The emission spectrum of a hydrogen atom consists of discrete frequencies, \( \nu \), of light forming the Rydberg series of groups of regular pattern obeying the relationship, \( \nu = R \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \) with integer values of \( n_i \) and \( n_f \).

The solution to the Schrödinger equation for a single electron moving in the attractive Coulombic potential of a positively charged nucleus produces quantized energy levels whose energy values are inversely proportional to the square of an integer quantum number, \( n \). The energy difference between pairs of these energy levels exactly accounts for the Rydberg series of the hydrogen atom emission spectrum.

The wavefunction solutions for an electron in an atom are called atomic orbitals. The boundary conditions impose three quantum numbers on the orbitals: principal quantum number, \( n \) \((1, 2, \ldots)\); orbital angular momentum quantum number, \( l \) \((0, 1 \ldots n - 1)\); magnetic quantum number, \( m_l \) \((-l, \ldots 0, \ldots l)\). All orbitals with the same value of \( n \) constitute a shell. Orbitals with different values of \( l \) constitute sub-shells of the shell. Orbitals with \( l = 0, 1, 2, 3 \) are called \( s, p, d, f \) orbitals respectively. All orbitals in a sub-shell of a hydrogenic atom are degenerate.

All \( s \) orbitals are spherically symmetric about the center of the atom whereas the shapes of \( p \) and \( d \) orbitals vary with angular direction. The three \( p \) orbitals have lobes pointing along the \( x, y, \) and \( z \) axes, respectively. The five \( d \) orbitals have more complex angular shapes. The radius of maximum probability of electron location in a shell of \( s, p, \) or \( d \) orbitals increases with principal quantum number.

**Related topics**
- Quantization of energy and particle-wave duality (G3)
- The wave nature of matter (G4)
- Many-electron atoms (G6)
- Valence bond theory (H2)
- Molecular orbital theory of diatomic molecule I (H3)

A hydrogen atom emission spectrum is obtained by passing an electric discharge through a tube of low-pressure hydrogen gas (to form excited hydrogen atoms) and dispersing the emitted light into its constituent wavelengths using a prism or diffraction grating. The resulting spectrum consists of light emitted at discrete frequencies only. The emitted frequencies, \( \nu \), occur in distinct groups with a regular pattern in different regions of the electromagnetic spectrum (Fig. 1). The frequencies conform to a very simple expression:

\[
\nu = R \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad n_i = 1, 2, \ldots \quad n_f = (n_i + 1), (n_i + 2), \ldots
\]
The sequence is known as the Rydberg series and the quantity $R_n = 109,677 \text{ cm}^{-1}$ is called the Rydberg constant. The emission with frequencies corresponding to $n_1 = 1$ is called the Lyman series and occurs in the ultraviolet. The Balmer series ($n_1 = 2$) occurs in the visible region. The Paschen, Brackett and Pfund series ($n_1 = 3, 4, 5$, respectively) are in the infrared.

The existence of discrete spectroscopic frequencies is evidence that the energy of the electron in the hydrogen atom is quantized. A photon of light is emitted when the electron moves from a higher to a lower energy level separated by energy difference, $\Delta E = h\nu$.

The Rydberg series of lines in the hydrogen emission spectrum is accounted for by solving the Schrödinger equation for the electron in the hydrogen atom. The potential energy $V$ of an electron (one negative unit of elementary charge) at a distance $r$ from a central nucleus of positive charge $Ze$ ($Z$ is the atomic number) is described by the Coulomb potential:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

where $\varepsilon_0$ is the vacuum permittivity. For hydrogen, $Z = 1$. The minus sign indicates attraction between the opposite charges of the electron and the nucleus. $V$ is zero when the electron and nucleus are infinitely separated and decreases as the particles approach.

The Schrödinger equation for a single particle moving in this potential energy can be solved exactly. The imposition of appropriate boundary conditions (that the wavefunctions approach zero at large distance) restricts the system to certain allowed wavefunctions and their associated energy values. The allowed quantized energy values are given by the expression:

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 \hbar^2 n^2} \quad n = 1, 2, \ldots$$

where $\mu = m_e m_n / (m_e + m_n)$ is the reduced mass of the electron $m_e$ and nucleus $m_n$. The energy level formula applies to any one-electron atom (called hydrogenic atoms), e.g., H, He$^+$, Li$^+$, Be$^+$, etc.

The difference between any pair of energy levels in a hydrogenic atom is:

$$\Delta E = E_n - E_{n'} = \frac{\mu e^4 Z^2}{8\varepsilon_0^2 \hbar^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

and the values of the physical constants give exact agreement (using appropriate units) with the Rydberg constant derived experimentally from the frequencies of the lines in the hydrogen emission spectrum ($Z = 1$), $\mu e^4/8\varepsilon_0^2 \hbar^2 = hcR_n$.

The distribution of energy levels for the hydrogen atom:
the quantity $R_n = \frac{\alpha}{n}$ with frequencies in the ultraviolet. Paschen, Brackett, and CIK that the energy of light is emitted in levels separated by

-\text{um is accounted for hydrogen atom. The transition charge) at a zero of the atomic number.}

The minus sign indicates the energy of the nucleus. The energy level decreases as the potential energy increases (that is rights the system to values. The allowed

-\text{m}, and nucleus $m_e$ (called hydrogenic) hydrogenic atom is:

\text{atomic quantum numbers and orbitals}

The full solution of the Schrödinger equation for hydrogenic atoms contains three different quantum numbers to specify uniquely the different allowed wavefunctions and energies of the states of the electron. The principal quantum number, $n$, is the only one of the three to appear in the formula for the energy of the various allowed states, and is sufficient to explain the Rydberg series of the hydrogen atom emission spectrum.

\[ E_n = -\frac{\hbar c R_H}{n^2} \quad n = 1, 2, \ldots \]

is shown in Fig. 2. The quantum number $n$ is called the principal quantum number. The energies are all negative with respect to the zero of energy at $n = \infty$ which corresponds to the nucleus and electron at infinite separation. The energy of the ground state (the state with the lowest allowed value of the quantum number, $n = 1$) is:

\[ E_1 = -\hbar c R_H \]

and is an energy $\hbar c R_H$ more stable than the infinitely separated electron and nucleus. The energy required to promote an electron from the ground state ($n = 1$) to infinite distance from the nucleus ($n = \infty$) is called the ionization energy, $I$. For hydrogen, $I = \hbar c R_H = 2.179 \times 10^{-18}$ J, which corresponds to 1312 kJ mol$^{-1}$ or 13.59 eV.

\[ \text{Fig. 2. The energy levels of the hydrogen atom expressed in units of the Rydberg constant $R_H$, relative to a zero energy of infinitely separated proton and electron.} \]

The energy levels in Fig. 2 are widely spaced at small values of $n$ but converge rapidly as $n$ increases. At small $n$ the electron is confined close to the nucleus by the electrostatic charge and the energy levels are widely spaced as for a particle in a narrow box. At large $n$ the electron has sufficient energy to move at large distances from the nucleus and the energy levels are closer together like those of a particle in a large box (see Topic G4).
In addition to the principal quantum number, \( n \) (= 1,2,3...) are the orbital angular momentum quantum number, \( l \), which takes the values, \( l = 0,1,2...(n-1) \) and the magnetic quantum number, \( m_l \), which takes the values, \( m_l = -l, -(l-1), ... (l-1), l \). Therefore, for a given value of \( n \) there are \( n \) allowed values of \( l \), and for a given value of \( l \) there are \((2l+1)\) allowed values of \( m_l \). For example, when \( n = 2 \), \( l \) can have the value 0, for which \( m_l \) can have the value 0 only, or 1, for which \( m_l \) can have the values \(-1, 0 \) and \( 1 \).

Each wavefunction, which is specified by a unique set of the 3 quantum numbers, is called an atomic orbital. All orbitals with the same principal quantum number \( n \) are said to belong to the same shell of the atom. Orbitals with the same value of \( n \) but different values of \( l \) are known as the sub-shells of the given shell. The sub-shells are usually referred to by the letters \( s \) (for sub-shells with \( l = 0 \)), \( p \) (for sub-shells with \( l = 1 \)), \( d \) (for sub-shells with \( l = 2 \)), \( f \) (for sub-shells with \( l = 3 \)) and \( g, h, j,... \) etc. for larger values of \( l \), if required. Thus the \( n = 2 \) shell contains four orbitals (sub-shells), one \( s \) orbital and three \( p \) orbitals. Electrons that occupy an \( s \) orbital are called \( s \) electrons. Similarly, electrons can be referred to as \( p, d, ... \) electrons.

A fourth quantum number, the electron spin quantum number, \( m_s \) is required to uniquely specify each electronic wavefunction. This quantum number can take the value \(+\frac{1}{2} \) or \(-\frac{1}{2} \) (see Topic G6). No two electron wavefunctions can have the same four quantum numbers so each atomic orbital can accommodate a maximum of two electrons. The pattern of allowed combinations of atomic quantum numbers is shown in Table 1.

<table>
<thead>
<tr>
<th>Shell</th>
<th>Sub-shell</th>
<th>Orbitals</th>
<th>Maximum no. of electrons per sub-shell</th>
<th>Maximum no. of electrons per shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 4 )</td>
<td>( l = 3 )</td>
<td>( 4f )</td>
<td>(-3, -2, 1, 2, 3 )</td>
<td>14</td>
</tr>
<tr>
<td>( l = 2 )</td>
<td>( 4d )</td>
<td>(-2, 1, 2 )</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>( l = 1 )</td>
<td>( 4p )</td>
<td>(-1, 1 )</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( l = 0 )</td>
<td>( 4s )</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( n = 3 )</td>
<td>( l = 2 )</td>
<td>( 3d )</td>
<td>(-2, 1, 2 )</td>
<td>10</td>
</tr>
<tr>
<td>( l = 1 )</td>
<td>( 3p )</td>
<td>(-1, 1 )</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( l = 0 )</td>
<td>( 3s )</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( n = 2 )</td>
<td>( l = 1 )</td>
<td>( 2p )</td>
<td>(-1, 1 )</td>
<td>6</td>
</tr>
<tr>
<td>( l = 0 )</td>
<td>( 2s )</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( n = 1 )</td>
<td>( l = 0 )</td>
<td>( 1s )</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Only hydrogenic atoms have sub-shells that are degenerate (of the same energy). For many-electron atoms the energy of the orbital (wavefunction) depends on both \( n \) and \( l \) so each sub-shell has different energy (Topic G6).

In general, the mathematical equation of each atomic wavefunction contains a radial part, describing the value of the wavefunction as a function of radial distance from the center of the atom, and an angular part, describing the value of the wavefunction as a function of all angles about the center, i.e., the value of the wavefunction at all points on the surface of the sphere at a given radius, \( r \).

For the 1s orbital \((n = 1, l = 0, m_s = 0)\) the mathematical form of the wavefunction is:
\( n = 1, 2, 3, \ldots \) are the values which take the principal quantum number, \( m_n \), which takes the value of \( n \) and \( l + 1 \) allowed values of \( m_l \), which can have the value 1.

- A set of the 3 quantum numbers with the same principal quantum number, \( n \), determines a sub-shell. The letters \( s \) (for sub-shells with \( l = 0 \)), \( p \) (for \( l = 1 \), if required). Thus the \( 1s \) and three \( 2p \) orbitals. Similarly, electrons can

<table>
<thead>
<tr>
<th>Quantum number, ( m_n )</th>
<th>32</th>
<th>18</th>
<th>8</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum no. of electrons per shell</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The angular dependence of the boundary surface of the hydrogen \( 1s \) orbital is given in Fig. 3.

\[ \psi = e^{-\frac{r}{a}} \]

where \( a \) is a constant known as the Bohr radius. The wavefunction contains no angular dependence so it has the same shape (an exponential decrease) in all directions from the center of the atom. For this reason the \( 1s \) orbital is called a spherically symmetrical orbital. The shape of the boundary surface (within which there is 95% probability of finding the electron) for the \( 1s \) orbital is shown in Fig. 3.

For the radial part of the wavefunction, the probability of finding the electron in the region between \( r \) and \( r + \delta r \) is given by:

\[ \text{radial probability distribution function} = 4\pi r^2 \psi^2 \delta r \]

where \( 4\pi r^2 \delta r \) is the volume of the spherical shell of thickness \( \delta r \) at radius \( r \). A plot of the radial probability distribution function for the \( 1s \) orbital is included in Fig. 4. The important feature of the radial probability distribution function is that it passes through a maximum. The location of the maximum indicates the most probable radius at which the electron in the orbital will be found. For a hydrogen \( 1s \) orbital the maximum occurs at the Bohr radius, \( a_0 \), which is 53 pm. As with all atomic orbitals, there is zero probability of finding the electron at the nucleus (\( r = 0 \)).

A \( 2s \) orbital (\( n = 2, l = 0, m_l = 0 \)) also has a spherically symmetric wavefunction. However, the radial wavefunction differs from that of the \( 1s \) orbital in that

\[ n = 1 \]

\[ n = 2 \]

\[ n = 3 \]
it passes through zero before it starts to decay to zero at large distances. The corresponding radial probability distribution function (shown in Fig. 4) therefore has a radius at which there is zero probability of finding the 2s electron. This is called a radial node. The radius at which the 2s electron is most likely to be located is greater than that for the 1s orbital, as expected for an electron possessing greater energy to overcome the nuclear attraction. The pattern repeats for the radial probability distribution of a 3s orbital which has two radial nodes and a yet larger radius for the most probable location of the electron (Fig. 4).

The angular wavefunctions of all p orbitals (orbitals with \( l = 1 \)) have two lobes pointing in opposite directions with a nodal plane passing through the center of the atom (Fig. 5). Consequently, unlike s orbitals, p orbitals are not spherically symmetrical and this is an important feature when considering the different types of bonds that can exist between atoms (see Topics H2–H4). A p sub-shell consists of three different types of p orbital (corresponding to \( m_l = -1, 0, +1 \)) and the three orbitals are normally represented at right angles to each other with the lobes pointing along each of the \( x, y, \) and \( z \)-axes for the \( p_x, p_y, \) and \( p_z \) orbitals, respectively. The radial probability distribution function along the axis of each 2p orbital does not contain a radial node; the radial probability distribution function of the 3p orbital contains one radial node, and so on (Fig. 4).

The five d orbitals (orbitals with \( l = 2, m_l = -2, -1, 0, 1, 2 \)) also have non-spherically symmetric shapes. The boundary surfaces are shown in Fig. 6. The \( n = 3 \) shell is the first shell that contains d sub-shells. There is no radial node in the radial probability distribution function along the axis of these orbitals (Fig. 4).
**H1 ELEMENTARY VALENCE THEORY**

**Key Notes**

Valence theories attempt to describe the number, nature, strength and geometric arrangements of chemical bonds between atoms. Although they have been superseded by more sophisticated theories, Lewis theory and VSEPR theory provide two complementary approaches to bonding which remain useful for elementary descriptions of simply bonded molecules.

Lewis theory is a primitive form of valence bond theory, with atoms forming bonds by sharing electrons. No attempt is made to describe the three-dimensional geometric shape of the molecule. The main group elements tend to adopt inert gas electron configurations (octets), although some elements, such as boron or beryllium are energetically stable with incomplete octets. Many larger elements display hypervalency, where it is energetically favorable for more than eight valence electrons to be held in an expanded octet.

Valence shell electron pair repulsion (VSEPR) theory explains the shapes of molecules by focusing on the bonding orbitals around each atom in isolation. VSEPR dictates that the geometry which maximizes the distances between the electron pairs in the orbitals is adopted. The basic geometry from the minimization of electron-electron repulsion is modified by the differing repulsion strengths of bonding and non-bonding pairs. In ammonia, NH₃, for example, there are four valence shell pairs, giving an underlying tetrahedral geometry, but the greater repulsive effect of the non-bonding pair forces the bonding pairs closer to one another than in the ideal tetrahedral geometry.

**Related topics**

- Many electron atoms (G6)
- Valence bond theory (H2)
- Molecular orbital theory of diatomic molecules I (H3)

**Valence theories**

Valence theories attempt to describe the number, nature and strength of chemical bonds between atoms. It also describes the geometric arrangement of the bonds, and so the shapes of molecules. The more sophisticated valence theories yield information about the electrical, magnetic, and spectroscopic properties of molecules.

Elementary valence theories invoke two principal bond types. In ionic bonding, electrostatic interactions generate bonds between ions formed by electron transfer from one element to the other. In covalent bonding two elements are held together by shared electrons in order that both may adopt an energetically favorable electron configuration. In reality, both are extreme forms
of the same bonding phenomenon. Pure covalent bonds are formed by elements with identical electronegativities, with more ionic bonding character being introduced to the bond as the electronegativity difference between the elements increases (see Topic H4). Even in extreme cases of ionic bonding, the degree of covalent character may still be quite high.

Two complementary theories were originally developed to explain the number and nature of covalent bonds (Lewis theory) and the shapes of molecules (VSEPR theory). More sophisticated theories have superseded these approaches for detailed investigations, but they remain useful in semi-empirical and non-rigorous discussions of molecular bonding.

**Lewis theory**

The Lewis theory of covalent bonding may be regarded as an elementary form of valence bond theory. It is nonetheless useful for describing covalent molecules with simple covalent bonds, and works successfully in describing the majority of, for example, organic compounds. Lewis theory recognizes both the free energy gains made in the formation of complete atomic electron shells, and the ability of atoms to achieve this state by sharing electrons. The sharing process is used as a description of covalent bonds.

The atoms are firstly drawn so as to represent their relative arrangement, with electron pairs (marked as pairs of dots) between neighboring atoms to indicate a shared bonding electron pair. No attempt is made to describe the three-dimensional geometric shape of the molecule. Multiple bonds are represented by two or three electron pairs as appropriate (Fig. 1a). Further electrons are added to each atom, so as to represent the non-bonding electrons and so

![Diagram](image)

Fig. 1. (a)–(c) Development of a Lewis bonding scheme for HCONH₂. Examples of (d) hyper-valency, and (e) resonance hybridization.
formed by elements the degree of an elementary form in describing the sharing ams to indicate the three-bonds are represented by electrons. The sharing relative arrangement, bonding covalent molecule in isolating, and describes the geometry of the bonds and non-bonding electron pairs around it. The basic assumption is that the electron pairs around an atom, both bonding and non-bonding, will adopt a geometry which will minimize repulsive forces by maximizing the distances between pairs.

The precise geometry of electron pairs around a central atom depends first of all upon the number of electron pairs which are present. For certain numbers of electron pairs (2, 3, 4, 6), it is possible to adopt a geometry in which the pairs are equidistant. For atoms with 5 or 7 electron pairs, this is not possible, and the maximum separation involves some compromise (Table 1).

Table 1. The dependence of molecular geometry on the number of electron pairs

<table>
<thead>
<tr>
<th>No. of electron pairs</th>
<th>Geometry</th>
<th>Interbond angles</th>
<th>Arrangement</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>180°</td>
<td>O-O</td>
<td>BeCl₂</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>120°</td>
<td></td>
<td>BF₃</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>109.5°</td>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramid</td>
<td>120° and 90°</td>
<td></td>
<td>PF₅</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>90°</td>
<td></td>
<td>SF₆</td>
</tr>
<tr>
<td>7</td>
<td>Pentagonal bipyramid</td>
<td>90° and 72°</td>
<td></td>
<td>IF₇</td>
</tr>
</tbody>
</table>

Examples of (d) hyper-
The basic geometry is modified by the variations in repulsion strengths between the electron pairs. Because the charge in bonding pairs is somewhat offset by the presence of the bonded nuclei, the repulsion increases in the order:

bonding pair:bonding pair < non-bonding pair:bonding pair < non-bonding pair:non-bonding pair

In determining the geometry of neighboring atoms around a central atom, the number of electron pairs is ascertained, so giving the underlying geometry. The pairs are then arranged so as to give the maximum distance between non-bonding pairs, giving the actual geometry of the neighboring bonded atoms. In CH₄, the bonding electron pairs adopt a perfect tetrahedral arrangement (Fig. 2a). In ammonia, NH₃, whilst there are four valence shell pairs, giving an underlying tetrahedral geometry, the greater repulsive effect of the non-bonding pair forces the bonding pairs closer to one another than in the ideal tetrahedral geometry (Fig. 2b). For a tetrahedral arrangement of four bonding pairs, the bond angle is 109.5°. With one non-bonding electron pair, this reduces to 107.3°, and with two non-bonding electron pairs (e.g. water, H₂O), the angle is further reduced to 104.5° (Fig. 2c).

A multiple bond, representing two or more electron pairs, is treated as a single electron pair, but with a greater electron density, and so has a greater electron repulsive effect than a non-bonding pair.

Fig. 2. VSEPR and the geometric arrangement of bonds in molecules with non-bonding electrons.
**H2 Valence Bond Theory**

**Key Notes**

Valence bond theory focuses attention on formation of the individual bonds in molecules. Bonds are generated from combinations of the atomic orbitals from each of the bonding atoms, and the bond is mathematically described as a function of these atomic orbitals. Where the resulting bond has cylindrical symmetry about the bond axis, it is termed a σ (sigma) bond. Elements with accessible p orbitals may generate bonds by sidelong overlap of the orbitals to give a π (pi) bond.

The valency of many elements is greater than that predicted from the number of unpaired atomic electrons. Promotion – raising one electron from a pair into a higher energy orbital – creates two additional unpaired electrons in an atom, and so increases the valency by two. The energy required for electron promotion is offset by the energy recouped in forming two additional chemical bonds.

The shapes of polyatomic molecules are poorly described by pure atomic orbitals. Deviation of actual bond angles from the angles between pure atomic orbitals is accounted for by hybridization.

Atomic orbitals are combined into hybrid orbitals, whose shape is defined by the geometry and proportion of the atomic orbitals. sp^3 hybrid orbitals are tetrahedrally arranged, sp^2 hybrid orbitals are arranged in a trigonal planar fashion, and sp orbitals are linearly arranged. More complex geometric configurations may be obtained by hybridization involving d and f orbitals.

**Related topics**

- The wave nature of matter (G4)
- The structure of the hydrogen atom (G5)
- Many-electron atoms (G6)
- Elementary valence theory (H1)
- Molecular orbital theory of diatomic molecules I (H3)

**Valence bond theory of diatomic molecules**

Valence bond theory is a quantum-mechanical description of molecular bonding which focuses attention on formation of the bond itself. As for Lewis theory (see Topic H1), bonds are generated by pairing up electrons on one atom with electrons on a second atom, but the nature of the atomic orbitals themselves are also considered. Electrons are paired in the course of bond formation and the spin of the individual electrons must be taken into account. Spin pairing is a requirement that the electrons from one atom are paired only with an electron of opposite spin. This ensures that a molecular bond is created in which the two electrons do not occupy the same quantum state, and so comply with the Pauli exclusion principle (see Topic G6).
Bonds are formed from combinations of the atomic orbitals from each of the bonding atoms, and the mathematical description of the molecular bond is therefore a function of these atomic orbitals. It is a fundamental requirement that the electrons in the molecular orbital are indistinguishable, and the simplest orbital function compatible with this is the **Heitler-London wavefunction**:

\[
\psi = \psi_1(1)\psi_2(2) + \psi_2(2)\psi_1(1)
\]

The first product describes the case of electron 1 in orbital A (\(\psi_1(1)\)) and that of electron 2 in orbital B (\(\psi_2(2)\)), with the second product describing the complementary situation. The two terms are not identical, as the electrons possess opposite spins. The resulting wavefunction describes the condition where either electron may be found on either of the bonded atoms.

In the simplest example, that of a hydrogen molecule, the atomic 1s orbitals are the sole contributors to the bond, and the wavefunction takes the form:

\[
\psi_{\text{H-H}} = \psi_{\text{H-A}}(1)\psi_{\text{H-B}}(2) + \psi_{\text{H-B}}(2)\psi_{\text{H-A}}(1)
\]

The physical results of this mathematical expression are illustrated in Fig. 1a and 1b. The resulting bond has cylindrical symmetry about the bond axis, and is termed a **\(\sigma\) (sigma) bond**.

In elements with accessible \(p\) orbitals, such as oxygen or nitrogen, more complex bonding may be obtained. The two atomic \(p\) orbitals which are parallel to the bonding axis (the \(p\) orbitals, by convention) may be combined so as to form a \(\sigma\) bond (Fig. 1c), but it is also possible for \(p\) orbital pairs which are perpendicular to the bonding axis (\(p\), on A and B or \(p\), on A and B) to combine to give \(\pi\) (pi) bonds (Fig. 1d). The strength of the \(\pi\)-bond is significantly less than

---

**Fig. 1.** (a) Two free hydrogen atoms and (b) the \(\sigma\)-bond formed from the combination of their 1s orbitals. (c) A \(\sigma\)-bond generated from two \(p\), orbitals. (d) A \(\pi\)-bond generated from two \(p\), orbitals.
bital from each of the mole cular bond is 
damental requirement 
able, and the simplest 
wavefunction:

\[ \psi_{1s}(1) \] and that of 
describing the comple 
ting the electrons possess 
condition where either 
the atomic 1s orbitals 
takes the form:

\[ V \]

illustrated in Fig. 1a and 
the bond axis, and is 
gen or nitrogen, more 
bital which are parallel 
y be combined so as to 
o orbital pairs which are 
A and B) to combine to 
ificantly less than

that of the σ-bond, as the ‘sidelong’ overlap of the p orbitals is less than that of the ‘direct’ overlap (the products \[ \psi_{p_1}(1)\psi_{p_2}(2) \] and \[ \psi_{p_1}(2)\psi_{p_2}(1) \] being cor 
 correspondingly reduced). Each pair of atomic p orbitals forms one molecular π-bond, giving a maximum of three molecular bonds from each set of p orbitals – one σ-bond and two mutually orthogonal π-bonds. The π-bonds do not have 
cylindrical symmetry, having instead a nodal plane parallel with the bonding 
axis.

Valency

The simple interpretation of the valence bond model fails to account for the 
valency (number of bonds) or multiple valency states of many elements. The 
valence electron configuration of silicon, \( 3s^23p^2 \), for example, suggests a 
valency of two arising from the two singly occupied p orbitals. The valency in 
fact increases through promotion, i.e., raising an electron into a higher energy 
orbital. This process breaks up an electron pair to give two additional unpaired 
electrons, and so increases the valency by two. In the case of silicon, promotion 
of an electron from the 3s to the 3p orbital results in a tetravalent configuration 
of \( 3s^23p^4 \). In some elements, the process may occur several times, each 
time increasing the valency by two. In all cases, the energy required for promo 
tion of the electron must be offset by the energy recouped in forming two additional 
chemical bonds for this process to occur.

Polyatomic 
molecules

The principle of spin pairing of electrons in singly occupied orbitals to form bonds 
may be extended to molecules with any number of atoms, with the available 
atomic orbitals on one atom combining with those on two or more other atoms.

The valence bond approach is broadly successful in predicting the number of 
available bonds, but is very unsatisfactory in its ability to predict the shape of 
molecules. In a commonly used example, the basic theory predicts that the 
bonding in water, \( \text{H}_2\text{O} \), would consist of two σ-bonds formed from pairing of 
electrons in the hydrogen 1s’ orbitals and two oxygen p orbitals. As the atomic p 
orbitals are orthogonal, valence bond theory predicts that the resulting σ-bonds 
are at 90° to one another. In fact, the inter-bond angle is closer to 104°. The devi 
ation of actual bond angles from the angles between pure atomic orbitals is 
accounted for by hybridization.

Hybridization

Hybridization is the process of combining pure atomic orbitals so as to circum 
vent the rigid geometry which the pure orbitals require. In this way, valence bond 
theory becomes far more able to account for molecular shapes. The pure orbital 
functions have both negative and positive signs. By directly combining the atomic 
orbitals, these negative and positive regions are added so as to enhance the ampi 
itude of the resulting orbitals in some directions, and to diminish their amplitude 
in others. The resulting combinations of pure orbitals are termed hybrid orbitals.

The most significant application of hybridization is in the shapes of the 
molecules involving the elements nitrogen, oxygen and particularly carbon. 
Combinations of one s and one p orbital give rise to two sp hybrid orbitals 
combinations (Fig. 2a). For a trigonal planar geometry, two p orbitals combine 
with one s orbital to yield three sp’ hybrid orbitals (Fig. 2b) and for a tetrahedral 
geometry, a combination of one s orbital and three p orbitals is used, gives rise 
to four sp’ hybrid orbitals (Fig. 2c).

The sp, sp’, and sp” hybrids represent limiting hybrids, and it is possible to 
combine the orbitals in such a way as to optimize the valence bonds to the 
required geometry. More complex geometric configurations may be obtained by
hybridization involving $d$ and $f$ orbitals, so that an $sp^3d$ hybrid orbital set generates a trigonal bipyramidal geometry, and an $sp^3d^5$ hybrid orbital set is octahedrally arranged.

The hybridization in an atom is imposed as a result of the molecular environment, and its precise nature is determined by the most effective way in which the free energy can be reduced through bonding. Hybridization is not a property of a free atom and does not occur prior to the bonding process, but takes place in parallel with bond formation. In practical bonding applications, however, the hybrid orbitals behave identically to pure atomic orbitals, and may be treated likewise. Hence the spatial arrangement of the bonds of methane, for example, may be accurately reproduced (within the constraints of the theory) from the four $sp^3$ hybrid orbitals of carbon, and the four $1s$ atomic orbitals of hydrogen (Fig. 2d).

Hybrid orbitals are invoked in order to enable formation of $\sigma$ bonds, whose geometry in turn defines the geometry of the molecule. In the case of carbon $sp$ and $sp^2$ hybrids, for example, this leaves one and two unused $p$ orbitals, respectively. In both cases, the remaining pure $p$ orbitals allow formation of multiple bonds with neighboring atoms via $\pi$ bonds (Fig. 2e and f).