

The effective potential: result of the solution of the angular part

- The solutions for the angular part results in a term in potential energy equal to:

$$V' = -\frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2}$$

- This term contains the contributions to the energy from angular terms.
- Together with the Coulomb potential the effective potential energy is:

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

The radial equation for hydrogen

Making the above approximations we have an radial hamiltonian (energy operator)

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

The solutions have the form: $R_{n,l} = N_{n,l} \rho^l e^{-\rho/2} L_{n,l}(r)$

where $\rho = 2Zr/na_0$ and $a_0 = 4\pi\epsilon_0 \hbar^2 / me^2$

$N_{n,l}$ is the normalization constant.

$L_{n,l}(r)$ is an associated Laguerre polynomial.

Solutions of the radial equation

The normalization constant depends on n and ℓ

$$N_{n,\ell} = \left\{ \frac{(n - \ell - 1)!}{2n(n + 1)!^3} \right\} \left(\frac{n}{2a_0} \right)^{\ell+3/2}$$

The associated Laguerre polynomials are:

$$n = 1, \ell = 0, L_1^1(x) = -1$$

$$n = 2, \ell = 0, L_2^1(x) = -2! (2 - x)$$

$$n = 2, \ell = 1, L_3^3(x) = -3!$$

$$n = 3, \ell = 0, L_3^1(x) = -3! (3 - 3x + 1/2x^2)$$

$$n = 3, \ell = 1, L_4^3(x) = -4! (4 - x)$$

$$n = 3, \ell = 2, L_5^5(x) = -5!$$

Normalization of the radial functions

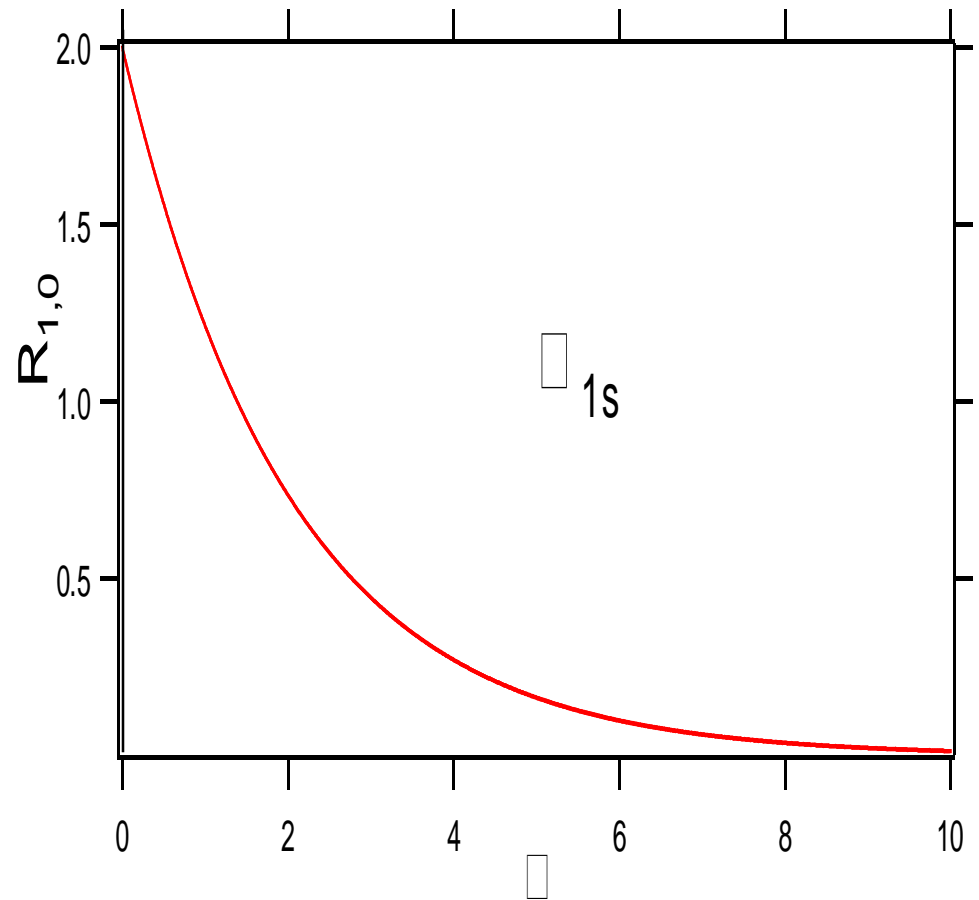
Each of the radial equation solutions is a polynomial multiplying an exponential. The normalization is obtained from the integral:

$$\int_0^{\infty} R_{n\ell}^* R_{n\ell} r^2 dr = 1$$

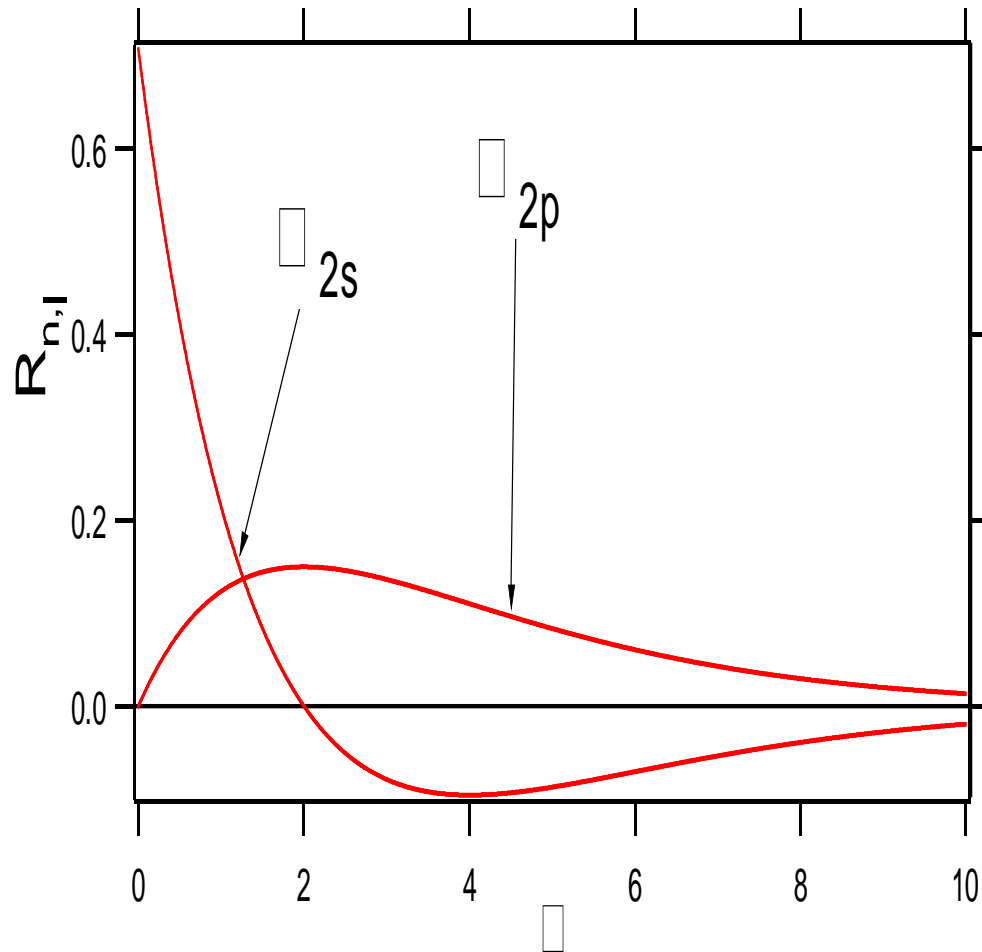
The volume element here is $r^2 dr$ which is the “r” part of the spherical coordinate volume element $r^2 \sin\theta dr d\theta d\phi$.

Hydrogen 1 s radial wavefunction

- The 1s orbital has no nodes and decays exponentially.
- $R_{1s} = 2(1/a_0)^{3/2}e^{-\rho/2}$
- For $n = 1$, $\rho = r/a_0$
- $n = 1$ and $\ell = 0$ are the quantum numbers for this orbital.



The Radial Distribution in Hydrogen 2s and 2p orbitals



Radial wave functions for H

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

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

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

$$R_{3s} = \frac{2}{3\sqrt{3}} \left(\frac{Z}{a} \right)^{3/2} \left(1 - \frac{2Zr}{3a} + \frac{2Z^2 r^2}{27a^2} \right) e^{-Zr/3a}$$

The Quantized Energy Levels

- The energy levels calculated using the Schrödinger equation are given by

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2} = -\frac{R}{n^2}$$

- In units of Bohrs the Rydberg constant is

$$R = \frac{me^4}{8\varepsilon_0^2 h^2} = \frac{e^2}{(4\pi\varepsilon_0)2a_0}$$

The Rydberg Constant

- The energy levels calculated using the Schrödinger equation permit calculation of the Rydberg constant.
- One major issue is units. Spectroscopists often use units of wavenumber or cm^{-1} . At first this seems odd, but $h\nu = hc/\lambda = hc\tilde{\nu}$ where $\tilde{\nu}$ is the value of the transition in wavenumbers.

$$\tilde{R} = \frac{1}{hc} \frac{me^4}{8\varepsilon_0^2 h^2} \quad \text{in cm}^{-1}$$

The simple form for H energy levels

Using the Rydberg constant the energy of the hydrogen atom can be written as:

$$E_n = -\frac{\tilde{R}}{n^2}$$

where $R = 109,690 \text{ cm}^{-1}$

In units of eV $R = 13.6 \text{ eV}$.

Shells and subshells

- All of the orbitals of a given value of n for a shell.
- $n = 1, 2, 3, 4 \dots$ correspond to shells K, L, M, N...
- Orbitals with the same value of n and different values of ℓ form subshells.
- $\ell = 0, 1, 2, \dots$ correspond to subshells s, p, d ...
- Using the quantum numbers that emerge from solution of the Schrödinger equation the subshells can be described as orbitals.

Spectroscopy of atomic hydrogen

- Spectra reported in wavenumbers, cm^{-1}
- Rydberg fit all of the series of hydrogen spectra with a single equation, $\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
- Absorption or emission of a photon of frequency ν occurs in resonance with an energy change, $\Delta E = h\nu$ (Bohr frequency condition).
- Solutions of Schrödinger equation result in further selection rules.

Spectroscopic transitions

- A transition requires a transfer from one state with its quantum numbers (n_1, ℓ_1, m_1) to another state (n_2, ℓ_2, m_2) .
- Not all transitions are possible: there are selection rules, $\Delta\ell = \pm 1, m = 0, \pm 1$
- These rules demand conservation of angular momentum. Since a photon carries an intrinsic angular momentum of 1.

The definition of an isosurface

A second way to view the hydrogen atom can be expressed by the question, "how big is the hydrogen atom?". We can define the size of the atom in terms of an isosurface. The isosurface is defined for a given probability. For example, we can calculate how large a sphere corresponds to a 90% probability for finding the electron. This 90% isosurface defines the radius of the atom. Assuming $Z = 1$ and units of Bohrs ($a_0 = 1$) the normalized radial 1s wave function is

$$R_{1s} = 2e^{-r}$$

The density contained within a 90% probability surface will have a radius A given by

$$\int_0^A R_{1s}R_{1s}r^2 dr = 0.9$$

The 90% isosurface of the H atom

Substituting in the 1s wave function we find

$$4 \int_0^A e^{-2r} r^2 dr = 0.9$$

This integral is readily solved to give the equation,

$$1 - (1 + 2A + 2A^2)e^{-2A} = 0.9$$

While this equation does not have analytic solution, it can readily be solved numerically to yield

$A = 2.66$. Thus, the 90% isosurface is defined as total density within 2.66 Bohrs of the nucleus.

