
Electron states in a diatomic molecule

- The hydrogen molecule
- The homonuclear diatomic molecule
- The diatomic molecule
- Bond order and bond energy
- The heteronuclear diatomic molecule
- Electronegativity

References

The material in this lecture closely follows:

- [Electronic Structure of Materials](#), A. Sutton ([chapter 2](#))

The diatomic molecule: H_2

- Consider the H_2 molecule in its ground ($1s$) state. There are 2 electrons in this molecule interacting Coulombically. Solving analytically the Schrödinger equation is not feasible.
- We can obtain a qualitative picture using a simple **molecular orbital approach**.
- Let $|\Psi\rangle$ denote **a state vector of an electron in the molecule**.
- We use a suitable basis to approximate this state: Let $|1\rangle$ and $|2\rangle$ denote the electron states in the first and second atoms, respectively ($1s$ states). Let the energy of the electron in these **atomic states** be E_f .

$$H_1|1\rangle = E_f|1\rangle \qquad H_2|2\rangle = E_f|2\rangle$$

where H_1 and H_2 are the Hamiltonians for the two isolated atoms.

- We expand the ground state of the molecule as: $|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$.

The diatomic molecule: H_2

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle.$$

- We assume that the basis states $|1\rangle$ and $|2\rangle$ are orthonormal, i.e.

$$\langle 1,2\rangle = \langle 2,1\rangle = 0 \text{ and } \langle 1,1\rangle = \langle 2,2\rangle = 1$$

- This assumption breaks down when the two H-atoms get close and the 1s orbitals overlap but should be a good starting point for our analysis.
- It follows that $c_1 = \langle 1|\Psi\rangle$ and $c_2 = \langle 2|\Psi\rangle$. Our task is to find c_1 and c_2 and the energy of the state $|\Psi\rangle$ for the molecule.

The diatomic molecule: H_2

- The Schrödinger equation for the molecular state is

$$H|\Psi\rangle = E|\Psi\rangle$$

- or using the basis approximation

$$H(c_1|1\rangle + c_2|2\rangle) = E(c_1|1\rangle + c_2|2\rangle).$$

- With projections into the basis states $|1\rangle$ and $|2\rangle$ (the same equations are obtained with the variational principle), we obtain:

$$\langle 1|H(c_1|1\rangle + c_2|2\rangle) = \langle 1|E(c_1|1\rangle + c_2|2\rangle)$$

$$\langle 2|H(c_1|1\rangle + c_2|2\rangle) = \langle 2|E(c_1|1\rangle + c_2|2\rangle)$$

The diatomic molecule: H_2

$$\langle 1|H(c_1|1\rangle + c_2|2\rangle) = \langle 1|E(c_1|1\rangle + c_2|2\rangle)$$

$$\langle 2|H(c_1|1\rangle + c_2|2\rangle) = \langle 2|E(c_1|1\rangle + c_2|2\rangle)$$

- Define the following:

Hamiltonian elements $H_{ij} = \langle i|H|j\rangle$

$E_0 = H_{11} = H_{22}$ (E_0 is not the same as E_f due to the presence of the potential from the nearby second atom).

H_{11} & H_{22} are referred to as the **on-site Hamiltonian matrix elements** because they involve states only on the same atom.

- Using the orthogonality of the basis, we finally simplify as follows:

$$E_0 c_1 + H_{12} c_2 = E c_1$$

$$H_{21} c_1 + E_0 c_2 = E c_2$$

The diatomic molecule: H_2

$$E_0 c_1 + H_{12} c_2 = E c_1$$

$$H_{21} c_1 + E_0 c_2 = E c_2$$

- The equations above result in the following:

$$\begin{vmatrix} E_0 - E & H_{12} \\ H_{21} & E_0 - E \end{vmatrix} = 0 \Rightarrow E^2 - 2E_0 E + E_0^2 - H_{12} H_{21} = 0.$$

- We assume a Hermitian Hamiltonian and the orbitals ($1s$) are real. Thus H_{ij} are real. Let $H_{12}=H_{21}=\beta$. We finally obtain:

$$E_b = E_0 + \beta$$

⇒

$$|\Psi_b\rangle = \frac{1}{(2)^{1/2}} (|1\rangle + |2\rangle)$$

$$E_a = E_0 - \beta$$

$$|\Psi_a\rangle = \frac{1}{(2)^{1/2}} (|1\rangle - |2\rangle)$$

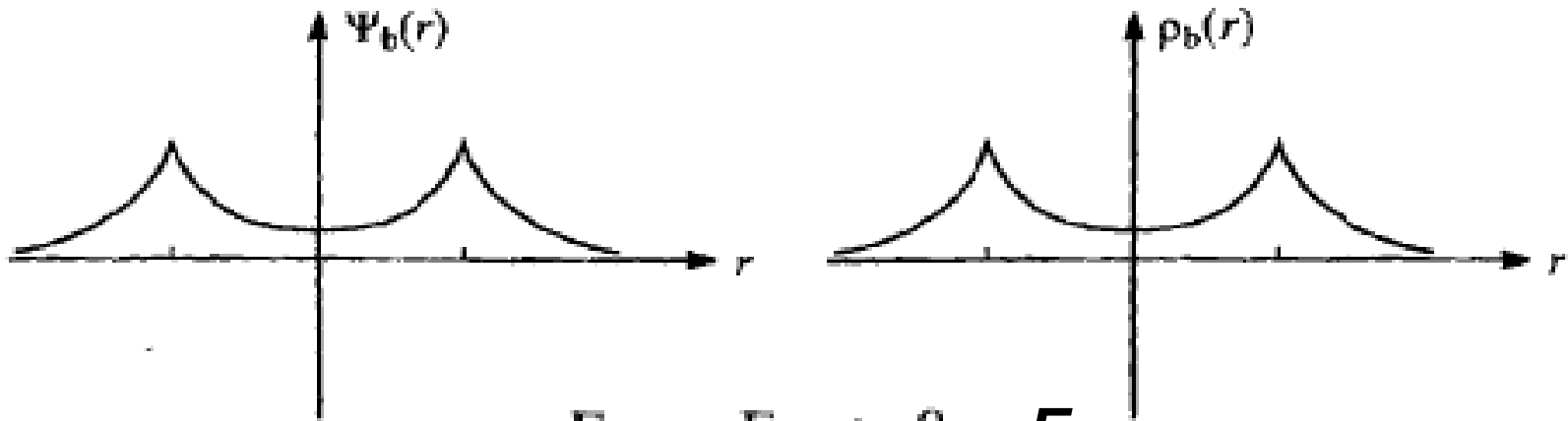
The hopping parameter or integral β

- We will see that β involves the transfer of an electron from one state (atom) to another.
- Here we will show that $\beta < 0$. Indeed:

$$\beta = \langle 1|H|2\rangle, \text{ where } H = -\frac{\hbar^2\nabla^2}{8\pi^2m} + V_1(\mathbf{r}) + V_2(\mathbf{r})$$

$$\begin{aligned} H_{12} &= \langle 1| -\frac{\hbar^2\nabla^2}{8\pi^2m} + V_1(\mathbf{r}) + V_2(\mathbf{r})|2\rangle \\ &= \langle 1| -\frac{\hbar^2\nabla^2}{8\pi^2m} + V_1(\mathbf{r})|2\rangle + \langle 1|V_2(\mathbf{r})|2\rangle \\ &= \langle 1|E_1|2\rangle + \langle 1|V_2(\mathbf{r})|2\rangle \\ &= \langle 1|V_2(\mathbf{r})|2\rangle < 0 \text{ (} V_2 \text{ is attractive to an electron} \\ &\quad \text{and thus } < 0 \text{)} \end{aligned}$$

Bonding state

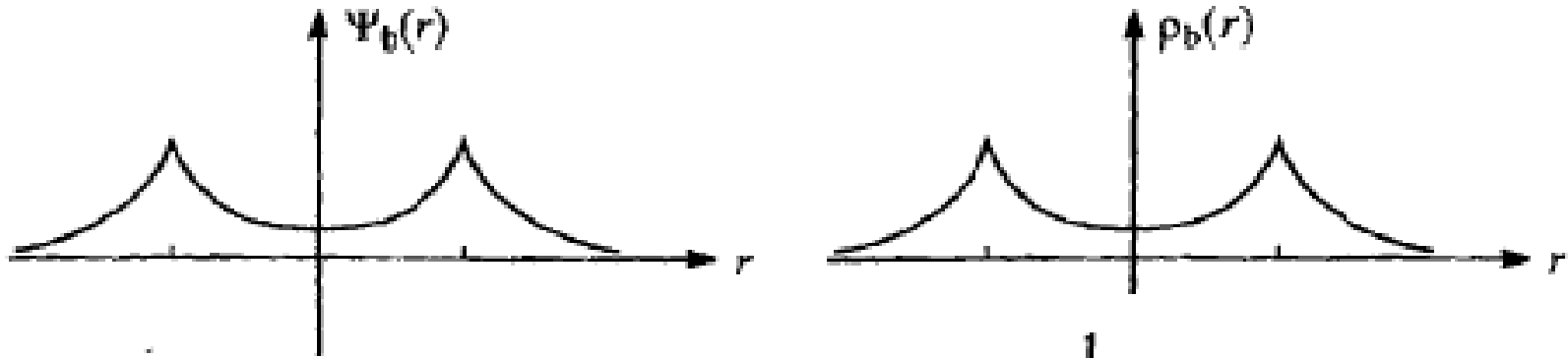


$$E_b = E_0 + \beta < E_0$$

$$|\Psi_b\rangle = \frac{1}{(2)^{1/2}} (|1\rangle + |2\rangle)$$

- It corresponds to a symmetrical combination of the basis states. The two electrons in the H_2 molecule occupy this molecular state with opposite spins.
- The electronic contribution to the total energy is lower in the molecule than for two isolated atoms by $2|\beta|$. This is the source of the cohesion in the molecule.

Bonding state



$$E_b = E_0 + \beta < E_0$$

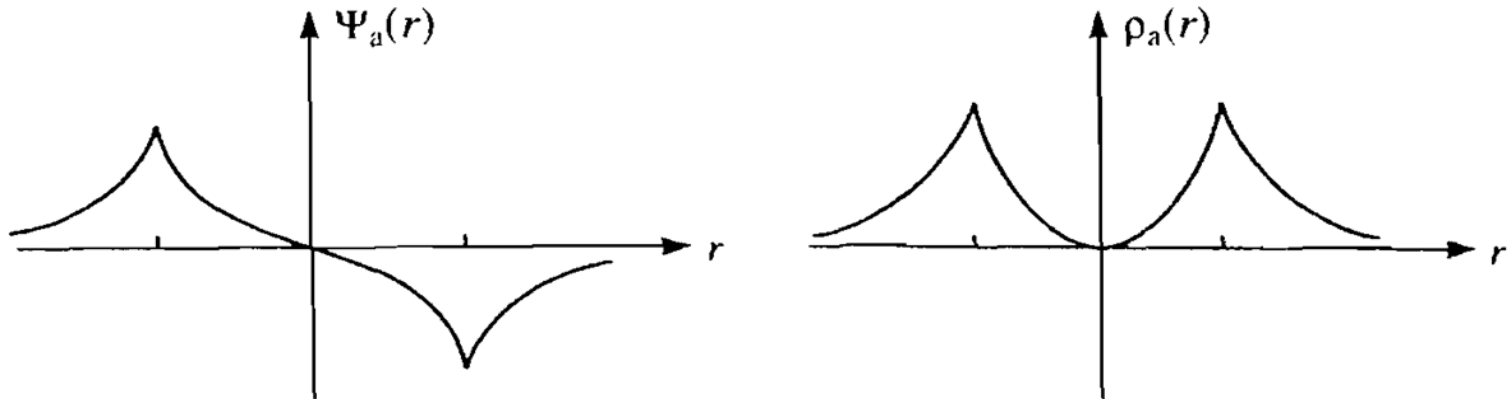
$$|\Psi_b\rangle = \frac{1}{(2)^{1/2}} (|1\rangle + |2\rangle)$$

$$\rho_b(r) = 2\Psi_b(r)\Psi_b(r) = \rho_1(r) + \rho_2(r) + \rho_{\text{bond}}(r)$$

$$\rho_{\text{bond}}(r) = 2\Psi_1(r)\Psi_2(r)$$

- The bonding state leads to charge being heaped up in the region between the atoms. This charge is electrostatically attracted to both nuclei and pulls the nuclei together.
- **Bonding arises from interference of quantum mechanical waves.**

Antibonding state

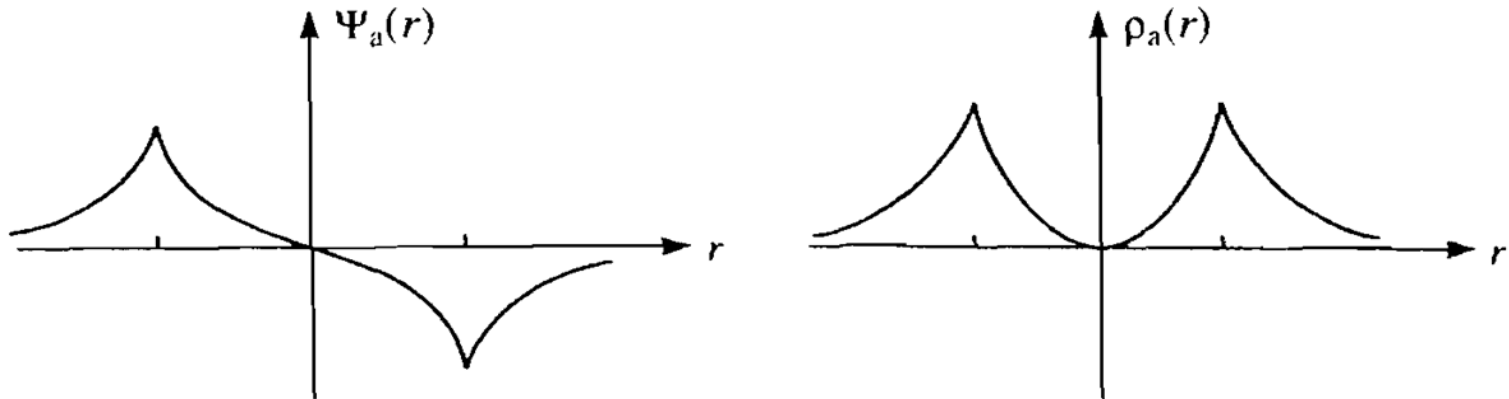


$$E_a = E_0 - \beta > E_0$$

$$|\Psi_a\rangle = \frac{1}{(2)^{1/2}} (|1\rangle - |2\rangle)$$

- It corresponds to an asymmetrical combination of the basis states.
- Since $E_a > E_0$, its occupation would not lead to bonding.

Antibonding state



$$E_a = E_0 - \beta > E_0$$

$$|\Psi_a\rangle = \frac{1}{(2)^{1/2}} (|1\rangle - |2\rangle)$$

- In the antibonding state, the charge density has a cusp at the mid-point between the atoms.

The H_2 molecule using a time-dependent analysis

- We repeat the same calculations but using the time-dependent Schrödinger equ.

$$i \frac{\hbar}{2\pi} \frac{d|\Psi\rangle}{dt} = H|\Psi\rangle$$

- Expanding the molecular state in the atomic orbitals, $|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$, we obtain:

$$i \frac{\hbar}{2\pi} \frac{dc_1}{dt} = H_{11}c_1 + H_{12}c_2$$

$$i \frac{\hbar}{2\pi} \frac{dc_2}{dt} = H_{21}c_1 + H_{22}c_2.$$

- We assume solutions of the form $c_1(t)=A_1e^{-i\omega t}$ and $c_2(t)=A_2e^{-i\omega t}$. Substitution gives:

$$\omega_b = 2\pi \frac{E_0 + \beta}{\hbar} \quad \omega_a = 2\pi \frac{E_0 - \beta}{\hbar}$$

The H_2 molecule using a time-dependent analysis

$$c_1(t) = a \exp\left(-2\pi i \frac{E_0 + \beta}{h} t\right) + b \exp\left(-2\pi i \frac{E_0 - \beta}{h} t\right)$$

$$c_2(t) = a \exp\left(-2\pi i \frac{E_0 + \beta}{h} t\right) - b \exp\left(-2\pi i \frac{E_0 - \beta}{h} t\right)$$

- We need initial conditions for $c_1(t)$ and $c_2(t)$. Assume that at $t=0$, the electron is in state 1 (atom 1). Thus $c_1(0)=1$ and $c_2(0)=0$. This leads to the following:

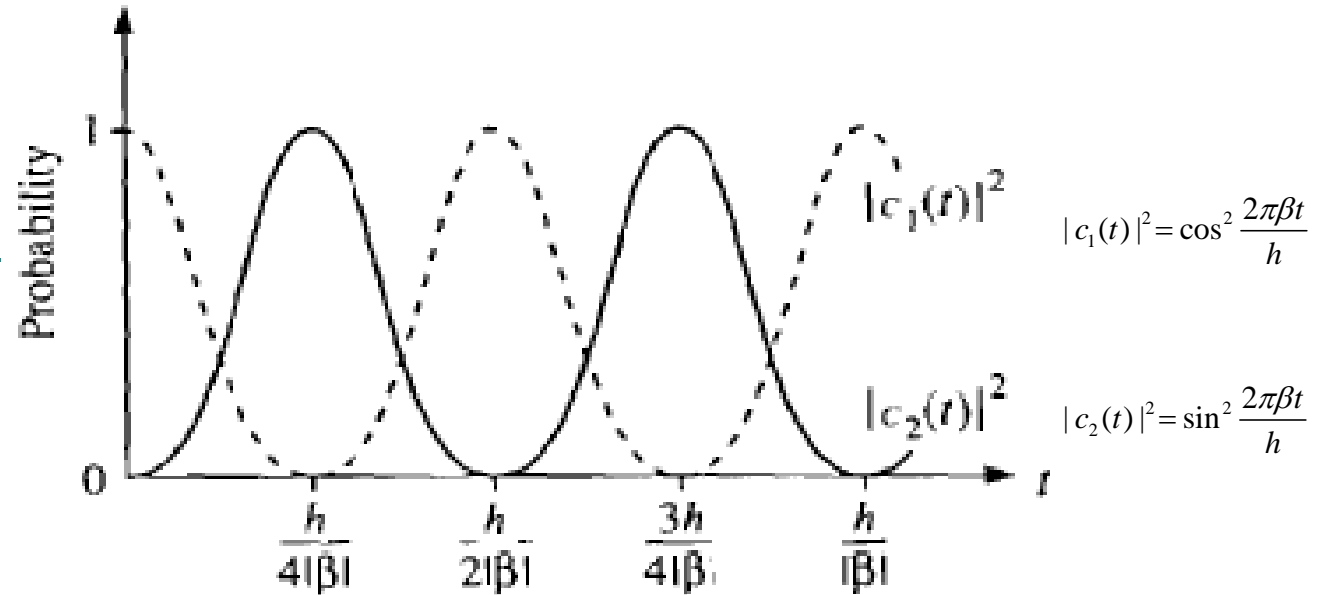
$$c_1(t) = e^{-2\pi i E_0 t/h} \cos(2\pi \beta t/h) \quad c_2(t) = e^{-2\pi i E_0 t/h} \sin(2\pi \beta t/h)$$

- The probability that the molecule is in state $|2\rangle$ is given as $|c_2|^2$.

$$|c_2(t)|^2 = \sin^2 \frac{2\pi \beta t}{h}$$

The H_2 molecule using a time-dependent analysis

From Sutton's
Electronic Structure of
Materials



Probabilities of an electron occupying the atomic states $|1\rangle$ and $|2\rangle$ as a function of time in a diatomic homo-nuclear molecule

- The electron tunnels through the energy barrier (ionization energy of a H-atom in its ground state is ~ 13.6 eV).
- The probability per unit time that the electron hops from one atom to the other is $2|\beta|/h$. β is called the hopping parameter (or integral).

Chemical bonding between homonuclear atoms

- Electrons become delocalized by tunnelling through the energy barrier separating neighboring atoms.
- When atoms are brought together electronic charge is piled up in the bonds. This is a result of tunneling and quantum interference between the free atomic states.
- The greater the tunneling rate $2|\beta|/\hbar$, the lower the energy of the bonding state relative to the free atomic state.

Heteronuclear diatomic molecules: covalency and ionicity

- The worked-out example for the H_2 molecule can serve as a template for the *hetero-nuclear diatomic* molecule (different atoms A and B in the molecule).
- The atomic states and energies are now different.
 - **The fact that the nuclei are not the same has some profound consequences**
 - **It can result in ionic bonding in the molecule**

Heteronuclear diatomic molecules: covalency and ionicity

- We assume an AB diatomic molecule with $E_A > E_B$.
- As before, we expand the molecular state in the atomic states as follows:

$$|\Psi\rangle = c_A|A\rangle + c_B|B\rangle$$

- Using the earlier process for the time-independent Schrödinger equ. leads to:

$$(E_A - E)c_A + \beta c_B = 0$$

$$\beta c_A + (E_B - E)c_B = 0.$$

- Solving these equations results in the following energies:

$$E_b = \varepsilon - (\Delta^2 + \beta^2)^{1/2}$$

$$E_a = \varepsilon + (\Delta^2 + \beta^2)^{1/2}$$

$$\text{with } \Delta = (E_A - E_B)/2 \text{ and } \varepsilon = (E_A + E_B)/2$$

Heteronuclear diatomic molecules: covalency and ionicity

- Inserting the bonding and antibonding energies in the secular equation, we obtain the following.

$$\frac{c_A^2}{c_B^2} = \frac{1}{1 + 2x^2 + 2x(1 + x^2)^{1/2}}$$

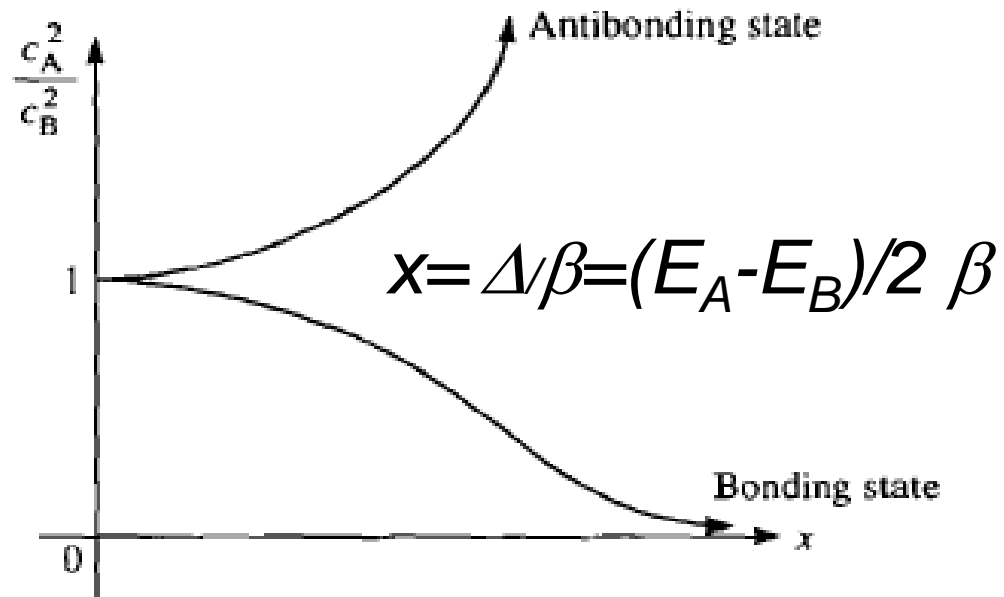
for the bonding state

$$\frac{c_A^b}{c_B^b} = -\frac{1}{x + \sqrt{x^2 + 1}}$$

$$\frac{c_A^2}{c_B^2} = \frac{1}{1 + 2x^2 - 2x(1 + x^2)^{1/2}}$$

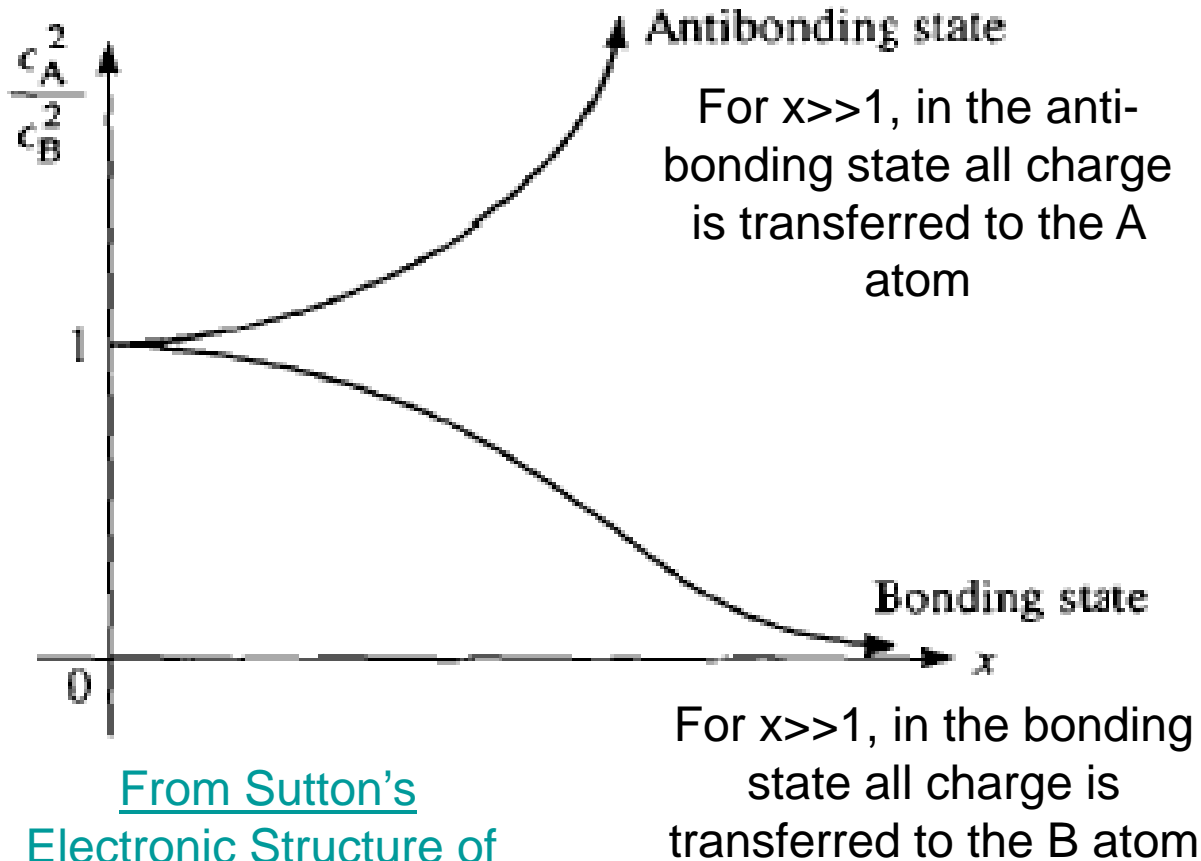
for the antibonding state

$$\frac{c_A^a}{c_B^a} = -\frac{1}{x - \sqrt{x^2 + 1}}$$



Occupation of the atomic state on the A atom to that on the B atom in an AB molecule, for the bonding and antibonding molecular states

Heteronuclear diatomic molecules: covalency and ionicity



[From Sutton's Electronic Structure of Materials](#)

- The bond becomes partially ionic since charge transfer occurs.
- We define the degree of polarity or covalency of the bond (extent of the ionic/covalent bonding) using:

$$\alpha_p = \frac{x}{(1 + x^2)^{1/2}}$$
$$\alpha_c = \frac{1}{(1 + x^2)^{1/2}}$$

Electronegativity

- For the case $E_A > E_B$ and in the bonding state charge is transferred from the A (atom with the higher on-site energy) to B (the atom with the lower on-site energy).
- **Electronegativity is defined as the power of an atom to attract electrons to itself from neighbouring atoms in its environment (Pauling).**
- **It is a property of the atom and the environment it finds itself in.**
- Mulliken defined electronegativity as follows:

$$\chi_A = \frac{1}{2}(\text{IP}_A + \text{EA}_A)$$

- IP_A is the **ionization potential** of atom A (the energy required to remove an outer electron) and EA_A is **the electron affinity** of atom A (the negative of the energy of adding an electron).

Electronegativity

$$\chi_A = \frac{1}{2}(\text{IP}_A + \text{EA}_A)$$

- The reasoning for arriving at this definition is as follows: We consider an A-B bond to be covalent if the energy of an A^+B^- bond is about the same as the energy of an A^-B^+ bond.
- The criterion for a non-polar bond is then the following:

$$\text{IP}_A - \text{EA}_B = \text{IP}_B - \text{EA}_A$$

Energy required to
make an A^+B^- bond

Energy required to
make an A^-B^+ bond

- Thus we conclude that for a covalent bond (i.e. with A and B having the same electronegativity):

$$\text{IP}_A + \text{EA}_A = \text{IP}_B + \text{EA}_B.$$

Electronegativity

- On the other hand, if $IP_A + EA_A > IP_B + EA_B$ then the energy cost of the A^+B^- bond is greater than the energy of the A^-B^+ bond.
- In that case charge transfer from the B atom to the A atom is favorable, i.e. A has higher electronegativity.
- This is entirely consistent with saying that χ_A is a suitable electronegativity scale.

$$\chi_A = \frac{1}{2}(IP_A + EA_A)$$

Electronegativity – Pauling scale

In [this table](#), the elements colored in pink are highly electronegative (readily attract electrons and form chemical bonds), while the elements in purple have lower electronegativity values. Values for the [noble gases](#) are not given on this list – they all have very low electronegativities and will not readily attract electrons.

2.1 H																	
1.0 Li	1.5 Be											2.0 B	2.5 C	3.0 N	3.5 O	4.0 F	
1.0 Na	1.2 Mg											1.5 Al	1.8 Si	2.1 P	2.5 S	3.0 Cl	
0.9 K	1.0 Ca	1.3 Sc	1.4 Ti	1.5 V	1.6 Cr	1.6 Mn	1.7 Fe	1.7 Co	1.8 Ni	1.8 Cu	1.6 Zn	1.7 Ga	1.9 Ge	2.1 As	2.4 Se	2.8 Br	
0.9 Rb	1.0 Sr	1.2 Y	1.3 Zr	1.5 Nb	1.6 Mo	1.7 Tc	1.8 Ru	1.8 Rh	1.8 Pd	1.6 Ag	1.6 Cd	1.6 In	1.8 Sn	1.9 Sb	2.1 Te	2.5 I	
0.8 Cs	1.0 Ba	1.1 La	1.3 Hf	1.4 Ta	1.5 W	1.7 Re	1.9 Os	1.9 Ir	1.8 Pt	1.9 Au	1.7 Hg	1.6 Tl	1.7 Pb	1.8 Bi	1.9 Po	2.1 At	
0.8 Fr	1.0 Ra	1.1 Ac															

- Less than 2.0
- 2.0 or greater

Bond order and bond energy

- Let us return to the AB diatomic molecule with $E_A > E_B$. The secular eqs. are:

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

- Let us apply this for the bonding state (we assume we already computed E_b).

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A^b \\ c_B^b \end{pmatrix} = E_b \begin{pmatrix} c_A^b \\ c_B^b \end{pmatrix}$$

- From this equation we can further compute:

$$(c_A^{b*} \quad c_B^{b*}) \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A^b \\ c_B^b \end{pmatrix} = (c_A^{b*} c_A^b + c_B^{b*} c_B^b) E_b.$$

- We can simplify by using the normalization condition:

$$(c_A^{b*} c_A^b + c_B^{b*} c_B^b) = 1$$

Bond order and bond energy

- We thus arrive at the following forms for the bonding (and similarly for the anti-bonding) energies:

$$E_b = c_A^b c_A^{b*} H_{AA} + c_B^b c_B^{b*} H_{BB} + \{c_A^b c_B^{b*} H_{BA} + c_B^b c_A^{b*} H_{AB}\}$$

$$E_a = c_A^a c_A^{a*} H_{AA} + c_B^a c_B^{a*} H_{BB} + \{c_A^a c_B^{a*} H_{BA} + c_B^a c_A^{a*} H_{AB}\}.$$

- $c_A^b c_A^{b*}$ is the probability of finding the electron on the A atom in the bonding state.
- $c_A^b c_A^{b*} H_{AA}$ is the energy contribution coming from the time spent by the electron on the A atom in the bonding state. Similarly, for $c_B^b c_B^{b*} H_{BB}$
- Finally $\{c_A^b c_B^{b*} H_{BA} + c_B^b c_A^{b*} H_{AB}\}$ is the part of the energy of the bonding state that comes from the time spent in the bond region (**bond energy contribution**).

Bond order and bond energy

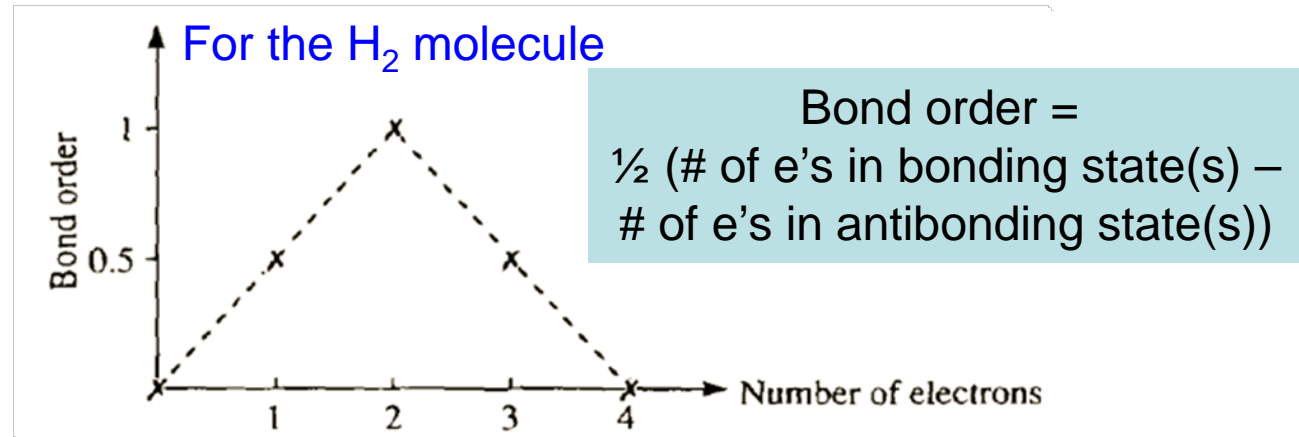
- Using $H_{AB}=H_{BA}$ and that the eigenvectors are real, we see that the bond energy contribution to the energy of the bonding state is the following:

$$\{c_A^b c_B^{b*} H_{BA} + c_B^b c_A^{b*} H_{AB}\} = (c_A^b c_B^{b*} + c_A^{b*} c_B^b) H_{AB} = 2c_A^b c_B^b H_{AB}$$

- $c_A^b c_B^b$ is called the 'partial bond' order of the AB bond (interference term)
- The **total bond order** is the sum of the partial bond orders taken over all occupied states.
- The **bond energy** is **twice** the bond order times the hopping parameter.

Bond order and bond energy

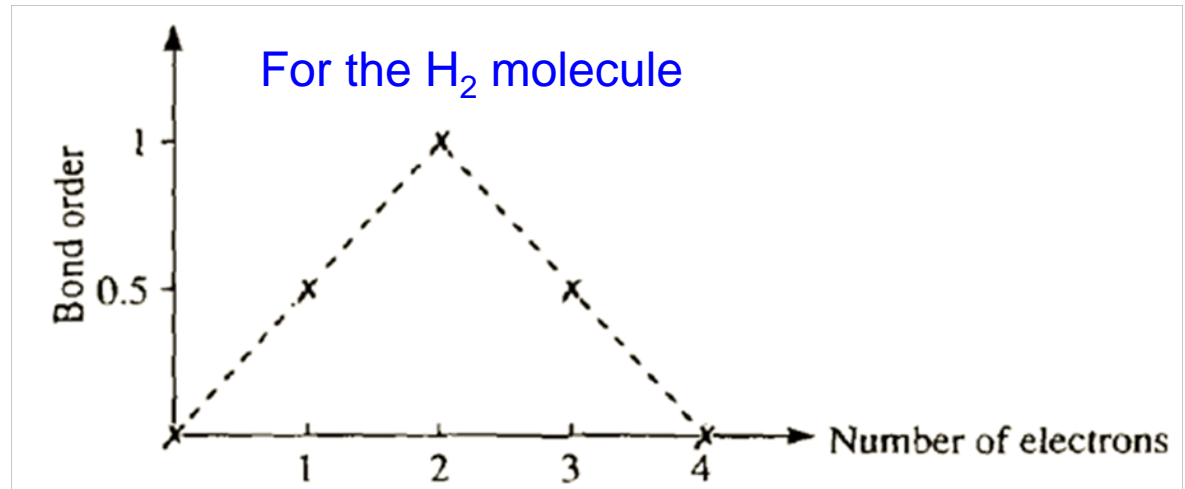
From Sutton's
Electronic Structure of
Materials



- When we only have one electron in the molecule, it fills half of the bonding state and the bond order is $C_A^b C_B^b$.
- Two electrons fill the bonding state and the bond order is $2 C_A^b C_B^b$.
- If a third electron is added, it will fill half of the antibonding state. The total bond order is then $2 C_A^b C_B^b + C_A^a C_B^a$.
- For 4 electrons, the bond order becomes: $2(C_A^b C_B^b + C_A^a C_B^a) = 0!$

Bond order and bond energy

From Sutton's
Electronic Structure of
Materials



- The bond order is zero when both the bonding and antibonding states are fully-occupied.
- If both the bonding and antibonding states are fully occupied (by two electrons each), then the total electronic energy is $2(H_{AA} + H_{BB})$ and there is no bond energy.
- This can also be seen from the invariance of the trace of a matrix under a similarity transformation: $E_{tot}^e = 2(E_b + E_a) = 2[H_{AA} + H_{BB}]$