

3.1: Review: The Hydrogen Atom

- The H atom wave functions (orbitals)
 - The electronic states of the simplest case
 - The 1-e orbitals form the basis for expanding approximate wave functions of many-e atoms
- The wave functions of H-atom (or H-like atom with an appropriate choice of the atomic number Z) depend on
 - the spatial variables, r , θ and φ
 - spin coordinate
- The spatial variable
 - The spherical polar coordinates, which allow the Schrodinger equation to be solved using separation of variables
 - Define the position of the electrons relative to the centre of mass of the atom – quite close to the position of the more massive nucleus
 - The polar coordinates r , θ and φ are related to the Cartesian coordinates x , y and z :
(C374a)

$$x = r \cdot \sin \theta \cdot \cos \varphi, \quad y = r \cdot \sin \theta \cdot \sin \varphi, \quad z = r \cdot \cos \theta$$

3.1-a: The Schrodinger Equation

- The spatial-dependent components of the wave functions can be obtained by applying the rigid-rotor model
 - For the H atom, an electron moves around the nucleus in a coulombic potential field, and the distance between the electron and the nucleus is not fixed.
- The Schrodinger equation for this system is thus,

$$\hat{H} \psi = E \psi$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{Ze^2}{4\pi \epsilon_0 r}$$

– It can also be expressed as

$$\hat{H} = -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} \right] + \frac{1}{2m_e r^2} \cdot \hat{\ell}^2 - \frac{Ze^2}{4\pi \epsilon_0 r}$$

– By applying the separation of variables, i.e., $\psi(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{\ell}^{m_{\ell}}(\theta) \cdot \Phi_{m_{\ell}}(\phi)$

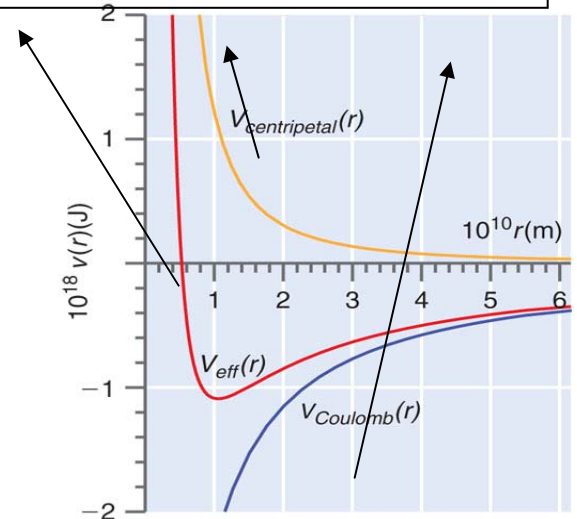
– Since the spherical harmonic function is the eigenfunction of the angular momentum operator, the Schrodinger equation is reduced to

$$\left\{ -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \left[\frac{\hbar^2 \cdot \ell \cdot (\ell + 1)}{2m_e r^2} - \frac{Ze^2}{4\pi \epsilon_0 r} \right] \right\} \cdot R_{nl}(r) = E \cdot R_{nl}(r)$$

• The Schrodinger equation for the H atom:

- It differs from the rigid rotor problem; r is not fixed, the potential depends inversely on r .
- However, the potential is not dependent on the angular coordinates for the H atom
 - The solutions to the Schrodinger equation for θ and ϕ are the same as those for the rigid rotor
- The separation of variables allows to separate the dependence of the wave function on the radial coordinate, r , from that on the angles.
 - The energy of the H-atom only depends on r
- The second term on the left-hand side can be viewed as an effective potential, V_{eff}

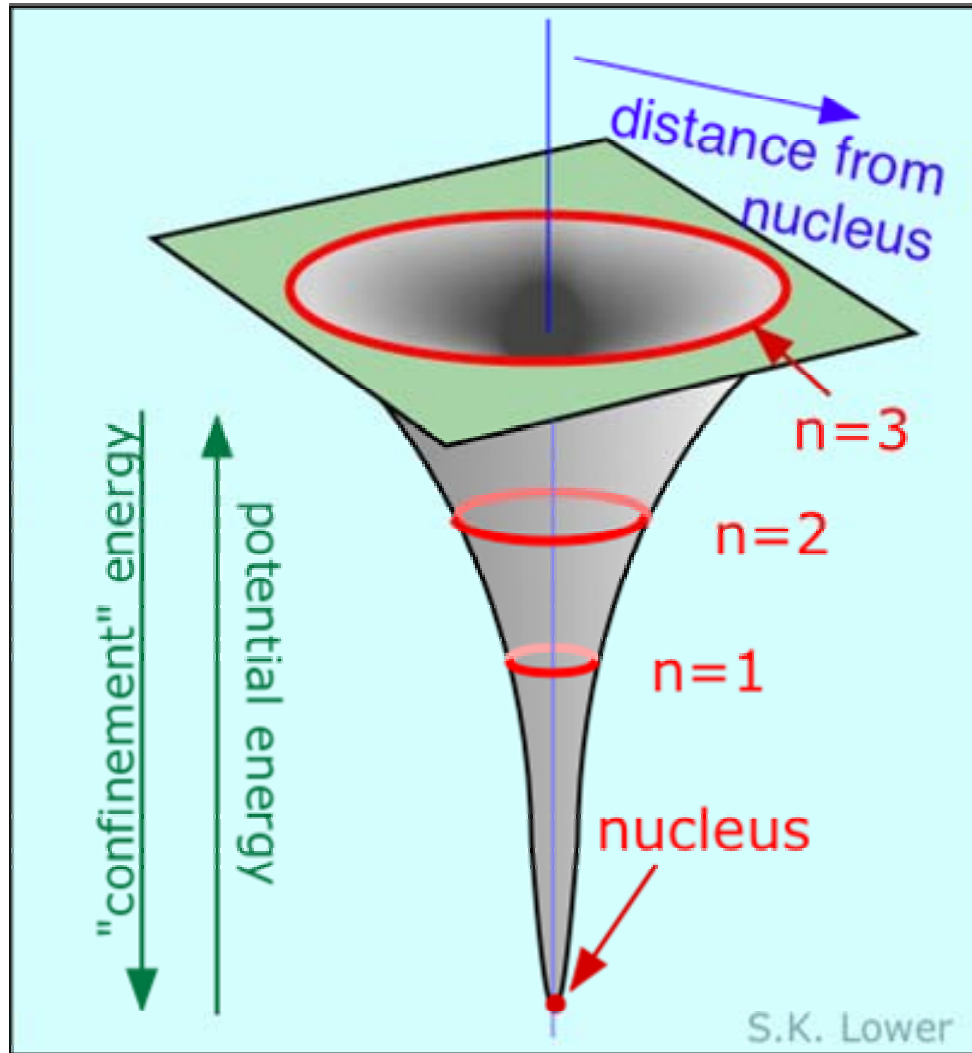
$$V_{\text{eff}}(r) = \frac{\hbar^2 \cdot \ell \cdot (\ell + 1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$



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• The Effective potential:

- Centripetal potential ($+1/r^2$ dependence) and Coulomb potential ($-1/r$ dependence)
 - If $\ell \neq 0$, the repulsive centripetal potential dominates at small distance
 - Both terms approach zero at large r .
 - The resultant potential is repulsive at short distance and more repulsive the greater the value of ℓ .
- The net result of the repulsive potential is to force the electrons in orbitals with $\ell > 0$ farther from the nucleus than s ($\ell = 0$) electrons



A close up of the Coulomb $1/r$ potential in 3-D.

3.1-b: The H-Atom Orbitals

- The radial component of the Schrodinger equation

$$\left\{ -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V_{eff}(r) \right\} \cdot R_{nl}(r) = E \cdot R_{nl}(r)$$

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

- The solutions of the radial component, $R_{nl}(r)$ are known as Laguerre Polynomials.
 - The overall solutions of the Schrodinger Eq. for the H-atom wave functions

$$\psi(r, \theta, \varphi) = R_{nl}(r) \cdot \Theta_{\ell}^{m_{\ell}}(\theta) \cdot \Phi_{m_{\ell}}(\varphi) = R_{nl}(r) \cdot Y_{\ell m_{\ell}}(\theta, \varphi)$$

The principal quantum number n is associated with r

- The solutions $Y_{\ell m}(\theta, \varphi)$, Legendre Polynomials, are those of the rigid-rotor (see C374a notes)
- The total energy eigenfunctions are also referred to as the orbitals
- A short-hand notation

$$\Psi_{n\ell m_{\ell}}$$

- Including the spin variable, the wave functions for the H atom are presented as

$$\Psi_{n\ell m_{\ell} m_s}(r, \theta, \varphi, \delta) = R_{nl}(r) \cdot Y_{\ell m_{\ell}}(\theta, \varphi) \cdot \begin{Bmatrix} \alpha \\ \beta \end{Bmatrix}$$

$$\begin{aligned} \ell = 0 & : \text{s - sharp} \\ \ell = 1 & : \text{p - principal} \\ \ell = 2 & : \text{d - diffused} \\ \ell = 3 & : \text{f - fundamental} \end{aligned}$$

–More on this later

3.1-c: The Energy Levels of the H Atom

- The wave functions

$$\Psi_{n\ell m_\ell m_s}(r, \theta, \varphi, \delta) = R_{n\ell}(r) \cdot Y_{\ell m_\ell}(\theta, \varphi) \cdot \begin{Bmatrix} \alpha \\ \beta \end{Bmatrix}$$

- The energy levels of the electronic states of one-e atoms

$$E_n = -\frac{Ze^2}{8\pi\epsilon_0 n^2 a_0} = -\frac{Z}{n^2} \times 13.6 \text{ eV}; \quad n = 1, 2, 3, \dots$$

$$a_0 = \text{Bohr radius} = 0.529 \text{ \AA} = \frac{4\pi\epsilon_0 \hbar^2}{\mu \cdot e^2}, \quad \mu = \frac{m_e m_N}{m_e + m_N} \approx m_e$$

where the degeneracy of each energy level, g_n , is specified by the principal quantum number n

$$g_n = 2n^2$$

ℓ, m_ℓ and m_s

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

$$m_\ell = -\ell, -\ell+1, \dots, 0, \ell-1, \ell$$

$$m_s = +\frac{1}{2}, -\frac{1}{2} \quad (\text{i.e., } s, -s); \quad s = \frac{1}{2}$$

The allowed values of these quantum numbers derive from the boundary conditions.

The spin quantum number, s is always equal to $\frac{1}{2}$, so it does not need to be specified for a one-e atom.