

Lecture 2 Summary Phys 402

We wrote down the Schrödinger equation in spherical coordinates and proceeded to solve it by separation of variables. We will solve it for a Hydrogen atom in which there is a (conservative) electrostatic (central) force between a proton and an electron, with potential $V(r) = -e^2 / (4\pi\epsilon_0 r)$, where e is the electronic charge, ϵ_0 is the permittivity of free space, and r is the radial coordinate, representing the distance from the proton to the electron (we shall discuss the QM 2-body problem in more detail during a discussion section later in the semester). We look for a solution with constant energy E such that $\psi(r, \theta, \phi, t) = u(r, \theta, \phi)e^{-iEt/\hbar}$. The resulting time-independent Schrödinger equation in spherical coordinates is given by Eq. [4.14] of Griffiths.

Separate variables as $u(r, \theta, \phi) = R(r)Y(\theta, \phi)$ to get an equation that has r -dependent terms (only) on one side, and θ, ϕ -dependent terms (only) on the other side (Griffiths, p. 134). Each side of the equation must separately equal a constant “ α ” (i.e. something independent of r, θ, ϕ), yielding the radial and angular equations, Griffiths [4.16] and [4.17], respectively.

Starting with the definition of the angular momentum operator $\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times (-i\hbar\vec{\nabla})$, the angular momentum squared operator in spherical coordinates is: $L^2 = \vec{L} \cdot \vec{L} = \frac{-\hbar^2}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) - \frac{\hbar^2}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}$. By comparison with Eq. [4.17] one sees that it contains the angular momentum squared operator: $L^2 Y = \hbar^2 \alpha Y$, which is a nice eigenvalue problem. The eigenvalues of L^2 will turn out to be $\hbar^2 \ell(\ell+1)$, where ℓ is zero or a positive integer, and the eigenfunction is the ‘spherical harmonic’ $Y_\ell^m(\theta, \phi)$, where m is another positive or negative integer or zero with $\ell \geq |m|$.

The radial equation has an infinite number of bound states ($E < 0$) for any given value of ℓ .

$$\frac{-\hbar^2}{2m} \frac{d^2(rR)}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2m r^2} \right] (rR) = E(rR)$$

The solutions are proportional to a finite polynomial called the Laguerre polynomial, which we will find later. The solution to this equation also results in a

quantization condition for the energy: $E_n = -\frac{1}{n^2} \frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$, where m is the electron (reduced) mass, and n is an integer that is bigger than ℓ , i.e. $\ell \leq n-1$. One also finds a characteristic length for the Hydrogen atom, called the Bohr radius: $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$, which is about 0.5 Angstroms.

The full solution of the time-independent Schrödinger equation for the H-atom is found by multiplying the $R(r)$ solution with the angular solution and properly normalizing the entire wavefunction:

$$\psi_{n\ell m}(r, \theta, \phi, t) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} \left(\frac{2r}{na_0}\right)^\ell e^{-r/na_0} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right) Y_\ell^m(\theta, \phi) e^{-iE_n t/\hbar}$$

There are three quantum numbers: n (principal), ℓ (ang. mom.) and m (magnetic). They have possible values given by:

$$n = 1, 2, 3, 4, \dots$$

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

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

The Hydrogen atom wavefunctions are orthonormal, Griffiths [4.90].

We shall examine the angular and radial equations in more detail next.