MOLECOLE bi-atomiche e poli-atomiche

Metodo VB (Valence Bond)

Promozione

Orbitali ibridi

Chimica Fisica 2

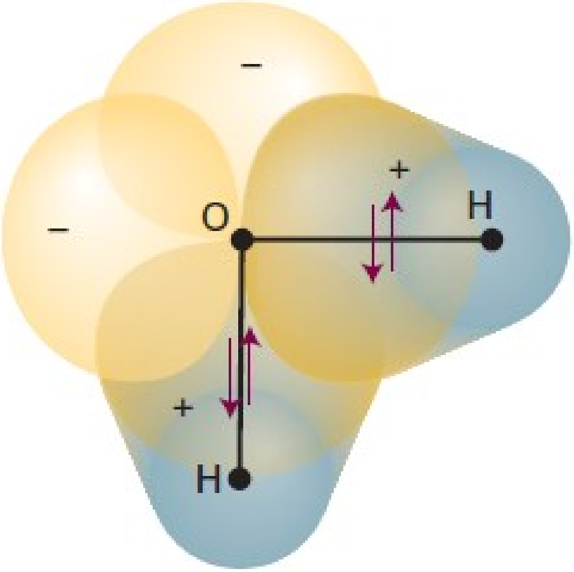
Laurea Tri. Chim. Ind. 2022-23

Mar. 23-5-2023 **CONTINUAZIONE**

Prof. Antonio Toffoletti

Teoria del legame di valenza (VB=Valence Bond)

Problema con gli angoli di legame – Molecola H_2O



ossigeno - O

config. elettronica $1s^2\ \ 2s^2\ \ 2p^4$

$2p_x^{\,1}\ 2p_y^{\,1}\ 2p_z^{\,2}$

idrogeno - H

config. elettronica $1s^1$

Fig. 10.6 A first approximation to the valence-bond description of bonding in an H_2O molecule. Each σ bond arises from the overlap of an H1s orbital with one of the O2p orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value. (≈104.5°)

Teoria del legame di valenza (VB=Valence Bond)

Promozione

Another deficiency of this initial formulation of VB theory is its inability to account for carbon's tetravalence (its ability to form four bonds). The ground-state configuration of C is $2s^2 2p_x^1 2p_y^1$, which suggests that a carbon atom should be capable of forming only two bonds, not four. This deficiency is overcome by allowing for **promotion**, the excitation of an electron to an orbital of higher energy. In carbon, for example, the promotion of a 2s electron to a 2p orbital can be thought of as leading to the configuration $2s^1 2p_x^1 2p_y^1 2p_z^1$, with four unpaired electrons in separate orbitals. These electrons may pair with four electrons in orbitals provided by four other atoms (such as four H1s orbitals if the molecule is CH_4), and hence form four σ bonds. Although energy was required to promote the electron, it is more than recovered by the promoted atom's ability to form four bonds in place of the two bonds of the unpromoted atom. Promotion, and the formation of four bonds, is a characteristic feature of carbon because the promotion energy is quite small: the promoted electron leaves a doubly occupied 2s orbital and enters a vacant 2p orbital, hence significantly relieving the electron–electron repulsion it experiences in the former. However, we need to remember that promotion is not a 'real' process in which an atom somehow becomes excited and then forms bonds: it is a notional contribution to the overall energy change that occurs when bonds form.

Teoria del legame di valenza (VB=Valence Bond)

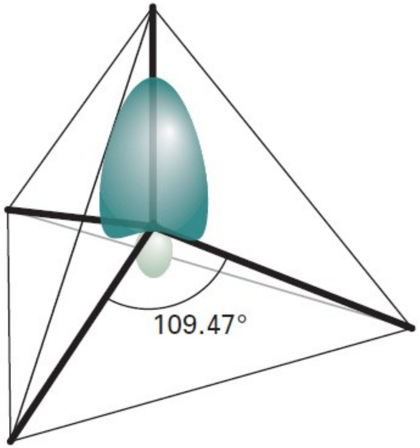
Orbitali ibridi **sp^3**

The description of the bonding in CH_4 (and other alkanes) is still incomplete because it implies the presence of three σ bonds of one type (formed from H1s and C2p orbitals) and a fourth σ bond of a distinctly different character (formed from H1s and C2s). This problem is overcome by realizing that the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a **hybrid orbital** formed by interference between the C2s and C2p orbitals of the same atom. The origin of the hybridization can be appreciated by thinking of the four atomic orbitals centred on a nucleus as waves that interfere destructively and constructively in different regions, and give rise to four new shapes.

As we show in the following *Justification*, the specific linear combinations that give rise to four equivalent hybrid orbitals are

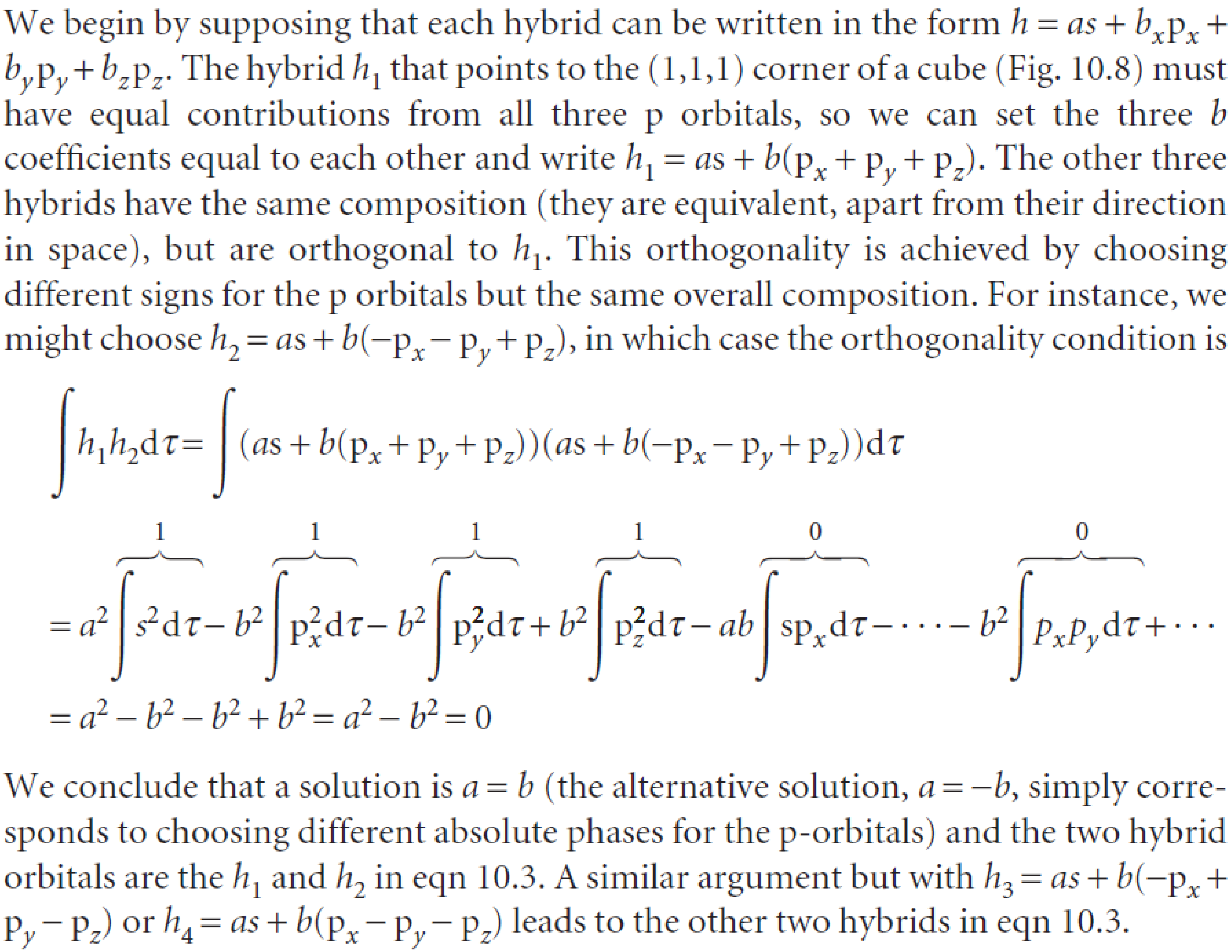
$$h_1 = s + p_x + p_y + p_z \qquad h_2 = s - p_x - p_y + p_z$$
$$h_3 = s - p_x + p_y - p_z \qquad h_4 = s + p_x - p_y - p_z$$

Orbitali ibridi sp^3



Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi **sp^3**



We begin by supposing that each hybrid can be written in the form $h = as + b_x p_x + b_y p_y + b_z p_z$. The hybrid h_1 that points to the (1,1,1) corner of a cube (Fig. 10.8) must have equal contributions from all three p orbitals, so we can set the three b coefficients equal to each other and write $h_1 = as + b(p_x + p_y + p_z)$. The other three hybrids have the same composition (they are equivalent, apart from their direction in space), but are orthogonal to h_1. This orthogonality is achieved by choosing different signs for the p orbitals but the same overall composition. For instance, we might choose $h_2 = as + b(-p_x - p_y + p_z)$, in which case the orthogonality condition is

$$\int h_1 h_2 \mathrm{d}\tau = \int (as + b(p_x + p_y + p_z))(as + b(-p_x - p_y + p_z))\mathrm{d}\tau$$

$$= a^2 \overbrace{\int s^2 \mathrm{d}\tau}^{1} - b^2 \overbrace{\int p_x^2 \mathrm{d}\tau}^{1} - b^2 \overbrace{\int p_y^2 \mathrm{d}\tau}^{1} + b^2 \overbrace{\int p_z^2 \mathrm{d}\tau}^{1} - ab \overbrace{\int s p_x \mathrm{d}\tau}^{0} - \cdots - b^2 \overbrace{\int p_x p_y \mathrm{d}\tau}^{0} + \cdots$$

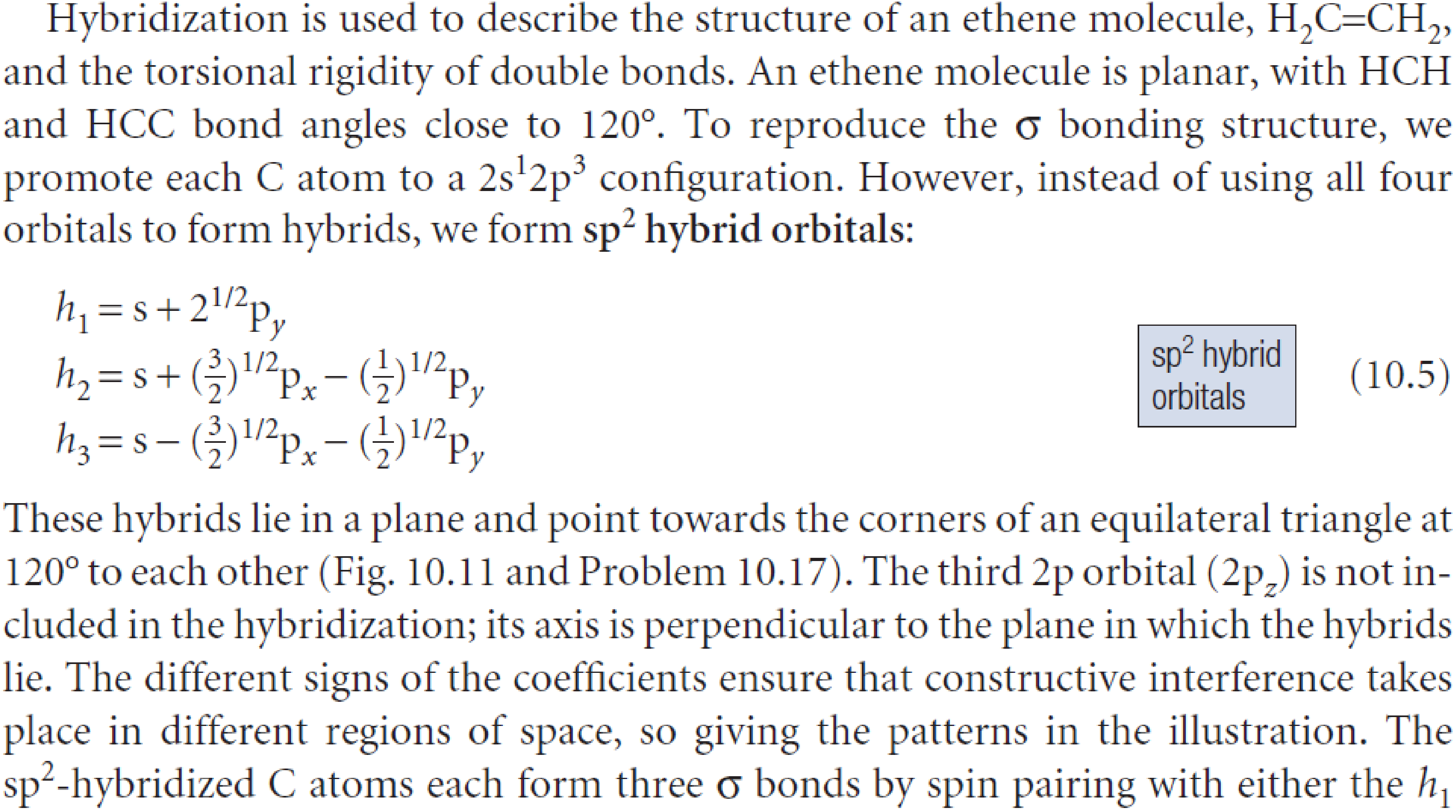
$$= a^2 - b^2 - b^2 + b^2 = a^2 - b^2 = 0$$

We conclude that a solution is $a = b$ (the alternative solution, $a = -b$, simply corresponds to choosing different absolute phases for the p-orbitals) and the two hybrid orbitals are the h_1 and h_2 in eqn 10.3. A similar argument but with $h_3 = as + b(-p_x + p_y - p_z)$ or $h_4 = as + b(p_x - p_y - p_z)$ leads to the other two hybrids in eqn 10.3.

Orbitali ibridi sp

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi **sp^2**



Hybridization is used to describe the structure of an ethene molecule, $H_2C{=}CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120°. To reproduce the σ bonding structure, we promote each C atom to a $2s^1 2p^3$ configuration. However, instead of using all four orbitals to form hybrids, we form **sp^2 hybrid orbitals:**

$$\begin{aligned} h_1 &= s + 2^{1/2}p_y \\ h_2 &= s + (\tfrac{3}{2})^{1/2}p_x - (\tfrac{1}{2})^{1/2}p_y \\ h_3 &= s - (\tfrac{3}{2})^{1/2}p_x - (\tfrac{1}{2})^{1/2}p_y \end{aligned} \qquad (10.5)$$

sp^2 hybrid orbitals

These hybrids lie in a plane and point towards the corners of an equilateral triangle at 120° to each other (Fig. 10.11 and Problem 10.17). The third 2p orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. The different signs of the coefficients ensure that constructive interference takes place in different regions of space, so giving the patterns in the illustration. The sp^2-hybridized C atoms each form three σ bonds by spin pairing with either the h_1

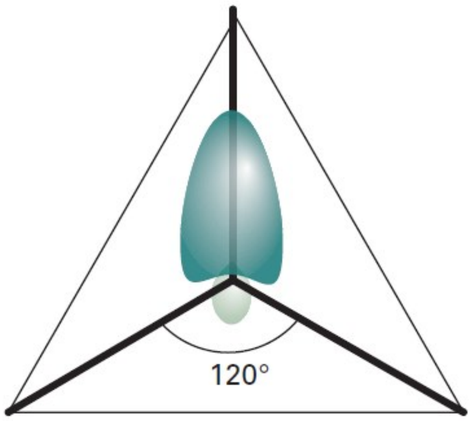
Orbitali ibridi sp^2

Teoria del legame di valenza (VB=Valence Bond)

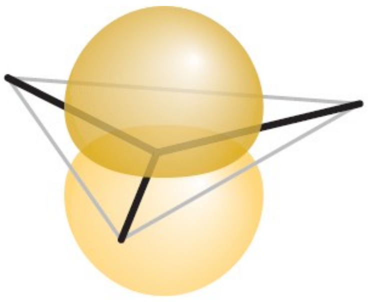
Orbitali ibridi **sp²**

$$
\begin{aligned}
h_1 &= \mathrm{s} + 2^{1/2}\mathrm{p}_y \\
h_2 &= \mathrm{s} + \left(\tfrac{3}{2}\right)^{1/2}\mathrm{p}_x - \left(\tfrac{1}{2}\right)^{1/2}\mathrm{p}_y \\
h_3 &= \mathrm{s} - \left(\tfrac{3}{2}\right)^{1/2}\mathrm{p}_x - \left(\tfrac{1}{2}\right)^{1/2}\mathrm{p}_y
\end{aligned}
\qquad \text{sp}^2 \text{ hybrid orbitals} \qquad (10.5)
$$

These hybrids lie in a plane and point towards the corners of an equilateral triangle at 120° to each other (Fig. 10.11 and Problem 10.17). The third 2p orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. The different signs of the coefficients ensure that constructive interference takes place in different regions of space, so giving the patterns in the illustration. The sp²-hybridized C atoms each form three σ bonds by spin pairing with either the h_1



Orbitali ibridi sp²



Il terzo orbitale 2p

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi **sp^2**

$$
\begin{aligned}
h_1 &= s + 2^{1/2}p_y \\
h_2 &= s + \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y \\
h_3 &= s - \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y
\end{aligned}
\tag{10.5}
$$

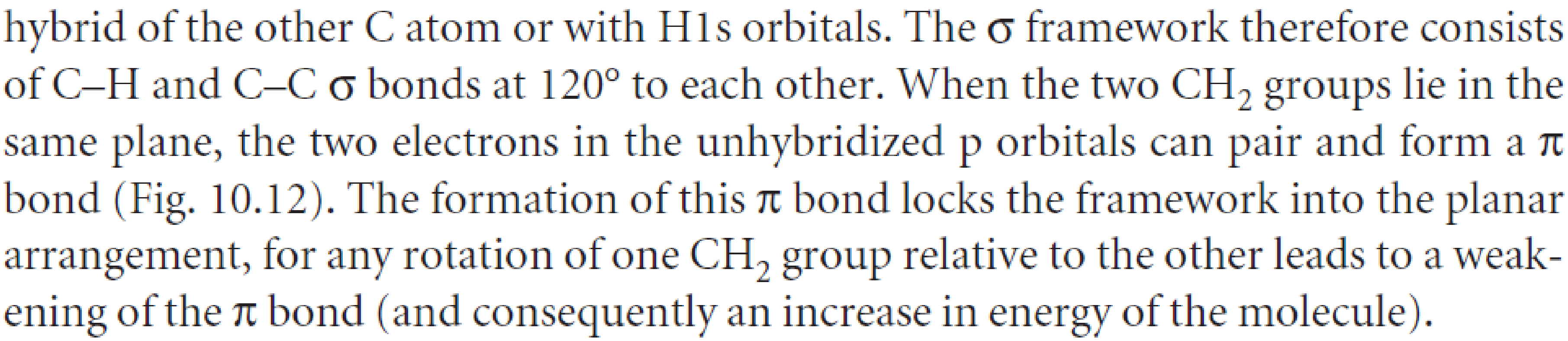
sp^2 hybrid orbitals

These hybrids lie in a plane and point towards the corners of an equilateral triangle at 120° to each other (Fig. 10.11 and Problem 10.17). The third 2p orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. The different signs of the coefficients ensure that constructive interference takes place in different regions of space, so giving the patterns in the illustration. The sp^2-hybridized C atoms each form three σ bonds by spin pairing with either the h_1 hybrid of the other C atom or with H1s orbitals. The σ framework therefore consists of C–H and C–C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized p orbitals can pair and form a π bond (Fig. 10.12). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

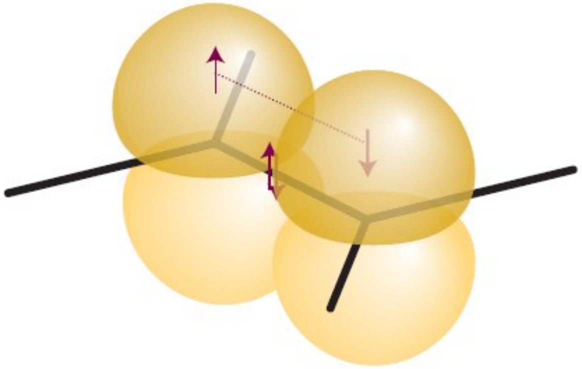
Orbitali ibridi sp^2

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi **sp^2**



hybrid of the other C atom or with H1s orbitals. The σ framework therefore consists of C–H and C–C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized p orbitals can pair and form a π bond (Fig. 10.12). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).



Orbitali ibridi sp^2

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi sp^2

$$\begin{aligned}
h_1 &= s + 2^{1/2}p_y \\
h_2 &= s + \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y \\
h_3 &= s - \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y
\end{aligned} \qquad (10.5)$$

sp^2 hybrid orbitals

	s	p_x	p_y	p_z
h_1	1	0	$\sqrt{2}$	0
h_2	1	$\sqrt{(3/2)}$	$-1/\sqrt{2}$	0
h_3	1	$-\sqrt{(3/2)}$	$-1/\sqrt{2}$	0

	QUADRATI				SOMMA
h_1	1	0	2	0	3
h_2	1	3/2	+1/2	0	3
h_3	1	+3/2	+1/2	0	3

Orbitali ibridi sp^2

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi **sp**

A similar description applies to ethyne, HC≡CH, a linear molecule. Now the C atoms are **sp hybridized**, and the σ bonds are formed using hybrid atomic orbitals of the form

$$h_1 = s + p_z \qquad h_2 = s - p_z \qquad \boxed{\text{sp hybrid orbitals}} \qquad (10.6)$$

These two hybrids lie along the internuclear axis. The electrons in them pair either with an electron in the corresponding hybrid orbital on the other C atom or with an electron in one of the H1s orbitals. Electrons in the two remaining p orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular π bonds (Fig. 10.13).

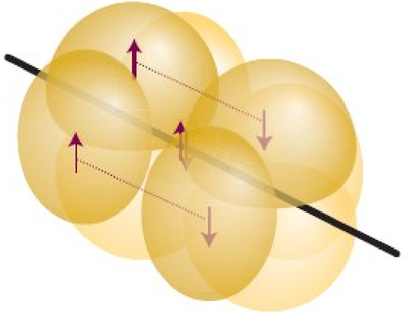


Fig. 10.13 A representation of the structure of a triple bond in ethyne; only the π bonds are shown explicitly. The overall electron density has cylindrical symmetry around the axis of the molecule.

Teoria del legame di valenza (VB=Valence Bond)

Orbitali ibridi di vari tipi

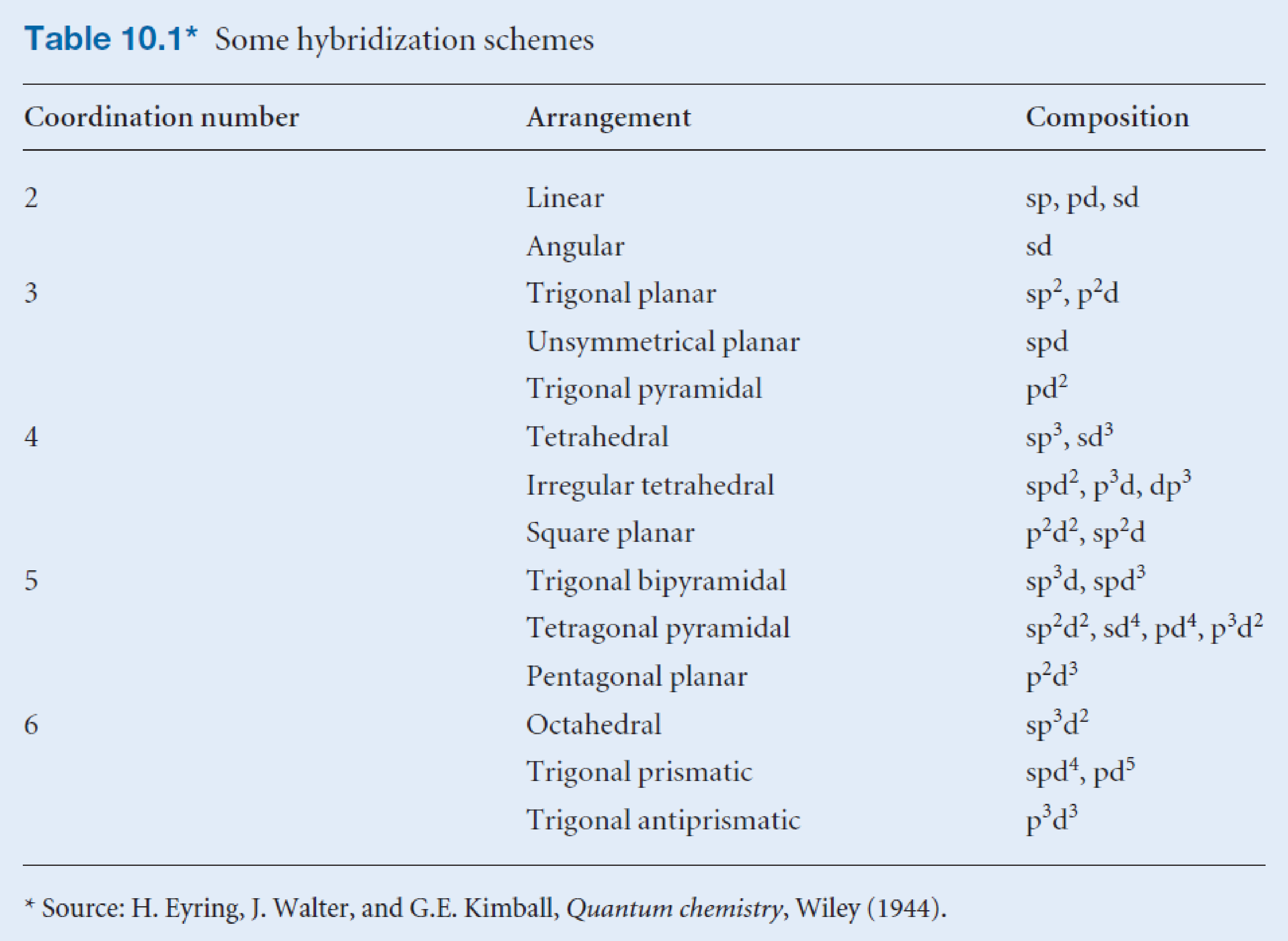


Table 10.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, dp^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

* Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*, Wiley (1944).

MOLECOLE bi-atomiche

ORBITALI MOLECOLARI

Chimica Fisica 2

Laurea Tri. Chim. Ind. 2022-23

Mar. 23-5-2023

Prof. Antonio Toffoletti

Struttura Molecolare

STRUTTURA MOLECOLARE

1. **Approssimazione di Born-Hoppenheimer (BO)**
2. **Teoria del legame di valenza (Valence Bond Theory)**
3. **Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)**

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Nella teoria MO, gli elettroni non appartengono a legami particolari ma si diffondono in tutto il intera molecola. Questa teoria è stata sviluppata in modo più completo rispetto alla teoria VB e fornisce il linguaggio ampiamente utilizzato nelle discussioni moderne sull'incollaggio. Introduce seguiamo la stessa strategia del capitolo 9, dove si trovava l'atomo H di un elettrone preso come la specie fondamentale per discutere la struttura atomica e poi sviluppato in una descrizione di atomi a molti elettroni. In questo capitolo usiamo il molecolare più semplice specie di tutte, la molecola ione di idrogeno, H_2^+, per introdurre le caratteristiche essenziali di legame e quindi utilizzarlo per descrivere le strutture di sistemi più complessi.

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Gli elettroni non appartengono a un particolare legame, ma sono distribuiti sull'intera molecola.

È la teoria più moderna per la descrizione del legame chimico.

Usa delle soluzioni **approssimate** all'equazione di Schroedinger:

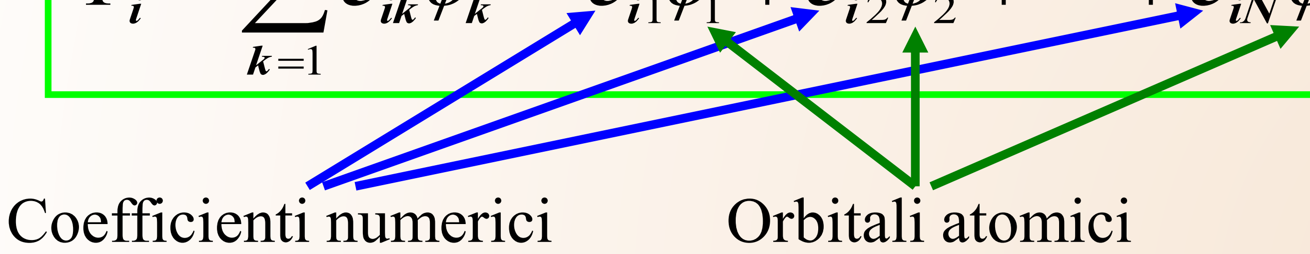
$$\boxed{\hat{H}\Psi = E\Psi}$$

Di solito queste soluzioni (Ψ_i), con energia E_i, vengono espresse come

combinazioni lineari di orbitali atomici
(LCAO - **L**inear **C**ombination of **A**tomic **O**rbitals)

della forma:

$$\boxed{\Psi_i = \sum_{k=1}^{N} c_{ik}\phi_k = c_{i1}\phi_1 + c_{i2}\phi_2 + \cdots + c_{iN}\phi_N}$$



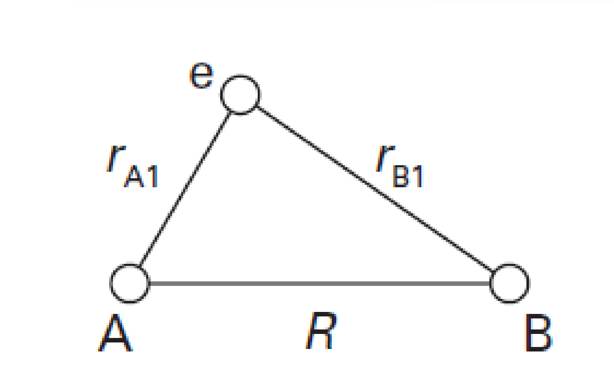
Coefficienti numerici

Orbitali atomici

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Hamiltoniano per H_2^+ :



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \qquad V = -\boxed{\frac{e^2}{4\pi\varepsilon_0}}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right)$$

Talvolta chiamato per brevità j_0

Attrazione dei nuclei

repulsione internucleare

Eq. di Schroedinger $\boxed{\hat{H}\Psi = E\Psi}$

Le soluzioni si chiamano Orbitali Molecolari **OM** (Molecular Orbitals **MOs**)

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Gli MOs permettono di calcolare, utilizzando Ψ^2, la distribuzione dell'elettrone nello spazio intorno ai nuclei.

Utilizza delle soluzioni **approssimate** all'equazione di Schroedinger

Di solito queste soluzioni (Ψ_i), con energia E_i, vengono espresse come

combinazioni lineari di orbitali atomici
(LCAO - **L**inear **C**ombination of **A**tomic **O**rbitals)

della forma:

$$\boxed{\Psi_i = \sum_{k=1}^{N} c_{ik}\phi_k = c_{i1}\phi_1 + c_{i2}\phi_2 + \cdots + c_{iN}\phi_N}$$

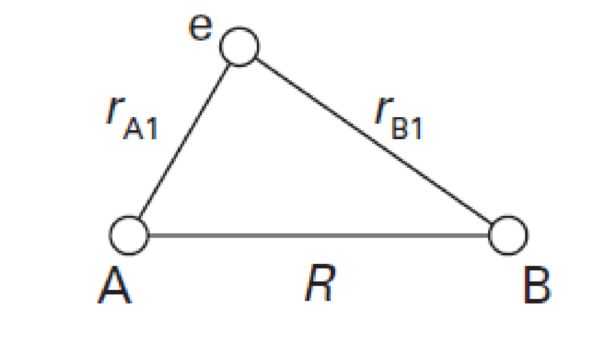
Coefficienti numerici

Orbitali atomici

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Per H_2+ può essere appropriato il seguente LCAO-MO



$$\Psi = N\phi_A + N\phi_B = N(\phi_A + \phi_B)$$

Dove ϕ_A e ϕ_B sono due orbitali atomici 1s di idrogeno cioè

$\phi_A = \phi_{H1sA}$ e $\phi_B = \phi_{H1sB}$

,

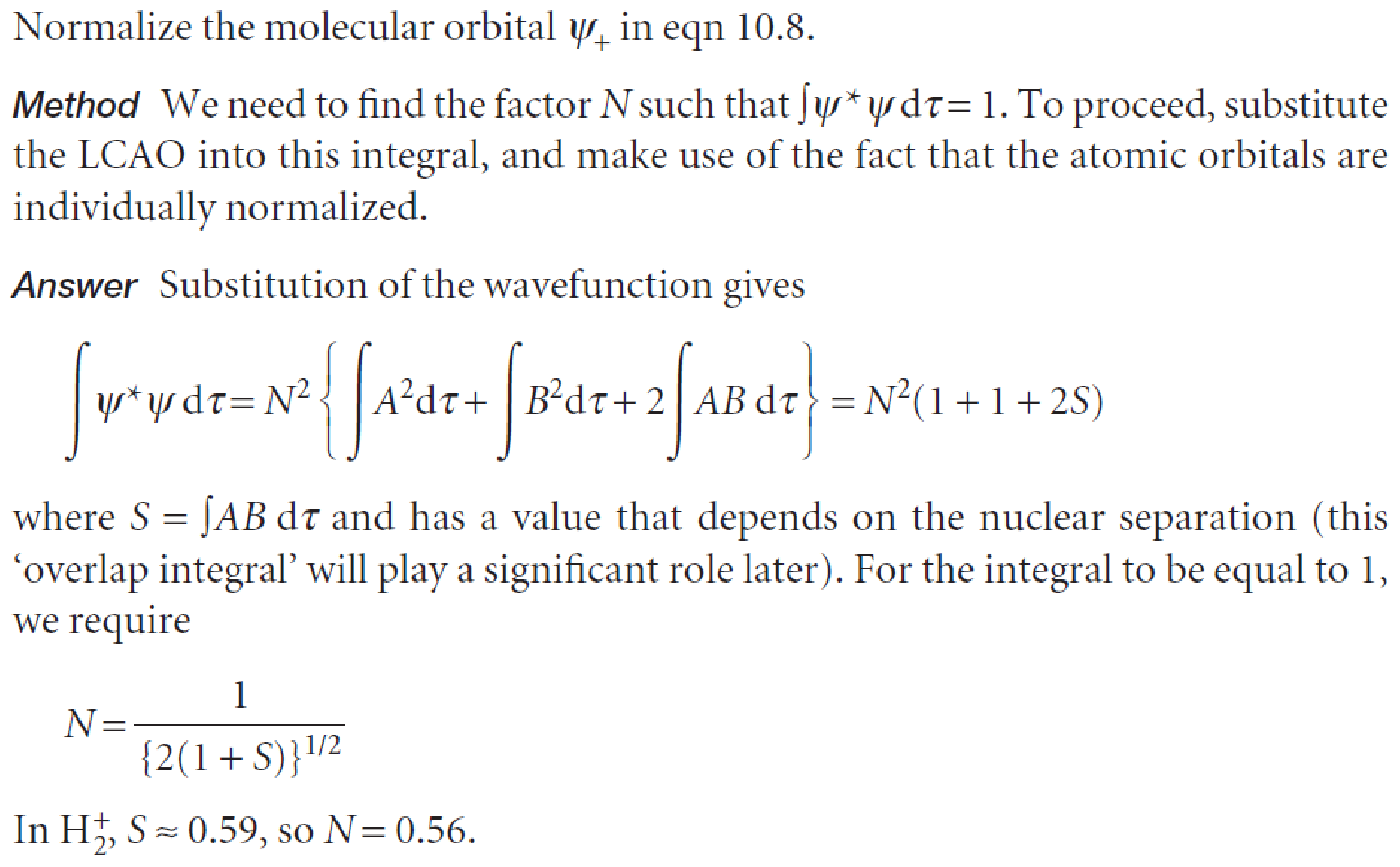
orbitale molecolare che ha la simmetria cilindrica attorno all'asse internucleare, come quella di cui stiamo discutendo, è chiamata s orbitale perché assomiglia a un orbitale se visto lungo l'asse e, più precisamente, perché ha un momento angolare orbitale pari a zero attorno all'asse internucleare.

Struttura Molecolare

Teoria dell’Orbitale Molecolare (Molecular Orbital - MO)

Normalizzazione di

$$\boldsymbol{\Psi_+ = N\phi_A + N\phi_B = N(\phi_A + \phi_B) = N(A + B)}$$



Normalize the molecular orbital ψ_+ in eqn 10.8.

Method We need to find the factor N such that $\int \psi^* \psi \, d\tau = 1$. To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.

Answer Substitution of the wavefunction gives

$$\int \psi^* \psi \, d\tau = N^2 \left\{ \int A^2 d\tau + \int B^2 d\tau + 2\int AB \, d\tau \right\} = N^2(1 + 1 + 2S)$$

where $S = \int AB \, d\tau$ and has a value that depends on the nuclear separation (this ‘overlap integral’ will play a significant role later). For the integral to be equal to 1, we require

$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

In H_2^+, $S \approx 0.59$, so $N = 0.56$.

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

ESERCIZIO

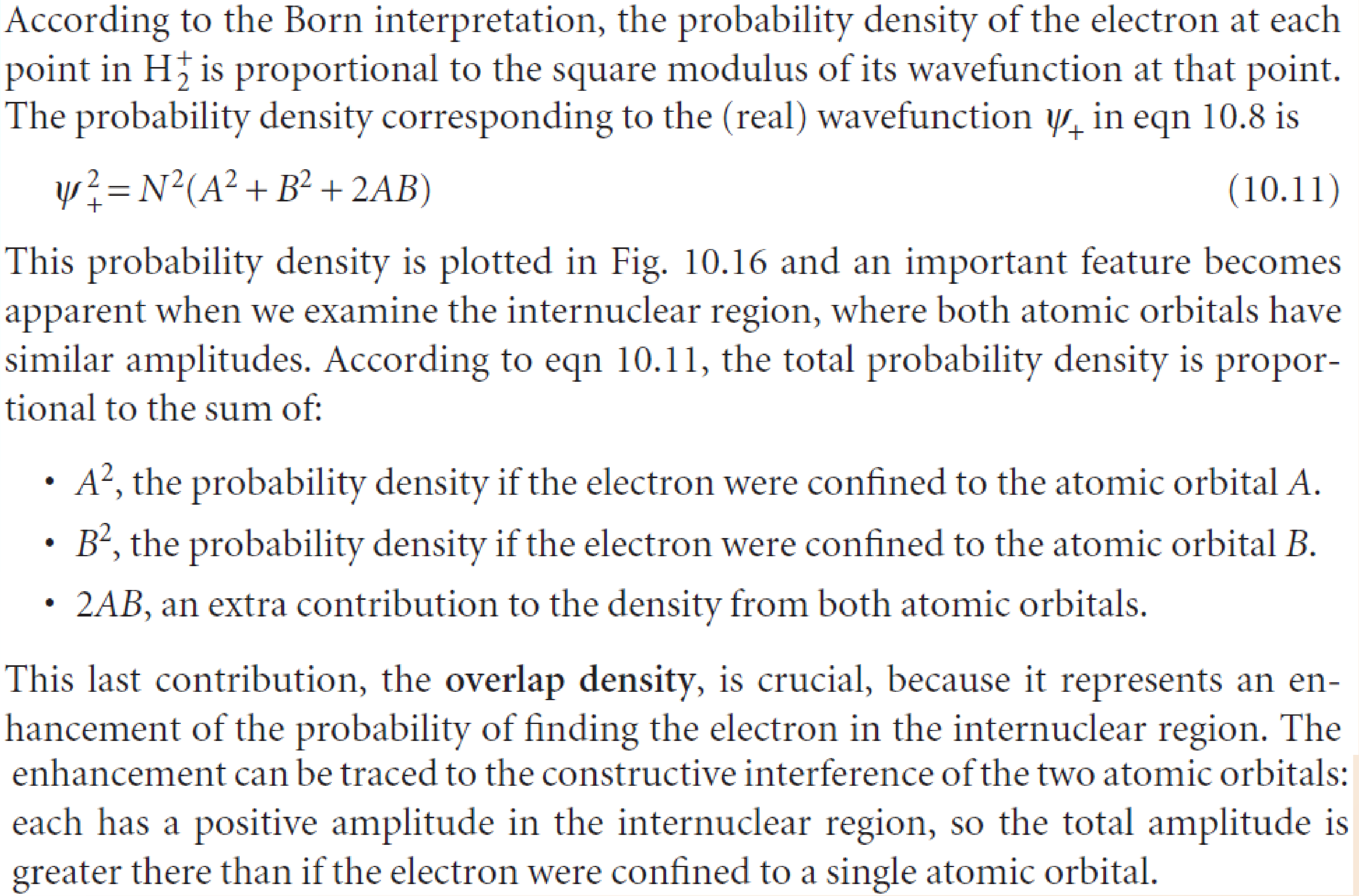
Normalizzare il seguente orbitale molecolare:

$$\boldsymbol{\Psi}_{-} = \boldsymbol{N}\boldsymbol{\phi}_{\boldsymbol{A}} - \boldsymbol{N}\boldsymbol{\phi}_{\mathrm{B}} = \boldsymbol{N}(\boldsymbol{\phi}_{\boldsymbol{A}} - \boldsymbol{\phi}_{\boldsymbol{B}}) = \boldsymbol{N}(\boldsymbol{A} - \boldsymbol{B})$$

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Bonding orbitals (Orbitali Molecolari leganti)



According to the Born interpretation, the probability density of the electron at each point in H_2^+ is proportional to the square modulus of its wavefunction at that point. The probability density corresponding to the (real) wavefunction ψ_+ in eqn 10.8 is

$$\psi_+^2 = N^2(A^2 + B^2 + 2AB) \tag{10.11}$$

This probability density is plotted in Fig. 10.16 and an important feature becomes apparent when we examine the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn 10.11, the total probability density is proportional to the sum of:

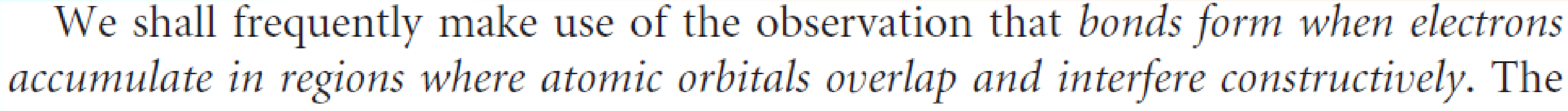
- A^2, the probability density if the electron were confined to the atomic orbital A.
- B^2, the probability density if the electron were confined to the atomic orbital B.
- $2AB$, an extra contribution to the density from both atomic orbitals.

This last contribution, the **overlap density**, is crucial, because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the constructive interference of the two atomic orbitals: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atomic orbital.

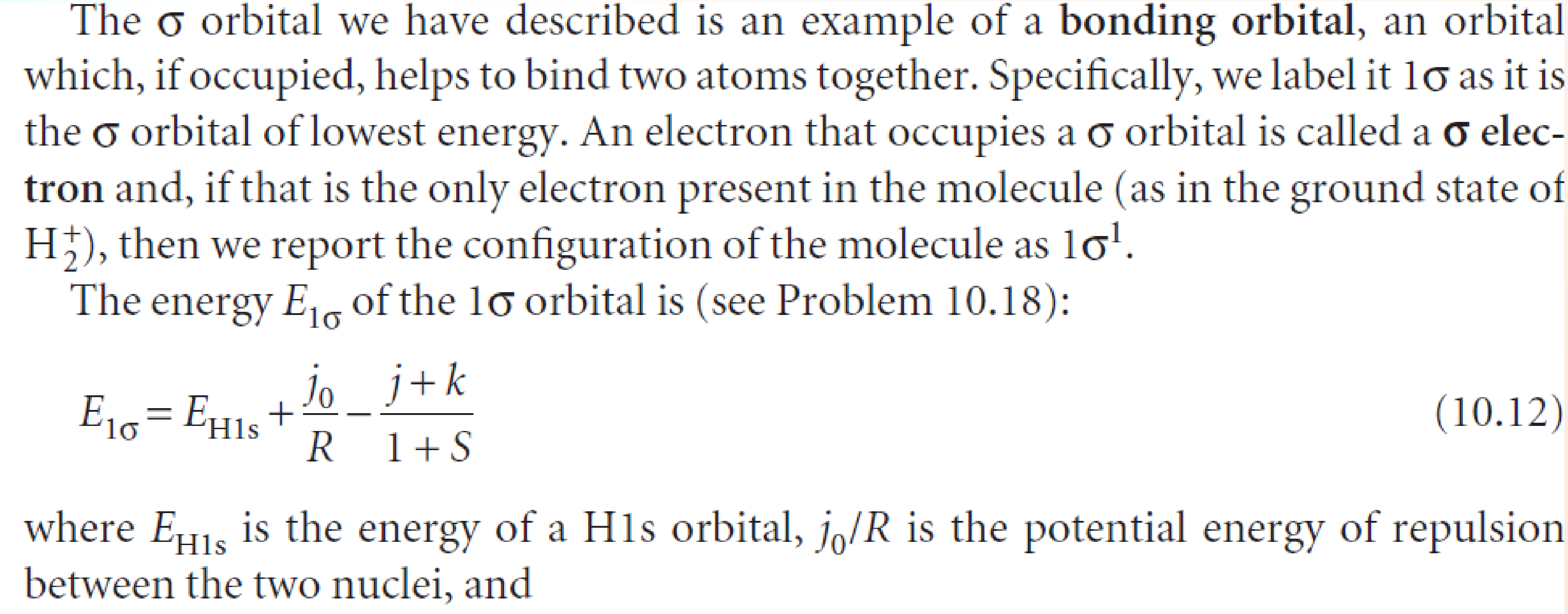
Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Bonding orbitals
(Orbitali Molecolari leganti)



We shall frequently make use of the observation that *bonds form when electrons accumulate in regions where atomic orbitals overlap and interfere constructively*. The



The σ orbital we have described is an example of a **bonding orbital**, an orbital which, if occupied, helps to bind two atoms together. Specifically, we label it 1σ as it is the σ orbital of lowest energy. An electron that occupies a σ orbital is called a **σ electron** and, if that is the only electron present in the molecule (as in the ground state of H_2^+), then we report the configuration of the molecule as $1\sigma^1$.

The energy $E_{1\sigma}$ of the 1σ orbital is (see Problem 10.18):

$$E_{1\sigma} = E_{H1s} + \frac{j_0}{R} - \frac{j+k}{1+S} \qquad (10.12)$$

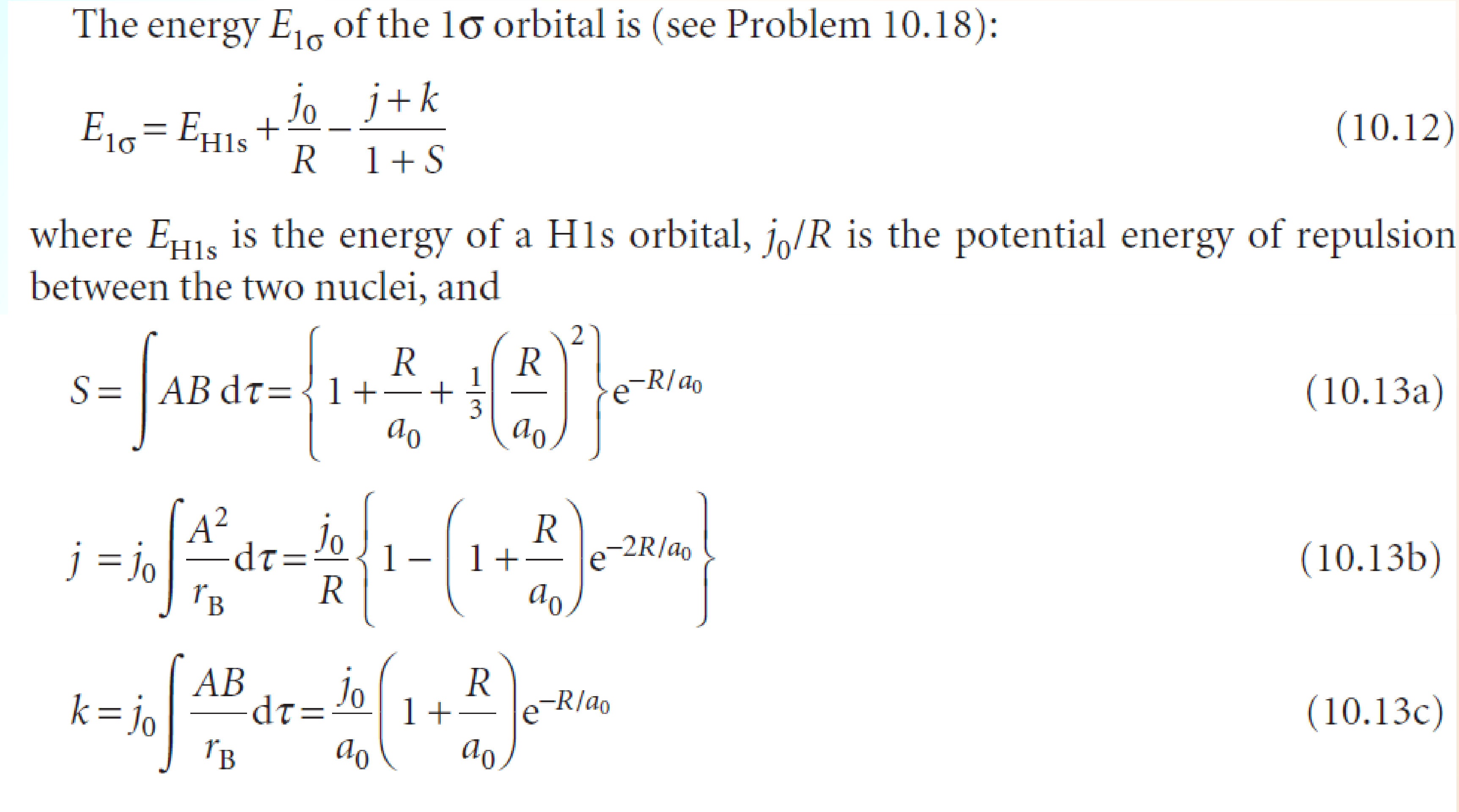
where E_{H1s} is the energy of a H1s orbital, j_0/R is the potential energy of repulsion between the two nuclei, and

$$j_0 = \frac{e^2}{4\pi\varepsilon_0}$$

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Bonding orbitals (Orbitali Molecolari leganti)



The energy $E_{1\sigma}$ of the 1σ orbital is (see Problem 10.18):

$$E_{1\sigma} = E_{\mathrm{H1s}} + \frac{j_0}{R} - \frac{j+k}{1+S} \tag{10.12}$$

where E_{H1s} is the energy of a H1s orbital, j_0/R is the potential energy of repulsion between the two nuclei, and

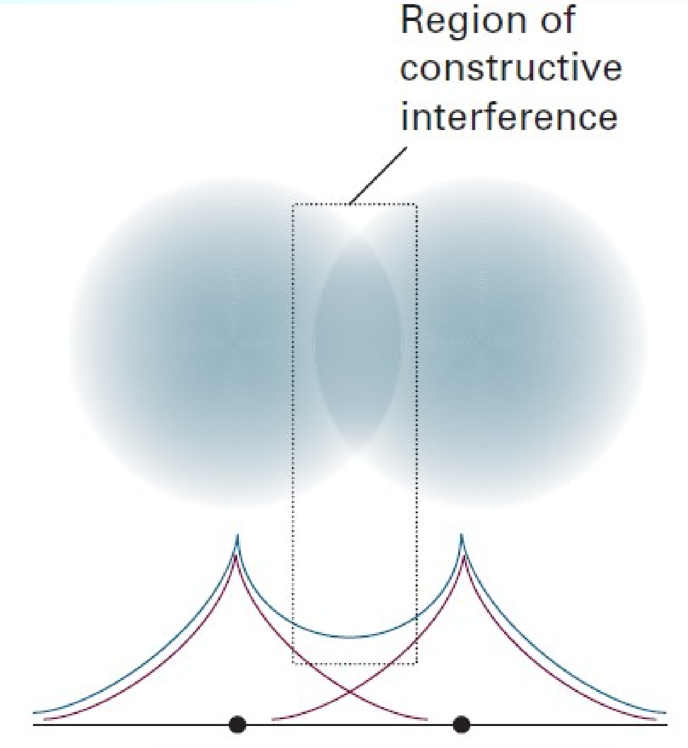
$$S = \int AB\,\mathrm{d}\tau = \left\{1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right\}\mathrm{e}^{-R/a_0} \tag{10.13a}$$

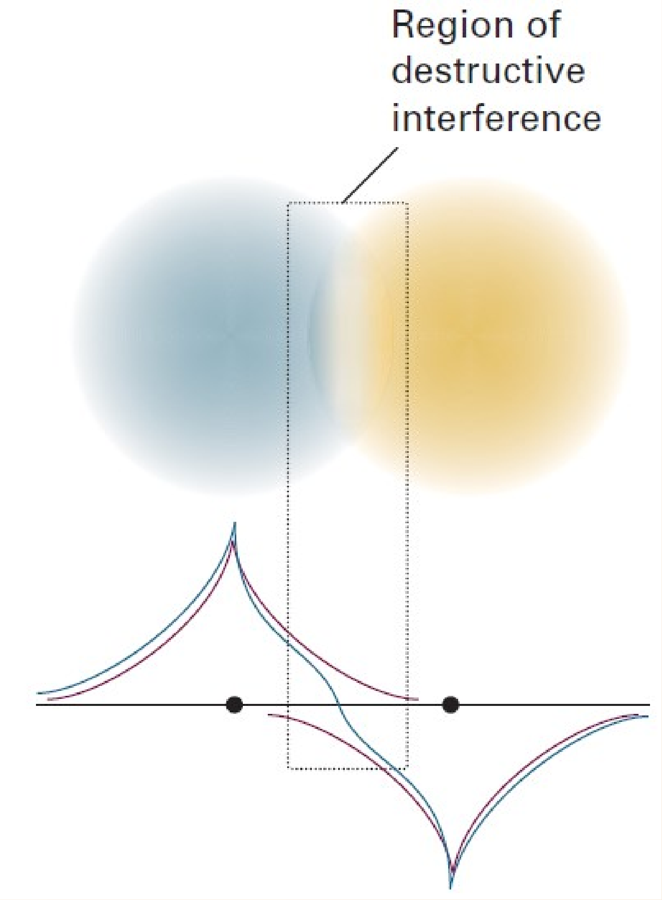
$$j = j_0\int \frac{A^2}{r_{\mathrm{B}}}\mathrm{d}\tau = \frac{j_0}{R}\left\{1 - \left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-2R/a_0}\right\} \tag{10.13b}$$

$$k = j_0\int \frac{AB}{r_{\mathrm{B}}}\mathrm{d}\tau = \frac{j_0}{a_0}\left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-R/a_0} \tag{10.13c}$$

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)





Orbitale Molecolare legante (bonding)

$$\boldsymbol{\Psi_{+} = N\phi_A + N\phi_B = N(\phi_A + \phi_B)}$$

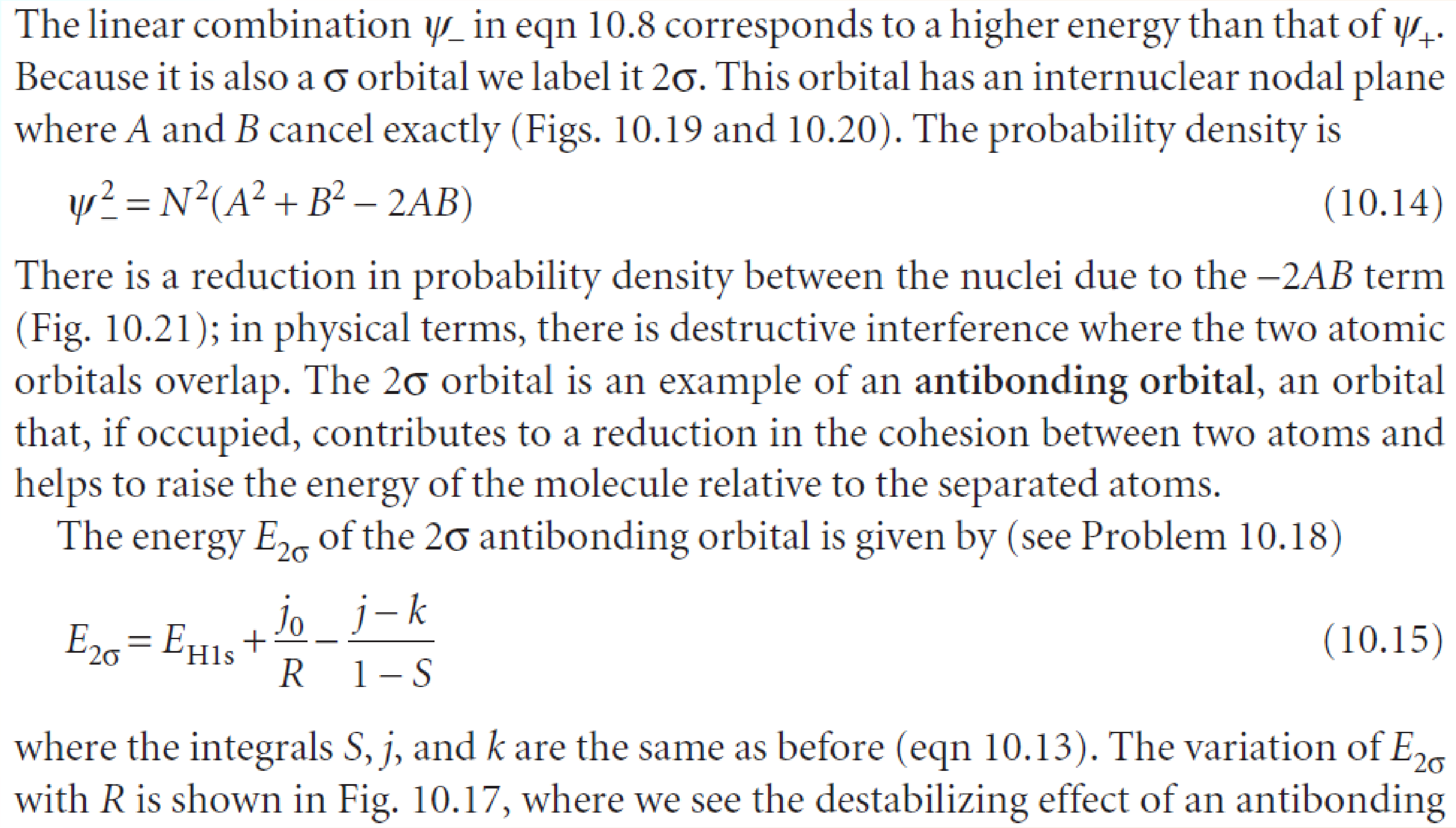
Orbitale Molecolare anti-legante (anti-bonding)

$$\boldsymbol{\Psi_{-} = N\phi_A - N\phi_B = N(\phi_A - \phi_B)}$$

Struttura Molecolare

Teoria dell'Orbitale Molecolare (Molecular Orbital - MO)

Antibonding orbitals
(Orbitali Molecolari antileganti)



The linear combination ψ_- in eqn 10.8 corresponds to a higher energy than that of ψ_+. Because it is also a σ orbital we label it 2σ. This orbital has an internuclear nodal plane where *A* and *B* cancel exactly (Figs. 10.19 and 10.20). The probability density is

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB) \qquad (10.14)$$

There is a reduction in probability density between the nuclei due to the $-2AB$ term (Fig. 10.21); in physical terms, there is destructive interference where the two atomic orbitals overlap. The 2σ orbital is an example of an **antibonding orbital**, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated atoms.

The energy $E_{2\sigma}$ of the 2σ antibonding orbital is given by (see Problem 10.18)

$$E_{2\sigma} = E_{\mathrm{H1s}} + \frac{j_0}{R} - \frac{j-k}{1-S} \qquad (10.15)$$

where the integrals *S*, *j*, and *k* are the same as before (eqn 10.13). The variation of $E_{2\sigma}$ with *R* is shown in Fig. 10.17, where we see the destabilizing effect of an antibonding