1 Atomic functions

a. Radial Functions

Solution: We know from solving the hydrogen atom that the solutions to the hydrogen atom consist of two parts, the radial and the angular part. For the case when $n = 2$ and $l = 0, 1$ the radial functions are

$$R_{20} = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}, \tag{1}$$

$$R_{21} = 2 \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}, \tag{2}$$

where a_0 is the Bohr radius and Z the nuclear charge. If we assume $Z = 1, a_0 = 1$ we get the following plot.

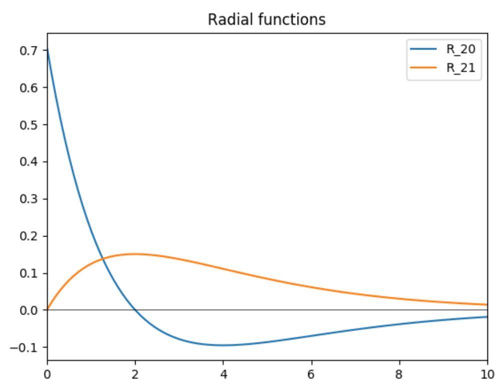


Figure 1: Radial functions R_{20} and R_{21}.

How many radial nodes are present? We don't consider $r = 0$ as a node. So taking that in mind, the number of radial nodes will be $n - l - 1$, therefore R_{20} must have 1 node and R_{21} none, as we can see in fig. 1

b. Qubic Harmonics

Solution:

From previous courses we know how to construct the cubic harmonics with $l = 0, 1$. By definition

$$s = Y_{00}, \tag{3}$$

$$p_z = Y_{10} \tag{4}$$

$$p_x = \sqrt{\frac{1}{2}}(Y_{1-1} - Y_{11}), \tag{5}$$

$$p_y = \sqrt{\frac{1}{2}}i(Y_{1-1} + Y_{11}), \tag{6}$$

The spherical harmonics for $l = 0, 1$ are

$$Y_{00} = \sqrt{\frac{1}{4\pi}}, \tag{7}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta, \tag{8}$$

$$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}, \tag{9}$$

Plugging eqs. 7-9 into eqs. 3-4 yields,

$$s = \sqrt{\frac{1}{4\pi}}, \tag{10}$$

$$p_z = \sqrt{\frac{3}{4\pi}} \cos\theta, \tag{11}$$

$$p_x = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi, \tag{12}$$

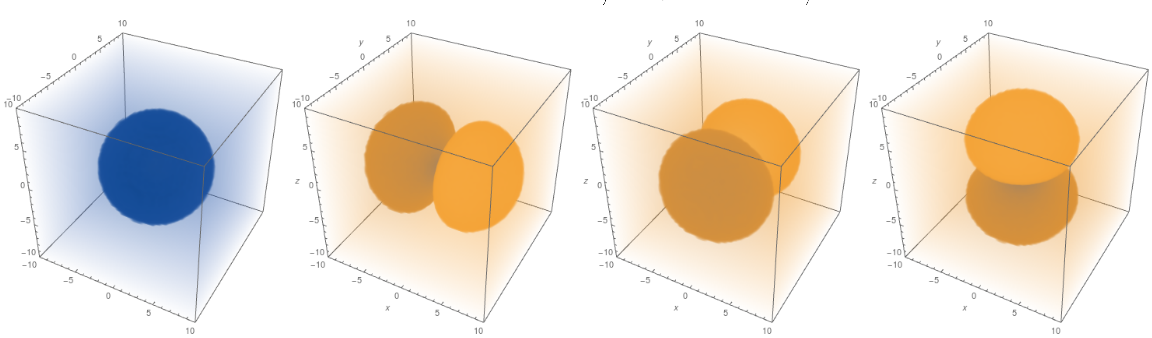
$$p_y = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi. \tag{13}$$

Now from this and our knowledge that the wavefunctions are given by

$$\psi_{nlm}(\vec{r}) = AR_{nl}(r)h_{l\alpha}(\theta, \phi), \tag{14}$$

we must be able to complete this exercise.

How do the wavefunctions look like for $n = 2, l = 0$ and $n = 2, l = 1$?

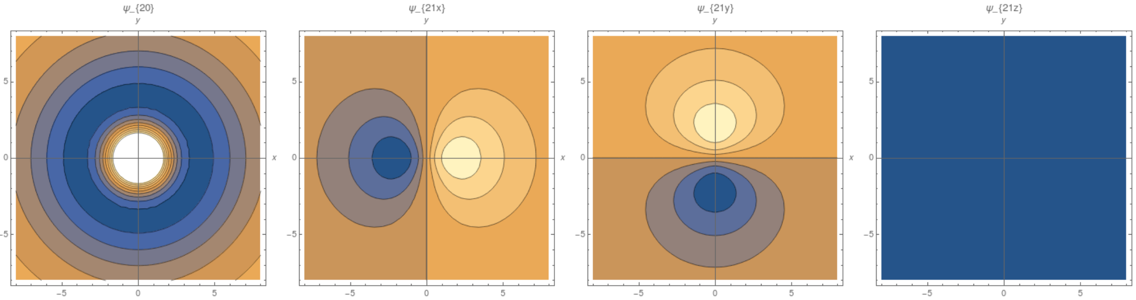


a) b) c) d)

Figure 2: 3D plots for the wavefunctions ψ_{200}, ψ_{21x}, ψ_{21y}, ψ_{21z}, from a) to b) respectively.

Here we can see that the p functions consist of two lobes with different sign each.

Draw contour plots on the xy plane



a) b) c) d)

Figure 3: Contour plots on the xy plane for the wavefunctions ψ_{200}, ψ_{21x}, ψ_{21y}, ψ_{21z}, from a) to b) respectively.

Which functions have inversion symmetry? If we don't consider signs only ψ_{200} has inversion symmetry. But if we are not that rigorous and we allow ourselves to take the absolute value of the functions then all of them have inversion symmetry with respect to the origin.

2 Slater determinants

a. 2 electrons

Solution: Let us write the concerning determinant

$$\begin{vmatrix} \phi_{m_a}(\vec{r}_1,\sigma_1) & \phi_{m_a}(\vec{r}_2,\sigma_1) \\ \phi_{m_b}(\vec{r}_1,\sigma_2) & \phi_{m_b}(\vec{r}_2,\sigma_2) \end{vmatrix} = \phi_{m_a}(\vec{r}_1,\sigma_1)\phi_{m_b}(\vec{r}_2,\sigma_2) - \phi_{m_a}(\vec{r}_2,\sigma_1)\phi_{m_b}(\vec{r}_1,\sigma_2). \tag{15}$$

Now if we decouple the wafunctions as $\phi_{n_a}(\vec{r},\sigma) = \psi_{n_a}(\vec{r})\chi_p(\sigma)$, and the orbital quantum numbers are the same ($m_a = m_b$) the right hand side of eq. 15 turns into

$$\psi_{m_a}(\vec{r}_1)\psi_{m_a}(\vec{r}_2)(\chi_1(\sigma_1)\chi_2(\sigma_2) - \chi_1(\sigma_1)\chi_2(\sigma_2)). \tag{16}$$

If we take $\sigma_1 = \sigma_2$ then all the quantum numbers of both electrons would be the same, since this is forbidden by Pauli's principle the conclusion is that in that case

$$\boxed{\Psi(\vec{r}_1,\vec{r}_2) = 0.}$$

If $m_a = m_b$ and the spins are different, then, using eq. 16 we will have

$$\boxed{\Psi(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\psi_{m_a}(\vec{r}_1)\psi_{m_a}(\vec{r}_2)(\chi_1(\uparrow)\chi_2(\downarrow) - \chi_2(\uparrow)\chi_1(\downarrow)).}$$

This state is *orbital symmetric, and spin-asymmetric*, as we can see, if we change the spin directions of the particles then the resulting wavefunction will change signs.

If the orbital quantum numbers are different then, we have two cases for the spins, when the spins are aligned and when they point in different directions. Let's take the case when they are aligned first, using eq. 15

$$\phi_{m_a}(\vec{r}_1,\sigma_1)\phi_{m_b}(\vec{r}_2,\sigma_1) - \phi_{m_a}(\vec{r}_2,\sigma_1)\phi_{m_b}(\vec{r}_1,\sigma_1).$$

Again, decoupling terms we'll have

$$(\psi_{m_a}(\vec{r}_1)\psi_{m_b}(\vec{r}_2) - \psi_{m_a}(\vec{r}_2)\psi_{m_b}(\vec{r}_1))\chi_1(\sigma_1)\chi_2(\sigma_1), \tag{17}$$

So we have, two possible wavefunctions

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_{m_a}(\vec{r}_1)\psi_{m_b}(\vec{r}_2) - \psi_{m_a}(\vec{r}_2)\psi_{m_b}(\vec{r}_1))\chi_1(\uparrow)\chi_2(\uparrow)} \tag{18}$$

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_{m_a}(\vec{r}_1)\psi_{m_b}(\vec{r}_2) - \psi_{m_a}(\vec{r}_2)\psi_{m_b}(\vec{r}_1))\chi_1(\downarrow)\chi_2(\downarrow)} \tag{19}$$

Both of them are *symmetric in spin, and antisymmetric in orbital*, i.e. if we exchange the spin of particle 1 and particle 2 the wavefunction keeps the same sign, but if we exchange the orbital quantum numbers a -1 sign will appear.

Now the only remaining case is when the spins point in opposite directions, for this case the slater determinant will yield

$$\phi_{m_a}(\vec{r}_1, \sigma_1)\phi_{m_b}(\vec{r}_2, -\sigma_1) - \phi_{m_a}(\vec{r}_2, \sigma_1)\phi_{m_b}(\vec{r}_1, -\sigma_1).$$

Here decoupling will not help us to spot symmetries, since *the result has neither spin nor angular symmetry.* So we will only write the resulting functions

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_{m_a}(\vec{r}_1, \downarrow)\phi_{m_b}(\vec{r}_2, \uparrow) - \phi_{m_a}(\vec{r}_2, \downarrow)\phi_{m_b}(\vec{r}_1, \uparrow)).} \tag{20}$$

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_{m_a}(\vec{r}_1, \uparrow)\phi_{m_b}(\vec{r}_2, \downarrow) - \phi_{m_a}(\vec{r}_2, \uparrow)\phi_{m_b}(\vec{r}_1, \downarrow)).} \tag{21}$$

b. 3 electrons

Solution: Now is the turn for a slater determinant of 3 electrons, with orbital quantum numbers ($m_a = m_b \neq m_c$). Let's remember that because of Pauli's principle the electrons that share the orbital quantum numbers need to have a different spin, to give a non-zero wavefunction. So the Slater determinant will look like

$$\begin{vmatrix} \phi_{m_a}(\vec{r}_1, \sigma_1) & \phi_{m_a}(\vec{r}_2, \sigma_1) & \phi_{m_a}(\vec{r}_3, \sigma_1) \\ \phi_{m_a}(\vec{r}_1, -\sigma_1) & \phi_{m_a}(\vec{r}_2, -\sigma_1) & \phi_{m_a}(\vec{r}_3, -\sigma_1) \\ \phi_{m_c}(\vec{r}_1, \sigma_3) & \phi_{m_c}(\vec{r}_2, \sigma_3) & \phi_{m_c}(\vec{r}_3, \sigma_3) \end{vmatrix} =$$

$$\begin{aligned} = \quad & \phi_{m_a}(\vec{r}_1, \sigma_1)\phi_{m_a}(\vec{r}_2, -\sigma_1)\phi_{m_c}(\vec{r}_3, \sigma_3) \\ & +\phi_{m_a}(\vec{r}_2, \sigma_1)\phi_{m_a}(\vec{r}_3, -\sigma_1)\phi_{m_c}(\vec{r}_1, \sigma_3) \\ & +\phi_{m_a}(\vec{r}_3, \sigma_1)\phi_{m_a}(\vec{r}_1, -\sigma_1)\phi_{m_c}(\vec{r}_2, \sigma_3) \\ & -\phi_{m_c}(\vec{r}_1, \sigma_3)\phi_{m_a}(\vec{r}_2, -\sigma_1)\phi_{m_a}(\vec{r}_3, \sigma_1) \\ & -\phi_{m_c}(\vec{r}_2, \sigma_3)\phi_{m_a}(\vec{r}_3, -\sigma_1)\phi_{m_a}(\vec{r}_1, \sigma_1) \\ & -\phi_{m_c}(\vec{r}_3, \sigma_3)\phi_{m_a}(\vec{r}_1, -\sigma_1)\phi_{m_a}(\vec{r}_2, \sigma_1) \end{aligned}$$

There are different ways to factorize terms on this product and make it more readable, here we show one that might be useful to spot symmetries

$$\begin{aligned} = \quad & \phi_{m_c}(\vec{r}_3,\sigma_3)(\phi_{m_a}(\vec{r}_1,\sigma_1)(\phi_{m_a}(\vec{r}_2,-\sigma_1) - \phi_{m_a}(\vec{r}_1,-\sigma_1)\phi_{m_a}(\vec{r}_2,\sigma_1)) \\ & +\phi_{m_c}(\vec{r}_1,\sigma_3)(\phi_{m_a}(\vec{r}_2,\sigma_1)\phi_{m_a}(\vec{r}_3,-\sigma_1) - \phi_{m_a}(\vec{r}_2,-\sigma_1)\phi_{m_a}(\vec{r}_3,\sigma_1)) \\ & +\phi_{m_c}(\vec{r}_2,\sigma_3)(\phi_{m_a}(\vec{r}_3,\sigma_1)\phi_{m_a}(\vec{r}_1,-\sigma_1) - \phi_{m_a}(\vec{r}_3,-\sigma_1)\phi_{m_a}(\vec{r}_1,\sigma_1)) \end{aligned}$$

Here is actually useful to decouple the terms again

$$\begin{aligned} = \quad & \psi_{m_c}(\vec{r}_3)\chi_3(\sigma_3)\psi_{m_a}(\vec{r}_1)\psi_{m_a}(\vec{r}_2)(\chi_1(\sigma_1)\chi_2(-\sigma_1) - \chi_1(-\sigma_1)\chi_2(\sigma_1)) \\ + \quad & \psi_{m_c}(\vec{r}_1)\chi_1(\sigma_3)\psi_{m_a}(\vec{r}_2)\psi_{m_a}(\vec{r}_3)(\chi_2(\sigma_1)\chi_3(-\sigma_1) - \chi_2(-\sigma_1)\chi_3(\sigma_1)) \\ + \quad & \psi_{m_c}(\vec{r}_2)\chi_2(\sigma_3)\psi_{m_a}(\vec{r}_3)\psi_{m_a}(\vec{r}_1)(\chi_3(\sigma_1)\chi_1(-\sigma_1) - \chi_3(-\sigma_1)\chi_1(\sigma_1)). \end{aligned} \tag{22}$$

Of course we are missing the normalization value, but that one must be $1\sqrt{6}$ since there are 6 terms of equal probability. We can also see that on this case the resulting function will be *orbitally symmetric, and spin-antisymmetric for changes of spin of the particles with the same orbital numbers.*

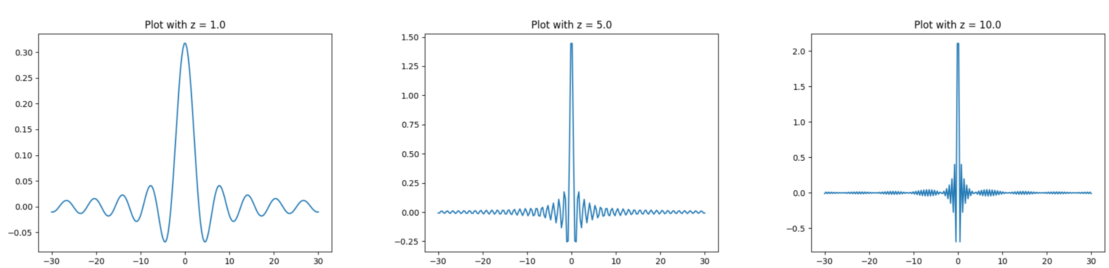
3 Dirac Delta

a. Sinc(x) definition of the delta function

Solution:

First we will calculate the given integral

$$\begin{aligned} \frac{1}{2\pi}\int_{-Z}^{Z} e^{ikx}dk &= \left.\frac{e^{ikx}}{2\pi ix}\right|_{-Z}^{Z}, \\ &= \frac{e^{iZx} - e^{-iZx}}{2\pi ix}, \\ &= \frac{1}{\pi x}\frac{e^{iZx} - e^{-iZx}}{2i}, \\ &= \frac{\sin(Zx)}{\pi x}. \end{aligned} \tag{23}$$



a) b) c)

Figure 4: Plots for eq. 23 using a) $Z = 1$, b) $Z = 5$, and c) $Z = 10$

Where does it have its maximum value? At x=0.

What happens when increasing Z? The peak rises but also narrows.

b. The integral of δ is one.

Solution:

Now we need to show that the integral of delta is one

$$\begin{aligned}\int_{-\infty}^{\infty}\delta(x)dx &= \int_{-\infty}^{\infty}\frac{1}{2\pi}\lim_{Z\to\infty}\int_{-Z}^{Z}e^{ikx}dk,\\ &= \int_{-\infty}^{\infty}\lim_{Z\to\infty}\frac{\sin(Zx)}{\pi x}, \quad \text{using eq. 23},\\ &= \lim_{Z\to\infty}\int_{-\infty}^{\infty}\frac{\sin(Zx)}{\pi x}, \quad \text{linearity},\\ &= \frac{1}{\pi}\lim_{Z\to\infty}\int_{-\infty}^{\infty}\frac{\sin(x')}{x'}dx', \quad \text{change of variable } x' = Zx,\\ &= \frac{1}{\pi}\lim_{Z\to\infty}\pi,\\ &= \frac{\pi}{\pi} = 1 \quad \blacksquare. \end{aligned} \tag{24}$$

Being strict we should have changed the Z on the limit when we changed variable, but as we saw the final result of the integral was not affected by the value of Z. So we can omit that step in order to avoid unnecessary calculations.

c. Fourier transform of δ

Solution: Let's begin with the definition

$$\begin{aligned}\delta(k') &= \int_{-\infty}^{\infty}e^{-ik'x}\delta(x)dx,\\ &= \int_{-\infty}^{\infty}e^{-ik'x}\left(\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ikx}dk\right)dx, \quad \text{definition of } \delta(x),\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-ik'x}e^{ikx}dkdx,\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{i(k-k')x}dkdx,\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{ik''x}dk''dx, \quad \text{variable change } k'' = k - k',\\ &= \int_{-\infty}^{\infty}\left(\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ik''x}dk''\right)dx,\\ &= \int_{-\infty}^{\infty}\delta(x)dx, \quad \text{by definition},\\ &= 1, \quad \text{using eq. 24}.\end{aligned}$$

d. Properties of Dirac's delta

Solution: Here we show a couple of properties of this distribution

$$\int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0). \tag{25}$$

$$\int_{-\infty}^{\infty} \delta(\alpha x)dx = \frac{1}{|\alpha|}. \tag{26}$$

$$\delta(-x) = \delta(x). \tag{27}$$

$$\int_{-\infty}^{\infty} f(t)\delta(t-T)dx = f(T). \tag{28}$$

$$\int_{-\infty}^{\infty} f(x)\delta(x-a) = \int_{-\infty}^{\infty} f(a)\delta(x-a). \tag{29}$$

$$\int_{-\infty}^{\infty} \delta(a-x)\delta(x-b)dx = \delta(a-b). \tag{30}$$

e. Properties of Fourier transforms

Solution: We will denote the Fourier transform operation with a hat. For $a, b \in \mathbb{C}$, if $h(x) = af(x) + bg(x)$ then

$$\hat{h}(\xi) = a\hat{f}(\xi) + b\hat{g}(\xi). \tag{31}$$

For $x_0 \in \mathbb{R}$, if $h(x) = f(x - x_0)$, then

$$\hat{h}(\xi) = e^{-2\pi i x_0 \xi}\hat{f}(\xi). \tag{32}$$

For $\xi_0 \in \mathbb{R}$, if $h(x) = e^{2\pi i x \xi_0} f(x)$, then

$$\hat{h}(\xi) = \hat{f}(\xi - \xi_0). \tag{33}$$

For $a \neq 0 \in \mathbb{R}$ if $h(x) = f(ax)$ then

$$\hat{h}(\xi) = \frac{1}{|a|} f\left(\frac{\xi}{a}\right). \tag{34}$$

If $h(x) = \overline{f(x)}$, then

$$\hat{h}(\xi) = \overline{\hat{f}(-\xi)}. \tag{35}$$

But we have to be careful with those 2π factors because they depend on the definition of the Fourier transform, and the inverse Fourier transform.