

# Lecture 10

## Exactly Solvable 1-e- Problem: The H-atom

The electronic motion is much much faster than the nuclear motion, the huge mass difference of the two essentially ended up giving us the reduced mass of the relative motion of the system to be dominated by the motion of the electron and that of the center of mass to be dominated by the nuclear mass resulting in a convenient separation of variables, which enables an exact solution of the problem possible!

From the point of view of chemistry, the H-atom is the lightest one around in a molecule and is important in many chemical reactions—including our vision process: The primary initial process of our vision is triggered by a proton motion in about  $6 \times 10^{-15}$  second timescale (R.W. Schoenlein, L.A. Peteanu, R.A. Mathies, & C.V. Shank, *Science* **254**, 412–414 (1991).).

The discrete emission spectrum of H, was noted as early as 1885 by Balmer, and quantified by Rydberg in 1890: long before quantum mechanics (~1925)! In fact, the discrete spectra of H-atom was one of the motivations in the development of QM.

Rutherford first argued planetary model of atoms followed by discrete stable ‘quantized’ states by Bohr but these old quantization models based on classical mechanics faced unanswerable questions of ad hoc orbit stabilizations, etc.

So, we have been discussing modern QM and the solution to the Schrödinger equation for the hydrogen atom.

For stable energy states (eigen-energies), the recipe is to time integrate the Schrodinger Equation and Solve:  $\hat{H}\psi = E\psi$

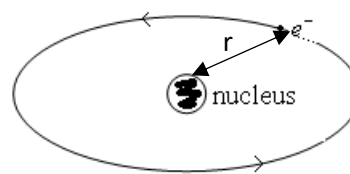
$$\hat{H} = \frac{1}{2m_e} \hat{p}_e^2 + \frac{1}{2m_N} \hat{p}_N^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\hat{p}_e = -i\hbar \left( \hat{i} \frac{\partial}{\partial x_e} + \hat{j} \frac{\partial}{\partial y_e} + \hat{k} \frac{\partial}{\partial z_e} \right)$$

$$\hat{p}_e^2 \rightarrow -\hbar^2 \left( \frac{\partial}{\partial x_e^2} + \frac{\partial}{\partial y_e^2} + \frac{\partial}{\partial z_e^2} \right) \equiv -\hbar^2 \nabla_e^2$$

$$\boxed{r = r_N - r_e} \quad \& \quad \mu = \frac{m_e m_N}{m_e + m_N} \approx m_e$$

$$\hat{H}_{relative} = \frac{-\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi \epsilon_0 r}$$



H-atom can be visualized as an electron of mass  $\mu$  on a sphere of radius  $r$ , while the C.M. is associated with translational motion of the body of mass  $(m_N + m_e)$

Solution:

Acceptable quantum state:  $\psi(r, \theta, \phi)$

From our previous discussion of rigid rotor, we suspect angular part will come with quantum numbers  $l, m_l$

Also, note that: PE part of the Hamiltonian depends only on the radial part 'r':  $V(r)$ .

So now, one more quantum number related to the radial distance.

$$\therefore \frac{-\hbar^2}{2\mu} \nabla^2 \psi(r, \theta, \phi) - \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

where,  $\nabla^2$  is now in spherical polar coordinates.

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}}_{\text{familiar from our } \hat{L}^2 \text{ operator.}}$$

Again, variables can be separated:

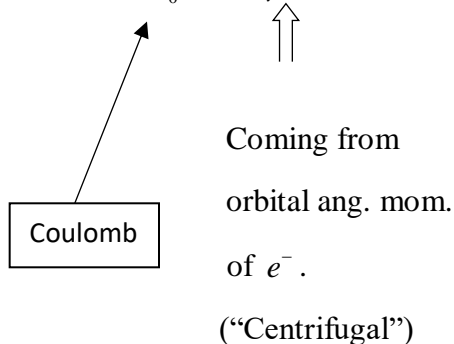
$$\psi(r, \theta, \phi) = N \cdot R(r) Y_{lm_l}(\theta, \phi)$$

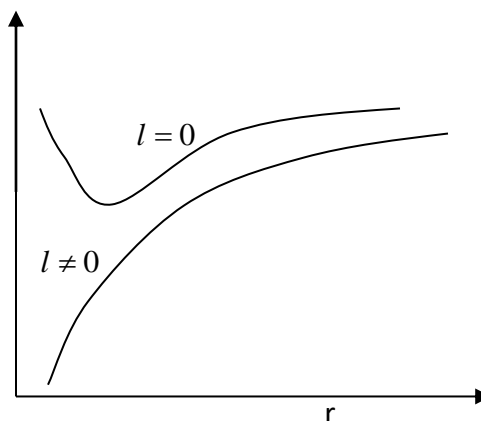
where  $R(r)$  : radial part  $\leftrightarrow$  Quantum number  $n$  (integer)

Since  $L^2$  is the eigenoperator for the Angular Momentum part of the wavefunction, finite PE arises due to angular contribution for non-zero  $l$  values, which can be considered as an effective potential, the problem can be written for central potentials as:

Radial part:  $R_{nl}(r)$  with

$$V_{\text{eff}} = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}; \quad \text{Effective potential} \quad l=0 \rightarrow (n-1)$$


  
 Coming from  
 orbital ang. mom.  
 of  $e^-$ .  
 ("Centrifugal")



Energy is quantized (as expected) for the H-atom:

$$E_n = \frac{-\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{1}{n^2}; \text{ with integer quantum number: } n = 1, 2, \dots$$

Note that  $E$  does not depend on  $l$  or  $m_l$ ; this is because this is a special case for the H-atom as there are no other electron to interact with.

Fundamental length scale, Bohr radius ( $a_0$ ):

$$a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2} \approx 53 \text{ pm} \approx 0.5 \text{ \AA}$$

$$\text{Rydberg constant } R_H = \frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \approx 109679 \text{ cm}^{-1}$$

$$\therefore E_n = \frac{-R_H}{n^2}$$

$$R_{n,l}(r) = N_{n,l,m_l} \left( \frac{2r}{n a_0} \right)^l L_{n-l} e^{-r/na_0}$$

the average radius for  $n^{\text{th}}$  orbital will be given by:

$$\langle r \rangle_n \sim n^2 a_0 \quad a_0 \rightarrow \text{Bohr Radius}$$

↑↑  
square of principal quantum number

The bound electronic motion obeys :

$$\left( \frac{-\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi \epsilon_0 r} \right) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

$(r, \theta, \phi)$  Spherical polar coordinates.

Surprisingly (or perhaps not so surprisingly!) the above can be exactly solved to yield :

$$E_{nlm_l} = \frac{-R_H}{n^2} \quad ; \quad n = 1, 2, 3, \dots$$

$$\psi_{nlm_l}(r, \theta, \phi) = \underbrace{N_{nlm_l}}_{\text{Normalization constant}} \underbrace{R_{nl} \left( \frac{2r}{na_0} \right)}_{\text{Radial part}} \underbrace{Y_{lm_l}(\theta, \phi)}_{\text{angular part}}$$

$$R_H \equiv \frac{-\mu e^4}{32\pi^2 \epsilon_0 \hbar^2} \text{ is the Rydberg Constant for Hydrogen}$$

(Note: To obtain the value of  $R_H$  in  $\text{cm}^{-1}$  as stated in the previous page, we have to divide this expression by  $hc$ )

- Energy, bound states, are negative.
  - No dependence on  $l$  &  $m_l \Rightarrow$  degeneracy.  $\left. \begin{array}{l} \text{For each } l : (2l+1) \text{ } m_l \text{ values} \\ \text{and for each } n : l = 0, 1, 2, \dots, (n-1). \end{array} \right\} n^2$
- e.g. :  $n = 2 \Rightarrow l = 0, 1$  and  $m_l : 0, (-1, 0, +1)$   
 $\therefore$  degeneracy  $2^2 = 4$ .

Thus, the energies are same ( $\therefore$  degenerate)

$$E_{200} = E_{211} = E_{210} = E_{21-2} = \frac{-R_H}{4}$$

However, the quantum states are different... For instance:

$$E_{200} \leftrightarrow \psi_{200}(r, \theta, \phi) = N_{200} R_{20} \left( \frac{r}{a_0} \right) \underbrace{Y_{00}(\theta, \phi)}_{\text{constant}}$$

$$E_{210} \leftrightarrow \psi_{210}(r, \theta, \phi) = N_{210} R_{21} \left( \frac{2r}{2a_0} \right) Y_{21}(\theta, \phi)$$

$$= N_{210} R_{21} \left( \frac{r}{a_0} \right) \cos \theta$$

Normalization :

$|\psi(r, \theta, \phi)|^2$  gives the probability density. This multiplexed by an infinite-small volume element in  $(r, \theta, \phi)$  will give the probability. Summing up all of these should yield 1.

But what is infinitesimal volume element in  $(r, \theta, \phi)$  ?

For Cartesian:  $dx dy dz$

Correspondingly, in case of spherical polar, it is:  $r^2 \sin \theta dr d\theta d\phi$

This comes from the fact that:  $\int_0^R dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin \theta = \frac{4}{3} \pi R^3$

Volume of a  
sphere of radius R

How do we visualize  $\psi(r, \theta, \phi)$  ? \* Orbitals—one electron wavefunctions ← very important!!  
→ difficult, 3-dimensional!

∴ Consider radial and angular part separately.

For  $l = 0$  (i.e., zero angular momentum) it is relatively easy:

Because,  $l=0 \Rightarrow m_l=0$ , ∴ angular part  $Y_{00}(\theta, \phi) = \text{constant}$

$\Rightarrow \psi_{n00}(r, \theta, \phi) = \text{function of } r \text{ alone.}$

For e.g.,

$$\psi_{100}(r, \theta, \phi) \propto e^{-r/a_0}$$

$$\psi_{200}(r, \theta, \phi) \propto \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

Note : cannot observe (experimentally) the orbital  $\psi(r, \theta, \phi)$  but perhaps the density  $|\psi(r, \theta, \phi)|^2$ .

For  $l \neq 0$  we even have complex  $\psi(r, \theta, \phi)$  !

Usually, chemists like to think in terms of real wave functions.  $\Rightarrow$  linear combinations.

What or which orbitals should be linearly combined?

These are typically the degenerate ones.

This is because, if  $\psi_1$  &  $\psi_2$  are such that

$$\hat{H}(\psi_1) = E \psi_1 \text{ and } \hat{H} \psi_2 = E \psi_2$$

$$\Rightarrow \hat{H}(a \psi_1 + b \psi_2) = E(a \psi_1 + b \psi_2)$$

i.e.,  $a \psi_1 + b \psi_2$  is also a valid solution.

So, for e.g. take  $\psi_{2,1,+1}$  and  $\psi_{2,1,-1}$  :

$$\left. \begin{aligned} \psi_{2,1,+1} &\propto R_{2,1}(r) \cdot \sin \theta e^{i\phi} \\ \psi_{2,1,-1} &\propto R_{2,1}(r) \cdot \sin \theta e^{-i\phi} \end{aligned} \right\} \text{degenerate}$$

$$\therefore (\psi_{2,1,+1} + \psi_{2,1,-1}) \propto R_{2,1}(r) \underbrace{\sin \theta \cos \phi}_x \quad p_x$$

$$(\psi_{2,1,+1} - \psi_{2,1,-1}) \propto R_{2,1}(r) \underbrace{\sin \theta \sin \phi}_y \quad p_y$$

$\therefore$  first one “directed” along x and second one along y.

These are all “Standing waves”. Also, there is the case:

$$\psi_{2,1,0} \propto R_{2,1}(r) \cos \theta \rightarrow Z\text{-axis.} \quad p_z$$

We call these orbitals as  $p_x, p_y$  and  $p_z$  orbitals.

$$\left. \begin{aligned} l=0 &: s\text{-orbitals} \\ l=1 &: p\text{-orbitals} \\ l=2 &: d\text{-orbitals} \end{aligned} \right\} \begin{aligned} &\text{given } \underline{n}. \\ &n = 1 \quad 2 \quad 3 \quad 4 \dots \\ &K \quad L \quad M \quad N \dots \\ &(\text{shells}) \end{aligned}$$

Total number of nodes :  $n-1$

Number of nodes in radial function :  $n-l-1$  (excluding  $r=0$ )

In Interstellar space: Very highly excited H – atom observed

i.e.,  $n \approx 200$  !!

This is possible only in interstellar space...

$$\langle r \rangle = \int \psi r \psi^* d\tau = \int r |\psi|^2 d\tau \approx n^2 a_0 \approx 4 \times 10^4 \times 0.53 \times 10^{-10} \text{ m} \approx 2 \times 10^{-6} \text{ m} \quad \text{Really a large atom!!}$$

Interstellar space provides such collision free space!!

These are called Rydberg states.

The zero at  $r=0$  is not a radial node as the radial wavefunction does not pass through zero at that point (because  $r$  cannot be negative). Nodes at the nucleus are all angular nodes.

Before we move on to multi-electron atoms, let me point out that the exact solutions (wavefunctions & energies) for the H – atom means we have the solutions for “Hydrogen like” atoms as well.

For e.g. these include,

$$He^+, Li^{2+}, Be^{3+}, \dots \text{etc.} \quad ; \quad \text{They are all } 1 e^- \text{ systems but nuclear charge } Ze.$$

Similarly, you could also combine s & p orbitals of the same energy (i.e., same  $n$  value) to produce hybrid orbitals. Depending on the % contribution of the contributing orbitals, the shape & properties of the hybrid orbitals are generated. Thus, for  $sp$ -hybrid orbitals equal contribution from s & p exists resulting in linear wavefunctions!!

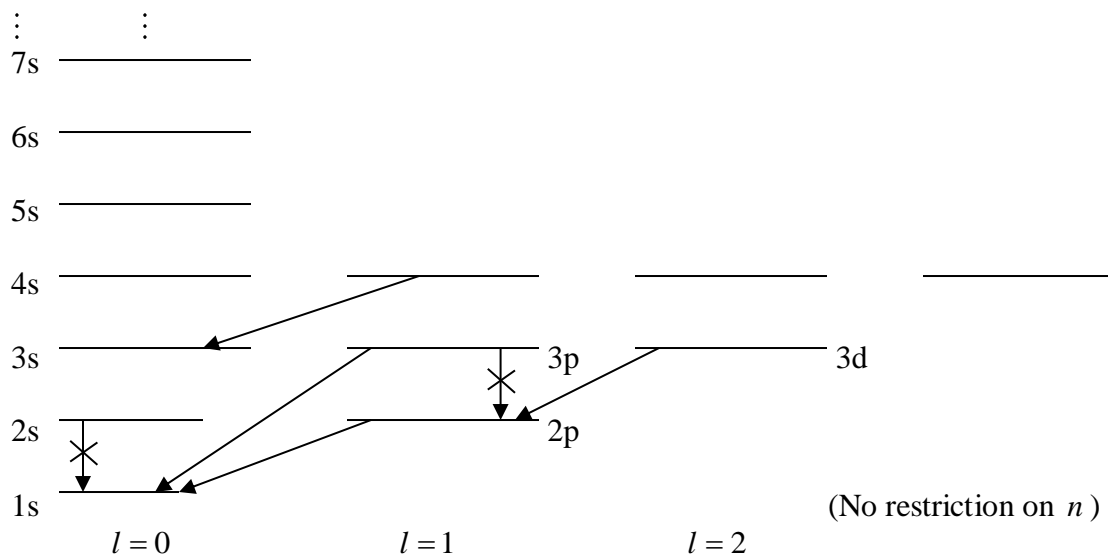
Thus,

$$\hat{H}(a\psi_{2s} + b\psi_{2p_z}) = E(a\psi_{2s} + b\psi_{2p_z})$$

$$\Rightarrow |a|^2 = |b|^2 = 0.5$$

Here,  $Z$  is the atomic number.  
(For the expressions of  $\psi$  &  $E$  look up Atkins.)

In any case of H – atom (or hydrogen like atom) spectrum result due to the electron undergoing transitions from a state  $n_1 l_1 m_{l_1}$  to  $n_2 l_2 m_{l_2}$ .



Arbitrary transition are not allowed. Only  $\Delta l = \neq \pm 1$ ,  $\Delta m_l = 0, \pm 1$   
(Selection rule)

For e.g. a 3d electron means  $n = 3$ ,  $l = 2$ .

Thus,  $\Delta l = \pm 1 \Rightarrow$  this 3d elec. Can make radiative transitions to levels with  $l = 2 + 1 = 3$  or  $l = 2 - 1 = 1$   
i.e,  $nf$  ( $l = 3$ ) or  $np$  ( $l = 1$ ); with condition  $\Delta m_l = 0, \pm 1$ .

But  $3d \not\rightarrow 3s$ , since, then  $|\Delta l| = 2$ .

Recently people have become interested in atoms excited to very high  $n$ .  
Typically,  $n \approx 100$  !

Such highly excited states are called as Rydberg states.

Making them in a lab are not easy – since they “bump into” other atoms way too often.  
But in interstellar space we have lots of room and very low pressures, and radius astronomers have detected transition  $n = 253 \rightarrow n = 252$ .