The Central Force Problem: Hydrogen Atom

B. Ramachandran

1 Separation of Variables

The Schrödinger equation for an atomic system with \( Z \) protons in the nucleus and one electron “outside” is

\[
\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0) r} \right) \psi = E\psi, \tag{1}
\]

where \( \varepsilon_0 \) is the permittivity of vacuum, which is a constant having the value \( 8.854187 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1} \) \( (4\pi\varepsilon_0 = 1.112650 \times 10^{-10} \text{ J}^{-1}\text{C}^2\text{m}^{-1}) \), and \( \mu \) is the reduced mass of the nucleus-electron system. The quantity \( \nabla^2 \) appearing above is the Laplacian which, in Cartesian coordinates, is given by

\[
\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.
\]

Transforming the Laplacian to spherical polar coordinates, we get

\[
-\frac{\hbar^2}{2\mu} \nabla^2 = -\frac{\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \tag{2}
\]

We recognize that

\[
\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).
\]

With this substitution, and making the well-justified assumption that \( \mu \approx m_e \), the mass of the electron, Eq. (1) becomes

\[
\left[ -\frac{\hbar^2}{2m_e} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r} - E \right] \psi(r, \theta, \phi) = 0. \tag{3}
\]

The presence of the \( \hat{L}^2 \) operator suggests that the angular part of the solution, i.e., the part that depends on the angles, are the spherical harmonics \( Y_l^m(\theta, \phi) \). Therefore, we choose the following function to attempt a separation of variables:

\[
\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi). \tag{4}
\]

Substituting Eq. (4) into Eq. (3) and simplifying, we get

\[
\frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} + \left[ \frac{2m_e}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\varepsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0. \tag{5}
\]

The notation can be further simplified by defining the following dimensionless parameters:

\[
\alpha^2 = \frac{-2m_e E}{\hbar^2}, \quad \beta = \frac{Ze^2 m_e}{4\pi\varepsilon_0 \hbar^2 \alpha}.
\]
Note that $\alpha^2$ will be positive only for negative values of $E$. This means that the parameter $\alpha$ will become complex for positive values of $E$, thereby restricting real solutions to those with negative energy. Since zero potential energy corresponds to infinite separation of the charges $(Ze)$ and $(-e)$, the negative energies correspond to the bound states of the atom. Using these definitions, Eq. (5) can be simplified to

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} - \left[ \alpha^2 - \frac{2\alpha \beta}{r} + \frac{l(l+1)}{r^2} \right] R = 0.$$  

(6)

2 Solving the Radial Equation

We could now attempt a series solution of Eq. (6) as was done in the case of the harmonic oscillator. However, this would lead to a three-term recursion relationship which is much harder to deal with than a two-term one. Therefore, we define a new variable $\rho = 2\alpha r$ and express Eq. (6) in terms of this variable as

$$\frac{\partial^2 T}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial T}{\partial \rho} - \left[ \frac{1}{4} \beta \rho + \frac{l(l+1)}{\rho^2} \right] T = 0,$$

(7)

where $T(\rho)$ is simply $R(r)$ expressed in terms of the new variable.

Let us examine the asymptotic behavior of the solution. As $\rho \to \infty$, Eq. (7) reduces to

$$\frac{\partial^2 T}{\partial \rho^2} - \frac{1}{4} T = 0,$$

which has the solution $T(\rho) = \exp(\pm \rho/2)$. The solution corresponding to the positive exponent grows exponentially as $\rho$ increases. This makes it impossible for the solution to be square-integrable. Therefore, we choose the solution corresponding to the negative exponent. Let us now assume that the general solution will be of the form

$$T(\rho) = G(\rho) \exp(-\rho/2).$$  

(8)

Substituting Eq. (8) into Eq. (7) and simplifying yields

$$\rho^2 G''(\rho) + (2\rho - \rho^2) G'(\rho) + \{ (\beta - 1)\rho - l(l+1) \} G(\rho) = 0.$$  

(9)

This equation must be valid for all values of $\rho$. Therefore, at $\rho = 0$, we have

$$l(l+1)G(\rho) = 0; \quad l = 0, 1, 2, ...$$

Since this equation has to be satisfied for nonzero values of $l$, this suggests that $G(\rho)$ must have the form $\rho^s L(\rho)$, with $s > 0$. We now expand $L(\rho)$ in a power series as

$$L(\rho) = \sum_{j=0}^{\infty} a_j \rho^j.$$  

(10)

Substituting this expression for $G(\rho)$ into Eq. (9) and collecting terms with the same power of $\rho$, we get the following recursion relationship for the coefficients $a_j$:

$$\frac{a_{j+1}}{a_j} = \frac{l + j + 1 - \beta}{(j+1)(j+2l+2)}.$$  

(11)
Now, we must verify whether the series will converge as $j \to \infty$. From Eq. (11), it is clear that
\[
\lim_{j \to \infty} \frac{a_{j+1}}{a_j} = \frac{1}{j}.
\]

To understand what such a series might resemble, consider a Taylor expansion of the function $e^\rho$:
\[
e^\rho = \sum_{j=0}^{\infty} \frac{\rho^j}{j!} = \sum_{j=0}^{\infty} b_j \rho^j,
\]
\[
\lim_{j \to \infty} \frac{b_{j+1}}{b_j} = \frac{j!}{(j+1)!} = \frac{1}{j+1} \approx \frac{1}{j} \text{ for large } j.
\]

### 3 Truncation of the Series: Quantized Energies

This suggests that $L(\rho)$, and therefore $G(\rho)$, behaves like $e^\rho$ asymptotically. This, of course, leads to a non-square-integrable solution, and is also in contradiction to the conclusion from Eq. (8) that $T(\rho)$ behaves like $e^{-\rho/2}$ as $\rho \to \infty$. The way out of this difficulty, of course, is to truncate the series at some value of $j$ (as in the case of the harmonic oscillator), say $j = k$, so that
\[
\frac{a_{k+1}}{a_k} = \frac{l + k + 1 - \beta}{(k+1)(k+2l+2)} = 0,
\]
i.e.,
\[
\beta = l + k + 1.
\]

Since $l + k + 1$ must be an integer, having possible values $1, 2, 3, \ldots, \infty$, we define $n = l + k + 1$ so $\beta = n; n = 1, 2, \ldots, \infty$. Also, since the truncation relationship must be valid for all values of $k$ including $k = 0$, we see that $n \geq l + 1$ or $l \leq (n - 1)$. Thus, the series truncation also imposes a limit on the values $l$ can assume. Now, substituting this into the definition of $\beta$, we get
\[
n = \frac{Ze^2 m_e}{4\pi \varepsilon_0 \hbar^2 \alpha}, \text{ or }
\]
\[
n^2 = -\left(\frac{Ze^2 m_e}{4\pi \varepsilon_0 \hbar^2 \alpha}\right)^2 \frac{\hbar^2}{2m_e E}.
\]

Rearranging, and recognizing that the energies depend on the integer $n$, we get
\[
E_n = -\frac{Z^2 e^4 m_e}{32 \pi^2 \varepsilon_0 \hbar^2 n^2}, \quad n = 1, 2, \ldots, \infty.
\]

We now define a parameter $\alpha_0 = \frac{4\pi \varepsilon_0 \hbar^2}{me^2}$, so that
\[
E_n = -\frac{1}{2} \left(\frac{e^2}{4\pi \varepsilon_0 \alpha_0}\right) \frac{Z^2}{n^2}.
\]
4 Atomic Units

The parameter \( a_0 \) has units of length (verify this!) and is equal to \( 0.529177 \times 10^{-10} \) m. This parameter has a special place in quantum chemistry because it is the unit of length (called the Bohr) in atomic units (au), which are a set of units commonly used in quantum chemistry calculations. In these units, the unit of mass is the mass of the electron (i.e., \( m_e = 1 \) au), and \( \hbar = 1 \) so that for the case of the Hydrogen atom (\( Z = 1 \)), the ground state energy is \( E_1 = -\frac{1}{2} \). The unit of energy is the quantity \( e^2 / (4\pi \varepsilon_0 a_0) \) called the Hartree and so, we see that the ground state of the hydrogen atom is half of a Hartree below the ionization limit (i.e., \( E = 0 \)). From this information, we calculate that

\[
1 \text{ Hartree} = 27.2115 \text{ eV} = 4.35979 \times 10^{-18} \text{ J},
\]

where “eV” stands for the electron volt, a commonly used unit of energy in quantum chemistry, defined as \( 1 \text{ eV} = e(\text{C}) \times 1.0 \text{ Volt} = 1.60219 \times 10^{-19} \text{ J} \).

5 The Rydberg Constant

The energy expression of Eqs. (13) or (14) can be used to calculate the value of the Rydberg constant appearing in Bohr’s original expression for the frequencies of the lines appearing in the emission spectrum of the hydrogen atom. Bohr’s expression was

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right); n_2 > n_1.
\]

Recognizing that \( \Delta E = h\nu = h\nu/\lambda \), we get from Eq. (14),

\[
\Delta E = \frac{\hbar^2}{2m_e} \left( \frac{Z}{a_0} \right)^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right); n_2 > n_1,
\]

\[
\frac{1}{\lambda} = \frac{\hbar}{4\pi^2 cm_e} \left( \frac{Z}{a_0} \right)^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).
\]

The value of the Rydberg constant \( R \) thus calculated is 109,677 cm\(^{-1}\). Modern experiments have established the correctness of this value to about 8 significant figures.

6 Atomic Orbitals

It is obvious from Eq. (5) that the solutions of the radial equation depend on the value of \( l \). Now, the series truncation condition above also brings in a quantum number \( n \). The radial solutions are, therefore, written as \( R_{nl}(r) \), and including normalization, are given by

\[
R_{nl}(r) = N_{nl} G_{nl}(\rho) e^{-\rho/2},
\]

\[
N_{nl} = -\left\{ \left( \frac{2Z}{n a_0} \right)^3 \times \frac{(n-l-1)!}{2n ![n+l]!]^3} \right\},
\]

\[
G_{nl}(\rho) = \rho^l I_{n+1}(\rho),
\]
where the polynomials denoted by $L^s_r(\rho)$ are called the associated Laguerre polynomials of degree $(r-s)$, and are defined as

$$L^s_r(\rho) = \frac{d^s}{d\rho^s} L_r(\rho),$$

where the $L_r(\rho)$ are the Laguerre polynomials given by

$$L_r(\rho) = e^\rho d^r d\rho d^r \rho e^{-\rho}.$$

Substituting for $\alpha$ in the definition of $\rho$, we get $\rho = 2Zr/(na_0)$. We now write the solutions to the hydrogen atom problem as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y^m_l(\theta, \phi),$$

(15)

$n = 1, 2, ..., \infty,$

$l = 0, 1, ..., (n-1),$

$m = 0, \pm 1, \pm 2, ..., \pm l.$

The convention followed in labeling atomic states is to use a letter symbol to denote various values of $l$, so that we use

<table>
<thead>
<tr>
<th>Value of $l$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Letter symbol</td>
<td>$s$</td>
<td>$p$</td>
<td>$d$</td>
<td>$f$</td>
<td>$g$</td>
<td>$h$</td>
</tr>
</tbody>
</table>

Therefore, the state $|nlm\rangle = |210\rangle$ is referred to as the 2p$^0$ state and so on. Each $|nlm\rangle$ state defines what is known as an atomic orbital.

Let us now examine the nature of the wave functions. We define two types of probability functions for this purpose. The quantity $|\psi_{nlm}(r, \theta, \phi)|^2 dr \sin \theta d\theta d\phi$ gives the probability of finding the electron in a volume element enclosed by the limits $(r, r + dr; \theta, \theta + d\theta; \phi, \phi + d\phi)$. However, when dealing with a “spherical” species like an atom, it is more useful to average over the angles and get the radial distribution function, $S_{nl}(r)$, which is obtained as

$$S_{nl}(r) = r^2 |R_{nl}(r)|^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi |Y^m_l(\theta, \phi)|$$

$$= r^2 |R_{nl}(r)|^2 dr.$$  

The final result comes about because the integrals over the angles yield unity because the spherical harmonics are normalized:

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi |Y^m_l(\theta, \phi)| = 1.$$  

(16)

The physical significance of this is that $r^2 |R_{nl}(r)|^2 dr$ gives the probability for finding the electron on a spherical shell of radius $r$ and thickness $dr$. We will examine the shapes of the radial functions and the two types of probability distribution functions using class handouts. We will also combine the radial functions with the spherical harmonics (i.e., generate atomic orbitals) and examine the nodal structure of these three-dimensional functions.

Below, we tabulate a few solutions of the Schrödinger equation Eq. (1). For convenience, we define
\[ \sigma = n\rho /2 = Zr /a_0. \]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( m )</th>
<th>( \psi_{nlm}(r) )</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>( \frac{\sqrt{\pi}}{a_0} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( e^{-\sigma} )</td>
<td>1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 0 0</td>
<td>( \frac{1}{4\sqrt{2\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( Z/a_0 )ue^{-\sigma/2}</td>
<td>2s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 1 0</td>
<td>( \frac{1}{4\sqrt{2\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma e^{-\sigma/2} \cos \theta )</td>
<td>2p_z</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 1 ( \pm 1 )</td>
<td>( \frac{1}{4\sqrt{2\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma e^{-\sigma/2} \sin \theta \cos \phi )</td>
<td>2p_x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 1 ( \pm 1 )</td>
<td>( \frac{1}{4\sqrt{2\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma e^{-\sigma/2} \sin \theta \sin \phi )</td>
<td>2p_y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 0 0</td>
<td>( \frac{1}{8\sqrt{16\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3} )</td>
<td>3s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 1 0</td>
<td>( \frac{\sqrt{3}}{8\sqrt{16\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma (6 - \sigma) e^{-\sigma/3} \cos \theta )</td>
<td>3p_z</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 1 ( \pm 1 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{16\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma (6 - \sigma) e^{-\sigma/3} \sin \theta \cos \phi )</td>
<td>3p_x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 1 ( \pm 1 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{16\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma (6 - \sigma) e^{-\sigma/3} \sin \theta \sin \phi )</td>
<td>3p_y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 2 0</td>
<td>( \frac{1}{8\sqrt{6\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma^2 e^{-\sigma/3} (3\cos^2 \theta - 1) )</td>
<td>3d_z^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 2 ( \pm 1 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{6\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \cos \phi )</td>
<td>3d_{xz}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 2 ( \pm 1 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{6\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \sin \phi )</td>
<td>3d_{yz}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 2 ( \pm 2 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{6\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma^2 e^{-\sigma/3} \sin^2 \theta \cos 2\phi )</td>
<td>3d_{x^2-y^2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 2 ( \pm 2 )</td>
<td>( \frac{\sqrt{3}}{8\sqrt{6\pi}} \frac{Z}{a_0} ) ( \frac{3}{2} ) ( \sigma^2 e^{-\sigma/3} \sin^2 \theta \sin 2\phi )</td>
<td>3d_{xy}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7 Most Probable and Average Values of \( r \)

The most probable and average distance of the electron from the nucleus is of considerable interest in chemistry and physics. The most probable distance of the electron from the nucleus is given by the position of the highest maximum in \( S_{nl}(r) \). Recall that the derivative of a function goes to zero at its maximum or minimum. For example, in the case of the 1s orbital, we set the derivative of \( S_{10}(r) = 0 \) and get

\[
\frac{d}{dr} \sigma^2 e^{-2\sigma} = (2\sigma - 2)e^{-2\sigma} = 0, \tag{17}
\]

where we have divided both sides by the multiplicative constants present in \( S_{10}(r) \) to eliminate them. Since the exponential term in the derivative is non-negative for all real values of \( \sigma \), we conclude that the most probable value of \( r \) corresponds to \( \sigma = 1 \), or \( r_{mp} = a_0 / Z \). For the hydrogen atom, this is exactly equal to the Bohr radius, which is the radius of the ground state orbit in Bohr’s planetary model of the
hydrogen atom. The average value of \( r \) is given by the expectation value

\[
\langle r \rangle_{nl} = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} r^n \psi_{nlm}^*(r, \theta, \phi) \hat{r} \psi_{nlm}^*(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi
\]

The final result is obtained by a somewhat lengthy and clever use of the method of integration by parts.\(^1\)

### 8 Hydrogenic atoms in a magnetic field

Note that the energy of a one-electron atom, given in Eq. (14), is independent of quantum numbers \( l \) and \( m \). This means that states with the same value of \( n \) but different values of \( l \) and \( m \) have the same energy. Let us examine what happens to these states when a magnetic field is applied along the \( Z \)-axis.

Consider a circular loop of conducting wire of radius \( r \) through which a charge \( Q \) is moving with velocity \( v \). Since current is the charge flow per unit time, we get

\[
I = \frac{Qv}{2\pi r}.
\]

The value of the magnetic dipole \(|\mu|\) associated with this current is given by \( IA \), where \( A \) is the area enclosed by the loop, i.e., \( A = \pi r^2 \). Therefore,

\[
|\mu| = \frac{Qv}{2\pi r} \times \pi r^2 = \frac{1}{2} Qvr = \frac{Qrp}{2m}.
\]

Therefore, the magnetic dipole vector is given by

\[
\mu = \frac{Qr}{2m} \times \mathbf{p} = \frac{Q}{2m} \mathbf{L}.
\]

For an electron,

\[
\mu = \frac{-e}{2m_e} \mathbf{L}, \quad (18)
\]

and

\[
|\mu| = \frac{\hbar}{2m_e} \sqrt{I(I+1)} = \mu_B \sqrt{I(I+1)}, \quad (19)
\]

where the quantity \( \mu_B \) is a constant called the **Bohr magneton**.

Now let us consider a magnetic field \( B \) applied to the atom. The potential energy of interaction between the field \( B \) and the magnetic dipole \( \mu \) is given by

\[
V_B = -\mu \cdot \mathbf{B} \quad (20)
\]

---

\(^1\)Yep. You guessed it. Homework assignment!
From Eq. (18), we get \( V_B = \frac{e}{(2m_e)} \mathbf{L} \cdot \mathbf{B} \). If we assume that the field is oriented along the \( Z \)-direction, i.e., the components of the field along the \( x \) and \( y \) directions are zero, then,

\[
V_B = \frac{e}{2m_e} \left( \hat{i} L_x + \hat{j} L_y + \hat{k} L_z \right) \cdot \hat{k} B = \frac{e}{2m_e} B L_z.
\]

In operator terminology, therefore,

\[
\hat{V}_B = \frac{eB}{2m_e} \hat{I}_z. \tag{21}
\]

Therefore, the Schrödinger equation for a hydrogen atom in a magnetic field is

\[
\left( \hat{H} + \hat{V}_B \right) R_{nl}(r) Y_{ml}^m(\theta, \phi) = (E_n + \mu_B B m) R_{nl}(r) Y_{ml}^m(\theta, \phi), \tag{22}
\]

where the Hamiltonian operator \( \hat{H} \) corresponds to the Schrodinger equation we started with in Eq. (1), \( E_n \) is given by Eq. (14), and \( \mu_B \) is the Bohr magneton defined in Eq. (19). Therefore, in a magnetic field, states with nonzero values of \( m \) will acquire different energies.