

One-electron atom radial functions

Notes on Quantum Mechanics

<http://quantum.bu.edu/notes/QuantumMechanics/OneElectronAtomRadialFunctions.pdf>
Last updated Friday, November 21, 2003 17:46:09-05:00

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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 spherical harmonics, $Y_{\ell m}$. These three-dimensional wave functions are called one-electron *orbitals*.

The spatial distribution of orbitals are the foundation of not only the periodic properties of the elements but also of chemical bonding. For this reason it is very useful to understand the distribution in three dimensions of the orbitals of an electron in a one-electron atom. The first step in doing this is to become familiar with the qualitative features of the radial wave functions, shell amplitudes, and shell densities.

■ Shell amplitudes

The shell amplitudes are determined by the Schrödinger equation

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

where the kinetic energy

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

is defined in terms of the effective potential energy

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

Here length is in bohr and energy is in rydbergs. Recall that 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. We'll use this notation here.

A general property of the shell amplitude $P_{n\ell}(\rho)$ is that for $\rho \ll 1$, it is proportional to $\rho^{\ell+1}$ (and so the radial wave function, $R_{n\ell} = P_{n\ell}/\rho$, is proportional to ρ^ℓ). This means that for $\ell = 0$ the shell amplitude leaves the origin as ρ and so with *zero curvature*; for all other values of ℓ , the shell amplitude leaves the origin with curving away from the zero line. This different behavior is due to the fact that for $\ell = 0$ there is no forbidden region near the nucleus, whereas for all other values of ℓ there is a forbidden region near the nucleus and so the shell amplitude must curve away from the zero line there.

Using the behavior of the shell amplitudes $P_{n\ell}(\rho)$ for $\rho \ll 1$, we can sketch the qualitative features of each possible shell amplitude in the potential energy curve for each value of the orbital momentum quantum number, ℓ .

Analytic expressions are available for the shell amplitudes $P_{n\ell}(\rho)$. It is very instructive to compare such sketches with the exact shell amplitudes. The exact shell amplitudes given by the following *Mathematica* function.

$$\mathbf{P}[\mathbf{z}_-, \mathbf{n}_-, \ell_-, \rho_-] := \rho^{\ell+1} e^{-z\rho/n} \left(\frac{2z}{n}\right)^\ell \frac{2}{n^2} z^{3/2} \sqrt{\frac{(n-\ell-1)!}{(n+\ell)!}} \times \\ \mathbf{LaguerreL}\left[\mathbf{n} - \ell - 1, 2\ell + 1, \frac{2z\rho}{n}\right]$$

The leading factor shows the $\rho^{\ell+1}$ dependence at small values of ρ . The exponential decay in the outer forbidden region is shown explicitly. Finally, the *Mathematica* function **LaguerreL**, known as the *Laguerre polynomial*, gives the oscillating part of the shell amplitude.

■ Classical turning points

We have learned that wave functions have an inflection point at each classical turning point—the boundary between allowed and forbidden regions—since the curvature vanishes there. In sketching and analyzing shell amplitudes $P_{n\ell}(\rho)$ the locations of the classical turning points are important guides. Here is how to determine these locations.

At classical turning points the kinetic energy vanishes and so the total energy is entirely potential energy. We can use this condition to get general expressions for the positions of the classical turning points.

Show that the inner and outer classical turning points are given by the following expressions.

$$\left\{ \frac{n \left(n - \sqrt{n^2 - \ell(1+\ell)} \right)}{z}, \frac{n \left(n + \sqrt{n^2 - \ell(1+\ell)} \right)}{z} \right\}$$

For example, here are the classical turning points for an electron in the hydrogen atom, with $n = 4$ and $\ell = 0, 1, 2$, and 3 .

n	ℓ	ρ_{inner}	ρ_{outer}
4	0	0.	32.
4	1	1.03337	30.9666
4	2	3.35089	28.6491
4	3	8.	24.

The inner forbidden region grows with ℓ , since the centrifugal repulsion is increasing; for $\ell = 0$, however, there is no inner forbidden region, since there is no repulsive term in the potential energy. The outer forbidden region starts at smaller distances as ℓ increases, since for a given n the total energy is fixed, and so the residual effect of centrifugal repulsion raises the potential energy curve in the outer region.

As another example, here are the classical turning points for an electron in the hydrogen atom, with $\ell = 1$ and $n = 2, 3$ and 4 .

n	ℓ	ρ_{inner}	ρ_{outer}
2	1	1.17157	6.82843
3	1	1.06275	16.9373
4	1	1.03337	30.9666

Now, since ℓ is fixed but the energy is increasing, for increased total energy the inner forbidden region decreases in size and the start of the outer forbidden region occurs at larger distances.

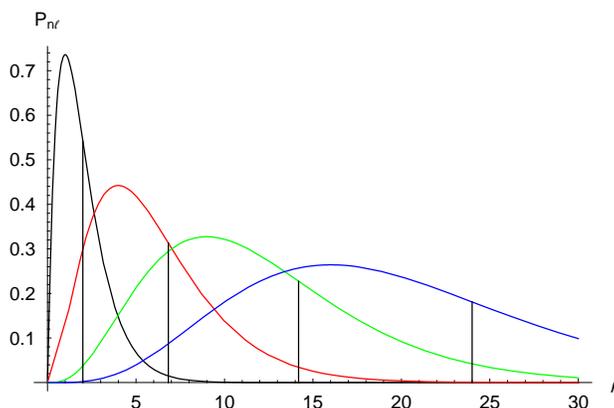
In the shell amplitude plots to follow, these effects on the classical turning points are seen in changes in the location of the inflection point in the first and last loops of the shell amplitudes. To help see the details of the plots, we'll use the following colors to distinguish different functions in the same plot.

■ Lowest energy hydrogen shell amplitudes and shell densities for different ℓ

Here are the classical turning points for the lowest energy shell amplitudes for $\ell = 0, 1, 2,$ and 3 .

n	ℓ	ρ_{inner}	ρ_{outer}
1	0	0.	2.
2	1	1.17157	6.82843
3	2	3.80385	14.1962
4	3	8.	24.

Here are the lowest energy shell amplitudes for $\ell = 0$ (black), 1 (red), 2 (green), and 3 (blue).



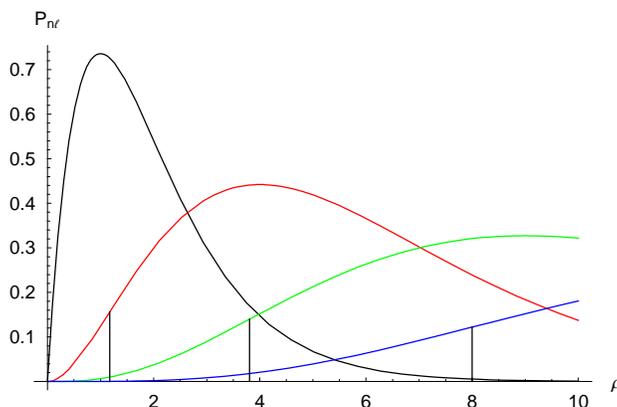
Since each shell amplitude is the lowest energy solution for the corresponding potential curve, each shell amplitude has a single loop. The vertical line extending downward from each shell amplitude marks the corresponding outer classical turning point. The total energy of these lowest energy solutions increases with ℓ .

n	ℓ	ϵ
1	0	-1.
2	1	-0.25
3	2	-0.111111
4	3	-0.0625

This means that in the outer forbidden region the negative kinetic energy is getting smaller, since each potential energy converges to the same value, 0, at very large distances from the nucleus. The lowered negative kinetic energy means that the shell amplitude in the forbidden region decays to zero over a larger and larger distance. The combined effect of the outer classical turning points moving

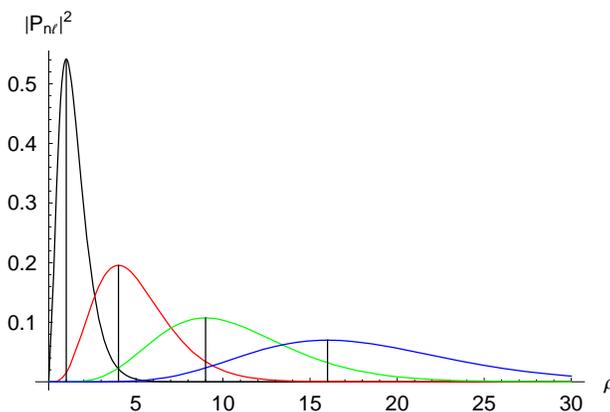
outward, due to increasing total energy, and the decay requiring greater distance in the outer forbidden region, due to decreased negative kinetic energy there, means that an electron in the lowest energy state for a given orbital momentum extends farther out into the space surrounding the nucleus for increased total energy and orbital momentum.

Here are the same shell amplitudes near the nucleus.



The vertical line extending downward from each shell amplitude (except for $\ell = 0$) marks the corresponding inner classical turning point; there is no inner forbidden region and so no inner classical turning point for $\ell = 0$. The inner forbidden region grows with increasing ℓ , due to the increasing centrifugal repulsion, with the result that as ℓ increases the shell amplitude is smaller and smaller near the nucleus; its centrifugal motion keeps the electron away from the nucleus. Only an s ($\ell = 0$) electron has appreciable amplitude near the nucleus, since only an s electron experiences no centrifugal repulsion.

Here are the corresponding shell densities, $|P_{n\ell}(\rho)|^2$.



The vertical lines extending downward from each shell density mark the maximum shell density. These maximum correspond to the radii predicted by the Bohr model,

n	Bohr ρ
1	1
2	4
3	9
4	16

In the Bohr model, the electron is assumed to be *only* at the single distance for a given total energy. We see now that instead, for each total energy, the electron may be found over a *range of distances* from the nucleus to the outer reaches of the atom.

Further, in the Bohr model, the allowed energies corresponded to circular orbits at distance from the nucleus such that the orbit circumference could fit an integer number of de Broglie waves. We see

now that instead the allowed energies correspond to those values that give radial probability amplitudes (rather than the circular probability amplitudes implied by the Bohr model) that converge to zero in the forbidden regions.

It is very important, now that we see this more accurate picture, to no longer think in terms of the Bohr-de Broglie circular orbits. The Bohr-de Broglie approach was helpful in getting us to the more accurate picture, but now that we have this more accurate picture, we can leave the Bohr-de Broglie picture behind.

■ Lowest energy $\ell = 0$ shell amplitudes for different Z

Here are the classical turning points for the lowest energy shell amplitudes for $\ell = 0$ for H, He⁺, and Li²⁺.

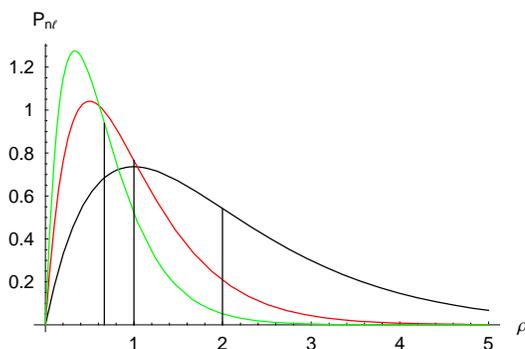
Z	ρ_{inner}	ρ_{outer}
1	0.	2.
2	0.	1.
3	0.	0.666667

The effective potential,

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

becomes deeper and narrower for increased nuclear charge, Z , because of the increased nuclear attraction. Since $\ell = 0$, there is no centrifugal repulsion and so no inner classical turning point.

Here are the lowest energy $\ell = 0$ shell amplitudes for H (black), He⁺ (red), and Li²⁺ (green).

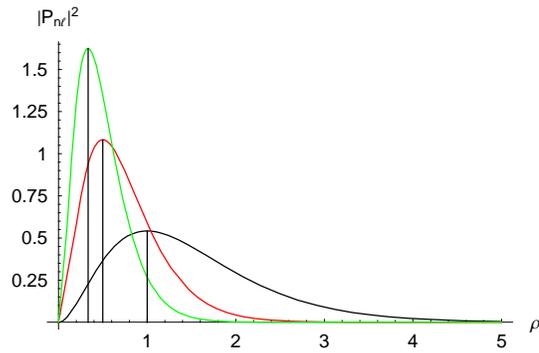


The vertical line extending downward from each shell amplitude marks the corresponding outer allowed-forbidden region boundary. The increased nuclear attraction shifts the turning point to smaller distances for larger nuclear charge. The increased nuclear attraction also lowers the total energy,

Z	ϵ
1	-1
2	-4
3	-9

This means that as nuclear charge increases the potential energy rises more steeply at the outer classical turning point. This in turn means the shell amplitude must decay more rapidly in the forbidden region as nuclear charge increases.

Here are the corresponding shell densities, $|P_{n\ell}(\rho)|^2$.



The vertical lines extending downward from each shell density mark the maximum shell density. These maximum correspond to the radii predicted by the Bohr model,

Z	Bohr ρ
1	1
2	$\frac{1}{2}$
3	$\frac{1}{3}$

We see that the lowest energy state of a one-electron atom shrinks as nuclear charge increases. We see also, once again, that the Bohr picture of an electron being at only the one distance from the nucleus is replaced by the electron distributed throughout space around the nucleus.

■ Hydrogen $\ell = 0$ shell amplitudes and shell densities for different levels of excitation

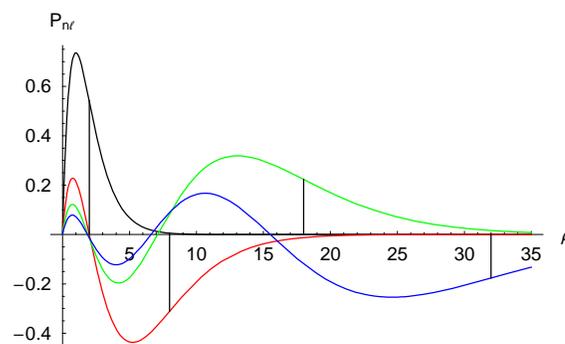
Here are the classical turning points for the four lowest energy hydrogen shell amplitudes for $\ell = 0$.

n	ℓ	ρ_{inner}	ρ_{outer}
1	0	0.	2.
2	0	0.	8.
3	0	0.	18.
4	0	0.	32.

As we have seen, there is no inner turning point, since $\ell = 0$ and so there is no centrifugal repulsion. The outer turning point is increasing since the total energy is increasing.

n	ℓ	ϵ
1	0	-1.
2	0	-0.25
3	0	-0.111111
4	0	-0.0625

Here are the lowest energy shell amplitudes for $n = 1$ (black), 2 (red), 3 (green), and 4 (blue).

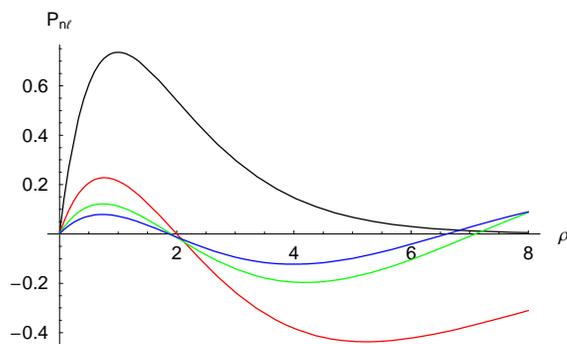


The lowest energy shell amplitude has one loop, the next lowest has two loops, etc. The vertical line extending downward from each shell amplitude marks the corresponding outer classical turning point.

n	l	ϵ
1	0	-1.
2	0	-0.25
3	0	-0.111111
4	0	-0.0625

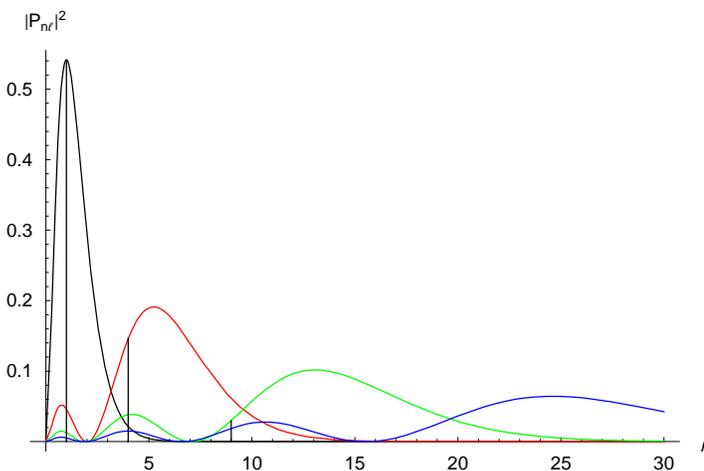
As the total energy increases, in the outer forbidden region the negative kinetic energy is getting smaller. The lowered negative kinetic energy means that the shell amplitude in the forbidden region decays to zero over a larger and larger distance. The combined effect of the outer classical turning points moving outward, due to increasing total energy, and the decay requiring greater distance in the outer forbidden region, due to decreased negative kinetic energy there, means that an electron in successively higher energy states for a given orbital momentum extends farther out into the space surrounding the nucleus.

Here are the same shell amplitudes near the nucleus.



Since there is no inner turning point, the shell amplitude leave the nucleus with non-positive curvature. Because near the nucleus the kinetic energy is so large, all of the functions have their first maximum at about the same place and, except for the lowest energy state, the first loops are all of nearly the same length. What is different, however, is the relative size of the loops: the higher the energy, the smaller the maximum of the initial loop.

Here are the corresponding shell densities, $|P_{nr}(\rho)|^2$.



The vertical lines extending downward from each shell density mark the radii predicted by the Bohr model,

n	Bohr ρ
1	1
2	4
3	9
4	16

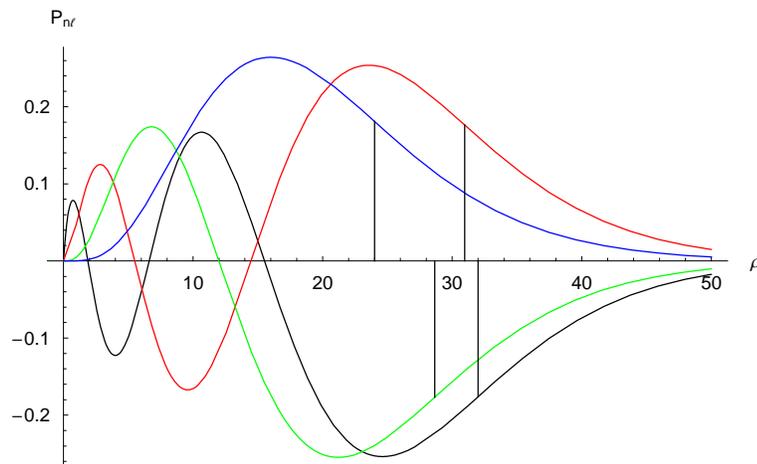
We see that only for the lowest energy solution does the maximum in the shell density agree with the predicted radius of the Bohr model. It is a general result that the Bohr model predictions only work for the lowest energy shell amplitude for a given orbital momentum.

■ Hydrogen shell amplitudes and shell densities at fixed total energy

Here are the classical turning points for hydrogen radial shell amplitudes and shell densities at fixed total energy $\epsilon = -1/16$, for $\ell = 0, 1, 2$, and 3.

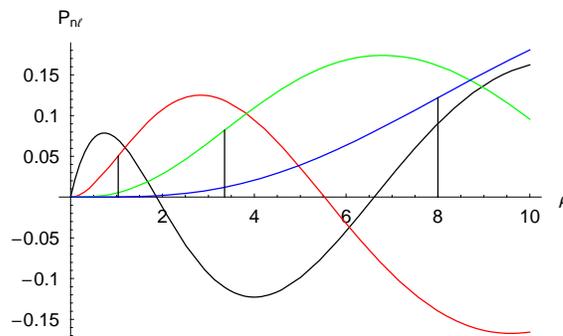
n	ℓ	ρ_{inner}	ρ_{outer}
4	0	0.	32.
4	1	1.03337	30.9666
4	2	3.35089	28.6491
4	3	8.	24.

Here are the shell amplitudes for $\ell = 0$ (black), 1 (red), 2 (green), and 3 (blue) at total energy $\epsilon = -1/16$.



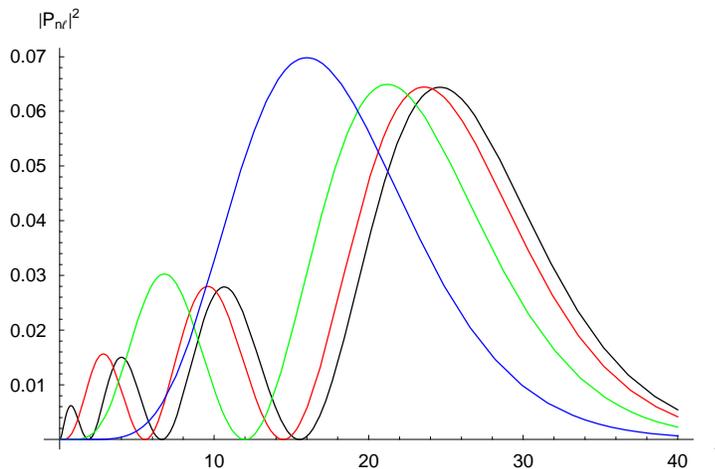
The vertical line extending downward from each shell amplitude marks the corresponding outer classical tuning point.

Here are the same shell amplitudes near the nucleus.



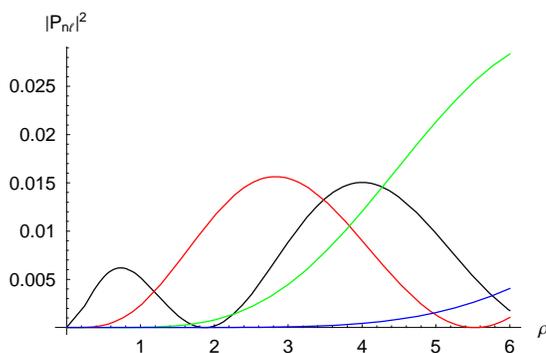
The vertical line extending downward from each shell amplitude (except for $\ell = 0$) marks the corresponding inner classical turning point; there is no inner forbidden region for $\ell = 0$. We see that the inner forbidden region grows with increasing orbital momentum. This makes sense since the effect of increased centrifugal repulsion is greatest at close to the nucleus.

Here is the plot of the shell densities, $|P_{n\ell}|^2$, for $\ell = 0$ (black), 1 (red), 2 (green), and 3 (blue) at total energy $\epsilon = -1/16$.



Even though the total energy is the same for all four shell densities, the electron distribution is quite different. The *higher* the orbital momentum, the *smaller* the allowed region, since the fixed total energy means that the total energy is *closer to the bottom of the corresponding potential curve*, where the allowed region is *smallest*.

Here are the shell densities close to the nucleus.



What is important to note is that the penetration of the electron into region near the nucleus is inversely proportional to the orbital momentum; the penetration is greatest for $\ell = 0$ (black) and least for $\ell = 3$ (blue). As orbital momentum increases, the increased centrifugal repulsion pushes the electron out from the center of the atom. We will see that this behavior, through its consequences for electrical shielding of the nuclear charge, will have profound effects on the structure of many electron atoms. Indeed, this behavior, together with the consequences of the antisymmetry requirement of many-electron shell amplitudes, accounts for the entire structure of the periodic table.

■ Radial loops

Here is a table of eigenvalues and number of loops for different values of the orbital momentum quantum number.

$n = j - \ell$	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 $-Z^2/(\ell + 1)^2$.

■ Study questions

Here are some questions to test your understanding. Keeping the effective potential energy curves in mind will be helpful in answering them.

Sketch the lowest energy hydrogen shell amplitude that has $\ell = 2$. How many loops does it have? What is its energy, in units $hc Ry$?

Sketch the third lowest energy hydrogen shell amplitude that has $\ell = 0$. How many loops does it have? What is its energy, in units of $hc Ry$?

Which hydrogen shell amplitude has the largest outer classical turning point: $3s$, $3p$, or $3d$?

Which hydrogen shell amplitude has the greatest amplitude near the nucleus: $4s$, $4p$, $4d$, or $4f$?

Which shell amplitude has the largest outer classical turning point: $H(1s)$, $He^+(1s)$, or $Li^{2+}(1s)$?

A hydrogen wave function has two loops and it has energy $-1/16$. What is the value of the orbital momentum quantum number?