Lecture in the course “Surface Physics and Nano Physics” 2008,

Chemisorption

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Outline :

Chemisorption models

- simpel 1D model
- more realistic 1D model
- realistic 3D calculation

Application of chemisorption

- hydrogen storage

PHYSISORPTION

weak bond

Electronic structure unperturbed. Van der Waals interaction - attractive force between the atom/molecule and the surface due to electron density fluctuation in the constituents.

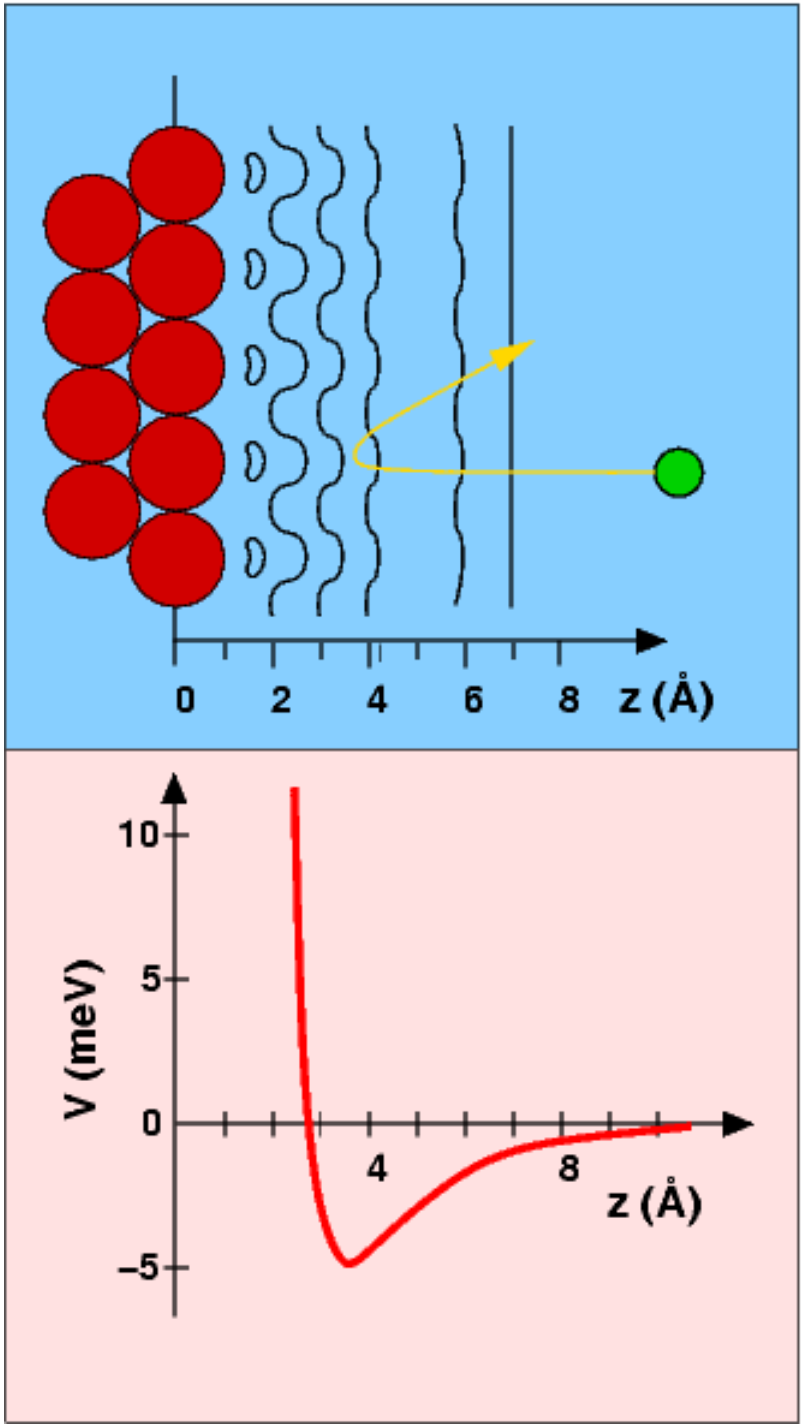
CHEMISORPTION

strong bond

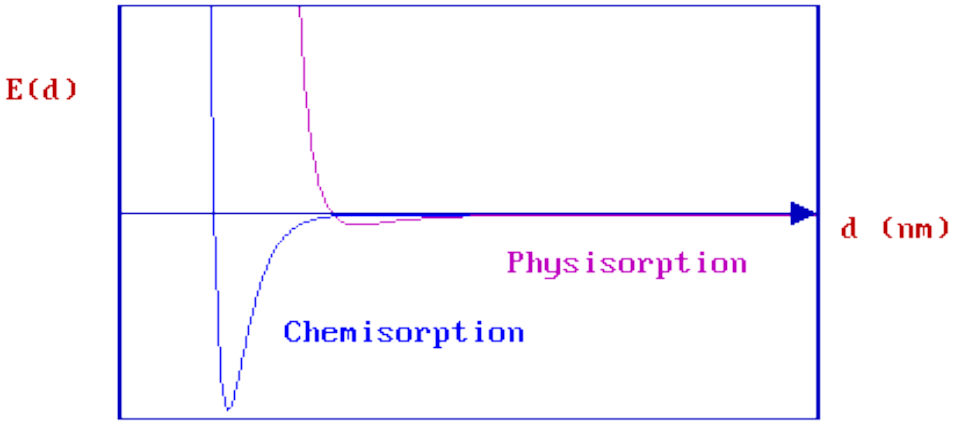
Like covalent bond in gas phase molecules. Electron structure strongly perturbed. Hybridized orbitals formed due to charge transfer.

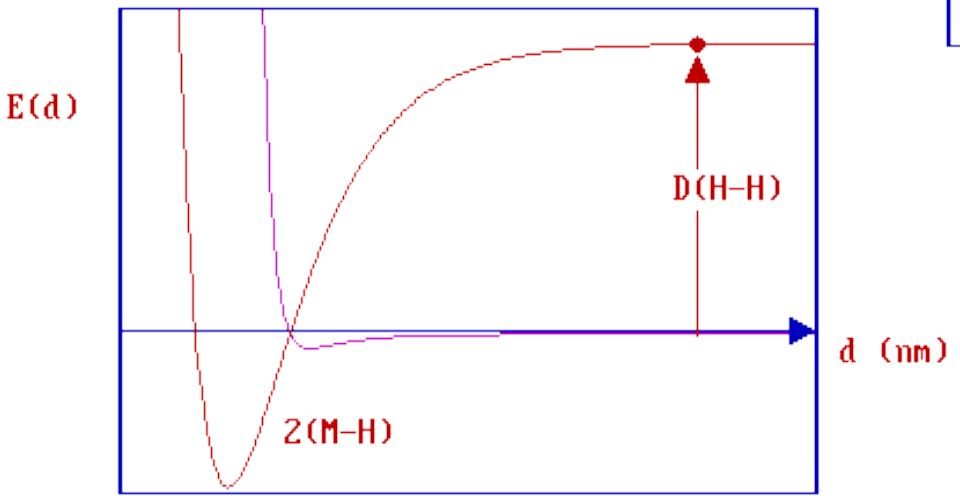
Example of Physisorption: He-Metal interaction :

The He-surface interaction potential has a long-range attractive part for large separation, and a short-range, repulsive component at small distance. The former is a dipole-dipole interaction due to quantum fluctuations in the charge density distribution, while the latter is caused by the overlap of the electron clouds of the He atoms with the outer electrons of the surface. The turning point of the He atoms is located about 3-4 Å from the surface atomic cores.



Example of Chemisorption: H_2-Metal interaction :

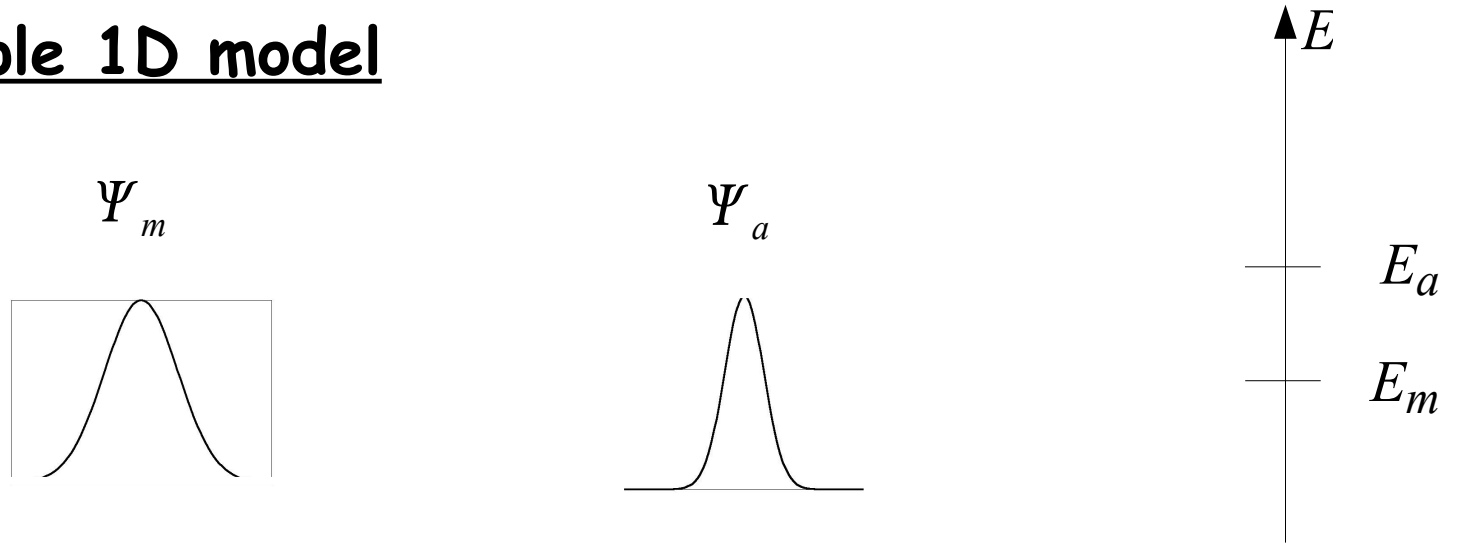




Consider the H_2 molecule. When the distance d is very large, a substantial amount of energy has to be supplied in order to dissociate H_2 to H + H . The energy required, the dissociation energy [D(H-H)], is about 4.5 eV.

CHEMISORPTION MODELS

(a) simple 1D model



Metal state

Adsorbate state

Hybridized orbital: $\Psi = c_m \Psi_m + c_a \Psi_a$ (1)

H = the Hamiltonian , $E_m = \int \Psi_m H \Psi_m d\vec{x}$ $E_a = \int \Psi_a H \Psi_a d\vec{x}$

$\int \Psi_a H \Psi_m d\vec{x} = \int \Psi_m H \Psi_a d\vec{x} = -V$ $\int \Psi_a \Psi_m d\vec{x} = S$

In short notation with "< bra |" and "| ket >" vectors

Schrödinger equation $H|\psi> = E|\psi>$ (2)

Multiply with ψ_a And then ψ_m and integrate

$<a|H|\psi> = E<a|\psi>$ ➔ $E_a c_a - V c_m = E(c_a + S c_m)$ (3)

$<m|H|\psi> = E<m|\psi>$ ➔ $E_m c_m - V c_a = E(c_m + S c_a)$ (4)

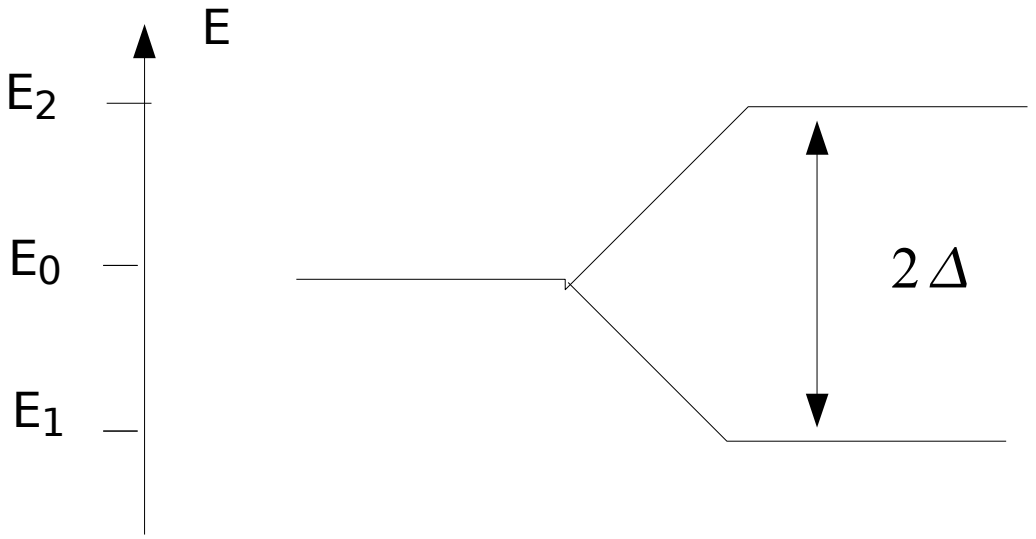
$$\begin{vmatrix} (E-E_a) & (V-ES) \\ (V-ES) & (E-E_m) \end{vmatrix} = 0$$

Assume $S \simeq 0$

➔ $E_{1,2} = 1/2\ (E_a + E_m) + / - \sqrt{((1/2\ (E_a - E_m))^2 + V^2)}$

$$E_0 = (E_a + E_m)/2 \quad \rightarrow \quad E_1 = E_0 - \Delta \quad and \quad E_2 = E_0 + \Delta$$

$$\Delta = \sqrt{((E_a - E_m)^2 + V^2)}$$



We now calculate the wave functions of the ground state, | 1 > and the excited state, | 2 > .

Insert $E_1 = E_0 - \Delta$ in Eq. (3)

$S \simeq 0$ ➔ $(E_a - E_0 + \Delta) c_a = V c_m$ *if* $E_a \simeq E_m$ ➔ $c_m \simeq c_a = c_0$

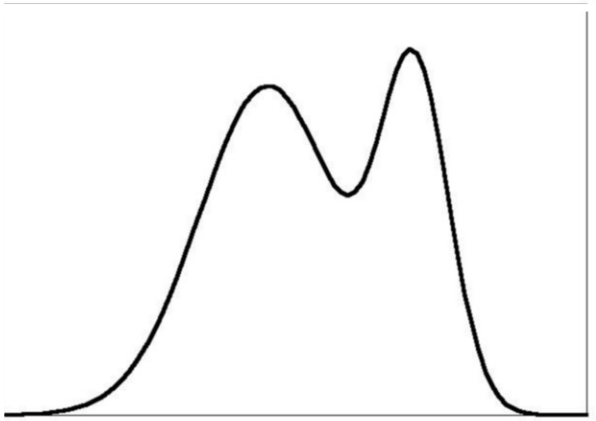
The wave function is given by Eq. (3)

$$|1> = c_0 (|a> + |m>)$$

We normalize $|1>$

$$<1|1> = c_a^2 + c_m^2 = 2\, c_0^2 = 1 \quad \Rightarrow \quad |c_0| = 1/\sqrt{2}$$

$$|1> = 1/\sqrt{2}\,(|a> + |m>)$$



$|1>$ *is a BONDING orbital*

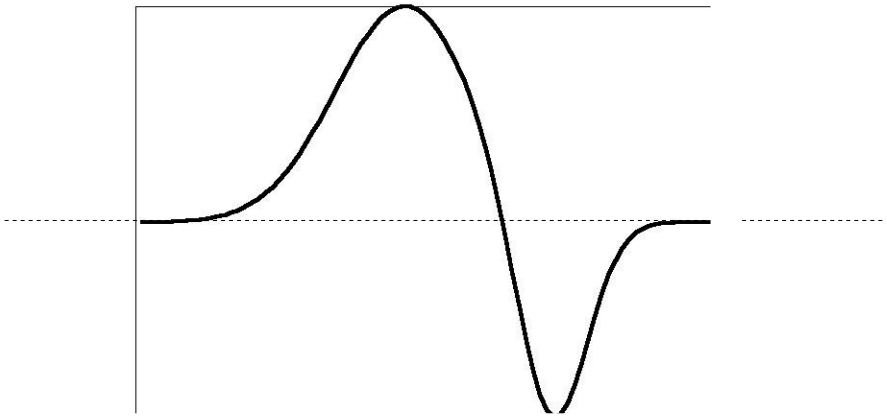
We now calculate the wave functions of the excited state| 2 > .

Insert $E_1 = E_0 + \Delta$ in Eq. (3)

$S \simeq 0$ ➔ $(E_a - E_0 - \Delta) c_a = V c_m$ *if* $E_a \simeq E_m$ ➔ $c_m \simeq - c_a$

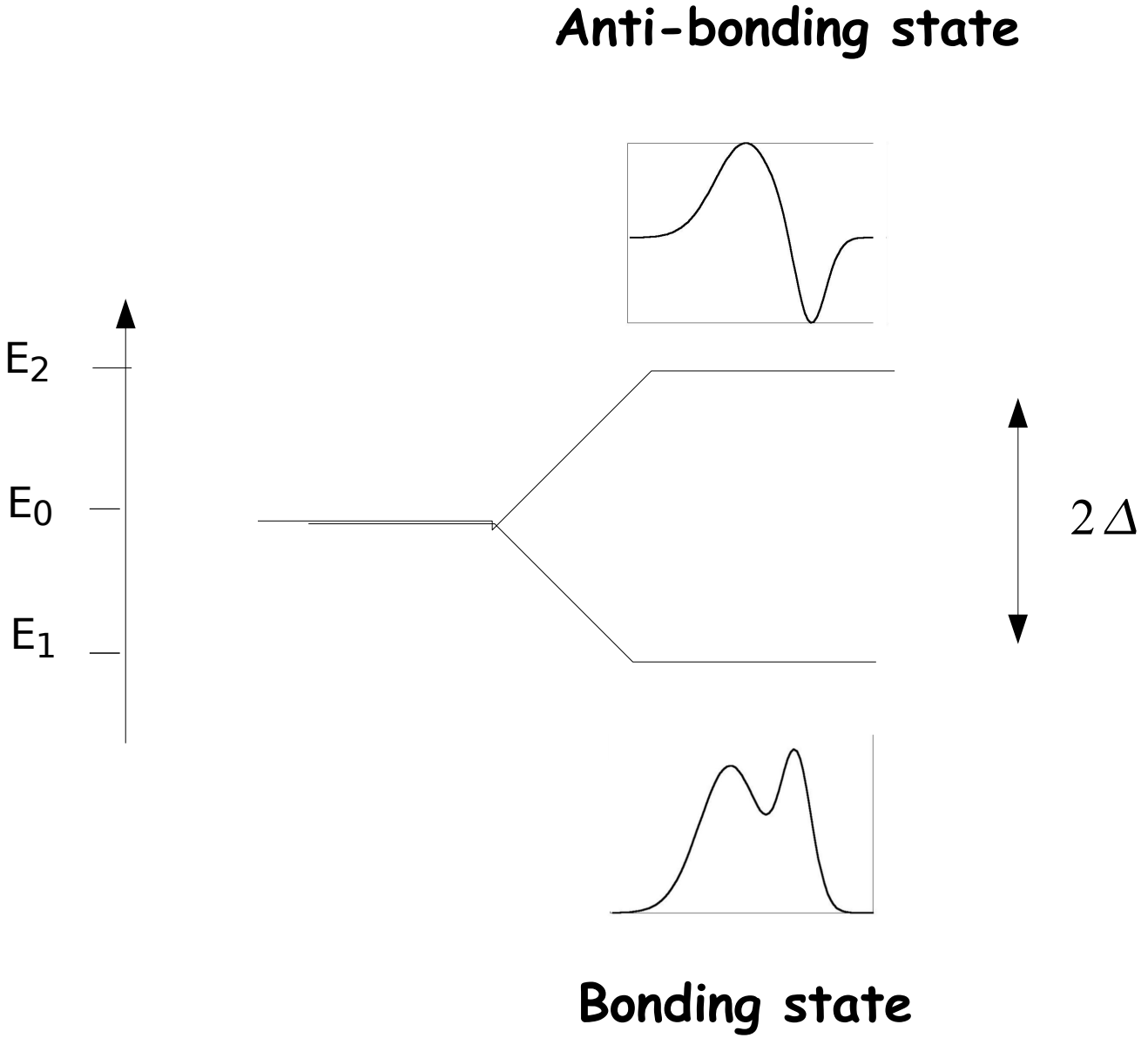
The wave function is given by Eq. (1)

$|2> = 1/\sqrt{2}\,(\,|a> - |m>\,)$



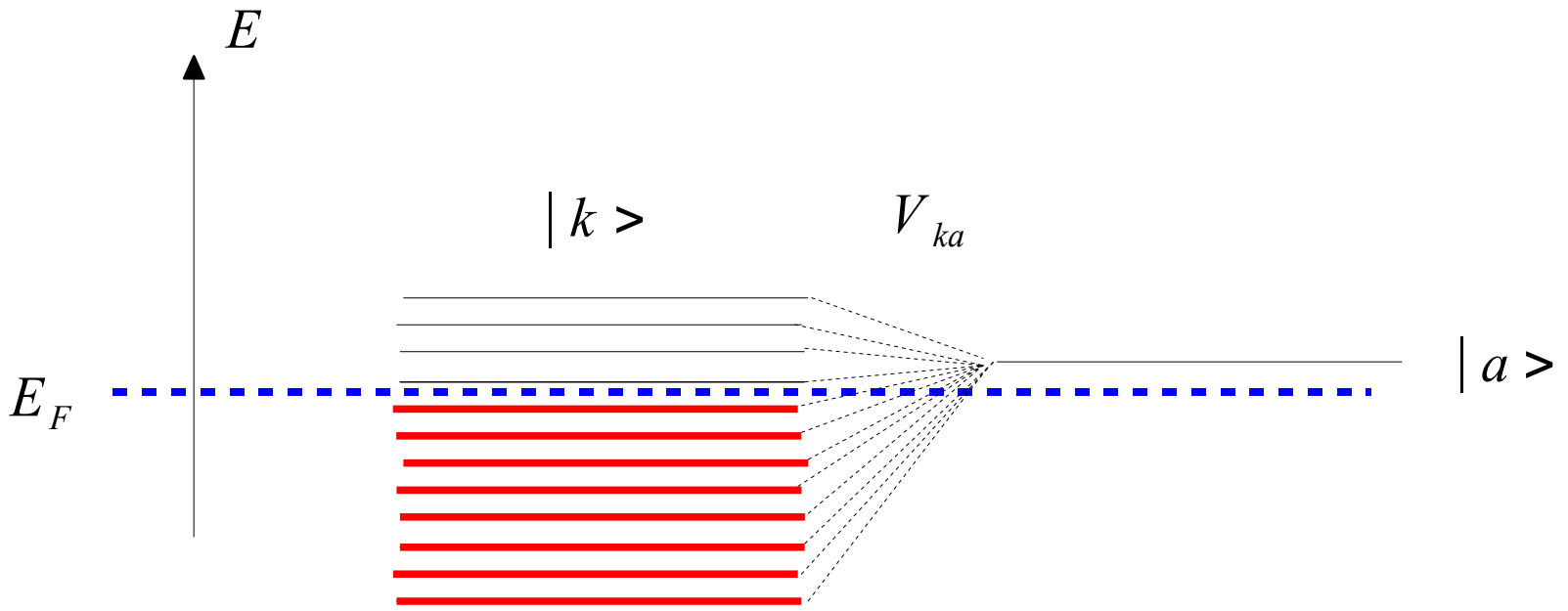
$|2>$ *is a ANTI − BONDING orbital*

In summary



(b) more realistic 1D model

Consider the atom-substrate interaction,
including many substrate states $|k>$



$E_F = Fermi\ energy = Highest\ occupied\ electron\ state$

$V_{ka} = \gg hopping\ \ matrix\ \ element \ll$

Newns-Anderson model for chemisortion (see litterature list).
The Hamiltonian:

$$H = \sum_k E_k c_k^+ c_k + E_a c_a^+ c_a + \sum_k V_{ak} c_a^+ c_k + \sum_k V_{ka} c_k^+ c_a$$

$$c_i^+ = electron\ creation\ \ operator$$

$$c_i = electron\ anhilation\ \ operator$$

$$V_{ka} = \int \Psi_k H \Psi_a d\vec{r} = <k|H|a>$$

Applying a Green's function technique to solve the equation of motion for the time dependent operators gives the adsorbate projected denstity of states

$$\rho_a(E) = \frac{1}{\pi} \mathrm{Im}\, G(E) = \frac{1}{\pi} \mathrm{Im} \frac{1}{E - E_a - \Sigma(E)}$$

$$= \frac{1}{\pi} \frac{\Delta(E)}{(E - E_a - \Lambda(E))^2 + \Delta^2(E)}$$

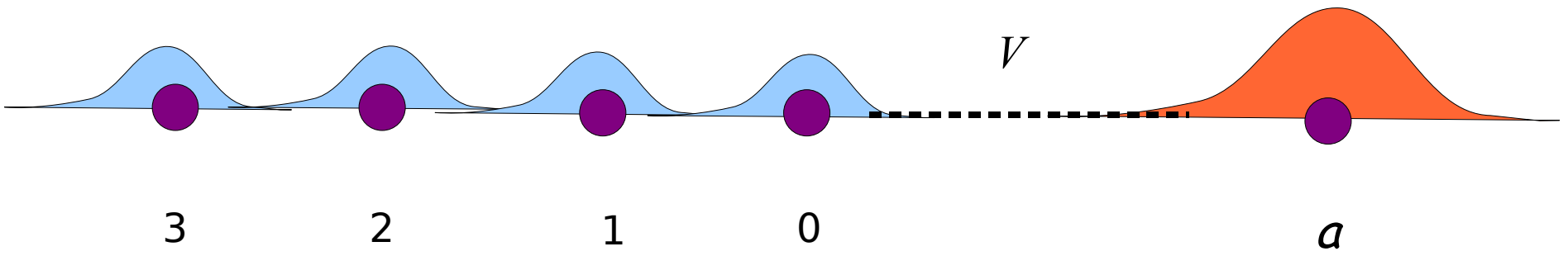
$$\textit{The Self-energy:}$$

$$\Sigma(E) = \mathrm{Re}\,\Sigma(E) + i\,\mathrm{Im}\,\Sigma(E) = \Delta(E) + i\Lambda(E)$$

$$\Delta(E) = \mathrm{Re}\,\Sigma(E) = \pi \sum_k |V_{ak}|^2\, \delta(E - E_k)$$ chemisorption function

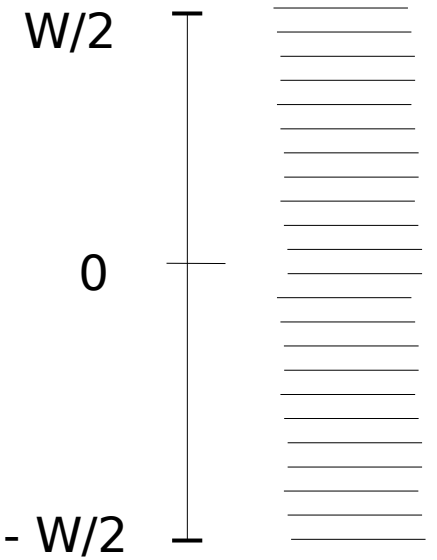
$$\Lambda(E) = \mathrm{Im}\,\Sigma(E) = \int \frac{\Delta(E')}{E - E'} dE' = \sum_k \frac{|V_{ak}|^2}{E - E_k}$$ shift function

1D Linear chain model



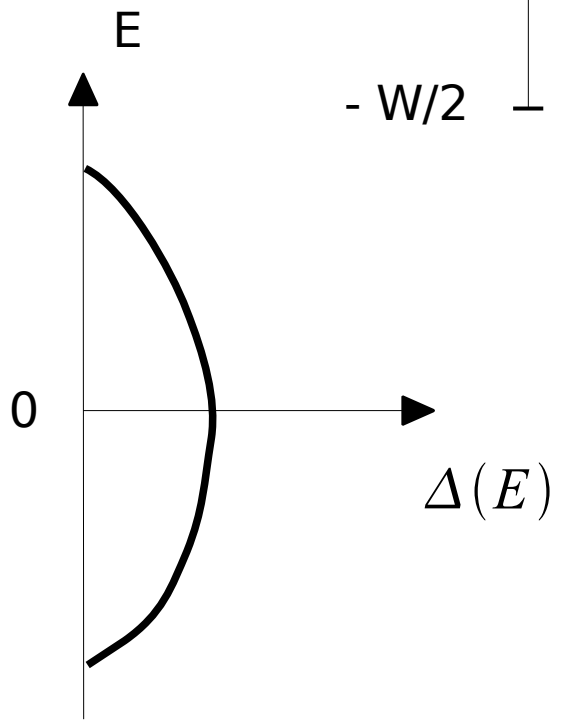
$$W = bandwidth = 4\,|<i|H|i+1>|$$

$|k>$



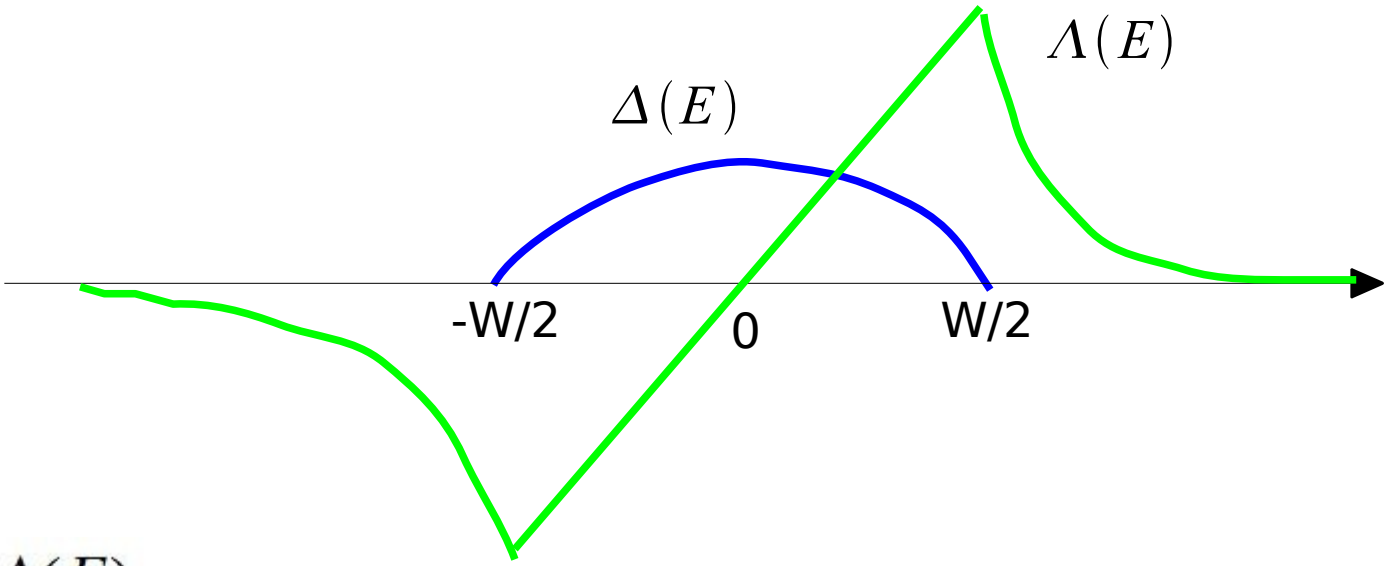
In this model we obtain a semi-eliptical chemisorption function

$$\Delta(E) = \frac{V^2}{W}\sqrt{1-(\frac{2E}{W})^2}$$



And the shift function is linear in energy within the band

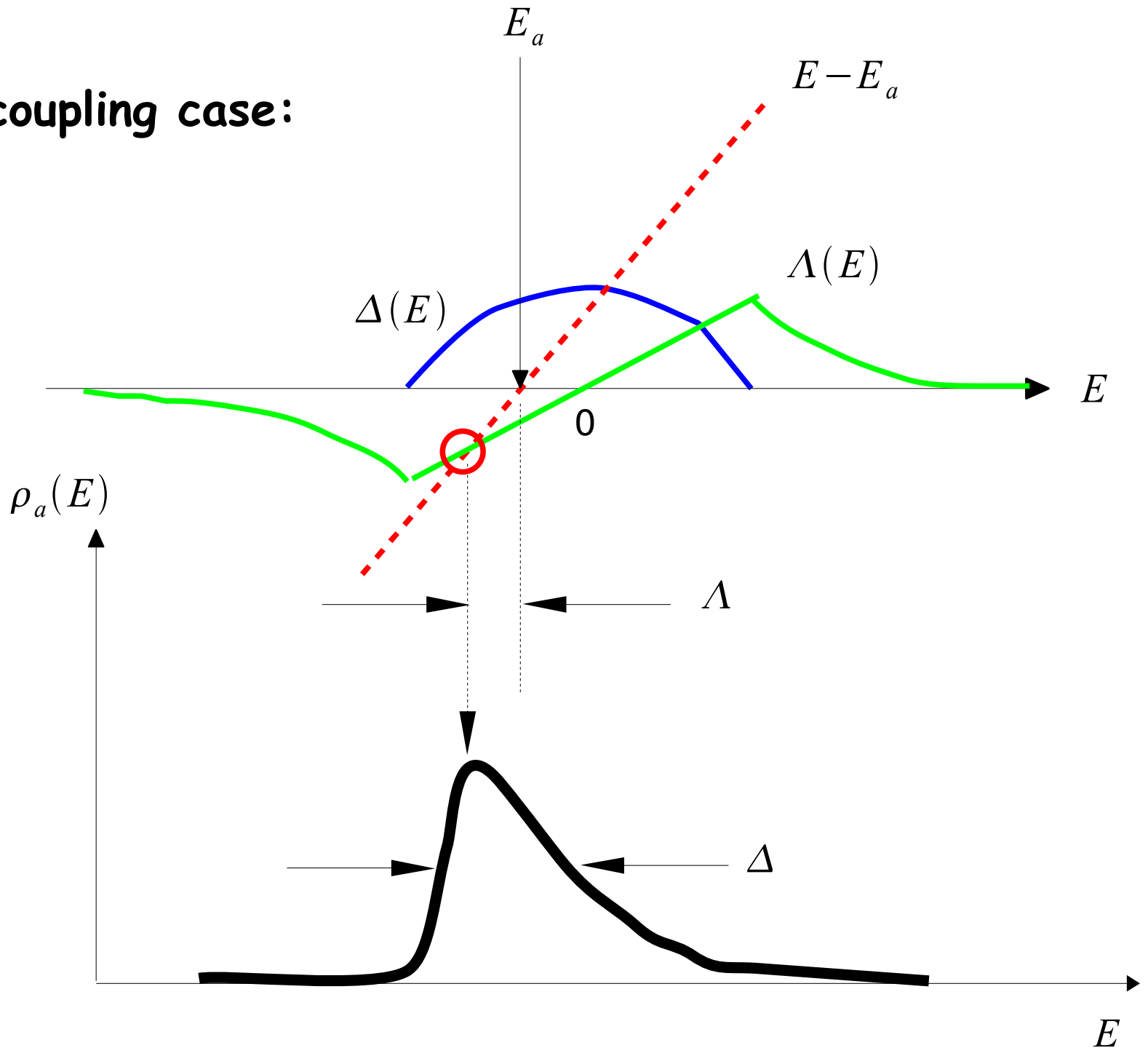
$$\Lambda(E) = 2(\frac{V}{W})^2 E \qquad when \ |2E/W| < 1$$



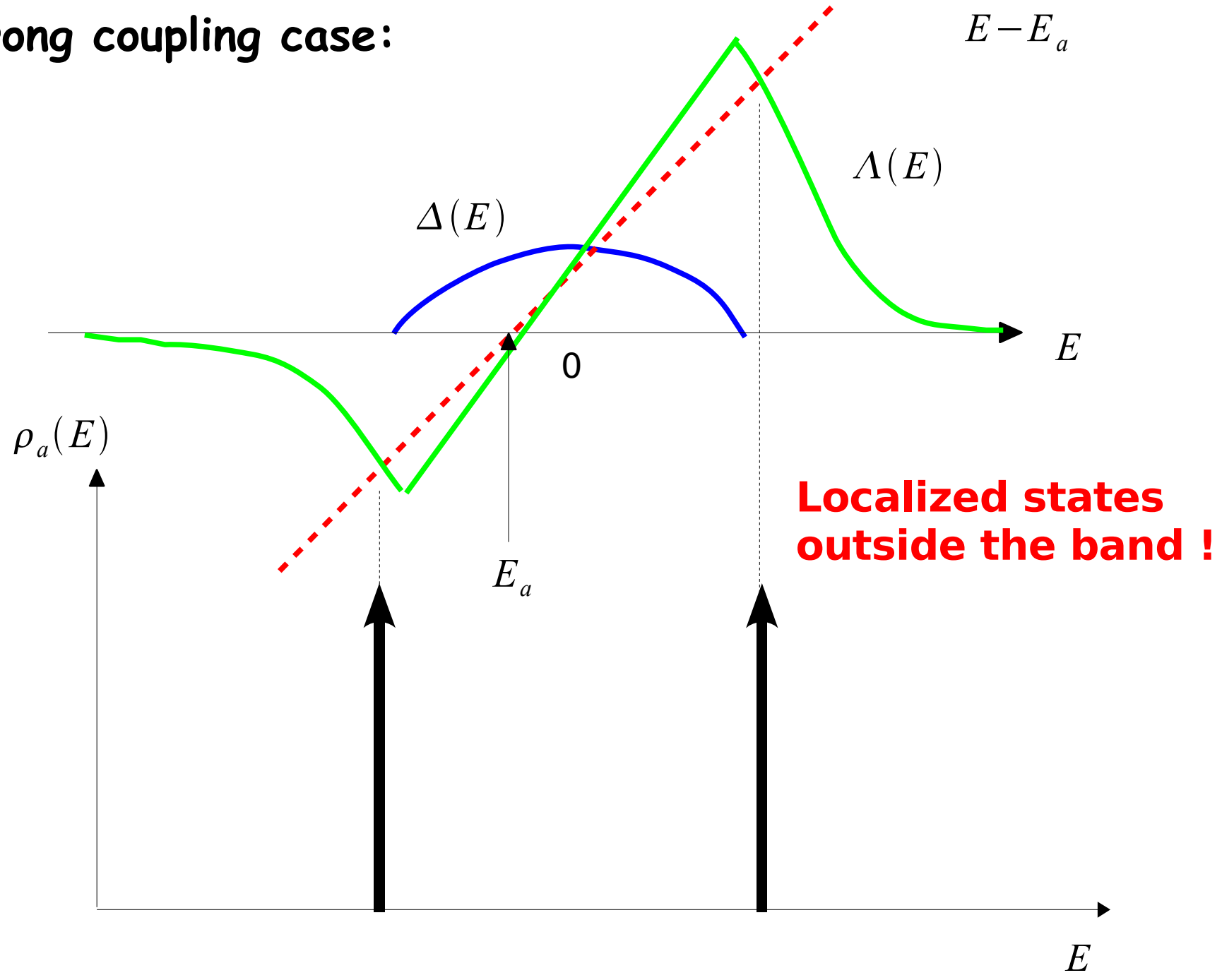
$$\rho_a(E) = \frac{1}{\pi} \frac{\Delta(E)}{(E - E_a - \Lambda(E))^2 + \Delta^2(E)}$$

We see that $\rho_a(E)$ is large when $\Lambda(E) = E - E_a$

Weak coupling case:

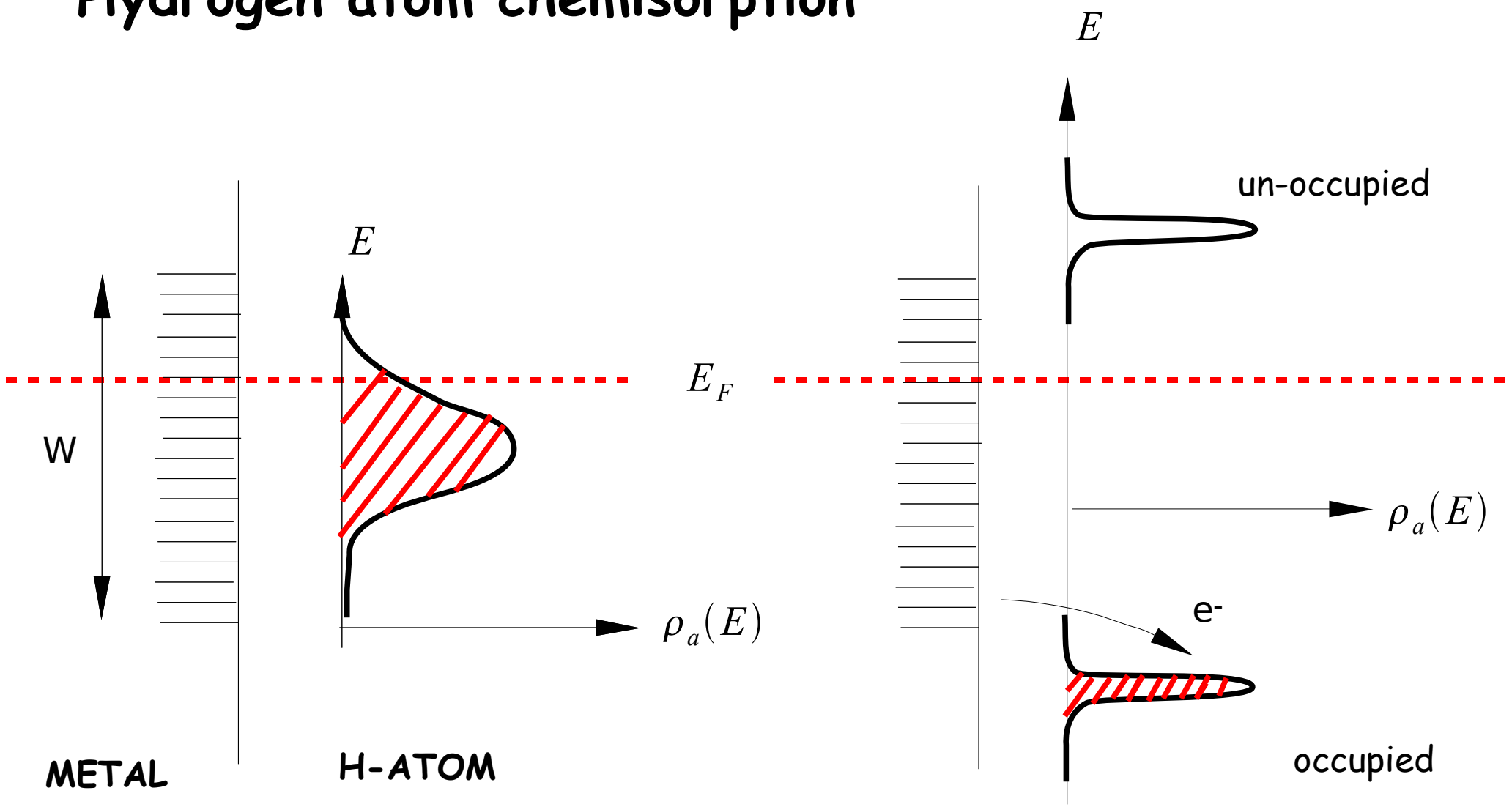


Strong coupling case:



Localized states outside the band !

Hydrogen atom chemisorption

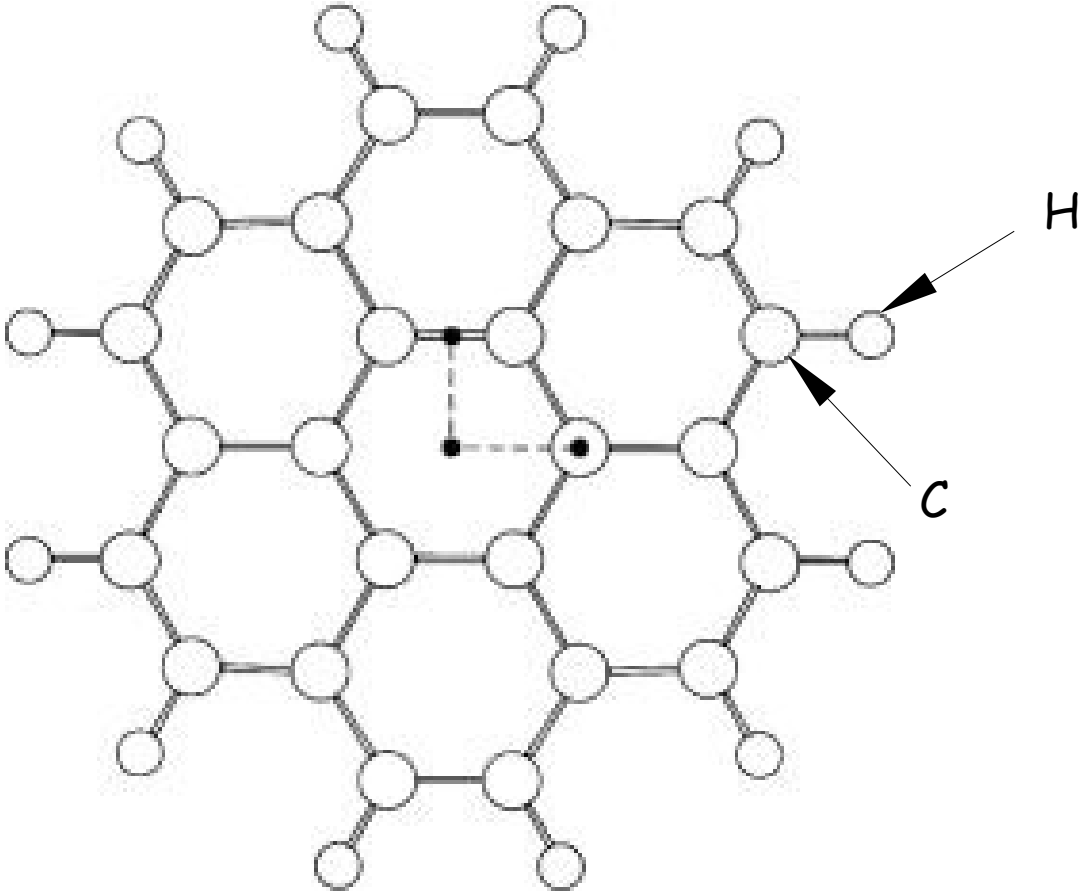


Weak coupling

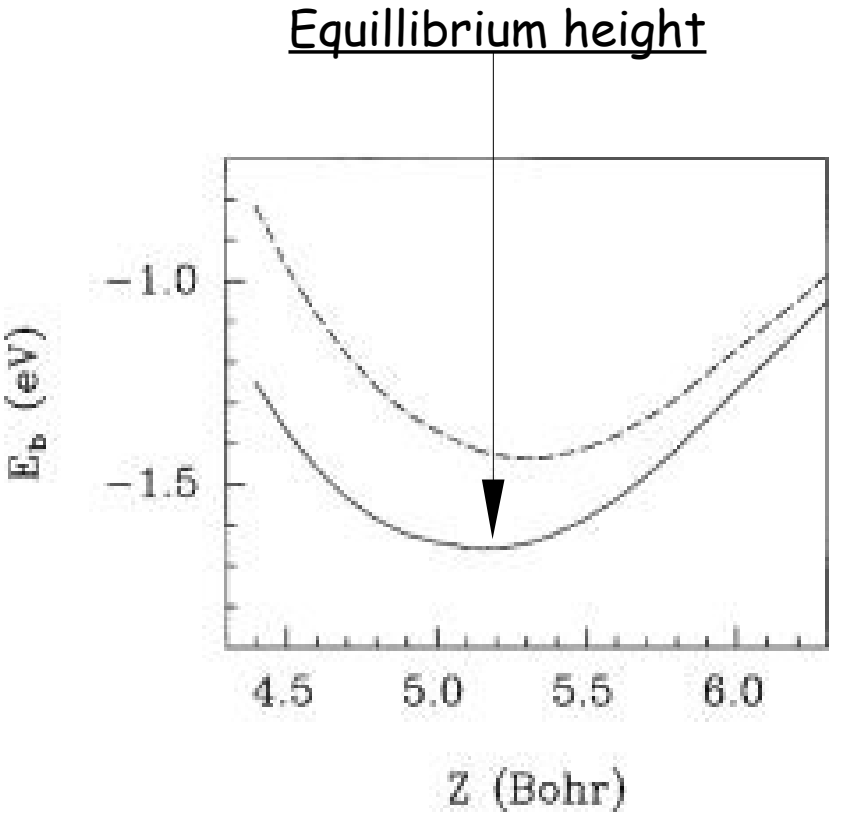
Strong coupling

(c) 3D realistic model

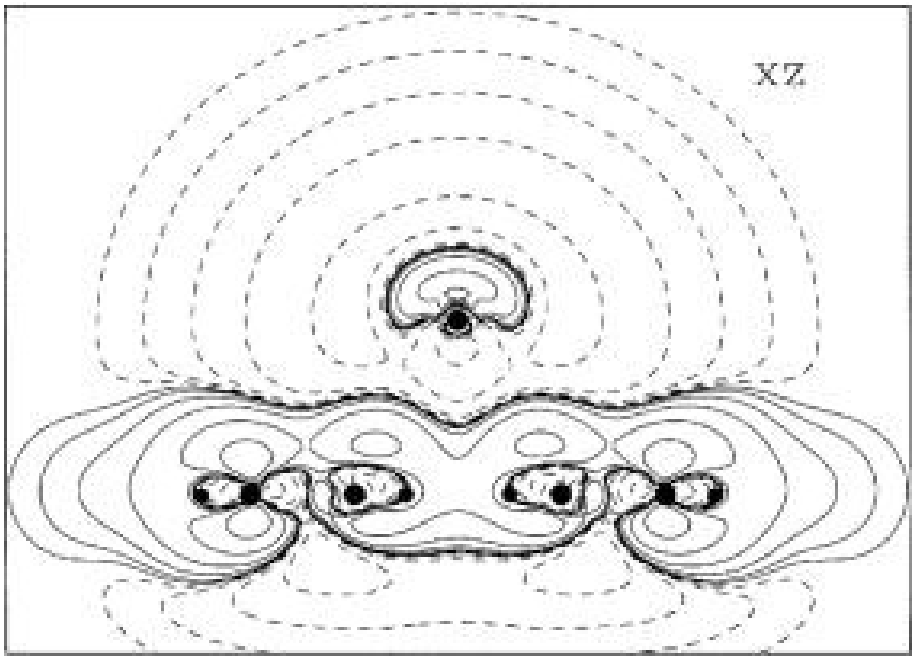
Chemisorption of K on graphite

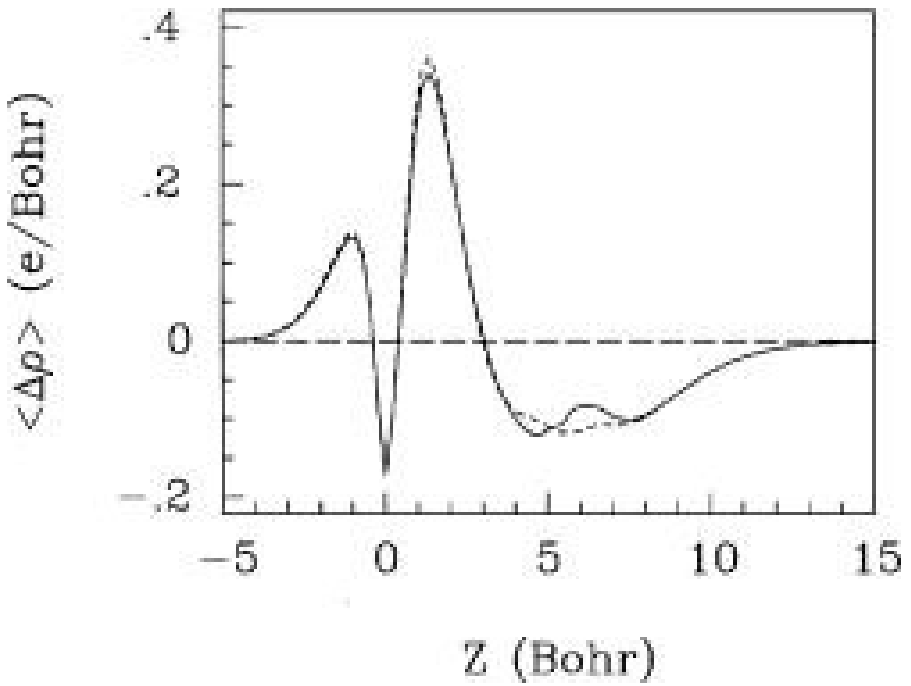


2D $C_{24}H_{12}$ graphite cluster



Chemisorption energy





Left figure:

Density difference contours for a $KC_{24}H_{12}$ adsorption system with the K atom above the hollow center at the equilibrium distance. The plane is made perpendicular to the substrate surface and passes through the center and a nearest carbon atom. The contour lines are separated by a factor of 3 increment starting from ±1.7×10-4 a_0^{-3}. Increases (decreases) in density are indicated by solid (dashed) lines. Filled circles represent projected positions of the substrate carbon atoms. Large (small) circles are for in-plane (off-plane) atoms.

Right figure: Density diff. Integrated over x and y

Chemisorption energy E_b determined from
thermal desorption experiment fitted to calcultaed spectra (see below)

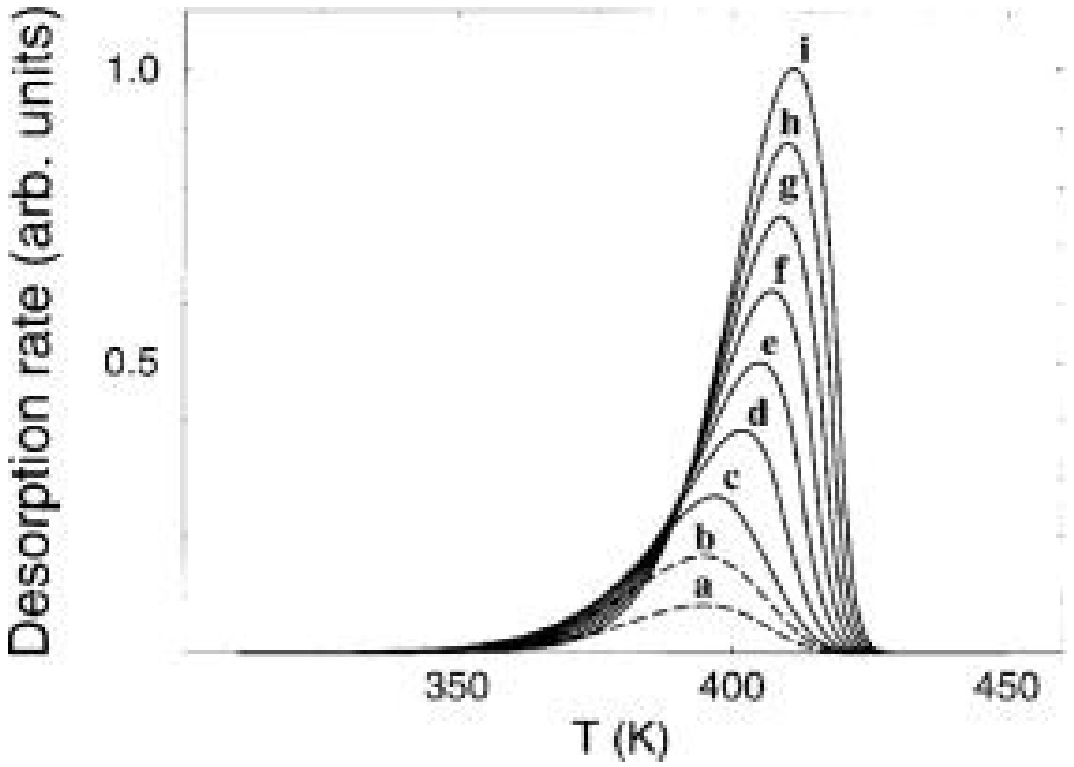


Figure:
Calculated desorption yield curves vs temperature for different initial coverages, 0.1 (a), 0.2 (b), 0.3 (c), 0.4 (d), 0.5 (e), 0.6 (f), 0.7 (g), 0.8 (h) and 0.9 (i). The two dashed lines correspond to coverages below the critical coverage 0.25.

Application of chemisorption

Hydrogen storage

Hydrogen fuel

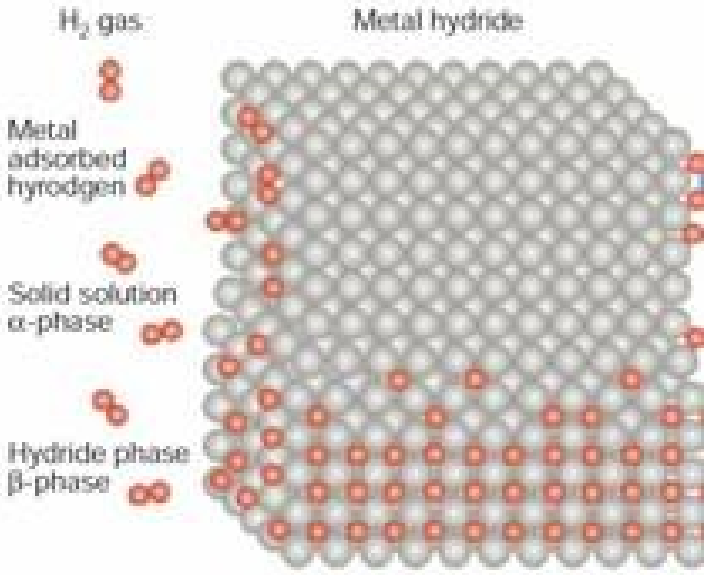
Hydrogen is a good candidate for reducing emissions since when it react with oxygen it produces only water as the reaction product. Hydrogen can be used to provide electricity and heat either through use in a fuel cell or combustion. A fuel cell generates electricity by combining hydrogen with oxygen from air; the only by-product is water. Hydrogen can also be burned in an internal combustion engine in the same way as petrol or natural gas. This produces water as the main by-product, however, small amounts of oxides of nitrogen (air pollutants) are also produced.

Solid-State Storage of Hydrogen

In order to achieve the environmental benefits of hydrogen the energy required to separate the hydrogen must be produced from renewable sources. Renewable energy such as solar, wind, hydro etc. is not a constant source; therefore if some of the electricity produced is used to produce hydrogen, which can be stored for later use, society has a continuous supply of power.

Storage is the key.

Hydrogen contains more energy on a weight for weight basis than any other substance. The most suitable method for storing hydrogen will depend on many factors including the volume to be stored, weight of the storage unit, storage time, space restrictions and the end use.
Hydrogen can be stored by the use of a reversible chemical reaction. This usually takes the form of the reaction of a metal with hydrogen to create a metal hydride. The reaction forms hydride at higher pressures and reverses to metal and hydrogen at lower pressures. These types of systems operate at room temperature and relatively low pressures. Storage is efficient in terms of volume but heavy due to the mass of metal hydride.

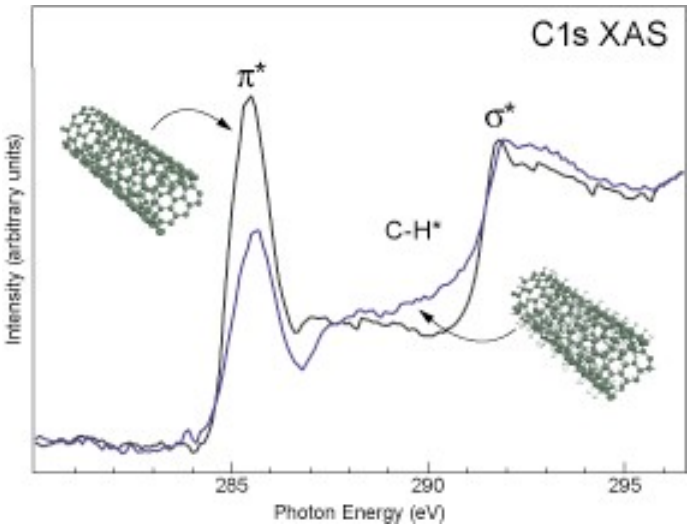


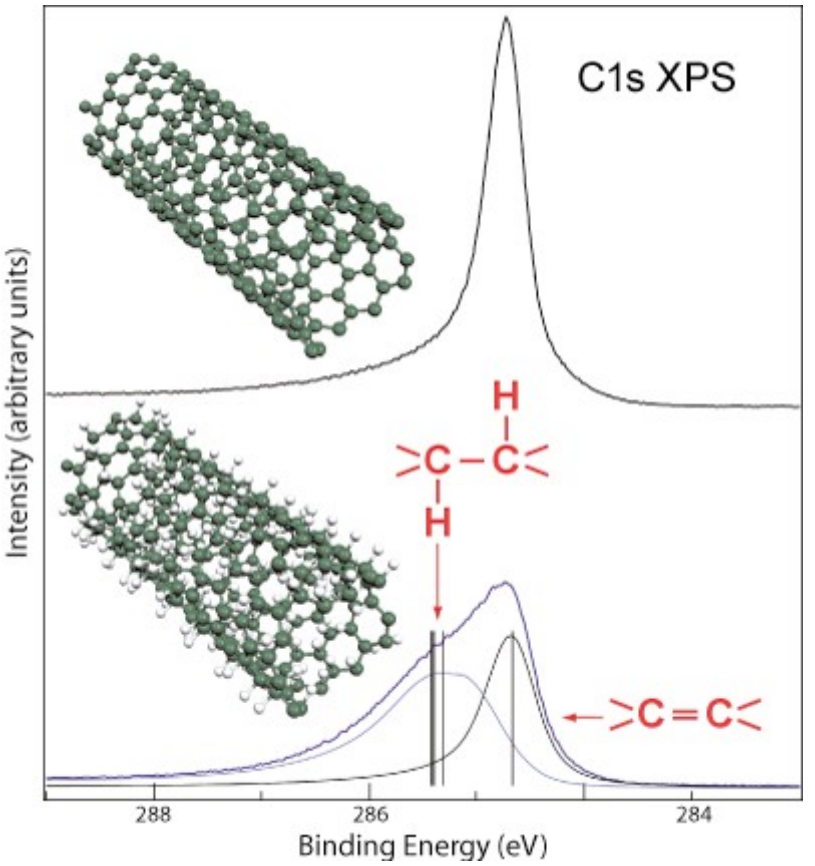
Reference:
www.aacg.bham.ac.uk/hydrogen/storage.htm

A Nanosolution to a Macroproblem?

Nanotubes

Since hydrogen exists in the form of gas at ambient pressure and temperature, the most appropriate way to store hydrogen is in an **adsorbed form** on media capable of adsorbing and releasing large quantities of this element easily and reliably. Carbon nanotubes are one of the most promising materials, and hydrogen storage through both physisorption and chemisorption mechanisms has been proposed. While most previous studies have focused on the potential of physisorption of molecular hydrogen, there is no direct reliable evidence of high hydrogen storage capacity at room temperature. It has been predicted that **the chemisorption mechanism could provide hydrogen storage capacity that fulfills the technological requirement through the saturation of C–C π bonds with atomic hydrogen.** However, direct experimental evidence of the feasibility of the hydrogen storage through chemisorption has not yet been demonstrated.





Carbon K-edge XAS spectra of a clean SWCN film (black) and a SWCN film after hydrogenation (blue). The decrease of the π* resonance intensity and increase of the intensity in the energy range of C–H* and σ* indicate that the hydrogenation causes the rehybridization of the carbon atoms in the SWCN film from sp2 to sp3 form along with the formation of C–H bonds.

Reference:
www-als.lbl.gov/.../sci_archive/129nanotube.html

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K chemisorption on graphite: Journal of Chemical Physics 112(2000)4788