

# Waveplot Documentation and Theory

Jon Kragoskow

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# 1 Atomic Wavefunctions

## 1.1 Radial Wavefunctions

The normalised forms of the radial part of the hydrogenic (atomic) wavefunctions are denoted  $R_{nl}(\rho)$ , and are defined as

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \rho^l L_{n-l-1}^{2l+1}(\rho) e^{-\rho/2} (n+l)! \quad (1)$$

$$\rho = \frac{2Zr}{na_0}$$

where  $L_{n-l-1}^{2l+1}(\rho)$  is an associated Laguerre polynomial. The  $R_{nl}(\rho)$  can be generated using the following Mathematica function

```
RadialWaveFunction[n_,
  l_] := ((2/n)^3 (n - l - 1)!/(2 n ((n + l)!)^3))^(1/2) (\[Rho])^
  l LaguerreL[n - l - 1, 2 l + 1, \[Rho]] Exp[-\[Rho]/2] (n + l)! Z^(3/2)
```

Unfortunately, Equation (1) does not match the definitions given in P.W. Atkins' *Molecular Quantum Mechanics 2nd Ed.* on Page 72 and in J.J. Sakurai's *Modern Quantum Mechanics* on page 455. This is due to the choices of nomenclature and normalisation used by those authors for the Associated Laguerre polynomials. The relationship between Sakurai/Atkins ( $\mathcal{L}_{p+q}^q(\rho)$ ) and Mathematica ( $L_p^{(q)}(\rho)$ ) is:

$$\mathcal{L}_{p+q}^q(\rho) = (p+q)!(-1)^q L_p^{(q)}(\rho)$$

## 1.2 List of Radial Wavefunctions

Here the Radial Wavefunctions for  $n = 0 \rightarrow 7$ ,  $l = 0 \rightarrow 4$  are listed in atomic units ( $a_0 = 1$ ). In Waveplot,  $r$  is in units of  $a_0$  (Bohr radius) and  $Z = 1$ .

$$\begin{aligned}1s &= R_{1,0}(\rho) = 2e^{-\rho/2} \\2s &= R_{2,0}(\rho) = \frac{1}{2\sqrt{2}}e^{-\rho/2}(2 - \rho) \\2p &= R_{2,1}(\rho) = \frac{1}{2\sqrt{6}}e^{-\rho/2}\rho \\3s &= R_{3,0}(\rho) = \frac{1}{9\sqrt{3}}e^{-\rho/2}(\rho^2 - 6\rho + 6) \\3p &= R_{3,1}(\rho) = \frac{1}{9\sqrt{6}}e^{-\rho/2}(4 - \rho)\rho \\3d &= R_{3,2}(\rho) = \frac{1}{9\sqrt{30}}e^{-\rho/2}\rho^2 \\4s &= R_{4,0}(\rho) = \frac{1}{96}e^{-\rho/2}(-\rho^3 + 12\rho^2 - 36\rho + 24) \\4p &= R_{4,1}(\rho) = \frac{1}{32\sqrt{15}}e^{-\rho/2}\rho(\rho^2 - 10\rho + 20) \\4d &= R_{4,2}(\rho) = \frac{1}{96\sqrt{5}}e^{-\rho/2}(6 - \rho)\rho^2 \\4f &= R_{4,3}(\rho) = \frac{1}{96\sqrt{35}}e^{-\rho/2}\rho^3 \\5s &= R_{5,0}(\rho) = \frac{1}{300\sqrt{5}}e^{-\rho/2}(\rho^4 - 20\rho^3 + 120\rho^2 - 240\rho + 120) \\5p &= R_{5,1}(\rho) = \frac{1}{150\sqrt{30}}e^{-\rho/2}\rho(-\rho^3 + 18\rho^2 - 90\rho + 120) \\5d &= R_{5,2}(\rho) = \frac{1}{150\sqrt{70}}e^{-\rho/2}\rho^2(\rho^2 - 14\rho + 42) \\5f &= R_{5,3}(\rho) = \frac{1}{300\sqrt{70}}e^{-\rho/2}(8 - \rho)\rho^3 \\6s &= R_{6,0}(\rho) = \frac{1}{2160\sqrt{6}}e^{-\rho/2}(-\rho^5 + 30\rho^4 - 300\rho^3 + 1200\rho^2 - 1800\rho + 720)\end{aligned}$$

$$\begin{aligned}
6p = R_{6,1}(\rho) &= \frac{1}{432\sqrt{210}} e^{-\rho/2} \rho(\rho^4 - 28\rho^3 + 252\rho^2 - 840\rho + 840) \\
6d = R_{6,2}(\rho) &= \frac{1}{864\sqrt{105}} e^{-\rho/2} \rho^2(-\rho^3 + 24\rho^2 - 168\rho + 336) \\
6f = R_{6,3}(\rho) &= \frac{1}{2592\sqrt{35}} e^{-\rho/2} \rho^3(\rho^2 - 18\rho + 72) \\
7s = R_{7,0}(\rho) &= \frac{1}{17640\sqrt{7}} e^{-\rho/2} (\rho^6 - 42\rho^5 + 630\rho^4 - 4200\rho^3 + 12600\rho^2 - 15120\rho + 5040) \\
7p = R_{7,1}(\rho) &= \frac{1}{11760\sqrt{21}} e^{-\rho/2} \rho(-\rho^5 + 40\rho^4 - 560\rho^3 + 3360\rho^2 - 8400\rho + 6720) \\
7d = R_{7,2}(\rho) &= \frac{1}{7056\sqrt{105}} e^{-\rho/2} \rho^2(\rho^4 - 36\rho^3 + 432\rho^2 - 2016\rho + 3024) \\
7f = R_{7,3}(\rho) &= \frac{1}{17640\sqrt{42}} e^{-\rho/2} \rho^3(-\rho^3 + 30\rho^2 - 270\rho + 720)
\end{aligned}$$

### 1.3 Angular Wavefunctions

The angular part of a hydrogenic wavefunction is a spherical harmonic  $Y_l^{m_l}$ , which can be written in either cartesian or spherical coordinates.

#### 1.3.1 Hybrid Orbitals

The hybrid orbitals  $sp$ ,  $sp^2$ , and  $sp^3$  are linear combinations of 2s and 2p orbitals. The expansion coefficients of these orbitals can be found using the orthonormality conditions of the atomic orbitals.

#### sp Orbitals

Two  $sp$  orbitals are formed from different linear combinations of a single  $s$  and a single  $p$  orbital

$$\Psi_{sp(1)} = a_1 \Psi_s + b_1 \Psi_p$$

$$\Psi_{sp(2)} = a_2 \Psi_s + b_2 \Psi_p$$

These two orbitals are orthonormal

$$\int_{-\infty}^{\infty} \Psi_{\text{sp}(1)}^* \Psi_{\text{sp}(1)} d\tau = \int_{-\infty}^{\infty} \Psi_{\text{sp}(2)}^* \Psi_{\text{sp}(2)} d\tau = 1 \quad (2)$$

$$\int_{-\infty}^{\infty} \Psi_{\text{sp}(1)}^* \Psi_{\text{sp}(2)} d\tau = 0 \quad (3)$$

Expanding the former in terms of s and p orbitals gives

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi_{\text{sp}(1)}^* \Psi_{\text{sp}(1)} d\tau = 1 &= \int_{-\infty}^{\infty} (a_1^* \Psi_s^* + b_1^* \Psi_p^*) (a_1 \Psi_s + b_1 \Psi_p) d\tau \\ &= \int_{-\infty}^{\infty} (a_1^* \Psi_s^* a_1 \Psi_s + b_1^* \Psi_p^* b_1 \Psi_p + a_1^* \Psi_s^* b_1 \Psi_p + b_1^* \Psi_p^* a_1 \Psi_s) d\tau \\ &= \int_{-\infty}^{\infty} (a_1^* a_1 \Psi_s^* \Psi_s + b_1^* b_1 \Psi_p^* \Psi_p + a_1^* b_1 \Psi_s^* \Psi_p + b_1^* a_1 \Psi_p^* \Psi_s) d\tau \end{aligned}$$

Since s and p orbitals are orthonormal, the integrals containing cross terms in  $\Psi_s$  and  $\Psi_p$  are zero, and the remaining integrals can be immediately evaluated since the s and p orbitals are normalised

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi_s^* \Psi_p d\tau &= \int_{-\infty}^{\infty} \Psi_p^* \Psi_s d\tau = 0 \\ \int_{-\infty}^{\infty} \Psi_s^* \Psi_s d\tau &= \int_{-\infty}^{\infty} \Psi_p^* \Psi_p d\tau = 1 \\ \rightarrow a_1^* a_1 + b_1^* b_1 &= |a_1|^2 + |b_1|^2 = 1 \end{aligned} \quad (4)$$

Then, considering the orthogonality relationship (Equation 3)

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi_{\text{sp}(1)}^* \Psi_{\text{sp}(2)} d\tau = 0 &= \int_{-\infty}^{\infty} (a_1^* \Psi_s^* + b_1^* \Psi_p^*) (a_2 \Psi_s + b_2 \Psi_p) d\tau \\ &= \int_{-\infty}^{\infty} (a_1^* \Psi_s^* a_2 \Psi_s + b_1^* \Psi_p^* b_2 \Psi_p + a_1^* \Psi_s^* b_2 \Psi_p + b_1^* \Psi_p^* a_2 \Psi_s) d\tau \\ &= \int_{-\infty}^{\infty} (a_1^* a_2 \Psi_s^* \Psi_s + b_1^* b_2 \Psi_p^* \Psi_p + a_1^* b_2 \Psi_s^* \Psi_p + b_1^* a_2 \Psi_p^* \Psi_s) d\tau \end{aligned}$$

repeating the above process this gives

$$a_1^* a_2 + b_1^* b_2 = 0 \quad (5)$$

From inspection, Equations (4) and (5) are fulfilled by

$$a_1 = b_1 = a_2 = \frac{1}{\sqrt{2}} \quad b_2 = -\frac{1}{\sqrt{2}}$$

### sp<sup>2</sup> Orbitals

A similar process can be carried out for the three sp<sup>2</sup> orbitals formed from linear combinations of two p orbitals and a single s orbital.

$$\Psi_{\text{sp}^2(1)} = a_1 \Psi_s + b_1 \Psi_{p_x} + c_1 \Psi_{p_y}$$

$$\Psi_{\text{sp}^2(2)} = a_2 \Psi_s + b_2 \Psi_{p_x} + c_2 \Psi_{p_y}$$

$$\Psi_{\text{sp}^2(3)} = a_3 \Psi_s + b_3 \Psi_{p_x} + c_3 \Psi_{p_y}$$

The orthonormality conditions

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(1)}^* \Psi_{\text{sp}^2(1)} d\tau &= \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(2)}^* \Psi_{\text{sp}^2(2)} d\tau = \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(3)}^* \Psi_{\text{sp}^2(3)} d\tau = 1 \\ \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(1)}^* \Psi_{\text{sp}^2(2)} d\tau &= \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(1)}^* \Psi_{\text{sp}^2(3)} d\tau = \int_{-\infty}^{\infty} \Psi_{\text{sp}^2(2)}^* \Psi_{\text{sp}^2(3)} d\tau = 0 \quad . \end{aligned}$$

can be expanded in terms of atomic orbitals to give

$$|a_1|^2 + |b_1|^2 + |c_1|^2 = 1$$

$$|a_2|^2 + |b_2|^2 + |c_2|^2 = 1$$

$$|a_3|^2 + |b_3|^2 + |c_3|^2 = 1$$

and

$$a_1^* a_2 + b_1^* b_2 + c_1^* c_2 = 0$$

$$a_1^* a_3 + b_1^* b_3 + c_1^* c_3 = 0$$

$$a_2^* a_3 + b_2^* b_3 + c_2^* c_3 = 0$$

The contribution of the s orbital to each sp<sup>2</sup> orbitals is equal, and so

$$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

Then, the first hybrid orbital  $\Psi_{\text{sp}^2(1)}$  can be arbitrarily defined as aligned along

the x axis, and so  $c_1 = 0$ . With these two simplifications, the remaining coefficients can be found

$$\begin{aligned} b_1 &= \sqrt{\frac{2}{3}} \\ b_2 &= b_3 = -\frac{1}{\sqrt{6}} \\ c_2 &= +\left|\frac{1}{\sqrt{2}}\right| \\ c_3 &= -\left|\frac{1}{\sqrt{2}}\right| \end{aligned}$$

### sp<sup>3</sup> Orbitals

An almost identical process can be carried out to find the expansion coefficients of the four sp<sup>3</sup> orbitals

$$\begin{aligned} \Psi_{\text{sp}^3(1)} &= a_1 \Psi_s + b_1 \Psi_{p_x} + c_1 \Psi_{p_y} + d_1 \Psi_{p_z} \\ \Psi_{\text{sp}^3(2)} &= a_2 \Psi_s + b_2 \Psi_{p_x} + c_2 \Psi_{p_y} + d_2 \Psi_{p_z} \\ \Psi_{\text{sp}^3(3)} &= a_3 \Psi_s + b_3 \Psi_{p_x} + c_3 \Psi_{p_y} + d_3 \Psi_{p_z} \\ \Psi_{\text{sp}^3(4)} &= a_4 \Psi_s + b_4 \Psi_{p_x} + c_4 \Psi_{p_y} + d_4 \Psi_{p_z} \end{aligned}$$

where again the s orbital contributes equally to all hybrid orbitals,  $\Psi_{\text{sp}^3(1)}$  is arbitrarily aligned along the  $x$  axis, and  $\Psi_{\text{sp}^3(2)}$  is in the  $x - z$  plane. Then the following coefficients are known

$$\begin{aligned} a_1 &= a_2 = a_3 = a_4 = \frac{1}{2} \\ c_1 &= d_1 = c_2 = 0 \end{aligned}$$

Then the conditions of orthonormality can again be exploited to find the re-

maining coefficients

$$\begin{aligned}b_1 &= \frac{\sqrt{3}}{2} \\b_2 = b_3 = b_4 &= -\frac{1}{2\sqrt{3}} \\c_3 &= +\left|\frac{1}{\sqrt{2}}\right| \\c_4 &= -\left|\frac{1}{\sqrt{2}}\right| \\d_2 &= \sqrt{\frac{2}{3}} \\d_3 = d_4 &= -\frac{1}{\sqrt{6}}\end{aligned}$$



## 2 Harmonic Oscillator

### 2.1 Definitions

The harmonic potential energy curve is defined as

$$E_{\text{PE}} = \frac{1}{2} k x^2 \quad ,$$

where  $x$  is the displacement in units of distance, and  $k$  is the force constant in force per unit area.

The energies of the harmonic oscillator states are

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega = \left( n + \frac{1}{2} \right) h \nu \quad ,$$

where  $n$  is the dimensionless harmonic oscillator quantum number,  $\omega$  is the angular frequency in radians per unit time,  $\hbar$  is the reduced Planck constant in energy per unit time per radians,  $\nu$  is the linear frequency in per unit time, and  $h$  is the Planck constant in energy per unit time.

The linear and angular frequencies are related by a factor of  $2\pi$ , as are the two forms of the Planck constant

$$\omega = 2\pi\nu$$

$$h = 2\pi\hbar$$

The force constant is related to the linear and angular frequencies

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\omega = \sqrt{\frac{k}{\mu}} \quad ,$$

where  $\mu$  is the reduced mass in units of mass.

The harmonic oscillator wavefunctions which correspond to the above energies

are

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left( \frac{\mu\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{\mu\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{\mu\omega}{\hbar}} x\right)$$
$$H_n(z) = (-1)^n e^{z^2} \frac{d^n}{dz^n} e^{-z^2}$$

where  $H_n$  are the Physicists Hermite polynomials.

An example set of units are

Quantity	Units
$x$	m
$k$	N m <sup>-2</sup>
$\mu$	kg
$E_{\text{PE}}$	J
$E_n$	J
$\omega$	rad s <sup>-1</sup>
$\nu$	s <sup>-1</sup>
$h$	J s <sup>-1</sup>
$\hbar$	J s <sup>-1</sup> rad <sup>-1</sup>

The units used in waveplot are

Quantity	Units
$x$	m
$k$	N m <sup>-2</sup>
$\mu$	g mol <sup>-1</sup>
$E_n$	cm <sup>-1</sup>
$E_{\text{PE}}$	cm <sup>-1</sup>
$\omega$	rad s <sup>-1</sup>
$\nu$	cm <sup>-1</sup>
$h$	cm <sup>-1</sup> s <sup>-1</sup>
$\hbar$	cm <sup>-1</sup> s <sup>-1</sup> rad <sup>-1</sup>

which, in particular, use the ‘literature’ units for the angular and linear ‘frequencies’ - cm<sup>-1</sup> - which technically correspond to the linear  $\bar{\nu}$  and angular  $\bar{\omega}$  wavenumbers, defined as

$$\bar{\nu} = \frac{\nu}{c}$$

$$\bar{\omega} = \frac{\omega}{c}$$

### 3 4f Electron Densities

Waveplot calculates and plots the free-ion electron density spheroid for a given  $m_J$  state of a  $J$  multiplet and superimposes these on a 3d model of a given molecule. The orientation and position of the spheroid on the molecule is completely defined by the user and is purely for visualisation purposes - the molecule itself is not considered when calculating the free-ion electron density.

Each spheroid is calculated using a radius vector  $R(\phi)$  which is solely a function of the polar angle  $\phi$ . This vector describes the angular dependence of the electron density of a given  $m_J$  state.

$$R(\phi) = \sqrt[3]{\tilde{c}_0 + c_2 Y_{20}(\phi) + c_4 Y_{40}(\phi) + c_6 Y_{60}(\phi)}$$

where  $\tilde{c}_0 = 3\pi/4$ .

The  $Y_{k0}$  are spherical harmonics, while the values  $c_k$  are calculated using a procedure outlined by Sievers.<sup>[1]</sup>

#### 3.1 Light lanthanides (<7 f electrons)

Here  $c_k$  is a function of the number of f electrons  $n$ , the total angular momentum  $J$  and its projection on the  $z$ -axis  $m_J$ , the total orbital angular momentum  $L$ , and the total spin angular momentum  $S$ .

$$\begin{aligned} c_k = & (-1)^{2J-m_J+L+S} \frac{7}{\sqrt{4\pi}} (2J+1) \sqrt{2k+1} \begin{pmatrix} J & k & J \\ -m_J & 0 & m_J \end{pmatrix} \\ & \cdot \begin{pmatrix} L & k & L \\ -L & 0 & L \end{pmatrix} \left\{ \begin{matrix} L & J & S \\ J & L & k \end{matrix} \right\} \begin{pmatrix} k & 3 & 3 \\ 0 & 0 & 0 \end{pmatrix} \\ & \cdot \sum_{i=1}^n (-1)^i \begin{pmatrix} k & 3 & 3 \\ 0 & 4-i & i-4 \end{pmatrix} \end{aligned} \quad (6)$$

where

$$\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$$

is a Wigner-3j symbol, up to a factor equal to Clebsch-Gordan coefficients, and

$$\left\{ \begin{array}{ccc} a & b & c \\ d & e & f \end{array} \right\}$$

is a Wigner-6j symbol.

### 3.2 Heavy lanthanides (>7 f electrons)

Here  $c_k$  is a function of the number of f electrons  $n$ , the total angular momentum  $J$  and its projection on the  $z$ -axis  $m_J$ .

$$c_k = (-1)^{J-m_J} \frac{7}{\sqrt{4\pi}} \frac{\begin{pmatrix} J & k & J \\ -m_J & 0 & m_J \end{pmatrix}}{\begin{pmatrix} J & k & J \\ -J & 0 & J \end{pmatrix}} \cdot \left[ \delta_{k0} + \sqrt{2k+1} \begin{pmatrix} k & 3 & 3 \\ 0 & 0 & 0 \end{pmatrix} \sum_i^{n-7} (-1)^i \begin{pmatrix} k & 3 & 3 \\ 0 & 4-i & i-4 \end{pmatrix} \right] \quad (7)$$

where  $\delta$  is the Kronecker delta.

[1] J. Sievers, Zeitschrift für Phys. B Condens. Matter, 1982, 45, 289–296.