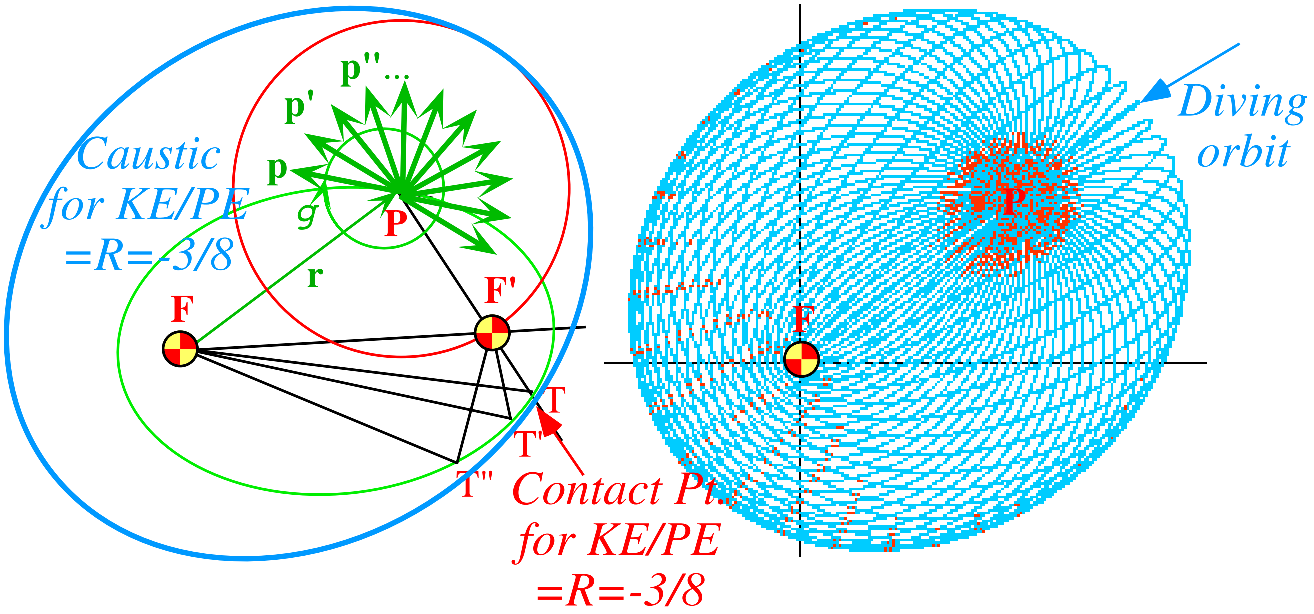
Quantum Theory for the Computer Age

Unit 9



Quantum Orbits

Unit 9 Quantum Orbits

Quantum theory of particle orbits has a long history beginning with the Bohr atomic Coulomb orbits introduced in Chapter 5 and 2D and 3D oscillator orbits introduced in Chapter 22 and shown to have U(3) and U(3) symmetry, respectively. Both are helped a lot by the R(3) rotational states and wavefunctions introduced in Chapter 23. The 3D Coulomb orbital problem has a higher symmetry R(4) that is something like the U(3) symmetry of the 3D isotropic oscillator. This connection will be explored.

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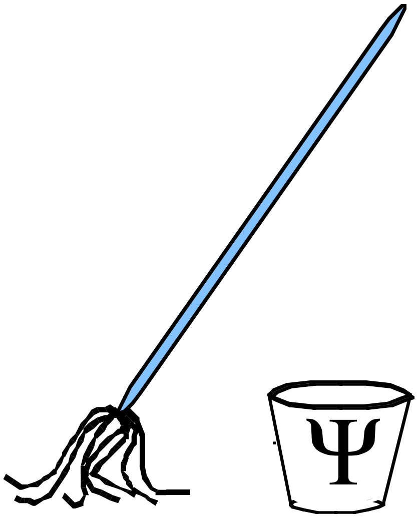

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for
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Ch. 26
Coulomb Orbits

W. Harter

The Bohr atomic Coulomb problem has nicely closed analytic solutions for both the classical and quantum versions. This is not an accident but due to symmetry. Like the 3D isotropic oscillator the 3D Coulomb orbital problem has a higher symmetry R(4) that is something like the U(3) symmetry of the 3D isotropic oscillator. This quantum symmetry connection will be explored and used to better understand the quantum orbitals and they will be compared with the classical orbits.

Unit 9 Quantum Orbits

Chapter 26 Coulomb Orbits

26.1 Introduction to Radial Hamiltonians

The ability to separate multi-dimensional equations into independent one-dimensional parts has generally been the prerequisite to finding exact analytic solutions for physics problems. This applies to classical equations of motion as well as the quantum mechanical equations of Schrodinger or Heisenberg. Further, such separation often depends on having some kind of symmetry which may or may not be obvious. Spherical rotational symmetry *R(3)* which has been exploited in the preceding sections is one of the more obvious ones. Closely related to *R(3)* is the *U(2)* symmetry of the isotropic two-dimensional oscillator.

For systems with spherical symmetry, the separation of the angular parts from the radial parts is to be expected. In the case of a single orbiting particle, such as an electron around a nucleus, the wave function for eigenstates has the simple product form $\Psi_{n,\ell,m}(r, \theta, \phi) = R_n(r)\, Y^{\ell}_{m}(\theta, \phi)$ where the angular part has already been given in closed analytic form in Chapter 23 by using the properties of rotational or *R(3)* symmetry operators.

Now we consider examples of possible radial functions $R_n(r)$. The radial functions will depend on the form of the radial potential function *V(r)*, and only for certain special potentials will symmetry analysis be helpful. Fortunately, two of the most common potentials, the harmonic oscillator $V(r)=kr^2/_2$ and the Coulomb potential $V(r)=k/r$ have high symmetries which allow symmetry analysis to aid in there analysis, as well. The three-dimensional oscillator has an obvious *U(3)* symmetry analogous to the *U(2)* symmetry of the two-dimensional oscillator. The Coulomb potential has a fairly non-obvious symmetry *R(4)* based on the eccentricity vector conservation.

For the vast majority of possible radial potentials *V(r)*, approximate solutions of their radial differential equations seem to be the only resort. Naturally, a modern approach offers numerical solution as a viable option in all cases.

So far, our only treatment of radial equations has been a brief analysis of the radial equation for the isotopic two-dimensional oscillator in Sec. 21.2(b). That technique will be used again here for some three-dimensional examples including that of the oscillator.

(a) Kinetic energy operator in polar form

For an isotropic or spherical potential that is a function $V(r)$ of radius alone, the separation of this degree of freedom from the angular ones is an obvious consequence of choosing polar coordinates.

$$x = r\cos\phi\sin\theta , \qquad y = r\sin\phi\sin\theta , \qquad z = r\cos\theta \tag{26.1.1}$$

From this follows the Jacobian transformation matrix.

$$\begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{pmatrix} = \begin{pmatrix} \cos\phi\sin\theta & r\cos\phi\cos\theta & -r\sin\phi\sin\theta \\ \sin\phi\sin\theta & r\sin\phi\cos\theta & r\cos\phi\sin\theta \\ \cos\theta & -r\sin\theta & 0 \end{pmatrix} \tag{26.1.2a}$$

The inverse (Kajobian) matrix is useful, too. It is inverse by chain rules: $\sum_\mu \frac{\partial x^a}{\partial r^\mu}\frac{\partial r^\mu}{\partial x^b} = \frac{\partial x^a}{\partial x^b} = \delta^a_b$, *etc.*

$$\begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial r}{\partial y} & \frac{\partial r}{\partial z} \\ \frac{\partial \theta}{\partial x} & \frac{\partial \theta}{\partial y} & \frac{\partial \theta}{\partial z} \\ \frac{\partial \phi}{\partial x} & \frac{\partial \phi}{\partial y} & \frac{\partial \phi}{\partial z} \end{pmatrix} = \begin{pmatrix} \cos\phi\sin\theta & \sin\phi\sin\theta & \cos\theta \\ \frac{\cos\phi\cos\theta}{r} & \frac{\sin\phi\cos\theta}{r} & \frac{-\sin\theta}{r} \\ \frac{-\sin\phi}{r\sin\theta} & \frac{\cos\phi}{r\sin\theta} & 0 \end{pmatrix} \tag{26.1.2b}$$

A transpose of the latter gives Cartesian momentum operators in terms of radial-polar angle derivatives.

$$\begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = \begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \phi}{\partial x} \\ \frac{\partial r}{\partial y} & \frac{\partial \theta}{\partial y} & \frac{\partial \phi}{\partial y} \\ \frac{\partial r}{\partial z} & \frac{\partial \theta}{\partial z} & \frac{\partial \phi}{\partial z} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix} = \begin{pmatrix} \cos\phi\sin\theta & \frac{\cos\phi\cos\theta}{r} & \frac{-\sin\phi}{r\sin\theta} \\ \sin\phi\sin\theta & \frac{\sin\phi\cos\theta}{r} & \frac{\cos\phi}{r\sin\theta} \\ \cos\theta & \frac{-\sin\theta}{r} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix} \tag{26.1.3a}$$

The inverse of this is a Jacobian differential operator relation based on the transpose of (26.1.2a).

$$\begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix} = \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} & \frac{\partial z}{\partial \theta} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = \begin{pmatrix} \cos\phi\sin\theta & \sin\phi\sin\theta & \cos\theta \\ r\cos\phi\cos\theta & r\sin\phi\cos\theta & -r\sin\theta \\ -r\sin\phi\sin\theta & r\cos\phi\sin\theta & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \tag{26.1.3b}$$

The radial part of the above, multiplied by r, is worth noting.

$$r\frac{\partial}{\partial r} = r\cos\phi\sin\theta\frac{\partial}{\partial x} + r\sin\phi\sin\theta\frac{\partial}{\partial y} + r\cos\theta\frac{\partial}{\partial z} = \mathbf{r}\bullet\frac{\partial}{\partial \mathbf{r}} = \mathbf{r}\bullet\nabla \tag{26.1.3c}$$

Classical Lagrangian mechanics begins with the first differential vector.

$$dx^a = \sum_{\mu} \frac{\partial x^a}{\partial r^\mu} dr^\mu = \frac{\partial x^a}{\partial r} dr + \frac{\partial x^a}{\partial \theta} d\theta + \frac{\partial x^a}{\partial \phi} d\phi , \text{ where: } x^a = \{x, y, z\}$$

Its square arc-length or metric has three terms (instead of nine) because polar coordinates are orthogonal.

$$(ds)^2 = \sum_a \left(dx^a\right)^2 = \sum_{a,\mu,\nu} \frac{\partial x^a}{\partial r^\mu} \frac{\partial x^a}{\partial r^\nu} dr^\mu dr^\nu = (dr)^2 + r^2 (d\theta)^2 + r^2 \sin^2 \theta (d\phi)^2$$

This gives a velocity-squared which, multiplied by half the mass, is the non-relativistic kinetic energy.

$$T = \frac{1}{2} M \dot{s}^2 = \dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \, \dot{\phi}^2$$

Hamiltonian mechanics uses momenta p_μ that use inverse (Kajobian) relations like (26.1.3).

$$p_a = M\dot{x}^a = \sum_{\mu} \frac{\partial r^\mu}{\partial x^a} p_\mu = \frac{\partial r}{\partial x^a} p_r + \frac{\partial \theta}{\partial x^a} p_\theta + \frac{\partial \phi}{\partial x^a} p_\phi , \text{ where: } \dot{x}^a = \left\{ \frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt} \right\} \tag{26.1.4}$$

Again, this gives a three-term expression for classical kinetic energy using polar momenta.

$$T = \frac{1}{2M} \sum_a \left(p_a\right)^2 = \sum_{\mu} \frac{\partial r^\mu}{\partial x^a} \frac{\partial r^\nu}{\partial x^a} p_\mu p_\nu = \frac{{p_r}^2}{2M} + \frac{{p_\theta}^2}{2Mr^2} + \frac{{p_\phi}^2}{2Mr^2 \sin^2 \theta} \tag{26.1.5a}$$

This is consistent with the fundamental Lagrangian definitions of momentum.

$$p_r = \frac{\partial T}{\partial \dot{r}} = M\dot{r}, \quad p_\theta = \frac{\partial T}{\partial \dot{\theta}} = Mr^2 \dot{\theta}, \quad p_\phi = \frac{\partial T}{\partial \dot{\phi}} = Mr^2 \sin^2 \theta \, \dot{\phi}, \tag{26.1.5b}$$

The quantum Hamiltonian is simplified by the square L^2 orbital momentum in Cartesian form.

$$\begin{aligned} L^2 = \mathbf{L} \bullet \mathbf{L} = (\mathbf{r} \times \mathbf{p}) \bullet (\mathbf{r} \times \mathbf{p}) &= \sum_{a,b,c,d,e} \varepsilon_{abc} r_b p_c \varepsilon_{ade} r_d p_e \\ &= \sum_{b,c,d,e} \left(\delta_{bd}\delta_{ce} - \delta_{be}\delta_{cd}\right) r_b p_c r_d p_e \\ &= \sum_{b,c} \left(r_b p_c r_b p_c - r_b p_c r_c p_b\right) \end{aligned} \tag{26.1.6}$$

The *Levi-Civita identity* $\Sigma_a \varepsilon_{abc} \varepsilon_{ade} = \delta_{bd}\delta_{ce} - \delta_{be}\delta_{cd}$ is used followed by commutation relations.

$$r_a p_b = p_b r_a + i\hbar \delta_{ab} , \qquad p_b r_a = r_a p_b - i\hbar \delta_{ab} . \tag{26.1.7}$$

This is rearranged to give **r•p** = $r_b p_b$ terms like (26.1.3c) wherever possible.

$$\begin{aligned} L^2 &= \sum_{b,c} \left(r_b r_b p_c p_c - i\hbar r_b p_c \delta_{bc} - r_b p_c p_b r_c + i\hbar r_b p_c \delta_{bc}\right) = \sum_{b,c} \left(r_b r_b p_c p_c - r_b p_b p_c r_c\right) \\ &= \sum_{b,c} \left(r_b r_b p_c p_c - r_b p_b r_c p_c + i\hbar r_b p_b\right) \end{aligned} \tag{26.1.8}$$

The result is concise expression involving the radial coordinate and momentum only.

$$L^2 = (\mathbf{r}\bullet\mathbf{r})(\mathbf{p}\bullet\mathbf{p}) - (\mathbf{r}\bullet\mathbf{p})(\mathbf{r}\bullet\mathbf{p}) + i\hbar(\mathbf{r}\bullet\mathbf{p}) = r^2p^2 - (rp_r)(rp_r) + i\hbar(rp_r)$$

The quantum kinetic energy reduces to the following. The classical T emerges if we ignore the tiny $\hbar\rightarrow 0$.

$$\begin{aligned} T = \frac{p^2}{2M} &= \frac{(rp_r)(rp_r) - i\hbar(rp_r)}{2Mr^2} + \frac{L^2}{2Mr^2} \\ &= \frac{p_r(rp_r) - i\hbar p_r}{2Mr} + \frac{L^2}{2Mr^2} \xrightarrow[\hbar\rightarrow 0]{} \frac{{p_r}^2}{2M} + \frac{L^2}{2Mr^2} \end{aligned} \tag{26.1.9}$$

The Jacobian relation (26.1.3c) gives a representation for rp_r equal to $(i/\hbar)r\partial_r$.

$$\mathbf{r}\bullet\mathbf{p} = rp_r = \frac{\hbar}{i}r\frac{\partial}{\partial r} = \frac{\hbar}{i}r\partial_r = \frac{\hbar}{i}\mathbf{r}\bullet\nabla$$

This gives the complete quantum kinetic energy operator in polar coordinates.

$$\begin{aligned} T = -\frac{\hbar^2}{2M}\nabla^2 &= -\frac{\hbar^2}{2M}\frac{(r\partial_r)(r\partial_r) + (r\partial_r)}{r^2} + \frac{L^2}{2Mr^2} \\ &= -\frac{\hbar^2}{2M}\frac{r^2{\partial_r}^2 + 2r\partial_r}{r^2} + \frac{L^2}{2Mr^2} \\ &= -\frac{\hbar^2}{2M}\frac{1}{r^2}\partial_r\left(r^2\partial_r\right) + \frac{L^2}{2Mr^2} \end{aligned} \tag{26.1.10a}$$

This may be compared with the polar coordinate Laplacian form arising from (26.1.3a).

$$T = -\frac{\hbar^2}{2M}\frac{1}{r^2}\partial_r\left(r^2\partial_r\right) - \frac{\hbar^2}{2Mr^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right) - \frac{\hbar^2}{2Mr^2\sin^2\theta}{\partial_\phi}^2 \tag{26.1.10b}$$

From this we infer the coordinate differential form for the square-angular momentum.

$$L^2 = \frac{\hbar^2}{\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right) + \frac{\hbar^2}{\sin^2\theta}{\partial_\phi}^2 \tag{26.1.10c}$$

(b) Angular-radial separation

The classical Hamiltonian for a radial potential $V(r)$ separates nicely by assuming angular momentum conservation in the kinetic part (26.1.9).

$$H = \frac{p^2}{2M} + V(r) \xrightarrow[\hbar\rightarrow 0]{} \frac{{p_r}^2}{2M} + \frac{L^2}{2Mr^2} + V(r) \tag{26.1.11}$$

The result is a 1-D potential $V(r)$ plus a $1/r^2$ *effective potential* known as the *centrifugal barrier* term. The quantum Hamiltonian Schrodinger energy eigenvalue equation has a purely radial form.

$$H\Psi = \left[-\frac{\hbar^2}{2M}\nabla^2 + V(r)\right]\Psi = E\Psi = \left[-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{L^2}{2Mr^2}\right]\Psi \tag{26.1.12}$$

This separates nicely by using the eigenvalues $\ell(\ell+1)$ from (23.1.10b)) for L^2 acting on spherical harmonics $\langle\theta\phi|^{\ell}{}_{m}\rangle = Y^{\ell}{}_{m}(\theta\phi)$, for which we have analytic expressions (23.1.15) and (23.1.16).

$$\left\langle \theta\phi \middle| \mathbf{L}^2 \middle| {}^{\ell}_{m} \right\rangle = L^2 Y^{\ell}_{m}(\theta\phi) = \frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y^{\ell}_{m}(\theta\phi)}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2 Y^{\ell}_{m}(\theta\phi)}{\partial\phi^2} = \hbar^2\ell(\ell+1)Y^{\ell}_{m}(\theta\phi) \tag{26.1.13a}$$

Then the equation for the radial part $R_n(r)$ of the product wave function

$$\Psi_{n,\ell,m}(r,\ \theta,\ \phi) = R_n(r)\ Y^{\ell}{}_{m}(\theta,\ \phi) \tag{26.1.13b}$$

is as follows.

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{\hbar^2\ell(\ell+1)}{2Mr^2} + V(r) - E\right)R = 0 \tag{26.1.13c}$$

Before proceeding with solutions for various radial potentials of this equation, it is instructive to note that a polar coordinate separation is possible in some cases even if the potential has angular dependence as well as radial, provide the angular dependency has the following form.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2} + \left(\varepsilon - v(r) - \frac{u(\theta)}{r^2} - \frac{w(\phi)}{r^2\sin^2\theta}\right)\Psi = 0 \tag{26.1.14a}$$

The energy and potential functions are in natural atomic units here.

$$\varepsilon = \frac{2M}{\hbar^2}E, \qquad v(r) = \frac{2M}{\hbar^2}V(r),\ etc. \tag{26.1.14b}$$

Substituting (26.1.13b) and multiplying through by r^2/RY gives the following.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + r^2(\varepsilon - v(r)) + \frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) - u(\theta)Y + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} - \frac{w(\phi)}{r^2\sin^2\theta}Y = 0$$

The radial part must equal a first *separation constant* k_1 since it is independent of the angular part. An ordinary radial differential equation like (26.1.13c) results. The separation constant is $k_1 = \ell(\ell+1)$.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\varepsilon - v(r) - \frac{k_1}{r^2}\right)R = 0 \tag{26.1.15a}$$

Also the angular part is a constant, too. It is minus the separation constant. A product wave function

$$Y(\theta,\ \phi) = P(\theta)Q(\phi) \tag{26.15.5b}$$

is assumed in order to separate the rest.

$$k_1 + \frac{Q}{PO\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right) - u(\theta)PQ + \frac{P}{\sin^2\theta}\frac{\partial^2 Q}{\partial\phi^2} - \frac{w(\phi)}{r^2\sin^2\theta}PQ = 0$$

Divide by $PQ/\sin^2\theta$ and rearrange so that a second *separation constant* k_2 is warranted.

$$\frac{\sin\theta}{P}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right) - \left(u(\theta) - k_1\right)\sin^2\theta \quad + \frac{1}{Q}\frac{\partial^2 Q}{\partial\phi^2} - w(\phi) = 0$$

The result is two more ordinary differential equations.

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) - \left(\left(u(\theta) - k_1\right)\sin^2\theta + k_2\right)P = 0 \tag{26.15.5c}$$

(26.1.15d)

The Q equation is a 1-D wave equation. For $w=0$ it reduces to Bohr orbital plane-wave exponentials.

$$Q=Q_m(\phi) = A\, e^{im\phi} + A\, e^{-im\phi} \qquad (26.1.16)$$

The separation constant is $k_2 = m^2$ according to (26.1.15d). It may be substituted in the $P=P(q)$ equation (26.1.15c).to give the following.

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)-\left(\left(u(\theta)-k_1\right)\sin^2\theta-m^2\right)P=0 \qquad (26.1.17a)$$

For $u=0$ this reduces to *Legendre's equation*. We use separation constant is $k_1=\ell(\ell+1)$.

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\left(\ell(\ell+1)\sin^2\theta-m^2\right)P=0 \qquad 5.1.17b)$$

Compare this to angular eigenfunction equation (26.1.13c) which has not yet separated θ and ϕ angles.

(c) Radial equations and solution

We now consider some special cases of the radial differential equation (26.1.13c) when well-known potentials are used. The simplest cases involve no potential at all.

1. Potential-free case

With $V(r)=0$ the radial equation (26.1.13c) becomes the following in atomic energy units.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\left(\frac{\ell(\ell+1)}{r^2}-\varepsilon\right)R=0 \qquad (26.1.18)$$

If the energy also happens to be zero $(E=0)$ then this is the radial part of the *Laplace equation* $\nabla^2\Psi=0$.

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\ell(\ell+1)R=0 \qquad (26.1.19a)$$

The solutions for the latter are the any combination of the following powers.

$$R=R_\ell(r)=Ar^\ell+B\frac{1}{r^{\ell+1}} \qquad (26.1.19b)$$

This is consistent with the multipole expansions (23.4.10), all of which are solutions to the Laplace equation for electrostatic potentials in a vacuum around charges.

However, the radial functions for quantum particles in free space are quite different. In general the solutions of (26.1.18) can be given in terms of spherical Bessel functions.

$$R=R_\ell(r)=Aj_\ell(r)+Bh_\ell(r)$$

These important functions will be discussed in connection with scattering theory.

2. Coulomb potential

With $v(r)=k/r$ the radial equation (26.1.13c) becomes the following in atomic energy units.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\left(\frac{\ell(\ell+1)}{r^2}+\frac{k}{r}-\varepsilon\right)R=0 \qquad (26.1.20a)$$

We shall here consider just the bound state case which requires a negative value for both the Coulomb constant (k=-$|k|$ makes the potential attractive) and the energy (ε=-$|\varepsilon|$ makes the wave bounded in space.)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\left(\frac{\ell(\ell+1)}{r^2}-\frac{|k|}{r}+|\varepsilon|\right)R=0 \qquad (26.1.20b)$$

For the Coulomb potential, several re-scaling factors are conventional and convenient. First, a radial scale

$$R(r)=\frac{X(r)}{r}\ ,\qquad \frac{dR}{dr}=\frac{1}{r}\frac{dX}{dr}-\frac{X(r)}{r^2}\ ,\qquad \frac{d^2R}{dr^2}=\frac{1}{r}\frac{d^2X}{dr^2}-\frac{2}{r^2}\frac{dX}{dr}-\frac{2X(r)}{r^3}$$

makes the radial integral $\int r^2R^2dr$ become simply $\int X^2dr$ and gives the standard form derived below. From

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{\ell(\ell+1)R}{r^2}+\frac{|k|R}{r}-|\varepsilon|R=0$$

we get an X-wave equation which has no first-derivative term.

$$\frac{1}{r}\frac{d^2X}{dr^2}-\frac{\ell(\ell+1)}{r^2}\frac{X}{r}+\frac{|k|}{r}\frac{X}{r}-|\varepsilon|\frac{X}{r}=0$$

or:

$$\frac{d^2X}{dr^2}-\frac{\ell(\ell+1)}{r^2}X+\frac{|k|}{r}X-|\varepsilon|X=0 \qquad (26.1.20c)$$

Finally, most Coulomb treatments use atomic units of distance and energy for radius $r=a\rho$ and $|E|=E_R\kappa^2$.

$$\frac{d^2X}{d\rho^2}-\frac{\ell(\ell+1)}{\rho^2}X+\frac{2}{\rho}X-\kappa^2X=0 \qquad (26.1.20d)$$

where $2/a = 2M|k|/\hbar^2$ and $\kappa^2/a^2 = 2M|E|/\hbar^2$ are given in terms of *Rydberg energy E_R* and *Bohr radius a*.

$$r=\rho a=\rho\frac{\hbar^2}{M\,|\,k\,|}=\rho\frac{4\pi\varepsilon_0\hbar^2}{Me^2Z}\ (26.1.20e)\qquad |\,E\,|=\kappa^2E_R=\kappa^2\frac{\hbar^2}{2Ma^2}\qquad (26.1.20f)$$

One should pause and realize that this equation has been solved on the average of at least once a day for over 75 years; that is, roughly 27,375 times. (And, here goes 27,376!) So, by now everyone thinks they have a pretty good scheme of units. The Bohr radius $a= 0.528$ Å was discussed in (5.6.3). The Rydberg energy for atomic number $Z=1$ (Hydrogen) is $E_R = 13.6eV$.

To begin solving such an equation it helps to check out how it behaves for large and small radii.

$$(for\ \rho\rightarrow\infty):\frac{d^2X}{d\rho^2}-\quad 0\quad +0-\kappa^2X=0\quad implies{:}\,X\sim e^{-\kappa\rho} \qquad (26.1.21a)$$

$$(for\ \rho\rightarrow 0):\frac{d^2X}{d\rho^2}-\frac{\ell(\ell+1)}{\rho^2}X+*-\quad 0\ =0\quad implies{:}\,X\sim\rho^{\ell+1} \qquad (26.1.21b)$$

This helps decide what factors to take out of the trial solution in order to possibly get a residual polynomial solution. Recall that the oscillator has an approximate e^{-ax^2} solution at large distances, and that turns out to ride on every exact solution including the ground state (for which it is the whole story!). The same happens here as we will see; an $e^{-\kappa\rho}$ factor will grace every bound-state Coulomb wavefunction.

So the trial solution taken here will be the following expansion around $\rho=0$.

$$X = e^{-\kappa\rho}\rho^{\mu}\sum_{\nu=0} f_\nu \rho^{\nu} = e^{-\kappa\rho}\sum_{\nu=0} f_\nu \rho^{\nu+\mu} \qquad (26.1.22)$$

With the factor ρ^{μ} we are pretending we don't know that (26.1.21b) suggests a factor $\rho^{\ell+1}$, and derive this later. Now we have the unenviable job of organizing the derivatives of the trial X.

$$\frac{dX}{d\rho} = -\kappa e^{-\kappa\rho}\sum_{\nu=0} f_\nu\rho^{\nu+\mu} + e^{-\kappa\rho}\sum_{\nu=0}(\nu+\mu)f_\nu\rho^{\nu+\mu-1}$$

$$\frac{d^2X}{d\rho^2} = \kappa^2 e^{-\kappa\rho}\sum_{\nu=0} f_\nu\rho^{\nu+\mu} - 2\kappa e^{-\kappa\rho}\sum_{\nu=0}(\nu+\mu)f_\nu\rho^{\nu+\mu-1} + e^{-\kappa\rho}\sum_{\nu=0}(\nu+\mu-1)(\nu+\mu)f_\nu\rho^{\nu+\mu-2}$$

To save space let us label $(\nu+\mu+a)$ by ν_a and write out enough terms to bring the sum power up to ρ^{ν_0}

.

$$\frac{d^2X}{d\rho^2} = e^{-\kappa\rho}\left(\kappa^2\sum_{\nu=0} f_\nu\rho^{\nu_0} - 2\kappa\sum_{\nu=0}\nu_0 f_\nu\rho^{\nu_{-1}} + \sum_{\nu=0}\nu_{-1}\nu_0 f_\nu\rho^{\nu_{-2}}\right) \quad \textit{where: } \nu_a = \nu+\mu+a$$

$$\begin{aligned}\frac{d^2X}{d\rho^2} = e^{-\kappa\rho}&\left(\sum_{\nu=0}\kappa^2 f_\nu\rho^{\nu_0}\right)\\ +e^{-\kappa\rho}&\left(-2\kappa\mu f_0\rho^{\mu-1} - \sum_{\nu=0} 2\kappa\nu_1 f_{\nu+1}\rho^{\nu_0}\right)\\ +e^{-\kappa\rho}&\left(+\mu(\mu-1)f_0\rho^{\mu-2} + (\mu+1)\mu f_1\rho^{\mu-1} + \sum_{\nu=0}\nu_1\nu_2 f_{\nu+2}\rho^{\nu_0}\right)\end{aligned}$$

In this way all the terms of the radial equation (26.1.20d) are assembled power-by-power. Let $L=\ell(\ell+1)$.

$$\begin{aligned}
-\kappa^2 X &= -\kappa^2 e^{-\kappa\rho}\sum_{\nu=0} f_\nu \rho^{\nu+\mu} &&= e^{-\kappa\rho}\left\{ \sum_{\nu=0}\left[-\kappa^2 f_\nu \right]\rho^{\nu+\mu}\right\} \\
\frac{2X}{\rho} &= 2e^{-\kappa\rho}\sum_{\nu=0} f_\nu \rho^{\nu+\mu-1} &&= e^{-\kappa\rho}\left\{ 2f_0\rho^{\mu-1} + \sum_{\nu=0}\left[2f_{\nu+1} \right]\rho^{\nu+\mu}\right\} \\
\frac{-LX}{\rho^2} &= -Le^{-\kappa\rho}\sum_{\nu=0} f_\nu \rho^{\nu+\mu-2} &&= e^{-\kappa\rho}\left\{ \text{-}Lf_0\rho^{\mu-2}\text{ - }Lf_1\rho^{\mu-1} + \sum_{\nu=0}\left[-L f_{\nu+2} \right]\rho^{\nu+\mu}\right\} \\
\frac{d^2X}{d\rho^2} &= && e^{-\kappa\rho}\left\{ \mu(\mu-1)\, f_0\rho^{\mu-2} + (\mu+1)\mu\, f_1\rho^{\mu-1} + \sum_{\nu=0}\left[\kappa^2 f_\nu \text{ - } 2\kappa\nu_1 f_{\nu+1} + \nu_1\nu_2 f_{\nu+2}\right]\rho^{\nu+\mu}\right\}
\end{aligned}$$

The sum of coefficients for each power must sum to zero. For the lowest power $f_0\rho^{\mu-2}$ the sum gives

$$\mu(\mu\text{-}1) = L = \ell(\ell+1) \text{ implies: } \mu = \ell+1 \text{ or: } \mu = \text{-}\ell \qquad (26.1.23)$$

This is known as an *index* or *indicial equation*. Here we only accept the first solution $(\mu=\ell+1)$ which also came from (26.1.21b) since the other possibility $(\mu = \text{-}\ell)$ would cause ρ^μ to blow up at $\rho=0$.

A formula for coefficients f_ν follows from zeroing the bracketed coefficients of $\rho^{\nu+\mu}$.

$$(2-2\kappa\nu_1)f_{\nu+1} = (\nu_1\nu_2 - L)f_{\nu+2} \qquad \text{where:} \qquad L=\ell(\ell+1),$$

or:

$$2\left(1-\kappa(\nu+\mu+1)\right)f_{\nu+1} = \left((\nu+\mu+1)(\nu+\mu+2) - \ell(\ell+1)\right)f_{\nu+2} \qquad (26.1.24)$$

This is called a *recursion relation*. Let us replace ν by $\nu-1$ and use indicial solution $(\mu=\ell+1)$.

$$\begin{aligned}
f_{\nu+1} &= \frac{2(\kappa(\nu+\mu)-1)}{(\nu+\mu)(\nu+\mu+1)-\ell(\ell+1)} f_\nu = \frac{2(\kappa(\nu+\ell+1)-1)}{(\nu+\ell+1)(\nu+\ell+2)-\ell(\ell+1)} f_\nu \\
&= \frac{2(\kappa(\nu+\ell+1)-1)}{(\nu+2\ell+1)(\nu+\ell+2)} f_\nu
\end{aligned} \qquad (26.1.25a)$$

Demanding that this recursion terminate for some integer $\nu = n$, that is, the radial wave is a polynomial of order is n, leads to the *Coulomb quantization condition* on the energy parameter κ.

$$f_{n+1} = 0 \quad \textit{implies:} \quad \kappa(n+\ell+1)-1 = 0 \quad \textit{or:} \quad \kappa = \frac{1}{(n+\ell+1)} \qquad (26.1.25b)$$

From the energy definition (26.1.20f) follows the famous *Rydberg energy level formula*.

$$|E| = \frac{1}{(n+\ell+1)^2}E_R = \frac{1}{2(n+\ell+1)^2}\frac{\hbar^2}{Ma^2} = \frac{1}{N^2}E_R \qquad (26.1.25c)$$

The energy is a function of only a single *principle quantum number N* .

$$N = n + \ell + 1 \qquad (26.1.25d)$$

N is a sum of *radial quantum number n* and the total angular quantum number ℓ. Since neither n nor ℓ may be negative the two quantum numbers are limited by each other in a given energy level belonging to a particular principle N, that is n is between zero and $N\text{-}\ell\text{-}1$ and ℓ is between zero to $N\text{-}n\text{-}1$. The $n\ell$-level structure for $n(\ell=0)=ns$, $n(\ell=1)=np$, $n(\ell=2)=nd$, $n(\ell=3)=nf$, and $n(\ell=4)=ng$ levels are sketched in Fig. 26.1.1 below. Recall that each orbital ℓ level has a $2\ell+1$ degeneracy due to magnetic or z-momentum *m* between ℓ and $-\ell$. Together, this makes each *(N = n + ℓ + 1)*-level have a degeneracy of N^2.

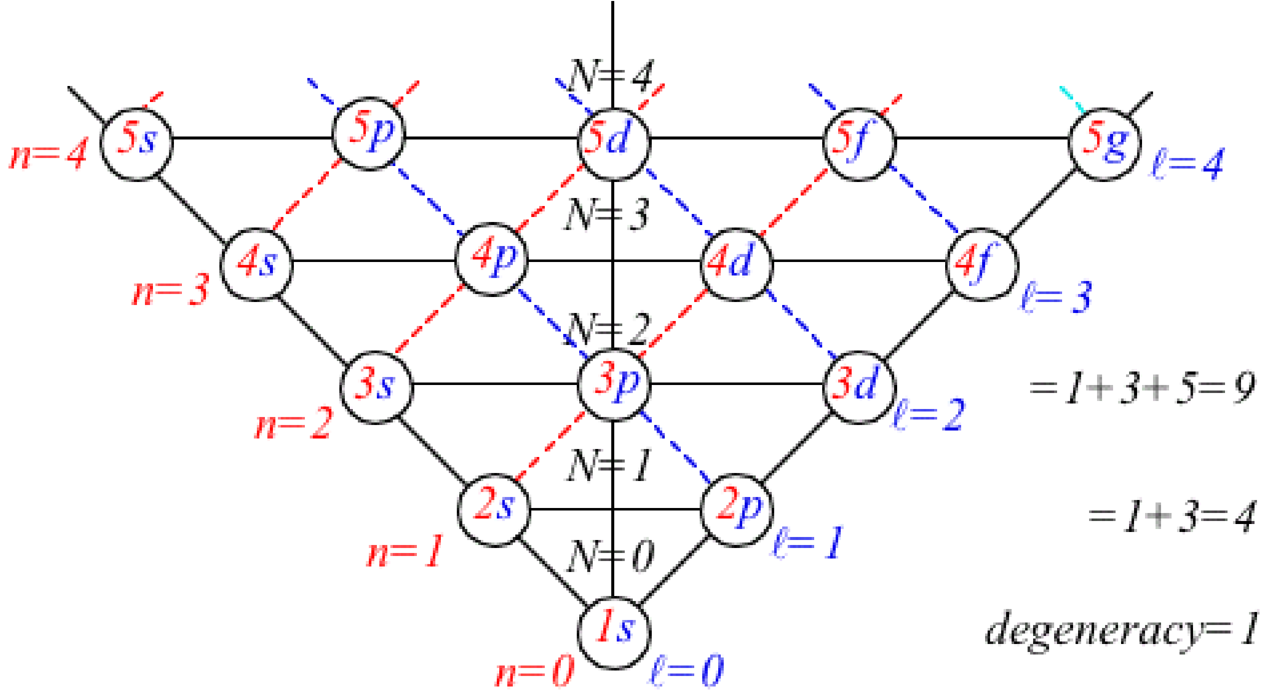

Fig. 26.1.1 Array of Coulomb states with their quantum numbers and degeneracy.

The recursion relation (26.1.25a) may be expressed in terms of the principle *N*-number using the quantization condition (26.1.25b).

$$f_{v+1} = \frac{2\left(\frac{v+\ell+1}{N+\ell+1}-1\right)}{(v+2\ell+1)(v+\ell+2)} f_v = \frac{2(v+\ell+1-N-\ell-1)}{N(v+2\ell+1)(v+\ell+2)} f_v \qquad (26.1.25e)$$

$$= \frac{2(v-N)}{N(v+2\ell+1)(v+\ell+2)} f_v$$

Radial wave functions have the polynomial following coefficients.

$$f_1 = \frac{2}{N}\frac{(0-n)}{(2\ell+2)} f_0\ , \quad f_2 = \frac{2}{N}\frac{(1-n)}{2(2\ell+3)} f_1\ , \qquad f_3 = \frac{2}{N}\frac{(2-n)}{3(2\ell+4)} f_2\ , \quad \cdots$$

$$= \left(\frac{2}{N}\right)^2 \frac{(0-n)(1-n)}{2(2\ell+2)(2\ell+3)} f_0\ , \quad = \left(\frac{2}{N}\right)^3 \frac{(0-n)(1-n)(2-n)}{2\cdot 3(2\ell+2)(2\ell+3)(2\ell+4)} f_0\ , \quad \cdots$$

The resulting wavefunction is an *N*-degree polynomial with a factor $f_0\rho^{\mu-2}e^{-\kappa\rho} = f_0\rho^{\ell}e^{-\rho/N}$

$$R_{N\ell}(r) = \frac{X_{N\ell}}{a\rho} \qquad \text{where: } r = a\rho$$

$$= f_0 \frac{e^{-\rho/N}\rho^{\ell}}{a}\left[1 + \frac{(0-n)}{(2\ell+2)}\left(\frac{2\rho}{N}\right) + \frac{(0-n)(1-n)}{2!(2\ell+2)(2\ell+3)}\left(\frac{2\rho}{N}\right)^2 + \frac{(0-n)(1-n)(2-n)}{3!(2\ell+2)(2\ell+3)(2\ell+4)}\left(\frac{2\rho}{N}\right)^3\right]$$

(26.1.26)

(d) Radial wavefunctions

Some examples of these waves are plotted in Fig. 26.1.2. The number and type of nodal surfaces for the complete Coulomb wave function $R_n(r)\ Y^\ell{}_m(\theta,\ \phi)$ are listed in the following table.

$n=N-\ell-1$	*concentric r-spheres*	
$\ell-m$	θ *- cones ("magic" angles)*	
m	ϕ*-planes (azimuthal nodes)*	
$N-1$	*nodal surfaces of some kind*	(26.1.27)

The principle or total quantum number N determines the number of nodal surfaces while the radial quantum number $n=N-\ell-1$ determines the number of radial nodes. The total angular quantum number ℓ determines the total number of angular modes and m determines the number of azimuthal nodes.

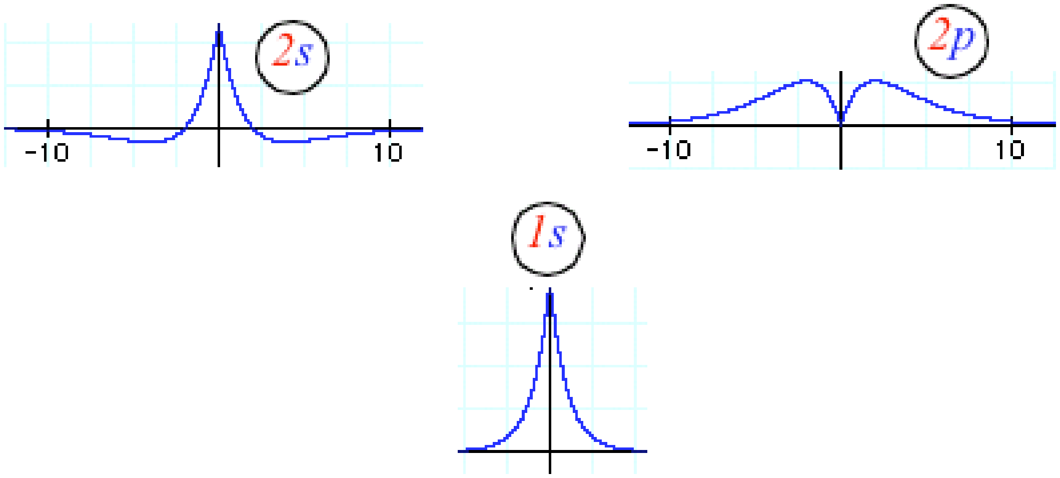

Fig. 26.1.2 Lowest Coulomb atomic radial wavefunctions