Quantum Mechanical Approaches to Molecular Bonding

• Two principal approaches have been taken to construct approximate wave functions for molecules, starting with the atomic orbitals of the atoms comprising the molecules.

1. Valence Bond (VB) theory

developed by Linus Pauling and co-workers, essentially puts the Lewis notion of electron pairs on a quantum mechanical footing.

2. Molecular Orbital (MO) theory

- developed by Robert S. Mulliken and co-workers, constructs new orbitals that are delocalized (i.e., "spread out") across the molecule.
- VB and MO theories take different mathematical approaches to constructing wave functions for the molecule, but their results are often equivalent.
- MO theory has historically been more popular as it is a computationally simpler method and more economical.

The Born-Oppenheimer Approximation

- The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated.
- This leads to a molecular wave function in terms of electron positions (r_i) and nuclear positions (R_i) :

$$\Psi_{\text{molecule}}(r_i, R_j) = [\Psi_{\text{electron}}(r_i, R_j)][\Psi_{\text{nuclear}}(R_j)]$$

- This involves the following assumptions
 - The electronic wavefunction depends upon the nuclear positions R_j but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
 - The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

- The Born-Oppenheimer approximation is the basis for modern computational chemistry.
- By assuming that the nuclear positions are fixed in space at arbitrary locations, we can then solve the Schrödinger equation for the wavefunction of the electrons alone.
- This allows us to select an internuclear separation and bond angle for each bond in a molecule and subsequently solve the Schrödinger equation for the chosen nuclear framework.
- Application of this method with 100's, 1000's of iterations allows us to build an image of the various geometric configurations of the molecule and with their respective energies.
- This data may then be plotted on a potential energy curve and the optimum lowest energy configuration is identified.

Note: the Born-Oppenheimer approximation is also the basis of the *Franck-Condon principle* (will study later in photophysics of excited state species).



A molecular potential energy curve

- The Born-Meyer potential U_1 represents the repulsive interaction of nearby wavefunctions.
- The total potential U_r is the sum of repulsive U_1 and attractive U_2 (Coulombic) potentials.
- The equilibrium bond distance r₀ and the binding energy can be calculated by setting the derivative of the potential wrt r to zero.

Valence Bond Theory

- Valence bond theory, developed by Linus Pauling and co-workers, approaches a molecular bonding scheme from the point of view of that *each shared electron pair occupies a localized orbital*, thus introducing concepts such as σ and π bonds and hybridization.
- The *atomic components of a molecule* are assembled by pairing up their unpaired electrons to form bonds through overlap of atomic orbitals on the bonded atoms.
- Localized bonding orbitals are then constructed from a linear combination of the atomic orbital wavefunctions from each of the paired atoms.
- **Principle of maximum overlap**: an AO on one atom should overlap as much as possible with an orbital on the atom to which it is bound.

(the greater the overlap the lower the energy of the system)

• **Modern valence bond theory** is the term used to describe computational valence bond methods that are competitive in accuracy and economy with molecular orbital based methods. It is only in the last decade that the programming of valence bond methods has truly developed.

Homonuclear Diatomic Molecules - Dihydrogen H₂

- In the classic case of covalent bonding, the H₂ molecule forms by the overlap of the wavefunctions of the electrons of the respective hydrogen atoms in an interaction which is characterized as an exchange interaction.
- When overlap creates an increase in electron density in the region between the two nuclei a sigma bond (σ bond) is formed.



Formation of sigma (σ) bond in H₂ from 1*s orbitals*

• The wavefunction Ψ for the H₂ molecule can be described in terms of the atomic wave functions $\Psi_{\rm H1}$ and $\Psi_{\rm H2}$ as follows

$$\Psi = \Psi_{H1}\Psi_{H2}$$

• For convenience purposes we will explicitly include the location of the valence electron for each atomic wavefunction

$$\Psi = \Psi_{\rm H1}(1s^{1}_{\rm H1})\Psi_{\rm H2}(1s^{1}_{\rm H2})$$

• As both H atoms approach each other and orbital overlap occurs, electrons $1s_{H1}^1$ and $1s_{H2}^1$ become indistinguishable from each other, thus an equally valid representation of Ψ is

$$\Psi = \Psi_{H1} (1s_{H2}^{1}) \Psi_{H2} (1s_{H1}^{1})$$

• As such, when the interatomic distance of both H atoms is within the bonding regime, the *true state of the system is more accurately described as a linear combination of both of the probable wavefunctions*

$$\Psi = N \left[\Psi_{H1} (1s_{H1}^{1}) \Psi_{H2} (1s_{H2}^{1}) \pm \Psi_{H1} (1s_{H2}^{1}) \Psi_{H2} (1s_{H1}^{1}) \right]$$

 $\Psi = N \left[\Psi_{A}(1s_{A}^{1})\Psi_{B}(1s_{B}^{1}) \pm \Psi_{A}(1s_{B}^{1})\Psi_{B}(1s_{A}^{1}) \right]$

- According to Pauli's exclusion principle, if the space component of the wavefunction (n, l, m_l) is identical, the electron spin component of the wavefunctions (m_s) for the two bonding atoms must be anti-symmetric.
- The electron spin component of the wavefunction (m_s) can be symmetric only when the space component of the wavefunction (n, l, m_l) is anti-symmetric.
- These conditions guarantee that the entire wavefunction (the product of the spin and space wavefunctions) is anti-symmetric.
- The two possibilities for the *radial wavefunctions* of distant hydrogens are shown below.



$$\Psi = N \left[\Psi_{A}(1s_{A}^{1})\Psi_{B}(1s_{B}^{1}) \pm \Psi_{A}(1s_{B}^{1})\Psi_{B}(1s_{A}^{1}) \right]$$

• In the bonding regime, overlap of these symmetric and anti-symmetric atomic wavefunctions give rise to σ bonding and σ^* antibonding molecular wavefunctions respectively:



 $\Psi = N \left[\Psi_{A}(1s_{A}^{1})\Psi_{B}(1s_{B}^{1}) \pm \Psi_{A}(1s_{B}^{1})\Psi_{B}(1s_{A}^{1}) \right]$

• In the bonding regime, overlap of these symmetric and anti-symmetric atomic wavefunctions give rise to σ bonding and σ^* antibonding molecular wavefunctions respectively:



- The symmetric wavefunction represented by Ψ_s interferes constructively (+) resulting in an enhancement in the value of the wavefunction in the internuclear region
 - \succ a σ bonding orbital is the result.
- A σ bond has a cylindrical geometry about the internuclear axis
 - \succ a σ orbital has zero orbital angular momentum about the internuclear axis (= 0 nodes)
- The anti-symmetric wavefunction represented by Ψ_A interferes destructively (–) resulting in an decrease in the value of the wavefunction in the internuclear region
 - \succ a σ^* antibonding orbital is the result
- The exchange interaction leads to a strong bond for the hydrogen molecule with dissociation energy 4.52 eV at a separation of 0.074 nm.



• If we explicitly show the spin component of the wavefunction $\sigma_{(H1, H2)}$ it is represented as:

 $Ψ = N [Ψ_A(1s_A^1)Ψ_B(1s_B^1) ± Ψ_A(1s_B^1)Ψ_B(1s_A^1)] σ_{(H_1, H_2)}$

• For simplicity, here we will not consider the radial distribution of electrons:

$$Ψ = (Ψ_{H1}Ψ_{H2}) σ_{(H1, H2)}$$

The possible distributions of spin states are

$$\alpha_{\text{H1}} \beta_{\text{H2}} \qquad \beta_{\text{H1}} \alpha_{\text{H2}} \qquad \alpha_{\text{H1}} \alpha_{\text{H2}} \qquad \beta_{\text{H1}} \beta_{\text{H2}}$$

• As the spin distributions $\alpha_{H1} \beta_{H2}$ and $\beta_{H1} \alpha_{H2}$ are indistinguishable it is appropriate to include their normalized linear combination in the expression for Ψ .

 $\sigma_{+} = N_{g} (\alpha_{H1} \beta_{H2} + \beta_{H1} \alpha_{H2})$ $\sigma_{-} = N_{u} (\alpha_{H1} \beta_{H2} - \beta_{H1} \alpha_{H2})$ $\sigma_{\alpha} = \alpha_{H1} \alpha_{H2}$ $\sigma_{\beta} = \beta_{H1} \beta_{H2}$

• The four possible expressions for Ψ can now be represented as:

$$\begin{split} \Psi(1) &= N_{g} \left(\Psi_{H1} \Psi_{H2} \right) \sigma_{+} \\ \Psi(2) &= N_{u} \left(\Psi_{H1} \Psi_{H2} \right) \sigma_{-} \\ \Psi(3) &= \left(\Psi_{H1} \Psi_{H2} \right) \sigma_{\alpha} \\ \Psi(4) &= \left(\Psi_{H1} \Psi_{H2} \right) \sigma_{\beta} \end{split}$$

• The four possible expressions for Ψ can now be represented as:

$$\Psi(1) = \textit{N}_{g} \left(\Psi_{\text{H1}} \Psi_{\text{H2}} \right) \left(\alpha_{\text{H1}} \beta_{\text{H2}} + \beta_{\text{H1}} \alpha_{\text{H2}} \right)$$

$$\Psi(2) = N_{u} (\Psi_{H1} \Psi_{H2}) (\alpha_{H1} \beta_{H2} - \beta_{H1} \alpha_{H2})$$

$$Ψ(3) = (Ψ_{H1}Ψ_{H2}) (α_{H1}α_{H2})$$

 $\Psi(4) = (\Psi_{H1}\Psi_{H2})(\beta_{H1}\beta_{H2})$

- Representations $\Psi(3)$ and $\Psi(4)$ are not possible as they contradict the Pauli exclusion principle.
- Only representation $\Psi(2)$ conforms with the Pauli exclusion principle.

(note: when the radial distribution of electrons is implicitly included in this calculation $\Psi(1)$ becomes allowed)

• Let us apply the Pauli exclusion principle to the following representation of Ψ

$$\Psi = (\Psi_{\text{H1}}\Psi_{\text{H2}})(\alpha_{\text{H1}}\alpha_{\text{H2}})$$

• According to the Pauli exclusion principle when electrons are exchanged Ψ must change sign

$$\Psi$$
 (1,2) = - Ψ (2,1)

• Therefore

$$\Psi = [-(\Psi_{H2}\Psi_{H1})][-(\alpha_{H2}\alpha_{H1})]$$

• However, as

$$\Psi_{H1}\Psi_{H2} = \Psi_{H2}\Psi_{H1}$$
 and $\alpha_{H1}\alpha_{H2} = \alpha_{H2}\alpha_{H1}$

this contradicts the Pauli exclusion principle as there is no overall change in sign

$$\Psi = [-(\Psi_{H1}\Psi_{H2})][-(\alpha_{H1}\alpha_{H2})]$$
$$= (\Psi_{H1}\Psi_{H2})(\alpha_{H1}\alpha_{H2})$$

• Now the *allowed* proof

$$\Psi = N_{u} (\Psi_{H1} \Psi_{H2}) (\alpha_{H1} \beta_{H2} - \beta_{H1} \alpha_{H2})$$

• Therefore applying the Pauli exclusion principle

$$\begin{split} \Psi &= N_{\rm u} \left[- \left(\Psi_{\rm H2} \Psi_{\rm H1} \right) \right] \left(- \alpha_{\rm H2} \beta_{\rm H1} + \beta_{\rm H2} \alpha_{\rm H1} \right) \\ \Psi &= - N_{\rm u} \left(\Psi_{\rm H2} \Psi_{\rm H1} \right) \left(\beta_{\rm H2} \alpha_{\rm H1} - \alpha_{\rm H2} \beta_{\rm H1} \right) \\ \Psi &= - N_{\rm u} \left(\Psi_{\rm H2} \Psi_{\rm H1} \right) \left(\alpha_{\rm H1} \beta_{\rm H2} - \beta_{\rm H1} \alpha_{\rm H2} \right) \\ \Psi &= - N_{\rm u} \left(\Psi_{\rm H1} \Psi_{\rm H2} \right) \left(\alpha_{\rm H1} \beta_{\rm H2} - \beta_{\rm H1} \alpha_{\rm H2} \right) \end{split}$$

• As there is a change in sign in Ψ upon application of the Pauli principle this representation of Ψ is allowed.

Sigma Bond Formation in F₂

• Valence configuration:



• The single bond in F_2 can be seen as a sigma bond formed by overlap of two 2*p* orbitals.



Formation of sigma (σ) bond in F₂ from 2p

Orbital Overlap in Double and Triple Bonds Pi Bonding (π **bonds)**

• Pi bonding results from side-by-side overlap of two orbitals, such as two 2px or two 2py orbitals.



Rotated about bond axis to show nodal plane:



• In the VB approach, there is never a π bond without a σ bond, too.

Pi Bonding in Dinitrogen N₂

- The essential features of VB theory are the pairing of electrons and the accumulation of electron density in the internuclear region that stems from that pairing.
- To construct the VB description of N_2 we must first consider its valence electron configuration

N:
$$1s^2 2s^2 2p_x^1 p_y^1 p_z^1$$

- By convention we align the σ bonding orbitals along the z-axis.
- At an appropriately short internuclear distance, the singly occupied $2p_z^1$ orbitals of both N atoms point towards each other hence overlap constructively and deconstructively forming a σ bonding (by spin pairing both electrons) and σ^* antibonding orbitals respectively.

$$\begin{split} \Psi(\sigma) &= N_{g} \left[\Psi_{A}(2p_{z}^{1}{}_{A})\Psi_{B}(2p_{z}^{1}{}_{B}) + \Psi_{A}(2p_{z}^{1}{}_{B})\Psi_{B}(2p_{z}^{1}{}_{A}) \right] \\ \Psi(\sigma^{*}) &= N_{u} \left[\Psi_{A}(2p_{z}^{1}{}_{A})\Psi_{B}(2p_{z}^{1}{}_{B}) - \Psi_{A}(2p_{z}^{1}{}_{B})\Psi_{B}(2p_{z}^{1}{}_{A}) \right] \end{split}$$

Pi Bonding in Dinitrogen N₂

- The $2p_x^{1}$ and $2p_y^{1}$ orbitals of each N atom of course remain perpendicular to the axis and cannot overlap with σ geometry as they have zero orbital angular momentum about the *z*-axis.
- The $2p_x^{1}$ and $2p_y^{1}$ orbitals do overlap constructively and deconstructively with their counterparts on the adjacent N atom in the *xz* and *yz* planes respectively giving rise to π bonding (by spin pairing both electrons) and π^* antibonding orbitals respectively

e.g.

$$\Psi(\pi_{x}) = N_{g} \left[\Psi_{A}(2p_{x}^{1}{}_{A})\Psi_{B}(2p_{x}^{1}{}_{B}) + \Psi_{A}(2p_{x}^{1}{}_{B})\Psi_{B}(2p_{x}^{1}{}_{A}) \right]$$
$$\Psi(\pi_{x}^{*}) = N_{u} \left[\Psi_{A}(2p_{x}^{1}{}_{A})\Psi_{B}(2p_{x}^{1}{}_{B}) - \Psi_{A}(2p_{x}^{1}{}_{B})\Psi_{B}(2p_{x}^{1}{}_{A}) \right]$$

Polyatomic Molecules

- Each σ bond in polyatomic molecule is formed by the spin pairing of electrons in atomic orbitals with cylindrical symmetry about the relevant internuclear axis.
- Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.
- Let us consider the H_2O molecule (σ only). The electron configuration of the O atom is

O:
$$1s^2 2s^2 2p_x^2 p_y^1 p_z^1$$

• We can see that the H 1s¹ orbital will overlap with the O $2p_y^{1} 2p_z^{1}$ orbitals which are at 90 ° to each other σ therefore the VB theory predicts a bond angle of 90 ° for the H₂O molecule.



- In reality an actual bond angle of 104.5 ° is observed.
- The VB theory initially failed when predicting actual bond angles and geometries for which the VSEPR theory had a better agreement with experiment.

- To enhance the overlap between an O orbital and the 1s orbital on the H atom, and in general to obtain orbitals consistent with the geometry of the molecule, Pauling introduced the concept of **hybridization**.
- In this process, orbitals *centered on the same atom* are combined to obtain new hybrid orbitals, each of which is more concentrated in one direction than in the opposite direction and thus has a greater overlap with a ligand orbital.



• For example, we can construct h_1 and h_2 , two hybrid orbitals for describing the bonds in the water molecule, by taking the two combinations:

$$h_1 = s + \lambda p_x$$
 $h_2 = s + \lambda p_y$

• Where λ is an adjustable mixing parameter. The value of λ determines the relative contribution of the *s* and *p* orbitals and also the angle between the hybrids, which is given by

$$\lambda = (-1 / \cos \theta)^{1/2}$$

e.g., for the H₂O molecule with a bond angle θ of 104.5° we calculate $\lambda = 2$ which tells us that h_1 and h_2 each contain a *p*:*s* ration of 2:1, i.e. *sp*² hybridized.

- Hybrids that are commonly used in the VB description of bonds, particularly for organic molecules sp, sp² and sp³.
- For example **sp** hybrids have $\lambda = 0.5$ corresponding to a bond angle θ of 180 °



Hybrid orbitals h_1 and h_2 formed from the 1s and 2p orbitals of the O atom in H₂O

	Molecule			
	Ethyne	Ethene	Methane	Water
Hybrid set	2(sp)	3(sp ²)	4(sp ³)	2(s ^{0.40} p ^{1.60})
Hybrid	s ^{0.5} p ^{0.5}	s ^{0.33} p ^{0.67}	s ^{0.25} p ^{0.75}	s ^{0.20} p ^{0.80}
Bond angle λ^{b}	180°	$120^{\circ a}$	109.5°	104.5°
	1	$\sqrt{2}$	$\sqrt{3}$	2.0

 Table 3.2
 Examples of Hybrid Orbitals Used to Describe Equivalent Bonds

Hybridization is not a physical phenomenon

- it is a mathematical operation that is used to

construct localized orbitals

to describe the bonding in a molecule.

Hybridization – CH₄

• The description of a tetrahedrally substituted C atom with the electron configuration

C: $1s^2 2s^1 2p_x^1 p_y^1 p_z^1$

implies the existence of non-equivalent C-H bonds at the same atom.

- This problem is overcome as the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a *hybrid orbital* consisting of 2*s* and 2*p* character.
- The generated sp³ orbitals have a greater bond strength than independent s_c s_H or p_c s_H bonds.
- As a result of constructive and destructive overlap of the 2s and 2p wavefunctions each of the four sp³ orbitals result in a tetrahedral geometry about the central C atom.

$$\Psi = N (\Psi_{sp3} \pm \Psi_{H})$$

• All four C-H bonds are therefore identical apart from their orientation in space.



Hybrid Orbital Formation on Carbon - A Hypothetical Process





- Contour diagram of a single sp³ hybrid orbital
 - X marks the position of the nucleus



Three-dimensional model (rotated 30° about a vertical axis)



Shape of an individual *sp³ hybrid orbital*



Cut-away rendering:



Set of four sp³ hybrid orbitals in a tetrahedral arrangement

• Boundary Surface Model of a single *sp*³ *Hybrid*

• Simplified sketches

Hybrids for 3 Electron Domains





• Boundary Surface Model of a single *sp*² *hybrid*

Hybrids for 2 Electron Domains





• Boundary Surface Model of a single *sp hybrid*

Summary of Hybrid Orbital Types

Domains	Geometry	Orbitals Used	Hybrids
2	linear	s, p	sp
3	trigonal planar	s, p_x, p_y	sp^2
4	tetrahedral	s, p_x, p_y, p_z	sp^3
5	trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp ³ d
6	octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2



• Boundary Surface Model of a single *sp*³ *Hybrid*



• Boundary Surface Model of a single *sp*² *hybrid*



• Boundary Surface Model of a single *sp hybrid*

Sigma and Pi Bonding in C₂H₄

• C *sp*² hybridized:



• Sigma bonding:



• Pi bonding:



(MO description ?)

Sigma and Pi Bonding in C₂H₂

• C *sp* hybridized:



• Sigma bonding:



• Pi bonding:



(MO description ?)



• Boundary Surface Models of the sigma and two Pi bonds in C₂H₂

Sigma Bonding in $C_2H_2 - VB \cong MO$

• C *sp* hybridized:



• Sigma bonding:





y







• The VB and MO descriptions are equivalent as the linear combination of hybrid orbitals results in the same internuclear probabilility electron density between the bonding atoms as calculated by the MO method.



Figure 3.20 (a) The σ - π model of the C=C double bond. (b) Taking the sum and difference of these orbitals produces two bent bond (τ) orbitals.



Figure 3.21 (a) Simplified representations of the two main bonding MOs of the water molecule. (b) Simplified representations of the localized equivalent bonding MOs in water.

The Group 14 Elements

Element	Electronic Configuration	1 st Ionization Energy (kJmol ⁻¹)	2 nd Ionization Energy (kJmol ⁻¹)	Covalent Radius (Å)
^{12.011} ₆ C	$1s^2 2s^2 2p^2$	1086	2352	0.77
^{28.0855} 14Si	[Ne] 3 <i>s</i> ² 3 <i>p</i> ²	786.1	1576	1.17
^{72.61} 32Ge	[Ar] $3d^{10} 4s^2 4p^2$	761.5	1537	1.22
^{118.710} 50Sn	[Kr] 4 <i>d</i> ¹⁰ 5 <i>s</i> ² 5 <i>p</i> ²	708.5	1412	1.41
^{207.2} 82Pb	[Xe] 4 <i>f</i> ¹⁴ 5 <i>d</i> ¹⁰ 6 <i>s</i> ² 6 <i>p</i> ²	715.5 [↓] ↑	1450 [↓] ↑	1.54

- All Group 14 elements have the valence configuration ns^2np^2 .
- Stable carbon and silicon compounds are observed in the +4 state.
- Going down the group the +2 state becomes more stable.

Group 14 Ionization Energies

- The ionization energies for Group 14 elements are irregular due to inner *d* orbitals (Ge, Sn, Pb), inner *f* orbitals (Pb) and relativistic effects (Pb).
- The exceedingly *high energies required to form M⁴⁺ ions (next slide)*, coupled to the fact that such ions would be small and highly polarizing, means that the existence of M⁴⁺ cations is highly unlikely.
- **Group 14 compounds are predominantly molecular** with only SnO₂, PbO₂ and the Sn,Pb fluorides thought to have significant ionic character.

In all these compounds, the oxidation state is merely a formalism, because all are molecular (not ionic) compounds.

Group 14 Ionization Energies – II vs IV



• Ionization energy drops dramatically after C, declining slowly through the rest of the group with Pb breaking this trend due to decreased shielding and enhanced relativistic effects.

Inert Pair Effect

- **The increasing stability of the lower state (+2) as we descend the Group** has been called the "inert pair effect" for the tendency of the ns² configuration to be retained (*most prominent for Sn and Pb*).
- This has nothing to do with inherent "inertness" of the ns² configuration, but rather *simply a consequence of thermodynamics*.
- Although energy "cost" of forming M(IV) is high for the lighter elements, the "pay-back" of bond formation is high, too.
- Bond strengths peak at Si, slowly decline through Sn, and then drop off significantly at Pb.
- At Ge and Sn, both M(II) and M(IV) states are stable.
- At Pb, the bond strength is too low to compensate for the slightly higher ionization energy requirement of the Pb(IV) state in many cases. Hence, the +2 state is favored.
- A similar "inert pair" effect is found in groups 13 and 15.

Group 14 MX₄ Bond Enthalpies



Electron Promotion and Multiple Valency of the Group 14 Elements

• An apparent deficiency of valence-bond theory is its inability to account for carbon's tetravalence. The ground state electronic configuration of the carbon atom is

C:
$$1s^2 2s^2 2p_x^1 p_y^1 p_z^0$$

which suggest C is only capable of forming two bonds.

• This deficiency is overcome by allowing for **promotion** of a 1*s* electron to the *p*_z orbital resulting in the excited state electronic configuration

C:
$$1s^2 2s^1 2p_x^1 p_y^1 p_z^1$$

which now suggests the possibility of forming four covalent bonds. The Group 14 elements (especially carbon) are typically surrounded by four other groups in a tetrahedral geometry.

- The energy consumed by the electron promotion is more than compensated for by the energy gained from the formation of two extra bonds.
- Promotion is a characteristic feature of the group IV elements, especially C due to its low promotion energy.

For C the $2s \rightarrow 2p$ promotion energy is 405.8 kJ mol⁻¹, with the $ns \rightarrow np$ promotion energy decreasing slightly as we descend the Group.

(promotion precludes electron-electron repulsion in the 2*s* orbital. This energy saving is less effective as we progress down the group due to the more diffuse n*s* orbitals)

- Although the ns → np promotion certainly leaves the element with four unpaired electrons, the electron have all their spins parallel. To obtain the element in its valence 'reacting' state work must be done to randomize the electron spins.^{*}
- Therefore to form MX_4 (X = halide) from the Group 14 element M and X_2 the following energy steps must be considered:

$$M_{(s)} \xrightarrow{\Delta H_{sub}} M_{(g)} \xrightarrow{P} M_{(g)}(s^{1}p^{1}p^{1}p^{1}) \xrightarrow{R} M_{(g)}(valence \ state)$$

$$2X_{2} \xrightarrow{\Delta H_{diss}} 4X \xrightarrow{\qquad}$$

$$P : \text{promotion energy} MX_{4}$$

R : electron spin randomization energy

Total energy input =
$$\Delta H_{sub} + P + R + 2\Delta H_{diss}$$

Total energy input = $\Delta H_{sub} + P + R + 2\Delta H_{diss}$

- This energy has to be regained by the formation of four strong M-X bonds.
- However, the production of MX₂ requires fewer energy-consuming steps:



Total energy input =
$$\Delta H_{sub} + R' + \Delta H_{diss}$$

• But only two M-X bonds are formed to compensate for the required energy input.

- Which process leads to the more thermodynamically stable molecule?
- MX₄ is favored for at least C, Si, Ge and Sn. For example, the enthalpy of formation at 25 °C for CH₂ and CH₄ is +343 kJ mol⁻¹ and -74.9 kJ mol⁻¹, respectively.
- Thus, although the utilization of the ns² electrons requires a higher initial input of energy, this is more than offset by the formation of two extra stabilizing M-X bonds.
- However, the *M-X covalent bond strength decreases as we descend the group*, with the result that not all Pb-X bonds are capable of supplying the energy required to stabilize the Pb(IV) state with respect to Pb(II).
- PbF₄, PbCl₄ and PbBr₄ readily decompose upon heating, e.g.

 $PbCl_4 + \Delta \rightarrow PbCl_2 + Cl_2$

• Pbl₄ is too unstable to exist at room temperature!!

(n/a = not applicable)		ionic	ionic model		<u>covalent model</u>	
<u>ц</u> 1	<u> </u>		formal charge	# of e⁻ donated	formal charge	# of e⁻ donated
Hydri	de	M—H	-1	2	0	1
Alkyl	(e.g. methyl)	M—CH₃ R″∖	-1	2	0	1
Alken	ıyl	M R	-1	2	0	1
Alkyn	ıyl	M—R	-1	2	0	1
Allyl			-1	2	0	1
Aryl		M	-1	2	0	1
Cyclo	ppentadienyl	M	-1	2	0	1
Carbo	ene	M R'	0	2	0	1
Carby	/ne	M R	0	4	0	3
Acyl		M-R	-1	2	0	1
Carbo	on monoxide	M—c≡o	0	2	0	1
Nitrile	9	M—C≡N	-1	2	0	1
Fulmi	inate	M—C≡N ⁺ _O ⁻	-1	2	0	1

		ionic	model	<u>covalen</u>	t model
<u>η¹ contd.</u>		formal charge	# of e⁻ donated	formal charge	# of e⁻ donated
Aqua	M-QH H	0	2	1	1
Hydroxyl	м—о	-	1 2	0	1
Охо	M=O	-2	2 4	0	2
Alkoxide (Thiolate O = S)	M—o	-	1 2	0	1
Ether (Sulfide/Thioether O = S)		0	2	1	1
Carboxylate		-1	1 2	0	1
Carbonate	M—O R	-1	1 2	0	1
Cyanate (Thiocyanate O = S)	M—o—c≡n	-1	1 2	0	1
Sulfoxide	^{δ+} −0 [−] ^K	0	2	0	1
	M ^{ð−} R ^Ř	0	2	2	1

		ionic	model	covaler	<u>it model</u>
<u>ղ1</u>		formal charge	# of e⁻ donated	formal charge	# of e⁻ donated
Isocyanate (Isothiocyanate O = S)	M—N=c=0	-1	2	0	1
Nitrogen	M—N≡N	0	2	1	1
Amine		0	2	1	1
Pyridyl	M—N	0	2	1	1
Imine	R M—N B"	0	2	1	1
Amide	M—NR ₂	-1	2	0	1
Isonitrile	M—N ⁺ ≡C	0	2	1	1
Nitrosyls	M—N	-1	2	0	1
	M—N≡O [⁺]	+1	2	1	1
Nitro	M-N	-1	2	1	1
Nitrito	M—0N=0	-1	2	0	1
Phosphine	M—PR ₃	0	2	1	1
Phosphide	M—PR ₂	-1	2	0	1
Halide (e.g. Cl)	M—CI	-1	2	0	1

$\mathbf{\eta}^1$ -coordination	Formal charge	# of e- donated	η^{x} -coordination	Formal charge	# of e- donated
η^{1} -aryl	-1	2	M y ⁶ -arene	0	6
γ^{1} -aikenyl	-1	2	μ M η ² -alkene	0	2
R—===−M η ¹ -alkynyl	-1	2	$\mathbf{R} = \mathbf{H}$ \mathbf{M} $\eta^2 \text{-alkyne}$	0	2
$\overbrace{ \begin{array}{c} \\ M \end{array}}^{H} H \\ \eta^{1} \text{-Cp (cyclopentadienyl)} \end{array}$	-1	2	M η ⁵ -Cp (cyclopentadienyl)	-1	6
η^1 -allyl	-1	2		м -1	4
η^{1} -acetate	-1	2	η ² -acetate	-1	4

		ior	nic model
Bridging ligands (multidentate non-chela	ating)	charge	# of e [−] donated
		-1	1/metal
μ-hydride	М—Н—М	-2	2/metal
μ-охо	M	-2	2/11/201
μ-alkoxide		-1	2/metal
μ-halide	M M	-1	2/metal
μ-CO	M M	0	1/metal
μ- ethylene diamine (μ- en)	H ₂ NM' /	0	2/metal
μ-pyrazine	M—N_N—M	0	2/metal
μ-4,4'-bipyridine	M—N_N_M'	0	2/metal
μ-1,2-bis(diphenyl phosphino)ethane (μ-dppe)	Ph Ph P-M' M-P Ph Ph Ph	0	2/metal

2		ior	<u>nic model</u>
η ² <u>Multidentate chelating ligands</u>		charge	# of e ⁻ donated
R = H: Ethylenediamine (en)	R ₂ N NR ₂	0	4
1-amino-2-(bisphenylphosphino)ethane	H ₂ N PPh ₂	0	4
R = Ph : 1,2-di(bisphenylphosphino)ethane (dppe) R = Me : 1,2-di(bismethylphosphino)ethane (dmpe)	R ₂ P PR ₂	0	4
1,2-di(biphenylphosphino)methane (dppm)	Ph ₂ P PPh ₂	0	4
allyl	M	-1	4
butadiene	M	0	4
cyclobutadiene		0	4
Cyclooctadiene (cod)	M	0	4
2,2'bis(diphenylphosphino)-1,1'-binaphtyl	PPh ₂ M		
	PPh ₂	0	4

2		ion	<u>ic model</u>
η ² <u>Multidentate chelating ligands</u>		charge	# of e [–] donated
2,2'-bipyridine (bpy)		0	4
Phenantroline (phen)		0	4
2-pyrimidylpyridine		0	4
2,2'-bipyrimidine (bpm)		0	4
2-pyrazylpyridine		0	4
2,2'-bipyrazine (bpz)		0	4
2-phenylpyridine (phpy)		-1	4
biphenyl (biph)		-2	4

2			<u>ionic model</u>			
η²	Multidentate chelating ligands		charge	# of e [−] donated		
	Oxalate		2-	4		
	Catecholate	M	2-	4		
	orthosemiquinone	M O	1-	4		
	Orthoquinone	M	0	4		
	Dithiolate	S R'	2-	4		
	Dithiocatecholate	M s	2-	4		
	Dithioorthosemiquinone	M S	1-	4		
	Dithioquinone	M S	0	4		

ionic model Multidentate chelating ligands (contd.) # of e⁻ donated charge R N Orthoiminophenolate 2-4 M R M Orthoiminosemiquinone -1 4 R Orthoiminoquinone 0 4 M R Μ Phenylenediamido 2-4 M Phenylenediiminosemiquinone 1-4 R

M

Ŕ

0

4

benzoquinonediimine

η²









Weakly coordinating anions generally have: 1. low charge, 2. high degree of charge delocalization (*i.e. no* individual atom has a high concentration of charge), 3. steric bulk.

CF₃

ĊF₃