One-electron atom
Notes on Quantum Mechanics

The prototype system for the quantum description of atoms is the so-called one-electron atom, consisting of a single electron, with charge $-e$, and an atomic nucleus, with charge $+Z\,e$. Examples are the hydrogen atom, the helium atom with one of its electrons removed, the lithium atom with two of its electrons removed, and so on.

There are two features of the one-electron atom that allow us to simplify our analysis. First, because the nucleus is so much heavier than the electron, to e very good approximation we can treat the nucleus as fixed in space, with the electron moving around it. Second, because there are no other electrons present, the potential energy, $-Z\,e^2/(4\,\pi\,\epsilon_0\,r)$, due to the Coulomb attraction of the electron and the nucleus, depends only on the distance, r, of the electron from the nucleus.

This means that the Hamiltonian of the one-electron atoms is simply the Coulomb potential energy added to the sum of the kinetic energy operators for motion of the electron in each dimension,

$$H = -\frac{\hbar^2}{2\,m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}.$$

Now, we have seen how to simplify the Schrödinger equation in more than one dimension by expressing the wave function is the *product* of the wave functions in each dimension. For this procedure to work, however, *the kinetic energy along each dimension must not be affected by the position in the other dimensions*. That is, the curvature at a particular position in a given coordinate must be the same for all positions in the other coordinates. Because the one-electron atom potential energy depends on $r = \sqrt{x^2 + y^2 + z^2}$, this is *not* the case here.

To illustrate this, let's set the origin of the coordinates at the nucleus and then plot how the kinetic energy changes in the hydrogen atom ($Z = 1$) in the $x\,y$ plane for two different values of the third coordinate, $z = 2\,a_0$ and $z = 0.2\,a_0$, for total energy equal to twice the first ionization energy.
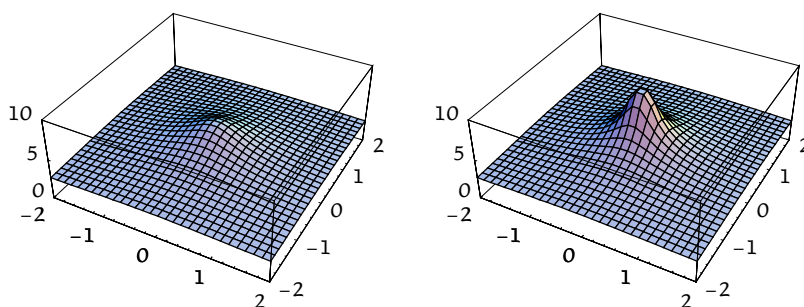
Kinetic energy, in units of the ionization energy of hydrogen, of the electron in the hydrogen atom ($Z = 1$) in the *xy* plane for two different values of the third coordinate, $z = 0.5$ (left) and $z = 0.2$ (right). The total energy is two units of the ionization energy of hydrogen. Lengths are in Bohr, $a_0 = 0.529$ Å.

The plots show three things. First, the closer the electron to the nucleus, the larger its kinetic energy, since the more negative the potential energy. Second, the closer the position in the third dimension is to the nucleus, the more pronounced the kinetic energy change, since the electron is able to come

closer to the nucleus. Third, and most important, the kinetic energy in one dimension is *not* independent of the position in the other dimensions.

What this analysis teaches is that in order to separate the Schrödinger equation of the one-electron atom, we need to transform the kinetic energy part of the equation to *spherical polar coordinates*, r, θ and ϕ.

We can use a similar approach to express the wave functions and energies of an electron in a one-electron atom. The key difference is that we need to analyze the curvature and so the kinetic energy in *spherical polar coordinates*, r, θ and ϕ, rather than Cartesian coordinates, x, y and z, since the Schrödinger equation is separable in spherical polar coordinates, but not in Cartesian coordinates.

■ Transformation to spherical polar coordinates

The details of transforming the kinetic energy operator from cartesian coordinates to spherical polar coordinates are a little complicated, but the result is the Schrödinger equation

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \longrightarrow \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2$$

where the angular part of the kinetic energy is expressed through the operator

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta}.$$

This operator, known as the *Legendrian*, determines the contribution to the kinetic energy of motion at constant distance from the nucleus. The Schrödinger equation in spherical polar coordinates is then

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} r + \frac{1}{r^2} \Lambda^2 \right) - \frac{Z e^2}{4 \pi \epsilon_0 r} \right\} \psi (r, \theta, \phi) = E \psi (r, \theta, \phi),$$

Because in this form of the Schrödinger equation the potential energy affects motion in only one coordinate, the wave function can be written as a product

$$\psi (r, \theta, \phi) = R (r) Y (\theta, \phi)$$

of two probability amplitudes. The amplitude $R (r)$ is called the radial wave function, and it depends only on the distance from the nucleus; the amplitude $Y (\theta, \phi)$ is called the angular wave function, or *spherical harmonic*, and it depends only on the coordinates θ and ϕ.

Since one quantum number indexes the wave function in each coordinate, two quantum numbers are needed to specify the spherical harmonic. The quantum number for motion in θ is called ℓ; it can have the values 0, 1, 2, …. The quantum number for motion in ϕ is called m; it can have the values $-\ell$, $-\ell + 1$, …, $\ell - 1$, ℓ. Spherical harmonics are thus usually written as $Y_{\ell m} (\theta, \phi)$.

> List the possible values of m when $\ell = 3$.

> List the possible values of m when $\ell = 2$.

> How many values of ℓ can have $m = 4$?

> Show that for a given value of ℓ, there are $2\ell + 1$ possible values of m.

The effect of the operator Λ^2 on spherical harmonics is very simple,

$$\Lambda^2\, Y_{\ell m}\,(\theta,\,\phi) = -\ell\,(\ell+1)\,Y_{\ell m}\,(\theta,\,\phi).$$

Using this relation, we can rewrite the Schrödinger equation as

$$\left\{-\frac{\hbar^2}{2\,m}\left(\frac{1}{r}\,\frac{d^2}{d\,r^2}\,r - \frac{\ell\,(\ell+1)}{r^2}\right) - \frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}\right\} R\,(r)\,Y_{\ell m}\,(\theta,\,\phi) = E\,R\,(r)\,Y_{\ell m}\,(\theta,\,\phi)$$

In this equation the spherical harmonic appears as a common factor on both sides and so we can cancel it out The result is the Schrödinger equation in the single coordinate r,

$$\left(-\frac{\hbar^2}{2\,m}\,\frac{1}{r}\,\frac{d^2}{d\,r^2}\,r + V_{\text{eff},Z\ell}\,(r)\right) R_{jZ\ell}\,(r) = E_{jZ\ell}\,R_{jZ\ell}\,(r),$$

in terms of an *effective potential energy function*

$$V_{\text{eff},Z\ell}\,(r) = \frac{\hbar^2\,\ell\,(\ell+1)}{2\,m\,r^2} - \frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}$$

This potential energy expression contains, in addition to the contribution from Coulomb attraction, a repulsive term due to the angular motion of the electron. We have indexed the radial wave function by its number of loops, j, and also by the Z and ℓ. This means that the energy values also depend on j, Z and ℓ.

Keep in mind that while j plays the role of the radial quantum numbers, Z and ℓ play the role of parameters in the radial Schrödinger equation.

■ Natural units of length and energy

We can simplify things by working in terms of units of length and energy that are typical for atoms. A convenient units of length is the Bohr radius,

$$a_0 = \frac{4\,\pi\,\epsilon_0\,\hbar^2}{m\,e^2} = 0.5292\,\text{Å}$$

in terms of the mass of the electron, which we write here simply as m. A convenient unit of energy is the magnitude of the Coulomb potential energy between two units of charge separated by the unit of distance,

$$E_h = \frac{e^2}{4\,\pi\,e_0\,a_0} = \frac{\hbar^2}{m\,a_0{}^2} = \frac{m\,e^4}{16\,\pi^2\,\epsilon_0{}^2\,\hbar^2} = 27.21\,\text{eV} = 4.360 \times 10^{-18}\,\text{J}$$

This unit of energy is called the *hartree*, and we write it as E_h.

In terms of length expressed as dimensionless multiples of the Bohr radius, $\rho = r/a_0$, and energy expressed as dimensionless multiples of the hartree, $\epsilon = E/E_h$, the kinetic energy part of the Schrödinger equation becomes

$$\frac{\hbar^2}{2\,m}\,\frac{1}{r}\,\frac{d^2}{d\,r^2}\,r$$

$$= \frac{\hbar^2}{2\,m}\,\frac{1}{r/a_0}\,\frac{d^2}{a_0{}^2\,d\,(r/a_0)^2}\,r/a_0$$

$$= \frac{\hbar^2}{2\,m\,a_0{}^2}\,\frac{1}{\rho}\,\frac{d^2}{d\,\rho^2}\,\rho$$

$$= \frac{E_h}{2}\,\frac{1}{\rho}\,\frac{d^2}{d\,\rho^2}\,\rho$$

and the potential energy part becomes

$$V_{\text{eff},Z\ell}\,(r)$$

$$= \frac{\hbar^2\,\ell\,(\ell+1)}{2\,m\,r^2} - \frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}$$

$$= \frac{\hbar^2\,\ell\,(\ell+1)}{2\,m\,a_0{}^2\,(r/a_0)^2} - \frac{Z\,e^2}{4\,\pi\,\epsilon_0\,a_0\,(r/a_0)}$$

$$= \frac{E_h\,\ell\,(\ell+1)}{2\,\rho^2} - \frac{E_h\,Z}{\rho}$$

Substituting these expressions into the Schrödinger equation, we get

$$\left(-\frac{E_h}{2}\,\frac{1}{\rho}\,\frac{d^2}{d\,\rho^2}\,\rho + \frac{E_h\,\ell\,(\ell+1)}{2\,\rho^2} - \frac{E_h\,Z}{\rho} \right) R_{jZ\ell}\,(\rho) = E_{jZ\ell}\,R_{jZ\ell}\,(\rho),$$

At this point we can simplify things a bit more by defining a new unit of energy known as the *rydberg*, $E_r = E_h/2$, defined as one half of the hartree. Dividing both sides of the Schrödinger equation by the rydberg, we get

$$\left(-\frac{1}{\rho}\,\frac{d^2}{d\,\rho^2}\,\rho + v_{\text{eff},Z\ell}\,(\rho) \right) R_{jZ\ell}\,(\rho) = \epsilon_{jZ\ell}\,R_{jZ\ell}\,(\rho),$$

in terms of the effective potential energy

$$v_{\text{eff},Z\ell}\,(\rho) = \frac{\ell\,(\ell+1)}{\rho^2} - \frac{2\,Z}{\rho}$$

and the total energy $\epsilon = E/(E_h/2) = E/E_r$, both in rydbergs.

■ Shell amplitudes

The Schrödinger equation

$$\left(-\frac{1}{\rho}\,\frac{d^2}{d\,\rho^2}\,\rho + v_{\text{eff},Z,\ell}\,(\rho) \right) R_{jZ\ell}\,(\rho) = \epsilon_{jZ\ell}\,R_{jZ\ell}\,(\rho),$$

is *very* similar to the curvature form of the Schrödinger equation. It turns out that we can transform it into curvature form by introducing a new radial function defined as $P(\rho) = \rho\,R(\rho)$. We call the function $P(\rho)$ the *shell amplitude* because, as we will see shortly, its squared modulus is the probability per unit length that the electron will be found anywhere on the shell of radius ρ centered at the nucleus.

Multiplying both sides of the Schrödinger equation from the right by ρ/ρ,

$$\left(-\frac{1}{\rho}\frac{d^2}{d\rho^2}\rho + v_{\text{eff},Z\ell}(\rho)\right)\frac{\rho R_{jZ\ell}(\rho)}{\rho} = \epsilon_{jZ\ell}\frac{\rho R_{jZ\ell}(\rho)}{\rho},$$

and then rewriting the equation using the definition of the shell amplitude, we get

$$-\frac{1}{\rho}\frac{d^2}{d\rho^2}P_{n\ell}(\rho) + v_{\text{eff},Z\ell}(\rho)\frac{P_{jZ\ell}(\rho)}{\rho} = \epsilon_{jZ\ell}\frac{P_{jZ\ell}(\rho)}{\rho}.$$

The essential point is that the factor ρ to the right of the second derivative has divided out, and that now each term contains the common multiplicative factor $1/\rho$. Multiplying both sides from the left by ρ we obtain finally

$$\left(-\frac{d^2}{d\rho^2} + v_{\text{eff},Z\ell}(\rho)\right)P_{jZ\ell}(\rho) = \epsilon_{jZ\ell}P_{jZ\ell}(\rho).$$

> Carry out the steps that result in this equation.

This is precisely the curvature form of the Schrödinger equation for the radial shell amplitudes. It is the *fundamental Schrödinger equation of one-electron atoms*. Remember that length ρ is the dimensionless multiple of the Bohr radius, $a_0 = 4\pi\epsilon_0\hbar^2/(me^2) = 0.5292$ Å and energy ϵ is the dimensionless multiple of the rydberg, $E_r = E_h/2 = \hbar^2/(2ma_0{}^2) = e^2/(8\pi\epsilon_0 a_0) = 13.61$ eV.

We have seen that the three-dimensional wave function for a one-electron atom can be expressed as

$$\psi_{j\ell m}(r,\theta,\phi) = R_{jZ\ell}(r)Y_{\ell m}(\theta,\phi) = \frac{1}{r}P_{jZ\ell}(r)Y_{\ell m}(\theta,\phi),$$

where the radial variation of the wave function is given by radial wave functions, $R_{jZ\ell}$, or alternatively by the shell amplitude $P_{jZ\ell}$, and the angular variation of the amplitude is given by the so-called *spherical harmonics, $Y_{\ell m}$*.

The fraction of the electron within a small volume $r^2\,dr\sin\theta\,d\theta\,d\phi$ of the point r,θ,ϕ is

$$|\psi_{j\ell m}(r,\theta,\phi)|^2\,r^2\,dr\sin\theta\,d\theta\,d\phi = |P_{jZ\ell}(r)Y_{\ell m}(\theta,\phi)|^2\,dr\sin\theta\,d\theta\,d\phi$$

The fraction of the electron anywhere within dr of the surface of a sphere of radius r is

$$\int_0^\pi\int_0^{2\pi}\left|\psi_{j\ell m}(r,\theta,\phi)\right|^2\,r^2\,dr\sin\theta\,d\theta\,d\phi = |P_{jZ\ell}(r)|^2\,dr$$

For this reason, $|P_{jZ\ell}(r)|^2$ is called the *shell density* of the electron, and this is why we call $P_{jZ\ell}$ the shell amplitude.

The fraction of the electron anywhere at all is

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}\left|\psi_{j\ell m}(r,\theta,\phi)\right|^2\,r^2\,dr\sin\theta\,d\theta\,d\phi = \int_0^\infty|P_{jZ\ell}(r)|^2\,dr = 1$$

That is, the total probability of finding the electron somewhere is unity.

■ Effective potential energy

The effective potential energy

$$v_{\text{eff},Z\ell}(\rho) = \frac{\ell(\ell+1)}{\rho^2} - \frac{2Z}{\rho}.$$

reflects the competition between the attractive (Coulomb) and repulsive (centrifugal) contributions. Because of their differing dependence on distance, the attractive term dominates at large distance, while the repulsive terms dominates at small distance.

The net potential energy changes from repulsive at small r to attractive at large r where the two contributions cancel.

> Show that two contributions cancel at $\rho_0 = \ell(\ell+1)/(2Z)$.

> Show that $V_{\text{eff},Z\ell}(\rho_0) = 0$.

The result is that there is a minimum in the effective potential energy at intermediate distances, except for $\ell = 0$, which has no repulsive component.

The distance at which this minimum occurs is where the slope of the potential energy curve vanishes.

> Show the minimum occurs at $\rho_{\min} = \ell(\ell+1)/Z$.

The effect of nuclear charge, Z, is to shift all of the minima inward. This is consistent with the Bohr model expression for the distance (in bohrs), $\rho = n^2/Z$.

> Show that the potential energy at the minima is given by $-Z^2/(\ell(\ell+1))$, in rydbergs.

The effect of nuclear charge, Z, is to shift all of the minima downward. Again, this is consistent with the Bohr model expression for energy (in rydbergs), $2\epsilon = -Z^2/n^2$.

The positions and energies at the minima for $Z = 1$ and orbital momentum quantum numbers $\ell = 1,\ 2,\ 3$ and 4 are

ℓ	$\rho_{\min}$	$\epsilon_{\min}$
1	2	$-\frac{1}{2}$
2	6	$-\frac{1}{6}$
3	12	$-\frac{1}{12}$
4	20	$-\frac{1}{20}$

Distance (in bohrs) and energy (in rydbergs) at the minima for $Z = 1$ and orbital momentum quantum numbers $\ell = 1,\ 2,\ 3,$ and 4.

Here are plots of the effective potential for hydrogen ($Z = 1$) for values of the orbital momentum quantum number $\ell = 0$ (black), 1 (red), 2 (green), and 3 (blue).
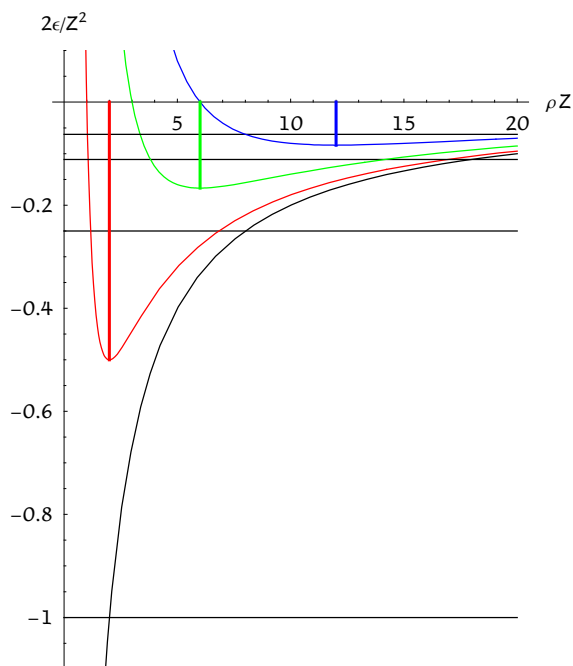
Effective potential energy curves for one electron bound to a nucleus of charge *Z*. Distance is measured in units of the Bohr radius, a_0, and energy is measured in units of the rydberg, $E_r = 2\,E_h$. The horizontal lines are the energies for $n = 1$ (lowest) to $n = 4$. The vertical lines mark the minimum, at $\rho_{\min} Z = \ell(\ell + 1)$, of the corresponding potential curve. The zero crossing of each curve is at $\rho_0 = \rho_{\min}/2$.

The vertical lines show the depth of the minimum of each potential curve, except for the curve for $\ell = 0$ for which the minimum is $-\infty$ at $\rho = 0$. Also shown are horizontal lines at the energies expected based on the Rydberg formula, for values of quantum number $n = 0, 1, 2,$ and 3, and vertical lines marking the kinetic energy at the minimum of each potential energy curve.

■ Eigenvalues of the one-electron atom Schrödinger equation

We have obtained the Schrödinger equation

$$\left(-\frac{d^2}{d\rho^2} + v_{\text{eff},Z\ell}(\rho) \right) P_{jZ\ell}(\rho) = \epsilon_{jZ\ell} P_{jZ\ell}(\rho).$$

for the shell amplitudes $P_{jZ\ell}$. We can express this in the curvature form as

$$\frac{d^2 P_{jZ\ell}(\rho)}{d\rho^2} = \text{curvature of } P_{jZ\ell} \text{ at } \rho = -t_{Z\ell}(\rho) \times P_{jZ\ell}(\rho)$$

in terms of the kinetic energy in rydbergs,

$$t_{Z\ell}(\rho) = \epsilon - v_{\text{eff},Z\ell}(\rho).$$

Since the potential energy

$$v_{\text{eff},Z\ell}(\rho) = \frac{\ell(\ell + 1)}{\rho^2} - \frac{2Z}{\rho}$$

depends only the distance from the nucleus, and not on θ and ϕ, but also since the effect of angular motion is already contained in the potential energy expression, the energy of the electron in the atom for a given number of loops will be different for different values of ℓ. Of course, since the potential energy also depends on the atomic number, Z, the energy for a given number of loops will also be different for different values of Z.

For a given ℓ and Z we can use

$$\text{curvature of } P_{jZ\ell} \text{ at } \rho = -t_{Z\ell}(\rho) \times P_{jZ\ell}(\rho)$$

to determine those energies for which the shell amplitudes converge to zero in the exterior, forbidden region of the atom. To do this, however, we need to know the form of the shell amplitude as ρ approaches zero.

The eigenvalues of the one-electron Schrödinger equation turn out to be

$$\epsilon_{jZ\ell} = -\frac{Z^2}{(j+\ell)^2} = \epsilon_{nZ} = -\frac{Z^2}{n^2},$$

where $j = 1, 2, \ldots$, is the number of loops in the shell amplitude $P_{jZ\ell}$ and $\ell = 0, 1, \ldots$, is the orbital momentum quantum number. These energies are shown by the horizontal lines in the potential energy diagram above. The reason that the energy depends on the orbital angular momentum quantum number is that the lowest energy must be above the minimum of the potential energy

$$v_{\text{eff},Z\ell}(\rho_{\min}) = -\frac{Z^2}{\ell(\ell+1)},$$

for otherwise there would be no allowed region, etc.

For historical reasons, the first four values of ℓ are usually expressed as a letter, as follows: s ($\ell = 0$), p ($\ell = 1$), d ($\ell = 2$), and f ($\ell = 3$). Again for historical reasons, $j + \ell$ is taken to define a new quantum number n, called the *principal quantum number*. The eigenvalues are exactly the energies that Bohr determined to be required to account for the Rydberg formula for one-electron spectra.

Because of the relation $n = j + \ell$, the shell amplitude $P_{jZ\ell}$ and radial wave function $R_{jZ\ell}$ are usually written instead in terms of the principal quantum number, as $P_{n\ell}$ and $R_{n\ell}$, with the additional understanding that the atomic number Z is not written explicitly.

Since the lowest energy solution the radial Schrödinger equation must have one loop, this means that the lowest possible value for the Bohr quantum number n for a given ℓ is

$$n_{\min} = 1 + \ell.$$

Thus, for $\ell = 0$ the lowest value of the Bohr quantum number is $n = 1$, for $\ell = 1$ the lowest value is $n = 2$, for $\ell = 2$ the lowest value is $n = 2$, etc.

To illustrate the role and relationship of these different quantum numbers, here is a table of eigenvalues and number of loops for different values of the orbital momentum quantum number.

n = j – ℓ	ϵ	s loops	p loops	d loops	f loops
6	$-Z^2/36$	6	5	4	3
5	$-Z^2/25$	5	4	3	2
4	$-Z^2/16$	4	3	2	1
3	$-Z^2/9$	3	2	1	
2	$-Z^2/4$	2	1		
1	$-Z^2/1$	1			

Eigenvalues, ϵ, and number of loops, j, for different values of the orbital momentum quantum number, ℓ. The unit of energy is rydbergs and Z is the atomic number of the one-electron atom.

The table shows that, as we have learned from the study of the curvature form of the Schrödinger equation, the lowest energy solution for each orbital momentum always has one loop, the next lowest has two loops, etc. It also shows, however, that the energy of the lowest solution is different for different orbital momenta. In particular the lowest energy state with orbital momentum quantum number ℓ has energy quantum number $n = \ell + 1$ and so energy $-Z^2/(\ell+1)^2$.

■ Qualitative form of one electron shell amplitudes $P_{jZ\ell}(r)$

To carry out the stepwise solution of

$$\text{curvature of } P_{jZ\ell} \text{ at } \rho = -t_{Z\ell}(\rho) \times P_{jZ\ell}(\rho)$$

to find the energies for which the shell amplitudes converge to zero in the exterior, forbidden region of the atom, we need to know the form of the shell amplitude as ρ approaches zero. The key to finding out is that kinetic energy

$$t_{Z\ell}(\rho) = \epsilon - v_{\text{eff},Z\ell}(\rho) = \epsilon - \frac{\ell(\ell+1)}{\rho^2} + \frac{2Z}{\rho}$$

approaches infinite magnitude as the electron approaches the nucleus. All else being equal, this would mean the curvature of the shell amplitude grows to extreme values, with the result that the shell amplitude would oscillate wildly near the nucleus. But such wild oscillations would rule out there being a lowest energy solution to the Schrödinger equation, since the lowest energy solution has only a single loop.

The way out of the difficulty that infinite kinetic energy presents is to offset its effect by requiring, as the electron approaches the nucleus, that the shell amplitude go to zero faster than the kinetic energy goes to infinity. Then the product $t_{Z\ell}(\rho) \times P_{jZ\ell}(\rho)$ approaches zero as the electron approaches the nucleus, and so wild oscillations in the shell amplitude are prevented.
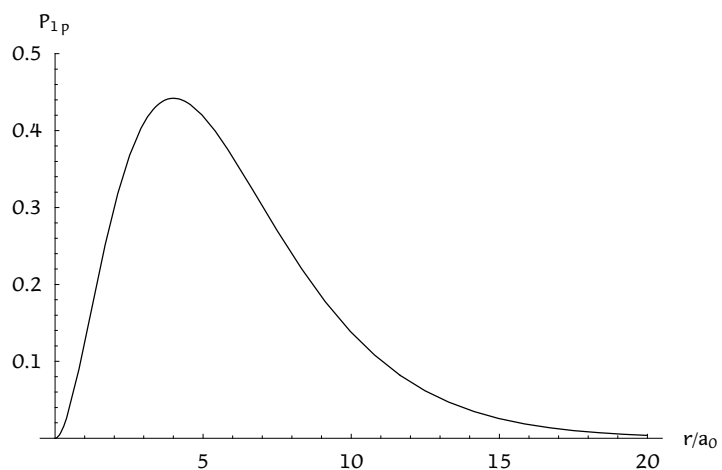
As example, here is the lowest energy s ($\ell = 0$) shell amplitude for the hydrogen.
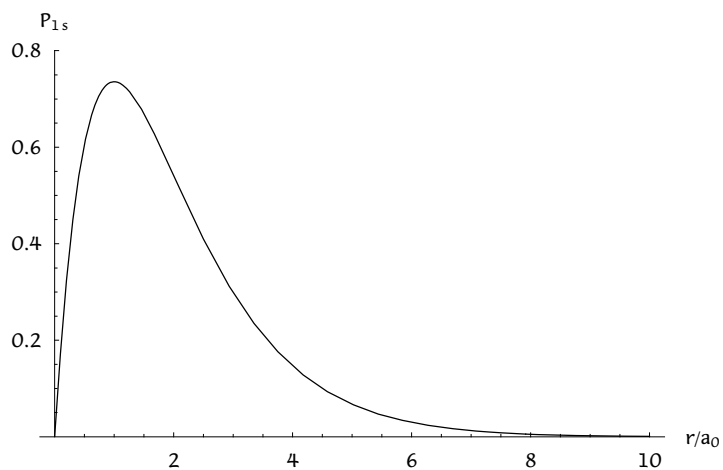
Lowest energy s ($\ell = 0$) shell amplitude for hydrogen atom.

Since there is no interior forbidden region when $\ell = 0$, there is not interior inflection point in the wavefunction.

As another example, here is the lowest energy p ($\ell = 1$) shell amplitude for the hydrogen.

Lowest energy p ($\ell = 1$) shell amplitude for hydrogen atom.

Since for $\ell > 0$ there is both an interior and an exterior forbidden region, there are now both interior and exterior inflection points in the wavefunction.