

Supplementary Course Topic 3:

Quantum Theory of Bonding

- Molecular Orbital Theory of H₂
- Bonding in H₂ and some other simple diatomics
- Multiple Bonds and Bond Order
- Bond polarity in diatomic and polyatomic molecules

Molecular Orbitals in Solids

- Bonding in Larger Molecules - electron delocalization
- Metals, Semiconductors and Insulators

Polar Bonds and Ionic Crystals

- Unequal Electron Delocalization
- The Ionic “Bond”
- Lattice Energy of an Ionic Solid

The Wave Equation for Molecules

Recall that for atoms the wavefunctions (atomic orbitals) and the allowed energy levels are obtained by solving the wave equation for electrons bound to a single nucleus (by an electrostatic potential).

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Molecular wavefunctions and their energy levels are simply the solutions to the wave equation for electrons bound by more than one nucleus.

E.g. In diatomic molecules, the potential energy function V describes the attraction of the electrons to two nuclei.

Current computational techniques allow us to numerically solve the wave equation for the electrons bound by an arbitrary set of nuclei, yielding information about the electronic structure of molecules and chemical bonding.

Why Do Atoms Form Molecules?

Molecules form when the **total energy** (of the electrons + nuclei) is lower in the molecule than in the individual atoms:



Just as we did with quantum theory for electron in atoms, we will use *molecular quantum theory* to obtain

- 1. Molecular Orbitals** What are the *shapes* of the orbitals (wavefunctions)?
Where are the lobes and nodes?
What is the electron density distribution?
- 2. Allowed Energies.** How do the energy levels change as bonds form?

We will use the results of these calculations to arrive at some simple models of bond formation, and relate these to pre-quantum descriptions of bonding. These will build a “toolkit” for describing bonds, compounds and materials.

Wavefunctions and Energies: Bonding in H₂

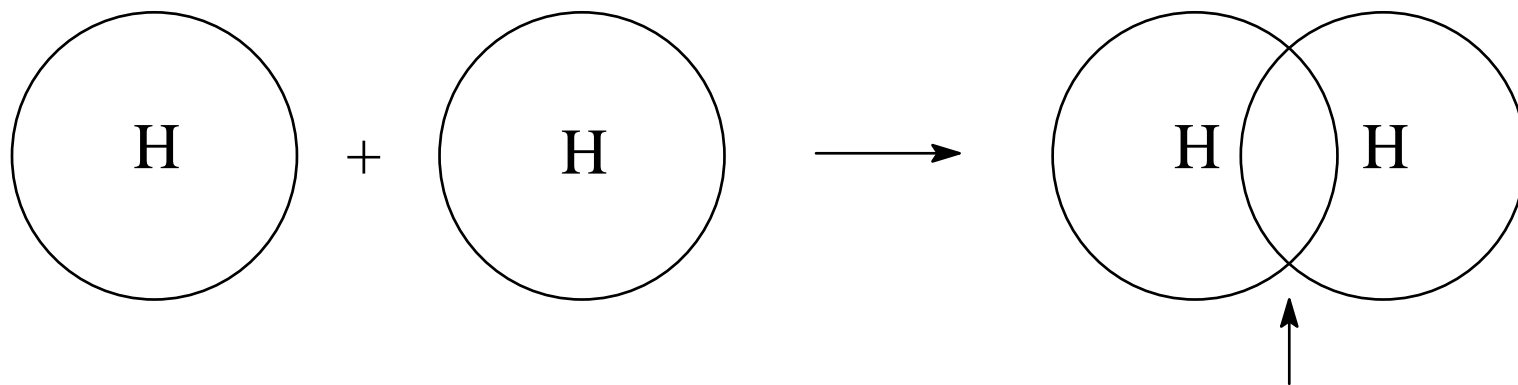
If we calculate the wavefunctions and allowed energies of a two proton, two electron system as a function of separation between the nuclei (the bond length), then we see how two atoms are transformed into a molecule.

Such a calculation can tell us

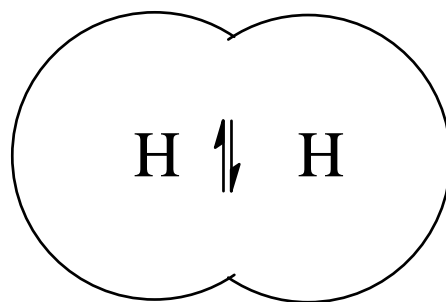
- **Whether a bond forms** - Is the energy of the molecule lower than for the two atoms?
- **The equilibrium bond length** - What distance between the nuclei corresponds to the minimum in the energy?
- **The charge rearrangement caused by bond formation** - What is the electron density (charge) distribution (ψ^2) for the molecule and how it differs from the atoms?
- **Electronic properties of the molecules** - Bond strength, spectroscopic transitions (colour...), dipole moment, polarizability, magnetic character...

Molecular Orbitals of H₂

As two H atoms come together their orbitals will overlap, allowing the electrons to move from one atom to the other and *vice versa*. The electrons no longer belong to just one atom, but to the molecule. They are now **delocalized** over the whole molecule, *i.e.* **shared** by the atoms.



Overlap of 1s atomic orbitals,
giving rise to a
molecular orbital (MO)
that encompasses both H atoms



The MO can hold 2 electrons
with opposite spins

In general, as

Atoms → Molecule
Atomic orbitals (AO) → Molecular Orbitals (MO)

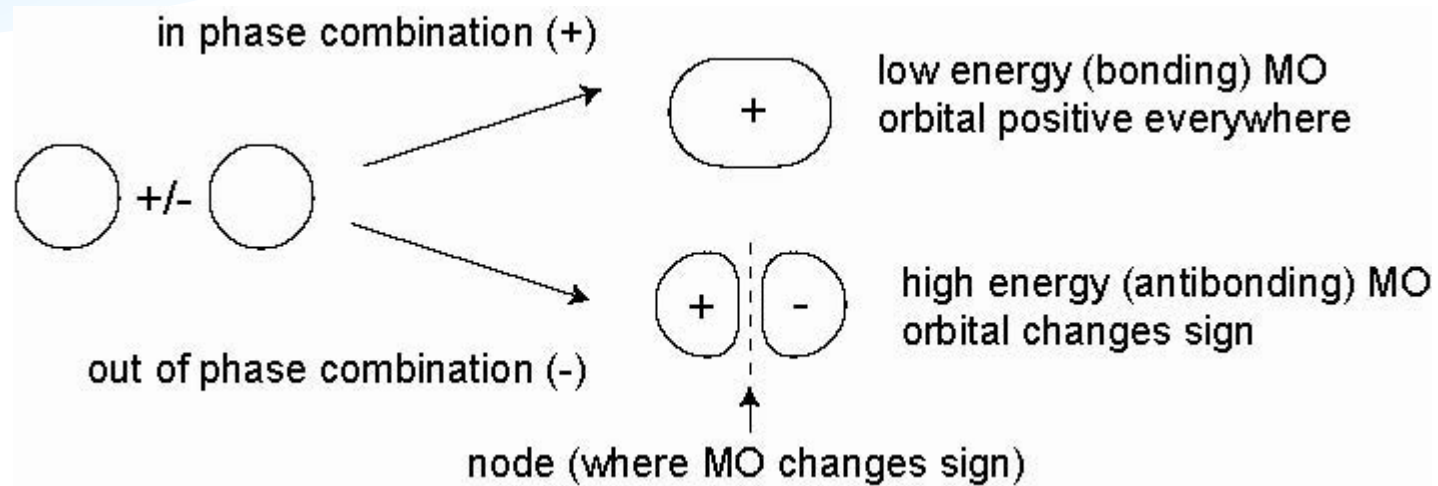
MO's are formed by combining (overlapping) AO's.

Bonding occurs if it's energetically more favourable for the electrons to be in MO's (*i.e.* in a molecule) rather than in AO's (*i.e.* in individual atoms).

Bonding and Antibonding MO's

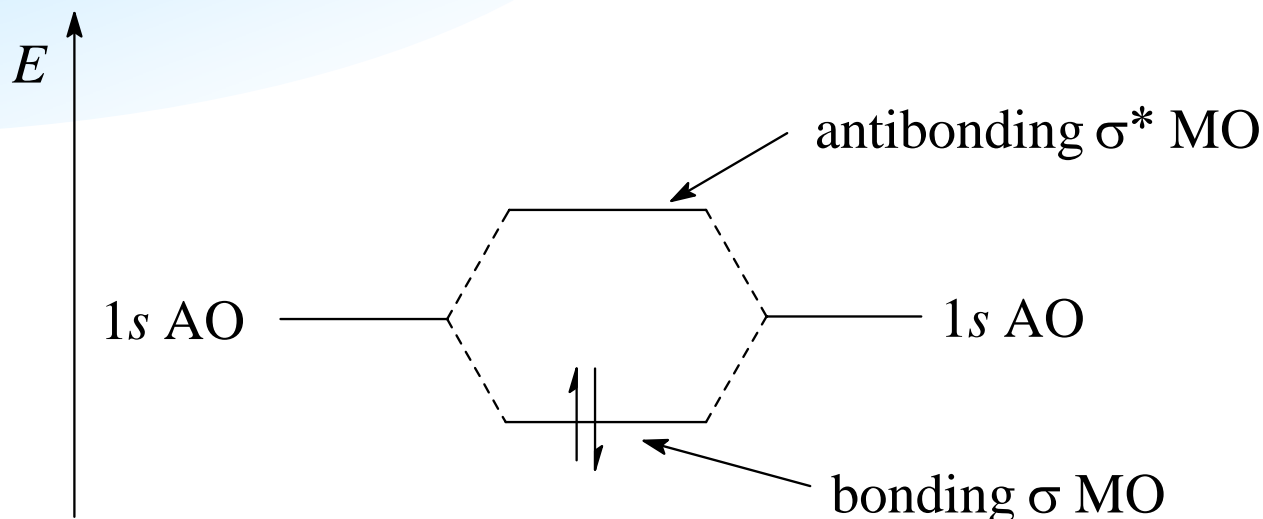
The combination of two AO's can be

in phase → low energy **bonding MO**
out of phase → high energy **antibonding MO**



The more rapidly a wave function (orbital) oscillates, the higher its energy and momentum become (as predicted by de Broglie's equation: $\lambda = h/mv$)

MO energy level diagram:



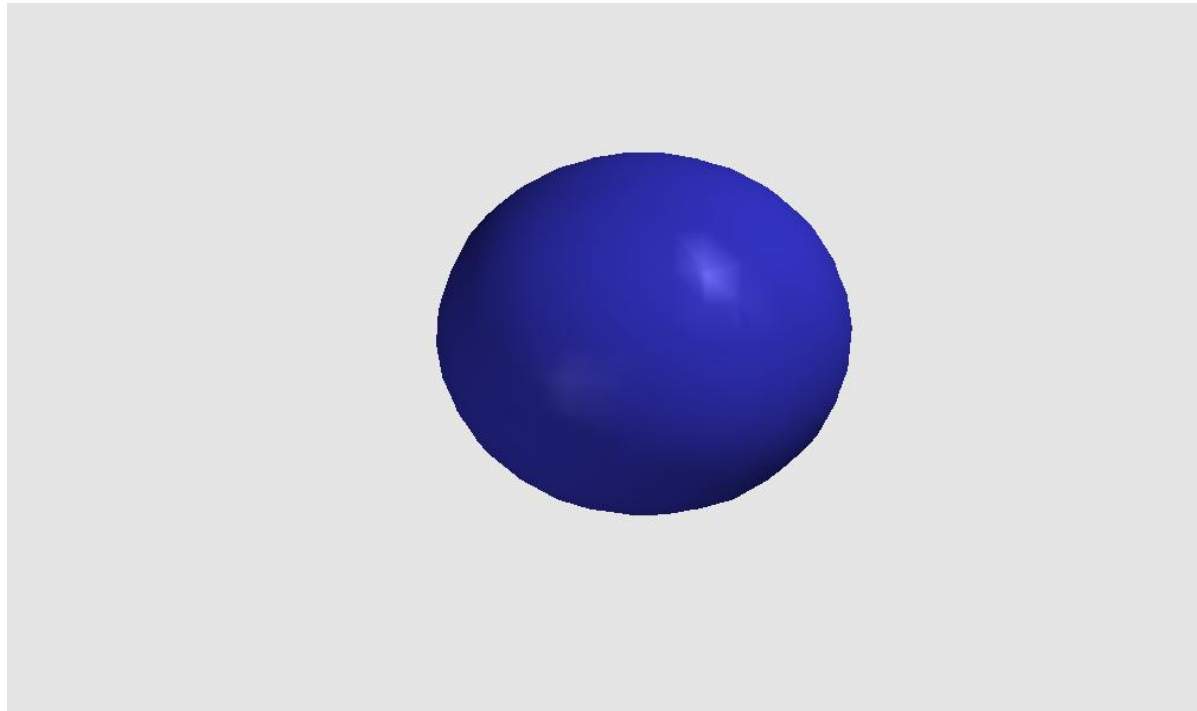
Now, feed in electrons

H ₂ ⁺	σ^1	stable	$E(\text{H}_2^+) < E(\text{H}) + E(\text{H}^+)$
H ₂	σ^2	stable	
He ₂ ⁺	$\sigma^2\sigma^{*1}$	stable	
He ₂	$\sigma^2\sigma^{*2}$	not stable!	$E(\text{He}_2) \sim 2E(\text{He})$

In fact, one electron in the (bonding) MO is sufficient for bonding to occur, *i.e.* H₂⁺ is predicted to be stable! (It has been verified by experiments.)
 Atoms will be bonded (in a molecule) provided there is an excess of bonding electrons.

Bonding Molecular Orbital of H₂

Recall that the lowest energy state of two isolated hydrogen atoms is two 1s orbitals each with one electron. As the nuclei approach each other, the lowest energy state becomes a *molecular orbital* containing two electrons (with opposite spins).



This lobe represents the molecular orbital or wavefunction of the electrons *delocalized* over the molecule, i.e. shared by the two protons. This results in energetic stabilization, i.e. *covalent bond* formation.

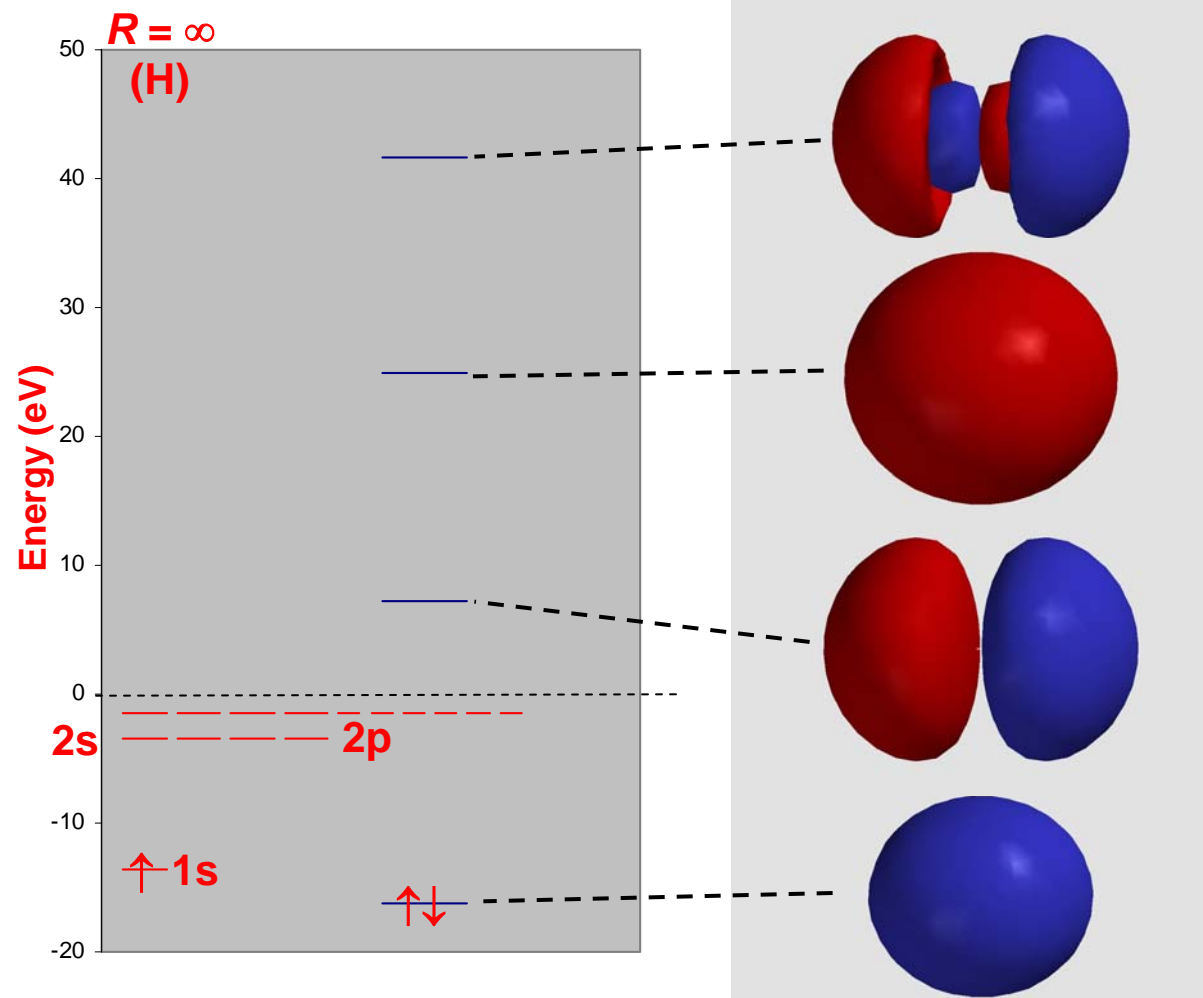
Quantum States in H₂ (as computed)

H₂, in addition to the lowest σ and σ^* MO's, has other higher energy MO's with corresponding allowed energies, formed from the 2s, 2p,...AO's. All these MO's have lobe structures and nodes reminiscent of atomic orbitals.

This diagram shows some of the allowed energy levels for **atomic H** and **molecular H₂**.

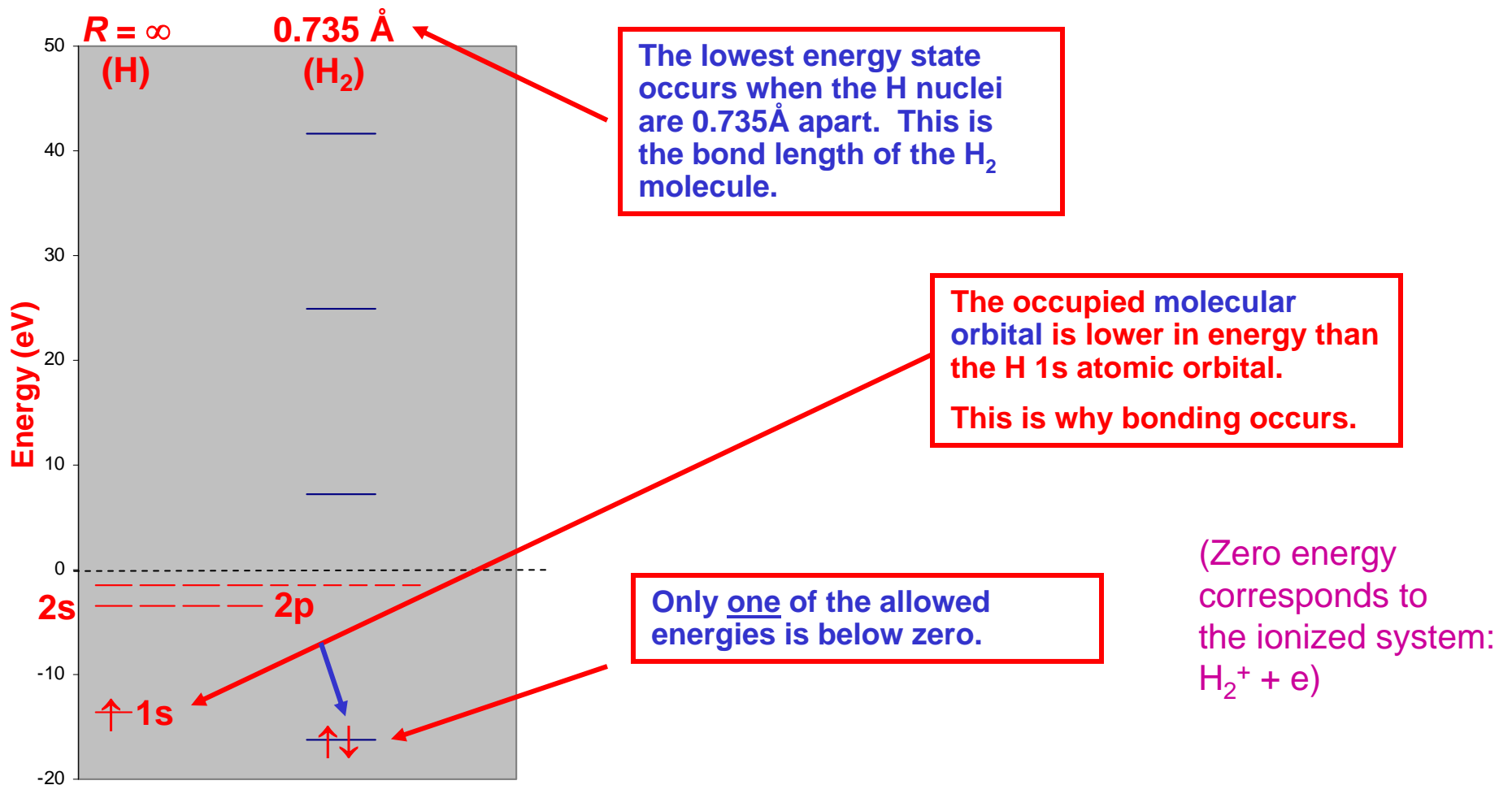
($R = \infty$ denotes the two atoms at *infinite separation* - no bond.)

The orbitals are filled with electrons *starting with the lowest energy*, just like atoms.



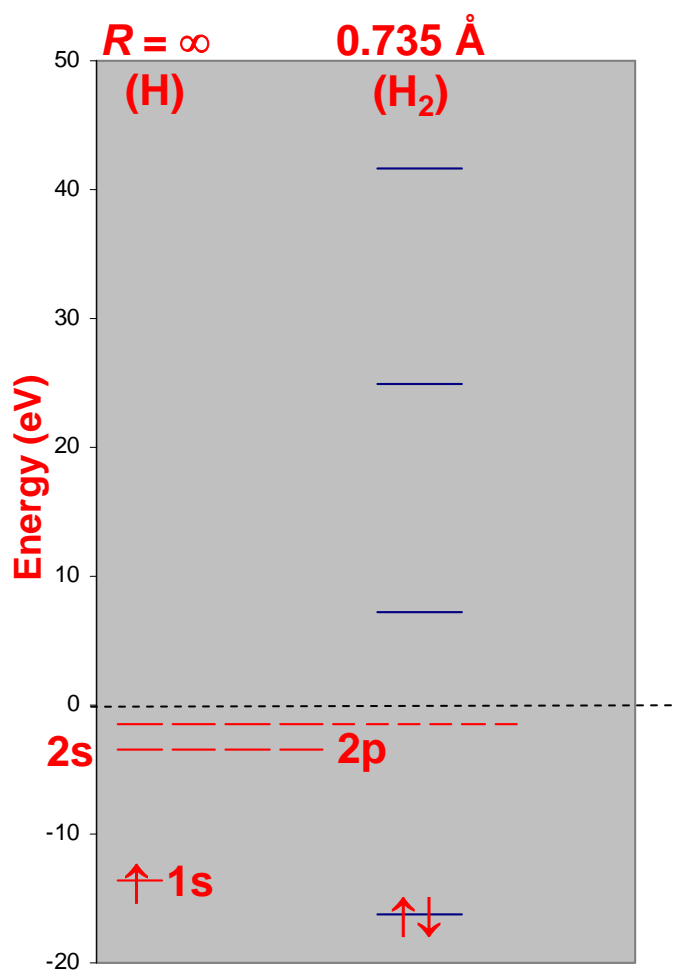
Quantum States in H₂: Allowed Energies

First let's ignore the wavefunctions (orbitals), and consider only the allowed energies, as obtained by computations. What do we observe?



Quantum States in H₂

The energy of the H₂ molecule is *lower than* the energy of two isolated H atoms. That is, the **energy change** associated with bond formation is negative.



We call this molecular orbital a **bonding orbital** for this very reason. It is symmetric to rotation about the interatomic axis, hence it's called a **σ MO**.

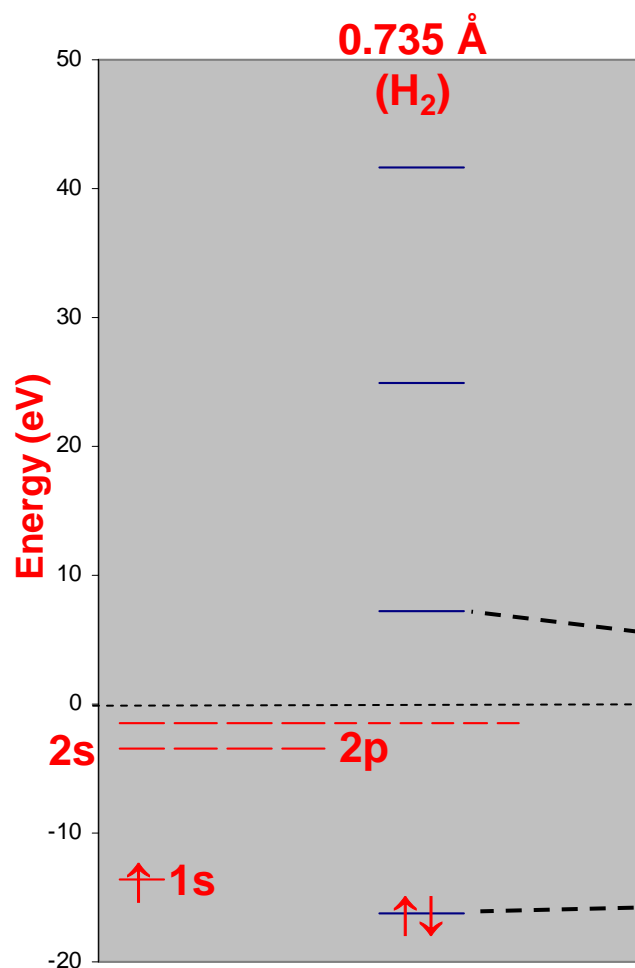
The other orbitals have higher energies than the atomic orbitals of H.

Electrons in these orbitals would not contribute to the stability of the molecule; in fact they would result in destabilization.

H₂ contains the simplest kind of bond, provided by a pair of **shared** electrons delocalised around two nuclei in a σ MO. The bond is therefore known as a **sigma (σ) bond**.

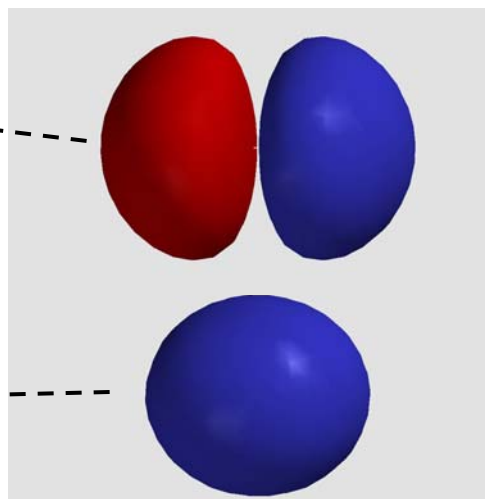
Molecular Orbitals in H₂

The next-lowest energy orbital is unoccupied. It lies above the energy of the 1s atomic orbitals (from which it's built), hence we refer to it as an *anti-bonding orbital*.



Look also at the shape of the lobes:
The *anti-bonding orbital* has a **node** between the two nuclei.

Where the bonding orbital has an electron density **build-up** between the nuclei, the anti-bonding orbital would have a **reduced** electron density (ψ^2).



This orbital is also called the Lowest Unoccupied Molecular Orbital (LUMO)

This (bonding) orbital is also called the Highest Occupied Molecular Orbital (HOMO)

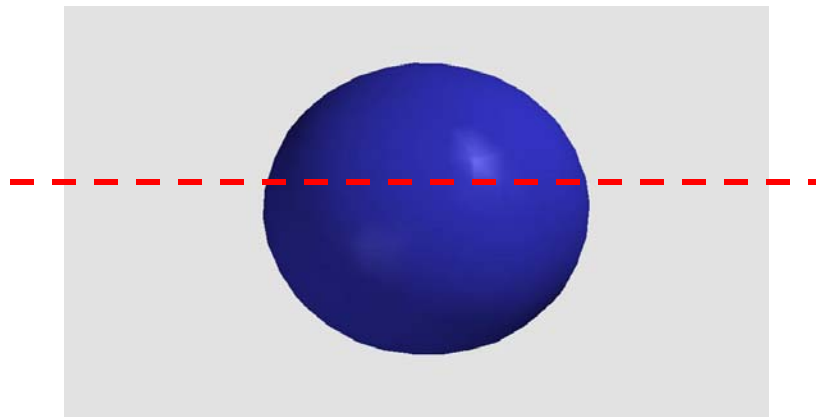
Molecular Orbital Theory

The solution to the Wave Equation for molecules leads to quantum states with discrete energy levels and well-defined shapes of electron waves (molecular orbitals), *just like atoms*.

Each orbital contains a maximum of two (spin-paired) electrons, *just like atoms*.

“Bonds” form because the energy of the electrons is lower in the molecules than it is in isolated atoms. Stability is conferred by electron *delocalization* in the molecule. This is a quantum effect: the more room an electron has, the lower its (kinetic) energy. Therefore the existence of molecules is a direct consequence of the quantum nature of electrons.

This gives us a convenient picture of a bond in terms of a pair of shared (delocalized) electrons. It also suggests simple (and commonly-used) ways of representing simple sigma bonds as:



1. A shared pair of electrons (in a bonding MO)
H : H
2. A line between nuclei (representing a shared delocalized pair of electrons)
H–H

Bonding of Multi-Electron Atoms

What kinds of orbitals and bonds form when an atom has more than one electron to share?

We will step up the complexity gradually, first considering other diatomic molecules. These fall into two classes

1. Homonuclear Diatomics. These are formed when two *identical* atoms combine to form a bond. E.g. H_2 , F_2 , Cl_2 , O_2 ...

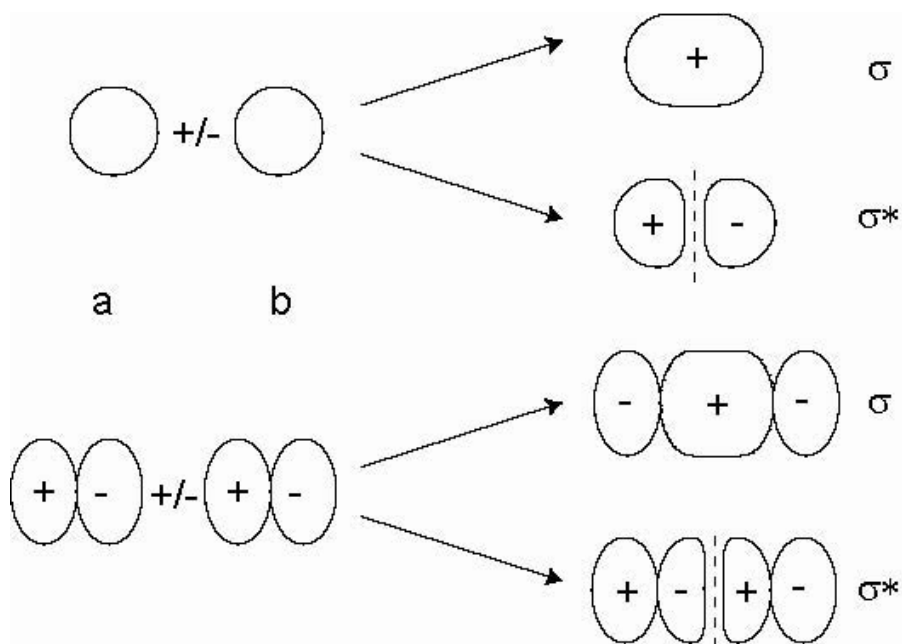
Bond lengths in homonuclear diatomic molecules are used to define the covalent radius of the atom [Lecture 5].

2. Heteronuclear Diatomics. These are formed when two *different* atoms combine to form a bond. E.g. HF, NO, CO, ClBr

Homonuclear diatomic molecules

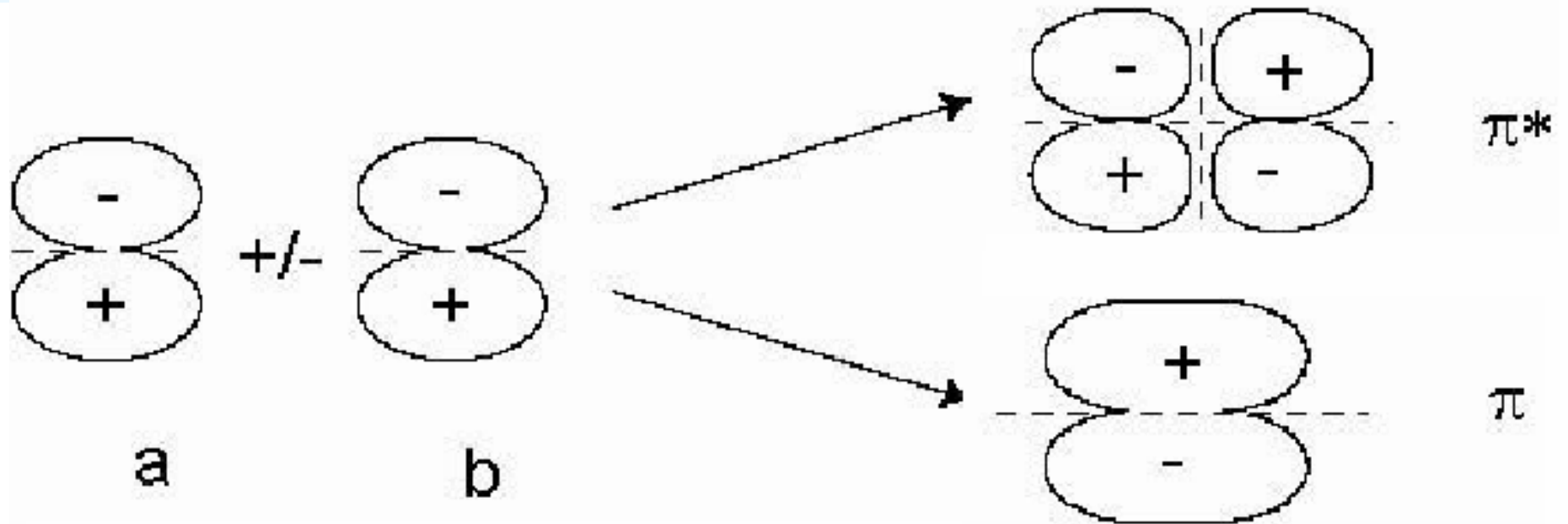
A general and systematic approach to the construction of MO's of a homonuclear diatomic molecule is to consider pair-wise interactions between atomic orbitals of the *same energy and symmetry*.

Given the $1s_a$, $2s_a$ and $2p_a$ AO's on atom a and $1s_b$, $2s_b$ and $2p_b$ AO's on atom b , we can form the following *bonding* and *antibonding* MO's of σ and π symmetry:



Head to head combination of p type AO's also results in σ and σ^* MO's

Homonuclear diatomic molecules

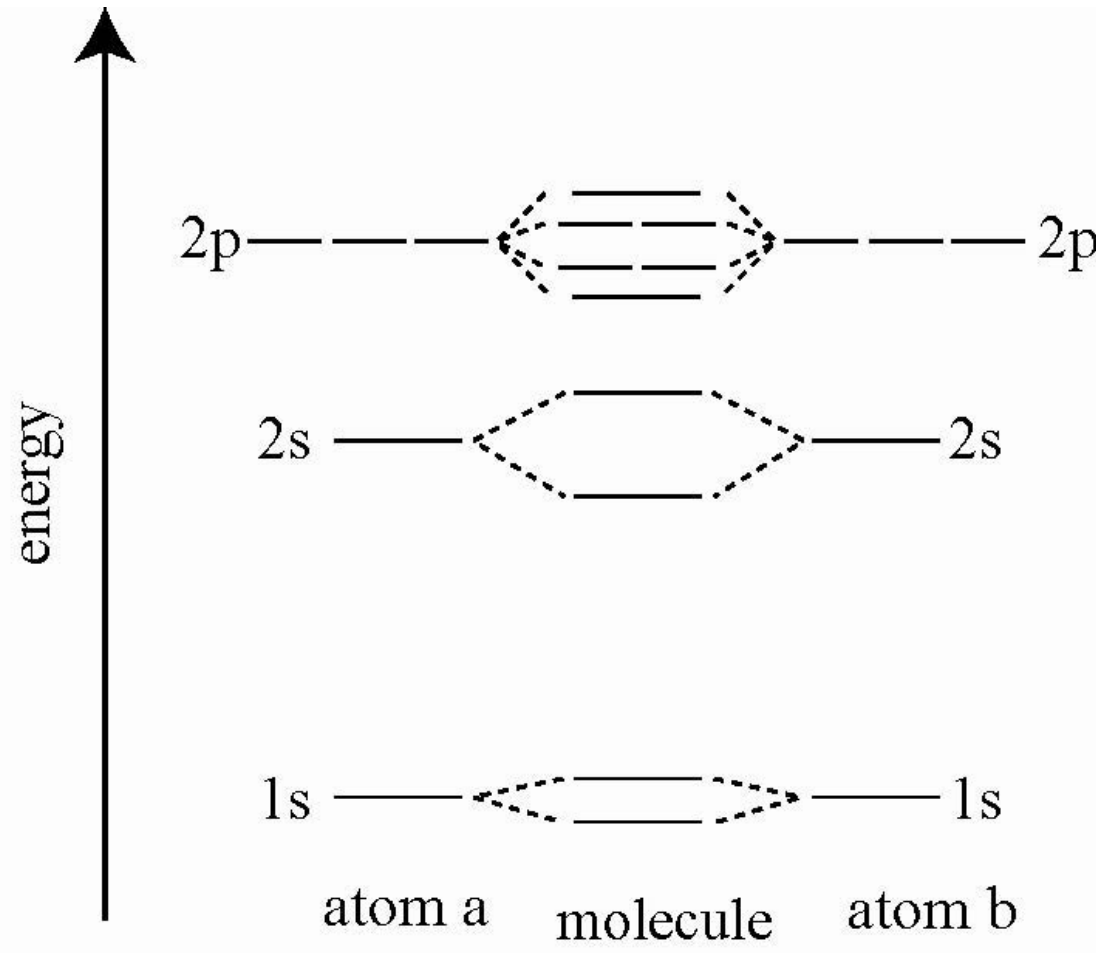


Sideways (parallel) combination of p type AO's results in π and π^* MO's.

As there are two equivalent parallel sets of p type AO's (p_x, p_y), as two atoms come together, there will be two equivalent sets of π MO's (π_x and π_y), lying in the xz and yz planes respectively (if z corresponds to the interatomic axis).

Homonuclear diatomic molecules

The following generic energy level diagram applies to **all** homonuclear diatomic molecules (with s and p valence AO's)

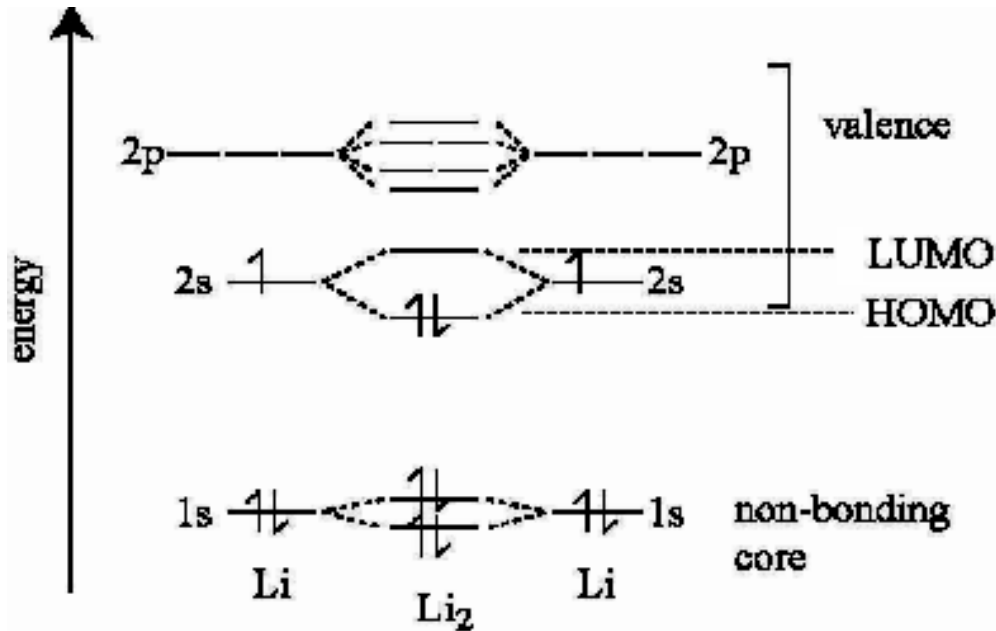


Homonuclear diatomic molecules

Next, to determine the ground state electronic configuration of the molecule, assign the electrons to the available molecular orbitals, as dictated by

- The Aufbau Rule (fill MO's in order of increasing energy)
- Pauli Exclusion Principle (a maximum of two electrons per MO with opposite spins)
- Hund's Rule (Maximize total spin when filling degenerate MO's)

As an example, consider Li_2



The two valence electrons of the Li atoms occupy a bonding σ MO in Li_2 . Hence, Li_2 is said to have a single σ bond (Li–Li).

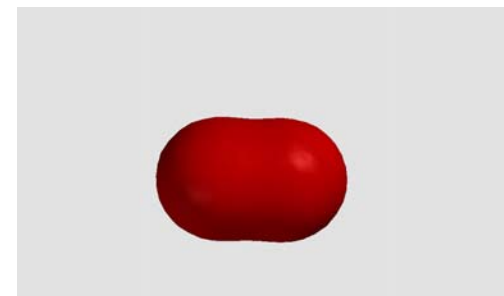
The lowest MO's are essentially the same as the 1s atomic orbitals and have the same energy. Therefore, the electrons occupying them do not contribute to bonding. These core MO's and the electrons in them are called non-bonding.

What do we take from all this?

Three simple kinds of molecular orbitals

1. Sigma (bonding) orbitals.

Electrons delocalized around the two two nuclei. These may be represented as shared electrons, e.g. H:H or Li:Li



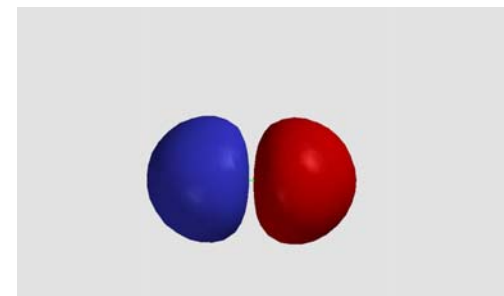
2. Non-bonding orbitals

Orbitals that are essentially unchanged from atomic orbitals, and remain *localized* on a single atom (unshared).

These may be represented as a pair of electrons on one atom.

3. Sigma star (anti-bonding) orbitals

Orbitals with a node or nodes perpendicular to the axis between two nuclei. If occupied, *these make a negative bonding contribution*, i.e. cancel the contributions of occupied bonding orbitals.



Bond Order

Simple models of bonding include the concepts of *single*, *double*, and *triple bonds*.

Molecular orbital theory provides us with a natural and general definition of bond order that includes all of these and also intermediate bonds as follows:

$$\text{Bond Order} = \frac{1}{2} (\text{No. of bonding electrons} - \text{No. of anti-bonding electrons})$$

E.g. H_2 bond order = 1 (2 electrons in a σ MO)

Li_2 bond order = 1 (2 electrons in a σ MO and 4 electrons in non-bonding core orbitals)

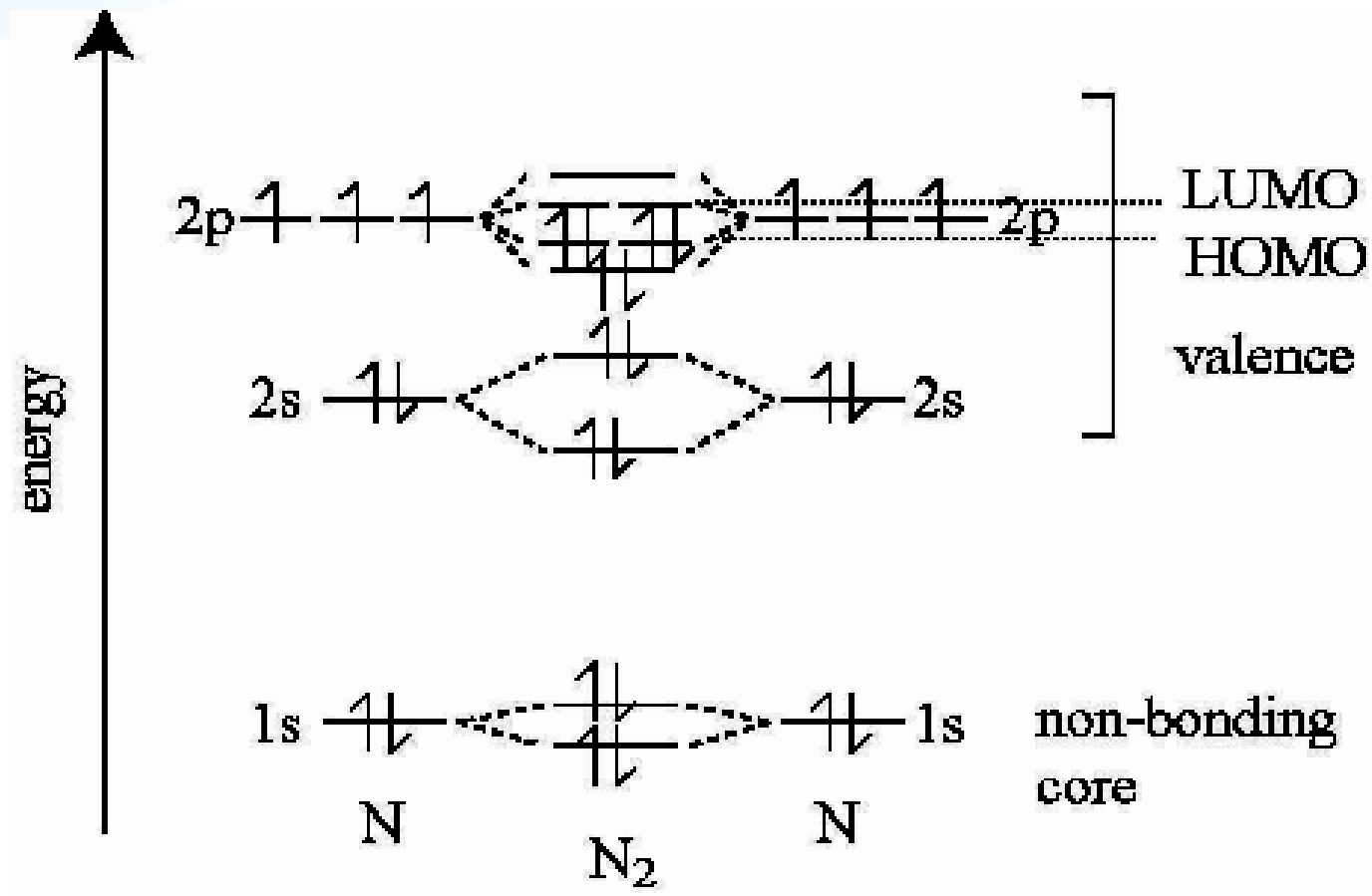
H_2^+ bond order = 0.5 (1 electron in a σ MO)

H_2^- and He_2^+ bond orders = 0.5 (2 electrons in a σ MO and 1 electron in a σ^* MO)

He_2 bond order = 0 (2 electrons in a σ MO and 2 electrons in a σ^* MO)

Homonuclear diatomics: The electronic structure of N₂

Using the standard MO energy level diagram allocate the 14 electrons of N₂



$$\text{Bond order} = \frac{1}{2}(8 - 2) = 3$$

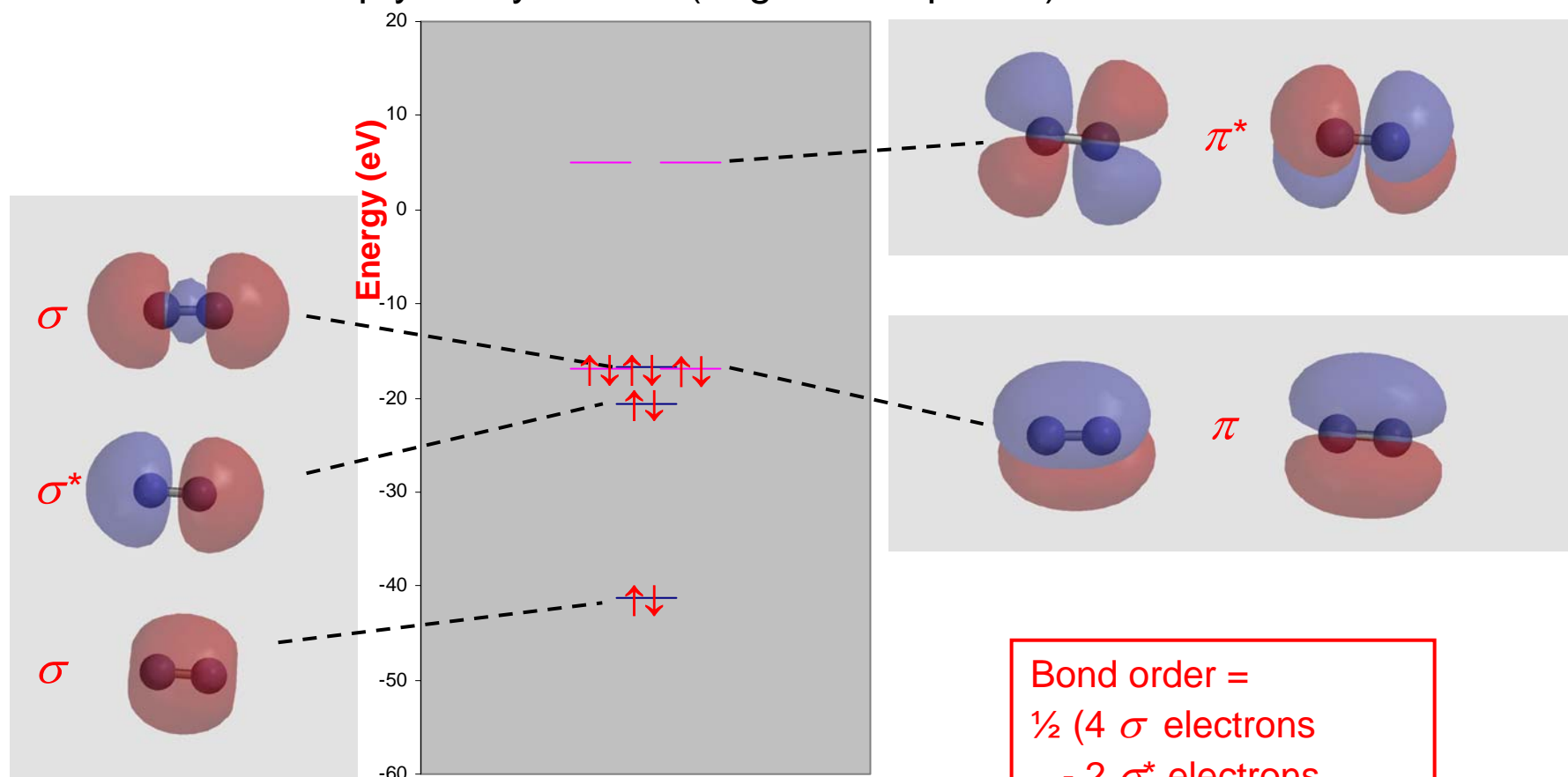
There is an excess of 6 bonding electrons, corresponding to a triple bond: **N≡N**

Valence MO's and energy levels in N₂ (as computed)

The 14 valence electrons of N₂ occupy bonding σ and π MO's and an antibonding σ^* MO.

The HOMO is actually a σ MO (lying slightly higher in energy than the π MO's.)

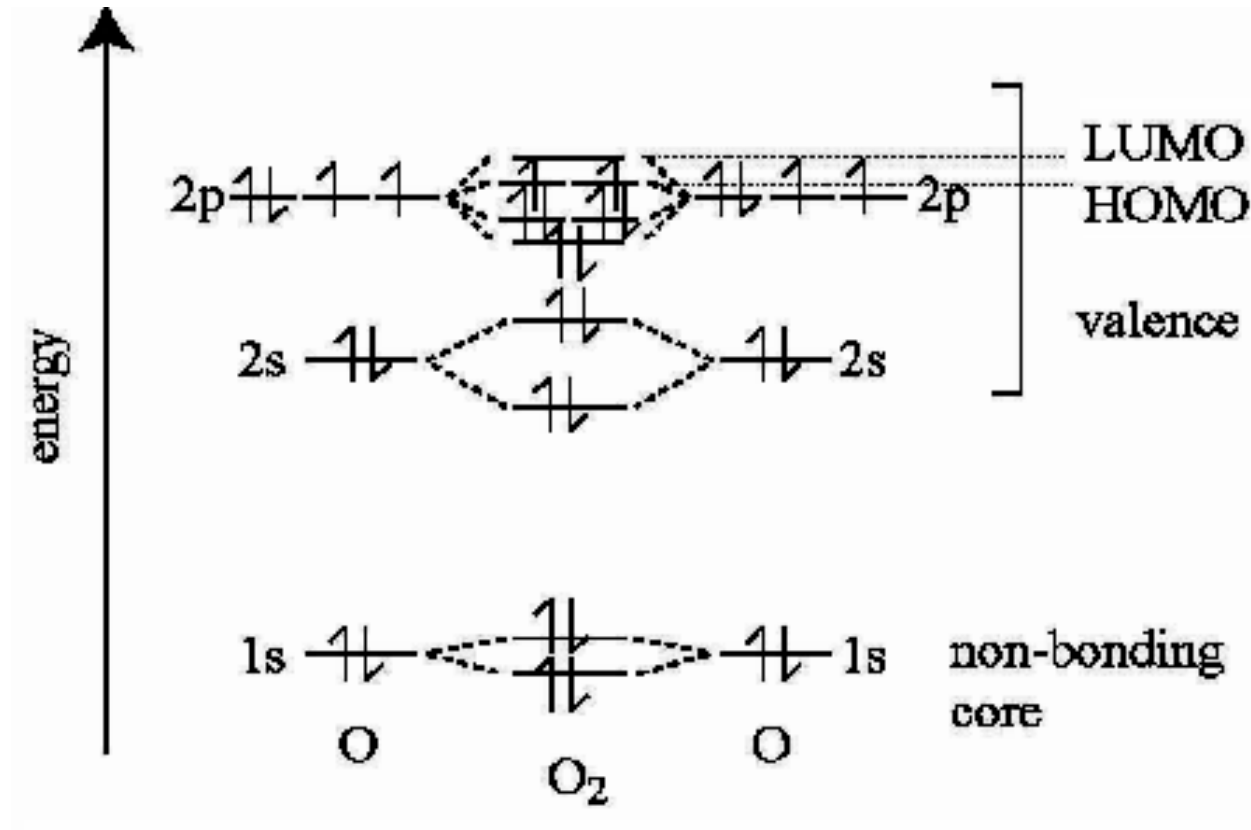
The π^* orbitals are empty - they are the (degenerate pair of) LUMO's.



$$\text{Bond order} = \frac{1}{2} (4 \sigma \text{ electrons} - 2 \sigma^* \text{ electrons} + 4 \pi \text{ electrons}) = 3$$

Homonuclear diatomics: The electronic structure of O₂

Following on from N₂, the extra two electrons are placed in the degenerate pair of π^* MO's (as required by Hund's Rule).



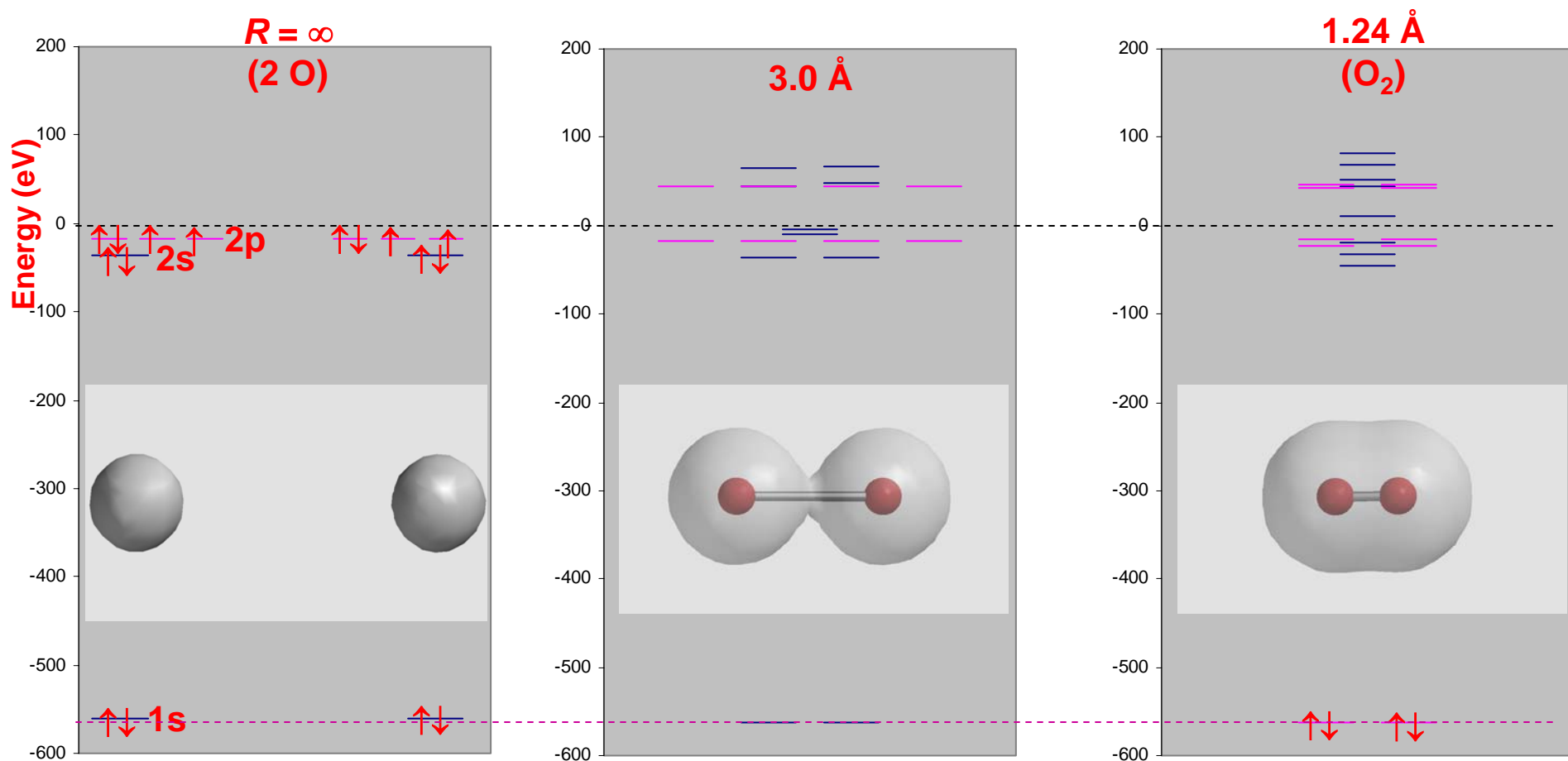
Bond order = $\frac{1}{2}(8 - 4) = 2$. This implies a double bond: **O=O**

MO theory also predicts that the O₂ molecule would be **paramagnetic**, due to the non-zero net electron spin, i.e. non-zero magnetic moment.

Oxygen is indeed paramagnetic!

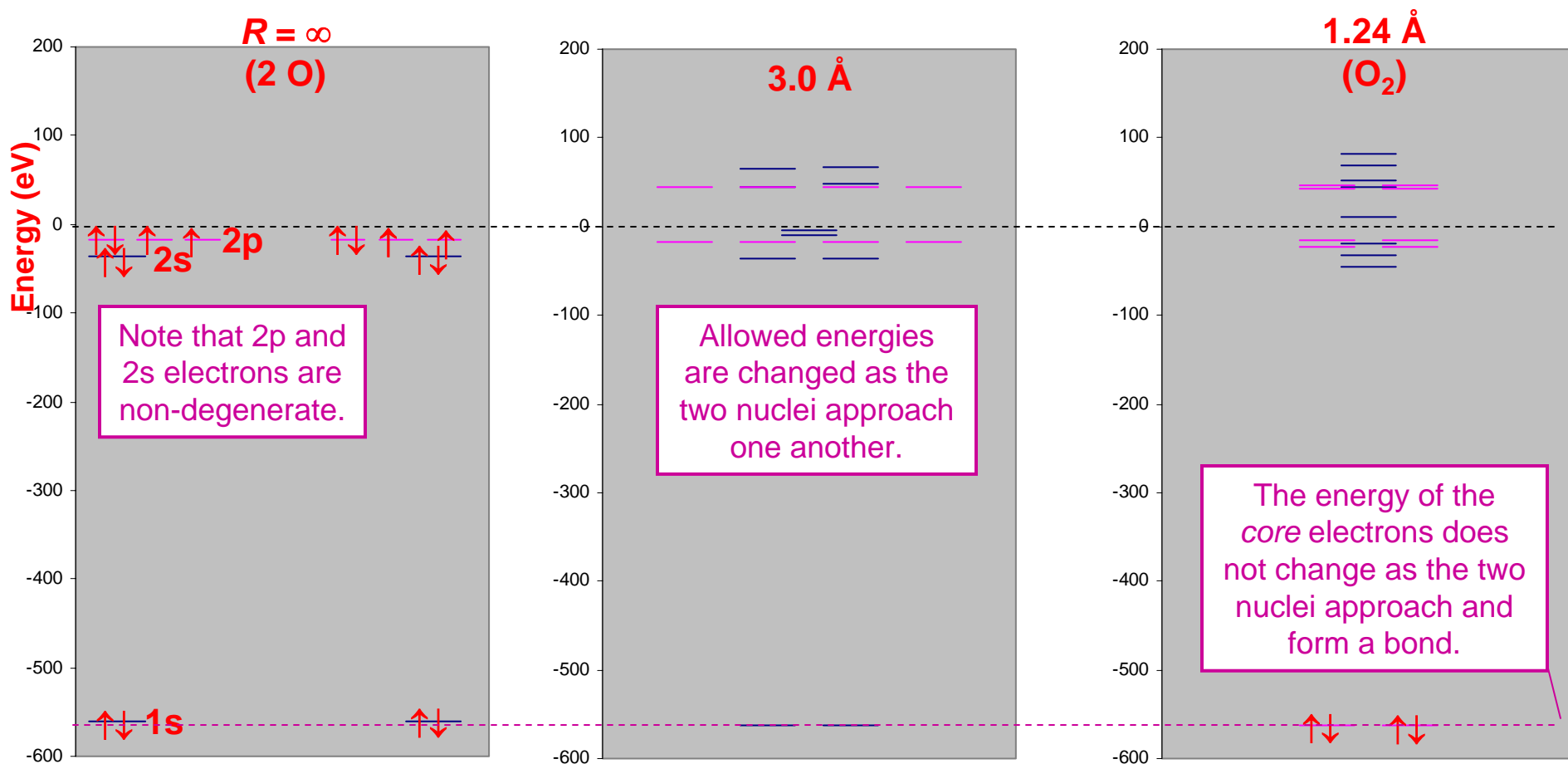
Bonding in O₂

As two O atoms approach one another, some of the electrons become delocalised and the allowed energy levels change, lowering the total energy of the system.



Energy Levels in O₂

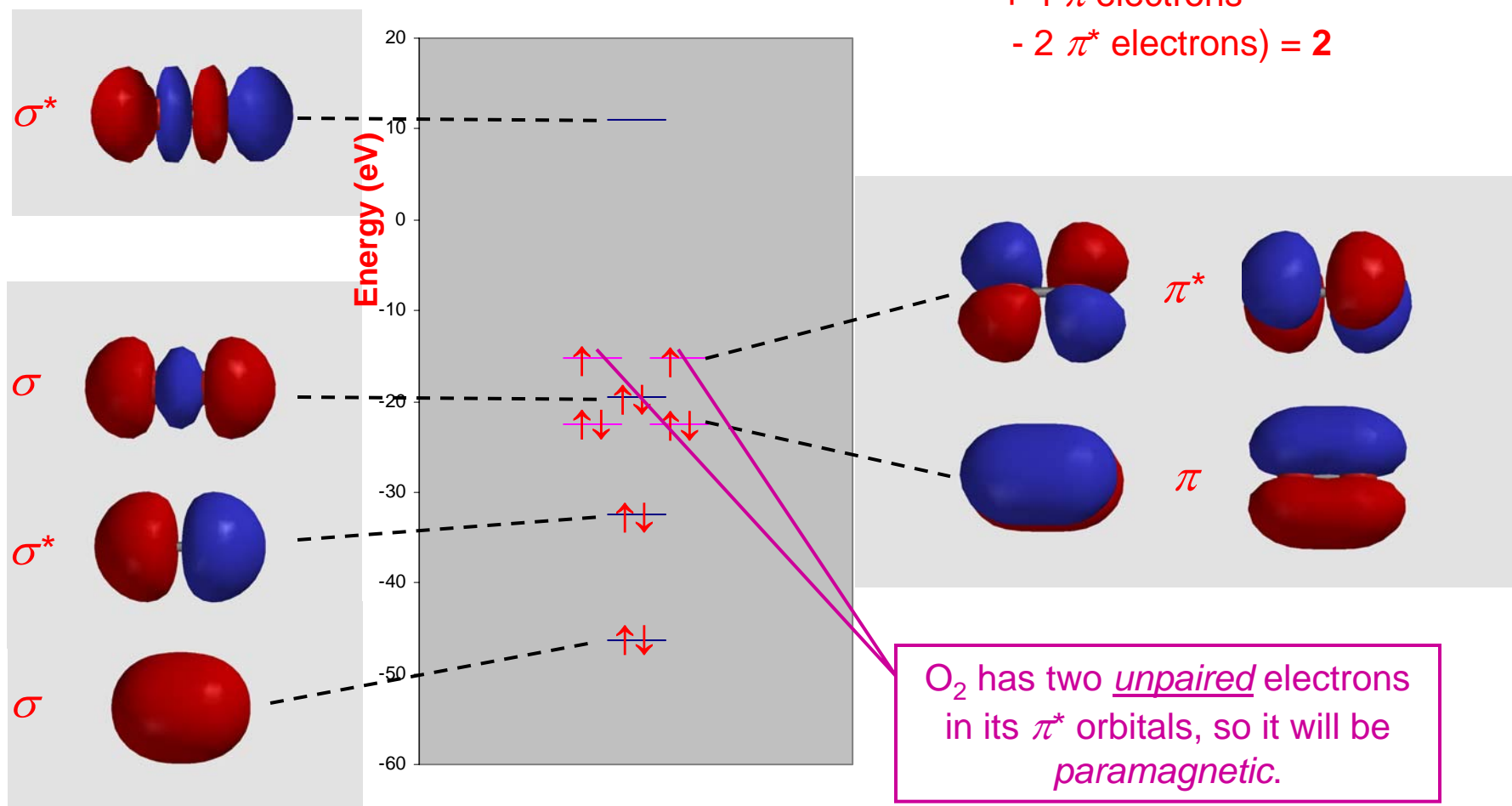
As the two nuclei approach each other, the energies of the valence electrons change, forming bonding and anti-bonding orbitals. The energy is a minimum at the equilibrium bond length (1.24Å).



Valence MO's and energy levels in O₂ (as computed)

As in N₂, the highest occupied σ MO is higher in energy than the π MO's). O₂ has 12 valence electrons and thus a bond order of

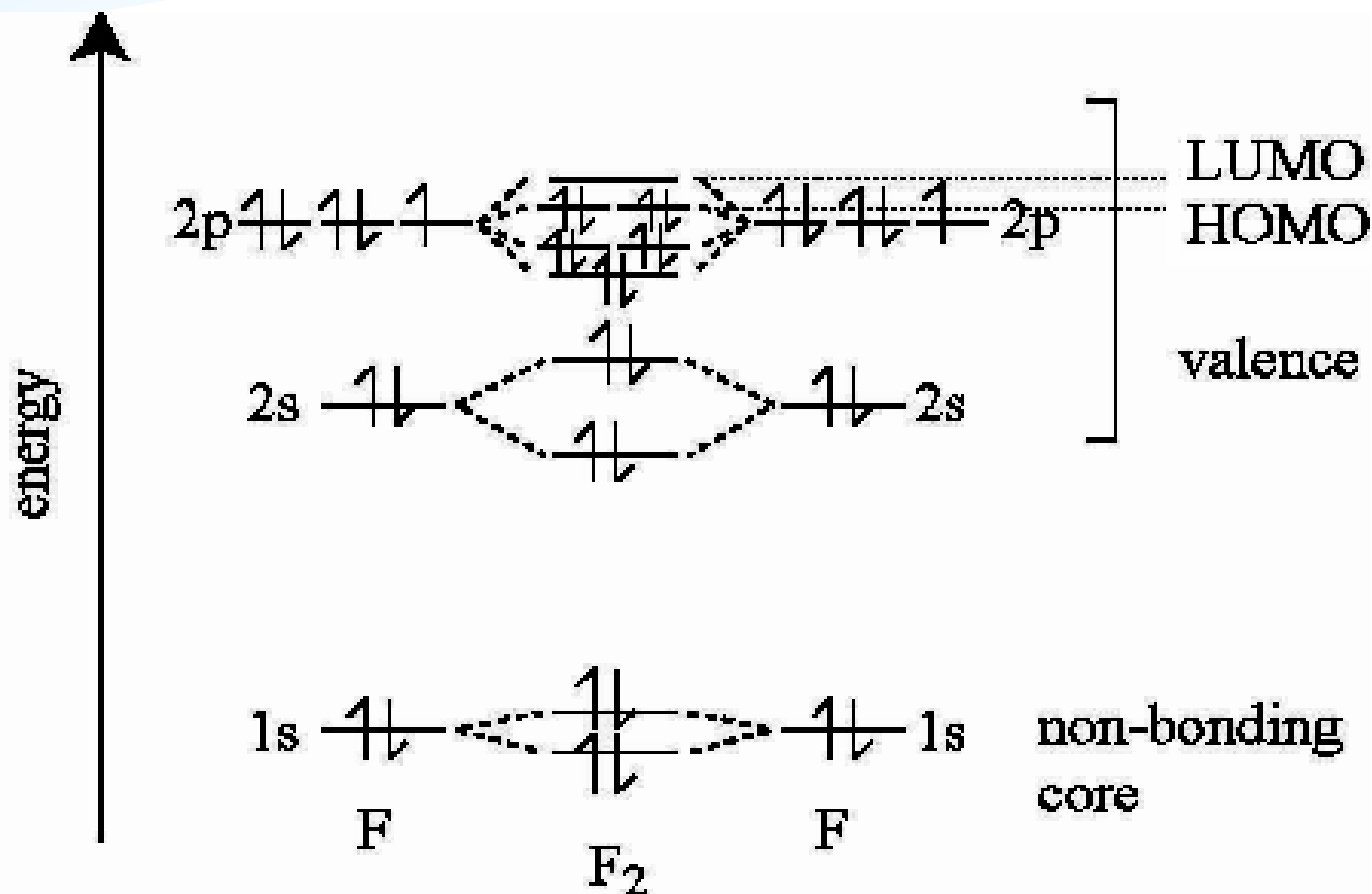
$$\frac{1}{2} (4 \sigma \text{ electrons} - 2 \sigma^* \text{ electrons} + 4 \pi \text{ electrons} - 2 \pi^* \text{ electrons}) = 2$$



Note that the antibonding MO's always have nodes between the nuclei!

Homonuclear diatomics: The electronic structures of F₂ and Ne₂

In F₂, the 18 electrons fill up all the MO's, up to and including the π^* MO's.



Bond order = $\frac{1}{2}(8 - 6) = 1$. This implies a single bond: F-F

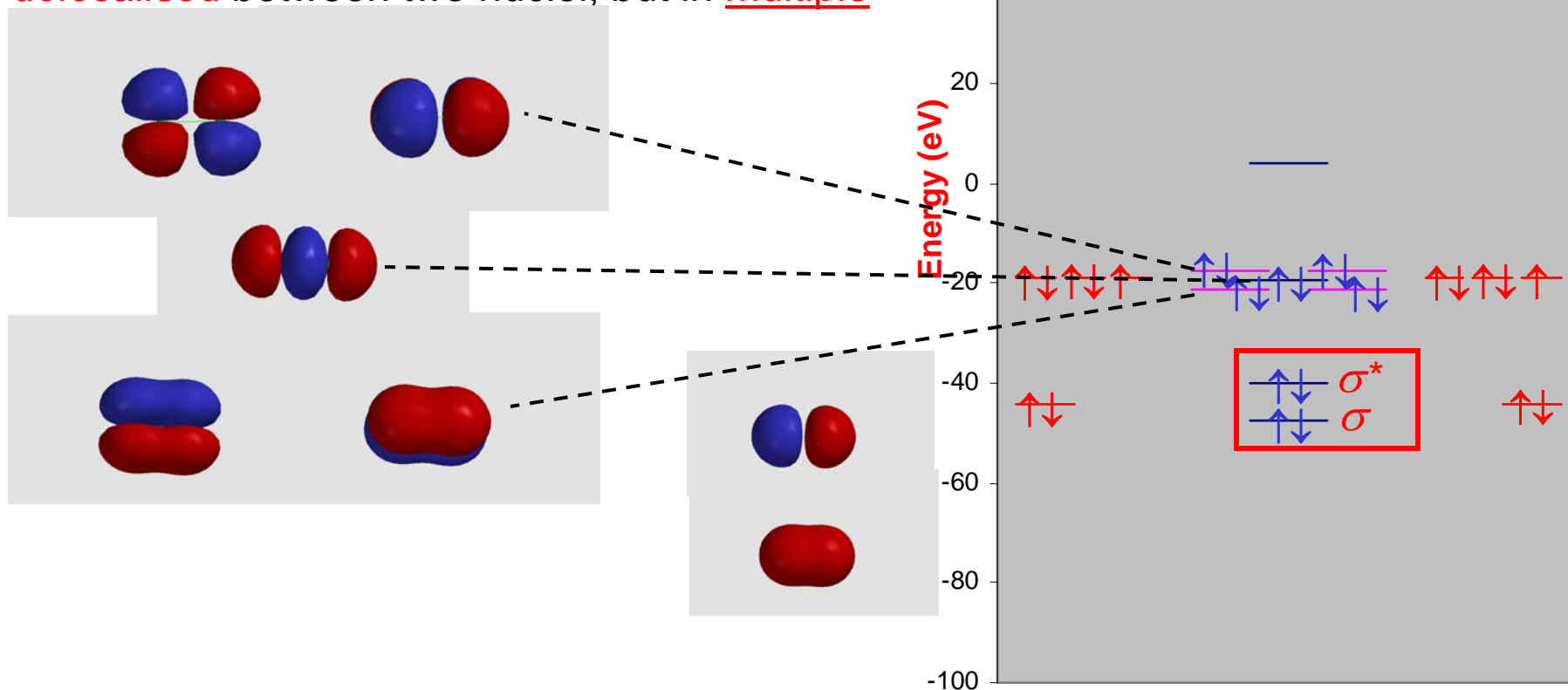
To obtain Ne₂ the extra two electrons are placed in the σ^* MO.

This results in a bond order of zero, i.e. **no bond and no Ne₂ molecule!**

Valence MO's and energy levels in F_2 (as computed)

The lowest two valence molecular orbitals are σ and σ^* .

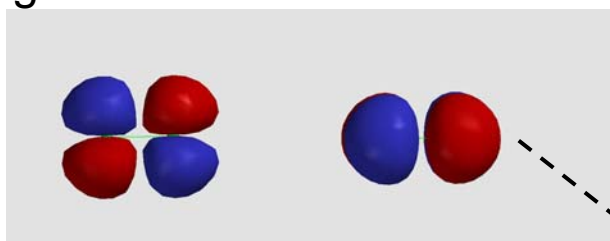
The other five filled orbitals have the same characteristics. Bonding orbitals have electrons *delocalised* between two nuclei, but in multiple



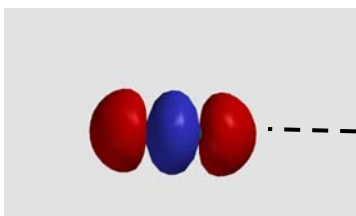
Valence MO's and energy levels in F₂ (as computed)

The highest energy occupied orbitals are π^* *antibonding* (nodes *between* the nuclei). There are also nodes along the internuclear axis.

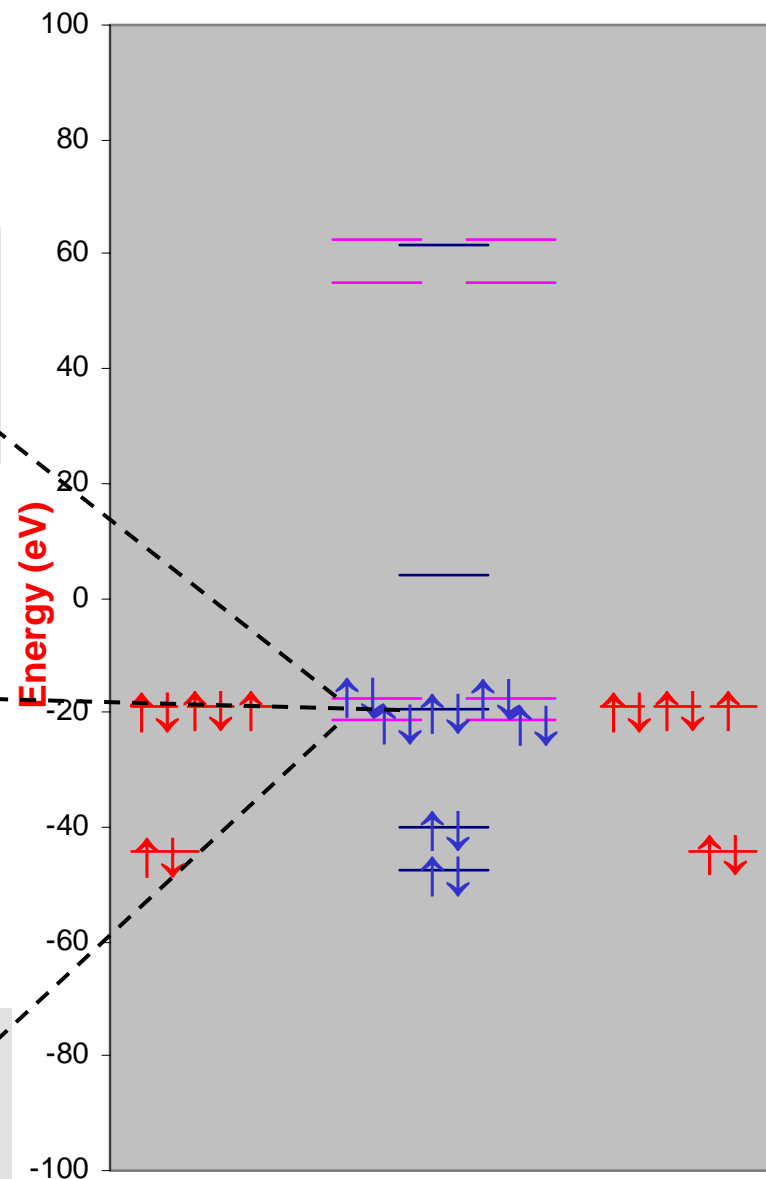
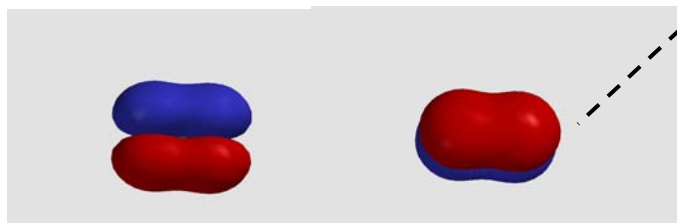
One orbital lies above & below the nuclei, and the other in & out of the page.



This orbital is a σ bonding orbital. No node between the nuclei, and symmetric about the internuclear axis.

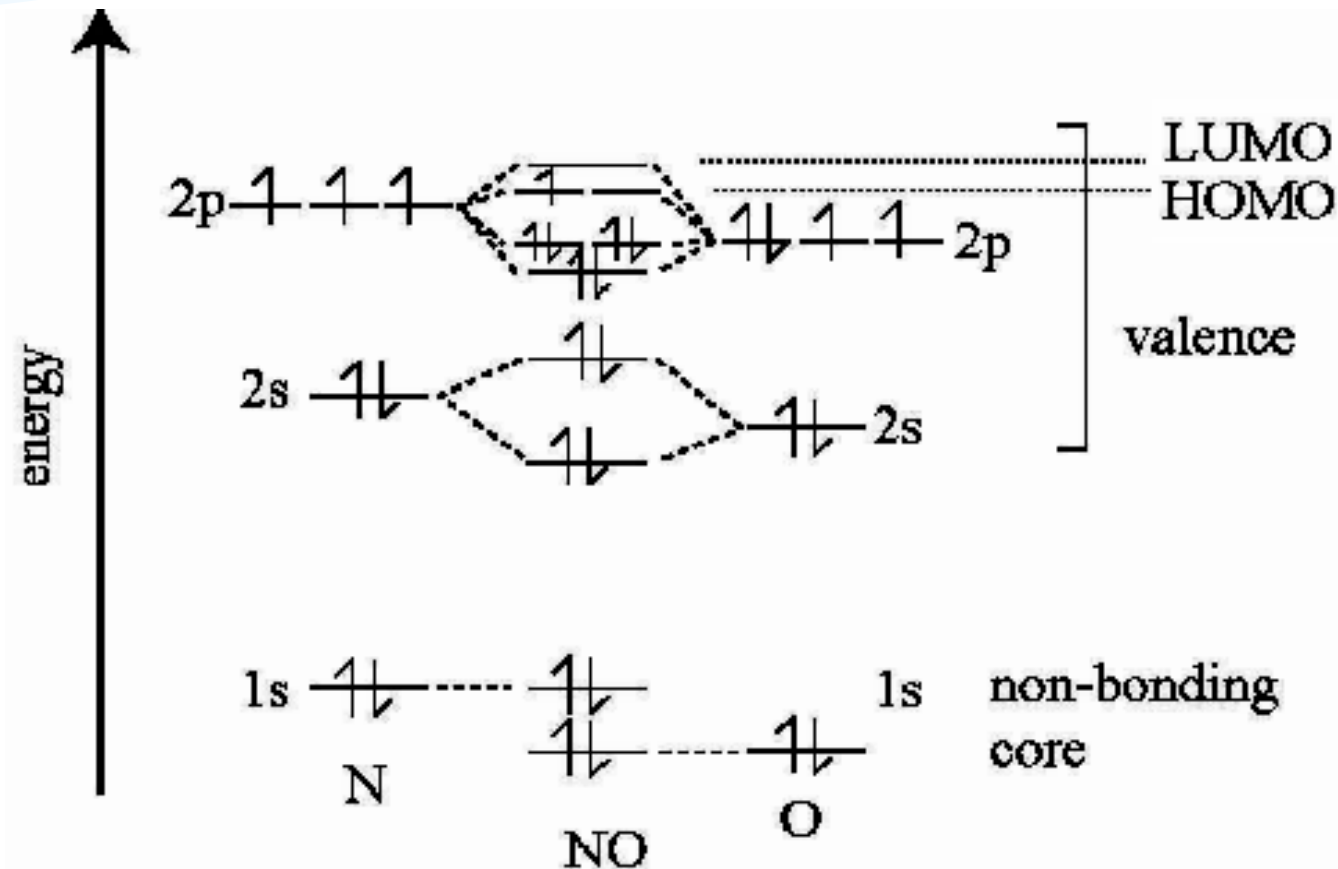


The lowest energy orbitals are π *bonding* - delocalised between the nuclei with nodes along the internuclear axis.



Heteronuclear diatomics: The electronic structure of NO

The energies of the AO's of N and O are very similar - those on O are slightly lower. The MO's of NO therefore can be constructed the same way as for N₂ or O₂.

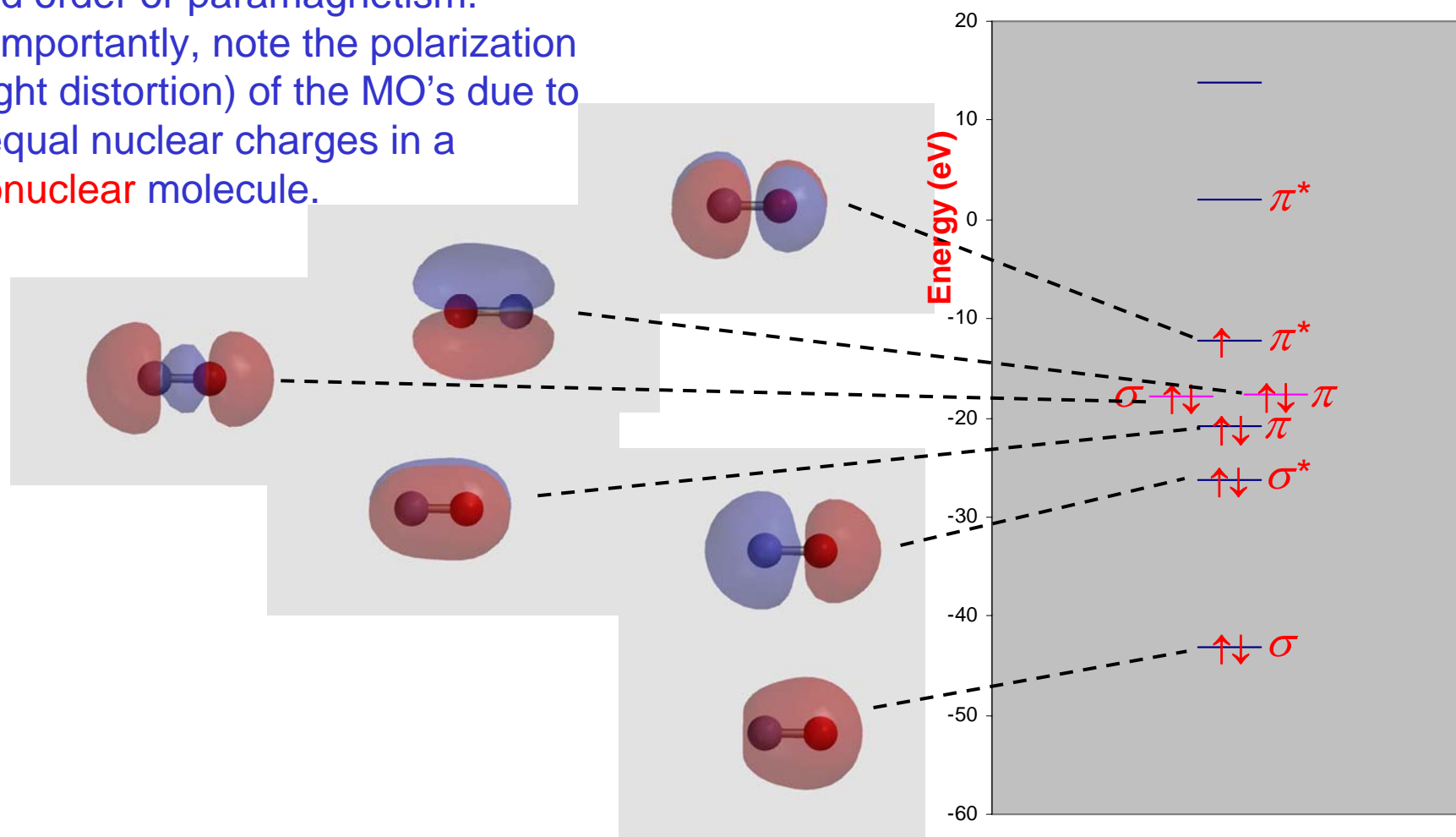


Bond order = $\frac{1}{2}(8 - 3) = 2\frac{1}{2}$. Strength of bond is between double and triple bonds. Molecule has an unpaired spin - therefore it is paramagnetic.

Valence MO's and energy levels in NO (as computed)

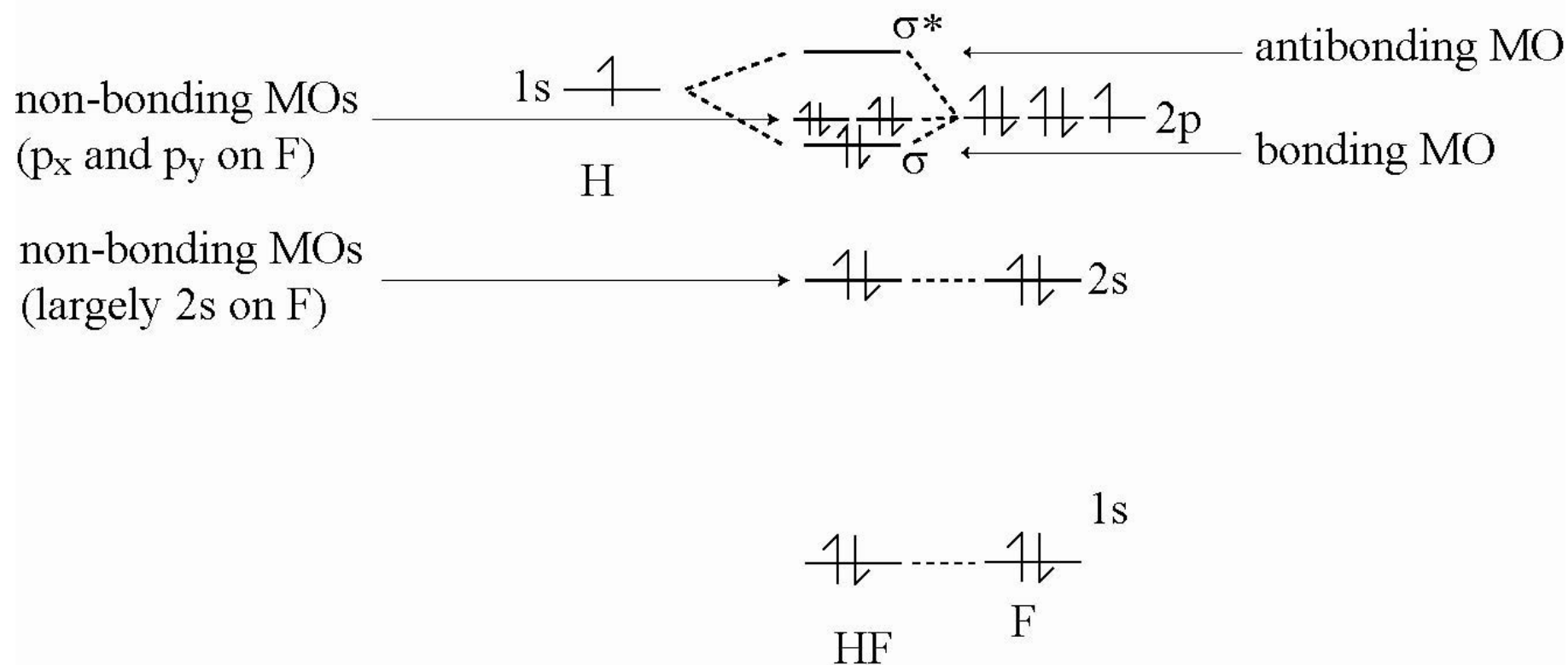
The computed energies of the four highest occupied MO's (π , π , σ , π^*) do not follow the expected pattern. This is due to effects, such as spin polarization (effect of electron in the singly occupied π^* MO on the π MO's), which are absent in the simple qualitative model we use. This has no effect on predictions of bond order or paramagnetism.

More importantly, note the polarization (left-right distortion) of the MO's due to non-equal nuclear charges in a **heteronuclear** molecule.

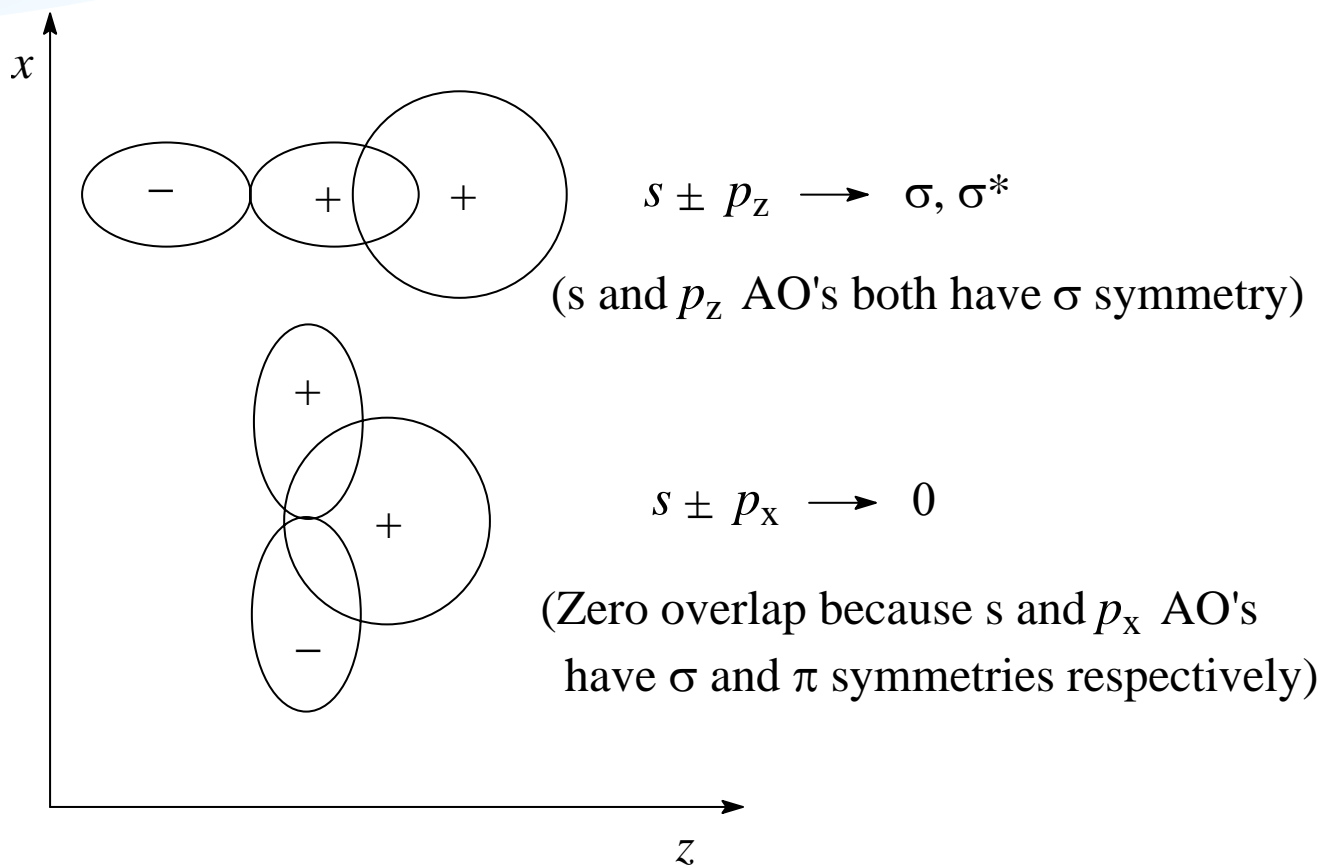


Heteronuclear diatomics: The electronic structure of HF

In hydrides, such as HF, the MO's need to be constructed from a single 1s AO of H and the 1s,2s,2p AO's of F. The 1s AO of H is closest in energy to the 2p AO's of F, but can only interact with the $2p_z$ AO of F (because of symmetry). As a result, all doubly occupied AO's of F remain largely unchanged, as non-bonding orbitals.



MO's from interaction of s and p orbitals



When forming MO's the parent AO's must have the same symmetry!

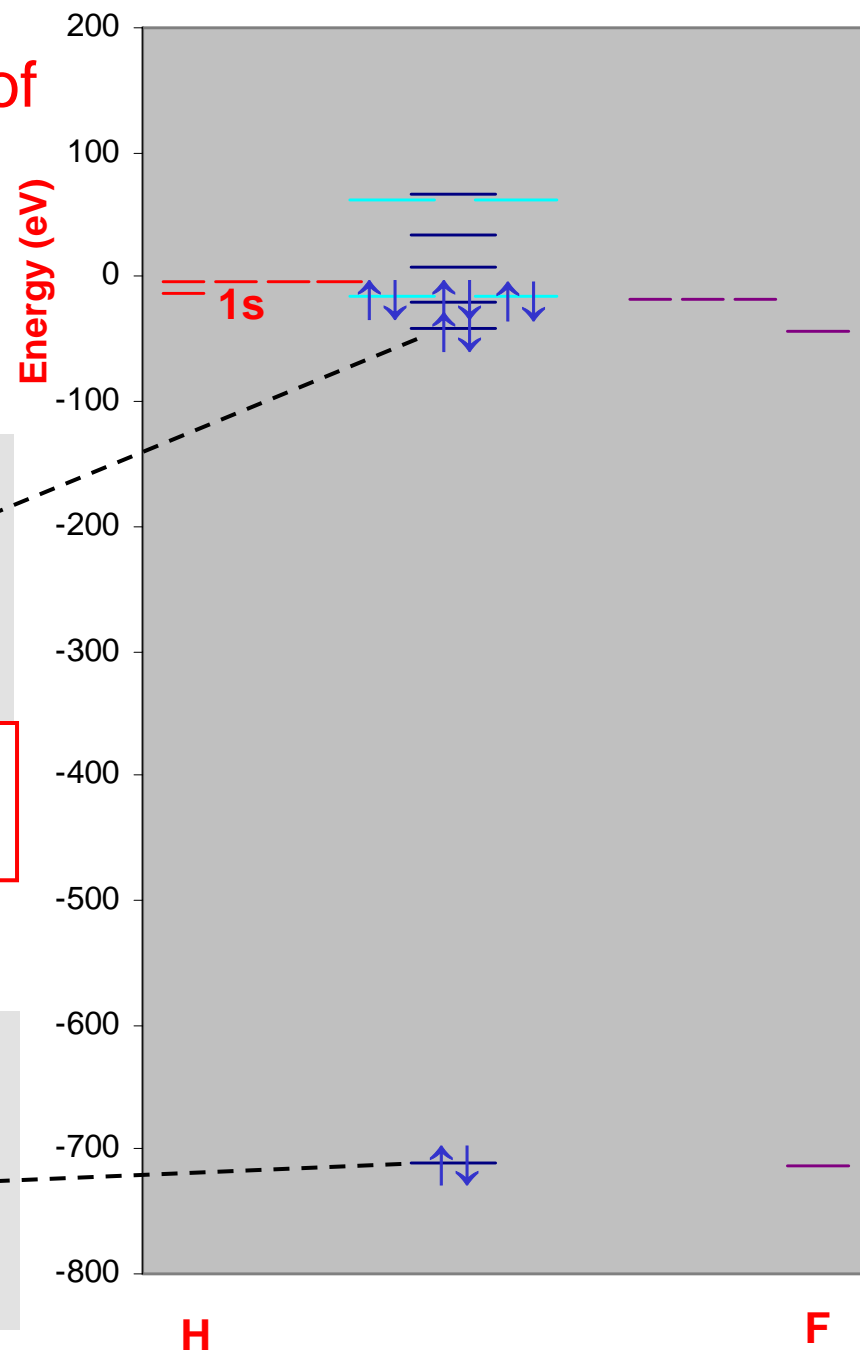
Molecular orbitals and energies of HF (as computed)

This is largely the **non-bonding 2s AO of F** (with small contributions from the 1s AO of H).



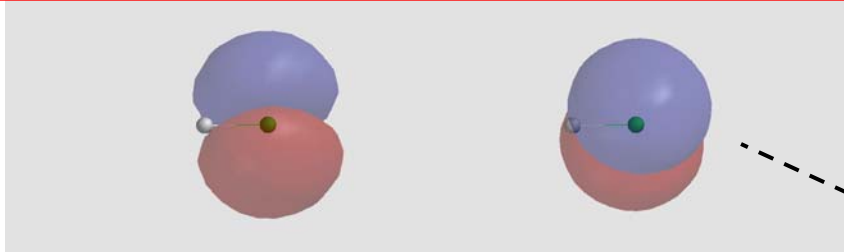
The electron density is mostly around the F atom.

This **non-bonding core orbital** is largely the F 1s orbital. The electrons are bound tightly to the F nucleus.

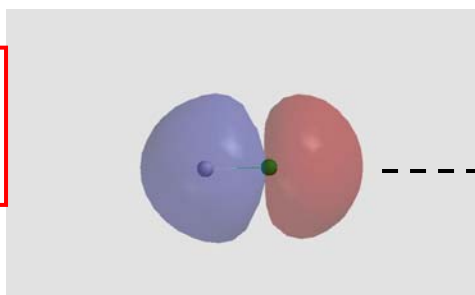


Molecular orbitals and energies of HF as computed

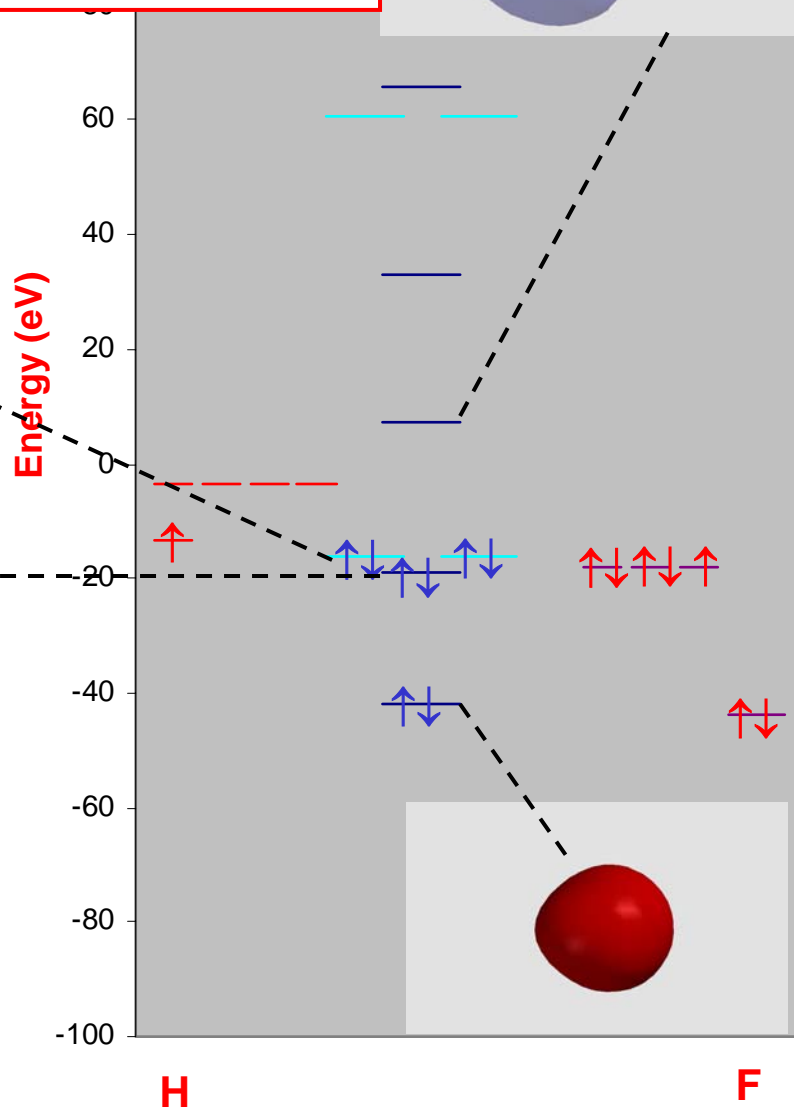
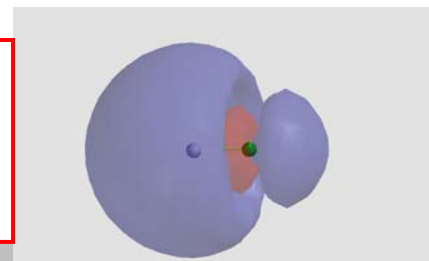
These two degenerate **non-bonding** HOMO's are the $2p_x$ and $2p_y$ orbitals of F.



This is the bonding MO consisting of the $2p_z$ AO of F and the $1s$ AO of H.



This (**empty**) LUMO is an antibonding orbital with a **node** on the interatomic axis between H and F.

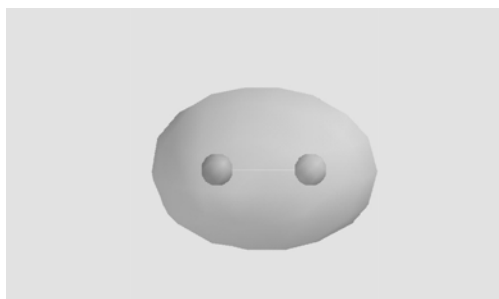


The only electrons which are shared by F and H are the two in the bonding σ MO. The rest are **non-bonding** - they are in orbitals which are largely localized on F.

Electron Densities in H_2 , F_2 , and HF

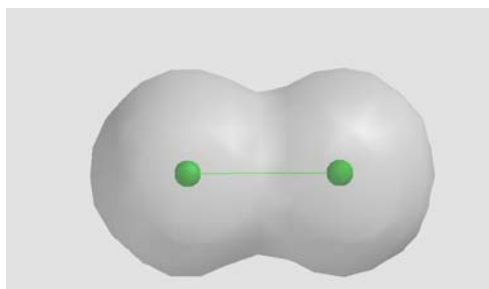
The square of a wavefunction (corresponding to an occupied orbital) tells us the charge density distribution of the electron(s) in the orbital. If we add up the charge densities from all the occupied molecular orbitals, we obtain the overall charge density distribution in the molecule.

1. H_2



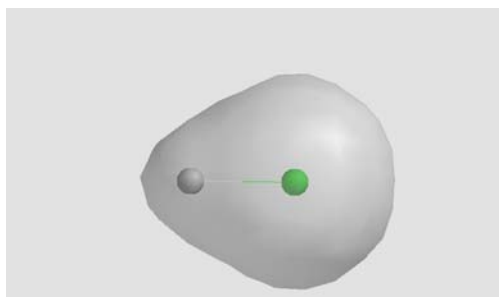
This shows the surface for H_2 within which the probability of finding an electron is 95%. It is simply the square of the occupied σ MO.

2. F_2



In F_2 the 95% surface includes all the occupied MO's. The *general effect* is seen by adding them together.

3. HF

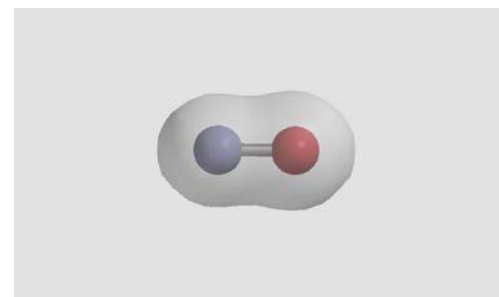


In HF the 95% surface looks like a simple sigma bond, but most of the electrons accumulate around the F atom.

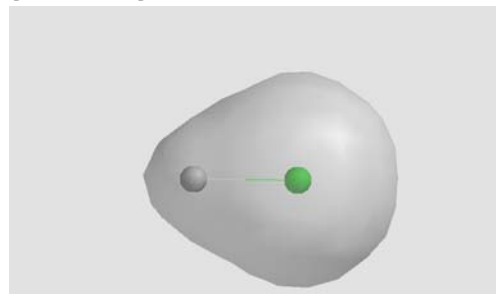
Charge Distribution in Heteronuclear Diatomics

The overall distribution of electron density in heteronuclear diatomic molecules is uneven due to the difference in nuclear charges and the different degree of attraction exerted on the electrons.

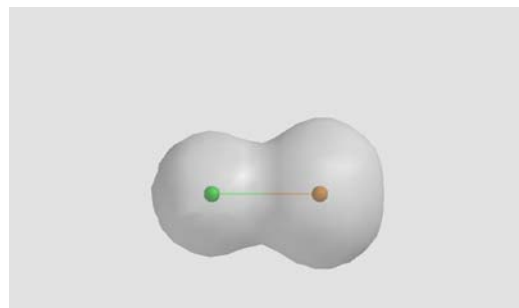
In NO the distribution of charge slightly favours O



In HF it strongly favours F (whereby H would appear quite positive and F would appear quite negative).



Similarly in HCl it favours Cl.



Bonds between unlike atoms are said to be *polar*. **Polar bonds** can occur in diatomic or polyatomic molecules.

Triatomic and Polyatomic Molecules

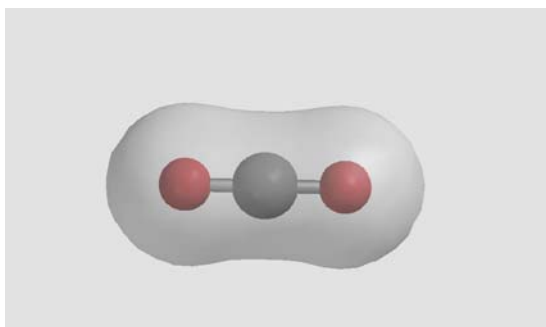
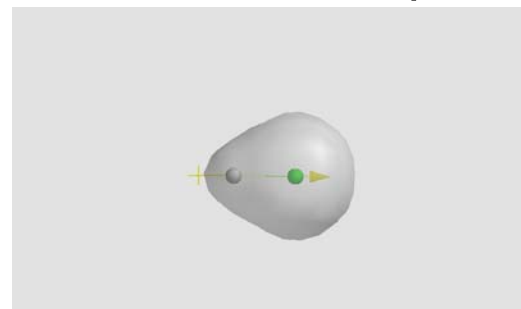
CO₂ is a simple triatomic molecule that can be represented O-C-O.

This representation says nothing about *bond order* or about *molecular shape*, only that in CO₂ both oxygen atoms are bonded to carbon.

Both C-O bonds in CO₂ are *polar*, as they are between different atoms (C and O). Each polar bond can be characterised by a dipole, and described by a *dipole moment*. A dipole is represented by an arrow from the positive to the negative end of the molecule.

E.g. HF has a large dipole. (NO has a small one.)

The equilibrium structure of CO₂ is shown below.



Although each C-O bond is polar, the two bond dipoles are equal and opposite, so this *linear triatomic molecule* has no net dipole. The electron density is symmetrical about the central C.

Review Types of Orbitals and Bonds in Diatomics

We now know of five kinds of molecular orbitals formed by valence electrons.

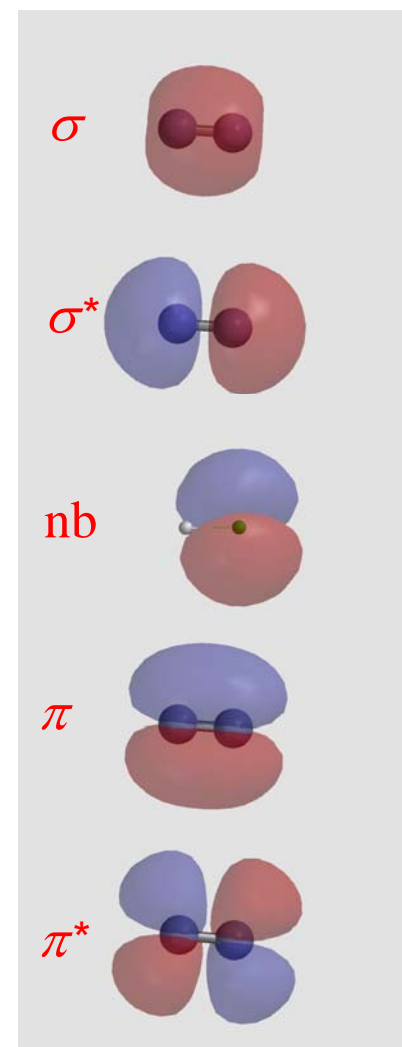
1. σ (bonding) orbitals. Electrons in these bonds lower the energy of the molecule (relative to its atomic orbitals). These are shared between two nuclei and **delocalised** *along the axis between two nuclei*.

2. σ^* (antibonding) orbitals. Electrons in these bonds raise the energy of the molecule (oppose bonding). These orbitals have a node or nodes along the axis between two adjacent nuclei.

3. Non-bonding (nb) orbitals are localised on only one atom and do not affect bonding.

4. π (bonding) orbitals. Electrons in these orbitals lower the energy of the molecule, and are delocalised between two nuclei in two lobes on opposite sides of the internuclear axis.

5. π^* (antibonding) orbitals. These orbitals have lobes on opposite sides of the internuclear axis, and a node between adjacent atoms.

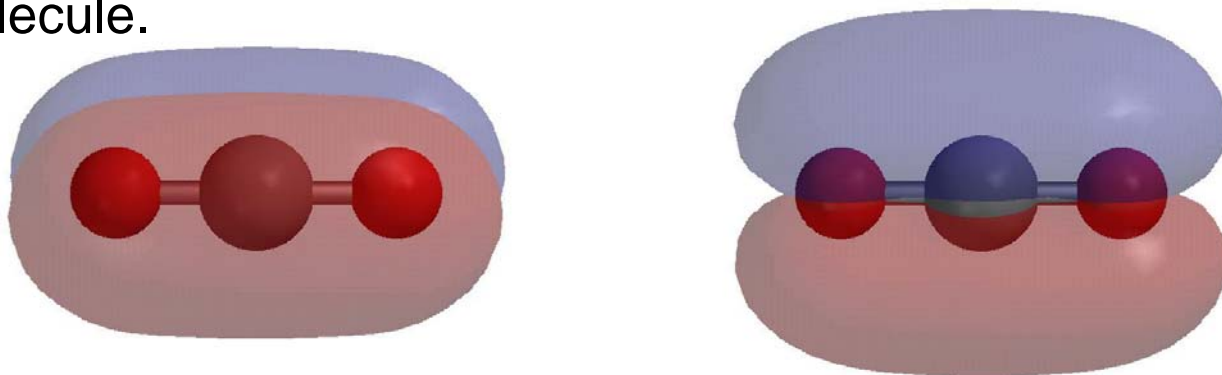


Orbitals in Polyatomic Molecules and Networks

Some of the general features we have seen in diatomic molecules can be generalised to larger molecules.

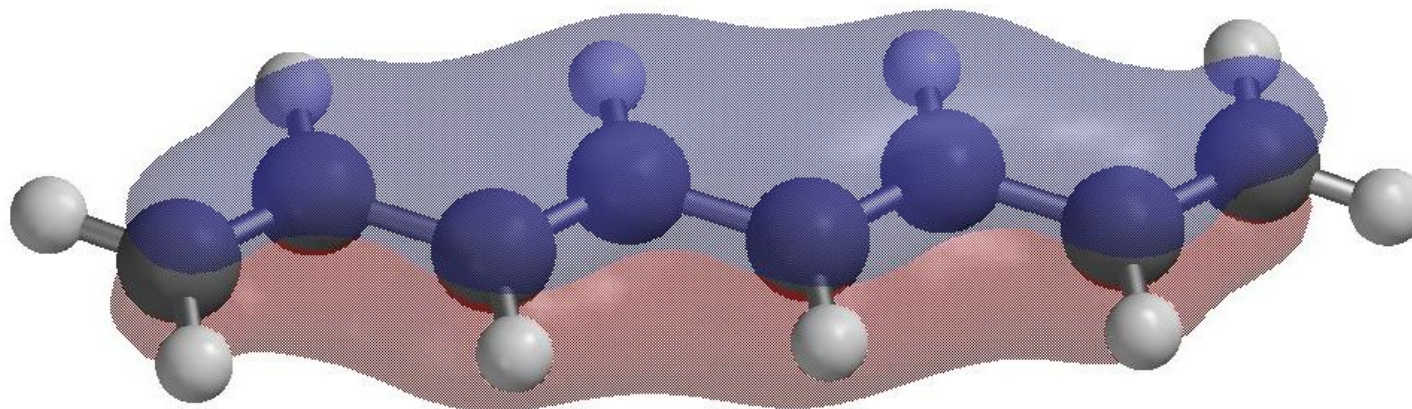
- All molecules yield discrete, allowed energy levels.
- Larger molecules generally contain more valence electrons, and have more allowed energies (= energy levels).
- Molecules are stabilised by lowering electron energies.
- **Stabilisation is achieved by greater delocalisation of the electrons** (i.e. a longer electron wavelength).

This can even be seen in a triatomic molecule like CO_2 , which has two π -type (two-lobed) MO's containing electrons delocalised along the whole molecule.

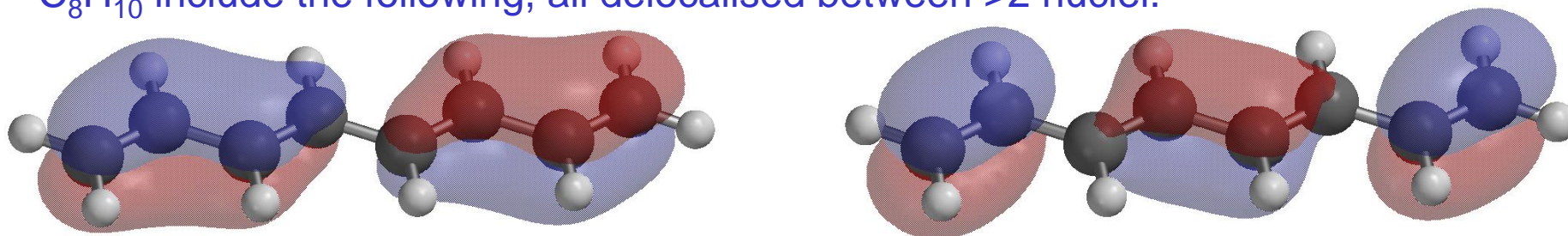


MO's in Larger Molecules

Octatetraene (C_8H_{10}) is an example of a molecule with electrons in highly delocalised orbitals such as the one shown below.



This and other π -type bonding orbitals are low energy quantum states in which the electron is *bound by more than two nuclei*. Other (higher energy) MO's of C_8H_{10} include the following, all delocalised between >2 nuclei.



You are not expected to recognise or define bonding and antibonding orbitals in polyatomic systems.

A Simple(r) Description of Bonding

We can now begin synthesise all this into a simple picture of bonding. Electrons in molecules can be divided into four classes.

1. **Core Electrons.** Electrons in these orbitals are unaffected by the presence of neighbouring atomic nuclei. Their energy is practically the same as in an isolated atom.

2. **σ or single covalent bonds.** Electrons in these orbitals are delocalised between neighbouring nuclei. The electron density is highest along the internuclear axis. **These are responsible for describing how the atoms are connected to each other and hence the three-dimensional structure of the molecule.**

3. **Non-bonding (nb) orbitals** are localised on only one atom and do not affect bonding.

4. **π bonds.** Electrons in these orbitals lower the energy of the molecule, and hence favour bonding. They are **delocalised between multiple nuclei** in lobes on opposite sides of the internuclear axis.

What we do with antibonding orbitals depends on what question we are asking (or being asked).

E.g. Bond energy? Bond Order? Electron Density?

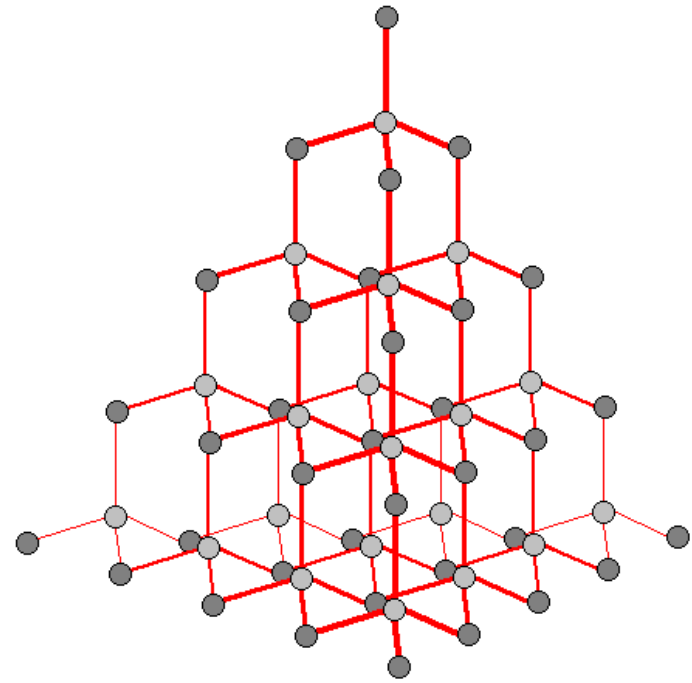
Bonding in Diamond

The structure of diamond is known to be a tetrahedral arrangement of carbon atoms organised in a three-dimensional, crystalline array. This can be measured by e.g. x-ray diffraction, and the internuclear distances are known very precisely.

In our simple bonding model, every carbon atom in diamond is bonded to four carbon neighbours by a simple σ bond. The electrons are not delocalised further.

This model is a typical description of many materials we refer to as *network solids*. They are effectively large molecules with neighbouring atoms connected by a covalent σ bond.

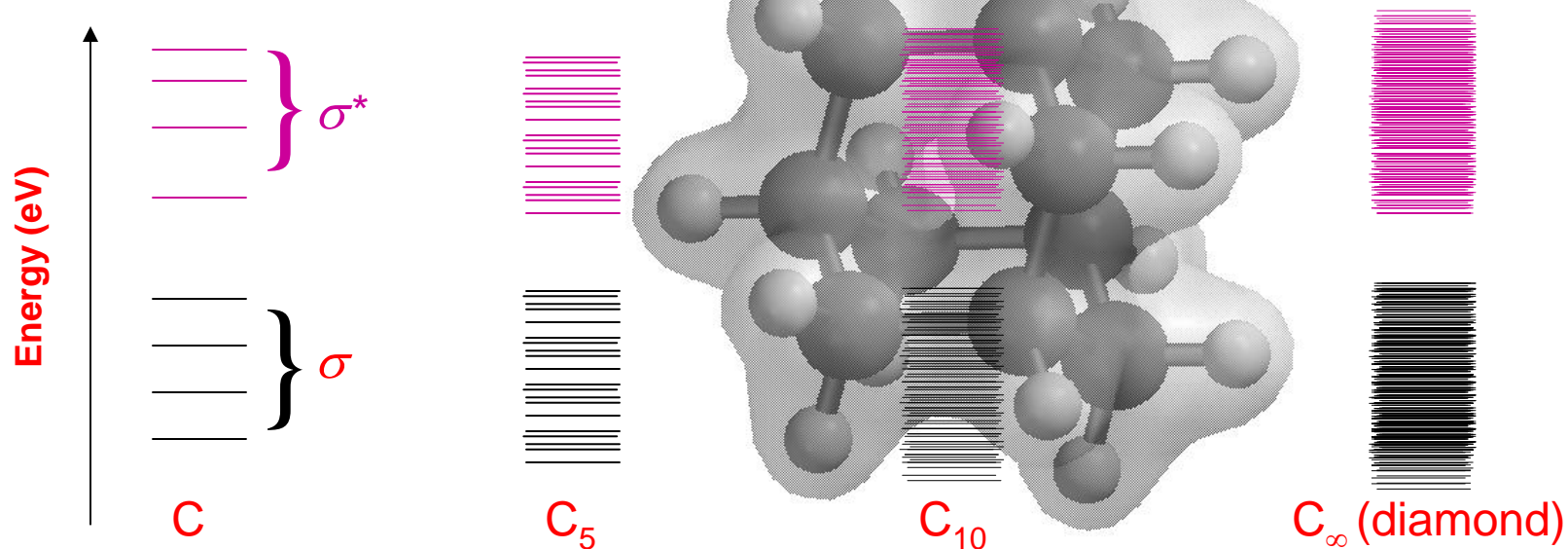
C and Si are two elements that form covalent network crystals. Compounds that form covalent network solids include SiO_2 , SiC, BN, and Si_3N_4 .



Energy Levels in Diamond

Network solids like diamond can be treated as one large molecule, which means that the entire material has a set of quantum states (allowed energies), and that only two electrons can be in each orbital (allowed energy).

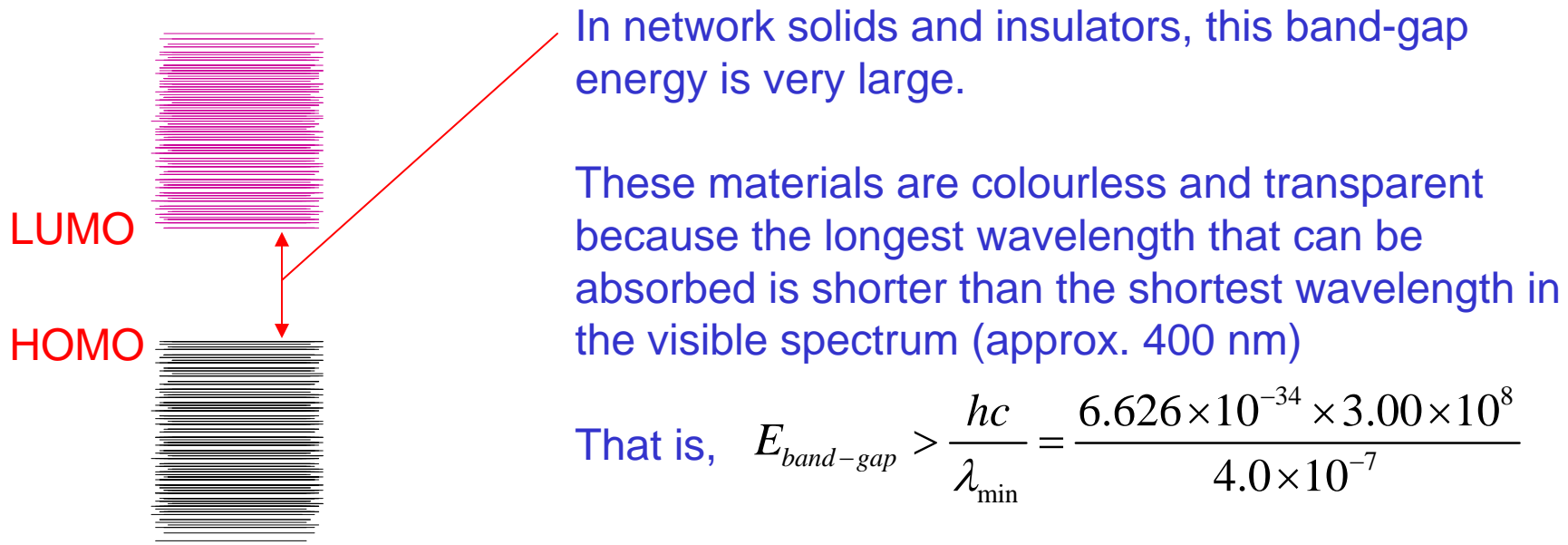
We can see the general effect of increasing molecular size by calculating the allowed energies in a fragments of a 3-dimensional diamond network of increasing size. The allowed states fall into two groups, bonding and antibonding, as we would expect. As the number of atoms in the network structure increases, so does the number of allowed states and the *density of states* (how close together in energy they are). E.g. (schematically)



Colour of Diamond and Network Solids

The ground state electronic configuration of network solids has all the σ energy levels filled, and all of the σ^* energy levels empty.

The lowest energy (HOMO \rightarrow LUMO) electronic transition is given by the *band gap*, the energy difference between the top of the (filled) band of allowed σ energies and the (empty) band of allowed σ^* energies.



In network solids and insulators, this band-gap energy is very large.

These materials are colourless and transparent because the longest wavelength that can be absorbed is shorter than the shortest wavelength in the visible spectrum (approx. 400 nm)

That is,
$$E_{band-gap} > \frac{hc}{\lambda_{min}} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.0 \times 10^{-7}}$$

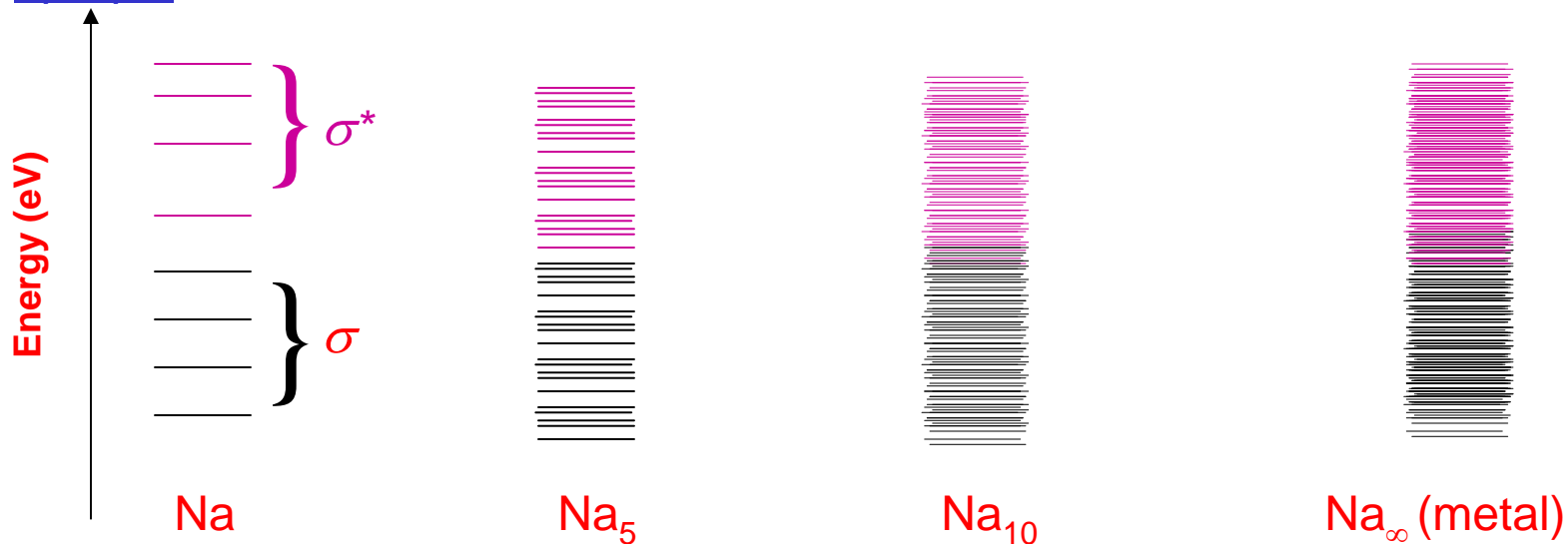
$$E_{band-gap} > 5.0 \times 10^{-19} \text{J or } 3.1 \text{eV.}$$

Bonding in Metals

Metals are also crystals in which the atoms are bonded to one another and can be treated as a single, large molecule. However in metals the bands of allowed energy levels are remarkably different from insulators.

If we take the same approach with, say sodium, as for diamond, we find that increasing the size of the fragment gives two bands of energy levels with no band gap. Energy levels in metals behave as a single, *partially-filled* band.

This means that there are many energy levels close together, and that the longest wavelength transition is much longer than 400nm, so the materials are opaque.



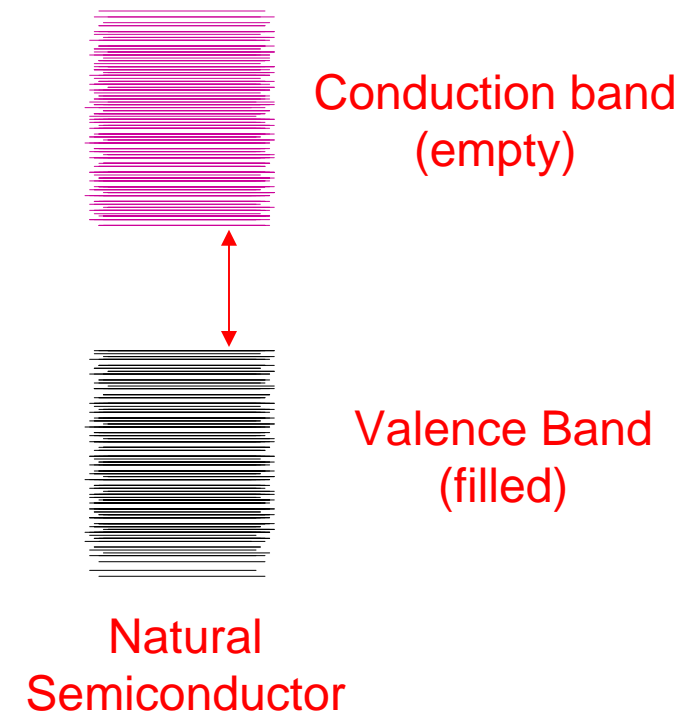
Natural or Intrinsic Semiconductors

Natural Semiconductors are network solids with band gap energies that lie in the visible or UV range. They may thus be transparent (UV absorbing) or coloured (visible absorbing).

Absorption of a photon promotes an electron from the lower, filled band into the unfilled upper band. Once in this band (the conduction band), the electron has enough thermal energy to *move* and hence to conduct electricity.

Promotion of an electron leaves a *vacancy* or *hole* in the lower (valence) band, so electrons there also become mobile, and have enough thermal energy to move between states within that band.

Conduction can be regarded as taking place through both electrons in the conduction band and holes in the valence band.

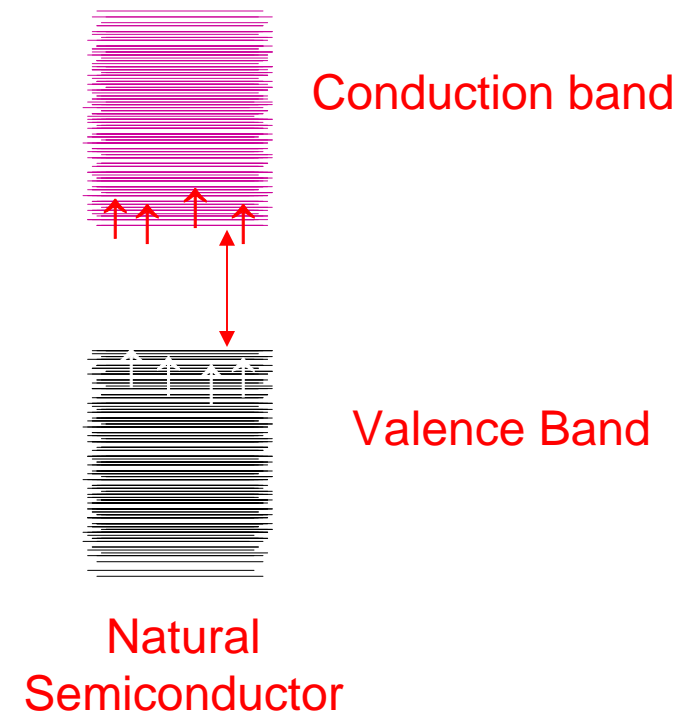


Natural or Intrinsic Semiconductors

Electrons can be promoted into conduction band states by light, or by thermal excitation (heat).

In natural semiconductors with small band gaps, some electrons are thermally excited into the conduction band. The fraction of excited electrons increases with temperature, and so does the conductivity.

Materials that are insulators at low temperatures become increasingly good semiconductors with increasing temperature.



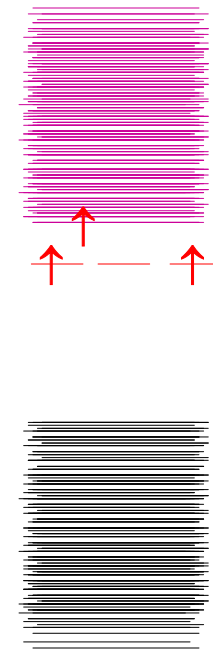
Doped Semiconductors

Semiconductors can be synthesised by introducing foreign atoms into an insulator to modify its electronic structure. There are two types of doped semiconductors.

N-type semiconductors are prepared by introducing atoms with occupied quantum states *just below the bottom of the conduction band*.

Some electrons from these *localised* electronic states are **thermally excited** into the conduction band, where they become mobile and act as (negative) charge carriers.

Typical n-type semiconductors are prepared by substituting group V elements (P, As, Sb) into the crystal lattice of Si or Ge (group IV). Group VI elements can act as double donors into these lattices.



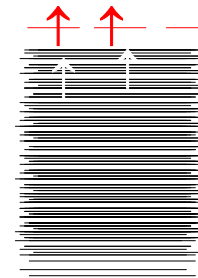
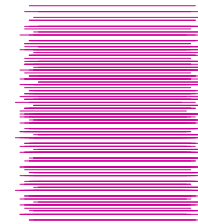
Doped Semiconductors

P-type semiconductors are prepared by introducing atoms with vacant quantum states *just above the top of the valence band*.

Some electrons from the filled valence band are **thermally excited** into these localised orbitals. This leaves vacancies or holes in the valence band that are mobile and act as (positive - “**p-type**”) charge carriers.

Typical p-type semiconductors are prepared by substituting group III (B, Al, Ga) or group II (Be or Zn) elements into the crystal lattice of an insulator.

Substitution into compound semiconductors - e.g. GaAs rather than Si or Ge - are a little more complex. For example, Group IV additives can act as donors or acceptors, depending on which element they substitute.



Solar Energy Conversion

A key application of semiconductors is in solar energy conversion. Excitation of electrons into the conduction band by light is a method for conversion of energy directly into electrical current (a photovoltaic device).

A variety of photovoltaic devices can be prepared consisting of layers of n-, p- and intrinsic semiconductors. The vast majority of these devices are based on Si, which absorbs light throughout the visible range and into the near infrared, making it an effective solar collector.

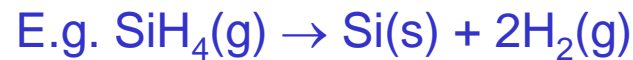
By creating a layer of n- and p-type semiconductors, electrons and holes can be prevented from recombining, leading to charge separation (an electrical potential difference) that can be used to run devices.

By using multiple layers of materials with different electronic states, it is possible to create multilayer solar cells that absorb in a wider wavelength range and collect more of the available solar energy.



Chemical Vapour Deposition

This is one of the key methods for preparing layered photovoltaic devices, especially with high-purity Si. Gases of *precursor compounds* such as silane (SiH_4) are exposed to a solid substrate at high temperature, so that they react when they come into contact with it.

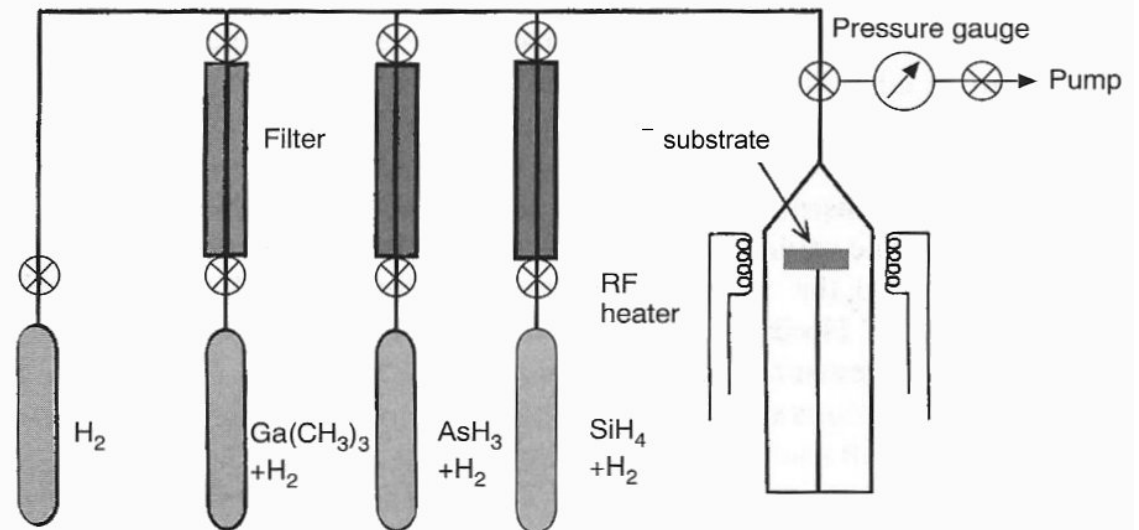


Dopants are included by introducing other precursors into the gas stream such as phosphine (PH_3) arsine (AsH_3) or trimethylgallium $\text{Ga}(\text{CH}_3)_3$.



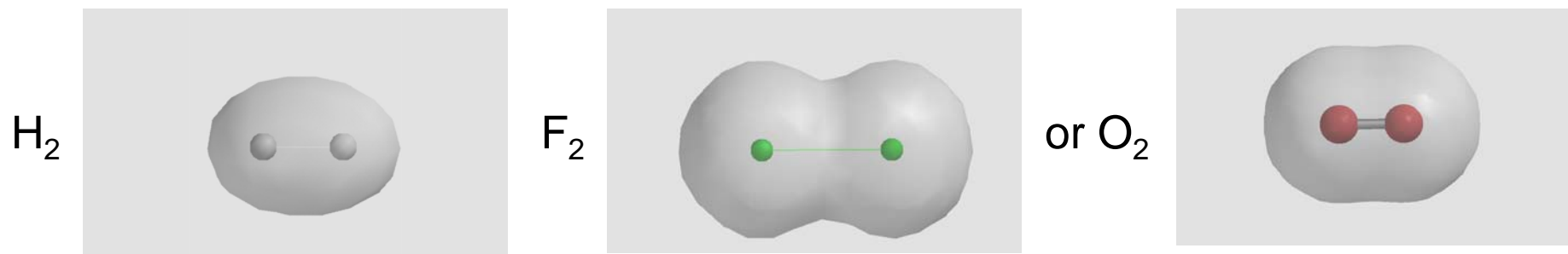
Includes H from SiH_4

Gas composition is changed as the film grows to create different layers.

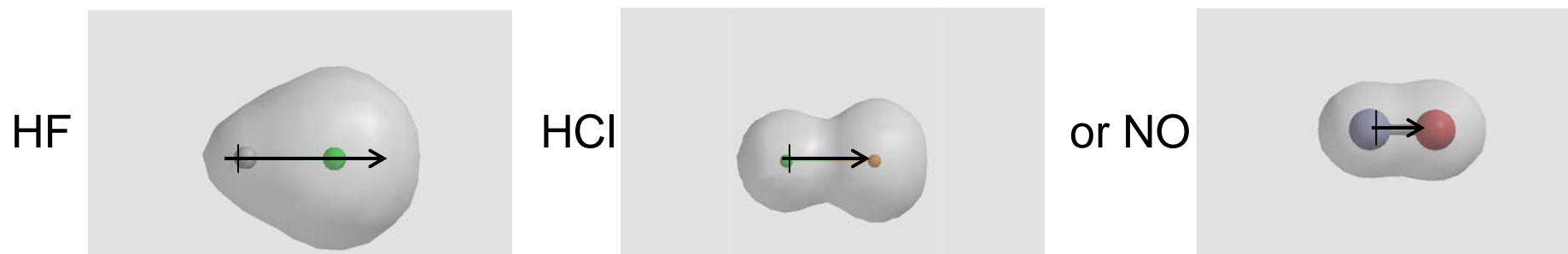


Unequal Delocalisation of Electrons

We have already seen in diatomic molecules that electrons in molecular orbitals can be delocalised *equally* about two identical nuclei like



or *unequally* about two different nuclei like



Unequal delocalisation of electrons is described by a dipole moment, in which a *partial charge* (a fractional electron charge) is assigned to each nucleus. The dipole moment, μ , is the product of the fractional charge and the distance between them (the bond length), represented as a crossed arrow pointing from the positive to the negative charge; Long Arrow = Big Dipole Moment.

Representing Unequal Delocalisation

The molecular orbitals contain all the information about charge distribution in a molecule. The dipole is a way of representing and quantifying how uneven the delocalisation is.

As a simple representation we may draw a single-bond (i.e. bond order =1) in a diatomic molecule as a shared pair of electrons or a line indicating connectivity, just as we did for H₂.

e.g. H:F or H-F

H:Cl or H-Cl

This discards a lot of the information we obtain from quantum theory.

Drawing in a dipole arrow or assigning a value for a dipole moment just adds back in some of that information about the way the electron charge is distributed along the bond or throughout a more complicated molecule.

Chemists use the concept of *Electronegativity* to describe the ability of a particular atom to attract or *withdraw* electrons around itself, and therefore create a polar bond.

Electronegativity

Electronegativity was a concept developed by Linus Pauling to describe the relative polarity of bonds and molecules.

The energy required to break the bond in H_2 is 432 kJ mol^{-1} , and for F_2 it is 159 kJ mol^{-1} . However the energy required to break a bond in HF is 565 kJ mol^{-1} , which is **much higher than expected** just by averaging the two homonuclear molecules (296 kJ mol^{-1}). Pauling argued that the difference could be assigned to an electrostatic attraction between the F and H “ends” of the molecule if the F end has more electron density (nett negative charge) and the H end less (nett positive charge).

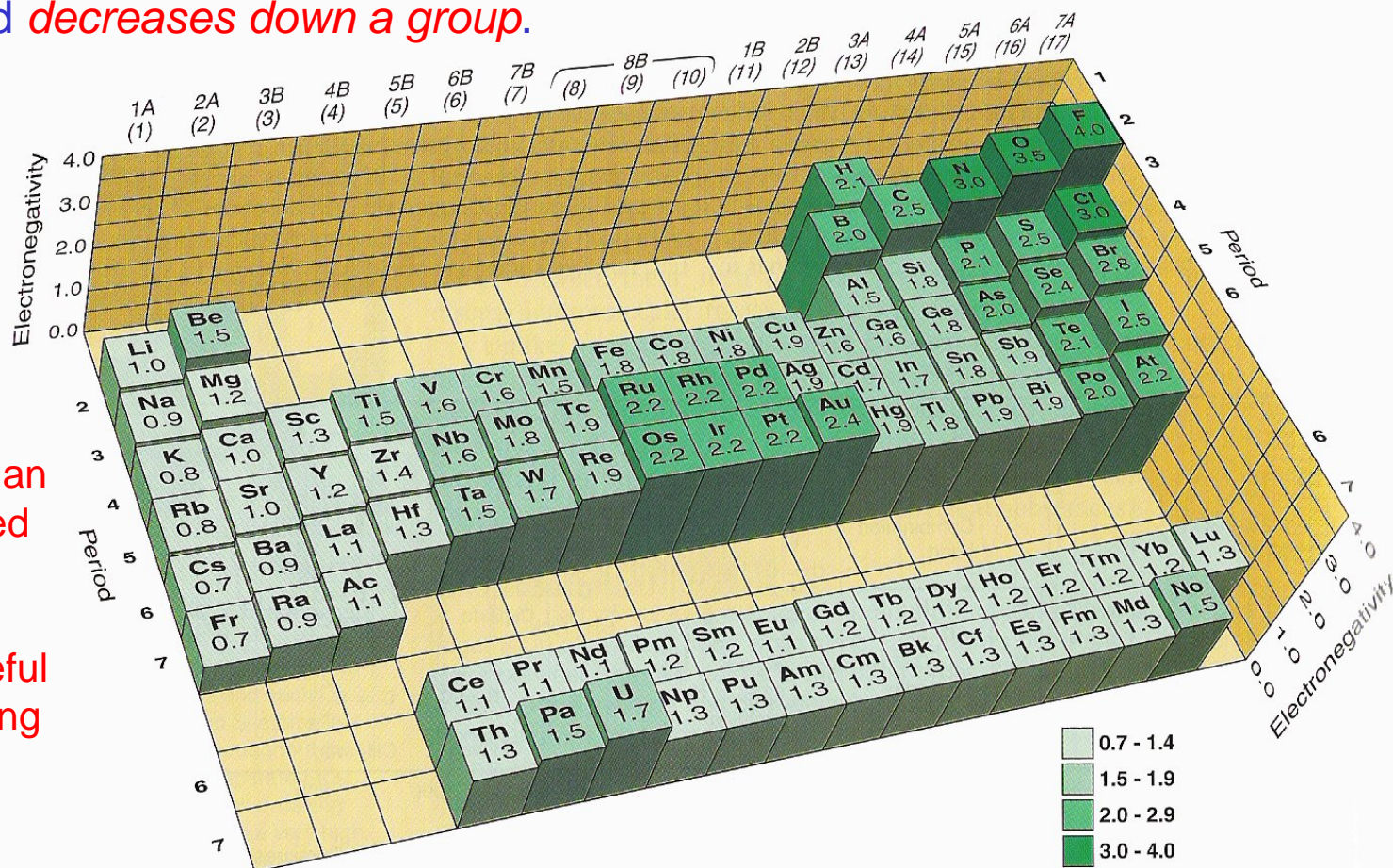
By examining many such systems, Pauling assigned each element an electronegativity on a scale between 0 and 4, which he assigned to fluorine as the most electronegative element. (As with all such things, this didn't happen in one go. He first assigned H to 0 and F to 2, but re-scaled his results later when he started to examine metals.)

The more electronegative atom in a bond will be the negative end of a dipole, and the bigger the electronegativity difference, the bigger the dipole moment.

Trends in Electronegativity

Electronegativity generally increases as atomic size decreases. That is, as the valence electrons are closer to the nucleus and more tightly bound.

In the periodic table, this means that electronegativity *increases left to right across a row*, and *decreases down a group*.



Electronegativity is an arbitrary scale based on a simple (non-quantum) model of bonding. It is a useful concept for predicting some molecular properties.

Ionic “Bonding”

Molecular Orbitals come about when the energy of delocalised valence electrons (bonding MO's) are lower than those localised on individual atoms.

In extreme cases where the allowed energies of electrons in two different atoms are very different, the lowest energy state of the two atoms together is not a bond but the transfer of one or more electrons from one atom to an atomic orbital of another.



We can see from this example that this kind of electron transfer leads to the formation of two ions.

In order for this to be favourable (even more favourable than delocalisation into a MO), the available atomic orbital of the acceptor atom must be much lower in energy than the highest filled atomic orbital of the donor atom. This usually means few outer shell electrons for the donor (**big atom**) and an almost filled outer shell for the acceptor (**small atom with tightly bound electrons**)

Ionic Bonding and the Periodic Table

Good electron donors - big atoms - are on the left of the periodic table; s^1 , s^2 and d (transition) elements.

Good electron acceptors - small atoms - are on the right of the periodic table; p^5 (p^4).

																				8A (18)	
	1 (1)																			2 He 4.003	
1	H 1.008	2A (2)																			
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18			
3	11 Na 22.99	12 Mg 24.31	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8) (9) (10)			1B (11)	2B (12)	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95			
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80			
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3			
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)			
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Ha (262)	106 Sg (266)	107 Ns (262)	108 Hs (265)	109 Mt (266)	110	111										
6	Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0						
7	Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (244)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)						

Ionic Character and Electronegativity

Electronegativity again proves to be a useful concept in dealing with ionic bonds. From the periodic table we can see that the **least electronegative** atoms are good electron donors (cation formers), and the **most electronegative** atoms are good electron acceptors (anion formers).

We can use the electronegativity difference between two atoms (ΔEN) to empirically define the *partial ionic character* of a bond as a fraction of the maximum possible difference, 4.0.

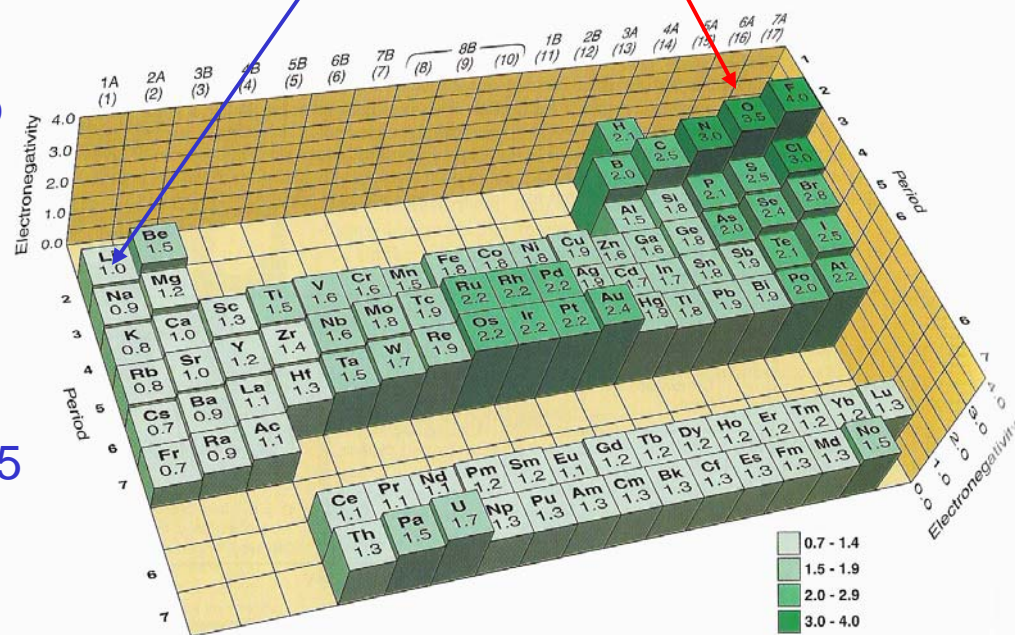
E.g. for HF, $\Delta EN = 4.0 - 2.1 = 1.9$
Partial Ionic Character = $1.9/4.0 = 0.495$

HCl: $(3.0 - 2.1)/4.0 = 0.23$

NO: $(3.5 - 3.0)/4.0 = 0.13$

LiF: $(4.0 - 1.0)/4.0 = 0.75$

MgCl₂: $(3.0 - 1.2)/4.0 = 0.45$



Electronegativity differences >2 generally give ionic bonds, whereas $\Delta EN < 1$ are covalent (delocalised MO's). This gives a good guide to the *character* of a bond.

Ionic Crystals

The ionic “bond” is unlike bonds formed by MO’s. The electrons are only delocalised in atomic orbitals on ions, **and not between 2 or more nuclei.**

What we call an ionic bond is simply the long-range electrostatic attraction between cation(+) and anion(-), together with the short-range repulsion between electrons in adjacent ions. The equilibrium distance between cation and anion nearest-neighbours occurs when the potential energy is a minimum. That is, when the attractive and repulsive forces are exactly equal and opposite.

Because the electrons do not change their allowed energies as the ions approach one another, their kinetic energy and delocalisation does not affect stability.

MO’s have a shape that we describe by lobes and nodes that gives a covalent bond a direction, however electrostatic interactions are *isotropic* - the same in all directions.

Ionic bonding does not readily lead to the formation of small molecules, but instead favours macroscopic crystals or, under certain circumstances, clusters.

Lattice Energy

An ionic crystal is an organised lattice of cations and anions. Many different crystals can form depending on the ionic radius, which can be quite different from the atomic radius due to the different number of electrons.

All ionic crystals share one characteristic. Oppositely-charged ions are nearest neighbours - It is the attraction between oppositely charged ions that makes the crystal stable.

The **Lattice Energy** is the energy change when **gas phase ions** combine to form a crystal lattice. E.g. For

$\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF}(\text{s})$, the lattice energy is $-1050 \text{ kJ mol}^{-1}$.

The negative value denotes that the energy of the crystal lattice is *lower than* that of the ions. This is the same idea as the negative potential energy that binds a negative electron to a positive nucleus.

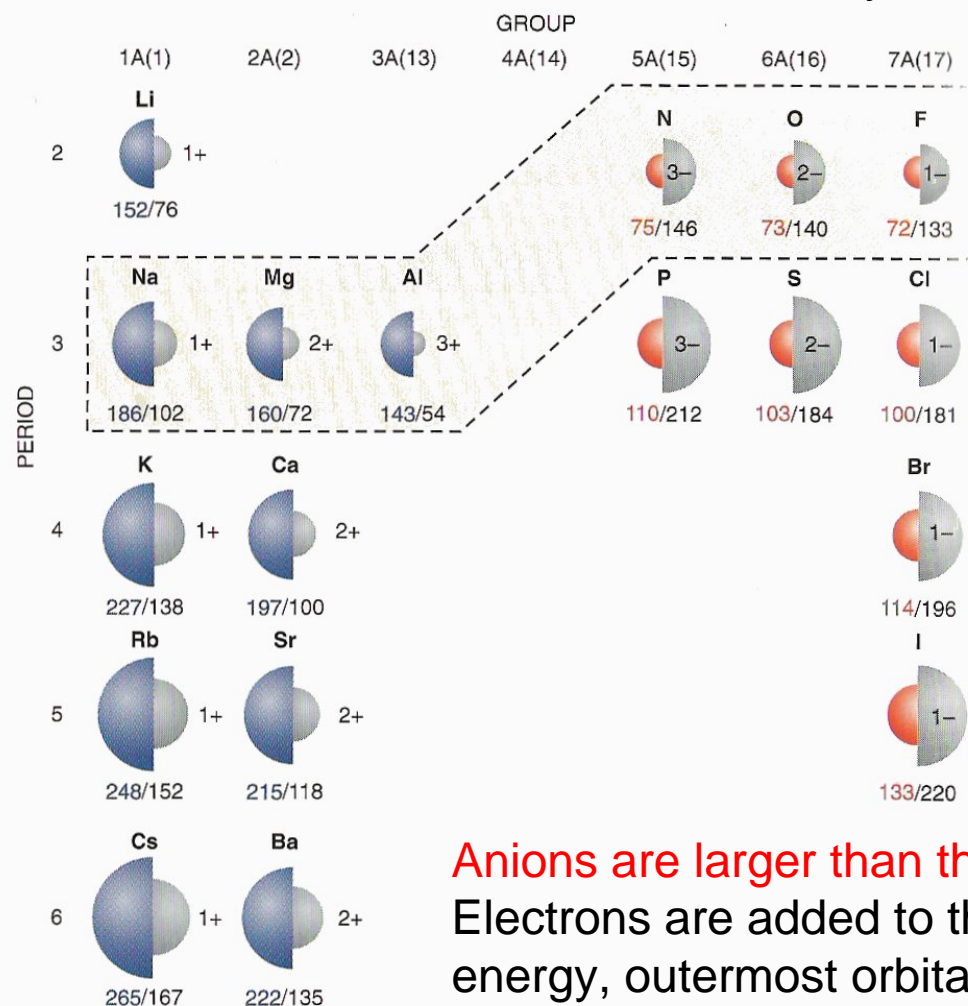
This denotes the energy change accompanying the formation of 1 mole of LiF.

Ionic Radii

The ionic radius is an estimate of the size of an ion in a crystal lattice.

Cations are smaller than their parent atoms.

Electrons are removed from the highest energy, outermost orbitals. The remaining orbitals also contract due to reduced electron-electron repulsions.



Anions are larger than their parent atoms.

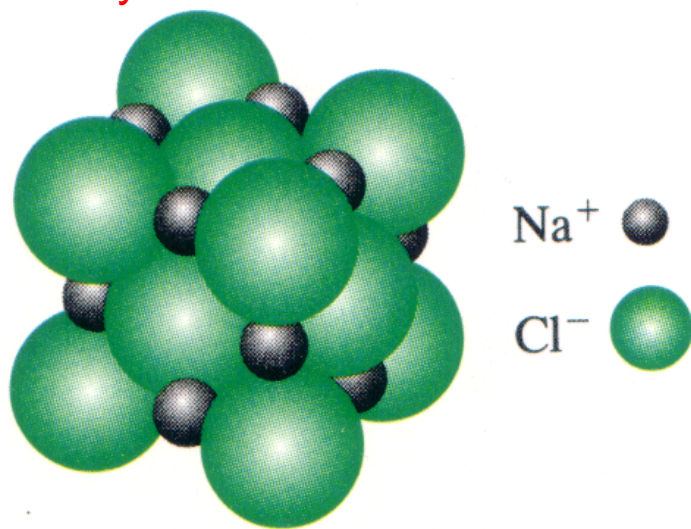
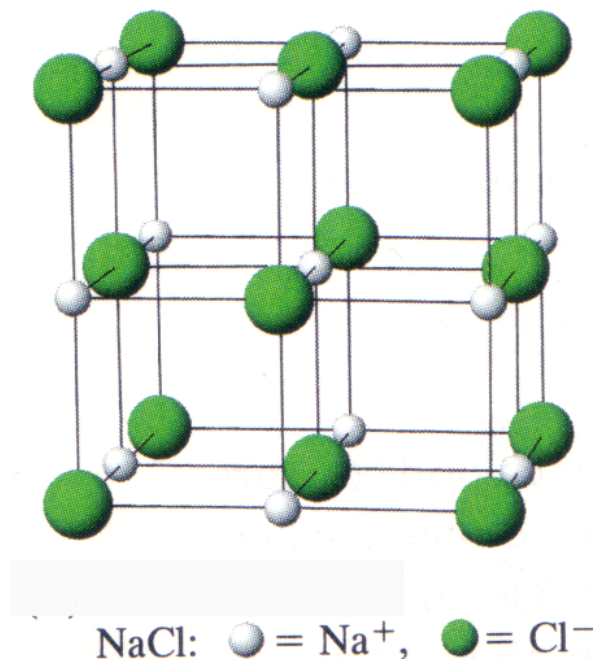
Electrons are added to the highest energy, outermost orbitals, which expand due to electron-electron repulsions.

Structures of Ionic Solids: The NaCl Structure

Sodium chloride may be represented as a *simple cubic* lattice, in which sodium and chloride ions alternate with each other.

Every sodium ion is surrounded by 6 chloride ions, and every chloride ion is surrounded by 6 sodium ions in an octahedral arrangement.

This representation masks the fact that Na^+ and Cl^- have very different ionic radii: 1.81 and 1.02 Å, respectively.



The larger Cl^- ions are actually **close packed** in a **face-centred cubic (fcc) lattice**, with smaller Na^+ cations in the **interstices** (spaces) between them.

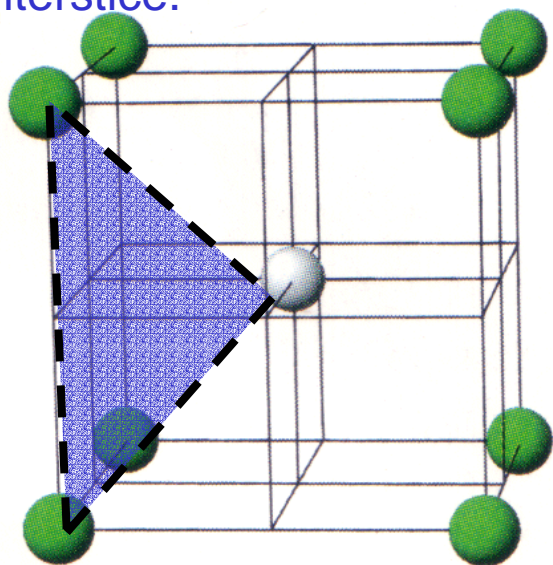
Close packing of anions is very common in ionic crystals. The arrangement of the cations depends on their size.

Structures of Ionic Solids: NaCl & CsCl

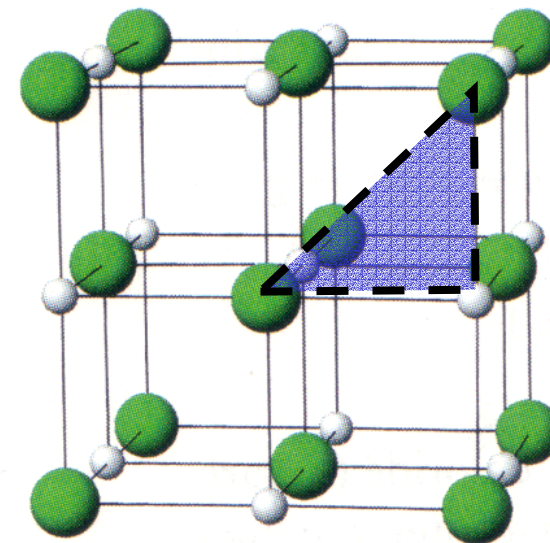
The chloride ion fcc lattice is an example of closest packing, where the anions are at their highest density. Only small cations like Na^+ can fit into the available interstices. The maximum cation radius can be estimated from simple geometrical considerations.

$$(2r_{\text{Cl}^-})^2 = 2(r_{\text{Cl}^-} + r_{\text{Na}^+})^2 \quad \Rightarrow \quad r_{\text{Na}^+} \leq 0.414r_{\text{Cl}^-}$$

Na^+ is a bit bigger than this. It *just* squeezes into the interstice.



CsCl: ● = Cs^+ , ● = Cl^-



NaCl: ● = Na^+ , ● = Cl^-

Larger cations such as Cs^+ (1.61\AA) cannot fit into these octahedral interstices, and so cannot form an fcc lattice. The ions pack in a different way, giving in this case a body-centred cubic lattice. The maximum cation radius for this lattice is

$$r_{\text{Cs}^+} \leq 0.732r_{\text{Cl}^-}$$

Once again, Cs^+ is a bit too big according to this model, but “squeezes” in the interstice.

Summary

You should now be able to

- Explain the reason for bond formation being due to energy lowering of delocalised electrons in molecular orbitals.
- Describe a molecular orbital.
- Recognise (some) sigma bonding, sigma star antibonding and non-bonding orbitals.
- Be able to assign the (ground) electron configuration of a diatomic molecule.
- Define HOMO and LUMO, and homonuclear and heteronuclear diatomic molecules.

Summary I

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- Explain the reason for bond formation being due to energy lowering of delocalised electrons in molecular orbitals
- Describe a molecular orbital
- Recognise (some) sigma bonding, sigma star antibonding and non-bonding orbitals
- Be able to assign the (ground) electron configuration of a diatomic molecule
- Define HOMO and LUMO, and homonuclear and heteronuclear diatomic molecules
- Distinguish between polar and non-polar bonds in diatomic molecules and relate it to electron attraction of a nucleus.
- Draw out ground state electronic configurations for molecules and molecular ions given their allowed energy levels.
- Calculate bond order from molecular electronic configurations.

Summary II

You should now be able to

- Explain how band structure in insulators, semiconductors and metals arise from delocalised orbitals.
- Describe the characteristics of natural and doped semiconductors, including band-gap energy.
- Describe chemical vapour deposition, and how it can be used to build up layers of different composition.
- Represent a dipole in a bond, and use electronegativity to identify the positive and negative ends.
- Describe and explain the periodic trends in electronegativity.
- Explain the origin of ionic bonding as a limiting case of MO theory.
- Explain why ionic interactions lead to crystals rather than small molecules.
- Explain how ionic radii influence crystal structure, and why they differ from atomic radii.