

Chapter 1. Atomic and molecular orbitals

1.1 Atomic orbitals

An [atomic orbital](#) is a function which describes the wave nature of the different electrons (or electron pairs) in an atom. They offer a way for evaluate the probability of finding an electron (interpreted as a charged particle) in any specific spatial region around the atom's nucleus.

There are four different kinds of orbitals appearing in the chemical elements of the Periodic Table, denoted by the letters *s*, *p*, *d* and *f*, each one with a different shape. Of the four types, *s* and *p* orbitals are the most common in organic and biological chemistry. An *s*-orbital is spherical with the nucleus at the center, a *p*-orbital is dumbbell-shaped, four of the five *d*-orbitals are cloverleaf shaped. The fifth *d*-orbital is shaped like an elongated dumbbell with a doughnut around its middle. *f*-orbitals have more complex shapes. Orbitals are organized into different layers or electron shells.

A useful aid to describe the three-dimensional (3D) probability density distributions of the various orbitals in the hydrogen atom is the Born interpretation of wave functions (M. Born, 1882-1970). Accordingly, the probability densities of the hydrogen atom orbitals can be represented and plotted as spatial surfaces which encompass most of the electron probability.

The wave function itself has no physical significance. However, the square of the wave function, is a quantity that is related to probabilities. Probability density distributions based on are three-dimensional, and it is these three-dimensional regions that we mean when we refer to the shape of an orbital.

Each point *P* possess a value of the wave-function, but its coordinates can be expressed in spherical or cartesian (orthogonal) coordinates

In the case of the wave function $\psi(\mathbf{P})$, spherical coordinates are preferable since they allow $\psi(\mathbf{P})$ to be factorized into the product :

$$\psi(\mathbf{P}) = \psi(r, \varphi, \theta) = R(r)Y(\varphi, \theta)$$

of the radial function $R(r)$ and of the angular function $Y(\theta, \varphi)$.

Angular wave function (table 1.1) are better suited to describe the 'shape' of the orbital, in a general sense, without a specific scale factor, whilst on the contrary radial part is able to fix the 'scale factor' of the same orbital. In this way one can plot the two different quantities and focus on each of the two concepts.

n	l	m		Polar coordinates	n	l	m		Polar coordinates
1	0	0	s	1	9	2	-2	d(xy)	$3 \sin^2 \theta \sin 2 \phi$
2	1	0	p(z)	$\cos \theta$	10	3	0	f(z ³)	$\frac{(5 \cos^2 \theta - 3) \cos \theta}{2}$
3	1	1	p(x)	$\sin \theta \cos \phi$	11	3	1	f(xz ²)	$\frac{3(5 \cos^2 \theta - 1) \sin \theta \cos \phi}{2}$
4	1	-1	p(y)	$\sin \theta \sin \phi$	12	3	-1	f(yz ²)	$\frac{3(5 \cos^2 \theta - 1) \sin \theta \sin \phi}{2}$
5	2	0	d(z ²)	$\frac{3 \cos^2 \theta - 1}{2}$	13	3	2	f(zx ² - zy ²)	$15 \sin^2 \theta \cos \theta \cos 2 \phi$
6	2	1	d(xy)	$3 \sin \theta \cos(\theta) \cos \phi$	14	3	-2	f(xyz)	$15 \sin^2 \theta \cos \theta \sin 2 \phi$
7	2	-1	d(yz)	$3 \sin \theta \cos(\theta) \sin \phi$	15	3	3	f(x ³ - 3xy ²)	$15 \sin^3 \theta \cos 3 \phi$
8	2	2	d(x ² -y ²)	$3 \sin^2 \theta \cos 2 \phi$	16	3	-3	f(3yx ² -y ³)	$15 \sin^3 \theta \sin 3 \phi$

Table 1.1 - angular wave functions $Y_{l,m}(\varphi, \theta)$ of hydrogen-like atoms

The first step for the graphics is to define a *meshgrid* of points, a job which is done by these following three lines of code. The first two lines create two row vectors (*theta*, *psi*) by mean of the function [linspace](#) . 60 elements are stuffed in *theta* , equally spaced starting from $-\pi$ (or *pi* in Octave) up to π ; 20 are stored in *phi* , from 0 to 2π .

```
theta = linspace(-pi,pi,60);
phi = linspace(0,2*pi,20);
[th1,ph1] = meshgrid(theta,phi);
```

The [meshgrid](#) function then generates two bidimensional arrays, *th1* and *ph1* , both 20 x 60 (20 rows , 60 columns), which are the basis for the following plotting function.

These arrays are someway redundant, indeed in *th1* all the colums have 20 equal elements and in *ph1* all the rows have 60 equal elements. In this fashion however for each point P (x_i , y_j) with $0 \leq i \leq 20$ and $0 \leq j \leq 60$ holds $x_i = th1(i, j)$; $y_i = ph1(i, j)$. This greatly speeds up following calculations.

Thereafter spherical coordinates are transformed in cartesian, with the function [sph2cart](#) .The inputs *theta*, *phi*, and *R* must be the same shape, therefore *R* is defined before, with the command $R=ones(20,60)$. It produces a 20x60 array (*R*) with all elements equal to unity. *Phi* describes the angle relative to the positive x-axis, (or azimuth angle), *theta* is the angle relative to the xy-plane (therefore the elevation angle is $90^\circ - \phi$,) and *R* is the distance to the origin (0, 0, 0), set to unity

```
[x,y,z] = sph2cart(ph1,pi/2 - th1,R);
surf(x,y,z);axis([-3 3 -3 3 -2 2]);
```

In such a way now $x, y,$ and z are three 20×60 matrices with everything is needed to plot in a cartesian reference (defined by *axis* instruction) the orbital surface.

In some instances, the resolution for ϕ angle has to be increased, so as to obtain a smoother picture (see figure captions below).

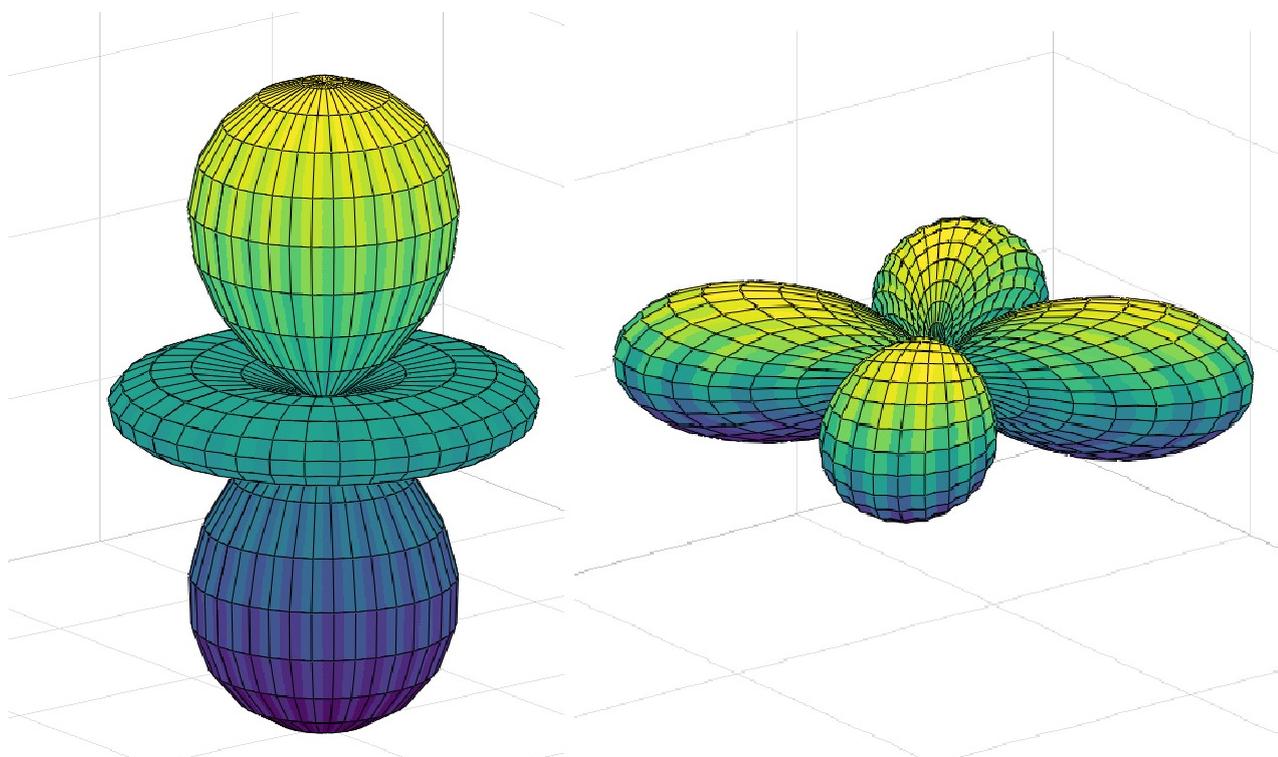


Fig. 1.1 $3d(z^2)$ left and $3d(xy)$ right. The meshgrid for the left orbital is 20×60 and for the right 40×60 .

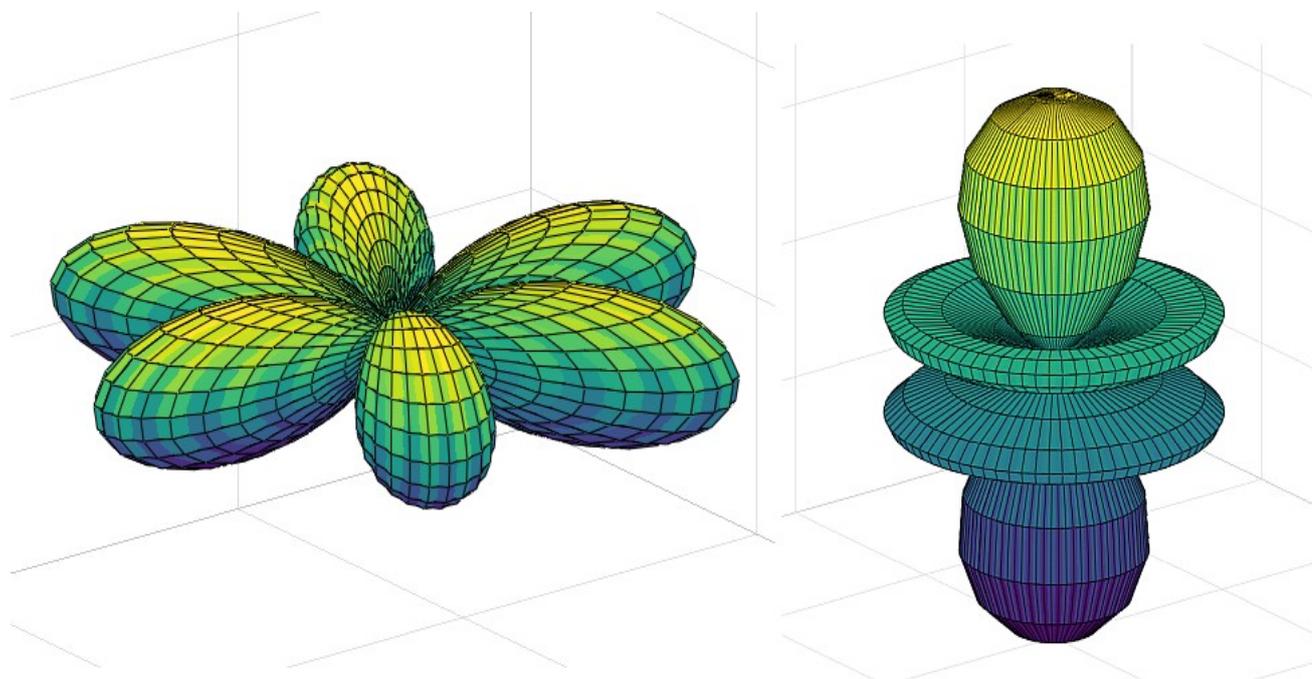


Fig. 1.2 $4f(x^3-3xy^2)$ left and $4f(z^3)$ right. The meshgrid is 60×60 for the left orbital and 40×60 for the the right.

```

clear;clc;R = ones(60);
orbital = 10; % <--- user choice
theta = linspace(-pi,pi,60); % <--- user meshgrid theta
phi = linspace(0,2*pi,40); % <--- user meshgrid phi
[th1,ph1] = meshgrid(theta,phi);

% Choose orbital type among those available.
switch orbital
  % 1s orbital
  case 1; T1='1s orbital'
  % 2p orbitals
  case 2; R = abs(sin(th1).*cos(ph1));T1='2p(x) orbital'
  case 3; R = abs(sin(th1).*sin(ph1));T1='2p(y) orbital'
  case 4; R = abs(cos(th1));T1='2p(z) orbital'
  % 3d orbitals
  case 5; R = abs(3*cos(th1).^2 - 1);T1='3d(z^2) orbital'
  case 6; R = abs(sin(th1).^2.*cos(2*ph1));T1='3d(x^2-y^2) orbital'
  case 7; R = abs(sin(th1).^2.*sin(2*ph1));T1='3d(xy) orbital'
  case 8; R = abs(sin(th1).*cos(th1).*cos(ph1));T1='3d(xz) orbital'
  case 9; R = abs(sin(th1).*cos(theta).*cos(ph1));T1='3d(yz) orbital'
  % 4f orbitals in standard set
  see--->https://winter.group.shef.ac.uk/orbitron/atomic\_orbitals/4f/index.html
  case 10; R = abs(5*cos(th1).^3 - 3*cos(th1));T1='4f(z^3) orbital'
  case 11; R = abs((5*cos(th1).^2 - 1).*sin(th1).*cos(ph1));T1='4f(xz^2)
orbital'
  case 12; R = abs((5*cos(th1).^2 - 1).*sin(th1).*sin(ph1));T1='4f(yz^2)
orbital'
  case 13; R = abs(sin(th1).^2.*cos(th1).*sin(2*ph1));T1='4f(xyz) orbital'
  case 14; R = abs(sin(th1).^2.*cos(th1).*cos(2*ph1));T1='4f(zx^2 - zy^2)
orbital'
  case 15; R = abs(sin(th1).^3.*cos(3*ph1));T1='4f(x^3 - 3xy^2) orbital'
  case 16; R = abs(sin(th1).^3.*sin(3*ph1));T1='4f(3yx^2 - y^3) orbital'
end

% Transforms spherical to cartesian coordinates.
% elevation angle is 90°-theta, azimuth angle equals phi.
[x,y,z] = sph2cart(ph1,pi/2 - th1,R);
surf(x,y,z);axis([-2 2 -2 2 -2 2]);
title(T1);

```

1.2 Hybrid orbitals

In chemistry, [orbital hybridization](#) is obtained by mixing atomic orbitals to form new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. For example, in a carbon atom which forms four single bonds the valence-shell s orbital combines with three valence-shell p orbitals to form four equivalent sp^3 mixtures which are arranged in a tetrahedral arrangement around the carbon to bond to four different atoms. Hybrid orbitals are useful in the explanation of molecular geometry and atomic bonding properties and are symmetrically disposed in space. Usually hybrid orbitals are formed by mixing atomic orbitals of comparable energies.

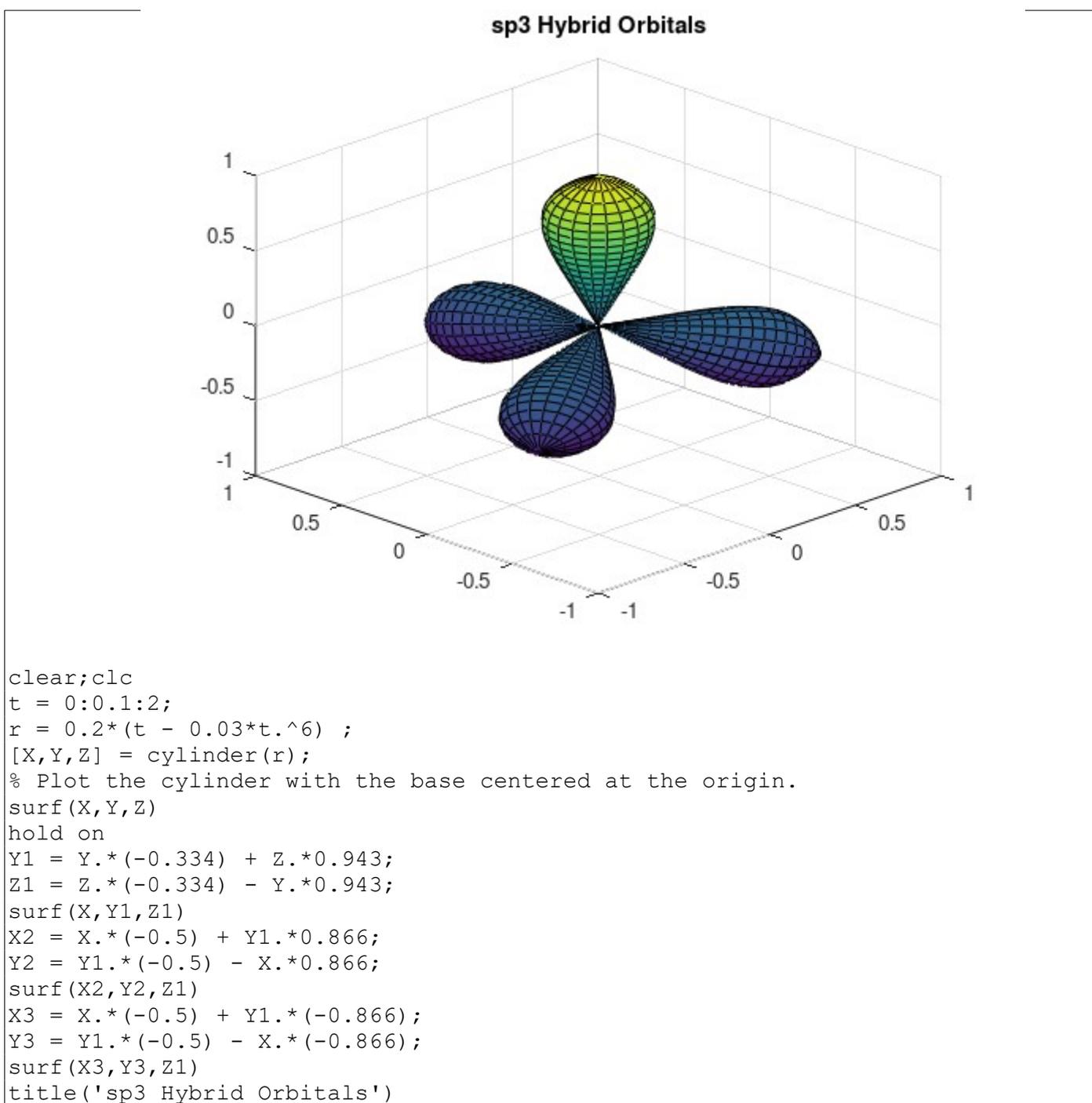
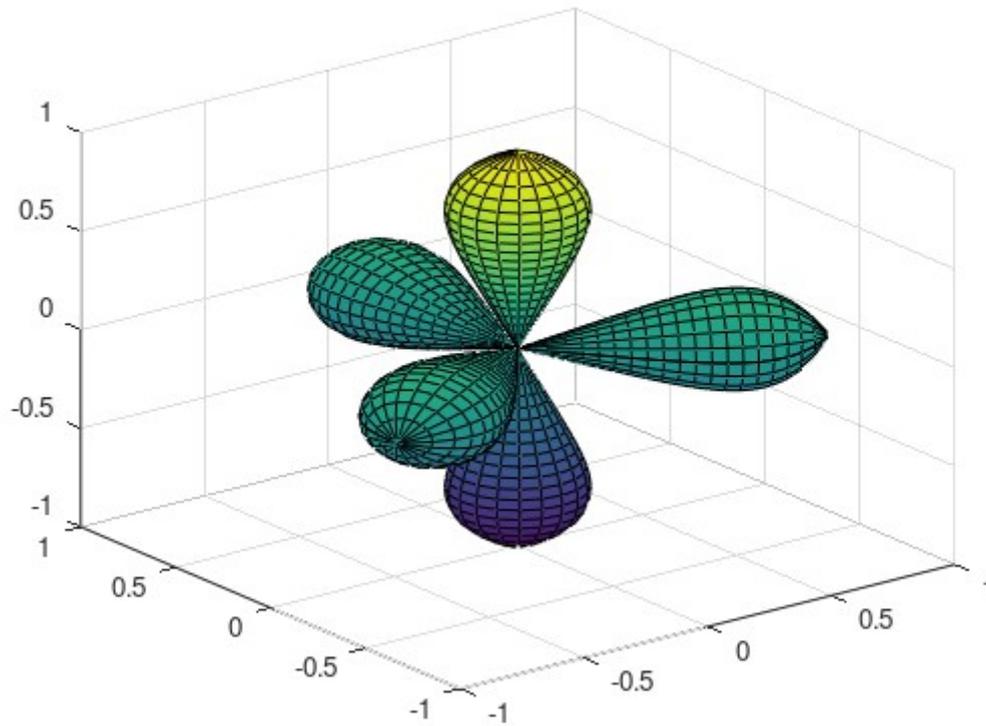


Fig. 1.3 sp^3 hybrid orbitals formation (with default meshgrid)

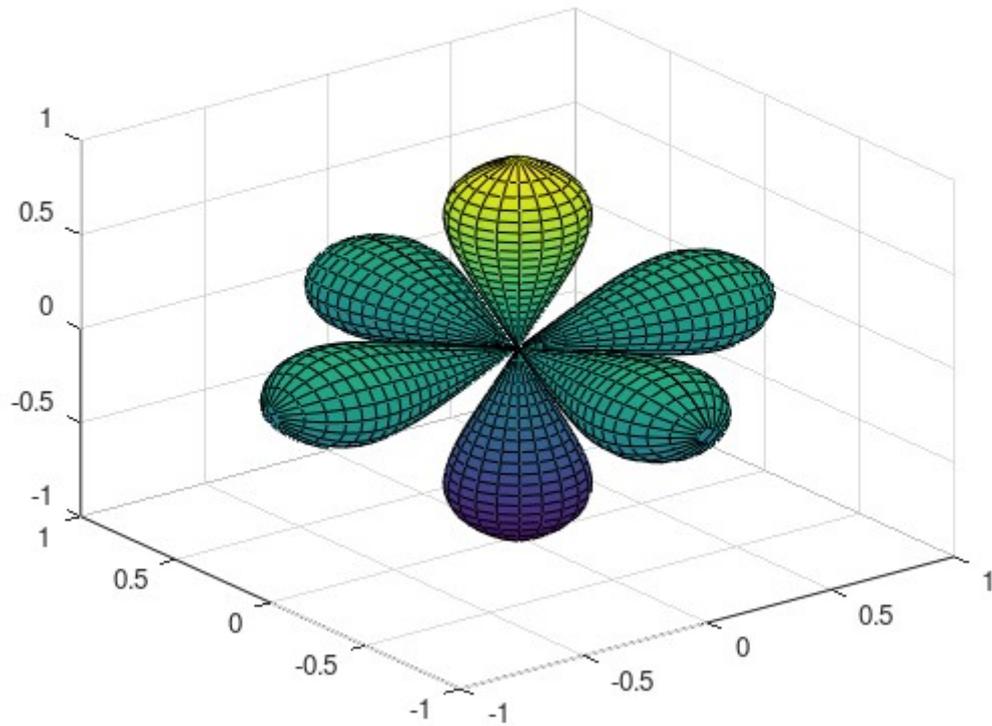
sp³d Hybrid Orbitals



```
clear;clc
t = 0:0.1:2;
r = 0.2*(t - 0.03*t.^6) ;
[X,Y,Z] = cylinder(r);
% Plot the cylinder with the base centered at the origin.
surf(X,Y,Z)
hold on
surf(X,Y,-Z)
Y1 = Z;
Z1 = -Y;
surf(X,Y1,Z1)
X2 = X.*(-0.5) + Y1.*0.866;
Y2 = Y1.*(-0.5) - X.*0.866;
surf(X2,Y2,Z1)
X3 = X.*(-0.5) + Y1.*(-0.866);
Y3 = Y1.*(-0.5) - X.*(-0.866);
surf(X3,Y3,Z1)
title('sp3d Hybrid Orbitals')
```

Fig. 1.4 sp³d hybrid orbitals formation (with default meshgrid)

sp3d2 hybrid orbitals



```
clear;clc
t = 0:0.1:2;
r = 0.2*(t - 0.028*t.^6) ;
[X,Y,Z] = cylinder(r);
% Plot the cylinder with the base centered at the origin.
surf(X,Y,Z)
title('sp3d2 hybrid orbitals');hold on
surf(Z,X,Y)
surf(Y,Z,X)
surf(X,Y,-Z)
surf(-Z,X,Y)
surf(Y,-Z,X)
```

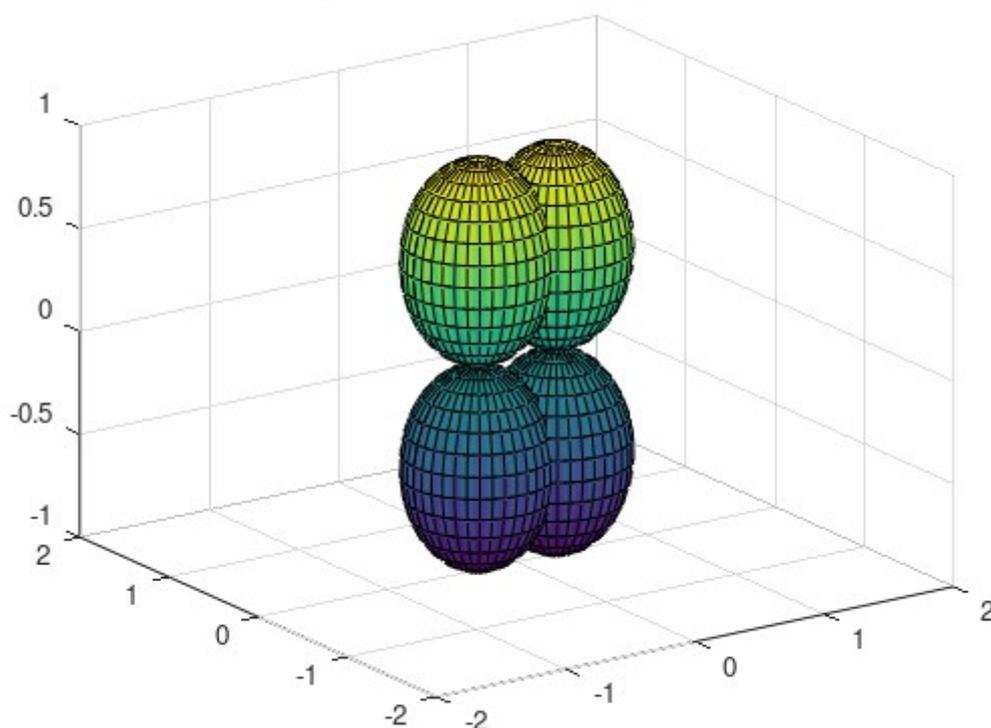
Fig. 1.5 sp^3d^2 hybrid orbitals formation (with default meshgrid)

1.3 Molecular orbitals

A [molecular orbital diagram](#), or MO diagram, is a qualitative descriptive tool explaining chemical bonding in molecules in terms of molecular orbital theory in general and the linear combination of atomic orbitals (LCAO) method in particular. A fundamental principle of these theories is that as atoms bond to form molecules, a certain number of atomic orbitals combine to form the same number of molecular orbitals, although the electrons involved may be redistributed among the orbitals.

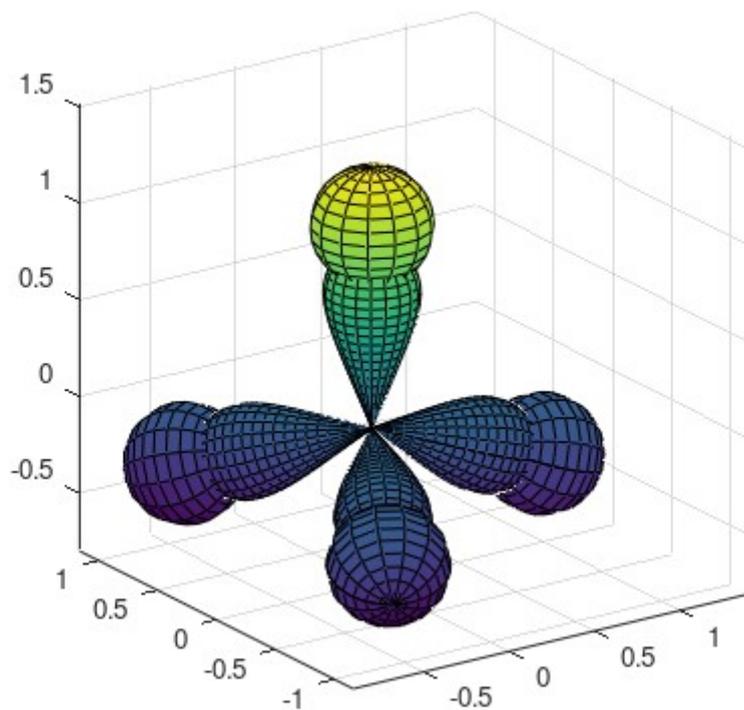
Linear combination of atomic orbital can be pictured in octave by simple overlapping of atomic orbitals. As an example molecular π orbitals in [ethylene](#) are portrayed in the following figure, whilst in fig. 1.7 the complete overlapping among 1s hydrogen orbitals and hybrid sp^3 of carbon in [methane](#) is to be seen.

pi bond formation in etylene



```
clear;clc;R = ones(20,60);
theta = linspace(-pi,pi,60);
phi = linspace(0,2*pi,20);
[th1,ph1] = meshgrid(theta,phi);
R = abs(cos(th1));T1='2p(z) orbital'
% Transforms spherical to cartesian coordinates.
% elevation angle is 90°-theta, azimuth angle equals phi.
[x,y,z] = sph2cart(ph1,pi/2 - th1,R);
surf(x+0.3,y,z);hold on;surf(x-0.3,y,z); % <--- duplicate surf function
axis([-2 2 -2 2 -1 1]);view(3);
title('pi bond formation in etylene');
```

sp³ Hybrid Orbitals in CH₄



```
clear;clc
t = 0:0.1:2;
r = 0.2*(t - 0.03*t.^6) ;
[X,Y,Z] = cylinder(r);
[x, y, z] = sphere (14);
x = 0.3*x;y = y*0.3;z = 0.3*z + 1.05;
% Plot the modified cylinder with the base centered at the origin.
surf(X,Y,Z); hold on;
surf(x,y,z);
T = rotz(30)*rotx(-109);
X1 = T(1,1)*X + T(1,2)*Y + T(1,3)*Z;
Y1 = T(2,1)*X + T(2,2)*Y + T(2,3)*Z;
Z1 = T(3,1)*X + T(3,2)*Y + T(3,3)*Z;
x1 = T(1,1)*x + T(1,2)*y + T(1,3)*z;
y1 = T(2,1)*x + T(2,2)*y + T(2,3)*z;
z1 = T(3,1)*x + T(3,2)*y + T(3,3)*z;
surf(X1,Y1,Z1);surf(x1,y1,z1);
T = rotz(120);
X2 = T(1,1)*X1 + T(1,2)*Y1;
Y2 = T(2,1)*X1 + T(2,2)*Y1;
x2 = T(1,1)*x1 + T(1,2)*y1;
y2 = T(2,1)*x1 + T(2,2)*y1;
surf(X2,Y2,Z1);surf(x2,y2,z1);
X3 = T(1,1)*X2 + T(1,2)*Y2;
Y3 = T(2,1)*X2 + T(2,2)*Y2;
x3 = T(1,1)*x2 + T(1,2)*y2;
y3 = T(2,1)*x2 + T(2,2)*y2;
surf(X3,Y3,Z1);surf(x3,y3,z1);
axis equal;
title('sp3 Hybrid Orbitals in CH4')
```