

BONDING IN SOLIDS, STRUCTURAL AND CHEMICAL PROPERTIES

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Summary

Ultimately the physical properties of all materials are governed by the characteristics of the bonds between their constituent atoms. In all cases these bonds are simply a consequence of the different ways in which electrons can be distributed between the nuclei of solids. Here we approach this problem by solving the Schrödinger equation, approximately, for simple systems, thereby developing the framework that allows us to understand much more complex systems. Initially, we consider solutions for atoms, which provide us with the hydrogen-like orbitals. These building blocks are used to construct solutions for simple molecules, such as H_2 , F_2 , HF and NaF. Consequently, ideas such as ionicity, covalency, bonding and anti-bonding become clearly established. By considering larger molecules and hybridization, such models explain the extreme differences in the bonding exhibited by diamond and graphite. This leads to an understanding of how bands arise as the infinite limit of a local orbital model, which is then applied to metals and semiconductors. However, an alternative free electron wave model for metals is also introduced and developed. By considering how a periodic lattice potential modifies electron waves, we finally converge on a model for metals, which shows aspects of both approaches.

Often the dominant term in the cohesive energy of a solid is long range, e.g., as in ionic solids. It is therefore important to introduce the semi-classical Born model based on a long-range Madelung Coulomb sum and short-range parameterized potentials. Molecular solids also exhibit longer range interactions although these are because of dipole–dipole interactions, again adequately modeled using a semi-classical approach (or more directional hydrogen bonds). In all cases these models lend themselves to application within quantitative predictive computer simulation codes. An understanding of bonding in solids can thereby directly complement experimental endeavor.

1. Introduction

Each element is defined by its atomic number, n . These n electrons are acted on by a central electrostatic potential and consequently, they are confined to move within specific areas of space called orbitals. Pauli's exclusion principle requires that only two electrons occupy each orbital. Therefore, two atoms, whose n values differ by only one, may have quite distinctly different overall shapes. This is important, because the shape of an atom dictates what types of bonds it can form with its neighbors. Consequently, elements side by side in the periodic table (i.e., those whose n values differ by one) can have quite distinct elemental forms. For example, moving across the periodic table, at 300 K and one atmosphere pressure,

fluorine ($n = 9$) is a diatomic gas (F_2), neon ($n = 10$) is a monatomic inert gas but sodium ($n = 11$) is a soft metallic solid. Clearly if we are to understand bonding in solids, we must begin by understanding the shapes of atomic orbitals.

A knowledge of orbital shape is thus the point from which we begin to understand why different materials exhibit such diverse bonding characteristics. Indeed the bonds are described by molecular orbitals, which are constructed from the appropriate atomic orbitals. Typically we then categorize bonding types as: covalent, ionic, metallic and molecular. Unfortunately, this division conceals the more interesting fact that a pure bonding type is very unusual. In fact, simple covalency only occurs between isolated homonuclear pairs, such as in the diamond allotrope of carbon. Conversely, the graphite allotrope of carbon exhibits both distinct covalent and molecular bonding types in the same crystal structure. Furthermore, bonds between heteronuclear species are never purely covalent—they may range from polar covalent to highly ionic. Covalent and ionic bonding types are better considered as two extremes of the same process. A molecular orbital approach will allow us to understand why this is so.

It is intended that this article should present techniques or theories that are predictive. After all, macroscopic properties of materials are a consequence of atomic scale bonding processes. However, in many engineering applications, compositions are regulated to control processes that are occurring at grain boundaries or perhaps within submicron scale precipitates. The atomic processes that occur are highly complex and it is not usual to analyze them at the atomic bonding level, except in a superficial manner. As we continue the trend to engineer at smaller length scales, subtle differences in local atomic distributions will have important consequences to materials properties. The rationale for studying atomic scale bonding processes is that it should lead to the engineering of materials at the atomic scale.

2. Atomic Orbitals: Their Origin and their Shapes

2.1. The Four Quantum Numbers

Each atom is composed of a positively charged nucleus surrounded by a number of negatively charged electrons. The electrons occupy allowed states, i.e., they move within regions of space known as atomic orbitals. Each atomic orbital is uniquely characterized by three quantum numbers, n , ℓ and m_ℓ . However, the values that these quantum numbers may assume are restricted, i.e., there are quantum conditions.

The first or *principle* quantum number, n , may take any integer value, i.e., $n = 1, 2, 3, \dots$

The second quantum number, ℓ , identifies the magnitude of the angular momentum of the electron and ℓ may take values, $\ell = 0, 1, 2, 3, \dots$. However, the values of ℓ for each energy level are restricted by the n quantum number of the energy level since ℓ may never exceed $(n-1)$. Therefore the values that ℓ may take are $\ell = 0, 1, 2, \dots, (n-2), (n-1)$. Consequently for each value of n there are n number of allowed values of ℓ . By

convention, the allowed values of ℓ are designated by letters (see Table 1).

Angular momentum ℓ	0	1	2	3	4
Symbol	s	p	d	f	g

Table 1. The Allowed Values of Angular Momentum and their Symbol

Thus:

$n = 1, \ell = 0$	1s-orbital
$n = 2, \ell = 0$	2s-orbital
$n = 2, \ell = 1$	2p-orbital
$n = 3, \ell = 0$	3s-orbital
$n = 3, \ell = 1$	3p-orbital
$n = 3, \ell = 2$	3d-orbital

In addition to its restriction with respect to magnitude, the angular momentum is restricted with respect to its direction; space quantization. In other words, the angle that the angular momentum makes with respect to a given axis, by convention the z-axis, is quantized. The values of L_z are given in Eq. (1)

$$L_z = m_\ell \hbar \quad (1)$$

where $m_\ell = 0, \pm 1, \pm 2, \pm 3, \dots, \pm \ell$. Thus, for each value of the angular momentum, there are $(2\ell + 1)$ values of m_ℓ or, $(2\ell + 1)$ different orientations. Consequently for an s-orbital, since $\ell = 0, m_\ell = 0$. However, for a p-orbital, $\ell = 1$, so that $m_\ell = -1, 0$ or 1 , that is three p-orbitals. There are five d-orbitals.

In addition to its charge and mass, each electron exhibits an intrinsic property known as spin. The spin of an electron may either be $+\frac{1}{2}\hbar$, also known as *spin up* (where \hbar is Plank's constant divided by 2π) or $-\frac{1}{2}\hbar$, also known as *spin down*.

We now invoke the Pauli Exclusion Principle which states that “no two electrons may have the same set of four quantum numbers; n, ℓ, m_ℓ, s .” Therefore, each atomic orbital may contain no more than two electrons.

The next step in determining atomic structure of an atom is to know in which order the electrons fill the orbitals. This is known as the Aufbau or building-up principle and relates to the way that the electrons around an atom are built-up, in terms of their quantum numbers. That is, their order of occupation, which leads to the ground state or

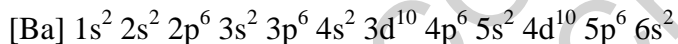
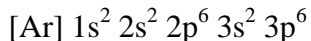
lowest energy configuration of the neutral atom. Initially the rule is quite simple. We start with the bare nucleus of atomic number Z , and allow the electrons to occupy orbitals of consecutively higher energy starting with $n = 1$ -orbitals then $n = 2 \dots$ For each value of n , the order of orbital energy is $s < p < d < f$ where $<$ implies more favourable, i.e., more negative. Thus the first is $1s$ then $2s$ then $2p$ then $3s$ then $3p$. Remember that each orbital can be occupied by two electrons, one with spin-up, one with spin-down, but that there are three p -orbitals so that the $2p$ -orbitals may contain up to six electrons.

Unfortunately once $3p$ is reached the situation becomes more complex. Although we would expect the $3d$ -orbitals to be occupied next, electron-electron repulsions interactions between the electrons in orbits changes the order of preference and the next orbitals to be filled are the $4s$ followed by the $3d$ and then $4p$. The order of occupation is shown in Table 2;

1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	5d	6p	7s	5f	6d
2	4	10	12	18	20	30	36	38	48	54	56	70	80	86	88	102	112
He	Be	Ne	Mg	Ar	Ca	Zn	Kr	Sr	Cd	Xe	Ba	Y	Hg	Rn	Ra	No	?

Table 2. Order of Occupation of Orbitals

Thus we can describe an atom in terms of its electron occupation.



One last question remains. What happens if there are less than six electrons available to fill all three $2p$ -orbitals? What is the distribution of the electron spin? In such circumstances, we invoke Hund's rule which states that "an atom in its ground state adopts a configuration with the greatest number of unpaired electrons." Thus if an orbital is unfilled (incomplete), the electrons in the unfilled orbital distribute themselves between the available orbitals.

One tool, which we will use to describe the distribution of electrons in atoms (and molecules), is the energy level diagram. In this, the energy of the orbital is designated by a horizontal line. The orbital with the lowest energy is at the bottom and that with the highest energy at the top. The number of electrons, which occupy that orbital is shown by the number of vertical lines. The spin of the electron is then identified by an arrowhead on the vertical line, thereby pointing either up or down. For example, a neutral manganese atom has the following electronic configuration: $[\text{Mn}] 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$. The corresponding energy level diagram is shown in Figure 1.



Figure 1. Energy Level Diagram for a Manganese Atom Showing the Electron Occupation.

2.2. The Schrödinger Equation

When a particle such as an electron is free it can exhibit any of a continuous range of energies. When it is confined, that is, acted on by a force, it may only be found in one of a discrete set of energy levels. This observation is utterly fundamental to all atomic structure, including atoms and molecules. It is a consequence of Heisenberg's uncertainty principle, Pauli's exclusion principle, and can be described by the mathematics of quantum mechanics using the Schrödinger equation.

Unfortunately it is not possible to solve the Schrödinger equation exactly, except in a few simple cases. However, the solutions for the hydrogen atom can be used to construct solutions for not only more complex atoms but also for complex molecules and even solids. Therefore, it is still very useful to consider the solution of the Schrödinger equation for hydrogen as this provides the basic building blocks (i.e., orbitals) with which we will be concerned in subsequent sections.

Nevertheless, a full derivation of the solution of the Schrödinger equation for hydrogen is beyond the scope of the present article (and is not necessary). However, we shall consider some aspects of the solution so that the origin of the atomic orbitals shapes will become apparent, as will the significance of the ℓ and m_ℓ quantum numbers. Full derivations for hydrogen are available in many advanced atomic theory textbooks.

2.2.1. Solutions to the Schrödinger Equation: The Wave Function

The Schrödinger equation is an eigenvalue equation so that it takes the form

$$\hat{H}\psi = E\psi \quad (2)$$

In equation 2 \hat{H} (known as the Hamiltonian operator) is composed of mathematical operations which are concerned with energy terms of the electrons, e.g., the kinetic and potential energies. When we solve this equation we find the functions, ψ , which when operated on by the Hamiltonian result in a single number, E , an energy, which multiplies the original function, ψ . In other words, ψ , the wave function, is a stationary state of the equation, a stable solution which is not altered by the mathematical operation \hat{H} . What this means physically is that we find the mathematical representation, ψ , for the electron orbiting around the nucleus. The wave function is the stable stationary state of the electron. The electron is allowed to exist in this orbital without alteration.

Clearly, the wave function will be of immense importance in much of what follows. Therefore we need to have a better understanding of exactly what it is. This was provided by Max Born, who suggested that if $\psi(r)$ is the amplitude of the wavefunction ψ at some point in space r , the probability of finding the particle within a small volume dt is proportional to $\psi^2 dt$. In other words, ψ^2 is the probability density and ψ is the probability amplitude.

Since the particle must be found somewhere in space, the integral over all space is equal to 1.

$$\int \psi^2 dt = 1 \quad (3)$$

Therefore a wavefunction must be finite at all points in space, but it may be negative, as indicated in Figure 2.

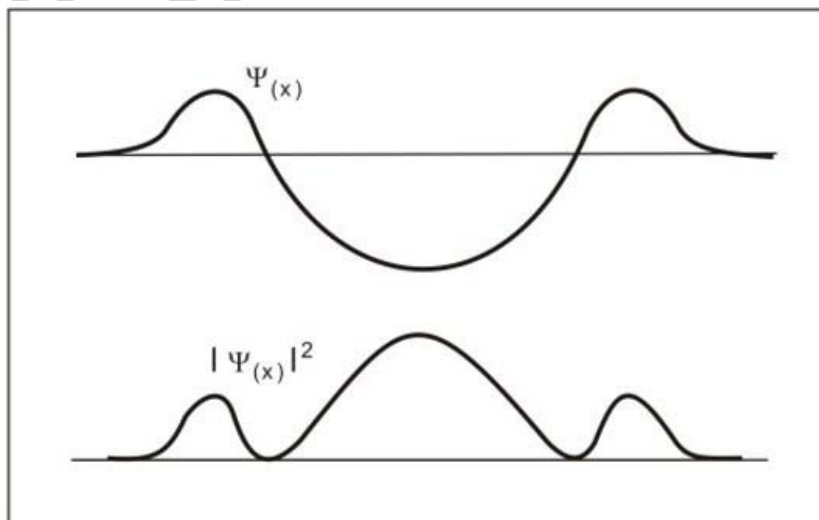


Figure 2. A Wavefunction ψ and its Corresponding Probability Amplitude ψ^2

2.2.2. Hydrogen as a Central Force Problem

The hydrogen atom is a two-body problem; a positive nucleus attracting a negative electron. However, by fixing the origin at the nucleus and by noting that the electron is subject to a central conservative potential, we can consider the problem to be a one-body problem; that of an electron moving under the influence of a spherically symmetric potential.

Since we are considering a central force, the influence that the nucleus has on the electron is only a function of how far radially the electron is from the nucleus. Thus we can write, $V(r)$; that is, the potential is only a function of r . This potential is represented in Figure 3. The smaller the value of r , the more negative the potential energy $V(r)$.

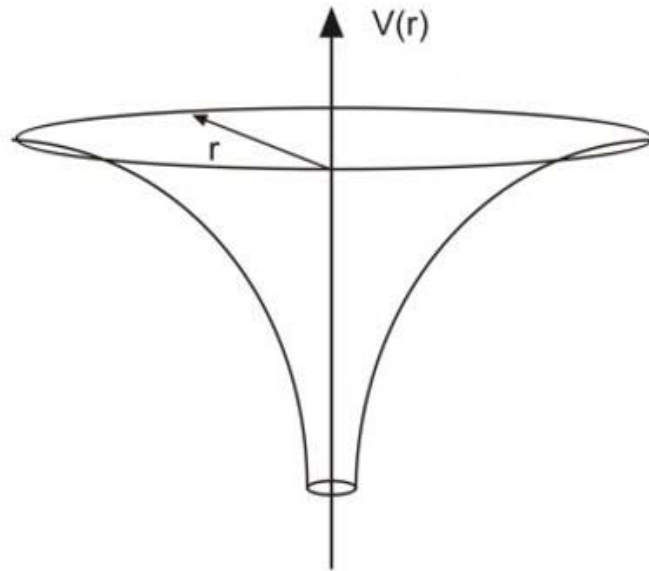


Figure 3. The Potential Energy $V(r)$ Acting on an Electron by the Nuclear Charge. Clearly given the spherical symmetry of the system, it is much easier to solve the hydrogen atom problem using the spherical polar coordinate system, r , θ , ϕ . Schrödinger's equation for the center of mass hydrogen atom problem therefore becomes

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi) \quad (4)$$

where

$$\frac{\hbar^2}{2\mu} \nabla^2$$

is the kinetic energy operator for the electron (μ is the electron mass) and $V(r)$ the

potential energy. We then make a simplification; the wavefunction is rewritten as a product of two factors, $\Psi(r,\theta,\phi) = R(r) Y(\theta,\phi)$, where $R(r)$ is the radial component and $Y(\theta,\phi)$ the angular component.

2.2.3. The Angular Component

It transpires that in a central-force problem, the angular part of the wave function is determined entirely by the magnitude, $|L|$, and the z-component, L_z , of the angular momentum of the electron. The reason we must specify both the magnitude and z-component is because the electron's angular momentum is a vector quantity, which may be pointing in a direction other than that of the z-direction. The magnitude of the angular momentum is determined by the ℓ quantum number since $L^2 = \ell(\ell + 1)\hbar^2$ and the z-component by is determined by m_ℓ . The resulting functions $Y(\theta,\phi)$ are called spherical harmonics and to indicate their origin we designate then

$$Y_{\ell,m_\ell}(\theta,\phi).$$

When $\ell = 0$ this is called the s-state. Notice that in this case the function

$$Y_{\ell,m_\ell}(\theta,\phi)$$

is a constant, that is, it is independent of angle; s-states are spherically symmetric. The polar diagram in Figure 4 shows that the locus of points of equal value form a sphere. This is reasonable since, if $\ell = 0$, i.e., the angular momentum of the electron is zero, there is no preferred orientation of the electron's orbit.

When $\ell = 1$ the three p-orbitals (see Figure 5) are formed which are characteristic of the three allowed orientations of the angular momentum corresponding to $m_\ell = -1, 0, 1$.

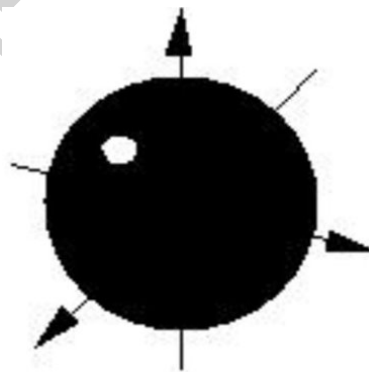


Figure 4. Angular Distribution of Electron Density in an s-Orbital

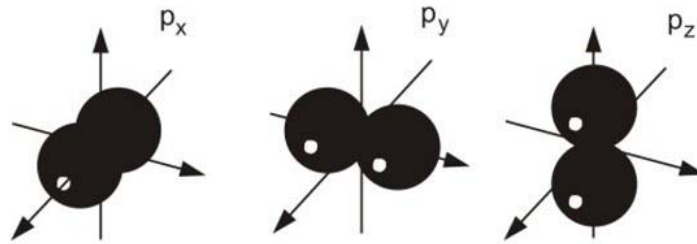


Figure 5. Angular Distribution of Electron Density in the p-Orbitals

When $\ell = 2$ the five d-orbitals are formed because there are five allowed orientations of the angular momentum corresponding to $m_\ell = -2, -1, 0, 1, 2$. The usual way in which the d-orbitals are drawn is shown in Figure 6. Although these do not correspond to the specific values of m_ℓ (they are actually linear combinations of the specific functions) this representation is more physically and chemically useful.

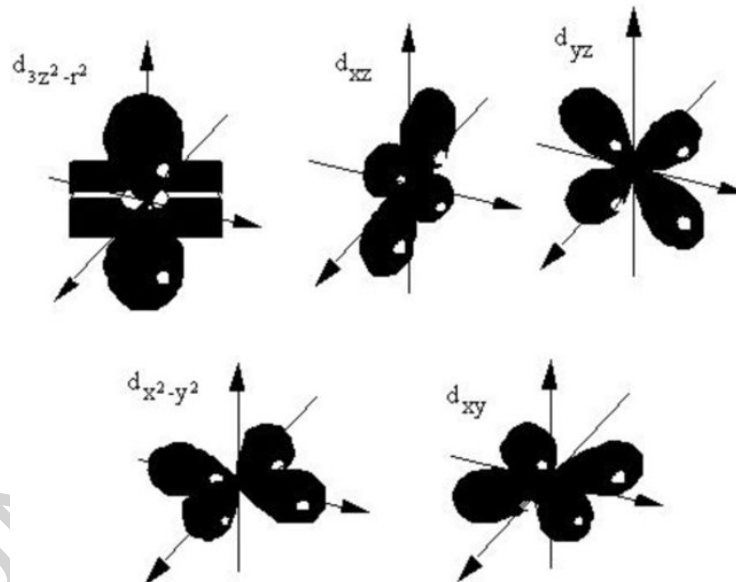


Figure 6. Angular Distribution of Electron Density in the d-Orbitals

What we have drawn above is the shape of the hydrogen wave functions from the point of view of their angular dependence. That is, how the wave functions look if we keep a constant radius from the nucleus. This will be very useful when we consider the angular orientation of bonds, since bonds are built up from different orbitals coming together. Clearly an s-orbital will not care about which orientation another atom is bonding from but p and d-orbitals will show specific angular preferences.

2.2.4. Parity

One property of the spherical harmonics that we must be aware of concerns their parity. Consider the P_x function. The function seems to show mirror symmetry about the y-axis. However, closer inspection reveals that at each positive values of x, the function has the same magnitude but opposite value as for the corresponding negative x value

(remember the value of the wave function can be positive or negative). Clearly an s-orbital has the same magnitude and sign at opposite sides of the origin. The d-orbitals show the same magnitude and sign on opposing points across the origin but different parity between x and y (or x and z or y and z) directions. Parity has important consequences for chemical bonding, as we shall see in Section 3.

To distinguish the sides of the wavefunction, they are represented in two dimensions as shown in Figure 7, where the hatched lines indicate opposite parity.

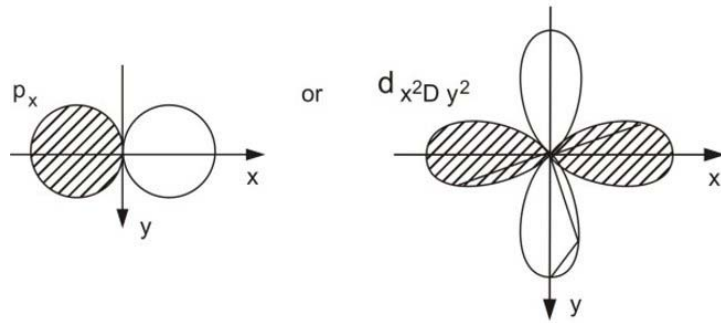


Figure 7. Representation of Parity in p- and d-Orbitals

2.2.5. The Radial Component

In many textbooks, atomic orbitals are only represented in terms of their angular component, as in the diagrams above. However, as stated in Section 2.2.2, the wave function is a product of both angular and radial components. Therefore we now consider the radial component.

It is possible to rewrite the Schrödinger equation, so that we explicitly consider the radial dependence and form a radial eigenvalue equation. The potential energy part of this equation, P , has the form:

$$P(r, \ell) = \frac{-Ze^2}{4\pi\epsilon_0 r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \quad (5)$$

What Eq. (5) describes is the total potential acting on an electron and is a function of the distance from the nuclear, r and the angular momentum of the electron, ℓ . The first term in this equation is the Coulomb interaction and the second term is known as the centrifugal potential. The first term has a negative sign indicating that it is responsible for attracting electrons to the positive charge of the nucleus. The second term has a positive value and clearly repels electrons away from the nucleus. For orbitals which have $\ell = 0$ (i.e., an s-orbital) this repulsion is zero and their orbitals are described as “penetrating.” Orbitals with higher ℓ values (e.g., p- and d-orbitals) are repelled more from the nuclear region.

The full radial eigenfunctions, i.e., the radial components of the wave function, $R(r)$, are

as represented in Figure 8.

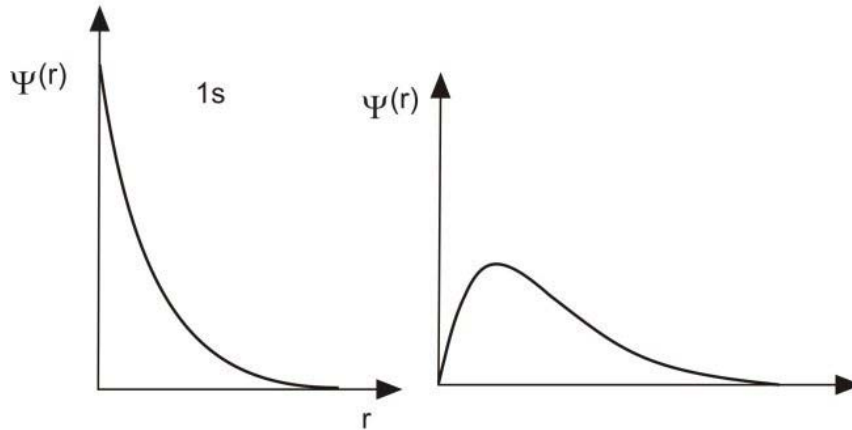


Figure 8. Radial Distribution of Electron Density in 1s- and 2p-Orbitals

Note that for the 1s-orbital $\psi(r)$ has a positive value when $r = 0$ whereas for 2p, $\psi(r) = 0$ when $r = 0$.

2.2.6. Energy Level Values

Finally, we should go back to the idea of orbital energy. For hydrogen, the energy of an electron in an orbital (the eigenvalue) is given by

$$E_n = \frac{-13.6}{n^2} \text{ electron Volts (eV)} \quad (6)$$

We can now draw these energies onto the potential energy function (see Figure 9). Remember, when $n = \infty$, it follows that $E_\infty = 0$. This is the vacuum level, when the electron has effectively escaped from the nucleus.

Note how the energy levels depend only on the n quantum number. Therefore in hydrogen the 2s and 2p-orbitals have the same energy as do the 3s-, 3p-, and 3d-orbitals.

2.3. Atoms with more than One Electron

As soon as we try to solve Schrödinger's equation for atoms with more than one electron, the situation becomes much more complex. The problem is that each electron experiences an electrostatic potential from not only the nucleus but from the other electrons. With hydrogen, we defined the center of the problem to be the nucleus so that only one particle was effectively moving: the electron. With more than one electron, the motion of the particles becomes an issue (this is known as correlation). In addition, since the electrons are indistinguishable, they may exchange with each other. The exchange interaction must also be taken into consideration.

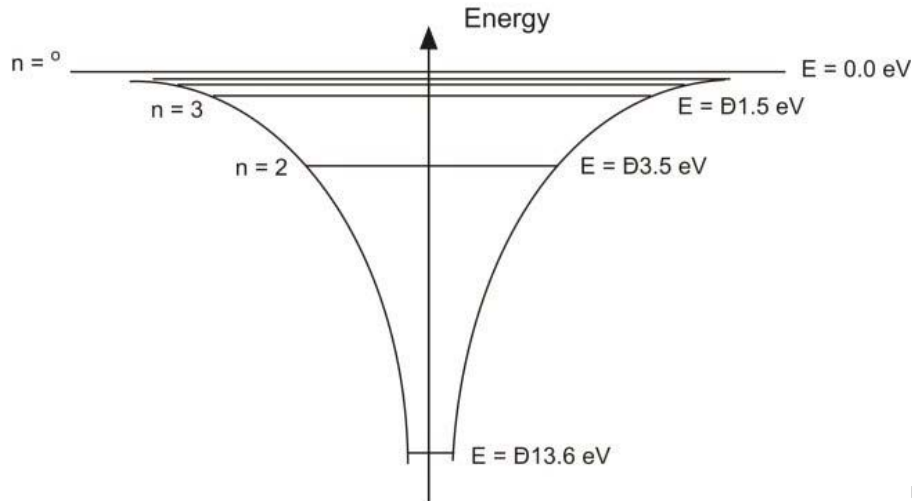


Figure 9. Potential Energy Well for an Electron with Superimposed Energy Levels

Fortunately, we are able to use an important simplification. The orbitals in which the electron reside have the same basic shape (i.e., functional form) as their associated hydrogen-like equivalents. This approximation is so good that we often forget that it is only approximately true. Using this, we can solve Schrödinger's equation (although numerically, not analytically) for atoms with even high atomic numbers. Of course, since the Z value of the nucleus changes, the orbital energies of these hydrogen-like solutions also change and by comparing with experiment we are able to see how good an approximation this is.

One important consequence of having more than one electron in an atom is that the 2s- and 2p-orbitals no longer have the same orbital energy. The reason for this lies with the different extents to which the 2s- and 2p-orbitals are able to penetrate the nucleus. The 2s-orbital is penetrating and spends more time closer to the nucleus. Consequently it screens the 2p electron which is not able to get so close to the nucleus. The 2p electron sees both the attractive nuclear charge and the repulsive 2s electron charge. The 2p electron energy is therefore slightly higher than the 2s.

For the same reason the energy of the 3s-orbital is lower than the 3p which is lower than the 3d-orbital. In other words the orbital energy depends on both the n and ℓ quantum numbers.

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Biographical Sketch

Robin Grimes is Reader in atomistic simulation at Imperial College in London, UK, where he has been since 1995. Prior to that he was assistant director of the Davy Faraday Research Laboratory at the Royal Institution of Great Britain. He spent the academic year 2000/2001 as Bernd T. Matthias Scholar at Los Alamos National Laboratory, US. His primary research interest is in the use of computer models to predict structural and dynamic properties of ceramic materials at the atomic level. Such models have been used to investigate a wide range of problems in: electronic and structural ceramics, catalysts, nuclear fuel, nuclear waste forms, fast ion conducting membranes and cement phases. He has authored over 110 publications in international journals.