ell^* < n$$


$$n_s^* \ll n_p^* < n_d^* < n_f^* \approx n$$

because high- ℓ cannot penetrate inside the core. So the inner lobe scales as n_ℓ^* .

Stationary Phase

Expectation values and matrix elements of r^k

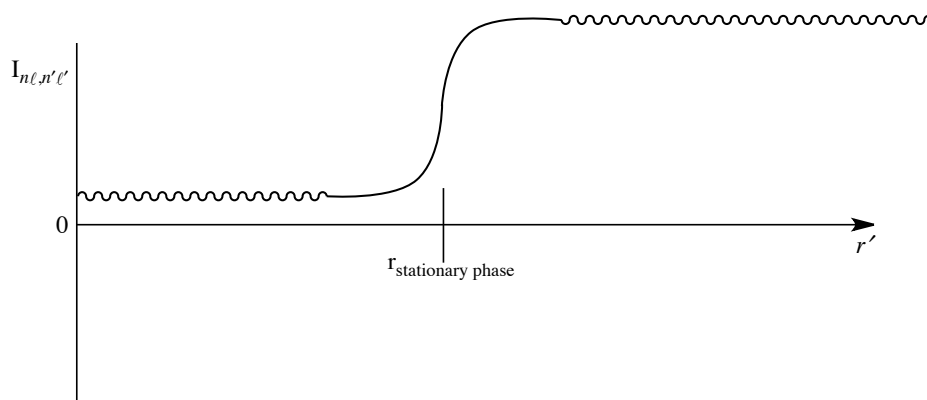
$$\int_0^\infty \chi_{n\ell}(r) r^k \chi_{n'\ell'}(r) dr$$



two rapidly oscillating functions

Integral accumulates only in the region where the two functions are oscillating at the same spatial frequency.

$$I_{n\ell, n'\ell'} = \int_0^{r'} \chi_{n\ell}(r) r^k \chi_{n'\ell'}(r) dr \text{ accumulates as}$$



For most $nl \neq n'l'$ integrals (as in transition moment from $1s$ to np) the only stationary phase region is in the innermost lobe.

$$I_{nl, n'l'} \approx n_l^{-3/2} n_{l'}^{-3/2}$$

This is a framework for training your intuition and then making intuition-based predictions about properties of many-electron systems for atoms and molecules!

Rydberg States!

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