

# Waveplot: Model proofs and further information

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# 1 The Particle in a Box

## 1.1 Proof

In the particle in a box model, an otherwise free particle is inserted into a one-dimensional box of length  $L$  bounded by walls of infinite potential at  $x = 0, L$ . These walls serve to constrain the particle such that its probability of existing outside of the box is zero, and its probability of being found somewhere within the box is unity.

The particle has an energy which can be computed as the sum of its kinetic and potential terms by applying the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}$$

to the particle's wavefunction  $\psi$ , as expressed by the time-independent Schrodinger equation

$$\hat{H}\psi = E\psi$$

The kinetic energy term  $\hat{T}$  describes the energy of translating the particle along the  $x$  direction.

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

Within the box ( $0 < x < L$ ) the potential energy is zero, and outside of the box it is infinity, therefore

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x \geq L \text{ or } x \leq 0 \end{cases}$$

We seek to find the wavefunction of the particle within the box, so the potential energy term is simply zero and the Hamiltonian consists only of the kinetic energy term.

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \tag{1}$$

Which has a solution of the form

$$\psi = A \sin(kx) + B \cos(kx)$$

where  $A, B$ , and  $k$  are constants which can be determined by the application of boundary conditions. The probability of finding the particle at  $x=0$  is zero, so

$$\int_{x-dx}^{x+dx} \psi^* \psi dx = 0$$

Hence  $\psi = 0$  and

$$\psi = 0 = A \sin(0) + B \cos(0) = B$$

Since  $B = 0$  for all  $x$  the wavefunction is simply

$$\psi = A \sin(kx) \tag{2}$$

where  $A$  and  $k$  are non-zero. Applying Equation (1) to this wavefunction gives

$$\begin{aligned} \hat{H}\psi &= -\frac{A\hbar}{2m} \frac{d^2}{dx^2} \sin(kx) = \frac{A\hbar^2 k^2}{2m} \sin(kx) = \frac{\hbar^2 k^2}{2m} \psi = E\psi \\ E &= \frac{\hbar^2 k^2}{2m} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \\ \psi &= A \sin\left(\sqrt{\frac{2mE}{\hbar^2}} x\right) \end{aligned}$$

In order to find the value of  $A$  we again consider what happens at the boundary of the box. At  $x = L$  the wavefunction must go to zero

$$\psi = A \sin\left(\sqrt{\frac{2mE}{\hbar^2}} L\right) = 0 \quad .$$

The trivial solution is  $A = 0$ , but this is invalid as it results in  $\psi = 0$  at all values of  $x$ . Instead, the sin term must go to zero and therefore the argument of sin must be an integer ( $n$ ) multiple of  $\pi$ .

$$\begin{aligned} \sqrt{\frac{2mE}{\hbar^2}} &= n\pi \\ E &= \frac{n^2 \pi^2 \hbar^2}{2mL^2} \\ \psi &= A \sin\left(\frac{n\pi x}{L}\right) \end{aligned} \tag{3}$$

The total probability of finding the particle in the box is unity

$$\int_0^L \psi^* \psi \, dx = A^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1$$

which can be evaluated using the identity

$$\sin^2(ax) = \frac{1 - \cos(2ax)}{2}$$

to give

$$A^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = A^2 \left( L - \frac{L}{2n\pi} \sin(2n\pi) \right) = 1$$

where since  $\sin(2n\pi) = 0$  for  $n = 1, 2, 3, 4$

$$\begin{aligned} A &= \sqrt{\frac{2}{L}} \\ \psi &= \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad . \end{aligned} \tag{4}$$

## 2 Quantum Harmonic Oscillator

### 2.1 Proof

This model is similar to the particle in a box, but uses a different potential term in the Hamiltonian which instead takes the form of a harmonic potential

$$V = V(x) = \frac{1}{2}kx^2 \quad (5)$$

which returns the particle back to equilibrium displacement ( $x=0$ ) with a restorative force  $F = -kx$ . In fact, this harmonic potential results in the mass oscillating between positive and negative displacements over time. Here however, we will only consider the position-dependence of the wavefunction.

To find the eigenfunctions of the time-independent Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

we first make a change of variables using

$$y = \sqrt{\frac{m\omega}{\hbar}} x \quad (6)$$

where  $\omega$  is the angular frequency of oscillation. The two terms in  $\hat{H}$  then become

$$\hat{T} = \frac{-\hbar}{2m} \cdot \frac{m\omega}{\hbar} \frac{d^2}{dy^2} = \frac{\hbar\omega}{2} \frac{d^2}{dy^2} \quad \text{and} \quad \hat{V} = \frac{k\hbar}{2m\omega} y^2 = \frac{\hbar\omega}{2} y^2 \quad (7)$$

where we have used the chain rule for second derivatives, and the definition of the angular frequency of a harmonic oscillator

$$\frac{d^2}{dy^2} = \frac{d^2x}{dy^2} \cdot \frac{dy}{dx} + \left( \frac{dy}{dx} \right)^2 \cdot \frac{d^2}{dx^2} \quad \omega = \sqrt{\frac{k}{m}}$$

Then the Schrodinger equation is

$$\begin{aligned} \hat{H}\psi &= \frac{-\hbar\omega}{2} \left( \frac{d^2}{dy^2} - y^2 \right) \psi = E\psi \\ \rightarrow \left( \frac{d^2}{dy^2} - y^2 \right) \psi &= -\lambda\psi \quad \text{where} \quad \lambda = \frac{2E}{\hbar\omega} \end{aligned} \quad (8)$$

which can be rewritten as the second order differential equation

$$\frac{d^2\psi}{dy^2} + (\lambda - y^2)\psi = 0$$

which has a solution of the form

$$\psi = f(y) \exp\left(\pm \frac{y^2}{2}\right)$$

where  $f(y)$  is a polynomial in  $y$ . If the exponent is positive, then the wavefunction is no longer square-integrable, i.e.

$$\int_{-\infty}^{\infty} |\psi|^2 dy = \int_{-\infty}^{\infty} \psi^* \psi dy = \infty$$

On the other hand, if the exponent is negative then the wavefunction remains square-integrable and so we adopt this in our wavefunction.

If we introduce the shorthand  $g(y) = \exp(-y^2/2)$ , then inserting this wavefunction into Equation (8) gives

$$\begin{aligned} \hat{H}\psi &= \left(\frac{d^2}{dy^2} - y^2\right) f(y)g(y) = -\lambda f(y)g(y) \\ f''(y)g(y) - 2yf'(y)g(y) - f(y)g(y) + y^2f(y)g(y) - y^2f(y)g(y) &= -\lambda f(y)g(y) \\ f''(y) - 2yf'(y) + (\lambda - 1)f(y) &= 0 \end{aligned}$$

which is a linear second order differential equation. Suppose that the solution to this can be written as the power series

$$f(y) = \sum_n a_n y^n$$

This will be valid so long as when  $y \rightarrow \infty$  this power series does not go to infinity faster than  $\exp(y^2/2)$ , else the wavefunction would no longer be square-integrable. Substituting this expression into the differential equation gives

$$\sum_n a_n (n(n-1)y^{n-2} - 2ny^n + (\lambda - 1)y^n) = 0$$

The trivial solution of  $a_n = 0$  is invalid since then the wavefunction would be zero everywhere. Instead, the coefficients of  $y^n$  must somehow sum to zero. For

a given  $m$ , the coefficients of  $y^m$  can be grouped and written as

$$(m+1)(m+2)a_{m+2} + (\lambda - 2m - 1)a_m$$

which must sum to zero if  $f(y)$  is a solution to the differential equation.

$$(m+1)(m+2)a_{m+2} + (\lambda - 2m - 1)a_m = 0$$

which can be rearranged to give

$$a_{m+2} = \frac{1 + 2m - \lambda}{(m+2)(m+1)} a_m$$

which is a recursive formula that allows all  $a_m$  to be defined in terms of  $a_0$  or  $a_1$ . To avoid an infinite series,  $f(y)$  must be truncated at some value of  $n$  which we shall call  $\nu$ . From the above recursive formula, this occurs when  $\lambda = 2\nu + 1$ , and since  $\lambda = 2E/\hbar\omega$  the energies of the harmonic oscillator are quantised with  $E = (\nu + \frac{1}{2})\hbar\omega$ . Finally, we can then write the wavefunction as

$$\psi_\nu = N_\nu \sum_{n=0}^{\nu} a_n y^n \exp\left(-\frac{y^2}{2}\right) = N_\nu H_\nu(y) \exp\left(-\frac{y^2}{2}\right) \quad (9)$$

where  $H_\nu(y)$  are the physicist's Hermite polynomials, and  $N_\nu$  is a normalisation constant

$$N_\nu^{-2} = \int_{-\infty}^{\infty} H_\nu(y) H_\nu(y) \exp(-y^2) dy = 2^\nu \nu! \pi^{\frac{1}{2}}$$

$$N_\nu = \left(2^\nu \nu! \pi^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

## 2.2 Useful definitions

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 waveplot, the user inputs the linear  $\bar{\nu}$  and angular  $\bar{\omega}$  wavenumber values rather than frequencies. These are defined as

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

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

For completeness a cohesive set of units for these quantities is given in Table 1.

Table 1: Units of Harmonic Oscillator Quantities

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



### 3 Atomic Orbitals

The hydrogenic orbitals can be written in spherical coordinates as a product of radial  $R_{n,l}(r)$  and angular  $Y_{l,m_l}(\theta, \phi)$  parts

$$\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m_l}(\theta, \phi) \quad . \quad (10)$$

Where  $n, l$ , and  $m_l$  are quantum numbers. The distance  $r$  can take values  $0 \leq r \leq \infty$ , while the polar and azimuthal angles  $\theta$  and  $\phi$  take values  $0 \leq \theta \leq \pi$  and  $0 \leq \phi \leq 2\pi$ .

#### 3.1 Radial Wavefunctions

The normalised forms of  $R_{nl}(\rho)$  are defined as

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \rho^l L_{n-l-1}^{2l+1}(\rho) e^{-\rho/2} (n+l)! \quad (11)$$

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

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_,
  1_] := ((2/n)^3 (n - 1 - 1)!/(2 n ((n + 1)!)^3))^(1/2) (\[Rho])^
  1 LaguerreL[n - 1 - 1, 2 1 + 1, \[Rho]] Exp[-\[Rho]/2] (n + 1)!(Z/a)^(3/2)
```

Unfortunately, Equation (11) does not match the definitions given in the main text of this publication, which themselves match Atkins and Sakurai, but results in the same expressions. 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:

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

#### 3.2 List of Radial Wavefunctions

Here the Radial Wavefunctions for  $n = [0, 7]$ ,  $l = [1, 4]$  are listed in atomic units ( $a_0 = 1$ ). Below,  $r$  is in units of  $a_0$  (Bohr radius).

$$\begin{aligned}
1s = R_{1,0}(\rho) &= 2Z^{\frac{3}{2}}e^{-\rho/2} \\
2s = R_{2,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{2\sqrt{2}}e^{-\rho/2}(2 - \rho) \\
2p = R_{2,1}(\rho) &= \frac{Z^{\frac{3}{2}}}{2\sqrt{6}}e^{-\rho/2}\rho \\
3s = R_{3,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{9\sqrt{3}}e^{-\rho/2}(\rho^2 - 6\rho + 6) \\
3p = R_{3,1}(\rho) &= \frac{Z^{\frac{3}{2}}}{9\sqrt{6}}e^{-\rho/2}(4 - \rho)\rho \\
3d = R_{3,2}(\rho) &= \frac{Z^{\frac{3}{2}}}{9\sqrt{30}}e^{-\rho/2}\rho^2 \\
4s = R_{4,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{96}e^{-\rho/2}(-\rho^3 + 12\rho^2 - 36\rho + 24) \\
4p = R_{4,1}(\rho) &= \frac{Z^{\frac{3}{2}}}{32\sqrt{15}}e^{-\rho/2}\rho(\rho^2 - 10\rho + 20) \\
4d = R_{4,2}(\rho) &= \frac{Z^{\frac{3}{2}}}{96\sqrt{5}}e^{-\rho/2}(6 - \rho)\rho^2 \\
4f = R_{4,3}(\rho) &= \frac{Z^{\frac{3}{2}}}{96\sqrt{35}}e^{-\rho/2}\rho^3 \\
5s = R_{5,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{300\sqrt{5}}e^{-\rho/2}(\rho^4 - 20\rho^3 + 120\rho^2 - 240\rho + 120) \\
5p = R_{5,1}(\rho) &= \frac{Z^{\frac{3}{2}}}{150\sqrt{30}}e^{-\rho/2}\rho(-\rho^3 + 18\rho^2 - 90\rho + 120) \\
5d = R_{5,2}(\rho) &= \frac{Z^{\frac{3}{2}}}{150\sqrt{70}}e^{-\rho/2}\rho^2(\rho^2 - 14\rho + 42) \\
5f = R_{5,3}(\rho) &= \frac{Z^{\frac{3}{2}}}{300\sqrt{70}}e^{-\rho/2}(8 - \rho)\rho^3 \\
6s = R_{6,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{2160\sqrt{6}}e^{-\rho/2}(-\rho^5 + 30\rho^4 - 300\rho^3 + 1200\rho^2 - 1800\rho + 720) \\
6p = R_{6,1}(\rho) &= \frac{Z^{\frac{3}{2}}}{432\sqrt{210}}e^{-\rho/2}\rho(\rho^4 - 28\rho^3 + 252\rho^2 - 840\rho + 840) \\
6d = R_{6,2}(\rho) &= \frac{Z^{\frac{3}{2}}}{864\sqrt{105}}e^{-\rho/2}\rho^2(-\rho^3 + 24\rho^2 - 168\rho + 336) \\
6f = R_{6,3}(\rho) &= \frac{Z^{\frac{3}{2}}}{2592\sqrt{35}}e^{-\rho/2}\rho^3(\rho^2 - 18\rho + 72) \\
7s = R_{7,0}(\rho) &= \frac{Z^{\frac{3}{2}}}{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{Z^{\frac{3}{2}}}{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{Z^{\frac{3}{2}}}{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{Z^{\frac{3}{2}}}{17640\sqrt{42}}e^{-\rho/2}\rho^3(-\rho^3 + 30\rho^2 - 270\rho + 720)
\end{aligned}$$

### 3.3 Angular Wavefunctions

The angular part of a hydrogenic wavefunction is a real spherical harmonic  $Y_{l,m_l}(\theta, \phi)$  which is a linear combination of complex spherical harmonics  $Y_l^{m_l}(\theta, \phi)$ .

$$Y_{l,m_l} = \begin{cases} \frac{i}{\sqrt{2}} (Y_l^{m_l} - (-1)^{m_l} Y_l^{-m_l}) & \text{if } m_l < 0 \\ Y_l^0 & \text{if } m_l = 0 \\ \frac{1}{\sqrt{2}} (Y_l^{-m_l} + (-1)^{m_l} Y_l^{m_l}) & \text{if } m_l > 0 \end{cases} \quad (12)$$

#### 3.3.1 Hybrid Orbitals

The hybrid orbitals  $sp$ ,  $sp^2$ , and  $sp^3$  are linear combinations of  $2s$  and  $2p$  orbitals and therefore cannot be separated into angular and radial parts. 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

$$\begin{aligned} \Psi_{sp(1)} &= a_1 \Psi_s + b_1 \Psi_p \\ \Psi_{sp(2)} &= a_2 \Psi_s + b_2 \Psi_p \end{aligned} .$$

These two orbitals are orthonormal

$$\int \Psi_{sp(1)}^* \Psi_{sp(1)} d\tau = \int \Psi_{sp(2)}^* \Psi_{sp(2)} d\tau = 1 \quad (13)$$

$$\int \Psi_{sp(1)}^* \Psi_{sp(2)} d\tau = 0 \quad (14)$$

where  $d\tau$  implies the integration is taken over all space, i.e.

$$\int d\tau = \int_0^\infty r^2 dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \quad (15)$$

Expanding the former in terms of s and p orbitals gives

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

Since s and p orbitals are orthogonal to each other, 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

$$\begin{aligned}
\int \Psi_s^* \Psi_p d\tau &= \int \Psi_p^* \Psi_s d\tau = 0 \\
\int \Psi_s^* \Psi_s d\tau &= \int \Psi_p^* \Psi_p d\tau = 1 \\
\rightarrow a_1^* a_1 + b_1^* b_1 &= |a_1|^2 + |b_1|^2 = 1 .
\end{aligned} \tag{16}$$

Then, from the orthogonality of the sp orbitals (Equation 14)

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

which can be evaluated to give

$$a_1^* a_2 + b_1^* b_2 = 0 . \tag{17}$$

From inspection of Equations (16) and (17) we obtain

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

### 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

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

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  $\text{sp}^2$  orbital 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 this information 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.

$$a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

Now we make the arbitrary choice of aligning  $\Psi_{\text{sp}^3(1)}$  along the  $x$  axis while placing  $\Psi_{\text{sp}^3(2)}$  in the  $xz$  plane, resulting in

$$c_1 = d_1 = c_2 = 0$$

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

maining coefficients

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