

Electronic Structure of Surfaces

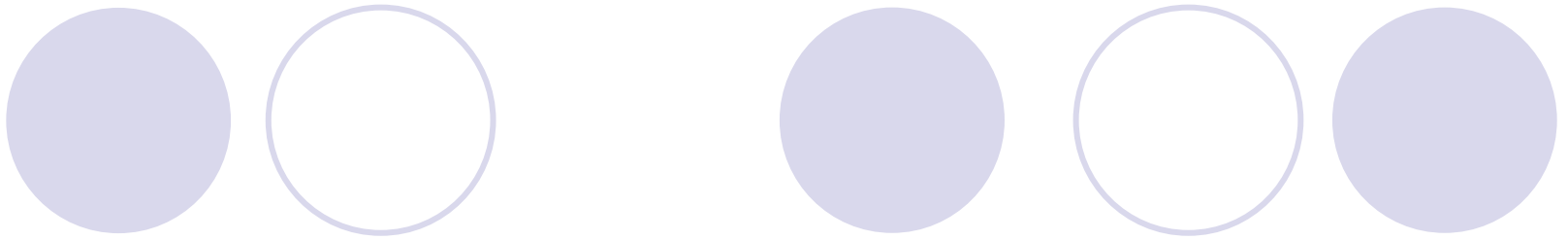
When solids made of an infinite number of atoms are formed, it is a common misconception to consider each atom individually. Rather, we must consider the structure of the solid as a whole. This provides the basis for the description of metals and other types of solids to account for their unique chemical and physical properties.

To fully understand the properties, it is essential to start with molecular orbital theory. In the basic theory, it was assumed that if atoms were brought together, they would form bonding, non-bonding and antibonding orbitals of different energies. These molecular orbitals are described by wave functions. The most important point to come out of the theory is that for N atomic orbitals in a molecule, N molecular orbitals must be the outcome.



The electronic structure of solids is usually described by a theory called Band Theory, a derivative of Molecular Orbital Theory. However, the best way to describe band theory is to go back and go through the process of forming molecular orbitals from the atomic orbitals for a simple diatomic like hydrogen.

To begin with, if one puts atomic orbitals into the wavefunction, and the Schrodinger equation holds true, then it is possible to make an orbital approximation where it is assumed to a reasonable first approximation that the wavefunction of the N electrons in the molecule can be written as the product of N one-electron wavefunctions.

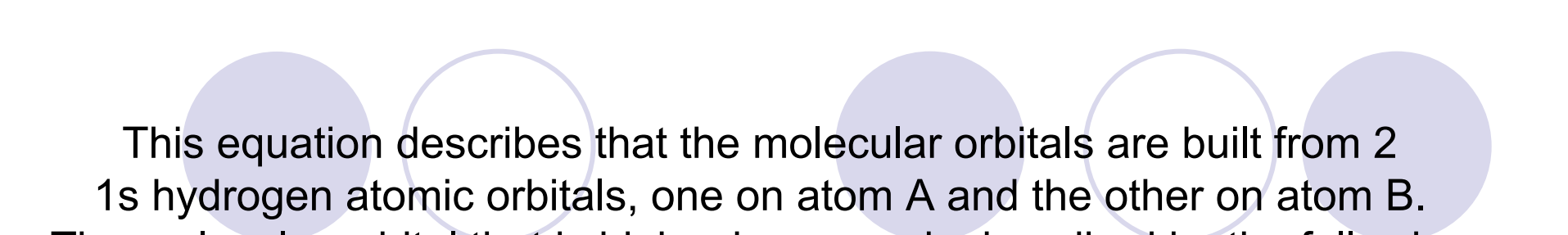


When an electron is close to the nucleus of one atom, its wavefunction closely resembles an atomic orbital of that atom. Therefore a reasonable first approximation of the molecular orbital can be achieved by adding together atomic orbitals contributed by each atom. **This is the Linear Combination of Atomic Orbitals.**

When constructing the molecular orbitals it is common practice to use the valence orbitals to form the molecular orbitals.

Therefore, for hydrogen, by adding together two 1s orbitals, one forms a **basis set** for the atomic orbitals that is described by the wavefunction:

$$\psi^+ = \phi_{1s}(A) + \phi_{1s}(B)$$



This equation describes that the molecular orbitals are built from 2 1s hydrogen atomic orbitals, one on atom A and the other on atom B. The molecular orbital that is higher in energy is described by the following equation:

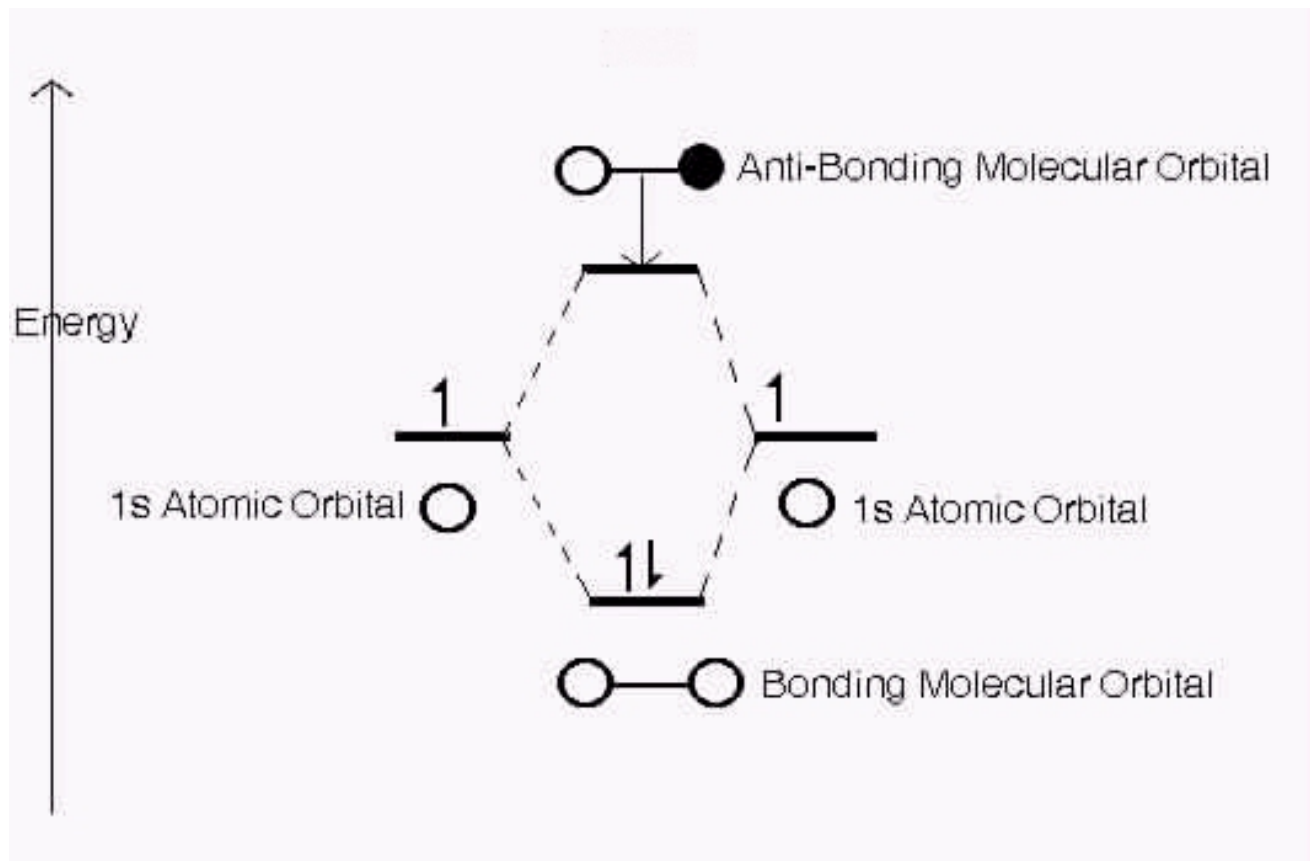
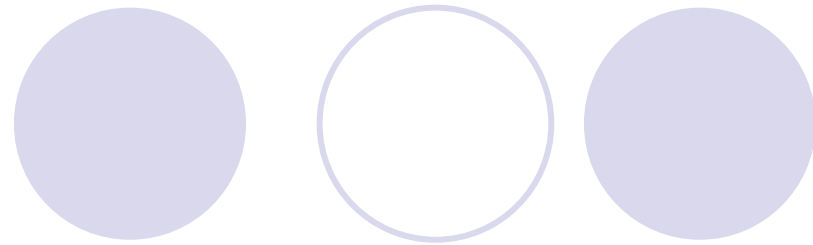
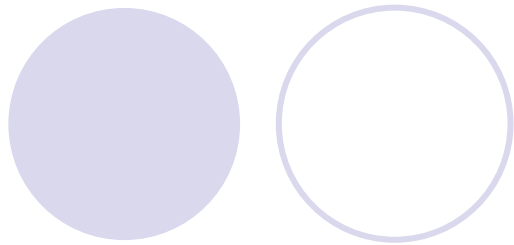
$$\psi_{-} = \phi_{1s}(A) - \phi_{1s}(B)$$

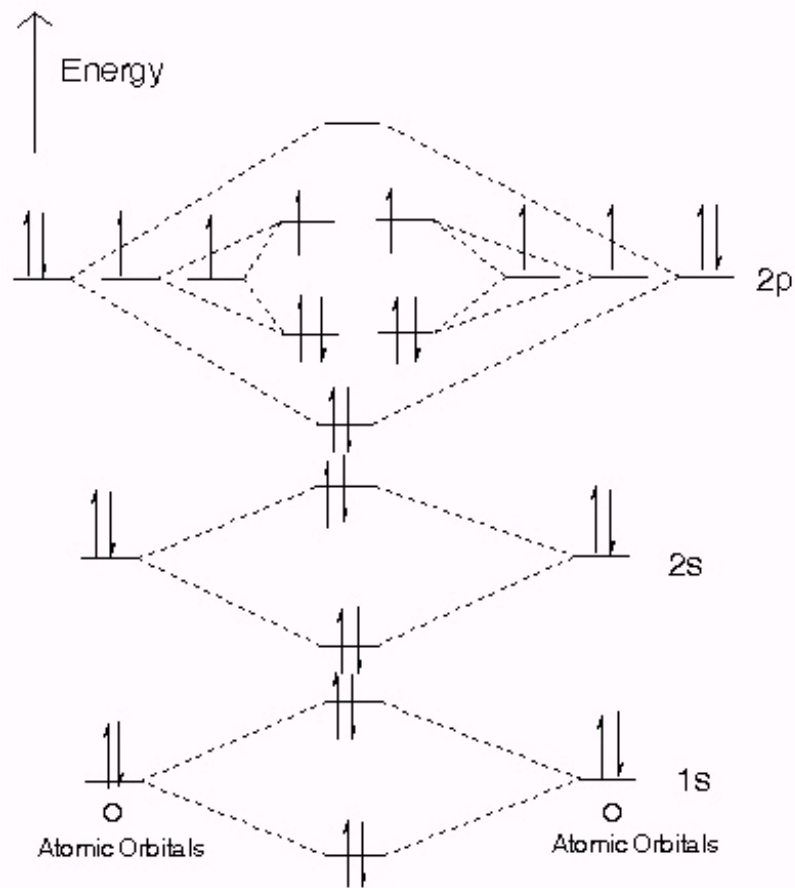
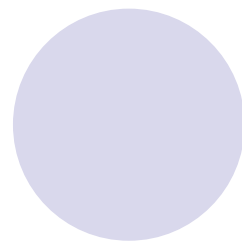
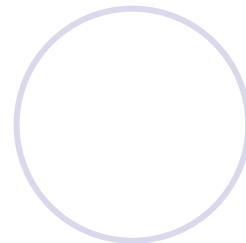
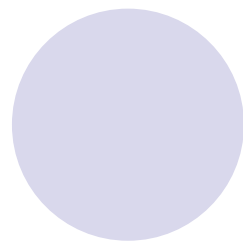
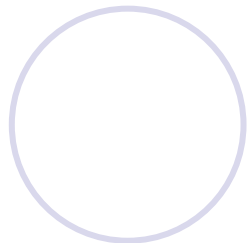
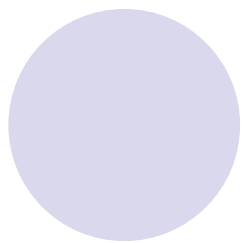
These wavefunctions are obtained by solving the Schrodinger equation for the solution that models both the highest and lowest molecular orbital.

This leads to equal contributions of each 1s orbital into each molecular orbitals.

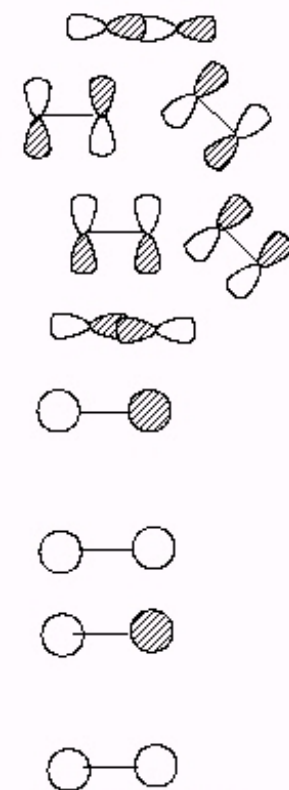
The signs of the coefficients determine if the atomic orbitals interfere constructively (positive coefficients) or destructively (negative coefficients).

This leads to an accumulation or reduction of electron density.

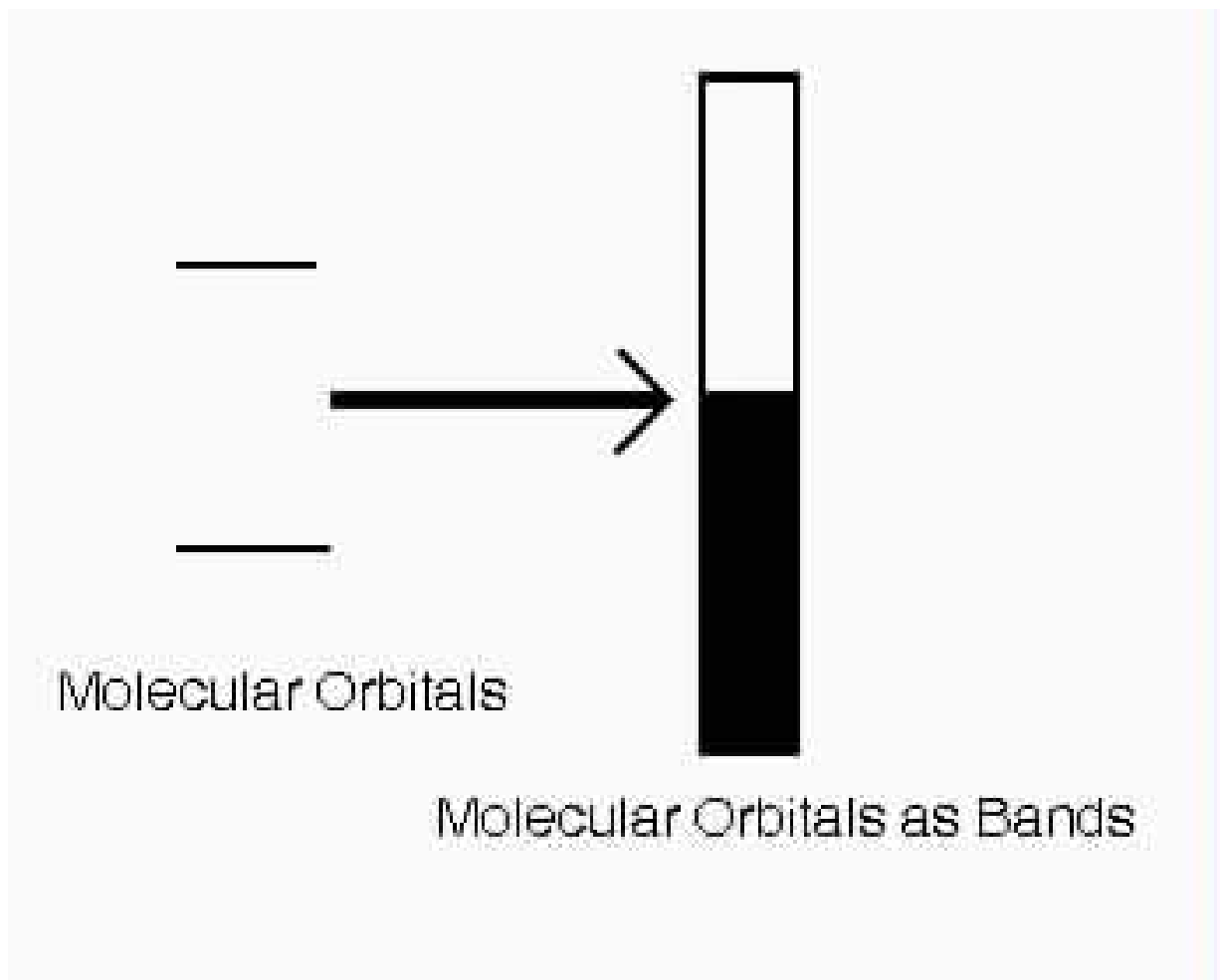
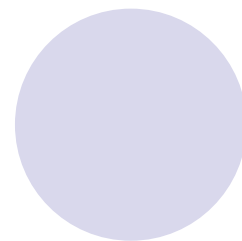
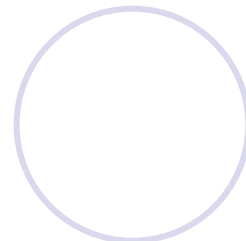
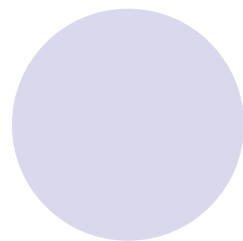
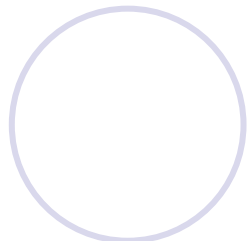
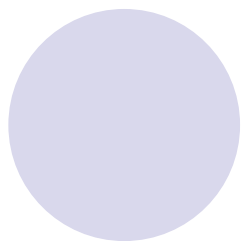




Molecular Orbitals Formed



Diagrams of the Molecular Orbitals Formed

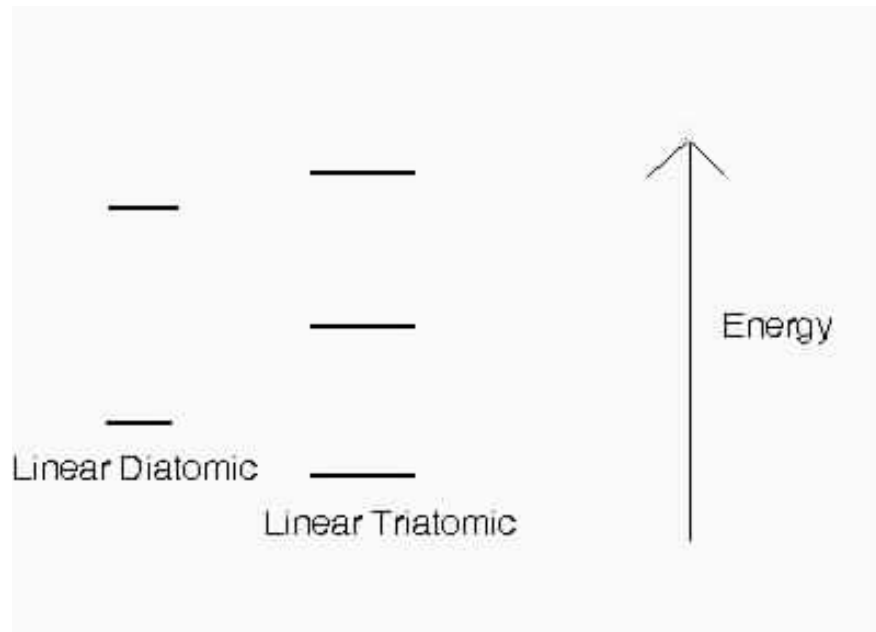


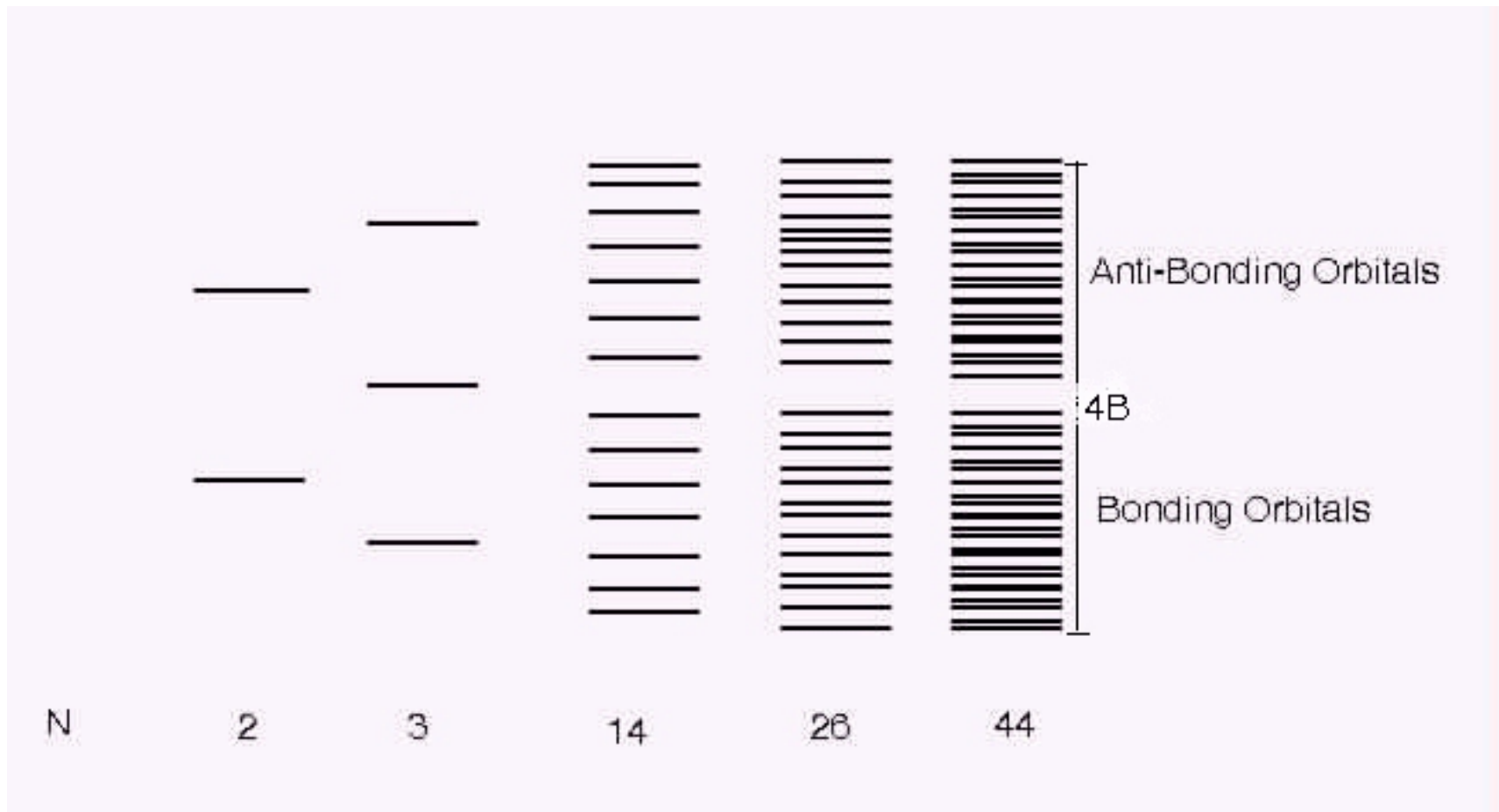
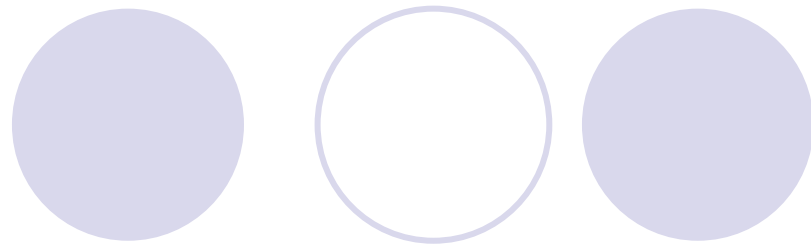
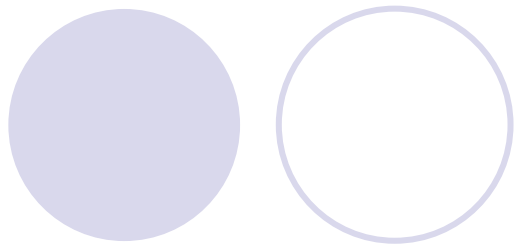


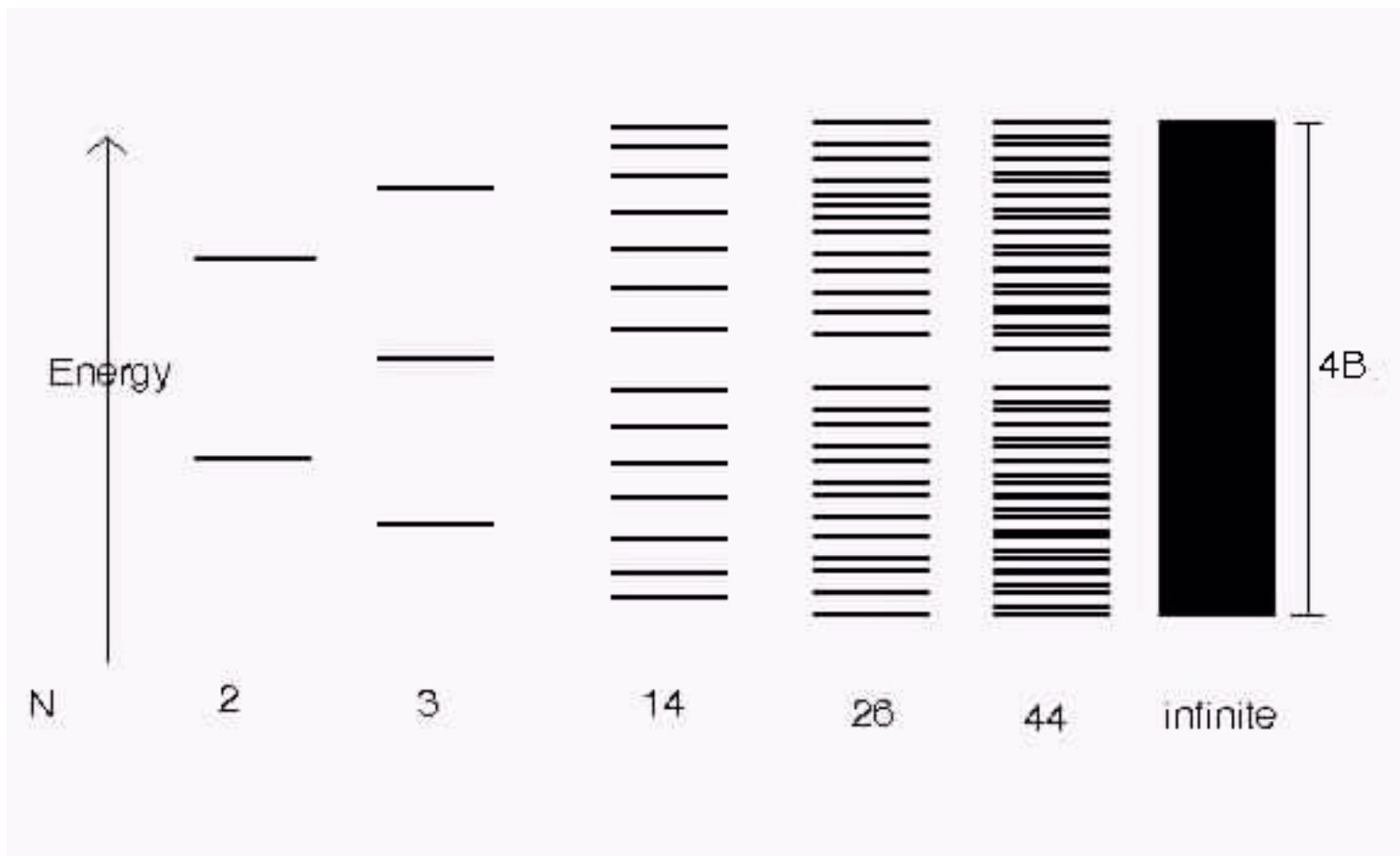
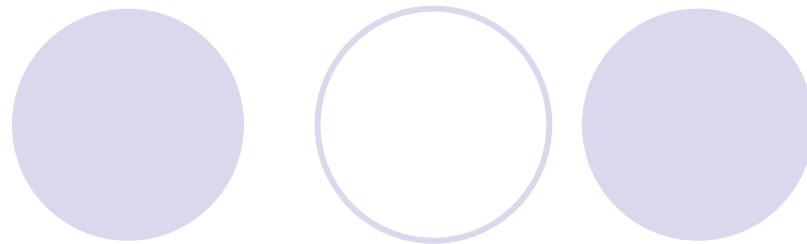
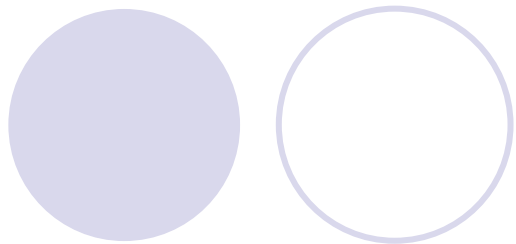
As observed for hydrogen, the number of molecular orbitals for which solutions were obtained from the Schrodinger equation are equal to the number of atomic orbitals put into the equation.

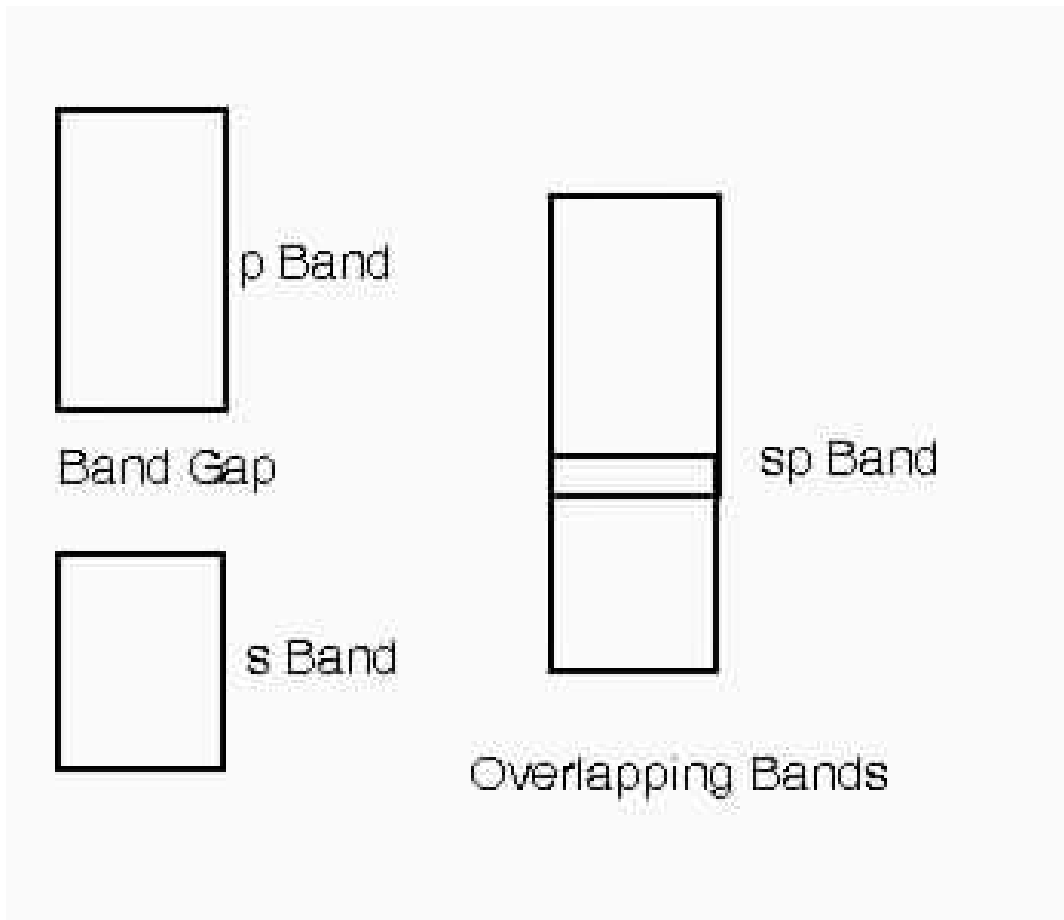
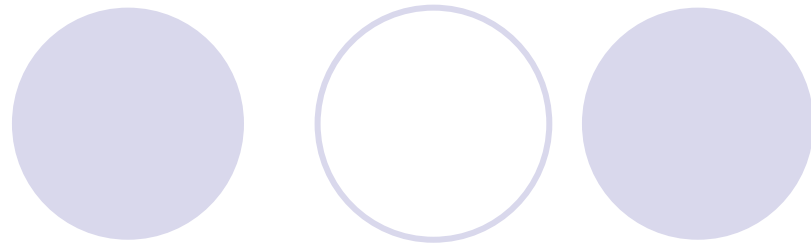
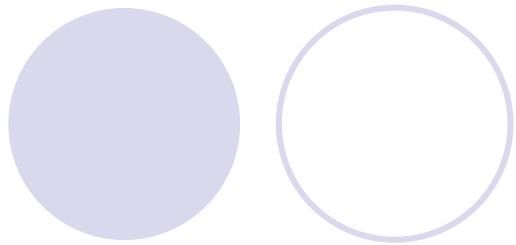
Now lets look at a triatomic linear molecule in which three atomic orbitals lead to three molecular orbitals.

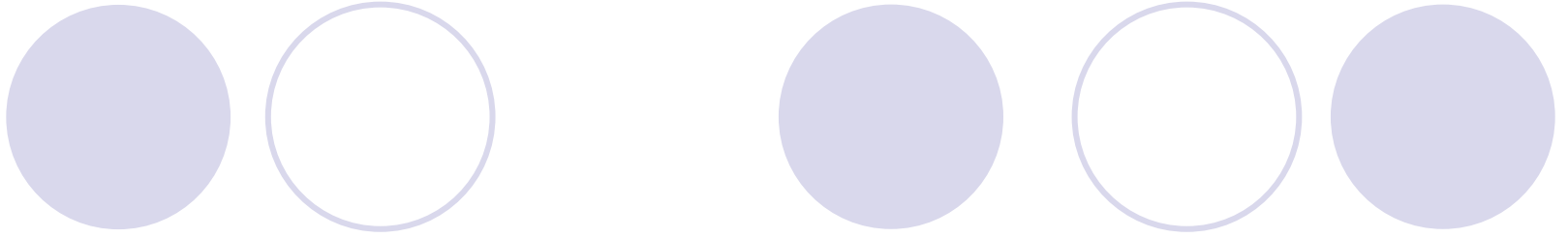
The first observation is that there is now an orbital between the antibonding and the bonding orbitals.











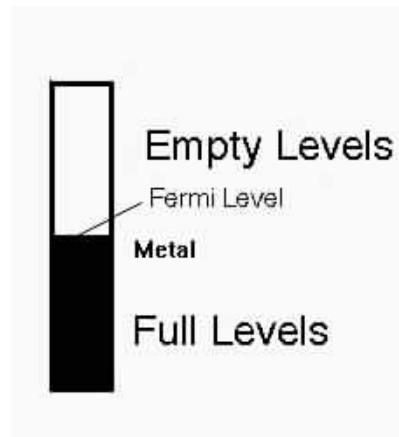
Metals

Metals are the elements found within the d-group on the periodic table.

The criterion for defining a metal lies

in its ability to conduct and its dependence on temperature.

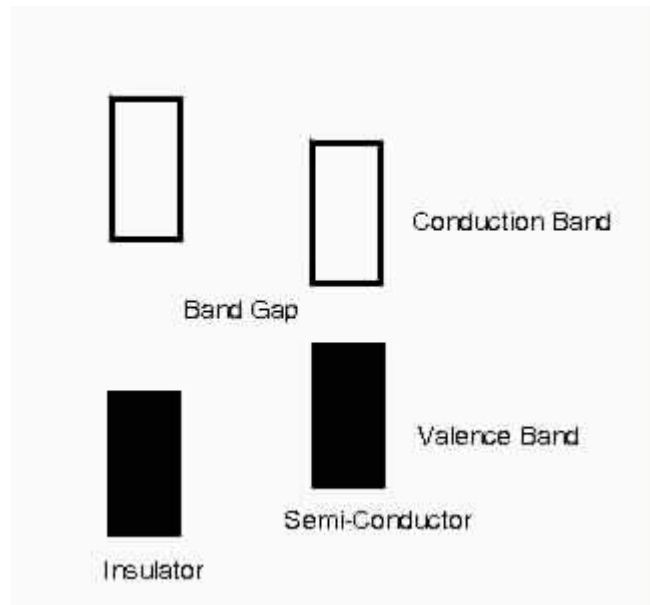
If a material is a metallic conductor, the electric conductivity decreases as the temperature increases. Usually the valence band is not completely filled. Other properties of metals are that they have a lustre and are very malleable. A diagram of the band structure can be seen below. An example of this is copper





Semi -conductors

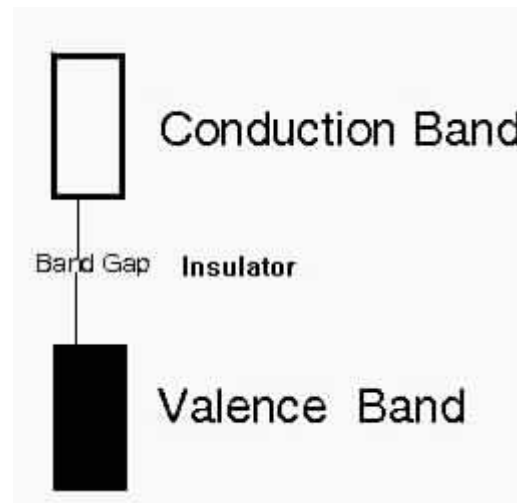
Semi-conductors are materials with an electrical conductivity that increases with increasing temperature, a trend that is opposite to that of metals. Semi-conductors characteristically have a band gap between the valence and conduction bands that is smaller than that found in the insulators. The reason the conductivity increases is because as the temperature increases more electrons become thermally excited and are able to jump the band gap between the valence and conduction band. An example of this is silicon.





Insulators

An insulator is a substance with very low electrical conductivity, but when measured, the conductivity is found to increase with an increase in temperature. In general, the bands of molecular orbitals are such that there is a huge band gap between both the valence band and the conduction band. An example of this is diamond.



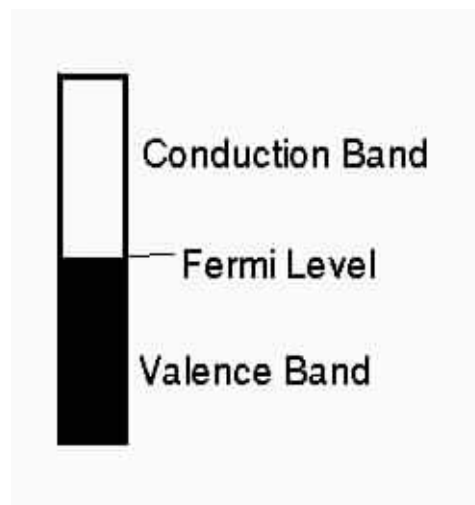


The Valence Band

The valence band is the band made up of the occupied molecular orbitals and is lower in energy than the so-called conduction band.

It is generally completely full in semi-conductors. When heated, electrons from this band jump out of the band across the band gap and into the conduction band, making the material conductive.

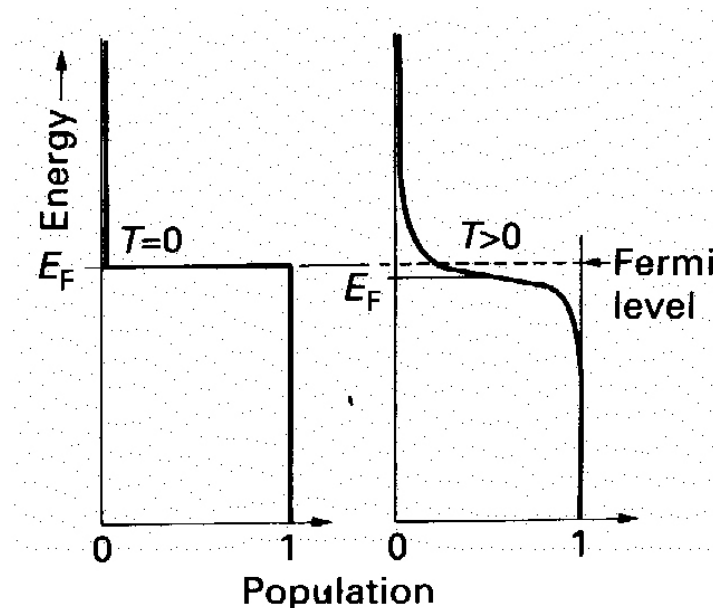
The valence band can be seen in the diagram below.



The Fermi Level

The Fermi Level is defined as the highest occupied molecular orbital in the valence band at 0 K, so that there are many states available to accept electrons, if the case were a metal.

It should be noted that this is not the case in insulators and semiconductors since the valence and conduction bands are separated. Therefore the Fermi-Level is located in the band gap





Electrons in Solids

In *free electron theory* the conduction electrons in a metal are assumed to be completely free except for the presence of a potential step at the surface.

The ion cores are replaced by a uniform positive background charge which has a density equal to the average ion core distribution.

This treatment ensures that charge neutrality is maintained.



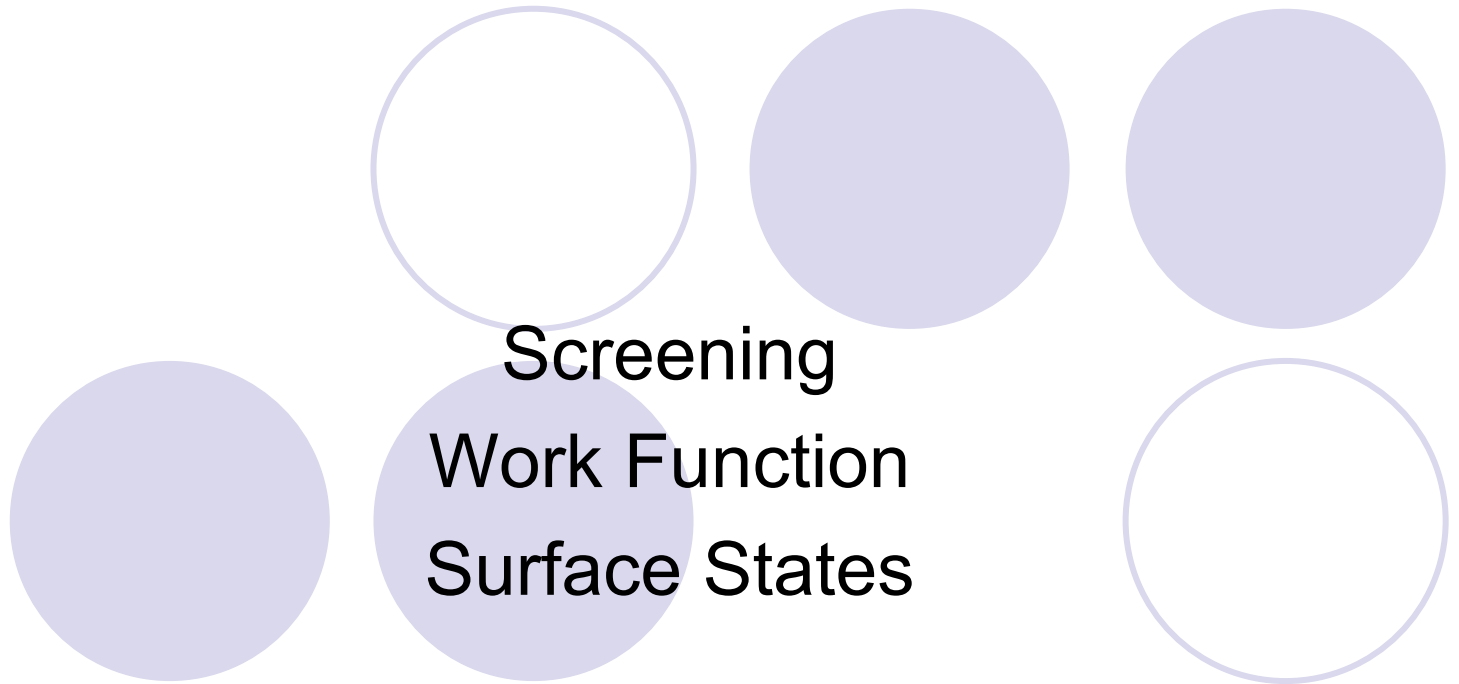
In the *nearly free electron model* the effects of the crystal lattice are accounted for by a weak periodic potential. That is, the electron behaves *essentially* as a free particle. The key result of the nearly free electron treatment is the development of energy gaps in the electron's dispersion (energy versus wavevector) curve.



The *tight binding model* represents the other extreme of electron-lattice interaction. In this approximation it is assumed that the atomic potentials are so strong that the electronic bands arise from the overlap of atomic wave functions.

This treatment is thus identical to the *linear combination of atomic orbitals* theory.

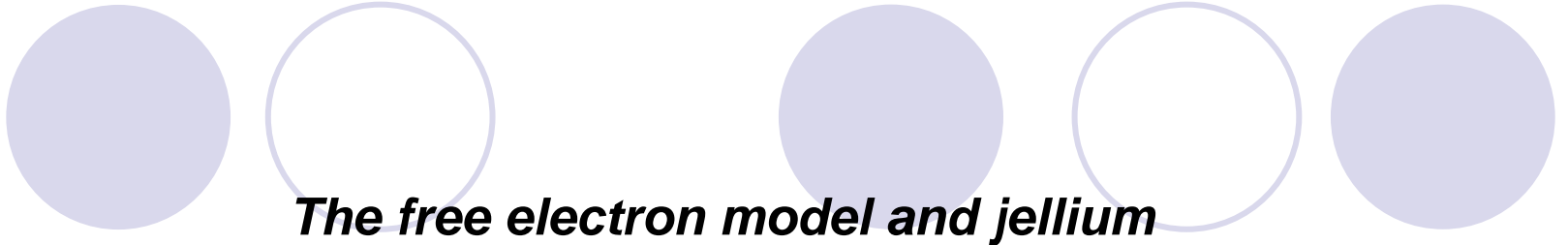
Electronic Structure of Solid Surfaces



Screening: if we take a positive charge and "bury" it in an electron gas, the electrons in the locality of the charge will rearrange to compensate – to *screen out* – the positive charge. The Coulomb potential associated with the isolated charge will thus differ from that for a charge in vacuum. The effectiveness of the medium in screening out the charge is related to the dielectric constant of the medium. We can write the Coulomb potential due to the charge as:

$$V(r) = \frac{-e^2}{4\pi\epsilon\epsilon_0 r}$$

where the magnitude of the isolated positive and electronic charges are the same and ϵ is the dielectric constant (or relative permittivity) of the medium. (The dielectric constant of most semiconductors is of the order of 10). The higher the electron density of the material the shorter the distance over which the electrons need to rearrange to screen the positive charge.



The free electron model and jellium

The free electron model replaces the ion cores with a fixed positive background charge.

The combination of this fixed background charge and the free electron gas produces a fictitious material that is normally termed *jellium*.

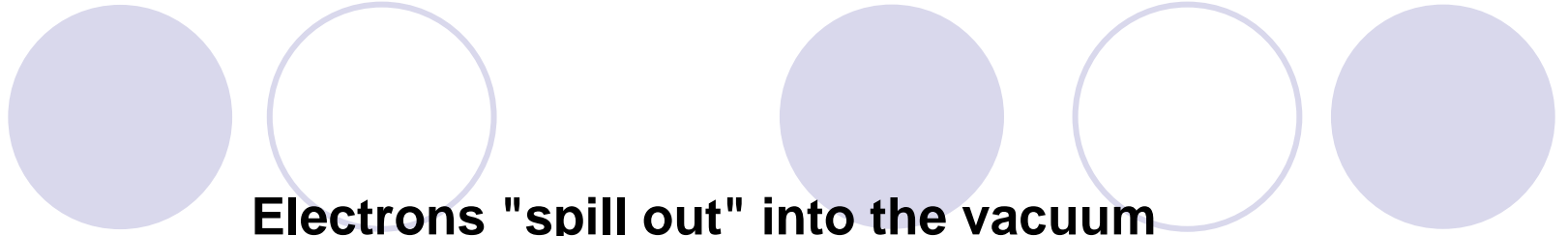
To deal with the surface the infinite jellium solid is replaced by a semi-infinite solid and the background charge density, n_+ , given simply by:

$$\begin{aligned}n_+(\mathbf{r}) &= n, z \leq 0 \\ &= 0, z > 0\end{aligned}$$

where z is the direction normal to the surface.

In the plane of the surface the electron density is uniform.

However, the electron density perpendicular to the surface behaves rather differently.



Electrons "spill out" into the vacuum and thus create an electrostatic dipole at the surface. The electron density oscillates strongly in the near surface region.

This is as a direct consequence of the presence of the sharp step in the background charge density.

The charge density oscillations (called *Friedel oscillations*) arise from the screening behaviour of the electrons.

That is, the electrons' spatial distribution is modified to account for (to screen out) the effects of the change in background charge density at the surface.



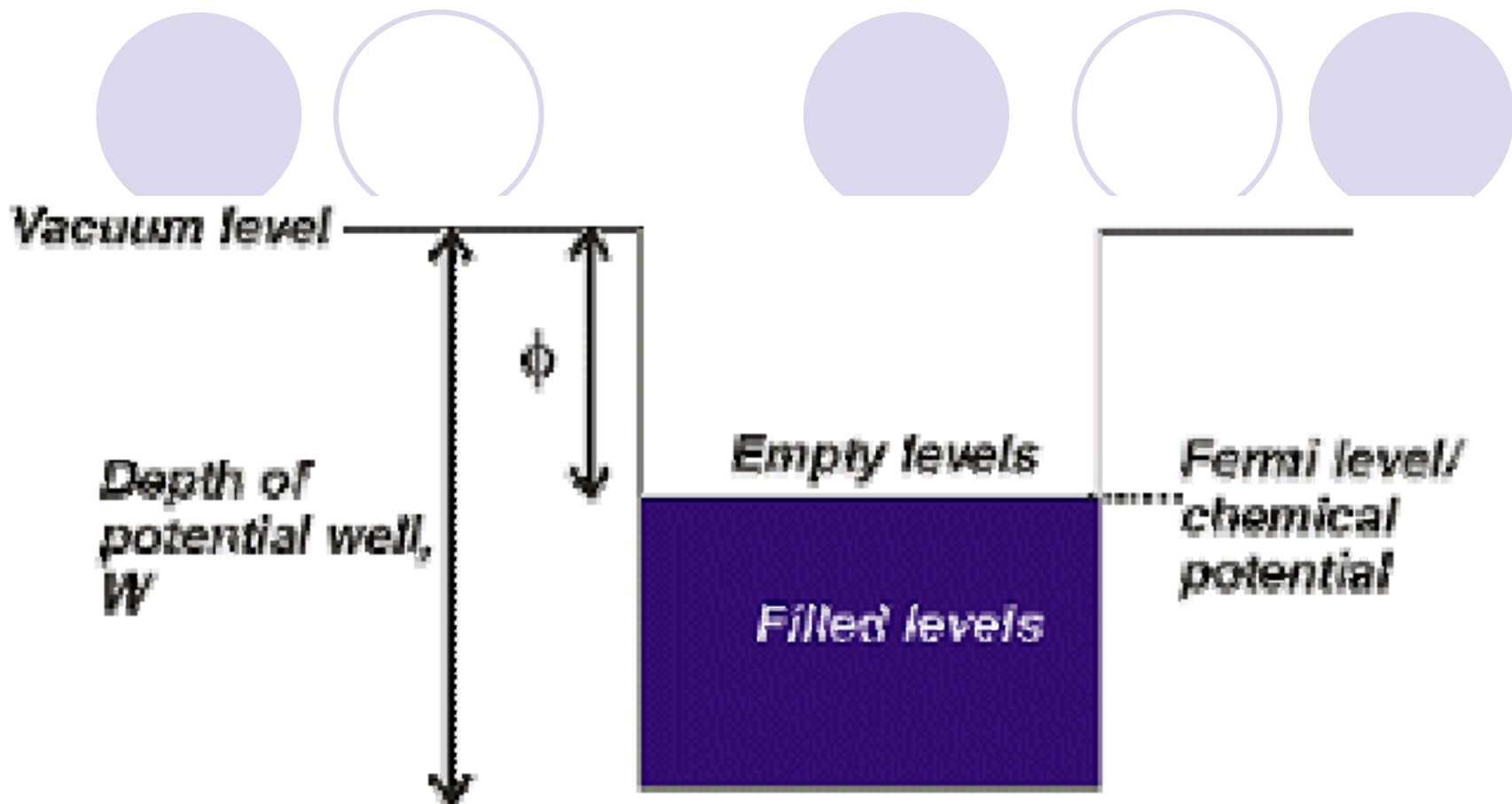
Work Function

One definition of the work function that is commonly used is that it is *the difference in energy between an electron at rest in the vacuum just outside a metal and an electron at the Fermi level*, i.e. the energy, typically a few eV, required to move an electron from the *Fermi Level*, E_F , to the vacuum level, E_0 .

The **work function** depends on the crystal face $\{hkl\}$ and rough surfaces typically have lower work function.

"Just outside" in this context means that the electron should be sufficiently distant from the surface that it does not interact with the solid. Thus, the electron-solid separation should be large enough so that the (Coulombic) force due to the electron's interaction with its image in the solid is not felt.

There are both bulk and surface contributions to the work function (ϕ). It is clear that ϕ will depend on the depth of the potential well for the conduction electron gas. This is dependent on the background charge density in the jellium model (a *bulk* property).



Electron overspill into the vacuum produces a surface dipole layer which makes a strong contribution to the work function. As the amount of overspill depends on the surface geometry, measurements of the work function provide information on surface properties.

Measurements of changes in work function following the adsorption of atoms/ molecules onto a clean surface may be used to derive the amount of substrate-adsorbate charge transfer. Treating the dipole layer as a parallel plate capacitor and noting that the work function change arises from an additional surface potential due to the adsorbed layer we can write:

$$\Delta\phi = n\mu / \epsilon_0$$

where n is the total number of adsorbates and μ the dipole moment between the adsorbate and its image charge.

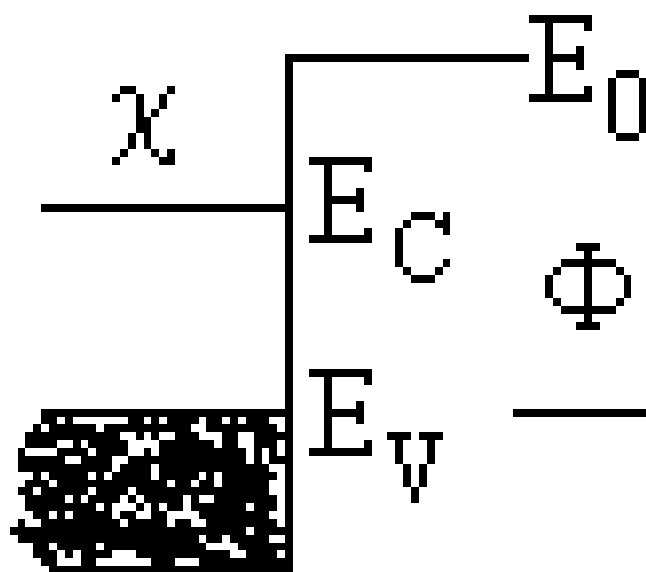
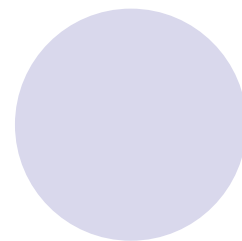
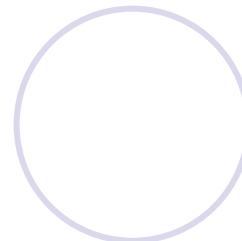
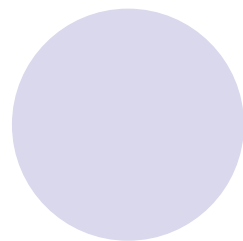
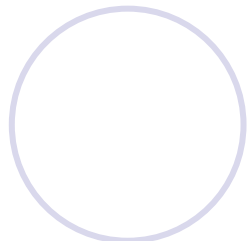
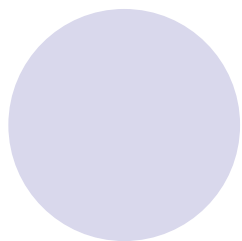


Electron Affinity and Ionisation Potential

Both of these would be the same for a metal, and equal to ϕ , but for a semiconductor or insulator, they are different.

The **electron affinity** is the difference between the vacuum level E_0 , and the bottom of the conduction band E_C .

The **ionisation potential** is $E_0 - E_V$, where E_V is the top of the valence band. These terms are not specific to surfaces: they are also used for atoms and molecules generally, as the energy level which a) the next electron goes into, and b) the last electron comes from.



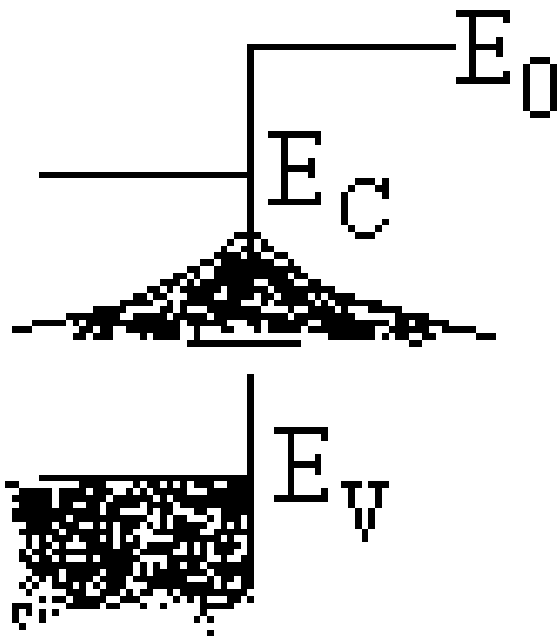
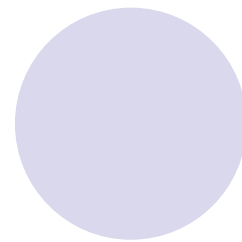
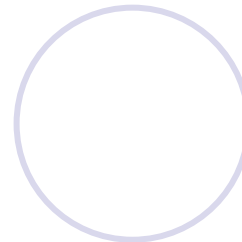
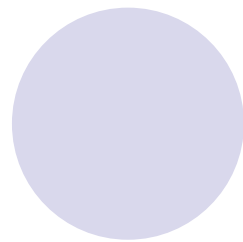
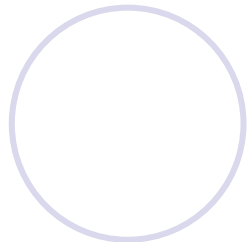
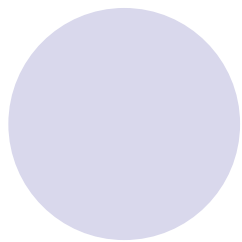


Surface States

A **surface state** is a state localised at the surface which decays exponentially into the bulk, but which may travel along the surface. The wave function is typically of the form

$$\psi \sim \mathbf{u}(\mathbf{r}) \exp(-i \mathbf{k}_\perp |z|) \exp(i \mathbf{k}_\parallel \cdot \mathbf{r}),$$

where, for a state in the band gap, \mathbf{k}_\perp is complex, leading to decay away from the surface on both sides. Such a state is called a **resonance** if it overlaps with a bulk band, as then it may have an increased amplitude at the surface, but evolves continuously into a bulk state. A **surface plasmon** is a collective excitation located at the surface, with frequency typically $\omega_p/\sqrt{2}$.

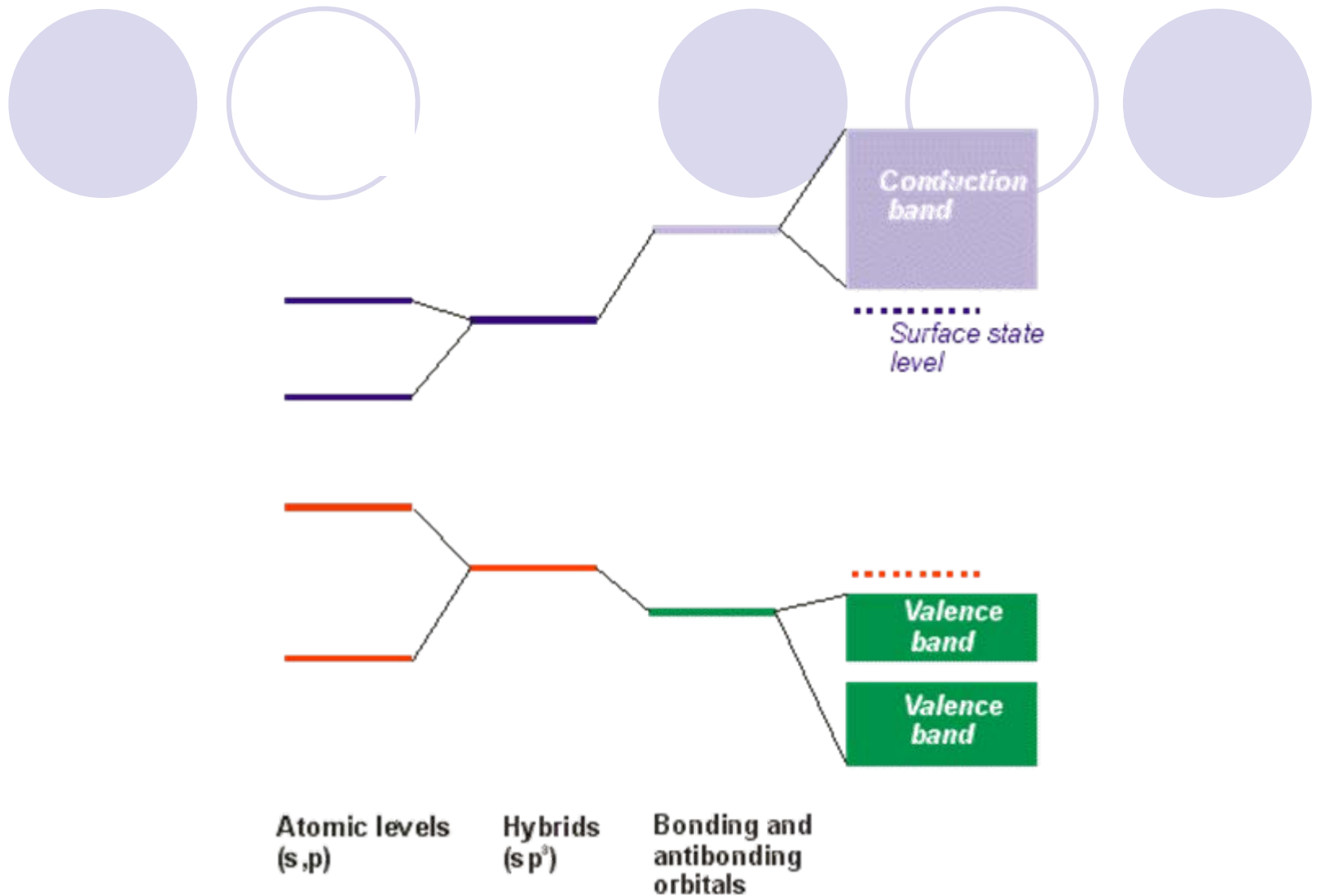




The existence
and character of surface states can be discussed
based on a nearly free electron model.

That a surface state will have an energy falling
within the bulk band gap can also be seen from simple qualitative
arguments based on
the tight binding ([LCAO](#)) model.

Atoms at a semiconductor surface have fewer neighbours
than their bulk counterparts,
there is thus less wavefunction overlap and the electronic
levels at the surface
will be closer to those in the free atom.



A simple schematic energy level/band diagram for a polar semiconductor (e.g. any III-V semiconductor).



Starting from the left, the s and p atomic levels of each atom combine to form sp^3 hybrids. The interaction of these hybrids leads to the formation of bonding and antibonding orbitals.

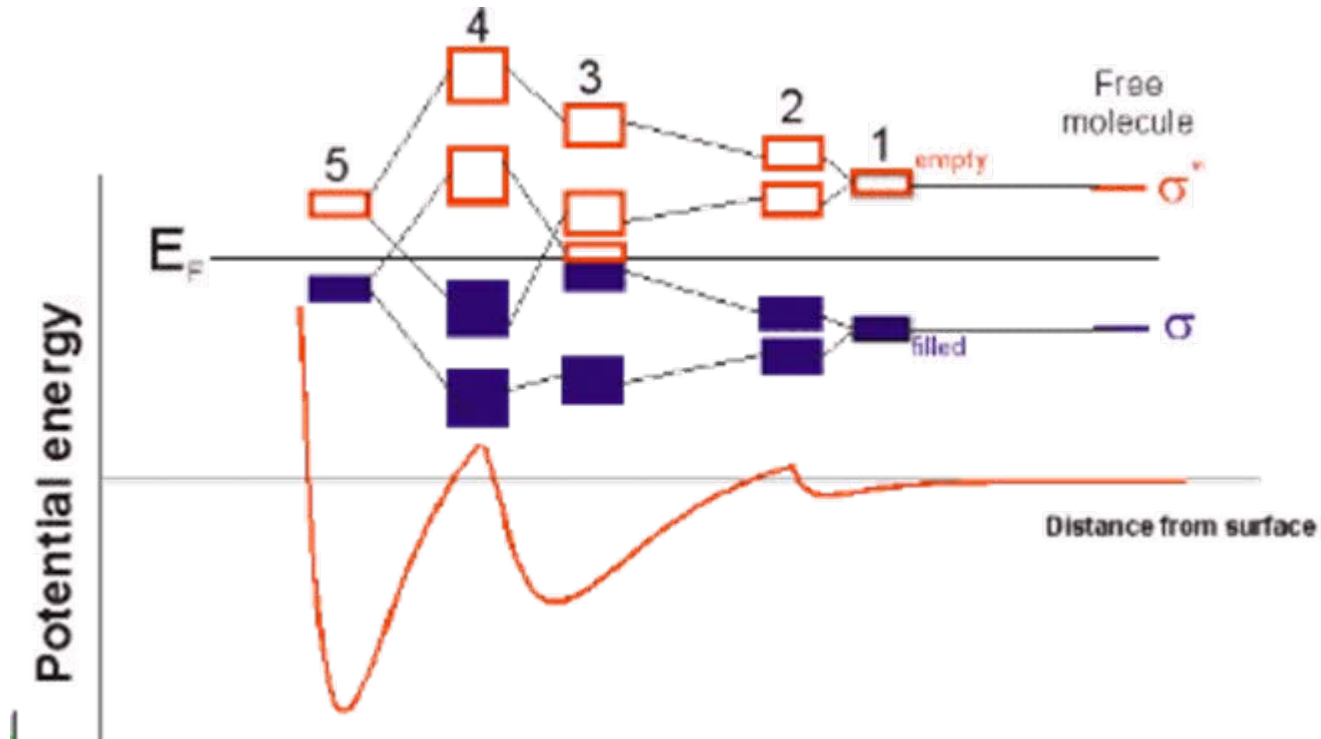
The mutual interaction of the bonding and antibonding orbitals throughout the crystal in turn leads to the formation of the conduction and valence bands.

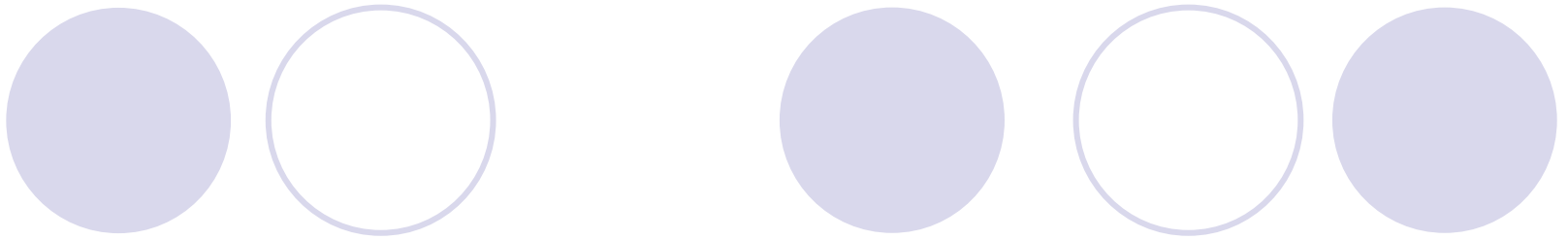


The electronic energy levels arising from the surface atoms lie closer to those of the free atoms and are thus split off from the bulk valence and conduction bands.

Therefore, as given also from the NFE model, the energy of a surface state falls within the bulk band gap. Every orbital/ hybrid broken at the surface (i.e. every dangling bond) will contribute an energy level. In addition to the dangling bond surface states arising from the uppermost surface layer, the bonding in the first few atomic layers will be modified to some extent (perhaps the most dramatic example of this is the Si(111)(7x7) reconstruction).

The Role of Electronic States and Molecular Orbitals in Chemisorption



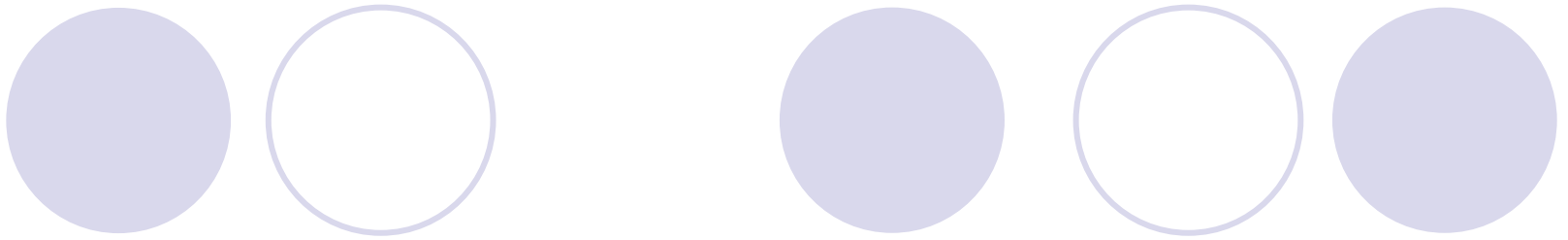


The figure shows how the s and s* molecular orbitals of a H₂ molecule are modified as the molecule approaches a metal surface.

Moving from right to left in the figure there are 5 distinct stages:

In the physisorbed precursor state the molecular levels are slightly broadened. The molecule is in a shallow potential well and, due to the interaction with the surface, the molecule's energy levels are broadened from that in the gas phase.

The molecule starts to surmount the small barrier associated with the activation energy for chemisorption.



The stronger interaction with the surface (greater overlap of surface and molecular wave functions) leads to a splitting of the original bonding and antibonding levels in the molecule.

The separation of these new broad levels increases as the molecule gets progressively closer to the surface.

The molecule surmounts the activation energy needed to form a chemical bond with the surface. In this molecular chemisorption state there is a large degree of overlap/hybridisation

of the surface and molecular wavefunctions.

In the example shown a filled molecular orbital level (derived from the original s level) has crossed the Fermi level resulting in a transfer of charge to the metal.



Given sufficient energy, the molecule will be able to surmount the dissociation barrier.

The key point to note in the molecular orbital diagram is that a broad level derived from an original antibonding level in the free molecule has dropped below the Fermi level and become filled. Occupation of the antibonding orbital will tend to weaken the interatomic bond.

Finally, due to occupation of the antibonding level, the molecule dissociates giving rise to two levels associated with each chemisorbed atom-metal bond.