

Chapter 12. Chemical Bonding

12.1. Chemical Bonds

Before Dalton's atomic theory there wasn't much reason to consider how atoms stick together, although it was clear that some force is necessary to bind compounds of elements together. The term "chemical affinity" referred more to the ability to react (undergo a chemical change) than to form a stable compound. When it was realized that chemical compounds were formed of discrete molecules containing fixed numbers of atoms, the need to explain molecular stability developed, leading to the notion of the **interatomic chemical bond** (Latin *inter* for among plus *band* for a fastening) holding atoms together. Early Nineteenth Century speculations about the origin of interatomic bonds were affected by contemporary discoveries in electricity, indicating that "opposites" attract. Positive and negative charges are electrical opposites, and north and south poles are magnetic opposites. Precisely just what constituted *chemical* opposites wasn't clear, however. Chemists had classified substances into metals and non-metals, and into acids and bases, both of which seemed opposite in the sense that they had "affinity" for each other and readily reacted together to form new compounds. Yet there was little evidence to support the hypothesis of Avogadro that non-metal gases were composed of two atoms of the *same* element, nor were there any explanations for the solid state of metallic elements, or the extreme hardness of non-metallic elements such as diamond.

The number of bonds an element could make, called the **valence** (Latin *valere* for strength) of the element, is suggested by the atom ratios of chemical formulas, and ordinarily limited to a small number. For example, hydrogen atoms never forms bonds to more than one another atom, so are assigned a valency of one. Oxygen has a valency of two (is **divalent**) as each oxygen atom combines with two hydrogen atoms in forming water (H_2O , more descriptively written showing atom connections as $\text{H}-\text{O}-\text{H}$). Carbon has a valency of four (is **tetravalent**) because it combines with a maximum of four hydrogen atoms (in methane, CH_4 more descriptively shown with C surrounded by 4 H), or, equivalently, a maximum of two oxygen atoms, each with a valency of two (in carbon dioxide, CO_2 , more descriptively written $\text{O}-\text{C}-\text{O}$).¹

¹ These are not the only possibilities; there are known compounds with alternative formulas, such as hydrogen peroxide (H_2O_2), methylene (CH_2), and carbon monoxide (CO), but these are less stable than the higher va-

12.2. Ionic and Covalent Chemical Bonds

Chemical salts are found to conduct electricity when melted or dissolved in water, suggesting the presence of charge carriers, called **ions** (from the Greek for traveler). Since salts are neutral compounds, the charge carriers must be divided into two groups, one positively charged and the other negatively charged. The oppositely charged ions would be bound through electrostatic attractions, or **ionic bonds**. Because chemical salts are known to be composed of metallic elements bound to non-metallic elements, the most reactive of which are found at opposite ends of the periodic table, ionic attraction can be explained in terms of the attraction of opposites.

When metals or nonmetals bond to elements of their own kind, the reason for the bonding is not so obvious. Compounds containing different elements might have some attraction due to the differences between the elements, but *homonuclear* (one-element) *polyatomic* (more than one atom) elements such as H_2 or sodium metal are bound by some *common* feature rather than by some difference between the atoms. Such bonds, called **covalent bonds** (Latin *co* + *valere* for joint strength), are not limited to homonuclear molecules but also occur between atoms of different elements that are close in behavior. The periodic table summarizes the properties of the elements, including bonding trends as well, and can be used to decide the basic type of bonding between atoms in molecules in a binary (two state) classification scheme.

lence counterparts. For this reason, valence sometimes denotes the *maximum* number of bonds an element forms.

Basic Bonding Heuristic

Purpose: To determine the types of bonding in a molecule.

Procedure:

1. Classify the possible bonds between pairs of atoms according to their relative positions in the periodic table. The closer to each other the atoms are in the periodic table, the more covalent the bonding. Metal to metal bonds and non-metal to non-metal bonds are covalent. Metal to non-metal bonds are ionic.
2. If the chemical formula (or name) is not available (or not recognizable), try to deduce it by analogy with known formulas of similar substances.

Example 12.1 Discuss the basic bonding in metallic Fe, gaseous XeF_4 and crystalline CaO.

1. Elemental Fe (iron) is a solid and is bonded only to itself, so must bond covalently to form a metal of n atoms (where n is a large number of the order of Avogadro's number).
2. The chemical formula shows the number of atoms of each element in the molecule, and should be written Fe_n . However, by convention the subscripts of formulas of pure elements consisting of one large molecule are dropped, Fe. This is justified because n varies, depending on the size of the sample.
1. Xe is a noble gas, and is not expected to form molecules, but fluorine is so greedy for electrons (*electronegative*) that a few noble gas compounds *do* exist. Since both elements are non-metals, XeF_4 is covalently bonded.
2. The formula is given in this case, and since the substance is a gas, the molecules exist essentially independent of each other.
1. Calcium is a metal and oxygen a non-metal. Therefore CaO is an ionic compound.
2. Again the basic molecular formula is given, but because crystals consist of a single large molecular network of subunits, the formula would be more correctly written $(\text{CaO})_n$. Again, by convention the subscript is dropped.

Sometimes a table of *electronegativities* is used to classify the possible bonds between each pair of atoms in a molecule into two categories, ionic or covalent (cf. Section 8.4 on Trends in the Periodic Table). Bonds between atoms which differ in electronegativity on a scale of 0 to 4 by more than 2 units may be assumed to be ionic. However, since electronegativities of metals vary between 1 and 2 and non-metals between 2 and 4, metal to non-metal bonds are the only ionic bonds. Electronegativities are useful for more refined classifications and trends in terms of the *percent ionic or covalent character* of a bond. In these terms, ionic bonds are those with more than 50% ionic character.² Because electronegativity is only a semiquantitative concept, there is no simple equation relating electronegativity to percent ionic or covalent character, and there is no standard table of electronegativities. This is due to the fact that atoms in molecules are only approximately localized and independent of the environment of the entire molecule. This prevents assigning unique electronegativities to atoms which experience a variety of bonding environments.

A parameter used to indicate the charge an atom has or would have if it were ionized in compounds is the **oxidation number**. Three rules help define the assignment of oxidation numbers to atoms in compounds (the “oxidation number game”).

² While purely (100%) covalently shared bonds exist in the case of homonuclear molecules, purely (100%) ionic bonds can only be approached in ionic compounds. *Polar bonds* result from varying degrees of “ionic character” in the imbalanced distribution of the electronic charge cloud.

Oxidation Number Heuristic

Purpose: To determine the oxidation number, ON, of an atom.

Procedure:

0. Oxidation numbers of elements range from a minimum equal to the group number in the periodic table minus 2 (first row) or 8 (beyond the first row) up to a maximum equal to the group number.
1. If the atom is not in a molecule, the oxidation number equals the charge on the atom.
2. If the atom is in a molecule, the oxidation number, ON_i , is determined algebraically by solving the equation

$$\sum_i^{\text{atoms}} ON_i = \text{molecular charge}$$

given the ON of each other element. More electropositive elements (such as metals) have greater oxidation numbers than more electronegative elements (such as nonmetals). Fluorine has only two possible oxidation numbers: zero (free element) and minus one (compounds).

Example 12.2 Oxygen being so electronegative commonly has an oxidation number of minus two, although it is -1 in peroxide ion (O_2^{2-}). and is +2 in oxygen difluoride (OF_2). Hydrogen is classified with the alkali metals (group 1) electronically and with the halogens (group 7) chemically. Its oxidation number ranges from -1 in metal hydrides (metals are more electropositive than H) to 0 as the free element to +1 in combination with more electronegative elements (most other nonmetal elements).

The oxidation number of Ca^{2+} is +2. Sulfur ranges from -2 in H_2S to +6 in $CaSO_4$, as $ON(Ca) + ON(S) + 4ON(O) = 0$ where $ON(Ca) = +2$, $ON(O) = -2$ implies $ON(S) = -ON(Ca) - 4ON(O) = -(+2) - 4(-2) = +6$.

12.3. Molecular Mass Spectrometry

Mass spectrometry provides a powerful analytical tool for probing molecules for their bonding structure. Mass spectrometers are instruments that fragment and ionize “parent” molecules with electron beams and analyze the products with electric and magnetic fields and detectors. According to the laws of electromagnetism, charged particles passing through electromagnetic fields follow trajectories determined by their mass to charge ratio. Thus fragments with different masses and/or different charges are separated by the external fields, except in the case where the mass to charge ratio happens to be the same. E.g. O^+ ($m/q = 16/1$) will be distinguished from O_2^+ ($m/q = 32/1$) but not from O_2^{2+} ($m/q = 32/2 = 16/1$). Relative amounts of parents and fragments measured by the detector reflect relative abundances in the sample.

Mass spectra patterns give clues to the bonding of molecules. The first direct evidence that hydrogen is diatomic came in the early 1920’s from a mass spectrometric analysis that showed two lines (“peaks”) in the mass spectrum of elemental hydrogen, one with twice the mass as the other. (Note that if there were insufficient energy in the ionizing beam of the mass spectrometer, the hydrogen molecule might be ionized but not ruptured, and only one mass species would be detected.)

More complicated molecules can have more complicated mass spectra, and computers are used to assist in the analysis. Complicating features include multiple combinations of possible “daughter” fragments, multiple ionizations of the parent and fragments, and multiple isotopes. If the molecules have a chance to react before analysis, fragments can recombine in new ways to confuse the analysis. A good way to analyze or predict a mass spectrum tabulates the possible combinations of parent and fragment masses, using isotope distributions to determine the spectral lines (peaks).

Molecular Mass Spectrum Algorithm

Purpose: To determine the mass spectrum (line positions and intensities) of a molecule.

Procedure:

1. If not given, assume some bonding structure for the molecule.
2. Determine the possible isotope masses and abundances of the elements in the molecule.
3. Tabulate all possible combinations of isotope masses for the parent molecule and each fragment, and compute their masses.
4. Mass peak intensities are proportional to isotope abundances.

Example 12.3 What should the mass spectrum of water look like?

1. The chemical formula for water is H_2O , which means there are two atoms of hydrogen and one of oxygen. To simplify the analysis we will assume that only singly ionized species are produced and no recombinations take place during the flight from the mass spectrometer ionizer to the analyzer. The type of bonding may not be known but may be inferred from bonding heuristics. Since hydrogen and oxygen are non-metals, it is safe to assume the molecule (and its fragments) are covalently bonded. *Which* atoms are bonded to which is another matter. Mass spectroscopy is one method used to determine the details of the bonding. If no assumptions are made about the bonding arrangement in water, possible fragments consist of HH and HO , H and O .
2. A table of isotopes shows that there are two stable isotopes of atomic hydrogen, having masses (and abundances) of 1.007825 (99.985%) and 2.0140 (0.015%), and three isotopes of atomic oxygen, having masses and abundances 15.99491 (99.76%), 16.99909 (0.04%) and 17.99917 (0.20%).
3. Considering only singly ionized species, *parent* water molecules should produce mass spectrum peaks at masses 18 through 22, with magnitudes corresponding to combined isotope abundances of the elements. The table below lists the possibilities of H_2O isotope combinations:

	^{16}O	^{17}O	^{18}O
$^1\text{H}_2$	18	19	20
$^1\text{H}^2\text{H}$	19	20	21
$^2\text{H}_2$	20	21	22

Note that (to two significant figures) there are two molecules contributing to the mass 19 peak, two to the mass 21 peak and three to the mass 20 peak (although the intensities, or contributions to peaks of equal mass are not equal because the isotope abundances differ).

Possible *fragments* are HO, HH, H and O. From the table below we see that HO would produce an additional peak at mass 17 as well as contribute to the peaks at masses 18, 19 and 20.

	^{16}O	^{17}O	^{18}O
^1H	17	18	19
^2H	18	19	20

HH would contribute to peaks at mass positions 2, 3 and 4:

	^1H	^2H
^1H	2	3
^2H	3	4

H would contribute to peaks at masses 1 and 2, and O would contribute to the peaks at masses 16, 17 and 18.

In all, there could be as as many as 11 peaks in the mass spectrum of singly ionized parents and fragments of water (corresponding to masses of 1, 2, 3, 4, 16, 17, 18, 19, 20, 21, 22). If *all* peaks were present, we would expect the mass spectrum to look something like Fig. 12.1, with the intensities reflecting the observed isotope abundances.

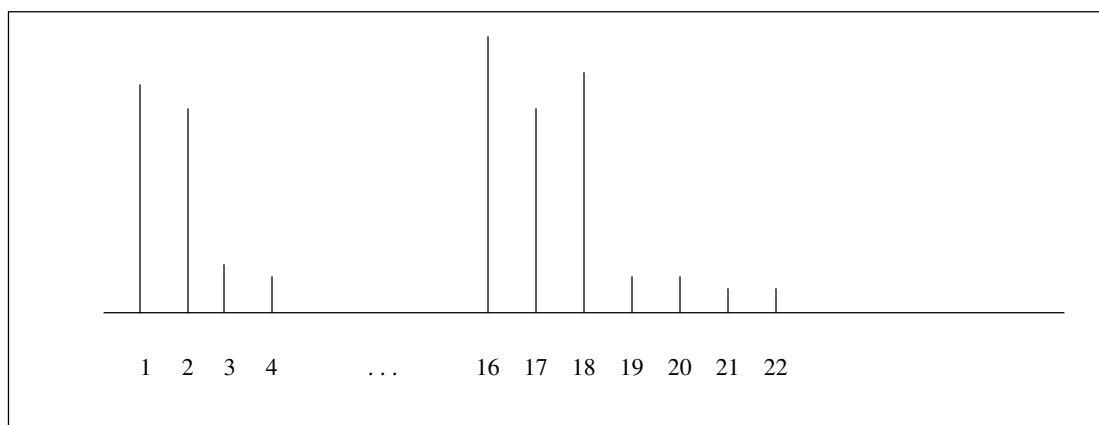


Fig. 12.1 Predicted Mass Spectrum for Water

An investigation of peaks at masses 2, 3 and 4 due to H_2 helps decide which atoms are bound to which in the parent water molecule. It turns out there is a small intensity at mass 2 due to ^2H , but zero intensities corresponding to masses 3 or 4 in the spectrum of water, suggesting no bond between H and H. Therefore hydrogen must be bound to oxygen if a molecule is to exist. This is supported by a sizable peak at mass 17. Therefore the bonding structure of water is H-O-H and not H-H-O.

Water is a rather simple (triatomic) molecule. The mass spectra of more complicated molecules can become enormously more complicated due to the increased number of possible combinations of fragments and isotopes.

12.4. The Electronic Theory of Chemical Bonding

Nowadays it is recognized that *the chemical bond is the most basic and essential feature of molecules*. Understanding the properties of the interatomic bonds in molecules is essential to understanding the physical structure and chemical reactivities of molecular matter. Chemical bonds result from the electrostatic (Coulombic) interactions of the electrons and nuclei of atoms. Basically, the outer-shell electrons on each atom in a molecule can be thought to be attracted to the nuclei of adjacent atoms as well as their own nuclei. Fig. 12.2 diagrams the electrostatic interactions for a classical particle model of the dihydrogen molecule, the simplest neutral polyatomic molecule. Actually this model, although useful, is an oversimplification on several counts; as was found for atoms, electrons in the presence of nuclei do not behave as particles and classical models fall short of accurate descriptions of electronic structure.

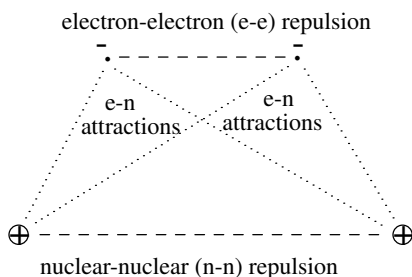


Fig. 12.2 Electrostatic Interactions in Dihydrogen

The wave mechanical model of electronic structure is the appropriate description for multiple electron systems, and applies to molecules as well as atoms (cf. Section 5.8 on Wave Mechanics and Section 8.3 on Periodic Electronic Configurations). *The nature of the chemical bond is revealed in the solutions to Schrödinger's equation for molecules.* As in the case of atoms, accurate solutions obtained for simple molecules are used to justify established bonding heuristics, as well as generate new molecular bonding principles.

A major feature that emerges in investigating chemical bonds through wave mechanics is *electrons prefer to be paired*. This fact explains the stability of the simplest neutral molecule, H_2 (with 2 paired electrons) with respect to H atoms, as well as the *instability* of He_2 with respect to He atoms (each having 2 paired electrons). The stability of paired electrons and filled subshell electronic configurations prove to be most useful general principles for explaining a variety of features of molecules.

Before delving further into the nature of the chemical bond as elucidated by the wave mechanics, we will explore a widely used powerful pre-wave mechanical bonding heuristic invented by G. N. Lewis³ early in the beginning of the Twentieth Century. Lewis considered electrons to be classical particles, which he represented graphically by dots. Pairs of electrons between atoms he represented with lines to represent bonds connecting the atoms together. Lewis's contribution consisted of a simple method of counting the dots to predict chemical formulas, molecular geometry, and various chemical properties.

By the beginning of the Twentieth Century, the sub-atomic structure of atoms was established and the stage was set for considering atomic attractions between atoms in terms of the interactive forces of the negatively-charged electrons and the positively-charged protons of the nucleus. In 1902 G. N. Lewis began using formulas of chemical compounds with little dots representing the electrons of the atoms in his lectures, which was the beginning of the *electronic theory of chemical bonding*. As Lewis searched for a theory to explain valency in terms of the electrons of an atom, he was led to the periodic table. We now know that columns of chemical families have similar properties because they have similar outer-shell electronic configurations, but that knowledge wasn't available at the beginning of the century.

³ Gilbert Newton Lewis (American, 1875-1946) emphasized the role of electrons in chemical molecules and their reactions. Contributed significantly to bonding theory, electrochemistry and chemical thermodynamics. Although he built the University of California at Berkeley Chemistry Department into the most prestigious in the world, he never received a Nobel Prize.

Lewis reasoned that families of elements have similar properties because they have similar *numbers* of electrons participating in the bonding. This led to dividing the electrons of an atom into two categories, now known as inner shell, or **core electrons** and outer shell or **valence electrons**. There may be multiple inner shells of electrons, but the outer shell valence electrons are the ones closest to neighboring nuclei and therefore dominate in the chemical bonding.

A chemically stable (inert) noble gas is found at the end of each row of the periodic table. The fact that each new noble gas has added at least eight more electrons, suggests some connection between eight electrons and stability. Atoms to the left and right of the noble gases have fewer than eight electrons, are less stable, and are hence chemically reactive. Lewis devised the **octet rule** to describe the tendency of atoms to gain stability by achieving an *octet* (8) of outer shell, or valence electrons. However, there are exceptions. Elements in the first three columns of the periodic table may form *suboctets* (less than 8 electrons) and elements beyond the second row of the periodic table can form *superoctets* (more than 8 electrons). Hydrogen is a notable exception, requiring merely a *duet* or pair of electrons to acquire the stability of the noble gas helium. The **duet/octet** heuristic, or “rule” states that *atoms like to be noble* (or have noble gas electronic configurations), or, in modern terms, *filled subshells in electronic configurations are particularly stable*. The octet heuristic was successful in describing the bonding in both ionic compounds (containing charged atoms or molecules) and covalent molecules (combinations of non-charged atoms) in terms of the valence electrons of atoms. In addition, the stability of paired electrons for the first time offered a rationalization⁴ of the stability of homonuclear diatomic gases, such as dihydrogen and dioxygen.

12.5. Lewis Structures

Covalent pairs of electrons Lewis called *bond pairs*. Atoms with valence greater than unity could possibly share more than one pair of electrons with a neighboring atom, producing stronger *multiple bonds*.⁵ Electrons left over after all the valences of the atoms were

⁴ The preference for pairing, like that for shoes and stockings, is, in fact, a rationalization, not justification or explanation, which waited until the first application of wave mechanics to the dihydrogen molecule in 1929 by Fritz London.

⁵ The octet rule limited the number of multiple pairs of electrons to four. In practice only single, double and triple bonds are observed.

satisfied, Lewis classified as **lone pair** electrons. The identification of different classes of electrons in molecules proved very powerful in explaining their structures and reactivities. Molecular formulas which show the bonding and free electrons are called **Lewis structure formulas**. *Lewis structures based on the duet/octet heuristic provide a simplified basis for explaining the properties of molecules.*

Writing Lewis structures is like a game with two rules, one of which determines how many valence dots an atom has, and the other determines how they are to be arranged. The number of valence electrons in an atom is determined by its electronic configuration. The electronic configuration, in turn, can be deduced from the position of the atom in the periodic table. *The number of valence (outer shell) electrons in an atom equals the group number of the atom in the periodic table, and the total number of valence electrons in a molecule is the sum of the valence electrons of its atoms, modified by any charge on the molecule.* Negative charge results from more electrons than protons in the system, and positive charge results from fewer electrons than protons.

Having determined the number of valence electrons, the next step is to *arrange* them in some fashion. The electrons in a molecule should be arranged to reflect the bonding; *ionic bonds result from transfer of electrons and covalent bonds are due to sharing of electrons.* The arrangements should also conform to the duet/octet rule of stability of filled subshells. The process of writing Lewis structures can be facilitated by recognizing that *electron pairs account for the covalent and ionic bonding, otherwise the molecule would not exist.* The remaining valence electrons may be arranged by trial and error into multiple bond pairs and lone pairs to satisfy the duet/octet rule.

Multiple Lewis structures satisfying the duet/octet rule for a given molecule are called **resonance structures**. The concept of **formal charge** can be used to resolve ambiguous structures. Formal charges on atoms result from an attempt to trace the electrons as the atoms (conceptually) come together to form molecules. They correspond to the charge each atom would have if it were fully ionic. Thus *the formal charge of an ion is equal to the charge on the hypothetical ion, and the formal charge of a covalently-bonded atom may be calculated as the group number of the atom in the periodic table minus the number of the bonds attached to the atom minus the number of nonbonding electrons.* The formal charge heuristic assumes that the most likely Lewis structure has the lowest set of formal charges, approaching neutral atomic character. This is not a provable theorem but a plausible guess based on the notion that electrons should not migrate very far when atoms form into

molecules.

Lewis Structure Algorithm

Purpose: To determine the Lewis structure of a given molecule.

Procedure:

1. *Compute the total number of valence electrons* (Lewis dots) in the molecule as the sum of group numbers of the atoms, minus the (algebraic) value of any charge.
2. *Classify the bonds.* If there are both metallic and non-metallic elements in the molecule, assign all the valence electrons to the non-metal portion of the molecule; this produces an imbalance of charge leading to ionic bonding. Metal-metal and non-metal-non-metal atoms are bound covalently through shared valence electrons.
3. *Write a molecular skeleton structure.* Assume some geometric arrangement for the atoms, noting that more electronegative elements tend to surround more electropositive elements. For covalent portions of the molecule connect the atoms together with lines representing the minimum bonding necessary to bind the molecule with electron-pair covalent bonds.
4. *Write molecular Lewis structures.* Subtract two electrons for each covalent bond (line) in step 3 from the total number of valence electrons in step 1, and attempt to distribute the remainder such that each first row element atom has two electrons (a duet) and other atoms have eight electrons each (an octet), noting that elements in the first three columns of the periodic table may form **suboctets** (less than 8 electrons) and that elements beyond row two of the periodic table may form **superoctets** (more than 8 electrons). Double and triple (but no higher) bond pairs are permissible, but single bonds are preferable.
5. *Determine the most stable Lewis structure.* Assign a formal charge to each atom, equal to the group number of the atom in the periodic table, minus the number of bonds attached to the atom minus the number of nonbonding electrons. The most stable Lewis structure is that with lowest negative (positive) formal charges on the more electronegative (electropositive) atoms.

Example 12.4 Determine the Lewis structure of water (H_2O).

Possible Lewis structures are obtained from the Lewis Structure Algorithm.

1. H is in group 1 of the periodic table, and oxygen in group 6. Therefore 1 dot is derived from the two hydrogen atoms and 6 from the oxygen atom, for a total of $2(1) + 6 = 8$ valence electron dots (4 pairs).
2. Apply the Basic Bonding Heuristic to determine the basic type of bonding for the molecules. All elements are non-metals, so neutral covalent compounds are expected.
3. Possible arrangements are HHO and HOH. HHO would require a super duet on hydrogen, so we will assume the symmetric skeleton structure, and use two pairs of electrons to provide the minimum bonding to hold the structure together, H-O-H.
4. There are $8 - 2(2) = 4$ electrons left to distribute. Since the hydrogen atoms have duets, only oxygen is deficient. Adding the 4 remaining electrons to oxygen gives it an octet, and we are finished. Note that the structure is consistent with the mass spectral evidence for the bonding in water given in Example 12.3.

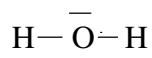


Fig. 12.3 Lewis Structure for Water

Example 12.5 Compare CO_2 (carbon dioxide) and N_2O (nitrous oxide).

Possible Lewis structures are obtained from the Lewis Structure Algorithm.

1. Carbon is in group 4 of the periodic table, and oxygen in group 6. Therefore 4 dots is derived from the carbon atom and 6 from each oxygen atom, for a total of $4 + 2(6) = 16$ valence electron dots (8 pairs). N_2O also has 16 valence electrons and is therefore *isoelectronic* with CO_2 .

2. Apply the Basic Bonding Heuristic to determine the basic type of bonding for the molecules. All elements are non-metals, so neutral covalent compounds are expected.
3. Possible bonding arrangements are two-bonded symmetrical OEO and unsymmetrical EOO, and a three-bonded triangular structure with all atoms bonded to neighbors, where E is C or N. We will consider the two-bonded structures and leave the three-bonded triangular arrangement to an exercise.
4. Lewis structures having two double bonds on the central atom are possible for all species. Figure 12.4 lists the possibilities. The last two OCO and NON structures are actually identical due to symmetry (by turning them around).

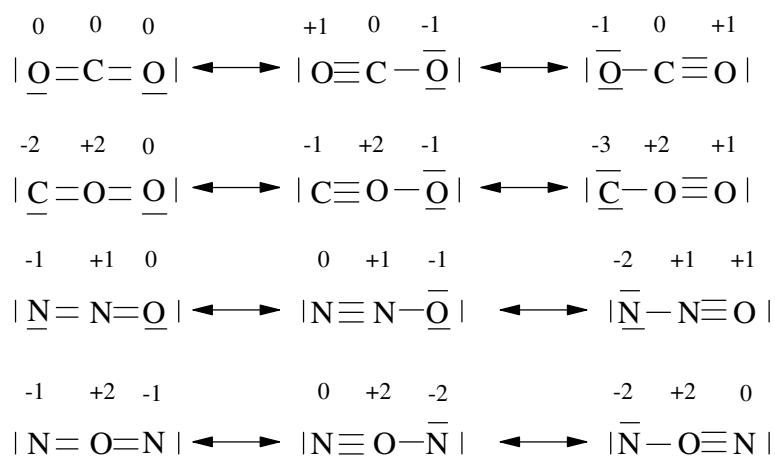


Fig. 12.4 Two-bonded Lewis Structures for CO_2 and N_2O

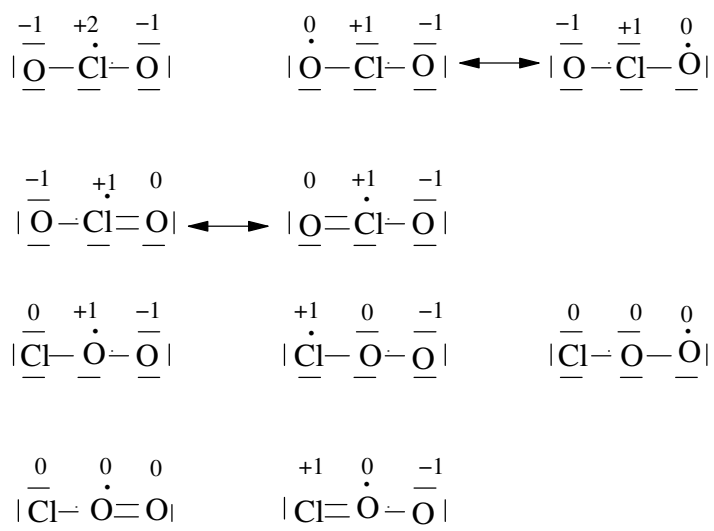
5. The smallest set of formal charges selects the symmetric OCO over unsymmetric COO but unsymmetric NNO over symmetric NON. This unusual situation is confirmed by experimental analysis. Although dinitrogen (N_2) and carbon monoxide (CO) (which are isoelectronic) have triple bonds (the only possibility satisfying the octet rule), double bonds are favored for carbon dioxide and nitrous oxide. A

avored triple bond for NNO is consistent with that of N_2 , but dioxygen (O_2) has a double bond, and double-bonded end oxygen structures are favored in the triatomics. Thus oxygen retains its double bond character at the expense of nitrogen's triple bond, consistent with oxygen being more electronegative than nitrogen. Nevertheless, the competition leads to two structures with the same formal charges.

Example 12.6 Discuss the chemical properties of chlorine dioxide.

Possible Lewis structures are obtained from the Lewis Structure Algorithm.

1. Chlorine is in group 7 of the periodic table, and oxygen in group 6. Therefore 7 dots are contributed by the chlorine atom and 6 by each oxygen atom, for a total of $7 + 2(6) = 19$ valence electron dots (9-1/2 pairs).
2. Apply the Basic Bonding Heuristic to determine the basic type of bonding for chlorine dioxide. Both elements are non-metals, so a neutral covalent compound is expected.
3. Possible bonding arrangements have the two oxygen atoms symmetrically placed around the chlorine atom, $\text{O}-\text{Cl}-\text{O}$, unsymmetrical $\text{Cl}-\text{O}-\text{O}$ and triangular ClO_2 . You can convince yourself the triangular arrangement requires superoctets.
4. Any attempt to distribute the remaining $19 - 4 = 15$ electrons will not produce octets everywhere, as there is an odd number. In general, *molecules with an odd number of odd-group elements have odd total numbers of valence electrons* and cannot totally satisfy an octet/duet rule. The best Lewis structures that can be obtained for ClO_2 contain two octets on two of the three atoms with one unpaired electron on the third. (The two pairs of resonance structures are equivalent by symmetry.)

**Fig. 12.5** Chlorine Dioxide Lewis Structures

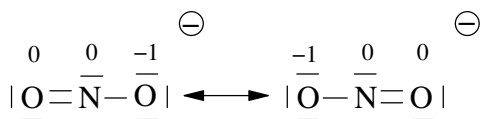
5. Determine the most stable Lewis structure for chlorine dioxide. For the symmetrical structures (OClO), if the unpaired electron is on chlorine, the formal charge on chlorine is $7 - 2 - 3 = +2$, and that on each oxygen atom is $6 - 1 - 6 = -1$. If the unpaired electron is on an oxygen atom, the formal charge on that atom is -1 , that on the chlorine atom is $7 - 2 - 4 = +1$, and that on the other oxygen atom is $6 - 1 - 5 = 0$. This set of formal charges is lower than that for the unpaired electron on chlorine, and is preferred. There is a redundancy regarding the oxygen atoms resulting in two equivalent (resonant) Lewis structures, indicated by the two-headed arrow. However, there are two *unsymmetrical* structures (ClOO) with zero formal charges which are preferred to the symmetrical structures. The double-bonded resonant Lewis structures cannot be distinguished from one of the single-bonded structures on the basis of formal charges. The higher electronegativity (electron greediness) of oxygen compared to chlorine, as well as the double bond in dioxygen weighs in favor of the double-bonded structures, consistent with short bond distances observed

experimentally.

The existence of an unpaired electron in a molecule suggests high reactivity. This is borne out by the experimental evidence. Gaseous chlorine dioxide explodes violently in air, and solutions of chlorine dioxide have superior bleaching power and germicidal activity.

Example 12.7 Predict a formula for the compound(s) that could exist between calcium, nitrogen and oxygen.

1. Calcium is in group 2, nitrogen in group 5 and oxygen in group 6. Therefore 2 dots are contributed by each calcium atom, 5 from each nitrogen atom and 6 to each oxygen atom in the compound.
2. The Basic Bonding Heuristic suggests an ionic compound will be formed. Calcium is a metal, nitrogen and oxygen are non-metals. Any compound will therefore be ionic, with two electrons transferred from each calcium atom to a negatively-charged covalently-bonded portion containing nitrogen and oxygen atoms. The molecular formula is not given, so some assumption must be made about the covalent portion of the molecule. Known negative ions containing nitrogen and oxygen are nitrite ion (NO_2^-) and nitrate ion (NO_3^-) (cf. Table 10.2). We will select the nitrite ion for further investigation, and leave the nitrate ion as an exercise. Since calcium transfers two electrons and since nitrite ions are singly charged, the formula for calcium nitrite is $\text{Ca}(\text{NO}_2)_2$.
3. There are $5 + 2(6) + 1 = 18$ electrons (9 pairs) to be distributed on the nitrite ion.
4. Assume a skeleton with two oxygen atoms surrounding a nitrogen atom: $\text{O}-\text{N}-\text{O}^{-1}$. (You can show unsymmetrical NOO has higher formal charges.) An attempt to place the remaining 7 pairs of electrons in octets evenly on all the atoms keeping single bonds leaves one atom deficient by one pair. Triple-bonded structures require superoctets, so single-bonded and triple-bonded structures are ruled out, leaving double-bonded structures as a possibility. Move one lone pair into the bond region to form a double bond between nitrogen and oxygen.
5. Since there are two oxygen atoms bound to nitrogen in nitrite, there are two choices for the double bond between nitrogen and oxygen. The two resonance structures are equivalent by symmetry and there is no need to assign formal charges to distinguish between them.

**Fig. 12.6** Nitrite Ion Resonant Lewis Structures

12.6. Molecular Geometry

Because the electrons surrounding an atom are negatively charged, repulsions exist which tend to move the electrons away from each other. *Bonding and lone pair electrons repel each other to arrange the atoms into the most stable (minimum repulsive) atomic spatial arrangement, referred to as the molecular shape, structure, or geometry.* This is known as the **Valence Shell Electron Pair Repulsion (VSEPR) Heuristic**, or “Theory”. The idea is not as complicated as the name.

A procedure to determine molecular geometry from the VSEPR heuristic identifies the type of bonding and counts regions of electron density. As far as electron density is concerned, multiple bonds form repulsive groups similar to single bond pairs (this is actually a first approximation assumption of the method). The possible spatial arrangements of equivalent groups of electrons are derived from solid geometry. Exploration with toothpicks or pencils should convince you of the possibilities.

The VSEPR Molecular Geometry Heuristic

Purpose: To determine the geometry of a molecule or molecular fragment.

Procedure:

1. Use the Basic Bonding Heuristic to classify the possible bonds. Ionic bonds form regular solid crystalline lattices.
2. The most stable geometry for the covalent (usually non-metal) portion is obtained by minimizing the repulsions between electrons.
 - a) Write the Lewis structure for the covalent portion using the Lewis Structure Algorithm.
 - b) Count the number of electron groups (regions of high charge density) on each atom in the molecule, where bonds of any multiplicity and lone single or pairs of electrons count one group each.
 - c) The arrangement of the groups of all *electrons* (bond and lone pairs) on each non-terminal atom which minimizes the repulsion is linear for two groups, triangular for three, tetrahedral for four, trigonal bipyramidal for five, octahedral for six, pentagonal bipyramidal for seven, etc. (cf. Fig 3.7.) Use the fact that lone pair electrons are more repulsive than bond pair electrons to distinguish ambiguous cases.
 - d) The geometric arrangement of the *atoms* (molecular geometry, or shape) describes where the *nuclei* are found when the electrons are arranged in step c) ((i.e. the atoms are “visible” and electrons are “invisible”).

Example 12.8 Describe the geometry of calcium nitrite, $\text{Ca}(\text{NO}_2)_2$.

1. The Basic Bonding Heuristic and Lewis Structure Algorithm suggest an ionic compound composed of calcium and nitrite ions. The ionic bonding between calcium and nitrite produces a solid crystalline lattice.
2. To determine the geometry of the nitrite ion, minimize electron group repulsions as follows:

- a) There is only one non-terminal atom, nitrogen. Fig. 12.6 shows the possible Lewis structures for the nitrite ion.
- b) From the Lewis structure for nitrite, there are three *groups* of repulsive electrons on the nitrogen atom: one from the single bond between the nitrogen and one of the oxygen atoms, one from the double bond between the nitrogen atom and the other oxygen atom, and one from the lone pair on the nitrogen atom.
- c) Three repulsive groups of electrons produces a triangular arrangement of electron groups surrounding the nitrogen atom.
- d) The oxygen nuclei are at two of the apices of the three groups of electrons attached to nitrogen atom (Fig. 12.7). The molecular geometry (describing the arrangement of the nuclei) is therefore *triangular*, or *bent* (either description is acceptable).

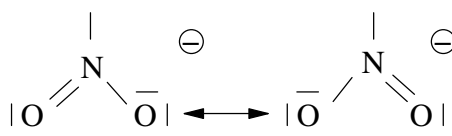


Fig. 12.7 Nitrite Ion Geometry

12.7. Molecular Polarity

Since dissimilar atoms have different attractions for electrons, all bonds between unlike atoms have **bond polarity** or imbalance of charge. Any *homonuclear molecule* (*molecule with only one type of element*) is *non-polar*, since there is no imbalance of charge. Any *heteronuclear molecule* (*molecule with more than one type of element*) has *polar bonds* between the unlike atoms. Since *bond polarities are additive*, the *net polarity of the entire molecule may be polar or non-polar, depending on the geometry: totally symmetric molecules have a total spatial balance of charge and are non-polar*, while *unsymmetric heteronuclear molecules are polar*. Non-polar means that any internal imbalance of charge (bond dipoles) cannot be detected outside the molecule. Classifying molecules on the basis of the bonding

and geometry can be codified into the following decision-making heuristic:

Molecular Polarity Heuristic

Purpose: To determine the polarity of a molecule.

Procedure:

1. Use the Basic Bonding Heuristic to determine the type of bonding in the molecule. If the bonding is ionic, individual diatom bonds of the molecule are polar, but *crystals* of the molecule (consisting of symmetrically paired submolecules) are *non-polar*. Homonuclear molecules (can only be covalent and) are *non-polar*.
2. If the molecule has heteronuclear covalent portions, determine the geometry from the Lewis Formula and VSEPR Molecular Geometry Heuristics. If the geometry is totally symmetric (spatially balanced), the molecule is *non-polar*; otherwise it is *polar*.

A graphic decision map for the Molecular Polarity Heuristic shows that polar molecules are simultaneously covalent, heteronuclear and nonsymmetric.

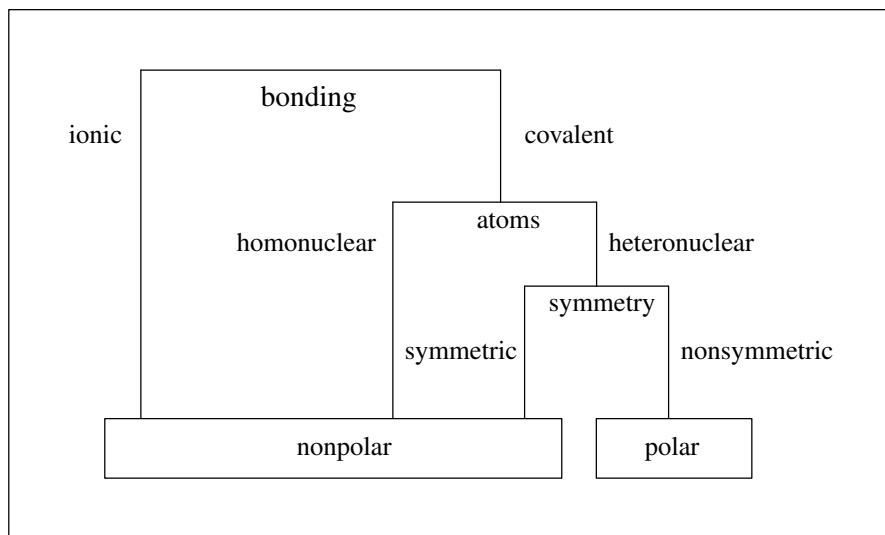


Fig. 12.8 The Molecular Polarity Map

Example 12.9 Discuss the polarity of water.

The polarity of the *molecule* is determined from the Molecular Polarity Heuristic.

1. Since the molecule involves two different non-metal elements, the bonds between the hydrogen and oxygen atoms will be covalent and polar.
2. The geometry of the molecule is determined from the Molecular Geometry Heuristic. From Example 12.4 it was determined that there are four groups of electrons around the oxygen. According to the VSEPR Heuristic, they are arranged tetrahedrally, causing a bent molecular geometry. Since the water molecule is bent, covalent, heteronuclear and nonsymmetric, it is *polar*. (This turns out to be a very important property of water.)

Example 12.10 Discuss the polarity of the nitrite ion.

Since the molecule involves two different elements, bonds between the nitrogen and oxygen atoms will be polar. The polarity of the *molecule* is determined from the Molecular Polarity Heuristic.

1. From Example 12.8 it is determined that the nitrite ion is bent.
2. A totally symmetric arrangement of ONO would be linear. Since ONO is bent, the molecule is covalent, heteronuclear, nonsymmetric, and therefore *polar*.

Note that the fact that one of the NO bonds is a double bond and the other is a single bond is not relevant. The two resonance forms balance out any differences in the bonds. In reality, the molecular bonding is symmetric; the structural ambiguity is a deficiency of Lewis bonding theory, which treats the electrons as localized classical particles.

12.8. Molecular Wave Mechanics

The Lewis structure model and its attending geometry and polarity heuristics provides an excellent technique for describing and predicting a variety of chemical properties in terms of chemical bonding, but no explanation is given for the duet/octet rule other than electrons preferred to be paired and atoms prefer to be noble. Furthermore it offers no explanation for the unusual stability of the noble gas elements, or differences in the relative stabilities of isoelectronic molecules. A rationalization of Lewis theory came with the development of wave mechanics during the scientifically creative period between the two World Wars.

The goal of Erwin Schrödinger and Werner Heisenberg in developing a new wave mechanics was to do for multiple-electron atoms what Niels Bohr had done for the hydrogen atom (explain atomic line spectra in fundamental terms; see Sections 7.4 and 7.5 on atomic spectra and wave mechanics). Bohr's quantized orbits were a modification of a classical model for the atom; Schrödinger's quantized waves broke with all classical particle notions and generated a picture of the electron which is still difficult to visualize in common experience (see Section 5.8 on Wave Mechanics). Still, the theory is eminently successful, and it has an added feature - it can convincingly describe the structure of multielectron systems with quantitative precision.

In Chapter 7 we have seen how wave mechanics is successful in explaining the aufbau heuristic, and the properties of atoms summarized by the chemical periodic table. We will now show how the Schrödinger equation is equally successful for molecules in providing quantitative information about molecules and in justifying simplifying models for chemical

bonding. In one sense there is little difference between atoms and molecules, as both atoms and molecules have nuclei and electrons, but significant differences result from the fact that molecules have more than one nucleus. It may seem strange to think of the dihydrogen molecule as being isoelectronic with the helium atom, but the identical electron count was precisely the basis of the duet rule for two-electron systems such as dihydrogen. Carbon monoxide and dinitrogen have identical Lewis structures, a triple bond and two lone pairs, with a resulting strong chemical bond, a striking success of the power of Lewis' classical electron model of chemical bonding. Yet while we breathe dinitrogen without noticeable effects, carbon monoxide is deadly. The detailed treatment of all the electrons and nuclei of a molecule is necessary to detect these differences, and wave mechanics is just the theory to apply to molecules as well as atoms.

One of the first insights obtained from applying Schrödinger's equation to molecules was the quantitative justification for the notion of the chemical bond. In the early days of atomic and molecular theory, Dalton criticized Avogadro's explanation for combining gas volumes that certain elements like hydrogen are made of diatomic molecules. Dalton questioned why hydrogen should be diatomic, and not triatomic, or tetraatomic, etc. for that matter? This was a difficult question to answer because nobody could explain why two or more identical atoms should be attracted, in the way that opposite charges are in the case of ionic compounds. The clue, as we have seen, came with the discovery of subatomic structure of oppositely charged fundamental particles (electrons and protons). Lewis gave a qualitative explanation for the chemical bond in terms of attraction of opposites, but could give no details about the bond itself. The duet/octet "rule" was nothing more than a useful heuristic, without theoretical justification, that is, until quantum mechanical wave mechanics was developed. It is not surprising that one of the first systems wave mechanics was applied to was the hydrogen molecule and, in 1929, calculations by Fritz London showed that dihydrogen was more stable than two isolated hydrogen atoms, justifying Avogadro's hypothesis of homonuclear covalent bonds for the first time.

We will assume at first that the nuclei in a molecule are fixed in space and that the electrons are moving in the electric field of the fixed nuclei. There is some justification for separating electronic and nuclear motion on the basis that the electrons are so much lighter than the nuclei that they can respond quickly to any changes of the positions of the much more massive nuclei. This simplification is named the **Born-Oppenheimer approximation**, after its originators. After developing the electronic structure of molecules, we will return to

molecular nuclear motion.

12.9. Valence Bond Theory

Of course it is extremely difficult to obtain the mathematical solution to Schrödinger's wave equation for multielectron systems, atoms as well as molecules.⁶ The solution to the dilemma of having an accurate theory for which only approximate solutions can be obtained is to reduce the original problem to a simpler one for which accurate solutions *can* be obtained. One of the early approximation approaches to the wave mechanics for molecules is based on Lewis structures. It was developed by Linus Pauling and is called **Valence Bond (VB) Theory**. In this model, the wave function describing the electron cloud localizes electrons into molecular orbitals surrounding the atoms similar to Lewis structures. Mathematical details are not important, but the picture of the chemical bond which emerges is. Atoms combine into molecules by sharing electrons. This sharing results from *overlapping* electronic orbitals on adjacent atoms. Molecular geometry is a consequence of the *directionality* of the atomic orbitals.

There are some problems with the explanation of the covalent bond in terms of atomic orbitals. In the first place, atoms with valence electrons in s orbitals should present no preferential direction to the bond, while atoms with electrons in p, d and f orbitals should present strong direction preference to the bonds formed with the orbitals of neighboring atoms (cf. Fig. 7.8). Consider simple compounds between carbon and hydrogen. The detailed electronic configuration of the carbon atom has two of the four valence electrons occupying the 2s orbital and the remaining two separately occupying two of the three 2p orbitals.⁷ If bonding results from the overlap of atomic orbitals on neighboring atoms, one would predict that the compound formed between carbon and hydrogen should have the molecular formula CH₂, since two of the four valence electrons are paired in a filled 2s subshell of the carbon atom. Further, molecule bonds of the CH₂ should be constrained to lie along the directions of the perpendicular 2p orbitals on carbon, where the remaining valence electrons reside. On this

⁶ This is a reflection of the famous three-body problem in classical mechanics. While it is possible to reduce the equations of motion for two bodies into a pair of one-dimensional equations for which closed solutions exist, no such reduction exists for more than two bodies, and approximate solutions are obtained by resorting to numerical techniques using computers (Section 5.4).

⁷ Recall Hund's rule: electrons occupy separate orbitals of a subshell.

basis, one predicts the hydride of carbon to be bent CH_2 with a bond angle of 90 degrees, resulting in a polar molecule. In fact, *none* of these properties is observed in nature. Seemingly oblivious to the occupancy and directional properties of orbitals, the simplest hydrocarbon, methane, CH_4 , has *four* hydrogen atoms, not two, is totally symmetric with a perfect tetrahedral geometry, and is non-polar.⁸

In order to retain Lewis structure notions in wave mechanics, Pauling conceived a *rationalization* of the bonding of methane. This rationalization is neither an explanation nor prediction, but a useful heuristic which can be applied to a wide range of molecules.⁹ According to Pauling's rationalization, the two 2s electrons on the carbon atom split, and one electron is "promoted" to the empty remaining p orbital. This results in *four unpaired*, and therefore highly reactive, electrons on the carbon atom. In this way carbon is able to combine with *four* hydrogen atoms to form an octet on carbon. Any expenditure of energy required to promote the 2s electron is recovered in forming two additional stable bonds (CH_4 vs. CH_2). To explain the *equivalence* of the four CH bonds, Pauling invented the concept of **hybridization**, which basically mixes the s and p orbitals to form "intermediate" orbitals, all equivalent. Since one s and three p orbitals are mixed and reformed, Pauling calls these sp^3 hybrid orbitals. Note that *in reorganizing atomic orbitals into hybrid atomic orbitals, the number of orbitals is conserved*.¹⁰

The Valence Bond Description Algorithm is useful for describing covalent molecular bonding in valence bond terms.

⁸ A CH_2 molecule has been detected experimentally, but it is unstable, short lived, and has a bond angle of 138 degrees, which defies explanation in terms of any simple atomic orbital model, including VSEPR theory (neither 90 nor 180 degrees). Careful quantum mechanical calculations confirm the experimental observations.

⁹ Note that methane is but the simplest of millions of known organic hydrocarbon molecules.

¹⁰ A good analogy for sp^3 hybridization is mixing three quarts of white paint with one can of red paint to form four cans of pink paint. Note that the superscript 3 is *not* a power, but rather denotes the *number* of p orbitals participating in the hybridization.

Valence Bond Description Algorithm

Purpose: To describe covalent bonding in valence bond terminology.

Procedure:

1. Write the Lewis structure of the molecule using the Lewis Structure Algorithm.
2. Classify the atomic orbitals. Single bonds and lone pairs result from σ hybrid orbitals, double bonds consist of one σ hybrid orbital plus one π (non-hybridized) bond, and triple bonds have one σ hybrid orbital and two π bonds.
3. Describe the bonding on each interior (non-terminal) atom by counting the number of σ bonds.

<i>Number of σ Orbitals</i>	<i>Hybridization</i>
1	no hybridization
2	sp hybridization
3	sp ² hybridization
4	sp ³ hybridization
5	sp ³ d hybridization
6	sp ³ d ² hybridization
7	sp ³ d ³ hybridization

4. Molecular geometry is explained by the VSEPR Molecular Geometry Heuristic, where the bonding groups (regions of high charge density) are identified with the σ bonds.

Example 12.11 Describe the bonding in the nitrite ion in valence bond terms.

1. The Lewis structure and geometry of the nitrite ion were discussed in Examples 12.7 and 12.8.
2. From the Lewis structure, there is one single (σ) bond, one double bond (one σ plus one π) and one (σ) lone pair on the nitrogen atom in the nitrite ion.
3. Three σ bonds on the nitrogen atom are described in valence bond terminology by sp^2 hybridization of the nitrogen atomic orbitals.
4. Three σ bonds produce a triangular electron arrangement, and a bent atom arrangement. The π electrons are not important since three atoms must lie in a plane.

In retrospect, it appears that the concept of promotion and hybridization is an overcomplicated rationalization of Lewis theory. Although expressed in impressive quantum mechanical terminology, equally valid predictions may be obtained by the much simpler VSEPR theory. However, the valence bond model does justify the Lewis heuristic, in terms of the correct mechanics (quantum mechanics). In common with the Lewis model, the valence bond description ignores the inner-shell electrons and considers the valence electrons to be localized in the chemical bonds. Thus large polyatomic molecules can be thought of as built up from independent diatomic bonds, much the way a “ball and stick” molecular model is constructed. For this reason the valence bond model is relatively easy to apply to large polyatomic molecules.

12.10. Molecular Orbital Bond Theory

One deficiency of valence bond theory is that it predicts, along with Lewis theory, that oxygen should be diatomic and have a double bond with two lone electron *pairs* on each oxygen atom. Experimentally, oxygen is observed to be diatomic with a bond strength and distance which correlates with other molecules known to have double bonds. However, completely paired electrons produce *diamagnetic* molecules (not attracted to magnets), and dioxygen is observed to be *paramagnetic* (has at least one unpaired electron and therefore attracted to magnets). An alternate method for solving the wave equation for molecules can account successfully for these properties of dioxygen.

The **Molecular Orbital (MO) Theory** of chemical bonding is based on an extension of the aufbau procedure for multi-electron atoms. Recall that in the aufbau method, one starts with a set of atomic orbitals arranged in ascending energy, and fills up the lowest available energy orbitals according to maximum occupancy restrictions (*Pauli exclusion*) (see the

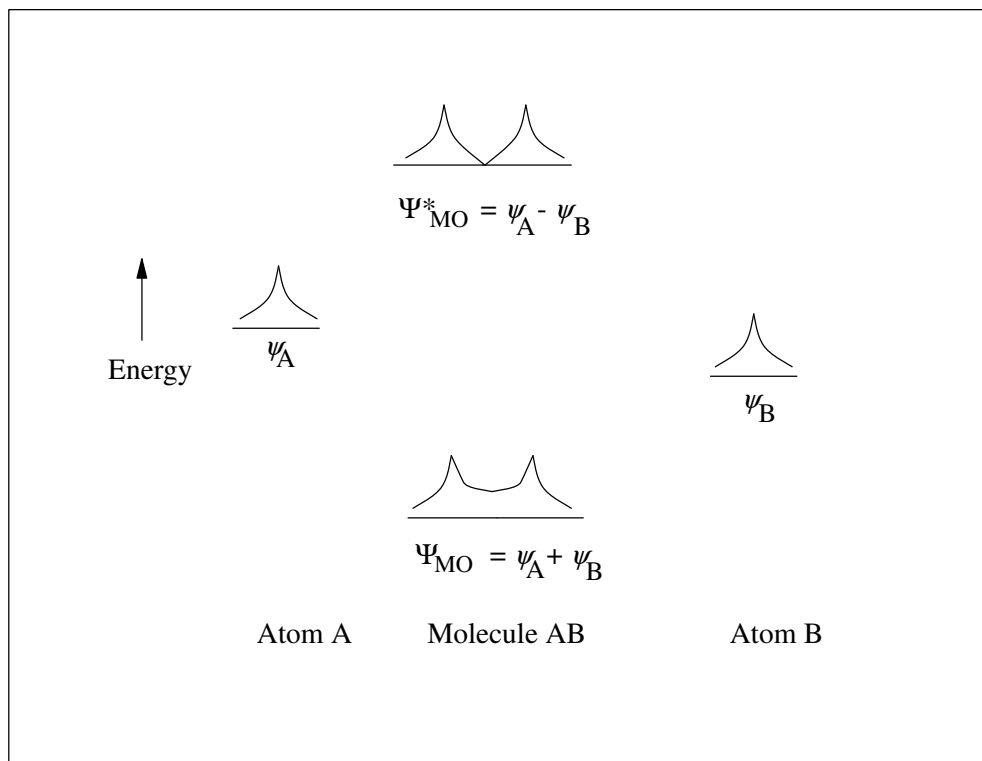
aufbau heuristic in Section 7.7 on Atomic Electronic Configurations). The *molecular orbital* method follows a similar procedure for molecules, with one important difference. In the case of molecules, when the charge clouds of a pair of atomic orbitals overlap (mix with) each other to some extent, two *molecular* orbitals with different energies result, one *lower* in energy than the atomic orbital energies, called a **bonding molecular orbital**, and one *higher* in energy, called an **antibonding molecular orbital**. Although there is a conservation of orbitals as they transform from atomic orbitals into molecular orbitals (i.e. the number of MOs on the molecule equals the number of AOs on the atoms) there is a splitting of energies into two sets. Electrons in the lower energy levels tend to stabilize molecule formation, while occupancy of the higher orbitals tends to *destabilize* the molecule.

Mathematically, the molecular orbital model combines atomic orbitals into molecular orbitals linearly (by addition):¹¹

$$\Psi_{\text{MO(AB)}} = \psi_{\text{AO(A)}} \pm \psi_{\text{AO(B)}} \quad (12.1)$$

Where $\psi_{\text{AO(A)}}$ and $\psi_{\text{AO(B)}}$ are atomic orbital wave functions for atoms A and B, and $\Psi_{\text{MO(AB)}}$ is the molecular wave function for molecule AB formed from the atoms. The two signs distinguish the bonding (+) molecular orbital from the antibonding (−) molecular orbital. Fig 12.9 portrays the electron densities of the separate atoms and of the bonding and antibonding molecular orbitals on the molecule, as well as the changes in energy when the molecule forms (electron densities are proportional to the square of the wave function).

¹¹ Refer to the discussion on Curve Fitting in Section 3.4.

**Fig. 12.9** Atomic and Molecular Orbitals and Energies

Note how the charge density builds up between the atoms in the bonding molecular orbital, and how it is diminished in the antibonding molecular orbital. In fact, the magnitude in the antibonding orbital (denoted with a superscript *) goes to zero at a point between the nuclei called a “node”.

In the case of dihydrogen, the bonding molecular orbital formed from two 1s atomic orbitals is denoted σ_{1s} . The sigma symbol is used to denote cylindrical symmetry about the internuclear axis. The two electrons occupy the bonding orbital and a stable molecule results,

giving a *molecular orbital electronic configuration* of $(\sigma_{1s})^2$. *Overlapping atomic orbitals is the molecular orbital explanation for the homonuclear diatomic bond in dihydrogen.* The antibonding molecular orbital formed from the 1s atomic orbitals is denoted by an asterisk superscript, σ_{1s}^* . It is unoccupied in dihydrogen, but would be occupied in dihelium (4 total electrons). The destabilization of the occupied antibonding orbital cancels the stabilization of the occupation of the bonding orbital, and dihelium is not stable, as is well known.

Similar to the way atomic multielectronic configurations are approximated as occupying one-electron atomic orbitals, molecular orbital configurations may be approximated in terms of the simplest one-electron molecule, the hydrogen molecule ion, H_2^+ .¹² By considering all the possible combinations of atomic orbitals on two atoms, the following *molecular orbital aufbau* energy ordering has been developed:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^* < \sigma_{3s} < \sigma_{3s}^* < \dots$$

The subscripts refer to hydrogen atom atomic orbital wave functions (the first two of which are shown in Fig. 12.9) which are used to construct the molecular orbitals according to Eq. (12.1). The superscript * distinguishes antibonding orbitals from their bonding counterparts. The Greek letter notation refers to the shape of the resulting molecular orbital. Cylindrical shape is denoted by σ and a “bridging” shape is reminiscent of the Greek letter π . A pair of s atomic orbitals produces bonding and antibonding cylindrical molecular orbitals. A pair of p_x atomic orbitals lying *along* an internuclear axis on the x coordinate also produces cylindrically symmetric molecular orbitals, but pairs of p_z atomic orbitals are *perpendicular* to the internuclear axis and produce π molecular orbitals.

Molecular orbital electronic configurations *specify the occupancy of the molecular orbitals in a molecule and are obtained from the molecular aufbau process given in the Molecular Orbital Aufbau Algorithm below.* Two significant features distinguish the *molecular* aufbau process from the atomic orbital *aufbau* process, however. First the x, y and z orbitals have different energy levels in molecules, so *the energies of molecular orbitals depend on the m, n and l quantum numbers. Orbitals with equal energies are said to be degenerate.*¹³ The p atomic orbitals lying perpendicular to the internuclear axis of a diatomic

¹² An alternative view considers the molecular orbitals to be approximated by atomic orbitals of atoms having the same number of electrons as the molecules they approximate. This is called the *united atom* view.

¹³ Recall that a circle is a degenerate ellipse, with major axis length equal to minor axes length.

molecule combine into two degenerate π molecular orbitals. Like atomic orbitals, *the maximum occupancy of any molecular orbital is two*. However, there are no destabilizing antibonding orbitals in atomic orbitals as there are in molecules. Consequently, *the stability of a molecule is determined by the both bonding as well as antibonding molecular orbital occupancy*. This is a second distinguishing feature of molecular orbitals. Note that MO theory considers *all* the electrons of the molecule whereas VB theory considers only the valence (outer shell) electrons. A useful formula for estimating the number of classical bonds in a molecule is the **bond order** formula,

$$\text{BO} = \frac{1}{2} (\text{total number of bonding electrons} - \text{total number of antibonding electrons}) \quad (12.2)$$

Molecular Orbital Aufbau Heuristic

Purpose: To determine the molecular orbital electronic configuration of a diatomic molecule.

Procedure:

1. Sum *all* the electrons for a given molecule from the atomic numbers of its atoms. In the case of ions, add one electron for each unit of negative charge, or subtract one electron for each unit of positive charge.
2. Fill the molecular orbitals with electrons in ascending energy order according to the molecular aufbau ordering, each with a maximum of two electrons:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} \approx \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^* < \sigma_{3s} < \sigma_{3s}^* < \dots$$

For elements beyond group 5 the σ_{2p} orbital is lower in energy than the π_{2p} orbital.

3. Estimate the number of classical bonds as one-half the difference between the number of bonding and number of antibonding electrons.

Example 12.12 Describe the bonding in dioxygen in terms of the molecular orbital theory.

1. The atomic number of oxygen is 8. Thus dioxygen has 16 electrons.
2. Since oxygen is in group 6 (beyond group 5), the σ_{2p} orbital is lower in energy than the π_{2p} orbital.

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^1 (\pi_{2p_y}^*)^1$$

3. Counting up the total number of bonding and antibonding electrons, the number of classical bonds (bond order) is $(1/2)(10 - 6) = 2$.

The dioxygen molecule has a double bond, in accord with the experimental facts (and Lewis and VB theory). The paramagnetism of the oxygen molecule emerges as a consequence of the degeneracy of the final π^* molecular orbitals and Hund's rule of single occupancy where possible in degenerate molecular orbitals.

Similar to the atomic aufbau heuristic, the molecular orbital heuristic is supported by calculations and experiments. For example, the photoelectron spectrum (Sections 5.7 and 7.6) of dioxygen shows emission peaks (from MOs) at 53,000(1s), 3860 (σ_{2s}), 2700 (σ_{2s}^*), 1753 (σ_{2p}), 1603 (π_{2p}), 1187 (π_{2p}^*) kJ/mol. Note that the core electrons are essentially atomic orbitals (i.e. similar energy as oxygen atoms - Example 7.6), and the large differences between the bonding and antibonding valence (2s and 2p) MOs.

It is possible to correlate MO theory with Lewis structures and VB theory by noting that the lowest energy electrons occupy inner-shell molecular orbitals, are balanced with equal bonding and antibonding occupancy, and therefore don't participate significantly in the bonding of the molecule. In the case of dioxygen, the MO configuration which distinguishes between core and valence electron configurations becomes

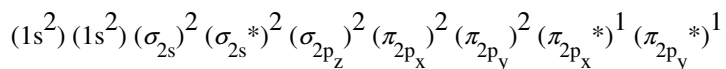


Fig. 12.10 depicts the atomic orbital energies of separated oxygen atoms and the molecular orbital energies of molecular dioxygen relative to a singly ionized state.

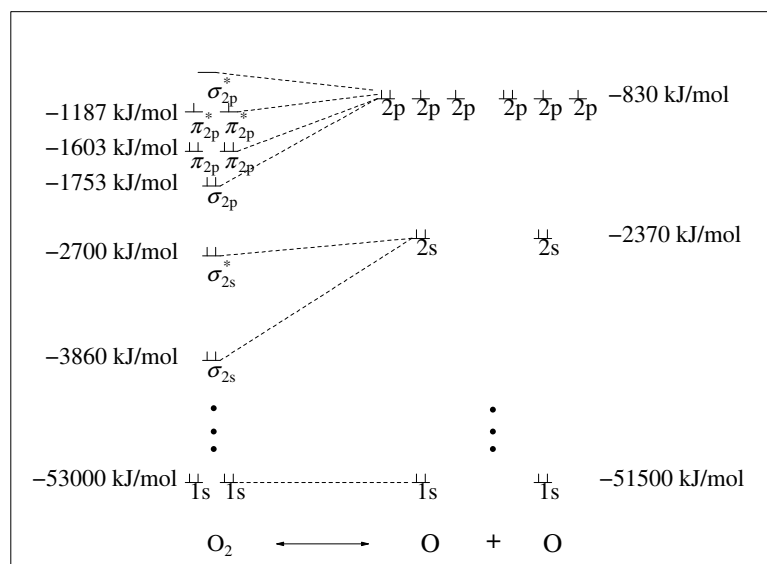


Fig. 12.10 Orbital Energies of Atomic and Molecular Oxygen

12.11. Bond Strength

So far we have been assuming that the nuclei of molecules are fixed at a certain distance and we have concentrated on the electronic configurations. Separating the electronic motion from that of the nuclei simplifies the situation, but the nuclei should not be ignored. In concentrating on the electrons, nuclear coordinates enter the wave equation as *parameters* (fixed values) and electronic coordinates as *variables* (variable values). But what values should be assigned to the nuclear separations? It is apparent that nuclei separated to large internuclear distances describe more a collection of atoms than a molecule. As the atoms approach, there should be a continuous transition to form a molecule. The wave mechanical equation can be solved for the energy of the system as a function of internuclear separation. What is the functional form of such a “binding energy” curve? As bonds form, the potential energy falls due to the attractions between the electrons and the nuclei, but as the nuclei move closer, the

nuclei repel each other more strongly, as do the electrons, according to Coulomb's law (refer to Fig. 12.2, Fig. 5.1 and Eq. (5.14b)). At some intermediate position, the potential energy of the molecule reaches a minimum, signifying a stable configuration, referred to as the "equilibrium" configuration. Fig. 12.11 depicts how the potential energy depends on the internuclear separation in a bond.

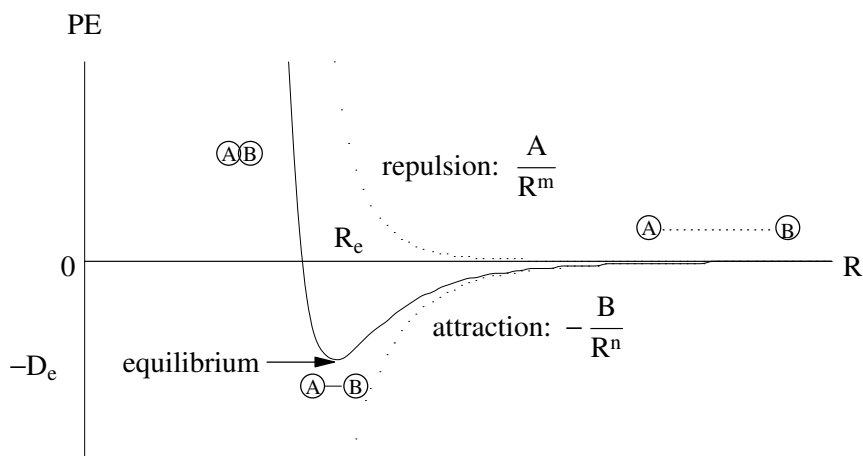


Fig. 12.11 Diatomic Binding Potential Energy (PE) vs Internuclear Distance (R)

The zero of interaction is arbitrarily assigned to separated fragments (atoms for diatomics) at infinite separation, R . As separated fragments come closer together, attraction increases, as indicated by a *decrease* in potential energy of the system. When the fragments become too close, the potential energy of attraction crosses the zero value and the system becomes repulsive. The equilibrium point at the minimum corresponds to the classical model of rigid molecules. In the figure, the equilibrium point is indicated by the separation value of R_e , and energy of $-D_e$. Molecules with more than two atoms have multidimensional potential energy surfaces, each dimension corresponding to the bond between a pair of atoms.

Bond strengths are measured as the energy differences between the minimum potential energy (initial state) and the energy of the dissociated atoms (final state). For a diatomic

molecule the bond energy ΔE_{bond} is

$$\Delta E_{\text{bond}} = E_{\text{final}} - E_{\text{initial}} = 0 - (-D_e) = D_e \quad (12.3)$$

The bond dissociation process can be expressed in terms of a “chemical equation” with “reactants” on the left (initial state of diatomic and input energy) converting into “products” on the right (final state of dissociated atoms).

$$A_2 + \Delta E_{\text{bond}} = 2A \quad (12.4)$$

The energy input to break a bond and dissociate the molecule can come from a variety of sources, including heat (thermal energy), light, and electricity. Note that while the bond strength usually connotes a single parameter, D_e , there is in reality a range of bond dissociation energies, corresponding to different points on the potential energy curve. In order to be above the minimum (equilibrium) state, molecules must have internal rotational and/or vibrational energy.

There have been many attempts to model bond energy curves with analytic functions. An early form, due to Mie in 1903 and developed by Lennard-Jones,¹⁴ combines repulsive and attractive contributions as the sum of simple hyperbolic curves:

$$PE(R) = \frac{A}{R^m} - \frac{B}{R^n} \quad (12.5)$$

The parameters m and n represent the strengths of the repulsive and attractive contributions; in order for repulsions to dominate over attraction at small separation R , it is necessary that $m > n$.¹⁵ Consideration of the value of PE at R_e expresses A and B in terms of D_e and R_e .¹⁶

¹⁴ John E. Jones changed his surname when he married Kathleen M. Lennard in 1925.

¹⁵ Typical values are $m = 12$, $n = 6$.

¹⁶ The slope of the curve at the minimum is zero. From calculus:

$$\left(\frac{dPE}{dR}\right)_{R_e} = \frac{-mA}{R_e^{m+1}} + \frac{nB}{R_e^{n+1}} = 0$$

$$PE(R) = \frac{-D_e}{(n-m)} \left[n \left(\frac{R_e}{R} \right)^m - m \left(\frac{R_e}{R} \right)^n \right] \quad (12.6)$$

Another expression, due to P. M. Morse, can be derived from the Mie potential and has the form¹⁷

$$PE(R) = D_e [1 \pm e^{-\frac{n}{R_e}(R-R_e)}]^2 - D_e \quad (12.7)$$

D_e is subtracted to shift the zero of energy from the minimum to separated particles ($R \rightarrow \infty$) and the plus sign has been added to describe repulsive antibonding curves as well as bonding curves (minus sign).

The product of the parameters m and n can be shown to be related to the molecular vibration frequency, ν_e (discussed in the next section):

Eliminate A and B between this equation and Eq. (12.5), evaluated at R_e , so that $PE(R_e) \equiv -D_e$.

$$-D_e = \frac{A}{R_e^m} \left(1 - \frac{m}{n} \right) = -\frac{B}{R_e^n} \left(1 - \frac{n}{m} \right)$$

Then solve for A and B and replace their expressions in Eq. (12.5).

¹⁷ Add to Eq. (12.6) the following identity equal to zero: $D_e \frac{(n-m)}{(n-m)} - D_e$ and collect terms to get

$$PE(R) = \frac{D_e}{(m-n)} \left\{ m \left[1 - \left(\frac{R_e}{R} \right)^n \right] - n \left[1 - \left(\frac{R_e}{R} \right)^m \right] \right\}$$

Apply the expansion definition of the exponential function, Eq. (3.5)

$$e^{-\left(\frac{R-R_e}{R_e}\right)} \approx \frac{1}{1 + \left(\frac{R-R_e}{R_e}\right)} = \frac{R_e}{R}$$

and obtain Eq. (12.7) for the case $m = 2n$

$$\nu_e = \frac{1}{2\pi R_e} \sqrt{\frac{mnD_e}{\mu}} \quad (12.8)$$

where μ is the reduced mass (Section 5.4) of the molecule, defined by

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (12.9)$$

The Mie and Morse functions are *empirical*, or *phenomenological* equations because they are not derived from anything else. However they are relatively simple mathematical expressions and have the properties of describing approximately the correct shape, and correct limiting behaviors: $PE(R = \infty) = 0$, $PE(R = 0) = \infty$, $PE(R = R_e) = -D_e$.

For an actual case, Fig. 12.12 shows the lowest (of an unlimited number of) potential energy curves for the dihydrogen molecule. The lower curve is the ground-state potential energy curve and shows how a stable dihydrogen molecule forms from two hydrogen atoms. This is the wave-mechanical justification for Avogadro's hypothesis that hydrogen is diatomic¹⁸ and Lewis' duet rule. One or both of the electrons in dihydrogen can be excited to a higher electronic state by the absorption of energy. Fig. 12.12 shows the bond energy curve for the first excited electronic configuration which results from bringing two hydrogen atoms together having the same value of the spin quantum number. The electrons in such a case are said to be "unpaired". The exclusion principle states that each electron must have a unique set of quantum numbers, so if the two electrons have the same spin quantum number (either $-\frac{1}{2}$ and $-\frac{1}{2}$ or $+\frac{1}{2}$ and $+\frac{1}{2}$), they must occupy different spatial orbitals and the excited-state MO configuration $(\sigma_{1s})^1 (\sigma_{1s}^*)^1$ results. Since the energy of the excited state is everywhere greater than that of two separated hydrogen atoms (a repulsive curve), the first electronic excited state of dihydrogen is essentially unstable (an antibonding state).¹⁹ If such an electronically excited molecule is formed momentarily by absorption of the appropriate

¹⁸ This does not answer Dalton's criticism that if atoms of the same type prefer to be bound into diatomic molecules, why not triatomic, or higher? The answer is again given by wave mechanics that trihydrogen is stable, but it is *less* stable than dihydrogen.

¹⁹ An extremely shallow potential well 0.0514 kJ/mol deep at the large internuclear separation of 415.4 pm has been found for the first excited state of H_2 by sensitive quantum mechanical calculations. The average thermal energy at 3 K (comparable to the background radiation temperature in space) of 0.04 kJ/mol according to Eq. (14.1) would be nearly sufficient to dissociate it.

amount of energy (light in the visible or ultraviolet region of the electromagnetic spectrum), it immediately decays back to the ground state. Promoting the electrons to still higher electronic excited state configurations, produces additional attractive and repulsive curves, but they all dissociate to higher hydrogen atom electronic states than the ground state, and all such species are unstable.

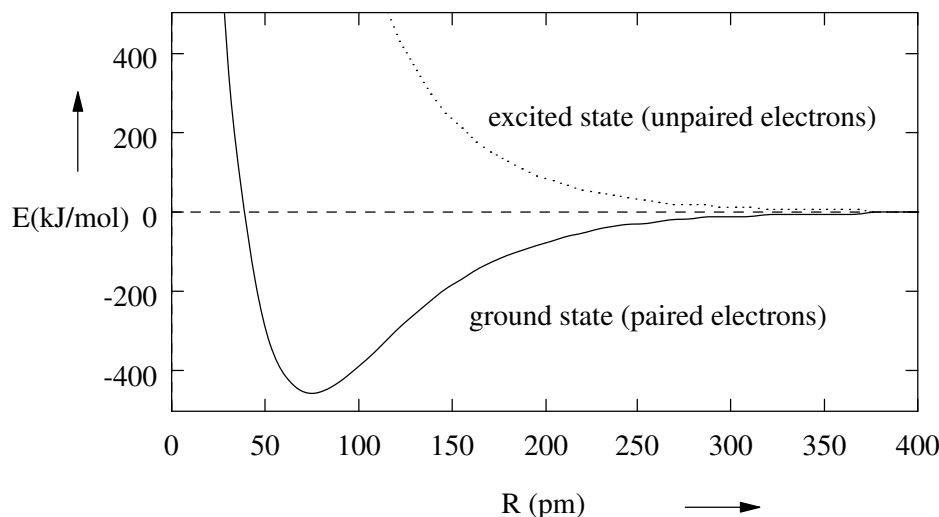


Fig. 12.12 Lowest Ground and Excited Electronic States of Dihydrogen

The Aufbau Heuristic is based on the wave-mechanical results for the one-electron dihydrogen molecule positive ion. The energy ordering of the bonding and antibonding molecular orbitals is derived from the potential energy curves for the ground and excited states (compare Figs. 12.9 and 12.12). Note that bonding and antibonding curves are interleaved so that electrons occupy antibonding as well as bonding molecular orbitals. The idea that chemical bonds are discrete in number, localized between atoms, and that interatomic distances are fixed are only useful heuristics, based on first approximations to the real situation. Given the approximations, bond strength is supposed to increase with number of bonds,

or bond order. Ionic bonds are considered in first approximation to be *electrostatic* in nature, that is, governed by the laws of electricity. The strength of ionic bonds therefore depends principally on electrostatic parameters such as charge and distance; bond strength increases with increasing charge and decreasing distance between oppositely charged ions. However, *according to the wave-mechanical description of bonding there is no distinction between ionic and covalent bonding*. Table 12.1 illustrates the correlation between bond order and bond strength for a variety of diatomic molecules.

Table 12.1 Diatomic Bonding Parameters

Molecule	MO Configuration	Bond Order	R_e (pm)	D_e (kJ/mol)	ν_e (s^{-1})
H_2^+	$(\sigma_{1s})^1$	$1/2$	106	268	6.886×10^{13}
H_2	$(\sigma_{1s})^2$	1	74	458	1.319×10^{14}
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$1/2$	108	241	5.090×10^{13}
He_2	$(1s_{He}^2)(1s_{He}^2)$	0	298	0.089	—
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^1(\sigma_{2s})^1$	1	105	175	5.426×10^{13}
LiH	$(1s_{Li}^2)(1s_H^2) = [He][He]$	1	160	242	4.213×10^{13}
Li_2	$[He_2](\sigma_{2s})^2$	1	267	110	1.053×10^{13}
Na_2	$[Ne_2](\sigma_{3s})^2$	1	308	73	4.773×10^{12}
K_2	$[Ar_2](\sigma_{4s})^2$	1	392	50	2.776×10^{12}
Rb_2	$[Kr_2](\sigma_{5s})^2$	1	420	46	1.718×10^{12}
Cs_2	$[Xe_2](\sigma_{6s})^2$	1	458	44	1.259×10^{12}
Be_2	$[He_2](\sigma_{2s})^2(\sigma_{2s}^*)^2$	0	?	9	?
B_2	$[Be_2](\pi_{2p})^2$	1	159	294	3.152×10^{13}
C_2	$[Be_2](\pi_{2p})^4$	2	124	613	5.560×10^{13}
BN	$[Be_2](\pi_{2p})^4$	2	128	394	4.542×10^{13}
BeO	$[He][Ne]$	2	133	453	4.458×10^{13}
LiF	$[He][Ne]$	1	156	579	2.728×10^{13}
NaCl	$[Ne][Ar]$	1	236	412	1.097×10^{13}
N_2^+	$[Be_2](\pi_{2p})^4(\sigma_{2p})^1$	$2 1/2$	112	859	6.617×10^{13}
N_2	$[Be_2](\pi_{2p})^4(\sigma_{2p})^2$	3	109	960	7.069×10^{13}
NO^+	$[Be_2](\pi_{2p})^4(\sigma_{2p})^2$	3	106	1050	7.126×10^{13}
CO	$[Be_2](\pi_{2p})^4(\sigma_{2p})^2$	3	113	1083	6.506×10^{13}
BF	$[Be_2](\pi_{2p})^4(\sigma_{2p})^2$	3	126	765	4.200×10^{13}
O_2^+	$[Be_2](\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)$	$2 1/2$	112	653	5.711×10^{13}
O_2	$[Be_2](\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$	2	121	503	4.737×10^{13}
F_2	$[Be_2](\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	1	144	159	2.755×10^{13}
Cl_2	$[Ne_2](\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^4$	1	199	243	1.678×10^{13}
Br_2	$[Ar_2](\sigma_{4p})^2(\pi_{4p})^4(\pi_{4p}^*)^4$	1	228	192	9.692×10^{12}

I ₂	[Kr ₂](σ _{5p}) ² (π _{5p}) ⁴ (π _{5p} [*]) ⁴	1	267	150	6.431 x 10 ¹²
Ne ₂	[Be ₂](σ _{2p}) ² (π _{2p}) ⁴ (π _{2p} [*]) ⁴ (σ _{2p} [*]) ²	0	310	0.260	—

A shorthand molecular electronic configuration similar to that for atoms has been employed, which summarizes completed-subshell configurations with atomic symbols. For example, complete occupancy of the two inner shell *atomic* orbitals can be abbreviated to [He₂]. [Be₂] is an abbreviation for the diberyllium MO configuration, with 1s inner shell atomic orbitals and 2s molecular orbitals. Note the inversion of the ground-state molecular orbital ordering for elements beyond the group 5 of the periodic table, similar to occasional atomic electronic configuration inversions.

Bond orders determined by molecular orbital occupancy often match the number of bonds in Lewis formulas for the molecules. There is a rough correlation between bond order and bond strength, with minimal bonding for zero bond orders in the case of molecular orbitals corresponding to pairing electrons from filled subshell atomic electronic configurations (e.g. noble gases), and maxima in the case of molecular orbitals corresponding to pairing electrons from half-filled atomic subshells (e.g. N₂ and CO). There is also a correlation between bond order and bond length; the stronger the bond, the shorter the separation (and the higher the vibrational frequency), in harmony with the notion that the chemical bond is due to build up of electronic charge between nuclei.

He₂ has a filled shell of electrons and bond order equal to zero. There is a small amount of binding between neutral helium atoms, but it is a thousand times smaller than ordinary chemical bonds. These so-called intermolecular bonds are considered in Chapter 14. When an electron in He₂ is promoted from an antibonding orbital to a bonding orbital, the molecule goes into an excited electronic state with a bond order of one, and shows a respectable binding energy. Electronically excited He₂ is not stable for any length of time because it decays back to the ground electronic state with the emission of radiation. On the other hand, the diatomic helium ion is stable in an isolated environment (such as outer space) because it has more bonding electrons than antibonding electrons.

Since the highest-energy electrons in dinitrogen occupy bonding molecular orbitals, the stability of the dinitrogen molecule would be expected to decrease when the bonding electrons are lost to ionization. Thus on ionization the bond strength of N₂ decreases, and the bond length increases. In contrast, the highest energy electrons in dioxygen occupy

antibonding molecular orbitals, and the stability of dioxygen *increases* and bond length decreases on ionization. Note that although O_2^+ is isoelectronic with N_2 , its dissociation energy is much less (653 kJ/mol vs 960 kJ/mol), illustrating that trends are better treated than absolute values.

The alkali metal (group 1A) and halogen (group 7A) diatomics demonstrate vertical trends in the periodic table of decreasing bond strength with increasing size, with an exceptional behavior of the top member of a family (which is extreme in the case of difluorine with its unusually weak bond).

Heteronuclear (different nuclei) diatomics (and polyatomics) can be treated by the MO model as well. For example, C_2 , BN, BeO and LiF are isoelectronic, but polarity increases as the atoms are further separated in the periodic table, and the bond strength for the heteronuclear diatomics increases accordingly. N_2 , NO^+ , CO and BF form another isoelectronic series containing triple bonds, but with a different trend. LiH would be isoelectronic with He_2 except for the fact that the atomic orbitals of Li and H differ. Because Li has a larger atomic charge (Z), 1s electrons are drawn in much closer to the Li nucleus than they are in H. On the other hand, the Li 2s orbital is much higher in energy than the 1s orbital of H, and when the bond forms, the Li 2s electron occupies the lower 1s orbital of H, giving rise to electron transfer and an ionic bond. This explains the MO configuration entry for LiH in Table 12.1. Similar considerations apply to LiF, BeO and NaCl, for which the ions have noble gas configurations. Dissociation energies for the ionic species are listed in the table relative to neutral atoms for consistency, however.²⁰

Example 12.13 Discuss the trends in bonding in the halogen hydrides.

The halogen hydrides form a series of similar diatomic molecules. As the halogen column of the periodic table is descended, the size of the halogen atom increases and the bond length is expected to increase and the bond strength is expected to decrease. Observed values for bond distances are 91.7 nm (HF), 127.5 nm (HCl), 141.4 nm (HBr) and 160.9 (HI), and bond strengths are 590 kJ/mol (HF), 447 kJ/mol (HCl), 378 kJ/mol

¹⁹ Ionized dinitrogen and dioxygen are not stable gas species in the lower atmosphere, where they are neutralized by encounters with other molecules, but they do persist in the rarefied “ionosphere” 100 km above the surface of the earth.

²⁰ For example, the dissociation energy of NaCl gas molecules to ionic $\text{Na}^+ + \text{Cl}^-$ is 550 kJ/mol.

(HBr) and 308 kJ/mol (HI). Hydrogen fluoride differs from its neighbor more than the others do.

MO bond theory has decided advantages over VB theory, including the more realistic picture of an electron “cloud” smeared over the molecule. A disadvantage is that MO theory becomes rapidly more complicated for polyatomic molecules. Therefore MO theory calculations have been largely (but not exclusively) restricted to small molecules.

The strength of the chemical bond between two given atoms varies from molecule to molecule because a bond is only part of a total electronic environment in a molecule. Nevertheless, the notion of a chemical bond between two atoms derives from the fact that electron clouds tend to be localized between atoms. Since adjacent atoms have the major influence on the electron cloud in a chemical bond, bond strengths tend to be fairly constant and independent of the remainder of the molecule.

Bond energies for many molecules have been measured experimentally,²¹ and the results confirm the speculation of the previous paragraph, namely *bond energy is relatively independent of environment*. For example, it takes 423 kJ to break the bonds in a mole of OH diatomic molecules, which is close to average energy to break the first and second OH bonds of water (H-O-H) molecules = $(499 + 428)/2 = 463$ kJ. Similarly, the energies to break the successive N-H bonds in ammonia are 449, 384 and 339 kJ/mol, leading to an average N-H bond energy of 391 kJ/mol. For methane (CH₄) the average is $(438 + 465 + 422 + 338)/4 = 416$ kJ/mol. For SF₆ the average is $(387 + 217 + 335 + 282 + 384 + 343)/6 = 325$ kJ/mol. Note that the values of bond energies do depend to some degree on the environment (neighbors, molecule) (for example, the bond strength first increases then decreases in methane as successive H atoms are removed). Further, bond strength depends on bond order, so bonds between the same atoms depend on the multiplicity of the bonds. However, under the assumption that bonds of the same bond order between the same atoms have similar values in different environments, it is permissible to speak of an *average* bond energy between a given pair of atoms. Table 12.2 lists average bond strengths for a selection of atom pairs. Note that single covalent bonds range between about 100-600 kJ/mol, double bonds between about 400-800 kJ/mol and triple bonds between 800-1000 kJ/mol. Bond strength is seen to increase

²¹ Bond energies are determined mostly from experiments, as accurate wave mechanical calculations for large molecules are not yet available in most cases.

with number of bonds, very roughly 300 kJ/mol for single bonds, 600 kJ/mol for double bonds and 900 kJ/mol for triple bonds.

Table 8.1 contains crystal lattice bond energies for alkali metal fluorides, which represent bond strengths of multiple bonds in crystals (cf. Sections 12.2 and 16.4), but the trends follow the expected decrease with increasing atom sizes. Fig. 12.13 shows trends in element-hydride bond energies across the periodic table. The large range in single bond strengths is illustrated. The expected decrease in bond strength in descending a column is due to increasing element size. Except for the first column, bond strength increases to the right as the chemical families become less metallic. As usual, hydrogen is exceptional, and bridges the trends in the alkali metals and the halogens.

Table 12.2 Typical Bond Energies (kJ/mol)*Single Bonds*

	Li	Na	Mg	C	N	P	O	S	H	F	Cl	Br	I
Li	106												
Na	90	77											
Mg	—	—	9										
C	—	—	—	347									
N	—	—	—	305	160								
P	—	—	—	264	209	213							
O	341	256	362	358	201	351	146						
S	—	—	234	259	464	444	—	266					
H	238	184	126	414	391	321	467	344	436				
F	577	519	462	485	270	439	197	327	570	155			
Cl	469	410	328	397	200	289	203	253	429	256	240		
Br	423	370	327	280	243	—	201	218	362	237	219	190	
I	352	301	285	209	159	—	201	—	295	<272	211	179	149

Double Bonds

	C	N	P	O	S
C	613				
N	615	418			
P	513	617	490		
O	799	627	597	498	
S	699	464	444	522	425

Triple Bonds

	C	N	O
C	839		
N	891	946	
O	1070	1063	—

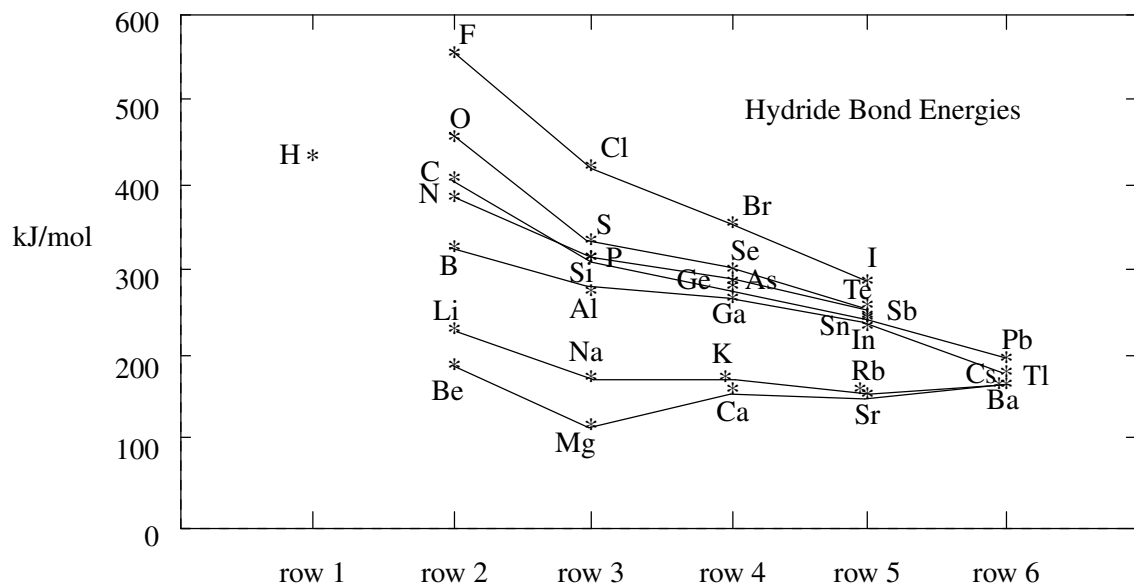


Fig. 12.13 Periodic Trends in Element Hydride Bond Strengths

Example 12.14 Compare the bond energies of dioxygen and ozone (trioxygen).

Lewis structures indicate a double bond for dioxygen and one double plus one single bond for ozone. According to Table 12.2, the energy of a dioxygen molecule is estimated to be $BE(O=O) = 498 \text{ kJ/mol}$, and that of ozone is $BE(O=O) + BE(O-O) = 498 + 146 = 644 \text{ kJ/mol}$. How is it that ozone is not more stable than dioxygen (which would cause the conversion of the atmosphere to ozone)? The answer is that if dioxygen is converted to ozone, the number of atoms must be conserved (matter cannot be created out of nothing), so the only fair comparison is to compare molecular energies relative to the same number of *atoms* (say, three molecules of O_2 with 2 molecules of O_3) or, equivalently, compare molecule energies *per oxygen atom*. When this is done, it is seen that dioxygen is more stable with 249 kJ/mol-O , whereas ozone has only 215 kJ/mol-O .

Example 12.15 Compare the total bond energies in methane, CH_4 , ethane, C_2H_6 , propane, C_3H_8 , and butane, C_4H_{10} .

These are the first in a series of *hydrocarbons*, molecules containing only the elements hydrogen and carbon. Since H can bond to only one other atom, hydrocarbon molecules containing multiple carbon atoms must have carbon bound to carbon. Methane contains 4 C–H single bonds. Ethane contains a C–C single bond and 6 C–H single bonds. Propane contains two C–C single bonds and 8 C–H single bonds. Butane contains four C–C single bonds and 10 C–H single bonds. According to Table 12.2, the total energy of a methane molecule is estimated to be $4 \times \text{BE}(\text{C} - \text{H}) = 4 \times 414 \text{ kJ/mol} = 1656 \text{ kJ/mol}$, that of an ethane molecule is $\text{BE}(\text{C} - \text{C}) + 6 \times \text{BE}(\text{C} - \text{H}) = 347 + 6 \times 414 = 2831 \text{ kJ/mol}$, that of propane molecule is $2 \times \text{BE}(\text{C} - \text{C}) + 8 \times \text{BE}(\text{C} - \text{H}) = 2 \times 347 + 8 \times 414 = 4006 \text{ kJ/mol}$, and that of butane molecule is $3 \times \text{BE}(\text{C} - \text{C}) + 10 \times \text{BE}(\text{C} - \text{H}) = 3 \times 347 + 10 \times 414 = 5181 \text{ kJ/mol}$.

Note that the estimated molecular energy per carbon atom is fairly constant (1656, 1415, 1335 and 1295 kJ/mol-C). The general formula for the saturated (single-bonded) hydrocarbons is $\text{C}_n\text{H}_{2n+2}$. Thus the general formula for the total bond energy per carbon atom is

$$\frac{(n-1) \times 347 + (2n+2) \times 414}{n} = 1175 + \frac{481}{n} \text{ kJ/mol-C}$$

which converges to 1175 kJ/mol-C for large n . Thus the fuel efficiencies of saturated hydrocarbons are basically equivalent in terms of carbon content.

12.12. Molecular Motion

Early notions of molecules considered them to be comprised of rigid collections of classical particles. However this is only a crude model of reality. We have discussed the implications of the non-classical (wave mechanical) behavior of the electrons in molecules. Now we will have a look at the nuclear motions.

To fairly good approximation, molecular motion can be separated into translational and rotational motion (tumbling) of the molecule as a whole, vibration of the nuclei within the molecule, and electronic motions. These motions are referred to as “degrees of freedom”. As a consequence of separability of these classes of motion, the total energy of a molecule is the *sum* of contributing parts.

$$E_{\text{total}} = E_{\text{translation}} + E_{\text{rotation}} + E_{\text{vibration}} + E_{\text{electronic}} \quad (12.10)$$

Each class of motion can be treated separately by wave mechanics. The quantum energy levels of translational motion are so closely spaced that translational motion is essentially classical (continuous). Rotation, vibration and electronic motions are quantized. Electronic states were discussed in the previous section. Here we will assume the molecule is in a single electronic state and translationally at rest, and explore the internal rotational and vibrational motions.

Rotational energy levels for diatomic molecules are given to a first approximation in terms of a rotational quantum number J :

$$E_{\text{rotation}}(J) = \frac{J(J+1)\hbar^2}{8\pi^2\mu R_e^2} \quad J = 0, 1, 2, \dots \quad (12.11)$$

where μ is the reduced mass, given by Eq. (12.9).

Molecules vibrate analogous to macroscopic springs, for which stretching from equilibrium results in a restoring attractive force (Hooke's Law, Eq. (5.7)). Note how the curves of Figs. 12.11 and 12.12 near their minima resemble the quadratic curve shown in Fig. (5.1). Microscopic molecules differ from macroscopic springs in that they are always vibrating in some amount. This is a consequence of the uncertainty principle, which says that it is not possible to know with certainty the positions and velocities of systems that obey wave mechanics. The uncertainty principle thus prevents molecules from resting at the minimum, and molecules are always in some state of vibration, a little above D_e . Wave mechanics shows the Hooke's Law vibrational energy to depend on a quantum number, symbolized by the letter v .

$$E_{\text{vibration}}(v) = (v + \frac{1}{2})h\nu_e \quad v = 0, 1, 2, \dots \quad (12.12)$$

where h is Planck's constant and ν_e ("nu sub e") the vibrational frequency. Additional (anharmonic) terms in ν_e can be added to account for deviations from Hooke's Law.

The value of D_e is the energy required to dissociate a molecule from the *minimum* energy configuration. The energy required to dissociate a molecule from the lowest *possible* vibrational state according to Eq. (12.12) is equal to $D_0 \equiv D_e - \frac{1}{2}h\nu_e$. Experimental dissociation energies measure the distance to the lowest vibrational state, D_0 (a little above D_e) and differ a little from equilibrium binding energies. Because the value of $h\nu/2$ is small compared to D_e , bond strength can be associated with either experimental dissociation energy or D_e , whichever is more convenient.

Polyatomic molecules containing a atoms have a total of $3a$ degrees of freedom (3 coordinates for each atom). Linear molecules have 2 degrees of rotational freedom, non-linear have 3, leaving $3a-5$ or $3a-6$ degrees of vibrational freedom. Each vibration is described by an equation of the form of Eq. (12.12), but with possibly different values of vibration frequency ν_e , corresponding to different bond strengths between different groups of vibrating atoms.

Each system has its own characteristic binding energy parameters, including R_e , $-D_e$, and ν_e . As seen in Table 12.1, the deeper the minimum, the stronger the bond, the shorter the equilibrium separation and the larger the vibrational frequency.

12.13. Molecular Spectroscopy

Since the rotation, vibration and electronic excitations are quantized, molecular spectra have discrete lines according to the Planck-Einstein rule relating the frequency of light to an energy transition (Eq. (7.5)). The quantum levels for rotation are about an order of magnitude more closely spaced than for vibration, which are in turn about an order of magnitude more closely spaced than for electronic motion, as can be seen by applying Eqns. (12.11) and (12.12) to the data of Table 12.1. Radiation energies to excite rotational degrees of freedom lie in the microwave region of the electromagnetic spectrum, infrared for vibration

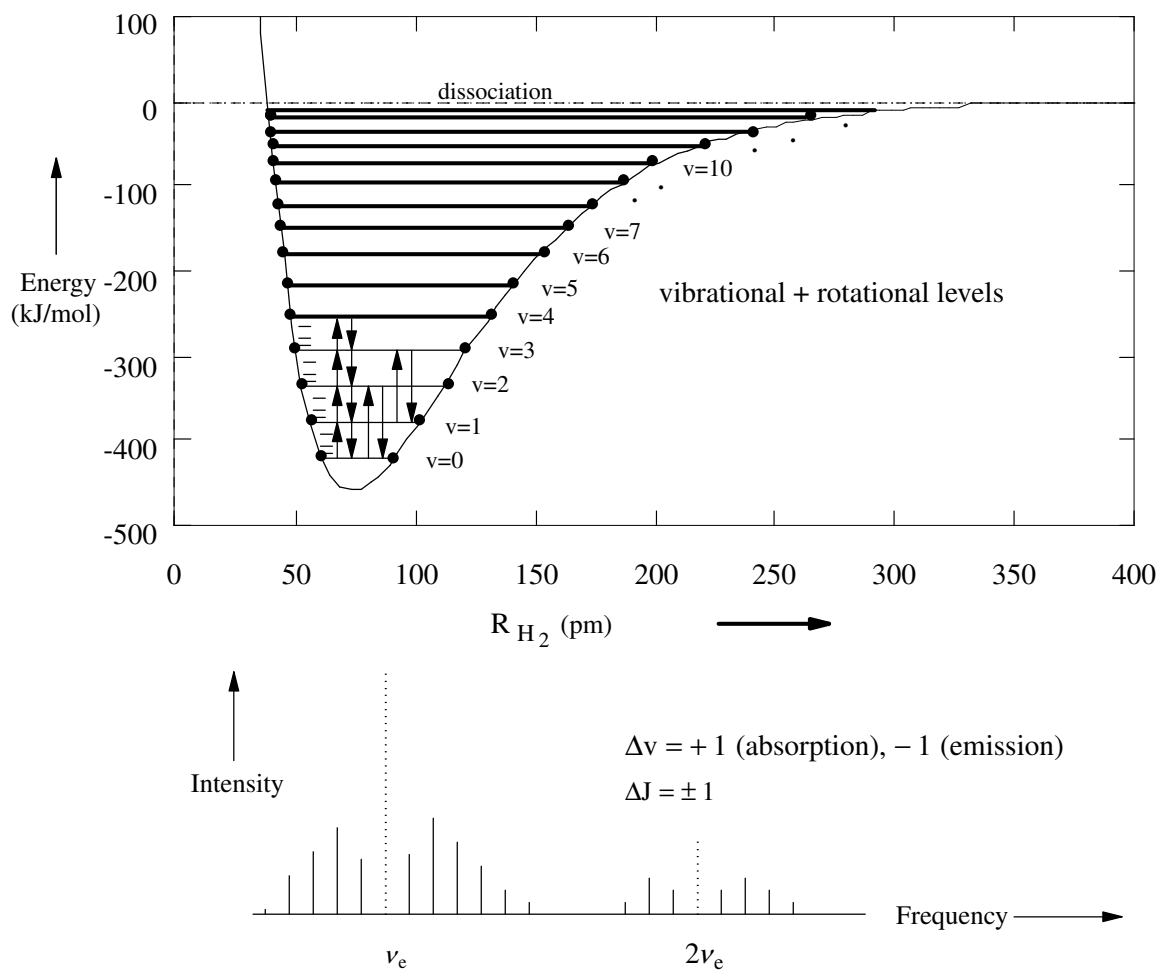
excitations, and visible and ultraviolet radiation for electronic excitations. Thus, light of the appropriate frequencies can be used to probe the structure of molecules, just as in the case of atoms (for which only electronic excitations are possible).

Vibrational and rotational transitions are limited to adjacent energy states according to wave mechanics ($\Delta v = \pm 1$, $\Delta J = \pm 1$). Application of Eqs. (12.12) and (12.11) to Eq. (7.5) generates one possible harmonic vibrational frequency and a series of possible equally spaced rotational frequencies. Rotational transitions combine with vibrational transitions to produce rotational-vibrational spectra.

The *intensities* (brightness) of the spectral lines corresponding to vibrational and rotational absorption transitions depends on the number of molecules available in the initial state. The population distribution of a collection of molecules among the various levels is determined by the amount of available thermal energy due to molecular collisions, according to the Boltzmann distribution function (Section 13.9). At room temperature, most typical molecules are in the lowest vibrational level and in the third rotational level, with fewer molecules in other levels. Molecules which can be “pumped” to higher levels may become trapped and released by light stimulation. This is *laser* action (Light Amplification by Stimulated Emission of Radiation).

Fig. 12.14 shows the vibrational energy levels in the ground electronic state of dihydrogen (compare it with Fig. 12.12). A few of the rotational levels (short horizontal lines) are shown superposed on the vibrational states (longer horizontal lines). A few vibrational transitions near the minimum where the greatest population of molecules reside are indicated (vertical arrows), and the corresponding rotational-vibrational spectrum is displayed. The dotted frequencies correspond to $\Delta J = 0$ and are forbidden according to the rules of wave mechanics. $\Delta J = \pm 1$ transitional frequencies accompany a vibrational transition and straddle the dotted vibrational frequency with intensities distributed according to population.²² Δv is limited to ± 1 values for harmonic vibrators, but anharmonicity allows $\Delta v = \pm 1, \pm 2$, etc. vibrational transitions as well, but with decreasing intensity. The first “overtone” vibrational series occurs at $2\nu_e$ and is much less intense than that at ν_e .

²² The population first increases then decreases even though the Boltzmann distribution causes a uniform decrease in population because rotational energy levels have degeneracies of $2J + 1$, where J is the rotational quantum number.



Vibrational/Rotational Spectrum

Fig. 12.14 Dihydrogen Vibrational and Rotational States

Larger molecules have greater numbers of energy levels and their molecular spectra can be quite complicated. Nevertheless, because bonds are localized to a degree in molecules, transition frequencies are somewhat characteristic of bond types. Looking back at Eqns. (12.11) and (12.12) we can see that knowledge of the energy levels of molecules allows a determination of molecular parameters, such as R_e and ν_e . Analysis of molecular spectra, like that of Fig. 12.14 for H_2 produced the entries in Table 12.1. Molecular spectroscopy is thus a powerful analytical tool in identifying the compositions and structures of molecules.

Summary

Chemical bonds result from electron attractions to the nuclei of molecules. Bonds are broadly classified into two extreme categories, ionic bonds with electrons transferred from one atom to another, and covalent bonds with electrons shared between two atoms.

Chemical bonds are described accurately by the quantum mechanical wave equation, which is difficult to solve for any but the simplest atoms and molecules. *In every case that has been tested, wave mechanical calculations agree with experimental observations quantitatively*, justifying the wave mechanical model.

Approximations to the wave equation leads to simplified models of bonding, such as Lewis structures, valence bond theory and molecular orbital theory. Valence bond theory is related to the Lewis duet/octet stability and VSEPR heuristics and is useful for describing the geometry of molecules, while molecular orbital theory is related to the orbital aufbau atomic electronic configuration and bond order heuristics and is useful for describing the stability of molecules.

Discrete molecular spectra are produced by electronic, vibrational and rotational transitions. Analysis of spectra in terms of the results of wave mechanics provides values of molecular parameters and identification of molecular composition and structure. Conversely, wave mechanics can be used to predict *ab initio* (from fundamental principles) molecular properties.

CHEMICAL BONDING EXERCISES

1. Which is the most favorable arrangement of atoms for the cyanate ion, which contains one carbon atom, one nitrogen atom, one oxygen atom and one negative charge. (Sodium cyanate is used in the treatment of sickle-cell anemia.)
2. Discuss the basic bonding and structure of sodium nitrate.
3. How many peaks are in the mass spectrum of HCl, assuming two isotopes of hydrogen, ^1H and ^2H , and two of chlorine, ^{35}Cl and ^{37}Cl ?
4. Determine Lewis structures for three-bonded triangular CO_2 and N_2O .
5. Based on the Lewis model of chemical bonding, how would you expect the chemical properties of Cl_2O to compare with those of ClO_2 ?
6. Compare the Lewis structure for phosphorous acid which has three OH groups bound to P with that which has two OH groups and one O and one H bound to P.
7. How would you expect the molecular geometry of Cl_2O to compare with that of ClO_2 ?
8. Discuss the bonding in the series O_2^{2+} , O_2^+ , O_2^0 , O_2^- and O_2^{2-} .
9. Discuss the bonding in hydrogen fluoride.
10. Discuss the relative energies of water and hydrogen peroxide.
11. Discuss trends in dihalogen and interhalogen bond strengths.
12. What is the average NH bond strength in ammonia, if it requires 449 kJ/mol to remove the first H, 384 kJ/mol to remove the second and 339 kJ/mol to remove the third?

CHEMICAL BONDING EXERCISE HINTS

1. Isocyanate ion is isoelectronic with carbon dioxide.
2. The formula for sodium nitrate is NaNO_3 . Review the calcium nitrite example.
3. Tabulate the possibilities, eliminate redundancies (and don't forget the atoms).
4. See Example 12.5.
5. Consider the electronic structures.
6. Phosphorous acid (Table 10.1) is observed to be diprotic (two removable protons).
7. Use the VSEPR heuristic.
8. Compare Lewis, VB and MO descriptions of the bonding in O_2^- and O_2^{2-} .
9. Note that HF is isoelectronic with B_2
10. Start with Lewis structures and compare estimated bond energies.
11. Interhalogens are compounds containing different halogen (Group 7A) elements.
12. Refer to Table 12.2.