

Visualizing Atomic Orbitals

Jing B. Wang, Paul C. Abbott, and Jim F. Williams

Department of Physics
University of Western Australia
Nedlands WA 6907, Australia
wang@physics.uwa.edu.au, paul@physics.uwa.edu.au

The Mathematica software package provides a range of tools for working with atomic systems. The symbolic tools include orthogonal polynomials and Clebsch-Gordan coefficients whilst the graphical capabilities cover polar plots; spherical plots; density plots; contour plots in two and three dimensions; and animation. These tools are applied to the manipulation and visualization of atomic orbitals.

■ INTRODUCTION

The probability distribution of the electron charge cloud in an atom, namely the atomic orbital, often reveals crucial information in atomic physics. Visual representation of such orbitals is invaluable to researchers working in this field and also helps teaching atomic structures to physics or chemistry students. The atomic orbital concepts were discussed in detail by Berry and the cited papers therein, including several visualization devices. However, the newly developed symbolic package *Mathematica* provides a wider range of graphical tools (including polar plots, spherical plots, density plots, contour plots in two and three dimensions, and animation), which can be applied to help visualise the radial and angular behaviour of multi-dimensional systems.

Mathematica also has a wide range of built-in special functions appropriate for the analysis of quantum systems. Orthogonal polynomials — Legendre, Laguerre, Chebyshev, Hermite and Jacobi (corresponding to the *Mathematica* functions $P_n(x)$, $L_n^a(x)$, $U_n(x)$, $T_n(x)$, $H_n(x)$, and $P_n^{(a,b)}(x)$) — arise when solving a wide class of eigenvalue and boundary value problems. The spherical harmonics, $Y_l^m(\theta, \phi)$, are eigenfunctions of the angular part of the Laplacian operator (which is the quantum mechanical angular momentum operator). Clebsch-Gordan coefficients arise in the study of angular momenta in quantum mechanics, and in other applications of the rotation group. These functions, taken together with the orthogonal polynomials and graphical tools, provide a powerful environment for the study of atomic systems. It is worth noting that these methods can be readily utilized in the studies of other multi-dimensional systems.

As this article is not intended to be a tutorial on *Mathematica*, commands and syntax will not usually be explained. However, it is hoped that by showing a well-chosen set of examples, even readers unfamiliar with *Mathematica* will be able to follow the examples. The graphical output is placed immediately after its corresponding input command as it appears in *Mathematica* notebooks. Arbitrary units are used in these graphs.

■ 1. NOTATION AND PREREQUISITES

The quantity

$$\Omega(r) dr = \begin{cases} |\psi_{n,l,m}(r)| dr & \text{pure basis state} \\ |\psi_{n,l}(r)| dr & \text{coherently mixed state} \end{cases} \quad \begin{matrix} \psi_{n,l,m}(r), \\ \psi_{n,l}(r) = \sum_m c_m \psi_{n,l,m}(r), \end{matrix}$$

where

$$\psi_{n,l,m}(r) \equiv |n l m\rangle = R_{n,l}(r) Y_l^m(\theta, \phi), \quad \mathbf{r} = (r, \theta, \phi), \quad dr = r^2 dr d\Omega, \quad d\Omega = \sin(\theta) d\theta d\phi,$$

represents the probability of finding an electron in the volume element dr . The spherical harmonics, $Y_l^m(\theta, \phi)$, give the angular distribution of the atomic orbitals and $R_{n,l}(r)$ is the corresponding radial distribution.

In the following, the general spherical harmonic will be denoted using the *Mathematica* shorthand $Y_l^m(\theta, \phi)$. For example,

$$Y_2^1(\theta, \phi)$$

$$-\frac{1}{2} e^{i\phi} \sqrt{\frac{15}{2\pi}} \cos(\theta) \sin(\theta)$$

Complex conjugation, required to yield real-valued charge densities, is easily achieved using a replacement rule:

```
exp_* := exp /. Complex(a_, b_) -> Complex(a, -b)
```

For example,

$$Y_2^1(\theta, \phi)^*$$

$$-\frac{1}{2} e^{-i\phi} \sqrt{\frac{15}{2\pi}} \cos(\theta) \sin(\theta)$$

Several *Mathematica* graphics packages are used in this work. Entering

```
<< Graphics`
```

causes these packages to be automatically loaded. We also set options for nice formatting of graphics labels,

```
$FormatType = TraditionalForm;
```

```
$TextStyle = {TraditionalForm, FontSize -> 10, FontFamily -> "Times"};
```

and for “pretty” plots:

```
SetOptions[DensityPlot, Mesh -> False, PlotPoints -> 200];
```

```
SetOptions[ParametricPlot3D, PlotPoints -> 40, PlotRange -> All, Axes -> True,
  AxesLabel -> {x, y, z}, Ticks -> None, Boxed -> True, BoxStyle -> Dashing[{0.001, 0.02}]];
```

```
SetOptions[ContourPlot3D, PlotPoints -> {4, 6}];
```

We make use of the **Notation** package to define custom input and output notations for the 3-*j*, 6-*j* and Clebsch-Gordan coefficients.

```
Utilities`Notation`AutoLoadNotationPalette = False;
```

```
<< Utilities`Notation`
```

```
SetOptions[Notation, WorkingForm -> TraditionalForm];
```

Symbolize[j']

Off[ClebschGordan::"tri"]

Off[ClebschGordan::"phy"]

Notation[$\left(\begin{array}{ccc} j1_ & j2_ & j3_ \\ m1_ & m2_ & m3_ \end{array} \right)_{3j} \Leftrightarrow \text{ThreeJSymbol}[\{j1_ , m1_ \}, \{j2_ , m2_ \}, \{j3_ , m3_ \}]$]

Notation[$\left\{ \begin{array}{ccc} j1_ & j2_ & j3_ \\ j4_ & j5_ & j6_ \end{array} \right\}_{6j} \Leftrightarrow \text{SixJSymbol}[\{j1_ , j2_ , j3_ \}, \{j4_ , j5_ , j6_ \}]$]

Notation[$\langle j1_ , j2_ , m1_ , m2_ | j_ , m_ \rangle \Leftrightarrow \text{ClebschGordan}[\{j1_ , m1_ \}, \{j2_ , m2_ \}, \{j_ , m_ \}]$]

Here is a palette for entering these special notations.

$\left(\begin{array}{ccc} \square & \square & \square \\ \square & \square & \square \end{array} \right)_{3j}$
$\left\{ \begin{array}{ccc} \square & \square & \square \\ \square & \square & \square \end{array} \right\}_{6j}$
$\left\langle \begin{array}{ccc} \square & \square & \square \\ \square & \square & \square \end{array} \right\rangle$
$\langle \square, \square, \square, \square \square, \square \rangle$

■ 2. ANGULAR DISTRIBUTION OF ATOMIC ORBITALS

■ 1. Pure states $\psi_{nlm}(r)$

For pure basis states, $\psi_{n,l,m}(r)$, the angular charge density distribution:

$$\Omega_{l,m}^{\text{ang}}(\theta) = |Y_l^m(\theta, \phi)|^2,$$

is axially symmetric with respect to the azimuthal angle ϕ . In this case, **PolarPlot** can provide a complete view of the atomic orbitals.

After defining the angular distribution function:

$$\Omega_{l,m}(\theta) := Y_l^m(\theta, \phi) Y_l^m(\theta, \phi)^*$$

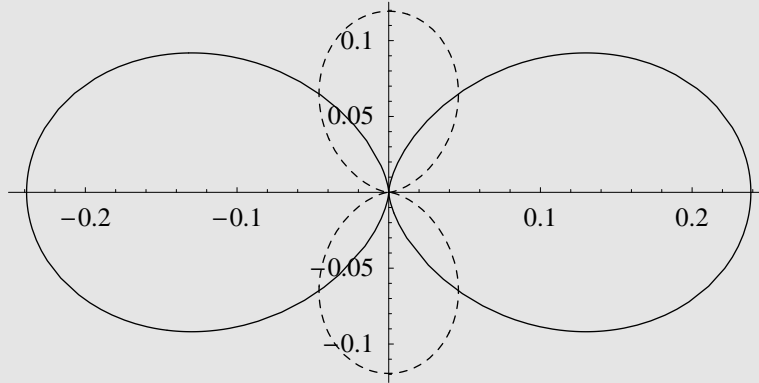
individual charge densities can be immediately examined, e.g.,

$$\Omega_{3,2}(\theta)$$

$$\frac{105 \cos^2(\theta) \sin^4(\theta)}{32 \pi}$$

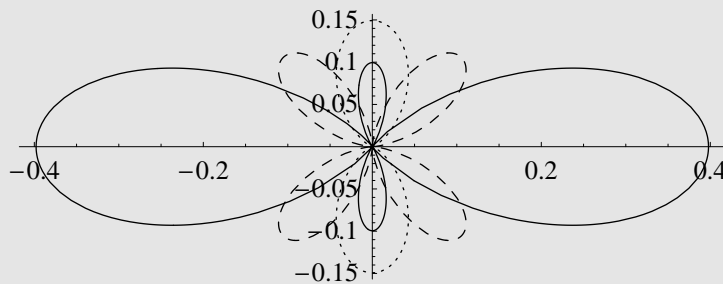
Here are plots of the atomic orbitals for the states $l = 1, m = 0, 1$:

DisplayTogether(PolarPlot($\Omega_{1,0}(\theta)$, $\{\theta, 0, 2\pi\}$), PolarPlot($\Omega_{1,1}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotStyle \rightarrow Dashing({0.01, 0.01})));

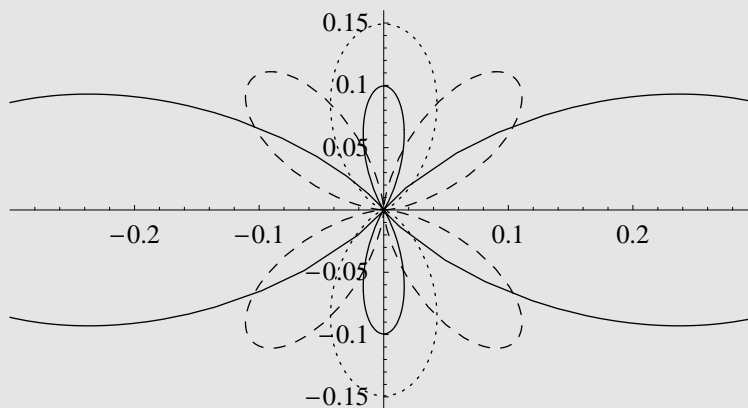


and $l = 2, m = 0, 1, 2$:

**DisplayTogether(PolarPlot($\Omega_{2,0}(\theta)$, $\{\theta, 0, 2\pi\}$), PolarPlot($\Omega_{2,1}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotStyle \rightarrow Dashing({0.015, 0.015})),
PolarPlot($\Omega_{2,2}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotStyle \rightarrow Dashing({0.003, 0.01})));**



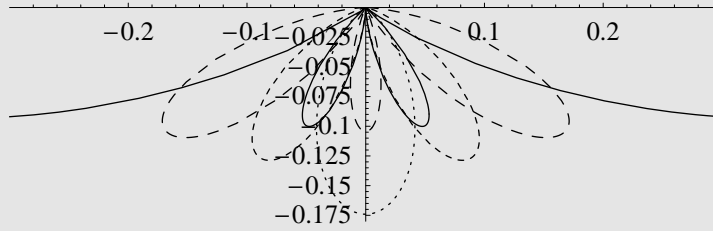
**DisplayTogether(PolarPlot($\Omega_{2,0}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotRange \rightarrow $\begin{pmatrix} -0.3 & 0.3 \\ -0.16 & 0.16 \end{pmatrix}$),
PolarPlot($\Omega_{2,1}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotStyle \rightarrow Dashing({0.015, 0.015})),
PolarPlot($\Omega_{2,2}(\theta)$, $\{\theta, 0, 2\pi\}$, PlotStyle \rightarrow Dashing({0.003, 0.01})));**



```

DisplayTogether(PolarPlot(Ω3,0(θ), {θ, 0, 2π}, PlotRange → {{-0.3, 0.3}, {-0.18, 0.18}}),
PolarPlot(Ω3,1(θ), {θ, 0, 2π}, PlotStyle → Dashing({0.015, 0.015})),
PolarPlot(Ω3,2(θ), {θ, 0, 2π}, PlotStyle → Dashing({0.008, 0.01})),
PolarPlot(Ω3,3(θ), {θ, 0, 2π}, PlotStyle → Dashing({0.003, 0.01})));

```



2. Mixed states $\sum_m c_m \psi_{nlm}(\mathbf{r})$

For coherently mixed states

$$\psi_{nl}(\mathbf{r}) = \sum_m c_m \psi_{nlm}(\mathbf{r}) = r R_{nl}(r) \sum_m c_m Y_l^m(\theta, \phi),$$

the angular probability distribution is

$$\Omega_l^{\text{ang}}(\theta, \phi) = \left| \sum_m c_m Y_l^m(\theta, \phi) \right|^2.$$

In this case, the charge cloud is no longer axially symmetric and its distribution is a function of both θ and ϕ . Three-dimensional plots are thus required to depict the structure of the coherently mixed atomic orbitals.

In general, the expression

$$\omega_l(\theta, \phi) = \sum_{m=-l,2}^l a_m e^{i b_m} Y_l^m(\theta, \phi),$$

where a_m (b_m) are the amplitude ratio (relative phase) of each state, can be evaluated in *Mathematica* using:

$$\omega_l[\mathbf{c}_-][\theta_-, \phi_-] := \omega_l[\mathbf{c}][\theta, \phi] = \sum_{i=0}^l c_{[i+1,1]} e^{i c_{[i+1,2]}} Y_l^{l-2i}(\theta, \phi)$$

The argument to c needs to be a list of $\{a_m, b_m\}$ pairs. The general angular charge distribution then reads:

$$\Omega_l[\mathbf{c}_-][\theta_-, \phi_-] := \text{Factor}[\text{ComplexExpand}[\text{Expand}[\omega_l(c)(\theta, \phi) \omega_l(c)(\theta, \phi)^*]]]$$

where the core of this expression is the product of $\omega_l(c)(\theta, \phi)$ with its complex conjugate, $\omega_l(c)(\theta, \phi)^*$. The other operations, **Expand**, **ComplexExpand**, and **Factor**, are used to simplify the expression to a human readable form.

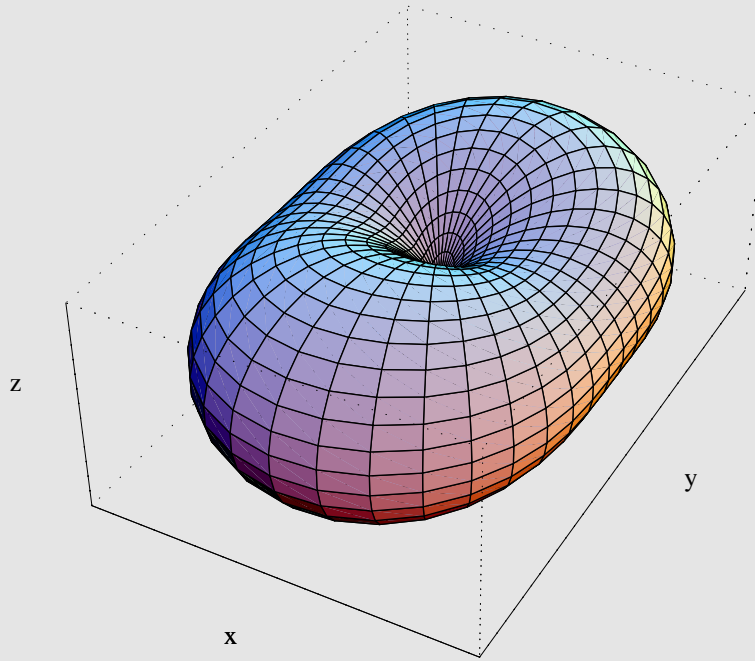
As an example, for the general P -state wavefunction can be obtained from the mixed state consisting of $l = 1$, $m = \pm 1$:

$$\psi_P(\mathbf{a}_-, \mathbf{b}_-) = \Omega_1\left[\begin{pmatrix} 1 & 0 \\ a & b \end{pmatrix}\right][\theta, \phi]$$

$$\frac{3(a^2 - 2\cos(b - 2\phi)a + 1)\sin^2(\theta)}{8\pi}$$

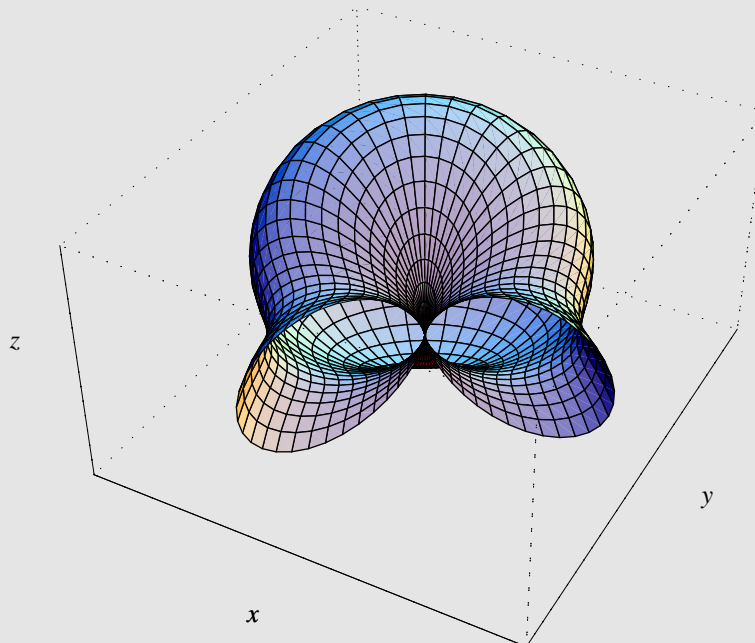
and then plot the orbitals for the states with parameters $\{a = 0.1, b = 0\}$:

`SphericalPlot3D(Evaluate[ψ_P [0.1, 0]], { θ , 0, π }, { ϕ , 0, 2π });`



and $\{a = 0.2, b = \pi/3\}$:

`SphericalPlot3D(Evaluate[ψ_P [0.2, $\frac{\pi}{3}$]], { θ , 0, π }, { ϕ , 0, 1.35π });`



Note that the full range of ϕ was not shown to highlight the structure of the orbital.

For a more complicated atomic orbitals, such as a coherently excited F -state atom, the charge density reads

$$\psi_F[\theta_-, \phi_-] := \Omega_3 \left[\begin{pmatrix} a_3 & b_3 \\ a_1 & 0 \\ a_{-1} & b_{-1} \\ a_{-3} & b_{-3} \end{pmatrix} \right][\theta, \phi]; \psi_F[\theta, \phi]$$

$$\begin{aligned} & \frac{1}{64\pi} \left(7 \sin^2(\theta) (75 a_{-1}^2 \cos^4(\theta) + 75 a_1^2 \cos^4(\theta) - 150 \cos(2\phi - b_{-1}) a_{-1} a_1 \cos^4(\theta) - \right. \\ & 30 a_{-1}^2 \cos^2(\theta) - 30 a_1^2 \cos^2(\theta) + 10 \sqrt{15} \cos(2\phi - b_{-3} + b_{-1}) \sin^2(\theta) a_{-3} a_{-1} \cos^2(\theta) - \\ & 10 \sqrt{15} \cos(4\phi - b_{-3}) \sin^2(\theta) a_{-3} a_1 \cos^2(\theta) + 60 \cos(2\phi - b_{-1}) a_{-1} a_1 \cos^2(\theta) - \\ & 10 \sqrt{15} \cos(4\phi - b_{-1} + b_3) \sin^2(\theta) a_{-1} a_3 \cos^2(\theta) + 10 \sqrt{15} \cos(2\phi + b_3) \sin^2(\theta) a_1 a_3 \cos^2(\theta) + \\ & 5 \sin^4(\theta) a_{-3}^2 + 3 a_{-1}^2 + 3 a_1^2 + 5 \sin^4(\theta) a_3^2 - 2 \sqrt{15} \cos(2\phi - b_{-3} + b_{-1}) \sin^2(\theta) a_{-3} a_{-1} + \\ & 2 \sqrt{15} \cos(4\phi - b_{-3}) \sin^2(\theta) a_{-3} a_1 - 6 \cos(2\phi - b_{-1}) a_{-1} a_1 - 10 \cos(6\phi - b_{-3} + b_3) \sin^4(\theta) a_{-3} a_3 + \\ & \left. 2 \sqrt{15} \cos(4\phi - b_{-1} + b_3) \sin^2(\theta) a_{-1} a_3 - 2 \sqrt{15} \cos(2\phi + b_3) \sin^2(\theta) a_1 a_3 \right) \end{aligned}$$

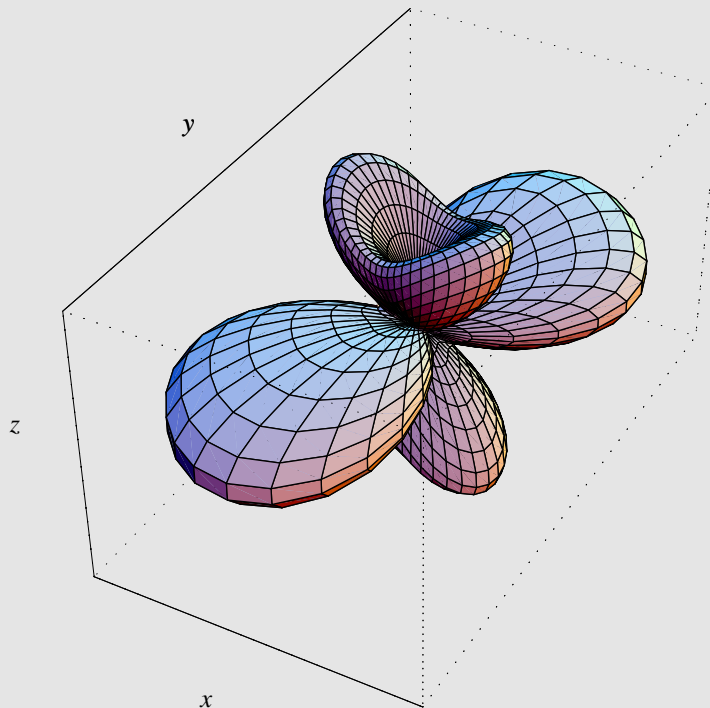
Choosing the parameters arbitrarily as

$$a /: a_1 = 1.0; a /: a_{-1} = 0.0; a /: a_3 = 0.8; a /: a_{-3} = 0.05;$$

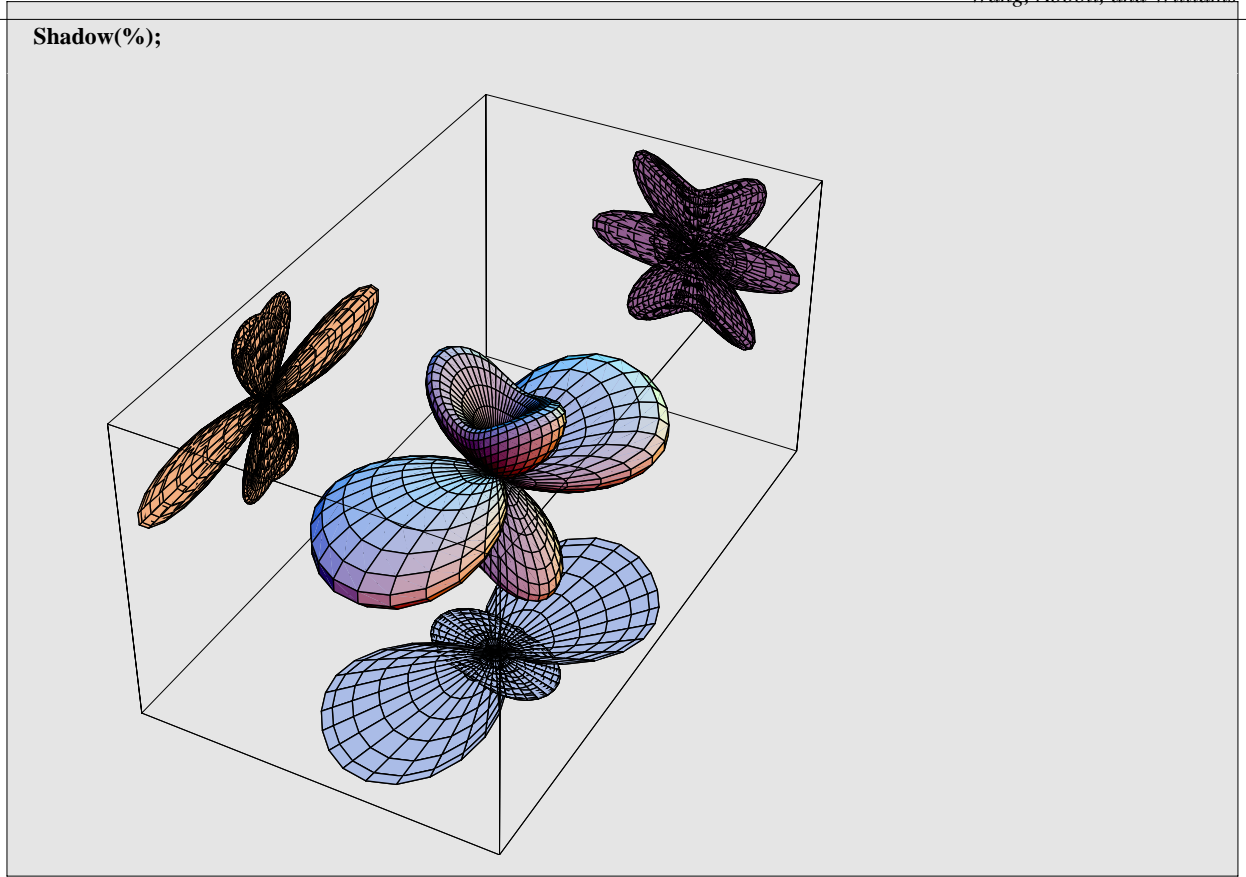
$$b /: b_{-1} = \pi; b /: b_3 = \frac{\pi}{5}; b /: b_{-3} = \frac{\pi}{4};$$

one can produce a three-dimensional graph:

SphericalPlot3D(Evaluate[$\psi_F[\theta, \phi]$], { θ , 0, π }, { ϕ , 0, 2π }, PlotPoints \rightarrow 50, PlotRange \rightarrow All);



We can use the **Shadow** command to display the projections along the x , y , and z directions:



3. Time evolution of atomic orbitals

Due to the interaction between the intrinsic magnetic dipole moment of the electron (spin) and the internal magnetic field of the atom (orbital angular momentum), the atomic charge density evolves with time. Animation provides views of such dynamic effects. Taking the spin-orbit (L - S) coupling into account, we obtained the time-dependent charge density function for a mixed state:

$$\psi_{nl}(\mathbf{r}) = \sum_m c_m \psi_{nlm}(\mathbf{r}),$$

$$\Omega_{nl}^{\text{ang}}(\theta, \phi, t) = \sum_{KQmm'} (-1)^{l-m'} \sqrt{2K+1} \begin{pmatrix} l & l & K \\ m & -m & -Q \end{pmatrix} Y_l^{m'}(\theta, \phi) (Y_l^m(\theta, \phi))^* \langle T(l)_{KQ}^\dagger \rangle G_K(ls; t),$$

where

$$\langle T(l)_{KQ}^\dagger \rangle = \sum_{mm'} (-1)^{l-m'} \sqrt{2K+1} \begin{pmatrix} l & l & K \\ m' & -m & -Q \end{pmatrix} c_{m'} c_m^*$$

implemented in *Mathematica* as

$$\mathcal{T}_{K,Q}[l] := \mathcal{T}_{K,Q}(l) = \sum_{m=-l}^l (-1)^{l-(m+Q)} \sqrt{2K+1} \begin{pmatrix} l & l & K \\ m+Q & -m & -Q \end{pmatrix}_{3j} c_{m+Q} c_m^*$$

are the so-called state multipoles and the corresponding time evolution factor is

$$G_K(ls; t) = \frac{1}{2s+1} \sum_{jj'} (2j'+1)(2j+1) \left\{ \begin{matrix} l & j' & s \\ j & l & K \end{matrix} \right\}^2 \cos\left((\mathcal{E}_{j'} - \mathcal{E}_j) \frac{t}{\hbar}\right).$$

implemented in *Mathematica* as

$$G_{K_}[l_ , s_ , t_] := G_K[l, s, t] = \frac{1}{2s+1} \sum_{j'=-|l-s|}^{l+s} \sum_{j=-|l-s|}^{l+s} (2j'+1)(2j+1) \left\{ \begin{matrix} l & j' & s \\ j & l & K \end{matrix} \right\}_{6j}^2 \cos((j'-j)t)$$

As an example, consider a general mixed P -state of a hydrogen atom:

$$l = 1; s = \frac{1}{2}; c /: c_1 = a + b i; c /: c_{-1} = d + e i; c /: c_0 = f + g i;$$

The time-dependent charge density function becomes

$$\begin{aligned} & \text{Collect[ComplexExpand[} \\ & \sum_{K=0}^{2l} \sum_{Q=-K}^K \sum_{m=-l}^l \mathcal{T}_{K,Q}[l] G_K[l, s, t] (-1)^{l-(m+Q)} \sqrt{2K+1} \left(\begin{matrix} l & l & K \\ m+Q & -m & -Q \end{matrix} \right)_{3j} Y_l^{m+Q}(\theta, \phi) Y_l^m(\theta, \phi)^*, \\ & \{\cos(\theta), \sin(\theta), \cos(2\phi), \sin(2\phi)\}, \text{Simplify}] \\ & \frac{(2a^2 + 2b^2 + 2d^2 + 2e^2 + 5f^2 + 5g^2 - 2(a^2 + b^2 + d^2 + e^2 - 2f^2 - 2g^2)\cos(t))\cos^2(\theta)}{12\pi} - \\ & \frac{(2\cos(t) + 1)\sin(\theta)((af - df + (b-e)g)\cos(\phi) + (-bf - ef + (a+d)g)\sin(\phi))\cos(\theta)}{2\sqrt{2}\pi} + \\ & \sin^2(\theta) \left(\frac{7a^2 + 7b^2 + 7d^2 + 7e^2 + 4f^2 + 4g^2 + 2(a^2 + b^2 + d^2 + e^2 - 2f^2 - 2g^2)\cos(t)}{24\pi} - \right. \\ & \left. \frac{(ad + be)(2\cos(t) + 1)\cos(2\phi)}{4\pi} + \frac{(bd - ae)(2\cos(t) + 1)\sin(2\phi)}{4\pi} \right) \end{aligned}$$

In a particular case, say $C_0 = 0$, $C_1 = 0.9$, $C_{-1} = 0.12 + 0.1i$, the charge density function is

$$\text{cdf}[t_] = \text{Chop}[\% /. \{a \rightarrow 0.9, b \rightarrow 0, d \rightarrow 0.12, e \rightarrow 0.1, f \rightarrow 0, g \rightarrow 0\}];$$

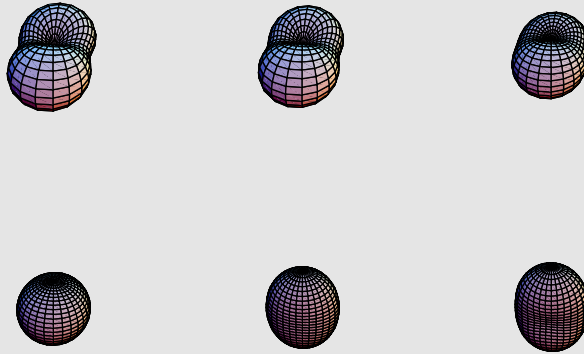
This can be plotted using the commands,

$$\begin{aligned} & \text{CDFPlot}(t_) := \text{SphericalPlot3D} \left(\text{Evaluate}[\text{cdf}(t)], \{\theta, 0, \pi\}, \{\phi, 0, 2\pi\}, \right. \\ & \left. \text{PlotPoints} \rightarrow 30, \text{PlotRange} \rightarrow \left(\begin{matrix} -0.14 & 0.14 \\ -0.14 & 0.14 \\ -0.12 & 0.12 \end{matrix} \right), \text{Boxed} \rightarrow \text{False}, \text{Axes} \rightarrow \text{False} \right); \end{aligned}$$

$$\text{Table}[\text{CDFPlot}\left(\frac{t\pi}{5}\right), \{t, 0, 5, 1\}];$$

This command displays a sequence of graphics objects in succession and thus simulates the time evolution of the orbitals. Alternatively, here is an array of animation frames:

```
Show[GraphicsArray[Partition[%, 3]], DisplayFunction -> $DisplayFunction];
```



We clear the values assigned in this section.

```
Clear[l, s, c];
```

■ 3. RADIAL AND ANGULAR DISTRIBUTIONS

■ 1. Radial function

For the hydrogen atom the radial wavefunction in atomic units is

$$R_{n,l}(r) = -\sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho),$$

where

$$\rho = \frac{2Zr}{n};$$

and $L_n^\alpha(x)$ denote the associated Laguerre Polynomials as defined by Abramowitz and Stegun. Although the definition of the associated Laguerre Polynomials differs from that used in many quantum mechanics texts, it has several advantages: it is the standard used by most mathematicians and several books of tables; the number of nodes of the radial wavefunction equals the order of the associated Laguerre Polynomial, i.e., $n-l-1$; and it is the definition used in *Mathematica*.

The radial wavefunction is easily defined:

$$N_{n,l,Z,1} = -\sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(l+n)!}};$$

$$R_{n,l,Z,1}(\mathbf{r}_-) = N_{n,l,Z} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho);$$

The syntax, $\mathbf{Z}_-; 1$, indicates that if the argument \mathbf{Z} is not supplied it will default to the value 1.

The radial distribution function,

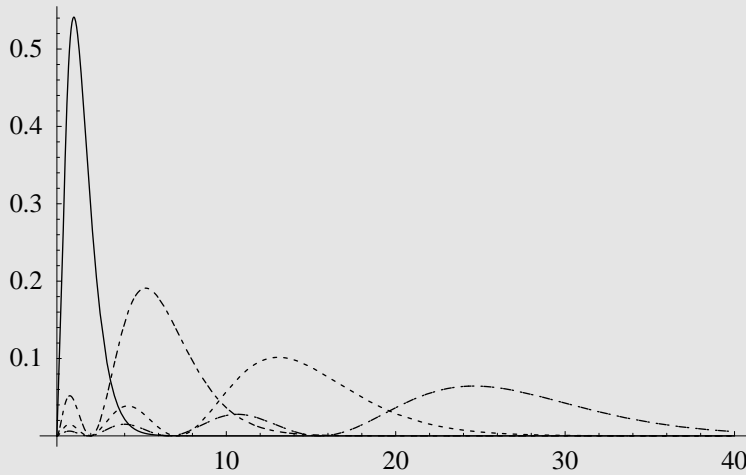
$$\mathcal{R}_{n,l}(r) = r^2 |R_{n,l}(r)|^2,$$

then becomes

$$\mathcal{R}_{n,l}(r) := r^2 R_{n,l}(r)^2$$

Here is a plot of three states with $n = 2, 3, 4, l = 1$:

```
DisplayTogether(Plot(Evaluate( $\mathcal{R}_{1,0}(r)$ ), {r, 0, 40}, PlotRange → All),
  Plot(Evaluate( $\mathcal{R}_{2,0}(r)$ ), {r, 0, 40}, PlotStyle → Dashing({0.008, 0.005, 0.01})),
  Plot(Evaluate( $\mathcal{R}_{3,0}(r)$ ), {r, 0, 40}, PlotStyle → Dashing({0.005, 0.01})),
  Plot(Evaluate( $\mathcal{R}_{4,0}(r)$ ), {r, 0, 40}, PlotStyle → Dashing({0.002, 0.01, 0.002})));
```



2. Density plots for pure basis states

We have so far plotted separately the angular and the radial distribution functions of various atomic orbitals. However, these pictures are incomplete on their own and one needs to imaginatively assemble the angular and the radial plots in order to obtain a complete picture of the charge distribution in three-dimensional space.

For the pure basis state the probability distribution $\Psi_{nlm}(r)$ is, as discussed earlier, axially symmetric, *i.e.*,

$$\Omega_{nlm}(r, \theta) = |r R_{nl}(r) Y_l^m(\theta, \phi)|^2.$$

Mathematica's **DensityPlot** is then adequate for showing the detailed distribution of the two-variable function, where the lighter region indicates higher charge density:

$$\mathcal{P}_{n,l,m}(r, \theta) := \mathcal{R}_{n,l}(r) \Omega_{l,m}(\theta)$$

Defining a set of rules to transform from spherical polar to Cartesian coordinates:

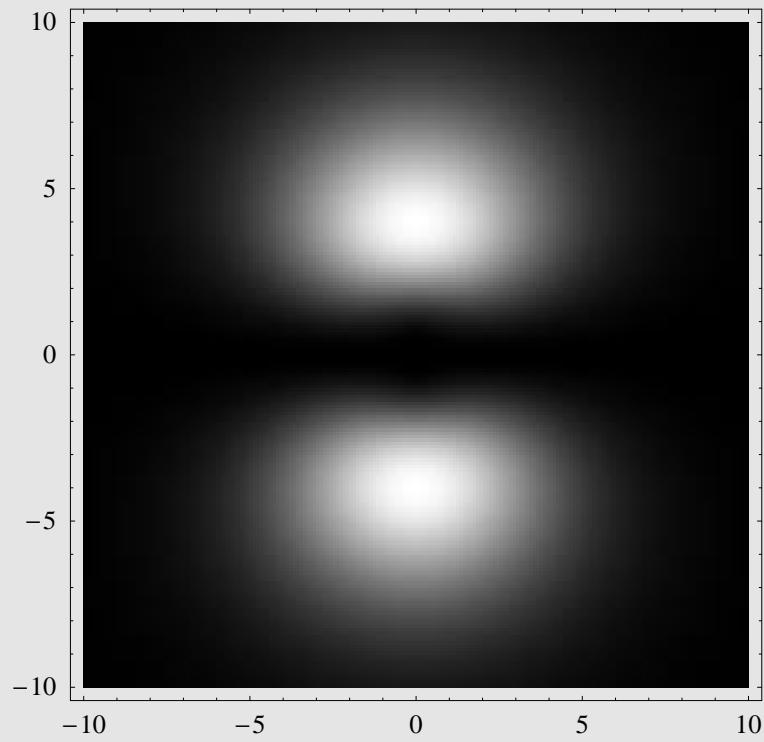
$$\text{PolarToCartesian} = \{r \rightarrow \sqrt{x^2 + y^2 + z^2}, \theta \rightarrow \cos^{-1}\left(\frac{z}{r}\right), \phi \rightarrow \tan^{-1}\left(\frac{y}{x}\right)\};$$

the distribution in Cartesian coordinates is easily obtained:

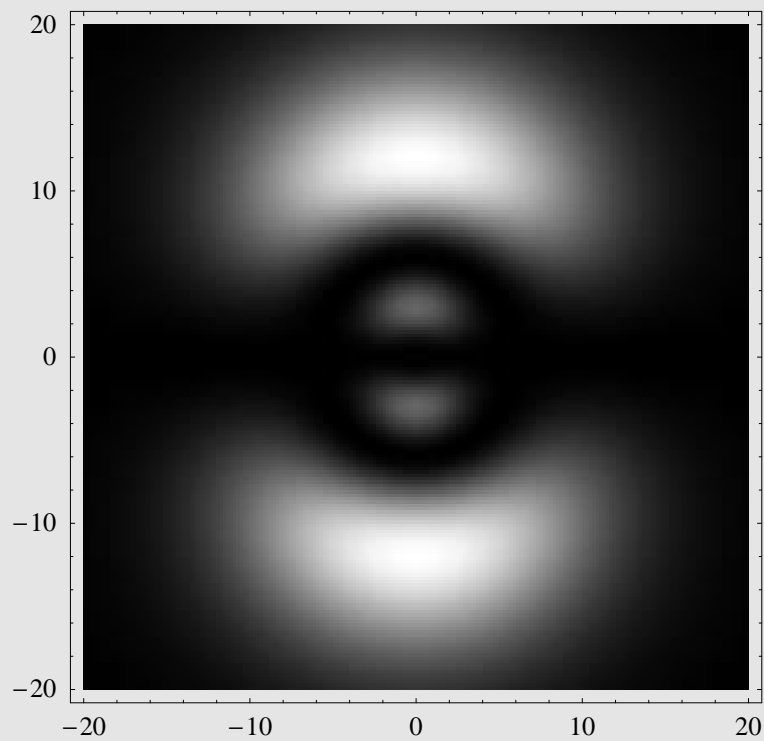
$$C_{n,l,m}(x, y, z) = \mathcal{P}_{n,l,m}(r, \theta) // \text{PolarToCartesian};$$

Here are plots of the charge density in the x - z plane for $n = 2, 3, 4, l = 1, m = 0$:

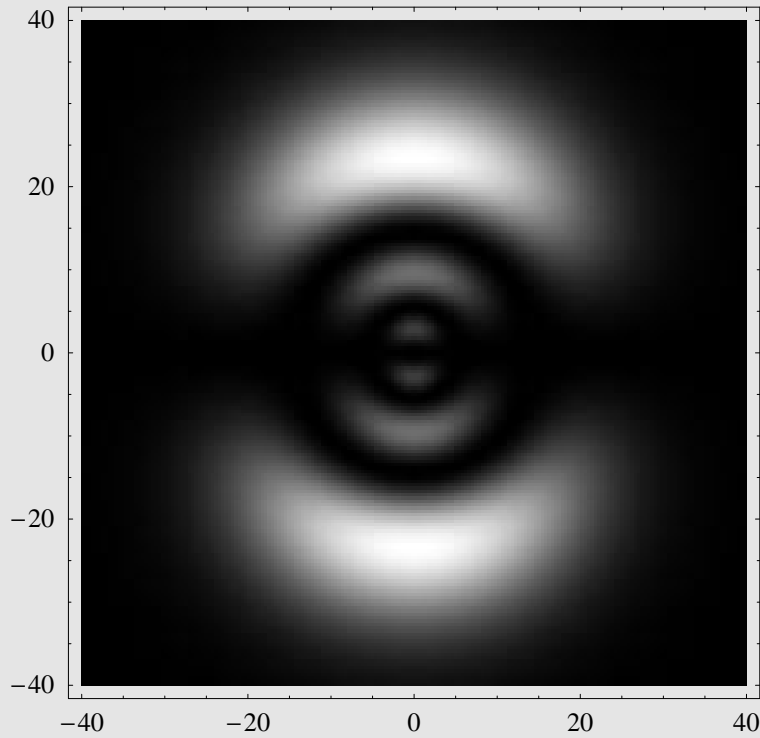
DensityPlot(Evaluate($C_{2,1,0}(x, 0, z)$), {x, -10, 10}, {z, -10, 10});



DensityPlot(Evaluate($C_{3,1,0}(x, 0, z)$), {x, -20, 20}, {z, -20, 20});



DensityPlot(Evaluate(C_{4,1,0}(x, 0, z)), {x, -40, 40}, {z, -40, 40});



3. Three dimensional contour plots for mixed states

Finally, for a general coherent mixture of several magnetic states

$$\psi_{nl}(\mathbf{r}) = \sum_m c_m \psi_{nlm}(\mathbf{r}) = r R_{nl}(r) \sum_m c_m Y_l^m(\theta, \phi),$$

the total charge density distribution is a function of three variables (r, θ, ϕ) :

$$\mathcal{P}_{n,l}[c][r, \theta, \phi] := R_{n,l}(r) \Omega_l[c][\theta, \phi]$$

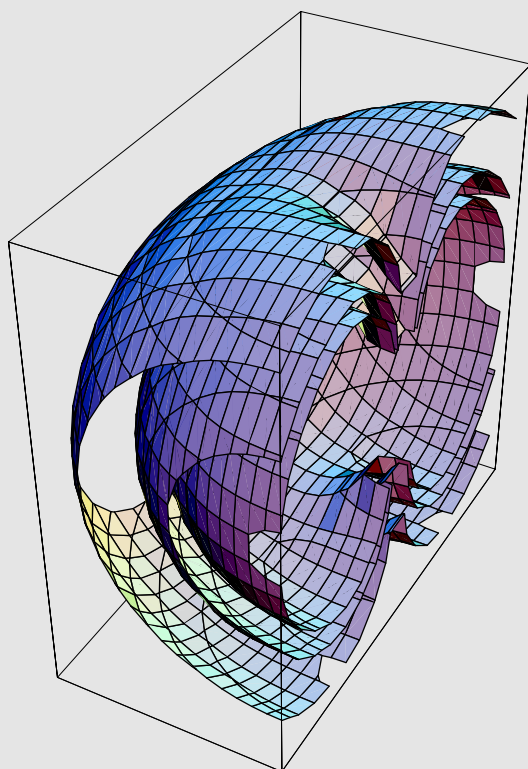
Arbitrarily choosing $C_1 = 1$, $C_0 = 0$, $C_{-1} = \frac{2}{10}$, three dimensional contour surfaces of the total charge distribution in Cartesian coordinates,

$$\text{Simplify}\left[\mathcal{P}_{2,1}\left(\left(\begin{array}{cc} 1 & 0 \\ \frac{2}{10} & 0 \end{array}\right)\right)(r, \theta, \phi) // \text{PolarToCartesian} // \text{TrigExpand}\right]$$

$$\frac{e^{-\sqrt{x^2+y^2+z^2}} (4x^2 + 9y^2)(x^2 + y^2 + z^2)}{400\pi}$$

can be plotted using **ContourPlot3D**. Here are the surfaces for the contour levels 0.0003, 0.0015, and 0.003.

```
ContourPlot3D(%, {x, -10, 0}, {y, -10, 10}, {z, -10, 10}, Contours -> {0.0003, 0.0015, 0.003});
```



■ 4. MOLECULAR ORBITALS

As an example of multi-dimensional systems other than atomic orbitals, we consider the hydrogen molecule-ion, which consists of two nuclei and one electron. Its wavefunction can be represented by a linear combination of two atomic hydrogen wavefunctions:

$$\psi = \sum_i c_i \phi_i = \begin{cases} \frac{1}{\sqrt{2(1+s)}} (\phi_1(x - r_0, y, z) + \phi_2(x + r_0, y, z)) & \text{bonding orbitals,} \\ \frac{1}{\sqrt{2(1-s)}} (\phi_1(x - r_0, y, z) - \phi_2(x + r_0, y, z)) & \text{antibonding orbitals,} \end{cases}$$

where $2r_0$ is the internuclear distance and S is a function of r_0 . In *Mathematica* syntax, we have for the atomic wavefunction,

$$\phi_{n,l,m}(x, y, z) = r R_{n,l}(r) Y_l^m(\theta, \phi) // \text{PolarToCartesian};$$

and for the molecular charge density of the bonding,

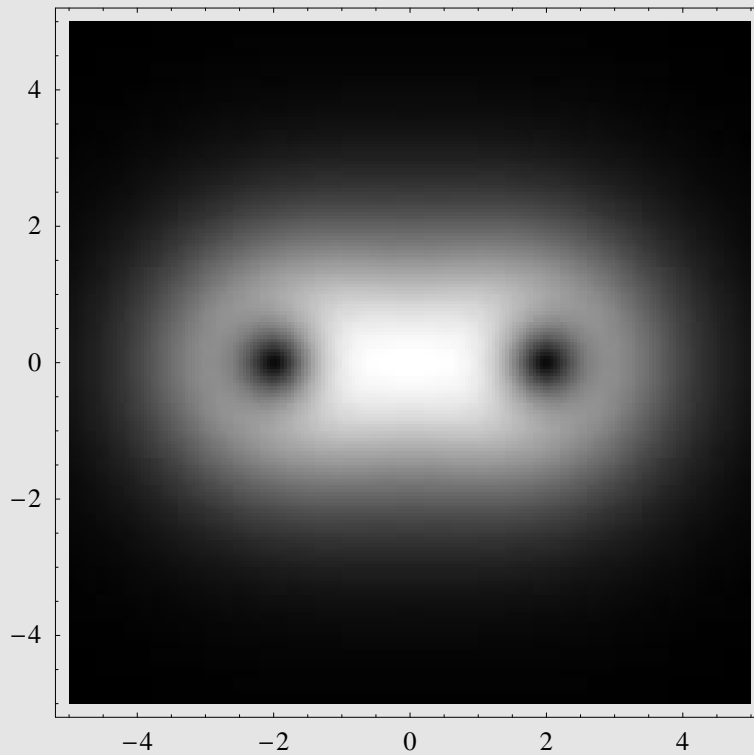
$$\psi_B \left[\begin{pmatrix} n1 & l1 & m1 \\ n2 & l2 & m2 \end{pmatrix} \right] [x, y, z] = (\phi_{n1,l1,m1}(x - 2, y, z) + \phi_{n2,l2,m2}(x + 2, y, z))^2;$$

and antibonding orbitals,

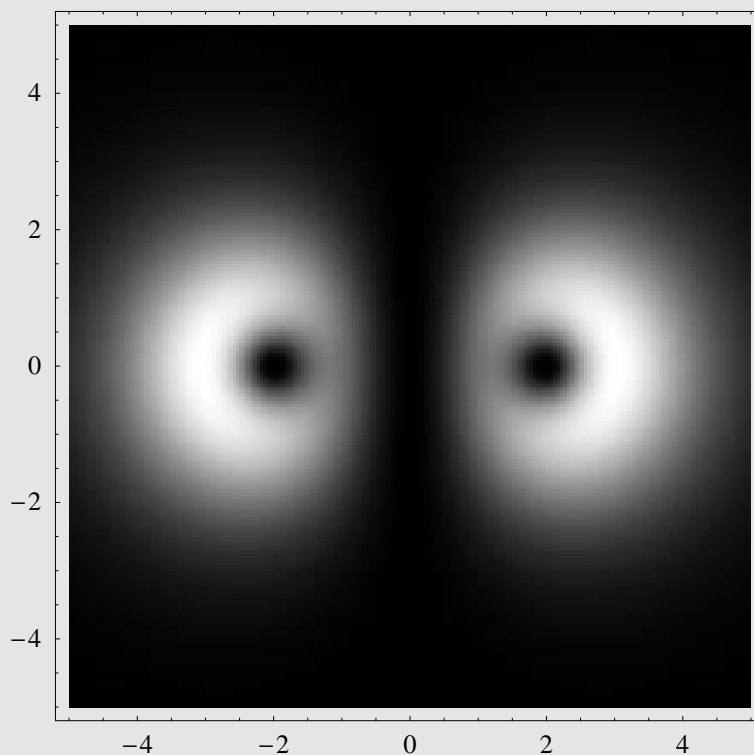
$$\psi_A \left[\begin{pmatrix} n1 & l1 & m1 \\ n2 & l2 & m2 \end{pmatrix} \right] [x, y, z] = (\phi_{n1,l1,m1}(x - 2, y, z) - \phi_{n2,l2,m2}(x + 2, y, z))^2;$$

If the hydrogen molecular-ion is in the state $n_1 = 1, l_1 = 0, m_1 = 0, n_2 = 1, l_2 = 0, m_2 = 0$, both bonding and antibonding orbitals have cylindrical symmetry along the internuclear x - z plane. The **DensityPlot** command is used to depict the projection of the charge distribution in this plane.

```
DensityPlot[Evaluate[ $\psi_B$ ][ $\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ ][x, 0, z], {x, -5, 5}, {z, -5, 5}];
```

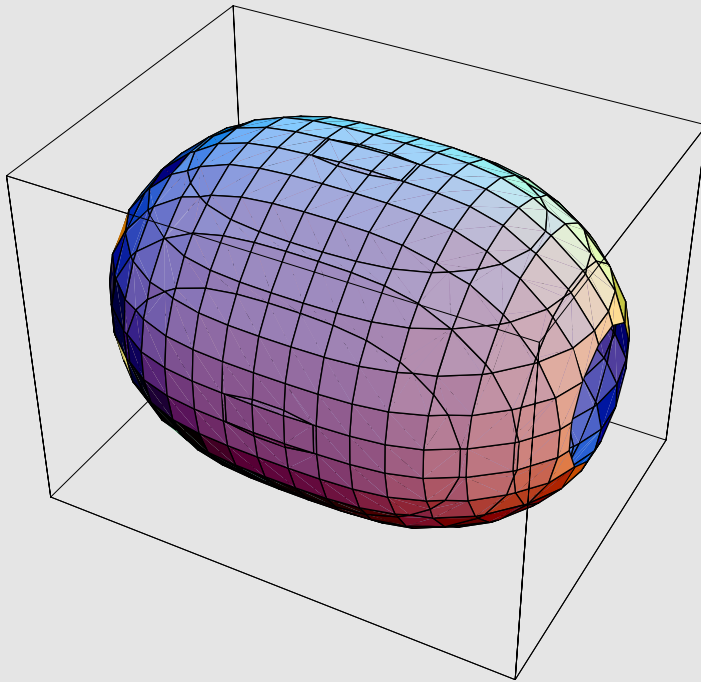


```
DensityPlot[Evaluate[ $\psi_A$ ][ $\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ ][x, 0, z], {x, -5, 5}, {z, -5, 5}];
```

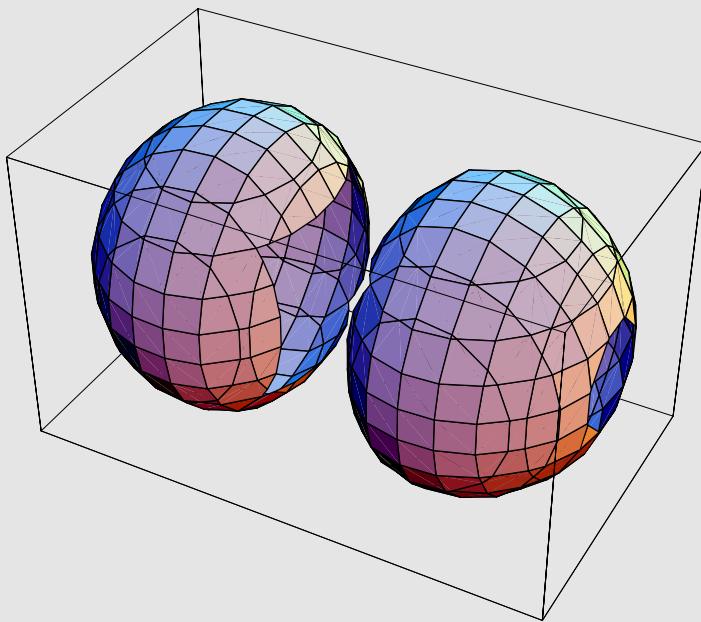


To see these orbitals in three dimensions, we also plot their contour surface at an arbitrary level of 0.005:

```
ContourPlot3D[Evaluate[ $\psi_B\left[\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}\right][x, y, z]$ ], {x, -5, 5}, {y, -5, 5}, {z, -5, 5}, Contours -> {0.005}];
```



```
ContourPlot3D[Evaluate[ $\psi_A\left[\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}\right][x, y, z]$ ], {x, -5, 5}, {y, -5, 5}, {z, -5, 5}, Contours -> {0.005}];
```



■ 5. EXAMPLES OF SYMBOLIC ANALYSIS

■ 1. Clebsch-Gordan coefficients

Clebsch-Gordan, 3- j , 6- j and 9- j coefficients (CGC) arise when coupling together angular momentum states or, equivalently, when linearizing products of or computing integrals over spherical harmonics. It is important to note that *Mathematica* can compute both numerical and symbolic CGC.

The notation

$$\langle l_1 l_2 m_1 m_2 | l m \rangle \equiv C_{m_1 m_2 m}^{l_1 l_2 l} = (-1)^{m+l_1-l_2} \sqrt{2l+1} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix},$$

is used in the following examples of the utility of symbolic CGC. The CGC required for spin-orbit coupling can be evaluated immediately, *e.g.*,

$$\left\langle j_1, \frac{1}{2}, m - \frac{1}{2}, \frac{1}{2} \left| j_1 - \frac{1}{2}, m \right. \right\rangle // \text{Simplify}$$

$$-\frac{\sqrt{-2m+2j_1+1}}{\sqrt{4j_1+2}}$$

2. Products and integrals of spherical harmonics

Products of spherical harmonics arise when computing the electron density of atomic states. Using the CGC, it is straightforward to linearize these products via

$$Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) = \sum_{l_3=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l_3}^{l_3} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} Y_{l_3}^{m_3}(\theta, \phi)^*.$$

This result can be used to evaluate the general integral of a triple product of spherical harmonics,

$$\int_0^{2\pi} \int_0^\pi Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) Y_{l_3}^{m_3}(\theta, \phi) \sin(\theta) d\theta d\phi =$$

$$\sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

In *Mathematica* this formula can be entered as follows:

$$\text{TripleProduct}[\{l1_ , m1_ \}, \{l2_ , m2_ \}, \{l3_ , m3_ \}] :=$$

$$\sqrt{\frac{(2l1+1)(2l2+1)(2l3+1)}{4\pi}} \begin{pmatrix} l1 & l2 & l3 \\ 0 & 0 & 0 \end{pmatrix}_{3j} \begin{pmatrix} l1 & l2 & l3 \\ m1 & m2 & m3 \end{pmatrix}_{3j}$$

$$\text{Notation}\left[\begin{pmatrix} j1_ & j2_ & j3_ \\ m1_ & m2_ & m3_ \end{pmatrix}\right] \Leftrightarrow \text{TripleProduct}[\{j1_ , m1_ \}, \{j2_ , m2_ \}, \{j3_ , m3_ \}]$$

This expression is used in the following example of the linear Stark effect.

3. Stark effect

The linear Stark effect requires the computation of the matrix elements $\langle n l m | r \cos(\theta) | n l \pm 1 m \rangle$. Noting that $\cos(\theta)$ is equivalent to $2\sqrt{\frac{\pi}{3}} Y_1^0(\theta, \phi)$,

$$2\sqrt{\frac{\pi}{3}} Y_1^0(\theta, \phi) == \cos(\theta)$$

True

$$Y_l^m(\theta, \phi)^* = Y_l^m(\theta, -\phi) = (-1)^m Y_l^{-m}(\theta, \phi),$$

the required non-vanishing angular integrals, *i.e.*, $\langle l m | \cos(\theta) | l \pm 1 m \rangle$, are easily evaluated.

$$\text{Simplify}\left[2\sqrt{\frac{\pi}{3}}(-1)^m \begin{Bmatrix} l & 1 & l+1 \\ -m & 0 & m \end{Bmatrix}, \{l, m\} \in \mathbb{Z}\right]$$

$$\frac{\sqrt{l-m+1}\sqrt{l+m+1}}{\sqrt{4l^2+8l+3}}$$

$$\text{Simplify}\left[2\sqrt{\frac{\pi}{3}}(-1)^m \begin{Bmatrix} l & 1 & l-1 \\ -m & 0 & m \end{Bmatrix}, \{l, m\} \in \mathbb{Z}\right]$$

$$\frac{\sqrt{l-m}\sqrt{l+m}}{\sqrt{4l^2-1}}$$

■ 6. CONCLUDING REMARKS

This article has demonstrated the capabilities of *Mathematica* for analyzing and visualizing atomic systems. The interplay between symbolic and graphical methods yields a tool that is more powerful than the sum of its parts and one that can be superior to special purpose visualization tools because of its flexibility.

Even for readers that have never used a computer algebra system, an examination of some of the code fragments presented above — say those implementing the radial wavefunctions for hydrogenic atoms or the triple integral of spherical harmonics — illustrates that implementing some quite complicated formulae in *Mathematica* is straightforward and transparent and, hence, less likely to contain or conceal an error. One of the goals of object oriented programming is to implement high-level structures. All of the computations in this article could, of course, be done in fortran or C (or C++). However, in general, the physicist or chemist does not want to write packages for computing orthogonal polynomials, spherical harmonics, Clebsch-Gordan coefficients or basic graphical tools. Of course, there exists libraries of public domain and commercial software which, when linked together, can provide equivalent capabilities. But, since all these capabilities, along with general symbolic manipulation, are built-in to *Mathematica* it can be seen to be an ideal tool for a wide range of analysis of atomic and molecular systems.

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