

QM Solution of Single Particle in $1/r$ Field

Bohr's explanation of the hydrogen atom spectra was one of the major scientific achievements of the last century. His arguments - the so-called Bohr-Sommerfeld quantization condition [1] - was not fully quantum mechanical in nature or correct in the rigorous sense and is therefore called the *semi-classical picture*. Today we seek rigorous, fully quantum mechanical solution to the one-body problem of a single particle in a $1/r$ attraction field based on solving Schrödinger's equation of the form,

$$\frac{-\hbar^2 \nabla^2}{2m} \psi(\mathbf{x}) - \frac{\alpha}{r} \psi(\mathbf{x}) = E \psi(\mathbf{x}), \quad (1)$$

where ψ depends only on a single vector coordinate \mathbf{x} . The hydrogen atom of course has two moving components, the electron and the proton, but it can be shown that this particular two-body system is trivially related to the one-body problem of (1), just like its classical counterpart, Newton's gravity problem. And this lecture is solely concerned with solving (1). Here α is a positive constant specifying the attraction strength, m is the effective mass. In the hydrogen atom case,

$$\alpha = \frac{e^2}{4\pi\epsilon_0}, \quad m = \frac{m_p m_e}{m_p + m_e}. \quad (2)$$

As a general rule, it is better to first reduce a PDE to a certain non-dimensional form before solving it. Because three constants have known values before (1) is solved: m , \hbar and α (E is unknown at this moment and acts like a parameter to be determined), one can use them to define a *reduced unit system* that requires *three independent* measures such as mass, length, energy, time, etc., from which all other reduced units can be determined. The first choice is straightforward: we choose the mass unit to be,

$$[\text{mass}] \equiv m. \quad (3)$$

To pick a length unit, let us compare the two terms on the LHS of (1). As they are added together, $-\hbar^2 \nabla^2 \psi / 2m$ must have the same unit as $-(\alpha/r)\psi$, and therefore if r and Cartesian coordinate \mathbf{x} are measured in certain [length] unit, one should have,

$$\nabla^2 = \frac{1}{[\text{length}]^2} \longrightarrow \frac{\hbar^2}{m[\text{length}]^2} = \frac{\alpha}{[\text{length}]}, \quad (4)$$

(it is customary to keep the signs and number constants like 2 on the denominator *out of the balance* for reasons we will shortly see), and therefore,

$$[\text{length}] \equiv \frac{\hbar^2}{m\alpha}. \quad (5)$$

Finally, if one compares $-(\alpha/r)\psi$ on the LHS of (1) with $E\psi$ on the RHS, one obtains,

$$\frac{\alpha}{[\text{length}]} = [\text{energy}], \quad (6)$$

and so,

$$[\text{energy}] \equiv \frac{m\alpha^2}{\hbar^2}. \quad (7)$$

From now on, everything is settled. For instance, from the kinetic energy expression $K = m|\mathbf{v}|^2/2$, we know there must be,

$$[\text{energy}] = \frac{[\text{mass}][\text{length}]^2}{[\text{time}]^2}, \quad (8)$$

and so the reduced time unit must be,

$$[\text{time}] = \sqrt{\frac{[\text{mass}][\text{length}]^2}{[\text{energy}]}} = \frac{\hbar^3}{m\alpha^2}. \quad (9)$$

What (3),(5),(7) mean together is that if mass, length and energy are measured by such units, the Schrödinger's equation can be re-expressed as,

$$-\frac{\nabla^2}{2}\psi(\mathbf{x}) - \frac{1}{r}\psi(\mathbf{x}) = E\psi(\mathbf{x}), \quad (10)$$

in the so-called dimensionless form, where r actually means $\tilde{r} \equiv r/[\text{length}]$, E actually means $\tilde{E} \equiv E/[\text{energy}]$, etc. in (10), but we just omit writing the tilde of \tilde{r}, \tilde{E} because we are lazy. It should be clear that r, E or \tilde{r}, \tilde{E} in (10) are dimensionless numbers, unlike r, E in (1) which carry units.

Another way of saying the same thing is that m, \hbar, α are all 1 in this particular unit system. Such would not be the case if one absorbs the number constant 2 in the process of definition. There is nothing wrong with any definitions, but it is easier to remember (10) as the result of setting m, \hbar, α to 1 from the original (1). If the number constant 2 is absorbed, we would

have,

$$-\nabla^2\psi(\mathbf{x}) - \frac{\psi(\mathbf{x})}{r} = E\psi(\mathbf{x}), \quad (11)$$

which may be confusing to physicists (but not mathematicians). A better case in point would be that one always likes to remember the kinetic energy K as $m|\mathbf{v}|^2/2$ with m taking convenient values in the new unit system, instead of $K = m|\mathbf{v}|^2$ which will result if the number constant 2 is absorbed into the definition of say [time], from known definitions of [length] and [energy].

(3),(5),(7) and (9) are not just mathematical devices but also have physical meaning. If we plug in the numbers for the hydrogen atom, we find that,

$$[\text{length}] = 0.529 \text{ \AA}, \quad [\text{energy}] = 27.21 \text{ eV}, \quad [\text{time}] = 0.0242 \text{ fs}, \quad (12)$$

which indeed are the typical length-, energy- and time-scales of electronic processes in hydrogen. The reason is quite simple: in the dimensionless differential equation (10), all the relevant quantities, be it the probability amplitude ψ , the dependent variables \mathbf{x}, r at significant ψ , or the energy eigenstate E , have *no compelling reasons* to differ greatly from unity. A rule of thumb in modeling is that it is uncommon to have these dimensionless quantities greater than 10^3 or smaller than 10^{-3} . Very often one does not really care to know or need to calculate behaviors of the model in these ranges. Furthermore, the model itself might become invalid for describing the system at such.

How does one go about solving (10)? The first thing to note is that the Hamiltonian,

$$\mathcal{H} = -\frac{\nabla^2}{2} - \frac{1}{r}, \quad (13)$$

is spherically symmetric, meaning under arbitrary change of variables (observation frame): $\mathbf{x}' = \mathbf{O}\mathbf{x}$, $\mathbf{O}\mathbf{O}^T = \mathbf{I}$, \mathcal{H} stays invariant (prove this). We shall not pursue the proof here, but the consequences of such symmetry is,

1. We *must* have degeneracy - meaning there are multiple linearly independent eigenfunctions sharing the same eigenenergy.
2. The eigenfunctions *can* be expressed as the product of radial and angular parts, since the symmetry operations do not involve the radial distance at all.

Such conclusions hold for any spherically symmetric potential $V(r)$, not just the $1/r$ poten-

tial. But as we shall see, the $1/r$ potential allows for additional (and more subtle) symmetry operations which *further* increase the degeneracy.

In spherical coordinates (r, θ, ϕ) , the Laplacian operator can be expressed as¹,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{r^2}, \quad (14)$$

where the \mathbf{L}^2 operator is defined as,

$$\mathbf{L}^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \quad (15)$$

As the name suggests, \mathbf{L}^2 is a *positive semidefinite* operator², so indeed all its eigenvalues are non-negative. The eigenfunctions of \mathbf{L}^2 are the so-called *spherical harmonics* $Y_l^m(\theta, \phi)$, with two integer labels l, m ,

$$\begin{aligned} \mathbf{L}^2 Y_l^m(\theta, \phi) &= l(l+1) Y_l^m(\theta, \phi), \\ l &= 0, 1, 2, 3, \dots \\ m &= -l, -l+1, \dots, l-1, l. \quad \leftarrow \text{degenerate} \end{aligned} \quad (16)$$

The lowest eigenvalue is $0 = 0 \times (0 + 1)$ for $l = 0$, which corresponds to a constant angular function:

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad (17)$$

in other words, no angular dependence. There is also no degeneracy for $l = 0$ (*s-wave*). But in general, the degeneracy is $2l + 1$; for instance, the *p-waves* ($l = 1$) have three-fold degeneracy, the *d-waves* ($l = 2$) have five-fold degeneracy and so on.

The general expression for the spherical harmonics is,

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\phi}, \quad (18)$$

¹(14),(15) is straightforward if one understands how the divergence operator ∇^2 truly operates.

² $\langle \psi, \mathbf{L}^2 \psi \rangle = \langle \psi, (\sum_{i=1}^3 L_i^2) \psi \rangle = \sum_{i=1}^3 \langle \psi, L_i^2 \psi \rangle = \sum_{i=1}^3 \langle L_i \psi, L_i \psi \rangle \geq 0$.

where P_l^m is the so-called associated Legendre polynomial, satisfying,

$$\left[(1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + \left(l(l+1) - \frac{m^2}{1-x^2} \right) \right] P_l^m(x) = 0, \quad (19)$$

(show this), which has the following explicit solution,

$$P_l^m(x) = \frac{1}{2^l l!} (1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l. \quad (20)$$

The reason (17),(18) have those particular constants is because of the orthonormality condition³:

$$\int d\Omega Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}, \quad (21)$$

where $\int d\Omega$ is the integral over 4π solid angle⁴, or more explicitly, $\int_0^\pi d\cos\theta \int_0^{2\pi} d\phi$.

The basis $\{Y_l^m(\theta, \phi)\}$ is not only orthonormal but also complete, meaning any arbitrary angular function $f(\theta, \phi)$ can be expanded in terms of $Y_l^m(\theta, \phi)$'s just like the Fourier series,

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_l^m(\theta, \phi) \times \int d\Omega' Y_l^{m*}(\theta', \phi') f(\theta', \phi') d\Omega'. \quad (22)$$

In reality, the above equation means that as l becomes sufficiently large, RHS of (22) approaches $f(\theta, \phi)$ in a vanishing squared-error-integral sense.

Going back to (10), let us propose that a solution has the form,

$$\psi(\mathbf{x}) = R(r) Y_l^m(\theta, \phi). \quad (23)$$

It is easy to check that $R(r)$ must satisfy,

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left(2E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right) R = 0. \quad (24)$$

When we seek bound-state solution to (24), E must be negative (prove this). Therefore let us introduce,

$$n \equiv \frac{1}{\sqrt{-2E}}, \quad (25)$$

³The mutual orthogonality is automatically guaranteed by being different eigenstates of (\mathbf{L}^2, L_z) , but their amplitudes need to be tuned to satisfy the normalization condition.

⁴The solid angle is defined by $dS \equiv r^2 d\Omega$ where dS is the differential area.

and then use n to rescale the distance,

$$\rho \equiv \frac{2r}{n}, \quad (26)$$

(the larger n is, the longer the characteristic length), and we shall obtain,

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left(-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2} \right) R = 0. \quad (27)$$

Before doing anything, let us deduce the asymptotic behaviors of $R(\rho)$ as $\rho \rightarrow \infty$, where,

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{1}{4} R \approx 0, \quad (28)$$

is correct to the leading order. For this to be satisfied, at least *two* of the three terms must balance each other in orders of magnitude, with the term left out having smaller or equal order of magnitude, but no greater. If they are to be the first and second term, then,

$$\frac{dR}{d\rho} \sim \rho^{-2} \longrightarrow R \sim \rho^{-1}, \quad (29)$$

but that is impossible because the third term would then dominate over both. If the second and third terms are to balance, then,

$$R \sim \exp(\rho^2/16), \quad (30)$$

which is absurd. So the only possibility left is that the first and third terms balance each other, in which case the asymptotic behavior is,

$$R \sim \exp(-\rho/2), \quad (31)$$

and so the second term would be insignificant and drop out, which is consistent. Therefore the only feasible leading behavior of $R(\rho)$ at $\rho \rightarrow \infty$ is $e^{-\rho/2}$.

Similarly, as $\rho \rightarrow 0$,

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R \approx 0, \quad (32)$$

is correct to the leading order, and $R(\rho)$ must have an algebraic behavior because if $R(\rho)$ is

a solution to (32), then $R(\lambda\rho)$ would also be a solution for any λ . Let $R \sim \rho^\gamma$, we see that,

$$\gamma(\gamma - 1) + 2\gamma - l(l + 1) = 0 \quad \longrightarrow \quad \gamma = l, -l - 1, \quad (33)$$

but $\gamma = -l - 1$ is not allowed because the probability integral diverges even for $l = 0$. Thus $R(\rho)$ can only behave like ρ^l when $\rho \rightarrow 0$.

Now we know the leading asymptotic behaviors of $R(\rho)$ in $0, \infty$ limits, it is quite natural to assume that $R(\rho)$ takes the form,

$$R(\rho) = \rho^l e^{-\rho/2} w(\rho), \quad (34)$$

and by plugging it into (27), we obtain,

$$\rho \frac{d^2 w}{d\rho^2} + (2l + 2 - \rho) \frac{dw}{d\rho} - (l + 1 - n)w = 0. \quad (35)$$

The solution to (35) which satisfies the condition that $w(\rho)$ approaches a constant when $\rho \rightarrow 0$ (otherwise it violates our asymptotic behavior prediction) is called the *confluent hypergeometric function*, labeled by $l + 1 - n$ and $2l + 2$,

$$w(\rho) = F(l + 1 - n, 2l + 2, \rho). \quad (36)$$

Furthermore, for $w(\rho)$ to not blow up non-algebraically at $\rho \rightarrow \infty$, the parameter $l + 1 - n$ must be a *non-positive integer*. So,

$$n = l + 1, l + 2, .. \quad (37)$$

for a fixed l . Or,

$$l = 0, 1, .., n - 1. \quad (38)$$

for a fixed n .

Because the eigenenergy is,

$$E = -\frac{1}{2n^2}, \quad (39)$$

by our own definition (25), E is only dependent on n , not l , although both n , l and m are needed in specifying the *eigenfunction* by virtues of (23), (34) and (36). n is therefore called

the *principal quantum number*, and by converting back (39) from the reduced unit system, we obtain,

$$E = -\frac{1}{2n^2} \left(\frac{m\alpha^2}{\hbar^2} \right), \quad n = 1, 2, 3, \dots \quad (40)$$

for any unit system.

The $1/r$ system is more degenerate than the general spherically symmetric $V(r)$ system where only different m states of the same l are destined to be degenerate with degeneracy count $2l + 1$. Here, if two states have the same principal quantum number n , *even if their l 's are different*, they still have the same energy. And the degeneracy count is,

$$\sum_{l=0}^{n-1} (2l + 1) = n^2. \quad (41)$$

This is not an accident, but because there is a “hidden” symmetry in the $1/r$ system involving mixed r and θ, ϕ operations, and in fact those operations constitute a rotational group in an appropriately defined 4-dimensional system. For details please see [1].

We thus obtained an exact solution to the hydrogen atom problem. Even though quantum mechanics is tremendously powerful, such exact solutions are very rare. For systems with more than one electron (simple as the Helium atom), there are no closed-form solutions. But, there are many well-developed approximations and computational methods such as the Density Functional Theory (DFT) which can handle thousands of electrons and performs admirably in practice, and one must rely on such methods. As a final remark, when there are multiple electrons, the *effective potential* (often called the pseudo-potential) that an electron “sees” is not the $1/r$ potential. So one would lose the n^2 degeneracy. For example, the ionization energy of a $2s$ electron in carbon atom is a far cry from the ionization energy of a $2p$ electron, even though both have principal quantum number 2.

References

- [1] L.D. Landau, E.M. Lifshitz, *Quantum mechanics: non-relativistic theory*, 3rd ed. (Pergamon Press, 1977).