ORBITALS: BACKGROUND MATERIAL FOR TEACHERS OF PRE-U CHEMISTRY

1. Introduction

In the author's experience of teaching sixth-form chemistry, the topic of orbitals causes the greatest upset among students, across the ability range. The abstract and counter-intuitive elements are difficult enough for students to grasp as it is, while the apparent contradiction of what was learnt at GCSE level can draw protest. Demands for justification and explanation can be tricky to field. Of course such enquiries lead inevitably to quantum mechanics.

The purposes of this document are several.

(1) Provide guidance to teachers on useful approaches to teaching this area. Some of the material in this chapter is worth conveying directly to all students; some could be useful extension material; parts could be useful reference for teachers to be able to draw upon if certain questions arise in discussion. At the beginning of each subsection will be advice about how the material may be employed.
(2) Explain the origin of atomic orbitals from first principles, and extend the treatment to bonding and antibonding molecular orbitals. This should give teachers greater confidence discussing orbitals.
(3) Treat the subject rigorously while remaining comprehensible at the level of a bright sixth former with knowledge of A-level further maths. Nothing in this chapter will be beyond the capacity of the brightest students.
(4) Provide figures that illustrate the subject matter exactly, rather than using the artists' impressions that are seen in many text books at this level. The resolution of the figures remain sharp after being expanded many times in a pdf viewer.
(5) Correct common misconceptions at this level about orbitals.

2. What are orbitals and why are they necessary?

Most students begin their sixth-form chemical studies thinking of electrons orbiting a nucleus like planets orbit the sun, *ie* with classical mechanics. How do orbitals and subshells fit into this picture? This is an ideal time to discuss what is meant by a model, how they can

be useful up to point, but may need refining under different circumstances. In this context it might also be worth pointing out that even the Schrödinger equation isn't the last word since it doesn't take into account the effects of special relativity (the Dirac equation does this) and more besides.

2.1. **Wave-particle duality.** At the root of it all is wave-particle duality, which is an experimental fact: electrons can impart momentum in collisions like particles do, and they can be diffracted and produce interference patterns like waves do. Pre-U students need to know that electrons in atoms are described by a wave function, and so this in itself implies the wave nature of the electron. Whether electrons behave as waves or particles depends on the experiment. For our purposes we are taking electrons in atoms to behave as standing waves. By analogy, a plucked guitar string holds a standing wave. We can imagine the string to be a one-dimensional object. The two-dimensional analogue might be the flat surface of a drum being struck. The three-dimensional analogue might be a rubber ball vibrating around its own centre. Electron wave functions have three spatial dimensions. Students are familiar with standing waves and so this will be a useful analogy.

Paul Dirac argued in his classic monograph on quantum mechanics (see the first section in [1]) that wave-particle duality could be justified on philosophical grounds. Considering the experimental fact that matter is not continuous but composed of fundamental particles, it follows that there must be some degree of indeterminacy at the level of these particles, since any observation made of a fundamental particle must involve disturbing it (with a photon, for example). In describing an electron as a wave we have introduced the required indeterminacy in the simultaneous measurement of its position and momentum.

2.2. **Wave functions.** Students who have seen the equations of simple waves in physics and maths may be interested or relieved that electron wave functions may be approached (initially, at least) from the same direction. More mathematically able students could be extended to consider the complex exponential form of the wave functions.

The Greek letter psi, ψ, is normally used to represent the wave function of an electron. A general formula for the amplitude at a given point on the x axis of a wave travelling from right to left is

$$\psi = A \sin(\omega t + \phi), \tag{1}$$

where A is the amplitude of the wave at the given point, ω is the angular frequency, t is time elapsed and ϕ is the phase of the wave in radians at $t = 0$. The angular frequency is defined as

$$\omega = 2\pi f, \tag{2}$$

where f is the frequency in Hertz (s^{-1}). ωt is therefore 2π times the number of wavelengths that passed the point in time t. It is therefore

the phase of the wave in radians at time t when $\phi = 0$. A general formula for a stationary wave on the x axis is

$$\psi = A \sin(kx + \phi), \tag{3}$$

where ϕ is the phase of the wave in radians at $x = 0$ and k is the wavenumber. Wavenumber is defined as

$$k = \frac{2\pi}{\lambda}, \tag{4}$$

where λ is the wavelength. This means that kx is 2π times the number of multiples of the wavelength along the x axis. k is therefore the spatial equivalent of the angular frequency, meaning that kx is a spatial equivalent of angular phase, and is also measured in radians. We can combine equations (1) and (3) to describe a wave in terms of both space and time coordinates,

$$\psi = A \sin(kx + \omega t + \phi), \tag{5}$$

where ϕ is the phase of the wave in radians at $x = 0$ and $t = 0$.

We could also have written equation (5) with a cosine function if we had adjusted the value of ϕ by $\pi/2$. Since there are multiple phases in the argument of the trig function it becomes mathematically convenient to express the wave function as a complex exponential function, which is related to trig functions through de Moivre's equation,

$$e^{i\phi} = \cos\phi + i \sin\phi. \tag{6}$$

where $i = \sqrt{-1}$. The complex exponential form is useful because the expression can be written as the product of complex exponentials of the component phases:

$$Ae^{i(\phi_1+\phi_2+\phi_3)} = Ae^{i\phi_1}e^{i\phi_2}e^{i\phi_3}. \tag{7}$$

It might seem unsettling to have the complex i appearing in a wave function, but there are mathematical tricks to make these complex exponentials real. For example,

$$Ae^{i\phi} + Ae^{-i\phi} = 2A\cos\phi, \tag{8}$$

since $\cos\phi = \cos(-\phi)$ but $\sin\phi = -\sin(-\phi)$. The properties of complex exponentials and their use in describing oscillating functions are explained in [2].

2.3. **Schrödinger and his equation.** When Schrödinger first constructed a wave function to describe fundamental particle he wrote it in terms of variables that might be measured: position, momentum, energy and time. He combined these with the Planck constant, h, since this was a measure of the smallest packets or quanta of energy that could be measured, as illustrated by the well-known equation relating the energy, E, of a photon of light to its frequency, f,

$$E = hf. \tag{9}$$

Equation (9) shows that Planck's constant has units of J s. These are the same units as momentum × distance and also energy × time. Students will all be familiar with this equation. Those with some ability in maths might be able to appreciate a generic wave function, comparable to equation (5) but expressed in the form of a complex exponential is

$$\psi = A \exp\left\{2\pi i \left(\frac{px - Et}{h} + \phi\right)\right\}. \tag{10}$$

There is a negative sign in front of the Et term as the wave is defined as travelling in the positive direction. (In equations (1) and (5) the wave is travelling in the negative direction.)

Schrödinger's famous equation is an eigenvalue equation. Such equations take the general form

$$\hat{O}\psi = \lambda\psi, \tag{11}$$

where $\hat{O}$ is an operator (as indicated by the hat symbol). An operator is something that acts on a function to produce another function. In an eigenvalue equation, when the operator acts on the function, called an eigenfunction, it returns the same function multiplied by a constant, λ, known as the eigenvalue. Schrödinger constructed operators that generated eigenvalues that correspond to physical observables. Most students won't have met eigenvalue equations, but will understand the concept, given some explanation. For example, if an operator is the second derivative with respect to x then the function $A \sin 2x$ will be an eigenfunction, giving the eigenvalue -4.

The operator for momentum along the x axis, $\hat{p}_x$, is $\frac{h}{2\pi i} \times \frac{\partial}{\partial x}$. The partial differential operator $\frac{\partial}{\partial x}$ denotes differentiating with respect to x while keeping other variables constant. Applying this operator to the generic wave function, $\hat{p}_x\psi$, returns the momentum, p, as the eigenvalue:

$$\begin{aligned}
\hat{p}_x\psi &= \frac{h}{2\pi i} \times \frac{\partial \psi}{\partial x} \\
&= \frac{h}{2\pi i} \times \frac{\partial}{\partial x}\left\{A \exp\left(2\pi i \left(\frac{px - Et}{h} + \phi\right)\right)\right\} \\
&= pA \exp\left(2\pi i \left(\frac{px - Et}{h} + \phi\right)\right) = p\psi
\end{aligned} \tag{12}$$

This is known as the position representation, as it is the position variable being operated on. The operator for position in this representation is trivially $\times x$.

These operators for momentum and position are used to construct the Schrödinger equation in the following sections. This field is known as wave mechanics.

2.4. **Properties of eigenvalue equations.** These equations have certain properties from which chemists can take advantage. In fact, many of the standard operations in quantum chemistry, such as normalising wave functions, creating bonding and antibonding combinations, and constructing hybrid orbitals, depend on the following properties.

(1) An eigenfunction may be multiplied by any constant and it remains an eigenfunction that produces the same eigenvalue from the operator.
(2) A linear combination, *ie* a sum, of eigenfunctions is also an eigenfunction of the operator. In this sense eigenfunctions add up rather like vectors and so wave functinos are often called eigenvectors. Using the arbitrary constants from the previous point, our eigenvectors can effectively all be normalised to the same length.
(3) A certain class of operator is particularly useful for quantum chemistry, namely Hermitian operators. When operating on a linear combination of n eigenvectors an $n \times n$ matrix is required. Such a matrix is Hermitian if it is self-adjoint. A self-adjoint matrix is equal to its conjugate transpose, which is formed by reflecting all the matrix elements in the leading diagonal and taking the complex conjgate of each element that has been reflected. The reason Hermitian operators are so useful is that their eigenvalues are always real, a requirement for physical observables.
(4) Another property of Hermitian operators is that their eigenvectors are all mutually orthogonal. Two vectors are orthogonal when their scalar, *ie* dot, product is zero. The analogous procedure with wave functions is to integrate the product of two wave functions over all space. This fact provides much simplification to quantum chemical calculations.

The properties of Hermitian operators are derived and discussed in detail in [3] and [4].

2.5. **The meaning of the wave function.** Quantum mechanics – dynamics on the smallest scales – raises many perplexing questions. One is on the physical meaning of the wave function itself (a question asked by many students being introduced to orbitals). As Dirac wrote (in the first part of [1]), it is "important to remember that science is concerned only with observable things". The wave function itself is not observable, so one might question the validity of employing them. However, predictions of observable quantities made using wave functions have been confirmed experimentally countless times. Despite the philosophical problems with quantum mechanics it is arguably science's most tested and successful theory.

For an eigenvalue to relate to a physical observable, it must be a real number. Wave functions are typically complex but can be made real by multiplication by their complex conjugate, denoted ψ^*, which is the wave function with the sign of the imaginary component reversed. Most students will be familiar with complex numbers, and will be able to appreciate this by writing a general complex function as $(a + ib)$, where a and b are real:

$$(a + ib)(a - ib) = a^2 - i^2b^2 = a^2 + b^2, \tag{13}$$

which is real. Hence a wave function only, in general, corresponds to an observable quantity when it is multiplied by its complex conjugate. Such a quantity is a mathematical function, typically of three spatial coordinates. The arbitrary constant that belongs to each wave function is chosen such that the function $\psi^*\psi$ integrated over all space gives 1. Thus, when the wave function $\psi^*\psi$ is integrated over a range of spatial coordinates, the resulting value is the probability of the electron being found in that volume. The wave nature of the electron implies that the position of the electron at any given instant is uncertain, and so only probabilities of position can be obtained with the wave function.

2.6. **What are orbitals?** This is another question that students persist in asking. Strictly, orbitals are the three-dimensional probability density functions, $\psi^*\psi$, that describe the location of an electron in that state. As we shall see in section 3.5, the radial functions decay asymptotically to zero as r increases. If we want to describe an orbital with a three-dimensional shape we have to decide what proportion of the function to show. Typically 90% of the probability density function is used, *ie* r is limited to the value such that 90% of the volume of the function (which, since it is defined as a probability, has a total value of 1) is shown. The boundary of this function is known as an isosurface since the wave function has a common value at all points on this surface.

Models and pictures of orbitals commonly involve lobes of different colour. These represent the phase or sign of the wave function in the different lobes. This sign has no significance in isolated atoms since once the wave function is multiplied by its complex conjugate this phase information is lost. It is significant, however, when orbitals on different atoms combine to make chemical bonds: there will be cancellation where orbitals lobes of opposite sign overlap, for example. This point will be considered further in section 4.

2.7. **Dirac notation.** For students who are extended in quantum matters, this notation can save a lot of writing. Multiplication of a wave function by its complex conjugation and integration over all space is such a common operation in quantum chemistry that Dirac developed a short-hand notation used by all in the field. The integral of $\psi^*\psi$ over

all space is abbreviated as

$$< \psi \,|\, \psi >= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(x,y,z)\psi(x,y,z)\,dx\,dy\,dz, \qquad (14)$$

where $< \psi \,|$ is known as the bra vector, and $|\, \psi >$ as the ket vector. The bra vector is a complex conjugate. Expressions involving operators can also be expressed with this notation. For example, equation (11) is written as

$$O \,|\, \psi >= \lambda | \, \psi > . \qquad (15)$$

It is only when the bra vector is included that an integration over all space is implied.

3. Orbitals in the hydrogen atom

3.1. **Spherical polar coordinates.** In the hydrogen atom, it is easiest to consider the nucleus to be at the centre of our coordinate system. Given the spherical symmetry of an isolated hydrogen atom, it is most practical to use spherical polar coordinates. Students will have met polar coordinates and some will be familiar with spherical polars too. These are illustrated in figure 1.

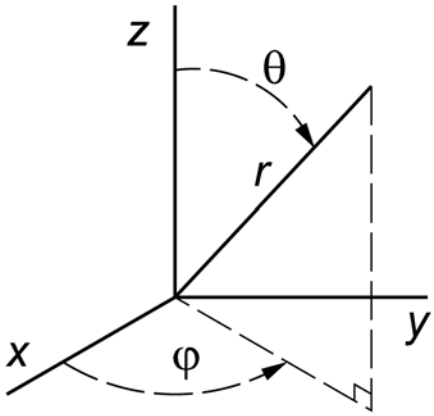

Figure 1. The spherical polar coordinate system

r is the radial distance, which is always positive. The angles θ and φ are a little like latitude and longitude when considering locations on the globe (except they are measured in degrees and latitude is measured from the equator). In spherical polar coordinates θ is known as the colatitude and lies in the range 0 to π radians; φ is known as the azimuth angle and lies in the range 0 to 2π radians. They are related

to Cartesian coordinates as follows.

$$r = \sqrt{x^2 + y^2 + z^2} \tag{16a}$$

$$\theta = \arccos\left(z/\sqrt{x^2 + y^2 + z^2}\right) \tag{16b}$$

$$\varphi = \arctan\left(y/x\right) \tag{16c}$$

The inverse relations are

$$x = r\sin\theta\cos\varphi \tag{17a}$$

$$y = r\sin\theta\sin\varphi \tag{17b}$$

$$z = r\sin\theta. \tag{17c}$$

A great advantage of using spherical polar coordinates to describe the hydrogen electron is that the wave function can factorise into a radial part, *ie* depending only on r, and an angular part, depending only on θ and φ which simplifies calculations.

3.2. **Degrees of freedom and quantum numbers.** Since the earliest spectroscopic experiments in the nineteenth century it has been evident that atoms absorb and emit energy in discrete amounts. (The first equation to describe the energy gaps in hydrogen atoms using what was effectively a quantum number was devised by the German schoolmaster J. J. Balmer in 1885.) This caused terrible problems for classical mechanics, which couldn't explain the results adequately.

Solving the Schrödnger equation and deriving quantum numbers, even for simple model systems, can be hard work mathematically for the uninitiated. However, this can be avoided, and much useful ground covered, by employing some simple analogies using standing waves to illustrate the origin of quantum numbers. Let us consider the standing wave on a plucked guitar string. The standing wave may only have certain wavelengths due to the constraint that the string is fixed at each end. In wave mechanics such a constraint is known as a boundary condition. The lowest energy, or fundamental, note is when the length of the string is half a wavelength, *ie* the only points on the string where the amplitude is fixed at zero are at the ends. These zero points are known as nodes. Higher energy standing waves have shorter wavelength. The next-highest energy wave, the first harmonic, has half the wavelength of the fundamental, so that a whole wavelength is held by the string and there is a third node half way along the string. In music, these harmonic differences are the octaves. The harmonic to higher energy has one third the wavelength of the fundamental. It turns out that the energy of the allowed standing waves is a function of $n - 1$, where n is the number of nodes on the string. ($n - 1$ is used so the fundamental takes a value of 1 and harmonics are multiples of this.) n here is analogous to a quantum number and its origin lies in the boundary condition imposed on the standing wave.

In the plucked guitar string example, there is only degree of freedom in the vibration as the string may be considered to be one-dimensional. A two-dimensional analogy would be a square drum in the xy plane. When the membrane is struck, its vibrations have two degrees of freedom as the membrane can be considered two-dimensional. (The x and y axes are independent in that they are mutually perpendicular, or orthogonal.) This leads to two quantum numbers, n_x and n_y, say, where n_x is the number of nodes on the x axis of the drum while n_y refers to the y axis. Each quantum number relates to a boundary condition: the fact that the amplitude at the ends of the drum on each axis are fixed at zero. The energy of these standing waves would, analogously, be a function of $(n_x - 1)(n_y - 1)$. The three-dimensional analogue, a vibrating cube, is harder to visualise, but we could extend the analysis to conclude that it has three degrees of freedom, that its vibrations are associated with three quantum numbers, n_x, n_y and n_z, and that the energy of its standing waves is a function of $(n_x - 1)(n_y - 1)(n_z - 1)$.

Analogies involving circular motion will bear a closer resemblance to the hydrogen atom. What about standing waves on a circular loop of wire? A circle may be thought to have no boundary but there is, in fact, a boundary condition. In order for a wave on the circular loop to be a standing wave, its amplitude at an angle φ from some reference point must be equal to its amplitude at the angle $\varphi+2\pi$. While we may consider a circle in the xy plane to be two-dimensional, if we describe it with spherical polar coordinates from the centre of the circle r and θ are constant, leaving only a single coordinate, φ. So the circle is one-dimensional with one degree of freedom, and there is one boundary condition for standing waves. We could describe the standing wave with a single quantum number, say m, that is the number of nodes of the standing wave on the loop. Being a circular standing wave, successive harmonics have two more nodes rather than one. It turns out that the energy of these circular standing waves is a function of $m/2$. This is a more natural quantum number than the number of nodes since angular momentum quantum numbers naturally go up in integer steps. By analogy with the harmonics on the one-dimensional string and equation (6), the general wave function for standing waves on a circular wire is

$$\psi = N_\varphi e^{im\varphi}, \tag{18}$$

where N_φ is the arbitrary constant in front of any eigenfunction and m is now defined as half the number of nodes on the standing wave.

The two-dimensional analogy of a circular standing wave is a vibrating elastic sphere. In spherical polar coordinates measured from the centre of the sphere r is constant, leaving θ and φ as the two degrees of freedom, each with their own boundary conditions, $\psi(r, \theta, \varphi) =$

$\psi(r, \theta + 2\pi, \varphi)$ and $\psi(r, \theta, \varphi) = \psi(r, \theta, \varphi + 2\pi)$. There are two resulting quantum numbers, m relating to φ and l relating to θ. The nodes relating to l will be discussed further in section 3.4.

The three-dimensional circular standing wave gives the solutions for the hydrogen electron. With r, θ and φ all variable there are three degrees of freedom, three boundary conditions and three quantum numbers. The boundary condition for r is that it must decay to zero at infinity – otherwise the electron wouldn't be localised on the atom. The quantum number associated with r is called n as there are certain parallels with the case of the vibrating string.

3.3. **Angular momentum.** Students studying physics may be interested in the important role that angular momentum plays in orbitals, and how the uncertainty principle affects angular momentum in quantum systems.

We saw in section 2.3 that there is an operator for determining the momentum of an electron using an eigenvalue equation. This was a linear momentum, $m\mathbf{v}$ which is a vector since velocity ($\mathbf{v}$) is a vector. A more relevant quantity for circular motion is the angular momentum, $\mathbf{l}$, also a vector, which is defined as the cross product $\mathbf{r} \times \mathbf{p}$. If a particle is moving in a circle, the vector describing its angular momentum points perpendicular to the plane of the circle. Rather than defining the kinetic energy as $\frac{1}{2}mv^2 = p^2/2m$ we use the rotational kinetic energy $\frac{1}{2}I\omega^2 = l^2/2I$, where I is the moment of inertia of the electron and ω is the magnitude of the angular velocity (which is the product of the magnitudes of the radius of the circle and the linear velocity). There are, however, three degrees of freedom to angular momentum, $l_x = xp_x$, $l_y = yp_y$ and $l_z = zp_z$.

The quantum mechanics of angular momentum is a complicated subject because Heisenberg's uncertainty principle (which is a manifestation of the indeterminacy of certain quantities being measured simultaneously) forbids all three components of angular momentum being known simultaneously. Only one component of angular momentum can be known exactly which, by convention, is l_z. It is, however, permissible to know simultaneously l_z and the square magnitude of the total angular momentum, $l^2 = l_x^2 + l_y^2 + l_z^2$. This result can be derived from the angular momentum operators [3]. Since there are only two simultaneously observable orbital angular momenta for an electron, these are the quantities described by the two angular quantum numbers, l and m. (The definition of m used by chemists is equivalent to the $m/2$ mentioned in section 3.2 in the context of nodes.) l relates to the magnitude of the orbital angular momentum of the electron in that state and so is always positive. It increases in integer steps, with its minimum permissible value being 0. m relates to the orientation of the angular momentum vector – specifically its projection on the z axis. It

also varies in integer steps, as discussed in section 3.2. It is not surprising, then, that the permissible range of m is $-l$, $-l+1$, ..., 0, 1, ..., $l-1$, l. It follows that for each value of l there are $2l+1$ possible values of m.

3.4. **Angular wave functions of the hydrogen electron.** Many students will at least be curious to see what the mathematical functions are that describe the orbital shapes. They are described in this subsection; their exact 3D rendering given in figures 2, 3 and 4 and the analytical wave functions are given table 2. The derivation of the orbitals' cartesian labels are given in equations (17) and (21). Students will need to be able to able to reproduce the approximate shapes of the orbitals with the relevant label.

Using the quantum theory of angular momentum it is possible to find simultaneous eigenfunctions of the operators for l_z and l^2 [3]. Following the arguments in sections 2.2 and 3.2, it is not surprising to find that the wave function involving φ, with its link to the one-dimensional circular motion and the m quantum number is the same as equation (18). The normalisation constant in front of each of the exponentials (see section 2.5) is

$$N_\varphi = \frac{1}{\sqrt{2\pi}} \tag{19}$$

The normalisation of this function is as follows. The complex conjugate of $N_\varphi e^{im\varphi}$ is $N_\varphi e^{-im\varphi}$. The product of these two functions is simply N_φ^2 since $e^{im\varphi}e^{-im\varphi} = e^0 = 1$. N_φ is chosen so that the integral of $\psi^*\psi$ with respect to φ between 0 and 2π (which is all space for φ) gives 1. Since N_φ is just a number it taken out of the integral:

$$N_\varphi^2 \int_0^{2\pi} d\varphi = 1. \tag{20}$$

The integral comes to 2π so N_φ must equal $1/\sqrt{2\pi}$.

Much algebra is required to derive the functions of θ that are simultaneous eigenfunctions of l_z and l^2 [3]. They are the associated Legendre functions, which actually depend on m as well as l. They are all real and given the symbol P_l^m; they are collected in table 1 with the arbitrary constants, N_θ required to normalise them [5], as discussed in section 2.5. The product of $P_l^m(\theta)$ and $\psi_m(\varphi)$ are the spherical harmonic functions, $Y_{lm}(\theta, \varphi)$, which describe the oscillations of an elastic sphere. There is more than one phase convention with these functions; here we follow those of Pauling [5].

The angular functions give the characteristic shapes of atomic orbitals. The l quantum number relates to the type of subshell, which are usually referred to by letter, as shown in table 2. For non-zero m the $\psi(\varphi)$ are imaginary. These are made real by taking linear combinations, as shown in equation (8). It is a property of eigenfunctions

P_l^m	N_θ	$P_l^m(\theta)$
P_0^0	$\sqrt{2}/2$	1
P_1^0	$\sqrt{6}/2$	$\cos\theta$
$P_1^{\pm1}$	$\sqrt{3}/2$	$\sin\theta$
P_2^0	$\sqrt{10}/4$	$(3\cos^2\theta - 1)$
$P_2^{\pm1}$	$\sqrt{15}/2$	$\sin\theta\cos\theta$
$P_2^{\pm2}$	$\sqrt{15}/4$	$\sin^2\theta$

TABLE 1. The associated Legendre functions, P_l^m, up to $l = 2$ with their normalisation constants, N_θ [5]

(discussed in section 2.4) that linear combinations are still solutions to the same eigenvalue equation. Similarly, subtracting the complex conjugate function is acceptable since the resulting orbital is wholly imaginary. When this is multiplied by its complex conjugate to obtain the probability density function the result is wholly real and positive. The real orbital functions together with their chemical labels are collected in table 2.

Orbital	N_θ	$\psi(\theta)$	Linear comb.	N_φ	$\psi(\varphi)$
s	$\sqrt{2}/2$	1	n/a	$1/\sqrt{2\pi}$	1
p_x	$\sqrt{3}/2$	$\sin\theta$	$\lvert 1> + \lvert -1>$	$1/\sqrt{\pi}$	$\cos\varphi$
p_y	$\sqrt{3}/2$	$\sin\theta$	$\lvert 1> - \lvert -1>$	$1/\sqrt{\pi}$	$\sin\varphi$
p_z	$\sqrt{6}/2$	$\cos\theta$	n/a	$1/\sqrt{2\pi}$	1
d_{xz}	$\sqrt{15}/2$	$\sin\theta\cos\theta$	$\lvert 1> + \lvert -1>$	$1/\sqrt{\pi}$	$\cos\varphi$
d_{yz}	$\sqrt{15}/2$	$\sin\theta\cos\theta$	$\lvert 1> - \lvert -1>$	$1/\sqrt{\pi}$	$\sin\varphi$
$d_{x^2-y^2}$	$\sqrt{15}/4$	$\sin^2\theta$	$\lvert 2> + \lvert -2>$	$1/\sqrt{\pi}$	$\cos 2\varphi$
d_{xy}	$\sqrt{15}/4$	$\sin^2\theta$	$\lvert 2> - \lvert -2>$	$1/\sqrt{\pi}$	$\sin 2\varphi$
d_{z^2}	$\sqrt{10}/4$	$(3\cos^2\theta - 1)$	n/a	$1/\sqrt{2\pi}$	1

TABLE 2. The orbital angular wave functions in real form for s, p and d orbitals with their normalisation constants, N_ϕ and the linear combintations of the $e^{im\varphi}$ functions required [5]

The cartesian labels for the real forms of the p and d orbitals can be obtained by converting the $\psi(\theta, \varphi)$ to $\psi(x, y, z)$ using equations (17). We need some trig identities to establish the cartesian labels for the d

orbitals that involve double-angle trig functins. These are collected in equations (21).

$$\sin^2\theta\cos 2\varphi = \sin^2\theta\cos^2\varphi - \sin^2\theta\sin^2\varphi = x^2 - y^2 \tag{21a}$$

$$\sin^2\theta\sin 2\varphi = 2\sin\theta\cos\varphi\sin\theta\sin\varphi = 2xy \tag{21b}$$

$$3\cos^2\theta - 1 = 3z^2 - (x^2 + y^2 + z^2) = 3z^2 - r^2 \tag{21c}$$

Figures 2, 3 and 4 show the exact forms of the probability density functions for the angular wave functions of the s, p and d orbitals, respectively. They appear to be three-dimensional plots, but are only two-dimensional in terms of spherical polar coordinates, since they are just functions of θ and φ. The nodes in these angular functions are planes. The number of nodal planes is equal to l, *ie* no nodal plane for s orbitals, one for p orbitals (the yz plane for the p_x orbital, *etc*) and two for d orbitals (the xz and yz planes for the d_{xy} orbital, *etc*). In the case of d_{z^2} the two nodal planes are conical, one above and one below the xy plane. When $m = 0$, $e^{im\varphi} = 1$ and so in these cases the angular function is just the appropriately normalised associated legendre function.

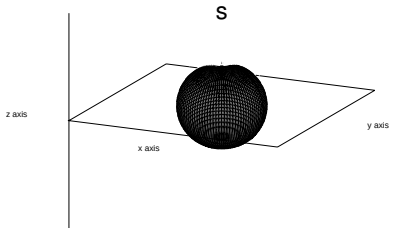

FIGURE 2. The angular probability density function for the H atom s orbitals

3.5. **Radial wave functions of the hydrogen electron.** Students often encounter radial wave functions or probability density functions in the context of subshells shielding one another, or the probabilistic nature of the electron, and may ask questions relating to the radial functions.

We consider now the Schrödinger equation for the hydrogen electron. As mentioned in section 2.3 it is an eigenvalue equation. The operator is known as the Hamiltonian, given the symbol $\hat{H}$, and is the operator for total energy, *ie* kinetic energy + potential energy. It therefore returns the total energy of the electron as its eigenvalue. Using the quantum operator for momentum and for distance we can translate the classical

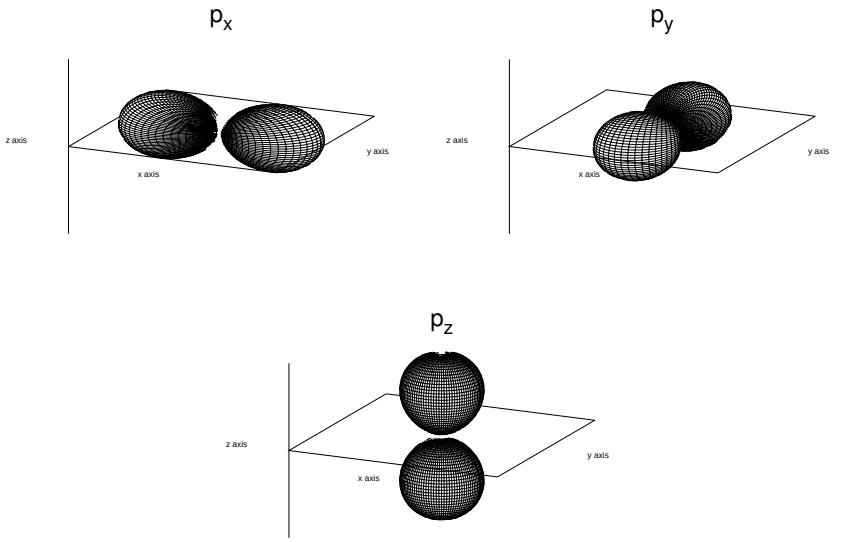

FIGURE 3. The angular probability density functions for the H atom p orbitals

expression for total energy,

$$E = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}, \tag{22}$$

into a wave mechanical equation. In equation (22) the second energy term is the potential energy of the electron. It is the Coulombic potential energy and is negative because of the attraction between the electron and the hydrogen nucleus. e is the fundamental charge and ε_0 is the permitivity of free space. Z is the number of protons in the nucleus. This is useful because ions like He^+ and Li^{2+} are "hydrogen-like" in that they only have one electron.

As explained in section 3.1 it is most convenient to express the wave function in spherical polar coordinates. The Hamiltonian operator will therefore need to be transformed so that it acts on spherical polar coordinates. This is achieved for functions using equations (17) but is more complicated for the differential operators required for the momentum operatorfor which the thery of partial derivatives is required.

It is a long and difficult process to construct the Schrödinger equation for the hydrogen electron in spherical polar coordinates and to find the radial eigenfunction solutions. Interested readers should consult one of the advanced texts in the bibliography ([3], [4] and [5]).

The crucial point in the algebra of finding the radial eigenfunctions is setting the boundary condition that the radial function should decay to zero as r approaches infinity. As with the examples in section 3.2 the boundary condition leads to a quantum number, which is the principal

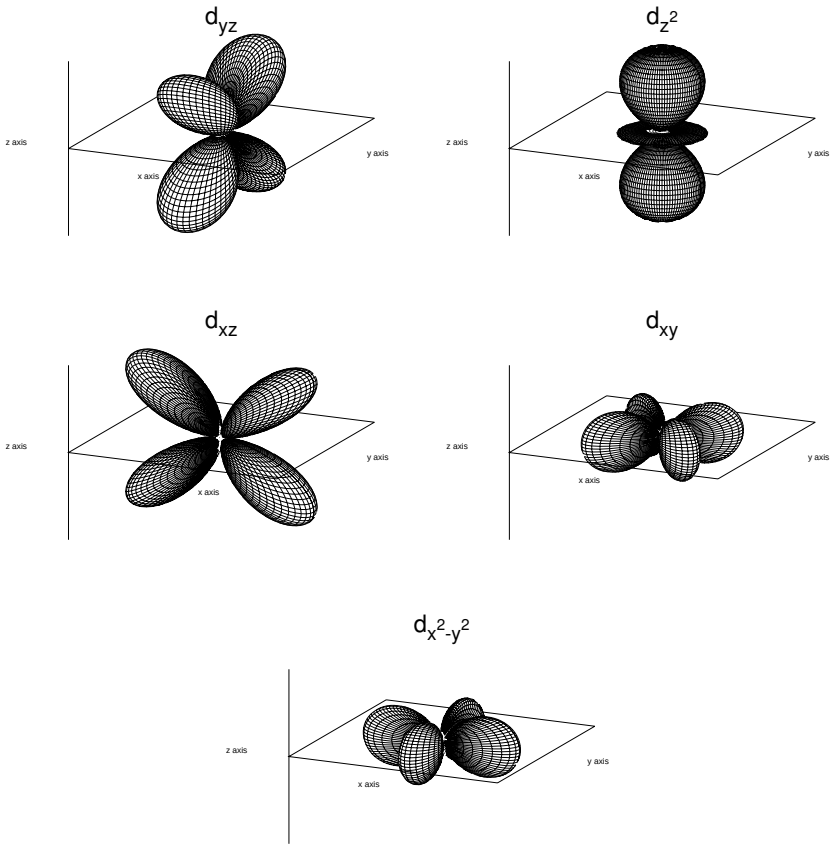

FIGURE 4. The angular probability density functions for the H atom d orbitals

(shell) quantum number n, which can take values 1, 2, 3,.... The full analysis [3] yields the following expression for n:

$$n = \frac{\mu Z e^2}{\hbar}\sqrt{\frac{K}{-2E}}, \tag{23}$$

where E is the total energy of the electron, which is defined to be negative (zero at the ionisation limit). It can also be shown that for a given value of n, l may take values in the range 0, 1, ..., $n-1$ [3]. In equation (23), $\hbar$ is $h/2\pi$. Planck's constant, h, is usually divided by 2π in the context of rotational motion, as this division converts frequencies in Hertz to angular frequencies in radians per second (radians are required for the calculus involving trig functions).μ is the reduced mass of the electron, which takes into account the fact that the electron and nucleus both rotate around a common centre of mass (rather than the nucleus being at the centre of the rotation of the electron).

$$\mu = \frac{m_e \times m_N}{m_e + m_N}, \tag{24}$$

where m_e is the mass of the electron and m_N is the mass of the nucleus. μ provides only a slight correction to the mass of the electron since its mass is so small compared to the mass of the nucleus. K is shorthand for the constants in the Coulomb expression:

$$K = \frac{1}{4\pi\varepsilon_0}. \tag{25}$$

The radial eigenfunctions turn out to be the associated Laguerre functions, which depend on the quantum numbers n and l, and therefore pertain to each subshell. They are shown in the table 3 with their normalisation constants, N_r.

Subshell	N_r	$\psi(r)$
1s	1	$(Z/a_0)^{3/2}.2e^{-\rho r/2}$
2s	$1/(2\sqrt{2})$	$(Z/a_0)^{3/2}.(2-\rho r)e^{-\rho r/2}$
2p	$1/(2\sqrt{6})$	$(Z/a_0)^{3/2}.\rho r e^{-\rho r/2}$
3s	$1/(9\sqrt{3})$	$(Z/a_0)^{3/2}.(6-6\rho r+\rho^2 r^2)e^{-\rho r/2}$
3p	$1/(9\sqrt{6})$	$(Z/a_0)^{3/2}.(4-\rho r)\rho r e^{-\rho r/2}$
3d	$1/(9\sqrt{30})$	$(Z/a_0)^{3/2}.\rho^2 r^2 e^{-\rho r/2}$

TABLE 3. The radial wave functions for the subshells of the first three shells, with their normalisation constants, N_r [5]

In table 3, a_0 is the Bohr radius, about 52.9 pm (1 pm = 10^{-12} m), which is the most probable distance of the electron from the nucleus in hydrogen. It can be expressed as a series of constants (see section 3.6).

$$a_0 = \frac{\hbar^2}{\mu e^2 K} \tag{26}$$

The value usually assigned to a_0 strictly only pertains to hydrogen as when there are more protons in the nucleus the reduced mass of the electron will be slightly different. From the definition of K in equation (25) and the Coulomb energy expression, the base units of K are kg m^3 s^{-2} C^{-2}. Given that the base units of h are kg m^2 s^{-1}, one can appreciate that equation (26) is dimensionally correct. The constant ρ that appears in the radial wave functions is a collection of constants that has dimensions of reciprocal distance.

$$\rho = \frac{2Z}{na_0} \tag{27}$$

Looking at the form of the radial eigenfunctions in table 3, bearing in mind that ρ has units of inverse distance, the eigenfunctions all

have dimensions of (distance)$^{-3/2}$. This is required for them to be normalised since the integral over all space of the square modulus of the wave function must equal 1. The integration over all space is the equivalent of summing over all spherical shells from $r = 0$ to ∞. Since the surface area of a sphere is given by $4\pi r^2$,

$$4\pi \int_0^\infty \psi(r)^2 \, r^2 \, dr = 1. \tag{28}$$

The square of the wave function multiplied by r^2 gives a function of inverse distance which, integrated over r, leads to a pure number, which is what's required for a probability. The normalised radial wave functions for the subshells of the first three shells are plotted in figure 5.

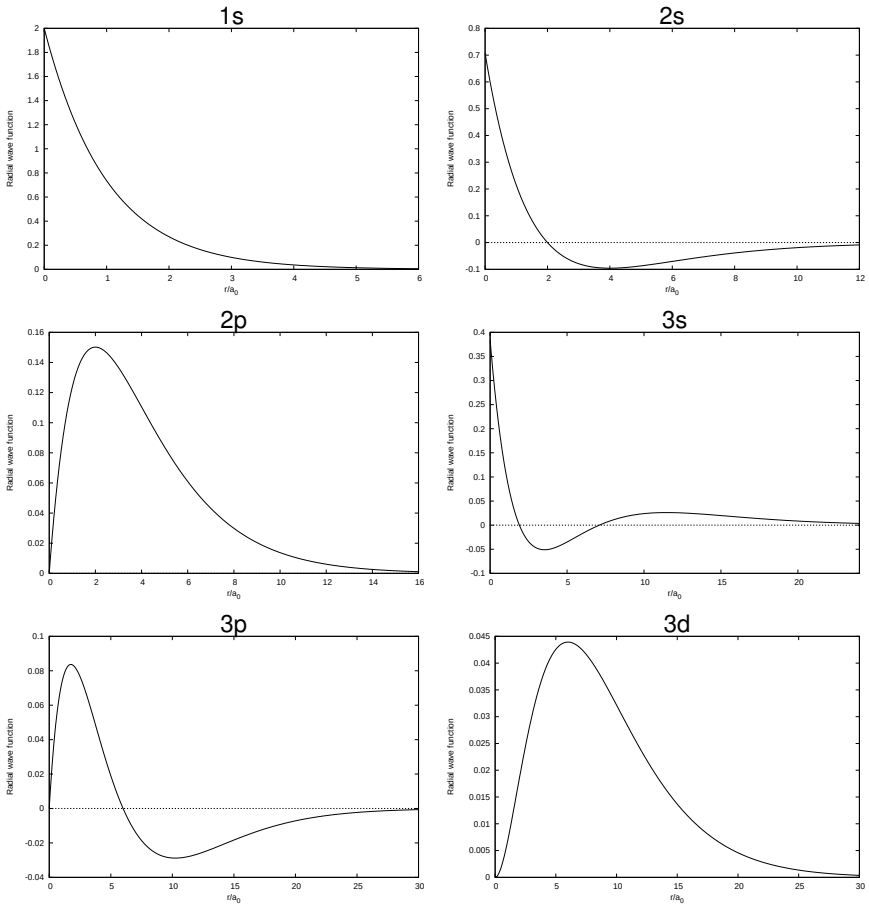

FIGURE 5. Radial wave functions for H atom orbitals of the first three shells

A common way to visualise radial wave functions is the radial density function (RDF). The RDF describes the probability of finding an electron a distance r from the nucleus, *ie* in the shell $4\pi r^2 \delta r$. Following equation (28) the RDF is defined as $4\pi r^2 \psi(r)^2$, which integrates over

all r to give 1. The radial density functions for the subshells of the first three shells are plotted in figure 6.

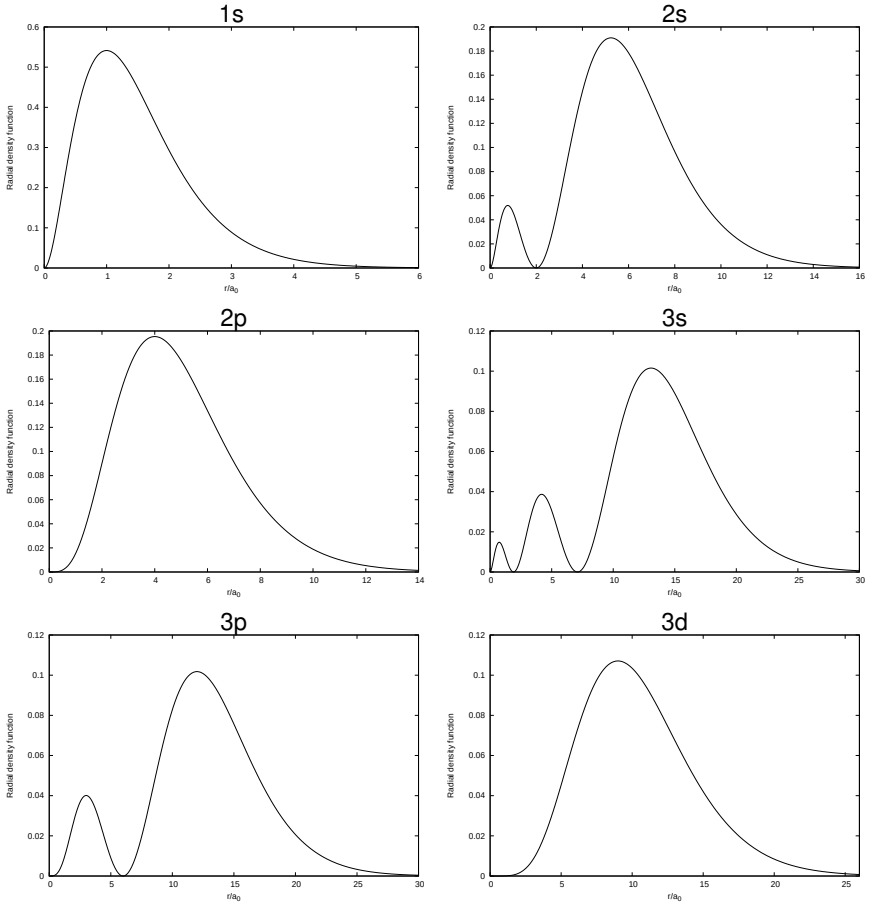

FIGURE 6. Radial density functions for H atom subshells of the first three shells

Inspection of figures 5 and 6 shows that the number of nodes shown by the radial density function, excluding $r = 0$ and ∞, is given by $n - l - 1$. These radial nodes are distinct from the angular nodes discussed in section 3.4. The radial and angular nodes are both visible in the probability density map of the xy plane for the 2s and $3d_{xy}$ orbitals in figure 7. The 2s orbital just has one radial node at the bottom of the spike. The $3d_{xy}$ orbital has no radial node but two angular nodal planes (xz and yz planes). Careful inspection of the 2s orbital probability density contour map in the xy plane of figure 8 reveals a radial node at about $r = 2$ Bohr radii. The contour map for the $3p_x$ reveals both an angular and a radial node. The angular nodal plane is the yz plane, and the radial node is at about $r = 5$ Bohr radii.

3.6. **The Bohr radius.** A remarkable fact about the expression for the Bohr radius in equation (26) is that it can be derived in a simple

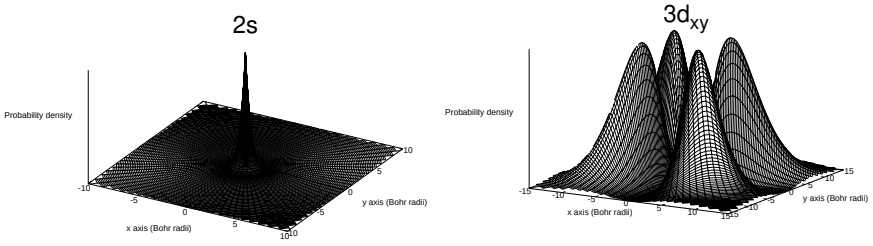

FIGURE 7. Probability density for the H atom $2s$ and $3d_{xy}$ orbitals in the xy plane

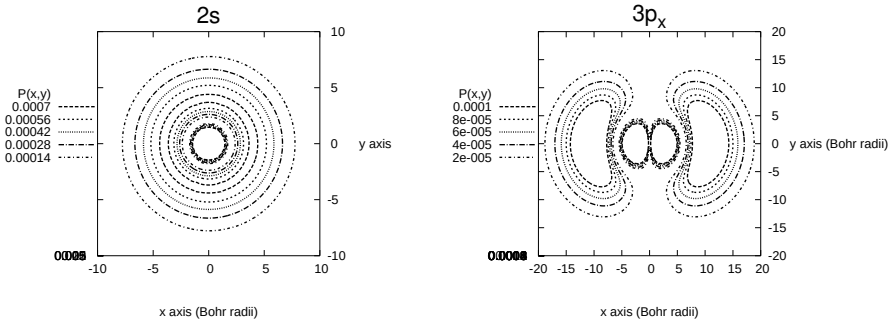

FIGURE 8. Probability density contour maps for the H atom $2s$ and $3p_x$ orbitals in the xy plane

classical calculation. If we picture an electron orbiting a proton such that the electrostatic force of attraction is equal to the centripetal force, then:

$$\frac{e^2K}{r^2} = \frac{\mu v^2}{r}. \tag{29}$$

We then quantise angular momentum, using a quantum number, n, and $\hbar$.

$$\mu v r = n\hbar \tag{30}$$

By equating equations (29) and (30), eliminating v and setting n to 1, we arrive at equation (26). This raises the question of why the solution for r is the most probable distance rather than the average distance. The answer is justified by Louis de Broglie in his discussion of least action (action has the units of momentum $\times$ distance, like $\hbar$) in part 5 of the first chapter of his classic book [6].

3.7. **Orbital energies in the hydrogen atom.** It is evident from the line spectrum of hydrogen that the energy of an electron in a hydrogen

atom depends only on the quantum number, n. Rearrangement of the expression for n (equation (23)) gives the energy of the electron as a function of the quantum number n.

$$E_n = -\frac{\mu^2 Z^2 e^4 K}{2\hbar^2 n^2} = -\frac{Z^2 e^2 K}{2n^2 a_0}. \tag{31}$$

The energy of the electron is defined to be negative since it is trapped in the attractive potential well of the nuclear attraction. This equation may be simplified using the Rydberg constant,

$$E_n = -\frac{Z^2 R}{n^2}, \tag{32}$$

where R is the Rydberg constant with dimenions of energy. It takes a value of 13.6 eV or 2.18×10^{-18} J.

It is interesting to note that the total energy of the electron in a one-electron atom depends only on the quantum number n, not the subshell quantum number l. Given knowledge of the Aufbau principle, students often ask why the hydrogen electron's energy doesn't depend on l; it is justified by equation (34). This raises some questions. Is the kinetic : potential energy ratio the same for electrons in the same shell but different subshell? Electrons with a greater l value have greater angular momentum (since l is the quantum number for the magnitude of the orbital angular mometnum) so they must possess greater rotational kinetic energy.

We can find the average value of observable quantities that are inherently probabilistic by working our their expectation values. In general the expectation value, $< \lambda >$, of an observable quantity, λ, with the quantum operator $\hat{O}$ is given by

$$< \lambda >=< \psi \,|\, O \,|\, \psi > . \tag{33}$$

The potential energy operator is $1/r$ multiplied by a constant. A very useful result is the expectation value for the operator $1/r$ when applied to the associated Laguerre functions, *ie* $\psi(r)$ [4].

$$\left\langle \frac{1}{r} \right\rangle =< \psi(r) \,|\, \frac{1}{r} \,|\, \psi(r) >= \frac{Z}{a_0 n^2} \tag{34}$$

The significance of this result is that the potential energy of an electron in a one-electron atom depends only on the shell quantum number n, not the angular momentum (subshell) quantum number l. A very general result known as the virial theorem, which applies to classical as well as quantum systems, imposes that the kinetic energy, T, and the potential energy, V, for system of conservative forces, *ie* one where energy isn't exchanged with the environment, are related. In the case of Coulombic attraction, the relation is

$$< T >= -\frac{1}{2} < V > . \tag{35}$$

So if the potential energy of the hydrogen electron is independent of the l quantum number then the same must be true of the kinetic energy. Since the angular momentum of the hydrogen electron does depend on l, then electrons with higher l must have greater rotational kinetic energy. Therefore they must have lower linear kinetic energy so that their total kinetic energy is constant.

Another useful result is the expectation value $< r >$ for the hydrogen electron. Its value for the associated Laguerre functions is [4]

$$< r >= \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right\}, \tag{36}$$

which shows that $< r >$ decreases as l increases. This is evident from inspection of the radial density functions in figure 6. While s orbitals have the greatest $< r >$ in a given shell one can appreciate how the $1/r$ is equal to other subshells since there is greater probability density for s electrons close to the nucleus due to larger number of radial nodes.

4. Orbitals in molecules

Students should know that the chemical bonds that hold together atomic nuclei in molecules are shared electrons between the nuclei: the electron-nuclear electrostatic forces of attraction bind the nuclei together. Electrons are shared in bonds as a result of the overlap and interaction between atomic orbitals on the two bonding atoms. Before going any further it is necessary to state the approximations involved with these atomic orbitals in multi-electron atoms.

4.1. **The orbital approximation and Slater's Rules.**

The orbitals derived for hydrogen atoms are exact solutions of the Schrödinger equation. There are no known exact solutions for the Schrödinger equation for multi-electron atoms due to the complication of electron-electron repulsion. Instead they are approximated to the hydrogen orbitals, with the atomic number, Z, being taken into account. However, we also need to take into account the shielding from the nuclear charge that outer electrons experience from inner electrons (and electrons in the same shell). A set of empirical rules was established by Slater to find the shielding contribution, σ, from each other electron in the atom. The sum of these shielding contributions gives the overall shielding factor S which, when subtracted from Z, gives the Z_{eff} experienced by the electron.

Slater's Rules

(1) $\sigma = 0$ for electrons of higher n.
(2) $\sigma = 0.35$ for electrons of the same n (0.30 for 1s)
(3) $\sigma = 0.85$ for s and p electrons with n one less
(4) $\sigma = 1.00$ for d and p electrons with n one less
(5) $\sigma = 1.00$ for electrons with n two or more less

4.2. **The linear combination of atomic orbitals (LCAO).** The overlap of atomic orbitals is normally considered pictorially, with lobes of the same phase reinforcing each other to form a bonding molecular orbital and those of different phase cancelling, leaving an antibonding molecular orbital. In the antibonding orbital most of the electron density is on the other side of each nucleus, so that the electrostatic repulsion between the atoms is maximised. When such a state is occupied, it may result in the two atoms becoming completely disconnected.

In this pictorial approach to LCAO theory, the relative orientation of the phases of the lobes determines whether interactions are bonding or antibonding. This is somewhat problematic for the overlap of two 1s orbitals, say, where the phase is only positive in both orbitals. However, following the properties of eigenfunctions (section 2.4) we know that we can choose any value for the constant in front of the eigenfunction, with it remaining a valid solution to the eigenvalue (Schrödinger) equation. The sign is therefore unrestricted so we can assign phases to orbital wave functions. In this way, one of two overlapping s orbitals can be given a negative phase arbitrarily, allowing for an antibonding combination. All of the possible phase combinations of orbitals need to be considered when constructing a molecular orbital diagram.

Figure 9 shows a sketch of the molecular orbital diagram for N_2. The relative energy levels of the valence atomic orbitals are shown on the right and left, with the molecular orbitals shown in order of energy up the middle. The dotted lines indicate which atomic orbitals combine to form a particular molecular orbital. The most important interactions are shown between atomic orbitals of the same type. Since it is a homonuclear diatomic, the like orbitals will have identical energy, which maximises the interaction between them. Antibonding orbitals are denoted with an asterisk. The bond order of the molecule is equal to the number of fully occupied bonding orbitals minus the number of fully occupied antibonding orbitals.

It is helpful to consider standing waves here too. In a bonding interaction the overlap of the orbitals extends the length of the orbital. This means that the resulting standing wave will have a longer wavelength and therefore a lower energy. The opposite applies to antibonding interactions. The bonding orbitals may be considered to be the result of

constructuve interference between wave functions causing an increase in amplitude, while antibonding orbitals result from destructive interference. This picture is easily understood by students who will have met constructive and destructive interference in physics, and adds further weight to the idea of electrons as waves.

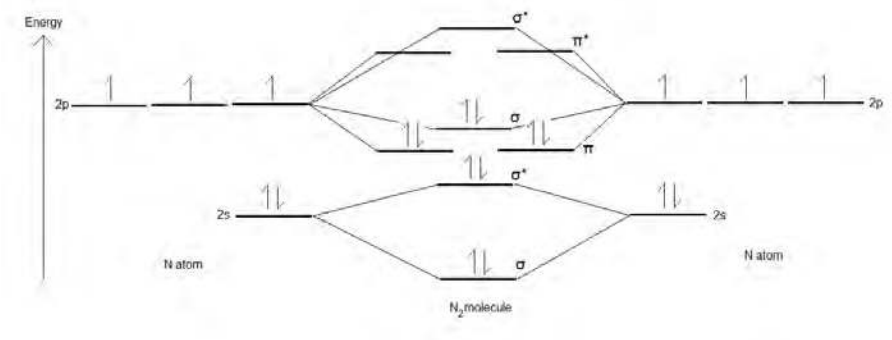

FIGURE 9. Sketch of the molecular orbital diagram for N_2

4.3. **Sigma and pi bonding and antibonding orbitals.** In figure 9 we see that the 2p orbitals on each N atom overlap in two different ways, giving molecular orbitals carrying σ or π labels. These labels relate to the geometry of the overlap involved. Single chemical bonds always involve sigma overlap, which is when the lobes of the two orbital are aligned head-on so that they meet directly between the two nuclei associated with the two orbitals. Pi overlap is when the orbitals overlap while they are sideways-on, *ie* the overlapping lobes are not pointing at each other. The regions of overlap therefore do not lie on the internuclear axis: they are between the nuclei but displaced from the internuclear axis. Pi bonds are found in multiple bonds, in addition to one sigma bond. Students will need to be able to represent these different types of overlap and know the difference between sigma and pi interactions.

Normally the head-on sigma alignment allows for greater overlap between orbitals. This leads to a larger interaction and a greater energy gap between the resulting bonding and antibonding orbitals. One way of breaking a chemical bond is to promote an electron from the bonding orbital to the antibonding one. The more energy required to do this, the stronger the bond is considered to be. Sigma bonds are therefore generally stronger than pi bonds. Pi bonds, however, are made stronger by delocalisation since extending the orbital lengthens the standing wave, increasing its wavelength and lowering its energy relative to its antibonding orbital.

In figure 9 the energies of the molecular orbitals from the overlap of the 2p electrons do not seem consistent with this approach: given the absence of pi delocalisation, one would expect the sigma bonding orbital to be lower in energy than the pi bonding one. The picture has been distorted by an effect known as s-p mixing. It was a simplification to assume that orbitals on one atom only combine with orbitals of the same type on the other atoms. In the full treatment the combinations of orbitals are determined by their symmetry label in the basis of the overall molecule's symmetry. Since the 2s and $2p_z$ orbitals have the same symmetry label in this homonuclear diatomic they can interact, which causes the sigma bonding orbital from the 2p overlap to increase in energy above the pi bonding orbitals. It is a smaller effect than the $2p_z$-$2p_z$ sigma overlap since the 2s and $2p_z$ atomic orbitals are at different energies.

In figure 10 the radial function of the 1s orbital of two hydrogen atoms a distance of 1.4 Bohr radii apart are added together and squared to give the probability density of the bonding orbital, and subtracted and squared to give the probability density of the antibonding orbital. This is the distance between H atoms in an H_2 molecule. The probability density of the molecular orbitals along the internuclear axis shows that most of the electron density is between the nuclei, consistent with section 4.2. Note that in the antibonding orbital there is a nodal plane perpendicular to the internuclear axis midway between the hydrogen nuclei.

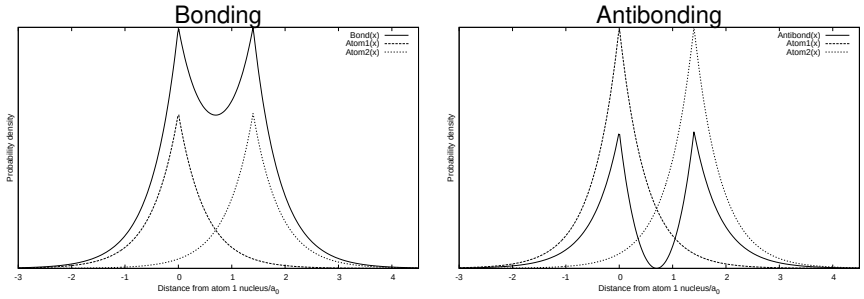

FIGURE 10. Sigma bonding and antibonding LCAOs of $1s$ orbitals in the H_2 molecule: probability density along the internuclear axis

Figure 11 shows the probability density of the molecular orbital in the xy plane using contour lines. It makes clear the nodal plane in the antibonding orbital.

Figures 12 and 13 show the molecular orbital probability densities for sigma overlap between p orbitals in two carbon atoms a distance of 2.5 Bohr radii apart. This is the distance between two carbon atoms in an ethene molecule. The sigma bonding of carbon atoms actually involves hybridised orbitals (see section 4.4); the figure is intended to

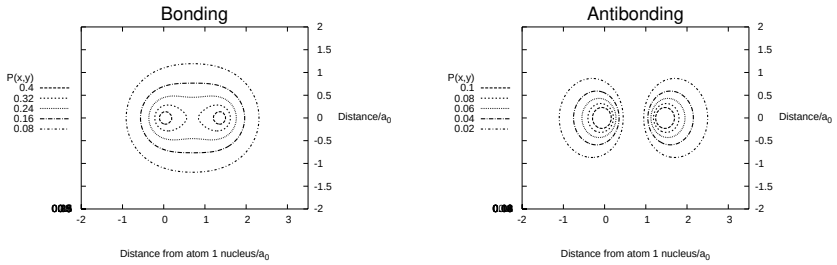

FIGURE 11. Sigma bonding and antibonding LCAOs of $1s$ orbitals in the H_2 molecule: probability density contour maps in the xy plane

illustrate the general principle of molecular orbitals from the overlap of atomic orbitals that have two lobes. Again, there is a nodal plane perpendicular to the nuclear axis midway between the nuclei in the antibonding orbital.

Wave functions for carbon atoms are hydrogen-like but with Z corrected for the extra protons in the nucleus and the shielding by other electrons. Following Slater's rules in section 4.1, Z_{eff} for the carbon 2p electron is $6 - 2.75 = 3.25$.

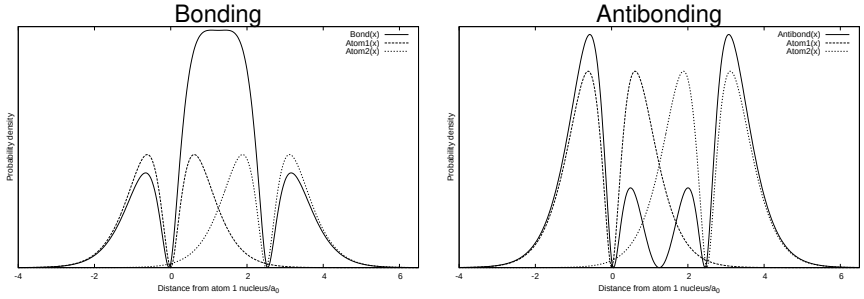

FIGURE 12. Sigma bonding and antibonding LCAOs of $2p_x$ orbitals: probability density along the internuclear axis

Figure 14 shows the molecular orbital probability densities for pi overlap between p orbitals in two carbon atoms a distance of 2.5 Bohr radii apart. As in all molecular orbitals from pi overlap, there is a nodal plane in the plane of the molecule. In the antibonding orbital there is a further nodal plane perpendicular to the internuclear axis, as is seen in the sigma antibonds.

4.4. **Hybridised atomic orbitals.** While hybridisation isn't explicitly in the Pre-U syllabus, many teachers find it such a useful concept

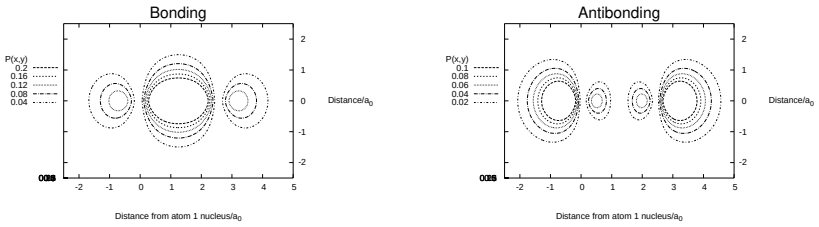

FIGURE 13. Sigma bonding and antibonding LCAOs of $2p_x$ orbitals: probability density contour maps in the xy plane

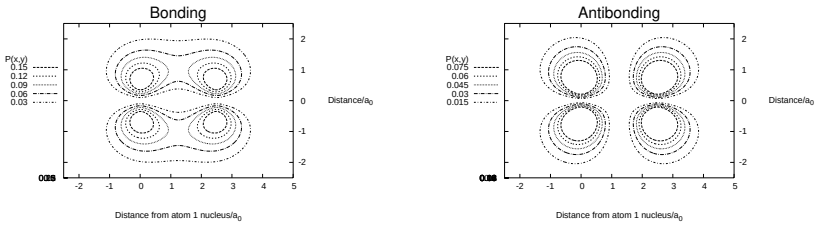

FIGURE 14. Pi bonding and antibonding LCAOs of $2p_y$ orbitals: probability density contour maps in the xy plane

when teaching organic chemistry that they teach it nevertheless. This may lead to questions of how their construction may be justified and what their wave functions look like. Their wave functions are given in table 4 and probability density contour maps of sp^2 orbitals are given in figure 16.

The bond angles in differently hybridised molecules can be predicted using Valence Shell Electron Pair Repulsion theory, and have been determined experimentally by x-ray diffraction (109° in methane, 120° in BF_3, *etc*). These bond angles are not consistent with the 90° bond angles between p orbitals. The angles are justified by the concept of orbital hybridisation, popular with organic chemists in particular. s and p orbitals are considered to "mix" to give these hybrids. What is this mixing?

We saw in section 2.4 that we can take linear combinations of the eigenfunctions with arbitrary constants in front of each eigenfunction, and the result is still a solution of the eigenvalue equation. Following the comparison of the addition of eigenfunctions to the addition of vectors in section 2.4, we can consider the p orbitals as vectors along

their given axis. Given that the eigenfunctions are all normalised, we can assume that the p orbital vectors are all the same length.

The hybridisation of a carbon atom involves the linear combination of the s orbital with $(3 - n)$ p orbitals where n is the number of pi bonds on the carbon atom (which may not exceed two).

In the case of sp^3 hybridisation, four bonds around carbon point to the corners of a tetrahedron. If we consider the carbon nucleus to be at the centre of a cube, then the bonds would point to four corners of the cube that are mutually diagonally opposite each other on each face. Considering the p orbitals to be vectors whose length is equal to half the length of an edge of the cube, we can construct the four hybrid orbitals as:

$$\mathrm{sp}^3(1) = N_s\mathrm{s} + N_p\mathrm{p}_x + N_p\mathrm{p}_y + N_p\mathrm{p}_z \tag{37a}$$

$$\mathrm{sp}^3(2) = N_s\mathrm{s} + N_p\mathrm{p}_x - N_p\mathrm{p}_y - N_p\mathrm{p}_z \tag{37b}$$

$$\mathrm{sp}^3(3) = N_s\mathrm{s} - N_p\mathrm{p}_x + N_p\mathrm{p}_y - N_p\mathrm{p}_z \tag{37c}$$

$$\mathrm{sp}^3(4) = N_s\mathrm{s} - N_p\mathrm{p}_x - N_p\mathrm{p}_y + N_p\mathrm{p}_z \tag{37d}$$

where the N represent normalisation constants. Since the x, y and z axes are equivalent in a tetrahedron, the normalisation constants in front of each p orbital are assumed to be equal. As well as being normalised, the hybrid orbitals should also be orthogonal to each other. To be orthogonal, the scalar (dot) product of any two of the sp^3 hybrids should come to zero. Any cross terms in the multiplication come to zero since the atomic orbitals are all defined to be orthogonal with one another. The dot product of any two different sp^3 hybrids gives the same expression from which the normalisation constants may be found:

$$< \mathrm{sp}^3 \,|\, \mathrm{sp}^{3\,\prime} >= 0 = N_s^2 < \mathrm{s} \,|\, \mathrm{s} > -N_p^2 < \mathrm{p} \,|\, \mathrm{p} > . \tag{38}$$

Since the atomic orbitals are normalised all the integrals come to 1, leaving $N_s^2 = N_p^2$. Normalisation of all the hybrids leads to the common expression, $N_s^2 + 3N_p^2 = 1$. These equations can be solved simultaneously, yielding $N_s = N_p = 1/2$. With the normalisation constants all equal to $\frac{1}{\sqrt{n}}$, where n is the number of normalised atomic orbitals in the linear combination, the hybrid orbital is evidently properly normalised. It is also evident that the s orbital makes up 1/4 of the probability density of the orbital, which is its fraction of the 4-orbital hybrid. The three p orbitals are equally weighted in the wave function as they are symmetrically equivalent in a tetrahedral environment.

Following the results from the previous paragraph, it is obvious that two sp hybrid orbitals, pointing along the z axis will have wave functions $|\,\mathrm{sp} >= \frac{1}{\sqrt{2}}(|\,\mathrm{s} > \pm |\,\mathrm{p}_z >)$, which are clearly normalised and orthogonal with one another.

The wave functions for the sp^2 hybrid orbitals are not quite so obvious. Following the arguments relating to sp^3 orbitals, the normalisation

constant for the s orbital component will be $\frac{1}{\sqrt{3}}$. The sum of the squares of the normalisation constants for the p orbitals in each hybrid must therefore come to 2/3. We define the three sp^2 orbitals to be in the xy plane such that one is pointing along the positive x axis, as shown in figure 15. The hybrid orbital pointing along the x axis will only have the p_x orbital combined with the s orbital. We can therefore immediately deduce that the normalisation constant in front of the p_x orbital in that hybrid is $\sqrt{2/3}$. In the other two sp^2 hybrid orbitals the normalisation constant in front of the p_x orbital must be negative and, due to the angles between the hybrids, will have the factor $\cos 60° = 1/2$. The normalisation constant in front of the p_y orbital will be positive in one of these hybrids and negative in the other. The angles dictate that a factor of $\cos 30° = \sqrt{3}/2$ appears with the p_y orbitals. Squaring and summing these trigonometric factors gives 1. As they account for two p orbitals the squares of these factors should sum to 2. This is achieved by multiplying these trigonometric factors by $\sqrt{2}$. Multiplying the trigonometric factors by the overall normalisation factor of $\frac{1}{\sqrt{3}}$ will therefore give the correct overall normalisation constants, which are collected in table 4. The reader is left to check that they are normalised and orthogonal.

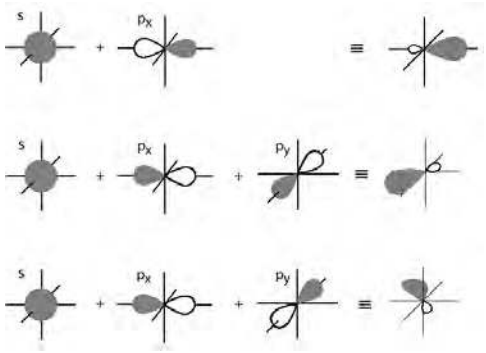

FIGURE 15. Sketches showing linear combinations of s and p orbitals that form the sp^2 hybrids

The geometry of the linear combinations for the sp^2 hybrid orbitals is shown in figure 15, which is a standard way of depicting the orbitals, with the shaded lobes having a positive phase. It is assumed that the s orbital has a positive phase, but this is not the case for 2s orbitals, where its radial node means that the exterior of the orbital (which will be overlapping with other orbitals) has a negative phase. Given that second-row elements most commonly exemplify these hybrid orbitals, the normalisation constant for the s orbital will have to be made negative so that the combinations of atomic orbitals follow the scheme in figure 15.

Figure 16 shows the probablility density functions in the xy plane using contour lines for the three sp^2 orbitals in a carbon atom using the linear combinations of atomic orbitals given in table 4.

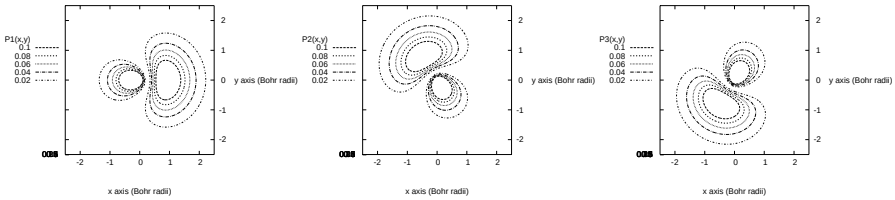

FIGURE 16. The three sp^2 hybrid orbitals: probability density contour maps in the xy plane

Hybrid orbital	Wave function
$sp^3(1)$	$(1/2)(-s + p_x + p_y + p_z)$
$sp^3(2)$	$(1/2)(-s + p_x - p_y - p_z)$
$sp^3(3)$	$(1/2)(-s - p_x + p_y - p_z)$
$sp^3(4)$	$(1/2)(-s - p_x - p_y + p_z)$
$sp^2(1)$	$(1/\sqrt{3})(-s + \sqrt{2}p_x)$
$sp^2(2)$	$(1/\sqrt{3})(-s - (1/\sqrt{2})p_x + \sqrt{3/2}p_y)$
$sp^2(3)$	$(1/\sqrt{3})(-s - (1/\sqrt{2})p_x - \sqrt{3/2}p_y)$
$sp(1)$	$(1/\sqrt{2})(-s + p_z)$
$sp(2)$	$(1/\sqrt{2})(-s - p_z)$

TABLE 4. The wave functions of all the sp^n orbitals for second-row elements

4.5. **Hybridised bonding and antibonding orbitals.** BF_3 is a classic example of a molecule with an sp^2 hybridised central atom, and is met by all students when studying VSEPR theory. Using the rule in section 4.4 one would expect the fluorine atoms to be sp^3 hybridised. However they may be considered to be sp^2 hybridised since there is also some pi bonding between a lone pair in a p orbital on each fluorine and the vacant p orbital on boron [7]. The average B–F bond energy in BF_3 is greater than any known single bond, at 646 kJ mol^{-1}; the B–F bond length is also surprisingly short [7], shorter than the C–F bond despite the smaller atomic radius of carbon.

Figure 17 shows the bonding and antibonding molecular orbitals in BF_3 from overlap of the sp^2 hybrid orbitals on boron and fluorine. The plot uses contour lines to visualise the probability density in the plane of the molecule. Electron density from the inner electrons on B and F, and from the pi interactions between boron and fluorine are not shown.

In the full molecular orbital treatment of a polyatomic molecule, all the atomic orbitals on all the atoms in the molecule need to be taken together, with their group theoretical label to determine which orbitals can interact. The overlap of hybridised orbitals is therefore a simplification, but very often a useful one to gain a reasonable general impression of the bonding.

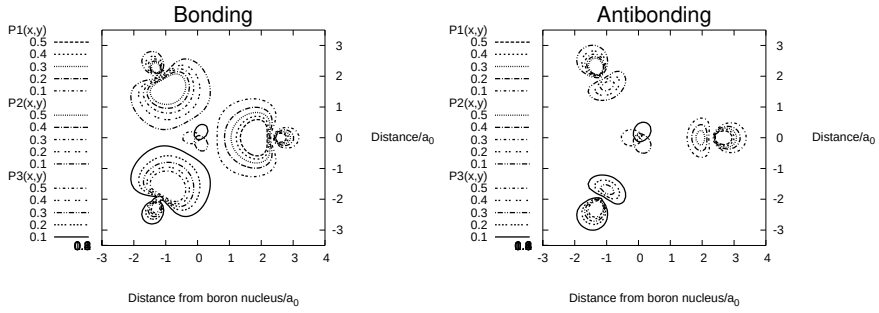

FIGURE 17. The three sigma bonds and the three sigma antibonds of BF_3 formed from overlap of sp^2 hybrid orbitals on boron and fluorine: probability density contour maps in the xy plane

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