

The Bohr Correspondence Principle

Kepler Orbits of the Electron in a Hydrogen Atom

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We consider the quantum-mechanical non-relativistic hydrogen atom. We show that for bound states with size much larger than the Bohr radius, one can construct a wave packet that is localized in space corresponding to a classical particle moving in a circular orbit.

1. Problems with the Bohr Theory of Hydrogen Atom

Bohr's theory to determine the energy levels of a hydrogen atom is well known to undergraduate students of physics. The algebraic steps in this calculation are quite straightforward, and easily understood even with XII grade algebra. To recall, Bohr assumed that an electron describes a circular orbit about the nucleus, and the angular momentum is quantized to be an integer multiple of \hbar . Of course, in general, the orbit can be elliptical, but let us restrict ourselves to circular orbits here for simplicity.

Many textbooks do not emphasize the important point that this is a good example of a theory that starts with *very wrong* premises, but makes predictions some of which give an excellent match with experimental data. In the correct quantum mechanical description, because of uncertainty principle, even the starting point of there being an orbit describing the electron's motion is invalid. In fact, while one is lucky to get the energy levels right using this wrong argument, properties of the quantum states are not correctly described in Bohr's theory. For example, in the ground state of the hydrogen atom, the



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Bohr theory of the hydrogen atom is only partly correct.

angular momentum of the electron is zero, not \hbar , as calculated in this theory. Also, one knows that there are only two distinct possible quantum-mechanical states of the hydrogen atom (corresponding to the two values of the electron spin), if it is known to have the minimum energy. But in Bohr's theory, the orientation of the plane of orbit is arbitrary, and hence the number of distinct states is infinite.

In fact, "Bohr theory of hydrogen atom had a scientifically useful life of a little more than a decade. The creation of quantum mechanics in the mid-1920's marked its demise" [1]. This does not belittle the importance of the Bohr theory, and the Bohr–Sommerfeld semiclassical quantization rules, in the development of ideas which eventually showed the way to a proper quantum mechanical theory. In the correct quantum mechanical description, the student learns a bit later that the state of the electron in the hydrogen atom is described by a wave function, which satisfies the Schrödinger equation. The allowed states of fixed energy are stationary states, and satisfy the eigenvalue equation

$$\mathbb{H}\Phi_n(\vec{r}) = E_n\Phi_n(\vec{r}), \quad (1)$$

where E_n is the eigenvalue, and $\Phi_n(\vec{r})$ is the corresponding eigenfunction. The corresponding wavefunction of the electron in the atom is $\Psi(\vec{r}, t) = \exp(-iE_n t/\hbar)\Phi_n(\vec{r})$. If the electron is in the stationary state, the corresponding probability density does not change in time, and there is no possibility of describing an orbit with a time-varying position-vector \vec{r} in any energy eigenstate of any quantum-mechanical system.

2. The Correspondence Principle

Once we agree that it is not possible to speak of orbits in describing the fixed-energy bound states of the hydrogen atom, we come to a different problem. Of course, the theory applies not only to the hydrogen atom, but also



to other hydrogen-like systems. In fact, one may want to describe the sun–earth system quantum mechanically. If the sun and earth may be represented as mass points (i.e., we ignore their internal structure), the quantum mechanical problem is formally the same as the hydrogen atom problem. How do we understand the Kepler orbits in this system in a quantum-mechanical description? The question is not of academic interest only, as now one can produce assemblies of several hydrogen atoms in excited states corresponding to principal quantum number $n \approx 300$ [1]. One would expect that for these states, called Rydberg states, the classical mechanical description may not be grossly wrong.

This question is addressed in standard textbooks, and the student is told that to describe time-dependent properties, one has to construct superposition of nearby energy-eigenstates, which then can show properties varying with time. In fact, there is a general proof that expectation values of the position \vec{r} and momentum \vec{p} for a single particle moving in a potential field satisfy the equations

$$\begin{aligned}\frac{d}{dt}\langle\vec{r}\rangle &= \frac{\langle\vec{p}\rangle}{m}, \\ \frac{d}{dt}\langle\vec{p}\rangle &= -\langle\vec{\nabla}V(\vec{r})\rangle,\end{aligned}\quad (2)$$

where $V(\vec{r})$ is the potential function. If the wavefunction is peaked near a value, and has small spread, the expectation value of $\vec{\nabla}V(\vec{r})$ is nearly equal to the value of the operator at the position where the wave function is sharply peaked, and the expectation values of rates of change satisfy classical equations of motion. This is the Bohr correspondence principle of similarity of predictions of classical and quantum systems at large scales.

While the explanation given above is not too complicated, and quite general, it is desirable to have some explicit cases where one can verify its working. In textbooks, one typically sees this verified for a free parti-

For large systems, the difference between classical- and quantum-mechanical descriptions must become small.



The quantum description of the hydrogen atom starts with determining eigenfunctions of the corresponding non-relativistic Schrödinger equation.

cle, where the mean value of the position of the particle evolves linearly with time. The case of hydrogen-like atoms is not much more difficult, does not involve too much algebraic manipulations, and hence would be an instructive exercise for students. For an earlier pedagogical discussion of this problem, see [2].

3. The Quantum Mechanical Description of Hydrogen Atom

We start with the non-relativistic Hamiltonian for the electron and the proton, with only the electrostatic interaction between them:

$$\mathbb{H}_{ep} = \frac{1}{2M} \vec{P}_p^2 + \frac{1}{2m} \vec{P}_e^2 - \frac{e^2}{r_{ep}}, \quad (3)$$

where \vec{P}_p is the momentum of the proton, \vec{P}_e is the momentum of the electron, M and m are their respective masses, e is the electron charge, and r_{ep} is the radial distance between the proton and the electron. We can separate out the center of mass motion, and write the wavefunction of the proton–electron system $\Psi(\vec{r}_p, \vec{r}_e)$ as

$$\Psi(\vec{r}_p, \vec{r}_e) = \exp(i\vec{K}_{cm} \cdot \vec{R}_{cm}) \psi(\vec{r}) \exp(-iEt/\hbar), \quad (4)$$

where $\vec{R}_{cm} = \frac{M\vec{r}_p + m\vec{r}_e}{M+m}$ is the center of mass coordinate, $\hbar\vec{K}_{cm}$ is the center of mass momentum, E is the total energy of the system, and $\psi(\vec{r})$ is the time-independent eigenfunction of the atom: it is a function only of the relative coordinate $\vec{r}_{ep} = \vec{r}_e - \vec{r}_p$. It satisfies the time-independent Schrödinger equation

$$\left[\frac{-\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r} \right] \psi(\vec{r}) = E' \psi(\vec{r}), \quad (5)$$

where $E' = E - \hbar^2 K_{cm}^2 / 2(m + M)$ is the energy of the atom in the center of mass frame, $\mu = mM / (m + M)$ is the reduced mass of the electron and we have dropped the subscript in \vec{r}_{ep} , for simplicity of notation.



The solution of this eigenvalue equation is quite straightforward, available in textbooks, and will not be repeated here [3]. The eigenfunctions can be labelled by three integers $\{n, \ell, m\}$ (we will ignore the spin of electron in this discussion). It is convenient to use the polar coordinates $\vec{r} \equiv (r, \theta, \phi)$. The eigenfunction corresponding to a bound state characterized by the quantum numbers $\{n, \ell, m\}$, having the energy $E_{n,\ell,m}$ is given by

$$\psi_{n,\ell,m}(\vec{r}) = R_{n,\ell}(r)Y_{\ell,m}(\theta, \phi), \quad (6)$$

where $R_{n,\ell}(r)$ is the radial wavefunction, $Y_{\ell,m}$ are the spherical harmonic functions, and $E_{n,\ell,m} = -\frac{me^4}{2\hbar^2n^2}$.

4. Constructing a Wave Packet From Eigenfunctions

Now, we want to construct a superposition of these eigenfunctions to form a wavefunction that is localized in space, say centered around the point $(r, \theta = \pi/2, \phi)$, with $r \gg a_0$, where a_0 is the size of the smallest Bohr orbit. Correspondingly, we want to consider $n \gg 1$.

Let us consider a wavepacket $W_0(r, \theta, \phi)$ at time $t = 0$, formed by simple superposition of the eigenstates $\psi_{n,\ell,m}$. We will consider the superposition using only the states with $m = \ell$ and $n = \ell + 1$.

$$W_0(r, \theta, \phi) = \sum_{\ell} f(\ell) \psi_{\ell+1,\ell,\ell}(r, \theta, \phi). \quad (7)$$

We choose the function $f(\ell)$ to be of the form

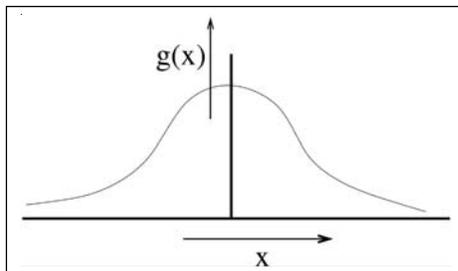
$$f(\ell) = g\left(\frac{\ell - \ell^*}{\Delta\ell}\right), \quad (8)$$

where the function $g(x)$ is a function peaked at $x = 0$, and with a width of order 1 (see *Figure 1*). Then, $f(\ell)$ is peaked at $\ell = \ell^*$, and is of width $\Delta\ell$. The reason for choosing this simple form may be understood as follows: we are trying to construct a wavepacket that corresponds to the classical Bohr orbit. Without loss of

To get a Kepler-like orbit, we superpose eigenfunctions of the Schrödinger equation to get a localized wavepacket.



Figure 1. A schematic plot of the function $f(l)$ used for superposition. It is expressed in terms of the window function $g(x)$, centred at $x = 0$, and of width of order 1.



generality, we choose such an orbit to be in the $\theta = \pi/2$ plane. In this plane, the z -component of the angular momentum is the largest possible. Hence, we choose $m = \ell$. Also, to consider superposition of states of nearly same energy, we will choose $\Delta\ell \ll \ell^*$.

We will need some properties of the eigenfunctions R_n and the spherical harmonics $Y_{\ell,m}$, for n, ℓ large.

In general, $Y_{\ell,m}$ is of the form $P_{\ell,m}(\cos\theta) \exp(im\phi)$, where $P_{\ell,m}(\theta)$ is called the associated Legendre function. This can be complicated, but it simplifies for the case $m = \ell$, and we have

$$Y_{\ell,\ell}(\theta, \phi) = K(\ell)[\sin(\theta)]^\ell e^{i\ell\phi}. \tag{9}$$

Here, the normalization constant $K(\ell)$ is a slowly varying function of ℓ , whose precise form is not needed here, and hence will not be discussed further.

Similarly, the radial function $R_{n,\ell}(r)$ is known to be of the form $L_n(r)e^{-cr}$, where L_n are called Laguerre polynomials. These also simplify in the case $n = \ell + 1$, and we get

$$R_{n,n-1}(r) = K' r^{n-1} \exp\left[-\frac{r}{na_0}\right], \tag{10}$$

where a_0 is the Bohr radius, and again, the precise value of the normalization constant K' is not needed.

This looks very promising, as we note that (9) implies that $|Y_{\ell,m}(\theta, \phi)|^2$ is sharply peaked around $\sin(\theta) = 1$, or $\theta = \pi/2$. In fact, it is appreciable only when $|\theta - \pi/2| \sim \mathcal{O}(\frac{1}{\ell^{1/2}})$.

The behavior of eigenfunctions for large quantum numbers is easily determined.



Similarly, from (10), we see that the radial function $R_{n,n-1}(r)$ is a sharply-peaked positive function, with maximum value at $r = r^* = n^2 a_0$. Also, the radial function is appreciable only if $|r/r^* - 1| \sim \mathcal{O}(\frac{1}{n^{1/2}})$. Thus, the function $\psi_{n,\ell,m}(r, \theta, \phi)$ from (6) is sharply peaked around $r = r^*$ and $\theta = \pi/2$. But $|\psi_{n,\ell,m}(r, \theta, \phi)|^2$ is independent of ϕ , and the probability distribution corresponding to this eigenfunction is uniformly distributed along the circle $r = r^*$, $\theta = \pi/2$.

A localized wave-packet of nearly constant energy moves in an approximately circular orbit, with right angular velocity.

Then, since the function $R_{\ell+1,\ell}$ and the θ -dependent part of $Y_{\ell,\ell}$ are only weakly dependent on ℓ , we may write (7) as

$$W_0(r, \theta, \phi) \approx \mathbf{R}^*(r) \Theta^*(\theta) \Phi^*(\phi) \exp(i\ell^* \phi). \quad (11)$$

Here, $\mathbf{R}^*(r)$ is a shorthand notation for $R_{\ell^*+1,\ell^*}(r)$, $\Theta^*(\theta) = [\sin \theta]^{\ell^*}$, and

$$\Phi^*(\phi) = \sum_{\ell} f(\ell) \exp[i(\ell - \ell^*)\phi]. \quad (12)$$

Let $\tilde{g}(y)$ be the Fourier transform of $g(x)$. Then, it is easy to see that (approximating sum over ℓ as integration over a continuous variable)

$$\begin{aligned} \sum_{\ell} f(\ell) \exp(i\ell\phi) &\approx \int d\ell g\left(\frac{\ell - \ell^*}{\Delta\ell}\right) \exp(i\ell\phi) \\ &= \Delta\ell \tilde{g}(\phi\Delta\ell) \exp(i\ell^*\phi). \end{aligned} \quad (13)$$

A convenient choice for the function $g(x)$ is a Gaussian, which corresponds to the ‘minimum uncertainty wavepacket’, minimizing the Heisenberg uncertainty product ($\Delta p \Delta x$). But we do not need to do so. The argument below is valid more generally.

Then, if $\tilde{g}(y)$ is small if its argument $y \gg 1$, we see that the function $\Phi^*(\phi)$ is localized around $\phi = 0$, with a spread of $\mathcal{O}(1/\Delta\ell)$. We have already seen that the



function $\mathbf{R}^*(r)$ is a sharply peaked function around $r = r^*$, and $\Theta^*(\theta)$ is sharply peaked around $\theta = \pi/2$.

5. Time Evolution of the Wave Packet

It remains now to determine the wave function of the system at time t , when it is prepared in the state $W_0(r, \theta, \phi)$ at time $t = 0$. Let the wave function at time t be denoted by $W_t(r, \theta, \phi)$. Then, from the Schrödinger equation, the wave function $W_t(r, \theta, \phi)$ is given by

$$\begin{aligned} &W_t(r, \theta, \phi) \\ &= \left[\sum_{\ell} f(\ell) \mathbf{R}_{\ell+1, \ell}(r) (\sin \theta)^\ell \exp(i\ell\phi) \exp(-iE_\ell t/\hbar) \right] \\ &\approx \mathbf{R}^*(r) \Theta^*(\theta) \left[\sum_{\ell} f(\ell) \exp(i\ell\phi) \exp(-iE_\ell t/\hbar) \right], \end{aligned} \tag{14}$$

where $E_\ell = -E_G/(\ell + 1)^2$, is the energy of the state with quantum numbers $(\ell + 1, \ell, \ell)$, with E_G being the ground state energy of the hydrogen atom.

We note that the expression in square brackets is just like the evolution of a wavepacket in a one-dimensional system, where ℓ acts like the wavenumber k , and E_ℓ is like the frequency ω_k . For that problem, we know that the wavepacket moves with the group velocity given by $\frac{\partial \omega_k}{\partial k}$. In this case, we put

$$E_\ell \approx E_{\ell^*} + (\ell - \ell^*)\hbar\omega^* + \text{higher order terms}, \tag{15}$$

where $\omega^* = \frac{\partial E_\ell}{\partial \ell} = 2E_G/\ell^*{}^3$, which is exactly the angular speed of the electron calculated in Bohr theory. Then, using similar arguments, it is easily seen that

$$\begin{aligned} &W_t(r, \theta, \phi) \approx \\ &\mathbf{R}^*(r) \Theta^*(\theta) \exp(i\ell^*\phi) \Phi^*(\phi - \omega^*t) \exp\left(-\frac{iE_{\ell^*}t}{\hbar}\right). \end{aligned} \tag{16}$$



Thus, we see that the wavepacket goes in a nearly circular orbit, with angular speed ω^* . For large ℓ^* , ω^* varies as ℓ^{*-3} , while r^* varies as ℓ^{*2} . Thus, $\omega^* \sim r^{*-3/2}$, which is Kepler's third law.

The higher order terms in $(\ell - \ell^*)$ lead to spread of the wavepacket over time scales much larger than the period of the orbit.

We have thus shown that the time-evolution of a wavepacket corresponding to an electron in a hydrogen-like atom, for large quantum numbers, is such that the wavepacket is nearly localized near the classical orbit for times over which the spreading of the wave packet can be neglected. There has been a lot of interest in studies of Rydberg atoms in recent years. They occur in Nature, and can be produced and manipulated in lab. Also, the use of the correspondence principle to study properties of Rydberg atoms (and deviations from it) has been investigated intensively. Discussion of these issues is outside the scope of this article. The interested reader is referred to [4] for a recent review.

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Suggested Reading

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