Wavefunction for Hydrogen-like Atom

1. Differential Equations

Coulomb potential $-e^2/(4\pi\varepsilon_0 r)$ is created for electron in hydrogen atom.

$$V(\mu) = -\frac{1}{4\pi\epsilon_0}\cdot\frac{Ze^2}{r}$$

Generally, the atom in the above Coulomb potential is called hydrogen-like atom. If we ignored electron-electron interaction, the electron in an atom with valency Z can be considered in such potential. The wavefunction for the electron is defined as:

$$\psi(\mathbf{r}) = R_l(r)Y_{lm}(\theta,\phi)$$

Then, the differenatial equation that radial wavefunction $R_l(r)$ should follow may be:

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}R(r)) + \left\{\frac{2m}{\hbar^2}(E+\frac{Ze^2}{r}) - \frac{l(l+1)}{r^2}\right\}R(r) = 0 \qquad (1)$$

Where,

$$\alpha^2 = \frac{8m|E|}{\hbar^2}, \lambda = \frac{2mZe^2}{\alpha\hbar_2} = \frac{Ze^2}{\hbar}(\frac{m}{2|E|})^{\frac{1}{2}}$$

2. Behavior at $r \sim 0$ and $r \sim \infty$

Convert the variant r with $\rho = \alpha r$, and the differential equation (1) will be:

$$\frac{1}{\rho^2}\frac{d}{d\rho}(\rho^2\frac{d}{d\rho}R) + \left\{\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right\}R = 0 \qquad (2)$$

Before directly solving for the equation (2), let's consider the behaviors at $r \sim 0$ and $r \sim \infty$.

For the large enough values ρ:

$$\square\ \rho \to \infty \quad : \quad \frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0$$

Thus, it is interacting with $R \sim e^{-\frac{1}{2}\rho}$

$$R \equiv e^{-\frac{1}{2}\rho}F(\rho) \quad \text{where,} \quad F(\rho) \to 0(\rho \to \infty)$$

At ρ near 0, and at an atomic nuclei vicinity:

$$\square\ \rho \to 0 \quad : \quad \frac{d^2}{d\rho^2}\upsilon - \frac{l(l+1)}{\rho^2}\upsilon = 0$$

$$R = \frac{\upsilon}{\rho} \to \upsilon = \rho^{l+1}, \rho^{-l}$$

So,

$$R \sim \begin{cases} \rho^l \\ \rho^{-l-1} \end{cases}$$

The other solution $R \sim \rho^{-l-1}$ is not allowed for the following reasons: (1) the solution cannot be normalized at $l \neq 0$. (2) $\nabla^2 r^{-1} = -4\pi\delta(\mathbf{r})$ where $l = 0$ so, it is not the solution for Schrodinger's equation at $r = 0$. Thus, only $R \sim \rho^l$ is valid in this situation.

3. **Series Solution Method**

Based on previous discussion, we can convert the equation as:

$$R = e^{-\frac{\rho}{2}} F(\rho)$$

The differential equation in terms of $F(\rho)$, we obtain:

$$\frac{d^2}{d\rho^2}F + (\frac{2}{\rho} - 1)\frac{d}{d\rho}F + \left\{\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right\}F = 0 \tag{3}$$

The differential equation above holds $\rho = 0$ as a regular singular point. The solution in need for the generalization can be obtained through the series in the following:

$$F(\rho) = \sum_{n=0}^{\infty} C_n \rho^{s+n} \tag{4}$$

To differentiate by each member:

$$\begin{aligned} F'' &= C_0 s(s-1)\rho^{s-2} + \sum_{n-1}^{\infty} C_n(s+n)(s+n-1)\rho^{s+n-2} \\ (\frac{2}{\rho} - 1)F' &= 2C_0 s\rho^{s-2} + \sum_{n=1}^{\infty}\left\{2C_n(s+n) - C_{n-1}(s+n-1)\right\}\rho^{s+n-2} \\ \left(\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2}\right)F &= -C_0 l(l+1)\rho^{s-2} + \sum_{n=1}^{\infty}\left\{C_{n-1}(\lambda-1) - C_n l(l+1)\right\}\rho^{s+n-2} \end{aligned}$$

In addition,

$$C_0\big(s(s+1) - l(l+1)\big)\rho^{s-2}$$
$$+\sum_{n=1}^{\infty}\left\{C_n(s+n)(s+n-1) + 2C_n(s+n) - C_{n-1}(s+n-1) + C_{n-1}(\lambda-1) - C_n l(l+1)\right\}\rho^{s+n-2} = 0$$

Set the coefficients of each term as 0, then:

$$s(s+1) - l(l+1) = (s-l)(s+l+1) = 0$$

$$C_n\left\{(s+n)(s+n+1) - l(l+1)\right\} = C_{n-1}(s+n-\lambda)$$

Since the solutions for $s = -l - 1$ is not acceptable from the previous discussion:

(5)

$$s = l$$
$$C_{n+1} = \frac{n+l+1-\lambda}{(n+1)(n+2l+2)} C_n \quad (6)$$

For a large n, this series may behave as:

$$\frac{C_{n+1}}{C_n} \to \frac{1}{n} \quad (n \to \infty) \quad (7)$$

Therefore, the behavior of r at large distance apart will be $F(\rho) \sim e^{\rho}$. In this case, $R(\rho) \sim e^{-\frac{\rho}{2}} e^{\rho} = e^{\frac{\rho}{2}} \to \infty$, and which does not satisfy the boundary condition $R(\rho) \to 0$ for the convergence. In order to avoid this to happen, it is important for the series to have a finite limit.

Based on the requirements from above:

$$\lambda = l + 1 + n' \quad (8)$$

$C_n = 0 \quad (n \geq n' + 1)$ is derived so, we can write $\lambda \equiv n \ (n = 1, 2, \ldots)$ while n is called principal quantum number. To put it all together:

$F(\rho) = \rho^l \times [\rho$'s $n - l - 1]$ degree of polynomial function (9)

$$C_k = \frac{k+l-n}{k(k+1+2l)} C_{k-1} \qquad k = 1, 2, \ldots, n-l \quad (10)$$

$$n = \frac{Ze^2}{\hbar}\left(\frac{m}{2|E|}\right)^{\frac{1}{2}} \quad (11)$$

The eigenenergy is determined by n

$$|E| = \frac{mZ^2e^4}{2\hbar^2 n^2} \quad (12)$$

And, the radial wavefunction can be obtained:

$$R(r) = \exp\left(-\sqrt{\frac{2m|E|}{\hbar}} r\right) \times \{r\text{の}\ (n-1)\ \text{次多項式} = r^l \times r\text{の}\ (n-l-1)\ \text{次多式}\}$$

Therefore, the nodes for $R(r)$ are determined by {in terms of r polynomials$n-(l+1)$} x {nodes of Y_{lm}} to be total $n-1$.

4. Wavefunction in Hydrogen Atom and Energy Eigenvalue

An extent of wavefunction is:

$$a_0 \equiv \frac{\hbar^2}{me^2} = 0.53 \times 10^{-8} cm \qquad \text{(Bohr radius)}$$

Then, the eigenenergy can be written as:

$$E_n = -\frac{Z^2e^2}{2a_0 n^2}$$

The energy of $n = 1,\ Z = 1$ is called 1 Ry (Rydberg) =13.6 eV, and the unit fixed by

$m=1,\ \hbar=1,\ e=1$ is called "atomic unit". 1 atomic unit of the energy is $2\ \mathrm{Ry}\simeq 27\ \mathrm{eV}$.
For specific radial wavefunctions, we define $a\equiv a_0/Z$:

$$
\begin{aligned}
R_{10}(r) &= a^{-\frac{3}{2}}2e^{-\frac{\rho}{2}} \\
R_{20}(r) &= (2\sqrt{2})^{-1}a^{-\frac{3}{2}}(2-\rho)e^{-\frac{\rho}{2}} \\
R_{21}(r) &= (2\sqrt{6})^{-1}a^{-\frac{3}{2}}\rho e^{-\frac{\rho}{2}}
\end{aligned}
$$

In short, the radial wavefunction can be generalized to be:

$$
F(p) = -\left[(\frac{2Z}{na_0})^3\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]^{\frac{1}{2}} \times \rho^l L_{n+l}^{2l+1}(\rho)
$$

$L_{n+l}^{2l+1}(\rho)$ in the equation is called the associated Laguerre polynomials.

$$
\begin{aligned}
L_{n+l}^{2l+1}(\rho) &= \sum_{k=0}^{n-l-1}(-1)^{k+2l+1}\frac{[(n+l)!]^2\rho^k}{(n-l-1-k)!(2l+1+k)!k!} \\
&= (-1)^{2l+1}e^{\rho}\rho^{-2l-1}\frac{(n+l)!}{(n-l-1)!}\frac{d^{n-l-1}}{d\rho^{n-l-1}}e^{-\rho}\rho^{n+l}
\end{aligned}
$$

This also satisfies the orthonormalization:

$$
\int_0^\infty r^2 R_{nl}(r)R_{n'l}(r)dr = \delta_{nn'}
$$