

Waveplot Documentation and Theory

Jon Kragoskow

January 2023

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

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

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

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 Ψ_s and Ψ_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

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

sp² Orbitals

A similar process can be carried out for the three sp² 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 sp² 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

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

sp³ Orbitals

An almost identical process can be carried out to find the expansion coefficients of the four sp³ 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

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

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, ω is the angular frequency in radians per unit time, \hbar is the reduced Planck constant in energy per unit time per radians, ν 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 2π , 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 μ 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.

For completeness, the units of each quantity are

Quantity	Units
x	m
k	N m ⁻¹
μ	kg
E_{PE}	J
E_n	J
ω	rad s ⁻¹
ν	s ⁻¹
h	J s
\hbar	J s rad ⁻¹

In waveplot, the user can input the linear $\bar{\nu}$ and angular $\bar{\omega}$ wavenumber values rather than frequencies. These are 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 ϕ . 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.^[1]

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 .

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

where δ is the Kronecker delta.

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