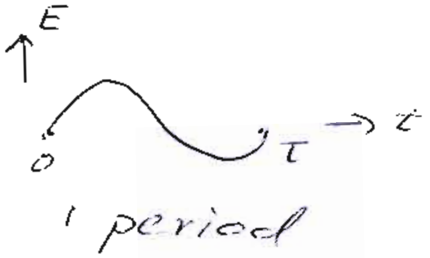
Review Chap. 11
1st Major

Electromagnetic radiation,
old quantum theory

$\lambda\nu = c$, $\nu = \frac{1}{\tau}$



angular velocity $\omega = 2\pi\nu = \frac{2\pi}{\tau}$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ natural frequency

k: force constant

more in use than ν: energy $E = h\nu$

or $\bar{\nu} = \frac{1}{\lambda}$ (cm^{-1}) $\nu = c\bar{\nu}$

harmonic motion:

$$\frac{d^2y}{dt^2} = \frac{F}{m} \qquad \frac{d^2y}{dt^2} = -\frac{k}{m}y$$

$$y = a\sin\left(\sqrt{\frac{k}{m}}\,t + b\right)$$

plane wave: $y = 2\sin\frac{2\pi}{\lambda}(x \pm ut)$

u: phase velocity: move of a phase

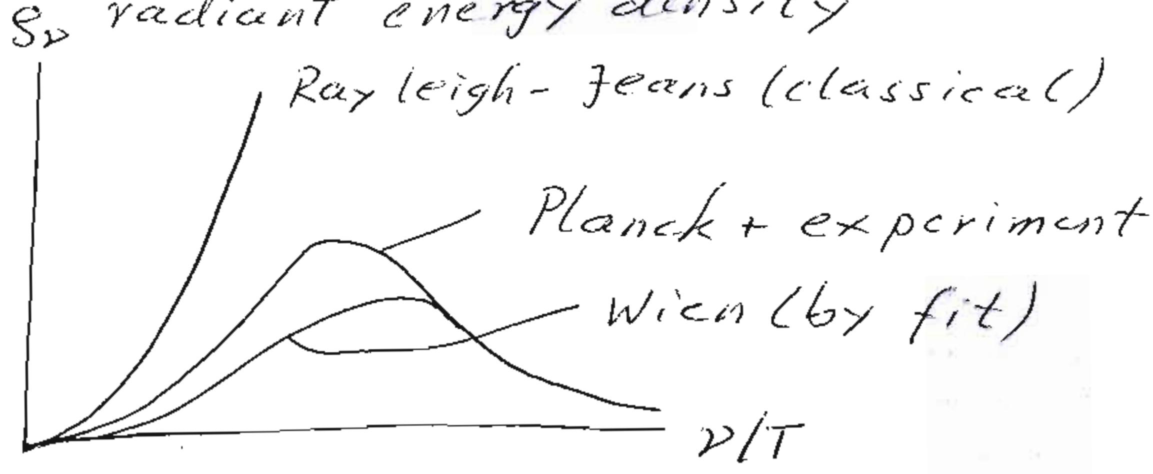
string

standing wave: $y = A\sin\frac{n\pi x}{\ell}\sin(2\pi\nu t + b)$

n: integer

Black body radiation

Planck: energy <u>only</u> in packets $h\nu$



Einstein: light as beam of photons, each with energy $h\nu$

$$h\nu = \frac{1}{2}mu^2 + W$$

u: e^--speed

W ↳ energy needed to cut an e^- free from a metal: work function

threshold frequency: $h\nu_0 = W$

light + bulk → wave
light + particle → particle

<u>Bohr's theory</u>

<u>classical</u>: e orbits round the nucleus like a planet round the sun
not stable

<u>Bohr</u> only special orbits stable

orbit stable when

angular momentum $L = mur = n\hbar$

$n = 0, 1, 2, \ldots$

$$E_n = -R_y \frac{z^2 hc}{n^2} \qquad R_y = \frac{e^2}{8\pi\varepsilon_0 a_0 hc}$$

E_n: ionization energy

good only for 1e atoms!

$H, He^+, Li^{2+}, Be^{3+}, B^{4+} \ldots$

line spectra, $Z=1$ for H:

$$\Delta E = -R_y hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = h\nu = h\frac{c}{\lambda} \qquad \frac{1}{\lambda} = \tilde{\nu} = \frac{\Delta E}{hc}$$

$$\tilde{\nu} = R_y\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Correspondence Principle

all QM must reduce to classical theory for classical experimental results cases

e.g. large masses

large boxes

Foundations of QM

de ~~Brg~~ Broglie wavelength for particles: $\lambda = \frac{h}{mu}$

→ Bohr H-atom: particle must be a standing wave on a circle (orbit, stable)

$$\rightarrow 2\pi r = n\lambda = \frac{nh}{mu}$$

Uncertainty principle

$$\Delta q \cdot \Delta p = \Delta E \Delta t \geq \frac{\hbar}{2}$$

Schrödinger's wave mechanics

reading assignment: plausibility

QM: Operators for physical quantities

$$\hat{x} \rightarrow x \quad , \quad \hat{p}_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\nabla^2 = \left(\hat{p}_x^2 + \hat{p}_2^2 + \hat{p}_z^2\right) / (-\hbar^2) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

time-dependent systems: $E \rightarrow -\frac{\hbar}{i}\frac{\partial}{\partial t}$

conservative systems $E \rightarrow \hat{H}$

$$H = E_k + E_p = \frac{p^2}{2m} + E_p(x,t)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + E_p(x,t)$$

wave function ψ:

$$\hat{H}\psi(x,t) = -\frac{\hbar}{i}\frac{\partial\psi(x,t)}{\partial t}$$

time independent (conservative):

$$\hat{H}\psi(x) = E\psi(x)$$

$$\psi(x,t) = \psi(x)\cdot e^{i\frac{Et}{\hbar}}$$

probability to find an e^- in $dV, d\tau$:

$$P = \psi^*\psi\, d\tau \qquad d\tau = dx\,dy\,dz$$

probability density:

$$\rho = \psi^*\psi$$

$\int\psi^*\psi\, d\tau = 1$ because it is prob. to find e^- anywhere in all space

any wave function: $\psi \rightarrow A\psi$

A such that $A^2\int\psi^*\psi\, d\tau = 1$

$$A = \frac{1}{\sqrt{\int\psi^*\psi\, d\tau}}$$

Postulates

solution of $\hat{H}\psi = E\psi$ gives the state of the system

ψ must be normalizable (= square integrable):

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \; \psi^* \psi (x,y,z) = \text{finite number}$$

every physical observable is ~~des~~ described by a <u>linear operator</u>

when 2 operators commute:

$$\hat{O}_1 \hat{O}_2 \psi = \hat{O}_2 \hat{O}_1 \psi$$

then they have the <u>same</u> eigenfunctions and <u>no</u> uncertainty when measurement of their observables

$\Rightarrow$ every operator that commutes with $\hat{H}$ has observables that can be measured precisely

$$\langle F \rangle = \frac{\int \psi^* \hat{F} \psi \, d\tau}{\underbrace{\int \psi^* \psi \, d\tau}_{}} \longrightarrow = 1 \text{ if normalized}$$

if ψ eigen function of $\hat F$:

$$\hat F \psi = f \psi$$

then all measurements give precisely f and $\langle F \rangle = f$

if ψ not eigenfunction of $\hat F$:

then $\langle F \rangle$ is the average of an infinite number of measurements

r does not commute with $\hat H$

$\Rightarrow$ since $\hat H \psi = E \psi$ $\rightsquigarrow$ $\langle r \rangle = \int \psi^* r \psi \, d\tau$ is average or expectation value

if ψ_1, ψ_2 eigenfunctions of $\hat F$ with different eigenvalues (non degenerate)

then $\int \psi_1^* \psi_2 \, d\tau = 0$ orthogonality

if ψ_1, ψ_2 eigen functions of $\hat F$ with the same eigenvalue (degenerate)

then all $a\psi_1 + b\psi_2$ are also eigenfunctions of $\hat F$ with the same eigenvalue

and can be chosen to be orthogonal

free particle

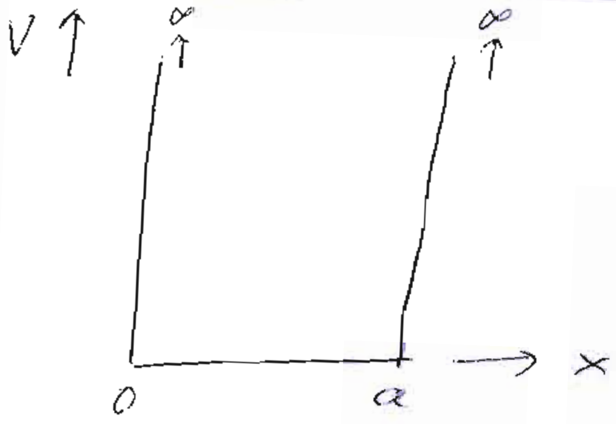
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$ no quantization if no box

$$\psi = A e^{\pm \frac{i}{\hbar}\sqrt{8\pi^2 mE}\, x}$$

delocalized along x-axis

momentum: precise, sharp: $p_x = \pm\sqrt{2mE}$

particle in a box



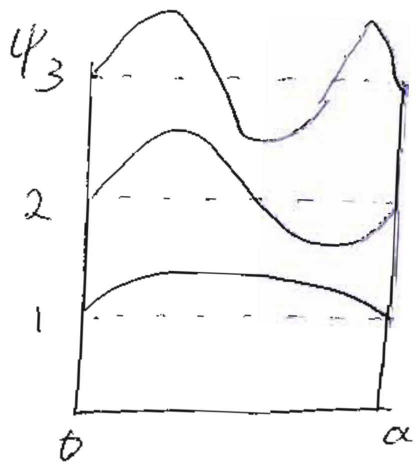
all integrals are from 0 to a, since

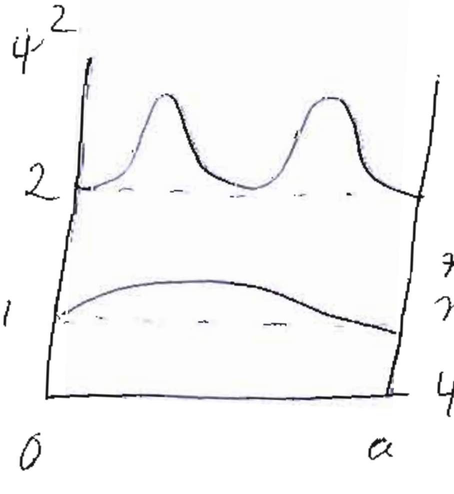
$\psi(x \leq 0) = \psi(x \geq a) = 0$

$$E_n = \frac{h^2}{8ma^2}n^2 \qquad n = 1, 2, 3, \ldots$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

3-dim. box: $E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$





of ~~maxi~~ maxima in ψ^2: n

$$E = -\frac{\hbar^2}{2m}\int_0^a \psi^* \frac{d^2}{dx^2}\psi \, dx$$

transitions: $\Delta E = \frac{h^2}{8ma^2}(n_2^2 - n_1^2)$ $n_1 \to n_2$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

Harmonic oscillator

reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$

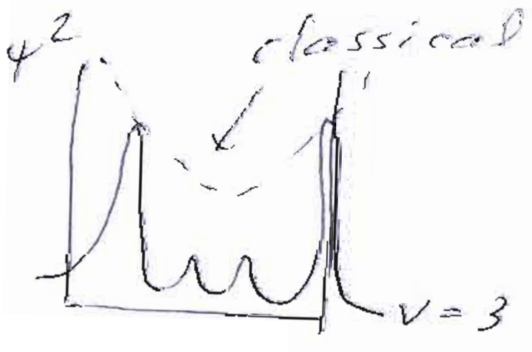
$E_p = \frac{1}{2}kx^2$ $\nu_0 = \sqrt{\frac{k}{\mu}}$

$E_v = h\nu_0 (v + \frac{1}{2})$ $v = 0, 1, 2$

$\nu = \bar{\nu} c$

$E_v = h\bar{\nu}_0 c (v + \frac{1}{2})$

zero-point energy $E_0 = \frac{1}{2}h\nu_0 = \frac{1}{2}hc\bar{\nu}_0$



approach to classical density for large v

all ψ_v with even v are even functions:

$$\psi_v(-x) = \psi_v(x) \quad v \text{ even}$$

all ψ_v with odd v are odd functions: $\psi_v(-x) = -\psi_v(x)$ v odd

ψ_0:

ψ_1

Hydrogen

separation if $\hat{H} = \hat{H}_1(x) + \hat{H}_2(y)$

then $\psi = \psi_1(x) \cdot \psi_2(y)$

polar coordinates:

$$\psi = R(r)\,\phi(\varphi)\,\Theta(\vartheta)$$

→ quantum numbers n, l, m_l

$n = 1, 2, 3, \ldots$ integer

$l = 0, 1, \ldots, n-1$

$m_l = -l, \ldots, -1, 0, 1, \ldots, l$

hydrogen: E_n

many electrons $E_{n,l}$

n: determines size of ψ

l: " shape of ψ

m_l: " direction of the shape

for the form of ψ-s, sketches of $\langle r_{1s} \rangle$, of R^2 and $4\pi r^2 R^2$ and of $[\Theta(\vartheta)\Phi(\varphi)]^2$ in general must be known

Angular momentum

$L = \sqrt{l(l+1)}\,\hbar \qquad L_z = m_l \hbar$

magnetic moment: $\mu = -\frac{e}{m_e} L$

Bohr magnetons $\frac{e}{m_e}$ as units

Ang. momentum, rigid rotor, spin, many electron atoms, approximations must be studied for 1st Major

in Lec. ⑬ is Exam

We have thus split the Schrödinger equation (Eq. 11.164) into three equations, one involving Φ and ϕ (Eq. 11.165), one involving R and r (Eq. 11.167), and one involving Θ and θ (Eq. 11.168). These equations must now be solved so as to eliminate the differentials. We will first solve the Φ equation so as to obtain the allowed values of m_l. These will then be used to solve the Θ equation so as to obtain the allowed l values. Finally, the l values will be used to solve the R equation.

Solution of the Φ Equation

Equation 11.165 is of a familiar form (compare Eq. 11.125) and its solution is

$$\Phi = Ae^{im_l\phi} \tag{11.169}$$

where A is a normalization constant. The function Φ must have the same value at $\phi = 0$, $\phi = 2\pi$, $\phi = 4\pi, \ldots$, because these angles correspond to the same position; this requires that

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{11.170}$$

The positive and negative values relate to distinct solutions. The quantity m_l has thus become a quantum number because of the mathematical constraints on the system and not in any arbitrary way.

The value of A is obtained by applying the normalization condition, the range of ϕ being 0 to 2π:

$$\int_0^{2\pi} \Phi_{m_l}\Phi^*_{m_l}\, d\phi = A^2 \int_0^{2\pi} e^{im_l\phi}e^{-im_l\phi}\, d\phi = A^2 2\pi = 1 \tag{11.171}$$

Therefore $A = 1/\sqrt{2\pi}$ and the solution becomes

$$\Phi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi} \tag{11.172}$$

When $m_l = 0$, the value of Φ_0 is $1/\sqrt{2\pi}$, but for other values of m_l the solutions involve imaginary exponents. This is awkward, and it is more usual to employ a linear combination of the functions, $\Phi_{m_l} \pm \Phi_{-m_l}$; as we have seen (Eq. 11.116), linear combinations of wave functions having the same eigenvalue are also solutions of wave equations. For example,

$$\text{for } m_l = 1, \qquad \Phi_1 = \frac{1}{\sqrt{2\pi}}e^{i\phi} \tag{11.173}$$

$$\text{for } m_l = -1, \qquad \Phi_{-1} = \frac{1}{\sqrt{2\pi}}e^{-i\phi} \tag{11.174}$$

We can take the sum of these and divide by $\sqrt{2}$ to preserve the normalization,

$$\Phi_x = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_{-1}) = \frac{1}{2\sqrt{\pi}}(e^{i\phi} + e^{-i\phi}) = \frac{\cos\phi}{\sqrt{\pi}} \tag{11.175}$$

We designate this orbital Φ_x since $\cos\phi$ has its maximum value when $\phi = 0$, which

The chemical bond

H_2^+

covalent bonds formed by sharing of electrons between atoms

Simplest example: H_2^+:

1 electron holds 2 protons (p^+) together

for H_2: already $2e^-$: not exactly solvable

bonding e^- pair

Approximation methods

MO (molecular orbital) theory

Linear combination of atomic orbitals (LCAO) + variation method to find combination coefficient

VB (valence bond) ~~thar~~ theory

wave function for bonding e^--pair as product of 2 atomic orbitals (AO) 1 for each electron

Essentially MO and VB lead to the same results but from different view-points and with different mathematics

covalent bonds: H_2, Cl_2, organic compounds

polar bonds: HCl: dipole moment
because different electronegativity of the atoms

large Δ(EN) → ionic bonds become stronger than covalent ones

hydrophobic bonds: indirect bonds in solutions of non-~~plo~~polar compounds in polar solvent like water.

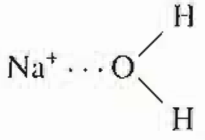
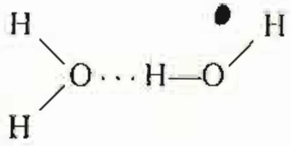
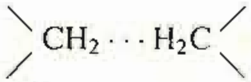
then the hydrophobic soluten disturb the hydrogen bonds in water
to keep the hydrogen bonds, the hydrophobic soluten are forced together

are present in aqueous solution, and they result from the fact that such groups have an effect on the hydrogen-bonded structure of water.

The Nature of the Covalent Bond

It took considerable time to understand the nature of the covalent bond. As early as 1902 the American chemist G. N. Lewis, who had already made pioneering contributions to thermodynamics (Section 3.8), had developed an important theory of the bond, but he did not publish his ideas until 1916. The essence of his concept was that chemical bonding can take place as a result of the sharing of electrons between two atoms. It had previously been realized that groups of eight electrons (octets) play some role in chemical bonding, and Lewis took this idea further. In his

TABLE 12.1 The Main Types of Chemical Forces

Type of Force or Chemical Bond	Example	Equilibrium Separation/nm	Dissociation, Energy*/kJ mol^{-1}
Ionic bond (ion-ion force)	$Na^+\cdots F^-$	0.23	670.0
Covalent bond	H—H	0.074	435.0
Ion-dipole force	 $Na^+\cdots OH_2$	0.24	84.0
Hydrogen bond (dipole-dipole bond)	 $H_2O\cdots H—OH$	0.28	20.0
Hydrophobic bond	 $CH_2\cdots H_2C$	≈ 0.30	≈ 4.0
Van der Waals (dispersion forces)	Ne · · · Ne	≈ 0.33	≈ 0.25

*This is the energy that would be required per mole to dissociate the species into its units (e.g., H—H into H + H or $Na^+\cdots OH_2$ into $Na^+ + H_2O$).

covalent bond

early, qualitative (no numbers) understanding

Lewis bonding by sharing of e^- between atoms

groups of $8e^-$ preferred in ~~n=2~~

$n=2$ atoms (noble gas $2s^2 2p^6$)

→ octet rule

Lewis: $8e^-$ or less at corners of cubes around atoms

bonds by overlaps of such corners

there: no motion of the e^-

concept was later improved

idea: bonding by pairs of e^-, shared by 2 atoms

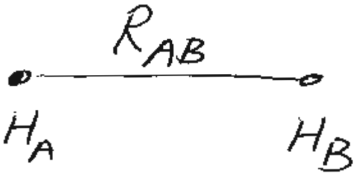
H_2^+: hydrogen molecular ion

$[H\overset{e^-}{-}H]^+$ not found in stable salts like $H_2^+B^-$

H_2^+ is found and studied in electrical discharges in H_2 gas:

experimentalpotential curve:

$E_{\text{[illegible]}}(R_{AB})$ (contains E_K and E_p of particles)



minimum at $R_{AB} = 106$ pm of $E_{\text{[illegible]}}$

(equilibrium bond length)

$$E_{\text{[illegible]}}(R_{AB} = 106\,pm) = -269.3\ \frac{kJ}{mol}$$
$$= -2.791\ eV$$

this $E_{\text{[illegible]}}$ is below the energy of $H + H^+$ at ∞ separation

~~$E_p(\infty$~~) $E_{\text{[illegible]}}(R_{AB} \to \infty) = 0$

Born-Oppenheimer approximation:

R_{AB} = const.

then equation (Schrödinger) for 1e⁻ can be solved exactly

done at different R_{AB} values → $E_{\text{[illegible]}}(R_{AB})$

In Born-Oppenheimer approx. ⑭-5

the Schrödinger equation can be separated and solved in confocal elliptical coordinates:

$$\varphi, \quad \xi = \frac{r_A + r_B}{R_{AB}} \quad ; \quad \eta = \frac{r_A - r_B}{R_{AB}}$$

R_{AB}: fixed distance between the p^+

r_A: distance $e^- - p_A^+$

r_B: distance $e^- - p_B^+$

exact solution possible

but good example to compare approximations with exact solution

$$E_p = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R_{AB}} - \frac{1}{r_A} - \frac{1}{r_B}\right)$$

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R_{AB}} - \frac{1}{r_A} - \frac{1}{r_B}\right)\right]\psi = E\psi$$

good first trial for use in a variation calculation:

$$\psi = e^{-b\xi}(1 + c\eta^2)$$

b, c such that E is lowest possible

→ dissociation energy:

$$E_{Diss} = -E_{minimum}$$

268.8 kJ/mol = 2.786 eV
(exp. 269 kJ/mol)

<u>but</u> at 206 pm which is much too large (exp: 106 pm)

<u>usual</u> way to find better trial function:
start from exact atomic wave-functions and then improve the trial function

H_2^+: 1s orbitals of the H atom
centered at nuclei A and B

$$\psi_{1s_A} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r_A/a_0}$$

$$\psi_{1s_B} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r_B/a_0}$$

each 1 alone cannot describe a bond, only 1 H atom

→ MO as LCAO:

$$\psi = N(1s_A + 1s_B)$$

ψ spreads over the complete molecule and must be normalized because $1s_A$ and $1s_B$ are normalized only for 1 atom alone

$$\int \psi^2 d\tau = N^2 \int (1s_A + 1s_B)^2 d\tau$$

↗ ψ^2 cause ψ in real

$$= N^2 \left(\underbrace{\int (1s_A)^2 d\tau}_{1} + \underbrace{\int (1s_B)^2 d\tau}_{1} + 2\int \overset{1s_A \cdot 1s_B\, d\tau}{\cancel{\psi_{1s_A}\psi_{1s_B}}} \right)$$

not 0, because $1s_A$ and $1s_B$ are on different centers

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

$$S = \int 1s_A 1s_B \, d\tau$$

e^- prob. density ρ, also called e^-- distribution, $\rho \sim \psi^2$

$\rightarrow \rho \sim \psi^2 \sim (1s_A)^2 + (1s_B)^2 + 2(1s_A)\cdot(1s_B)$

e^- near p_A^+ : r_A small, r_B large

$\rightarrow \psi \approx 1s_A$

e^- near p_B^+ : r_A large, r_B small

$\rightarrow \psi \approx 1s_B$

e^- near A or B : ψ similar to isolated atoms

e^- between A and B : distribution is not the sum of the atoms, but larger

1) shift e^- from p_A^+, p_B^+ to their center by term $2(1s_A)(1s_B)$ which accounts for the bonding :

raise of potential energy

$\rightarrow$ destabilization

2) e^- shift to the center

→ shrinking of ψ^2 at nuclei as compared to the atoms

→ larger e^--nuclei attraction

→ stabilization (lower energy)

3) decrease of kinetic energy

⇒ 1) + 2) + 3) → bonding

ψ is <u>no</u> longer spherical, as $1s_A$ and $1s_B$ are

<u>but</u> ψ has cylinder symmetry:

no change upon rotation around AB axis (φ)

MO with such symmetry:

σ-MO, σ-bond

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \underset{\substack{\uparrow \\ \text{if } \psi \text{ is normalized}}}{=} \int \psi^* \hat{H} \psi \, d\tau$$

simple ansatz

→ correct form of potential curve

but wrong numbers

$E_{Diss} = 170.7 \frac{kJ}{mol}$ at $R_{AB} = 169\,pm$

exp.: $269 \frac{kJ}{mol}$ at $R_{AB} = 106\,pm$

⇒ better must the same funtion,

<u>but</u> with a free parameter:

$$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left[e^{-\frac{Zr_A}{a_0}} + e^{-\frac{Zr_B}{a_0}}\right] \cdot \frac{1}{\sqrt{2(1+S)}}$$

and variation of Z:

find Z that makes the energy Smallest, then:

$Z = 1.23 \rightarrow E_{Dis} = 217.0 \frac{kJ}{mol}$

include more AO-s: 1s, 2s, 2p, ...

with 130 AO-s: exact E_{Diss} is obtained!

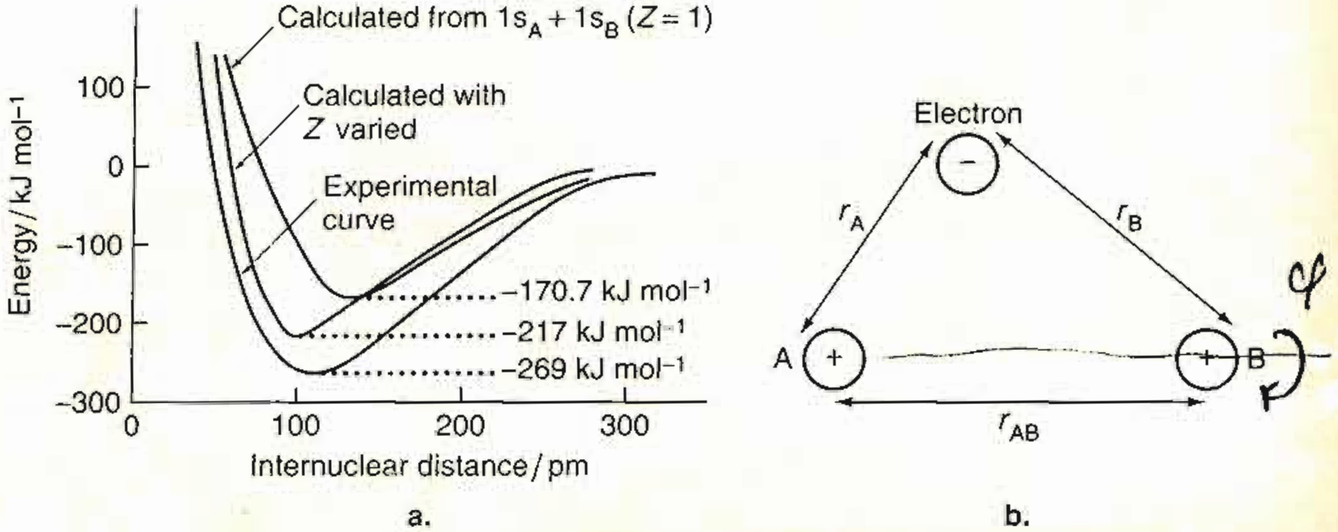
The remainder of this chapter is concerned with the quantum mechanics of the covalent bond. It is convenient to begin with the one-electron bond found in the hydrogen-molecular ion H_2^+.

12.1 THE HYDROGEN MOLECULAR-ION, H_2^+

The simplest molecular system is H_2^+, which consists of two protons and a single electron. This species forms no stable salts, but there is evidence for its existence in electrical discharges passed through hydrogen gas, and some of its properties have been studied by spectroscopic methods. The experimental potential-energy curve for H_2^+ is shown in Figure 12.1a. The minimum energy occurs at an internuclear separation of 106 pm and corresponds to an energy 269.3 kJ mol^{-1}(= 2.791 eV) below that of the separate particles $H + H^+$.

It is possible to obtain a satisfactory quantum-mechanical solution for the H_2^+ ion. The system of two protons and an electron is shown in Figure 12.1b, and we make use of confocal-elliptical coordinates in order to effect a separation of variables.

FIGURE 12.1
The hydrogen molecule-ion H_2^+. (a) Experimental and theoretical potential-energy curves for the ground electronic state. (b) The system of two protons and an electron.



a.

b.

Hydrogen molecule

H_2: simplest molecule with an electron-pair bond

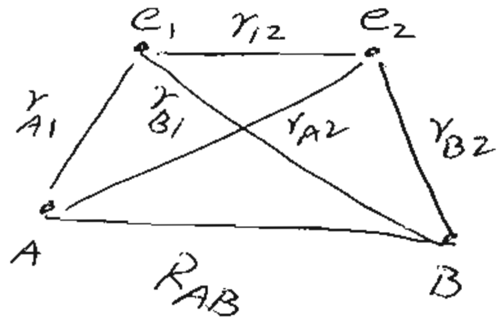
1) VB method:
starting with a product of 2 atomic wave functions (AO-s), one for each e^-

2) MO method:
orbitals for single electrons as in the H_2^+ treatment

electrons are filled into the MO-s following Pauli principle and Hund's rule

VB method

based on the chemical idea of resonance and resonance structures



$$E_p = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}}\right)$$

$$\rightarrow \hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + E_p$$

Born-Oppenheimer: R_{AB} fixed

$\rightarrow$ no $\nabla_A^2 + \nabla_B^2$

starting point: neglect of e^--e^- repulsion,

= neglect of $\frac{1}{r_{12}}$

$\rightarrow$ A —— ∞ ---- B   two isolated H atoms at ∞ distance

then: e_1 at A: $1s_A(1)$

e_2 at B: $1s_B(2)$

and $E = E_A + E_B$

and $\psi_1 = 1s_A(1) \cdot 1s_B(2)$ only then is

$$E = E_A + E_B \text{ at } R_{AB} \rightarrow \infty$$

an equivalent function has e_1 at B and e_2 at A:

$$\psi_2 = 1s_A(2)\, 1s_B(1)$$

bond energy $\simeq -90 \frac{kJ}{mol}$

vs exp. $-458 \frac{kJ}{mol}$

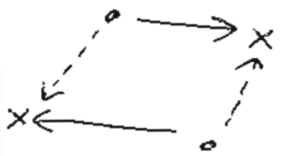
$\rightarrow$ bad approximation

Heitler-London: wrong ansatz:

It is not possible to distinguish electrons by giving them labels 1,2 and follow the path of e_1:

~~e_1 —— e_2 ×~~ · time 1 × time 2

measured e^- positions:



not possible to know and measure which way is the correct one to come from t_1 (∘) to t_2 (×)

But in ψ_1 it is always sure that e_1 is in $1s_A(1)$ at A and e_2 is in $1s_B(2)$ at B

analogous in ψ_2 → wrong ansatz

correct: linear combination of the 2:

symmetric combination: normalization

$$\psi_S = N_S\,(\psi_1 + \psi_2) = N_S\,(1s_A(1)1s_B(2) + 1s_A(2)1s_B(1))$$

now exchange of 1 and 2 gives back ψ_S → not possible to distinguish between the k electrons

⇒ S for symmetric

antisymmetric combination:

$\psi_A = N_A(\psi_1 - \psi_2) = N_A(1s_A(1)\,1s_B(2) - 1s_A(2)\,1s_B(1))$

here $1 \leftrightarrow 2$ exchange gives $-\psi_A$

$\Rightarrow$ antisymmetric A

but a - sign is unimportant for observable

→ also indistinguishable e-s

for stable bond: nuclear repulsion must be reduced

→ both e-s close together between the nuclei

there: $1s_A(1) \approx 1s_A(2)$, $1s_B(1) \approx 1s_B(2)$

because between the nuclei:

$r_{A1} \approx r_{A2}$, $r_{B1} \approx r_{B2}$

then $\psi_S \approx \frac{2}{\sqrt{2}}\, 1s_A(1)\,1s_B(2) = \frac{2}{\sqrt{2}}\,\psi_1$

if $N_S = \frac{1}{\sqrt{2}}$ $\psi_A \approx 0$

probability densities $\sim \psi_S^2, \psi_A^2$

very small density between the nuclei in ψ_A, but larger in ψ_S

$\swarrow R_{AB}$

$\Rightarrow E_{\cancel{B}}(R)$ for ψ_S has a

minimum $\Rightarrow$ attractive

$E_{\cancel{B}}(R)$ for ψ_A has no minimum

$\rightarrow$ repulsive

0 of energy to minimum:

classical dissociaten energy E_{Diss}

or classical binding energy

QM: 0-point energy of oscillator

$\rightarrow$ exp. E_{Diss} smaller than minimum

$E(\psi_A) > 0$ antibonding state

$E(\psi_{\cancel{B}S}) < 0$ and minimum:

bonding state

$E_{\psi_1} - E_{\psi_S}$ at the minimum of the

curves:

resonance or

resonance stabilization energy

energy decrease from spreading out of the e⁻ over both nuclei

→ built up of e-density between the nuclei

→ the electron clouds that are initially at the nuclei overlap

→ principle of maximum overlap for bonds.

ψ_S is a better approximation than ψ_1 or ψ_2 alone

but still gives only ≈ 66% E_{Diss}

evaluation of integrals

→ 2 contributions to the energy

a) Coulomb energy J: negative compared to isolated atoms

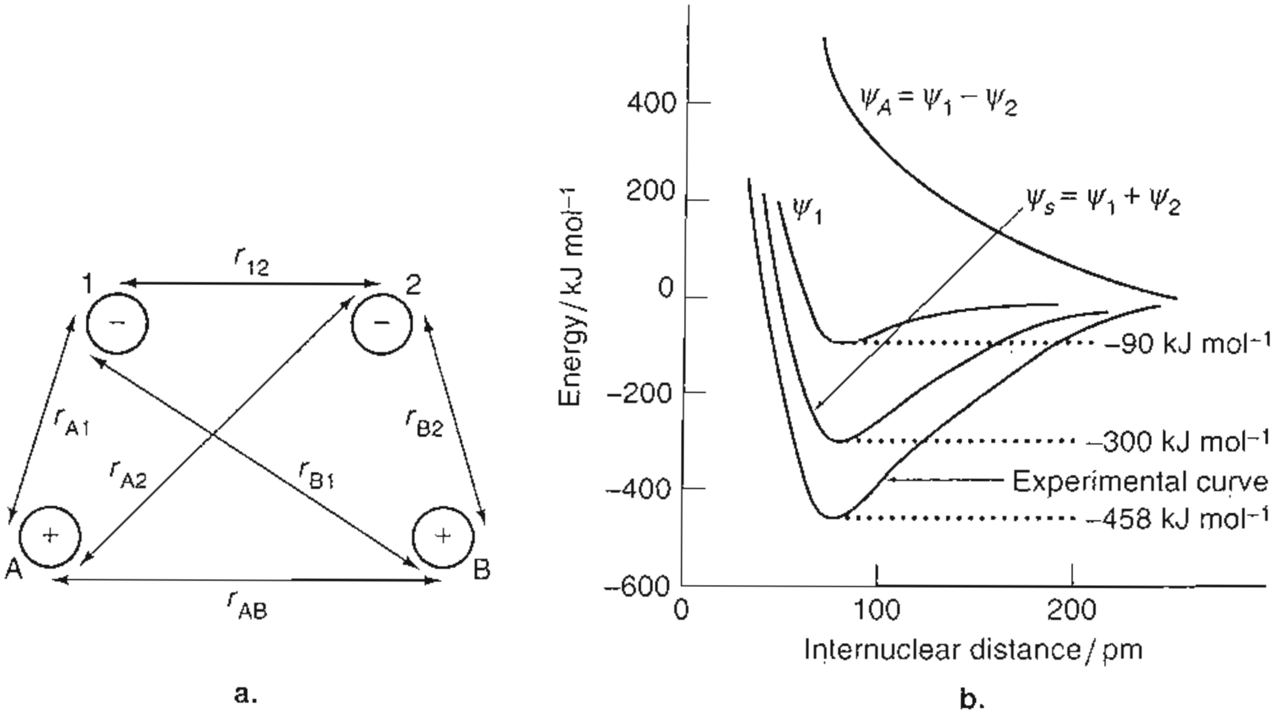
but <u>only</u> ≈ 10% of the binding

b) Exchange energy K: ≈ 90% of binding

Coulomb ≙ classical electrostatic repulsions and attractions

→ classical treatment false!

FIGURE 12.2
(a) The hydrogen molecule H_2, consisting of two protons and two electrons. (b) Experimental and theoretical potential-energy curves for the hydrogen molecule.



and the Hamiltonian operator is therefore

$$\hat{H} = -\frac{h^2}{8\pi^2\mu}\nabla^2 + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}}\right) \qquad (12.11)$$

We initially simplify the problem by ignoring the electrical repulsion between the electrons, which is the case if the two hydrogen atoms are infinitely far apart. The state of electron 1 on nucleus A is described by the wave function $1s_A(1)$, and electron 2 on nucleus B is described similarly by the wave function $1s_B(2)$. When the two atoms are infinitely far apart, their energy is simply the sum of the two atomic energies, $E_A + E_B$. To meet this requirement, the Schrödinger wave function for this system must be the *product* of the individual wave functions. Thus, a possible wave function is exchange: purely quantum-mechanically arising ~~a~~ effect from the possibility of e^- exchange

Improvements: various ones possible

important: to add ionic terms:

$$\psi_3 = 1s_A(1)\,1s_A(2) \quad H_A^- \; H_B^+$$
$$\psi_4 = 1s_B(1)\,1s_B(2) \quad H_A^+ \; H_B^-$$

because electrons are indistinguishable, the terms must come together as $(\psi_3 + \psi_4)$ just as $(\psi_1 + \psi_2)$

In symmetric H_2 both are equivalent

not e.g. in HCl, there H^+Cl^- more important than H^-Cl^+

trial: $\psi = c_1(\psi_1 + \psi_2) + c_2(\psi_3 + \psi_4)$

$$\hookrightarrow \approx 3\%$$

c_1, c_2 are determined by variation such that E is smallest

better approximations are possible, but not so easy to understand.

Electron spin

exchange of electron coordinates 1↔2:

ψ_S does not change: symmetric to exchange

ψ_A changes sign:
antisymmmetric to exchange

Pauli principle restricts e spins:

only $m_s = \pm\frac{1}{2}$ in 1 orbital possible:

The total wave function of a system (orbital · spin function) must be antisymmetric to e inter~~ex~~change

→ symmetric orbital ψ_S must have an antisymmetric spin function

antisymmetric orbital ψ_A must have a symmetric spin function

$\hat{S}^2\alpha = s(s+1)\hbar^2\alpha \quad \hat{S}\beta = s(s+1)\hbar^2\beta \quad s = \frac{1}{2}$

$\hat{S}_z\alpha = m_s\hbar\alpha \quad \hat{S}_z\beta = m_s\hbar\beta$

$m_s = +\frac{1}{2}$ for α

$= -\frac{1}{2}$ for β

for 2 electrons, 4 spin functions are possible:

$\alpha(1)\alpha(2)$ $\beta(1)\beta(2)$ symmetric
parallel spins

$\alpha(1)\beta(2)$ $\alpha(2)\beta(2)$

$\Rightarrow \psi_1 = \psi_A \alpha(1)\alpha(2)$ same energy
and
$\psi_2 = \psi_A \beta(1)\beta(2)$ antisymmetric

other 2 spin functions: not s, not as

Same as before: distinguishable electrons require a linear combination to be indist.:

symmetric: $\alpha(1)\beta(2) + \alpha(2)\beta(1)$

antisymmetric: $\alpha(1)\beta(2) - \alpha(2)\beta(1)$

$\Rightarrow \psi_3 = \psi_A \left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]$

same energy as ψ_1, ψ_2

antisymmetric

triplet excited state, becaus 3 degenerate wavefunction and excited: ψ_A repulsive
not stable

antisymmetric spin function goes to symmetric orbital

→ antisymmetric, bonding state

or groundstate:

$$\psi_g = \psi_s \left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

singlet groundstate, only 1 state ψ_g

other systems can have also singlet, doublet, triplet or higher degenerate states

also ~~at~~ as groundstate

MO method

alternative to VB, especially for large molecules

basic idea (Lennard-Jones): LCAO to construct MO-s

VB: e^- in pairs

MO construction of MO-s from AO-s without consideration ~~t~~ of the e-s during construction

The electrons are at the end filled into the MO-s following Pauli and Hund

⇒ MO-s for H_2 are the same as for H_2^+

→ MO of lowest energy: bonding

$1s_A + 1s_B$

→ high e^--density between the nuclei which holds them together

MO-s of diatomic molecules are eigenfunctions of $\hat{L}_z$ but <u>not</u> of $\hat{\underline{L}}^2$

→ labeling like AO-s (s, $l=0$; p, $l=1$; d, $l=2$) but greek letters:

$$\underset{\sigma}{\lambda = 0}, \underset{\pi}{1}, \underset{\delta}{2}, \ldots$$

bonding orbital $\sigma = 1s_A + 1s_B$

1e⁻: H_2^+ energy below $H + H^+$ → bonding

bond order: 1 bonding e⁻ contributes 0.5

in H_2, 2 electrons (↑↓) in the binding σ orbital → bond order 1

in H_2^+ bondorder 0.5

Subtraction: 2., antibonding orbital

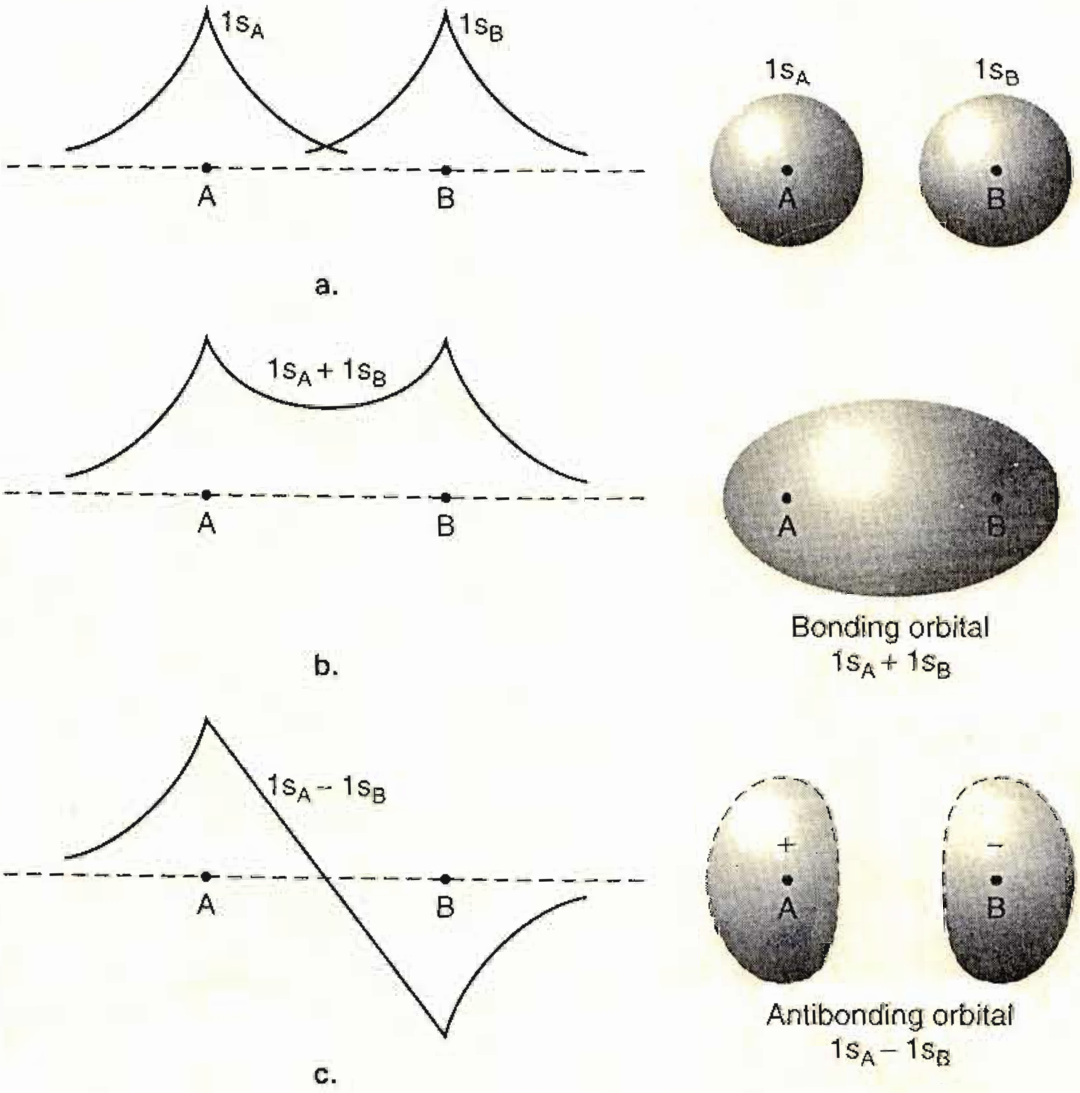
$$\sigma^* = 1s_A - 1s_B$$

lower density between the nuclei

→ antibonding, repulsive

also has $\lambda = 0$ → σ^*

* for antibonding



o the right
at represent
the orbitals.
nic orbitals
ogen atoms.
l $1s_A + 1s_B$.
bit $1s_A$ −

rbital
bonding)

is

al (bonding)

g and
he H_2
with
n in the

This corresponds to a low electron density between the nuclei, as shown in Figure 12.3c. It corresponds to $\lambda = 0$, and it is also a σ orbital; the fact that it is antibonding is shown by the asterisk. The two wave functions σ and σ^* are orthogonal to each other (see Problem 12.8).

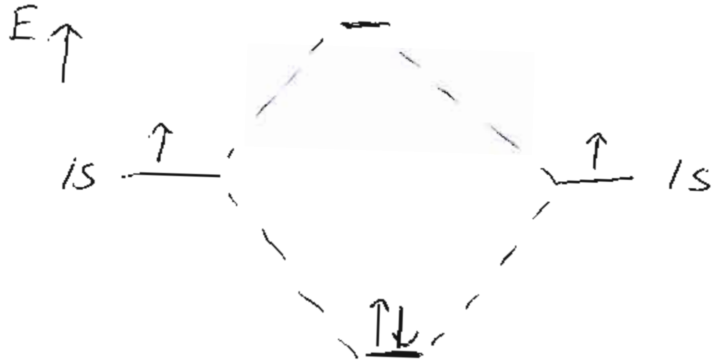
Figure 12.4 is an energy diagram showing the separated atoms and the bonding and antibonding levels. The ground state of H_2 is shown, with two electrons in the bonding orbital. If one of these is promoted into the antibonding σ^* orbital, the antibonding effect approximately overcomes the bonding.

The molecular orbital for the electron-pair bond in the hydrogen molecule is obtained by taking the product of the molecular orbitals for each of the two electrons, as given by Eq. 12.24. This description allows the electrons to move freely throughout the molecule. The wave function for electron 1 is written as

$$\sigma(1) = N_b[1s_A(1) + 1s_B(1)] \tag{12.26}$$

and that for electron 2 as

groundstate σ^2



1 electron promoted: $\sigma^1(\sigma^*)^1$

bonding is overcome → excited state not stable

MO for e-pair: product of the MO-s for each electron

$\sigma(1) = N_b\left[1s_A(1) + 1s_B(1)\right]$ $\sigma(2) = N_b\left[1s_A(2) + 1s_B(2)\right]$

N_b normalization factor

$\sigma = \sigma(1)\cdot\sigma(2) = N_b^2\left[1s_A(1) + 1s_B(1)\right]\left[1s_A(2) + 1s_B(2)\right]$

$$= N_b^2\Big[\underbrace{\underset{H-H}{1s_A(1)\,1s_B(2)} + \underset{H-H}{1s_B(1)\,1s_A(2)}}_{\text{Heitler-London}}$$

$$+ \underbrace{\underset{H^-H^+}{1s_A(1)\,1s_A(2)} + \underset{H^+H^-}{1s_B(1)\,1s_B(2)}}_{\text{ionic contribution to bonding } \approx 3\%}$$

here: weights of covalent and ionic terms equal

MO with weighting factors: no!

reduction of ionic contribution

→ MO, VB become more similar

Refinements in both → MO, VB identical

for energies, first normalization is needed:

$$\int \sigma(1)^2 \, d\tau = 1 = N_b^2 \int [1s_A(1) + 1s_B(1)]^2 \, d\tau$$

$$= N_b^2 \left[\underbrace{\int (1s_A)^2 \, d\tau}_{1} + \underbrace{\int (1s_B)^2 \, d\tau}_{1} + 2 \underbrace{\int 1s_A \, 1s_B \, d\tau}_{\text{overlap integral } S} \right]$$

$$\rightarrow N_b^2 (2 + 2S) = 1$$

$$\rightarrow \underset{\substack{\uparrow \\ \text{bonding } \sigma}}{N_b} = \frac{1}{\sqrt{2(1+S)}}$$

$$\int \sigma^*(1)^2 \, d\tau = 1 = N_a^2 \int [1s_A - 1s_B]^2 \, d\tau$$

$$\underset{\substack{\uparrow \\ \text{antibonding; } \sigma^*}}{N_a} = \frac{1}{\sqrt{2(1-S)}}$$

S: degree of overlap

$R_{AB} \to \infty \Rightarrow S = 0$

$1s_A$ large $1s_B$ small H_A	both small	$1s_A$ small $1s_B$ large H_B

$\to$ $1s_A 1s_B$ is <u>small</u>

but S is finite, not 0 for small R_{AB}

$\to$ $1s_A$, $1s_B$ not orthogonal

<u>but</u> $\int \sigma(1)\sigma^*(1)\,d\tau = N_a N_b \int (1s_A + 1s_B)(1s_A - 1s_B)\,d\tau$

$= N_a N_b \left[\int (1s_A)^2 d\tau - \int 1s_A 1s_B\,d\tau + \int 1s_B 1s_A\,d\tau - \int (1s_B)^2 d\tau \right)$

$= N_a N_b [\,1 - S + S - 1\,] = 0$

σ, σ^* are orthogonal

$$E_b = \frac{\int \sigma(1)\hat{H}\sigma(1)\,d\tau}{\int \sigma(1)\sigma(1)\,d\tau} = \int \sigma(1)\hat{H}\sigma(1)\,d\tau$$

$$= N_b^2 \underbrace{\int 1s_A(1)\hat{H}\,1s_A(1)\,d\tau}_{J} + N_b^2 \underbrace{\int 1s_B(1)\hat{H}\,1s_B(1)\,d\tau}_{J}$$

Coulomb integrals

$$+ \underbrace{2N_b^2 \int 1s_A(1)\hat{H}\,1s_B(1)\,d\tau}\ ]$$

exchange or resonance integral K

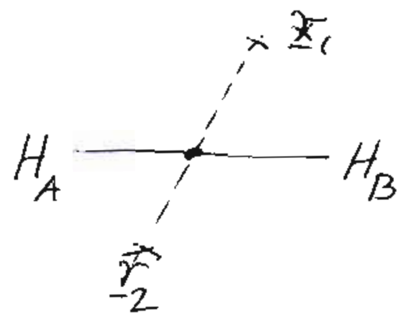
$$\rightarrow E_b(\sigma) = \frac{2(J+K)}{2(1+S)} = \frac{J+K}{1+S} \approx \underset{\uparrow}{J+K}$$

if S small enough

E_b is below the energy of the atoms, because $K<0$

a molecular wave function must be symmetric or antisymmetric when the nuclei are interchanged

= inversion of the MO through the center of symmetry



$\sigma(\underline{r}_1) = \sigma(\underline{r}_2)$ symmetric

$\sigma(\underline{r}_2) = -\sigma(\underline{r}_2)$ antisymmetric

symmetric: label g for "gerade"
= even

antisymmetric: label u for "ungerade"
= odd

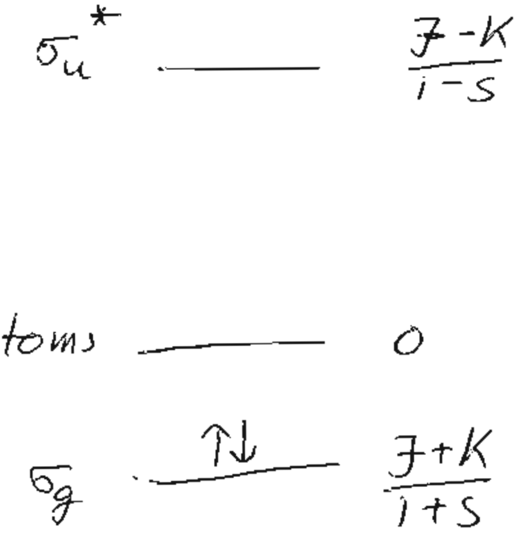
$\sigma_g(1) = N_b[1s_A(1) + 1s_B(1)]$

$\sigma_u^*(1) = N_a[1s_A(1) - 1s_B(1)]$

$$E_b = \frac{J+K}{1+S} \approx J+K$$

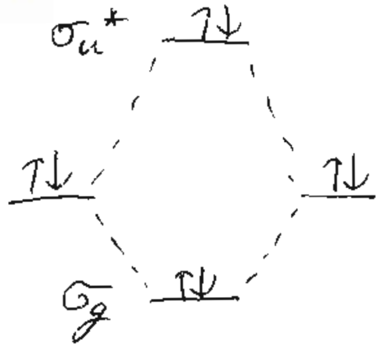
$$E_a = \frac{J-K}{1-S} \approx J-K$$

$K<0 \Rightarrow \sigma_u^*$ energy above J, which is the energy of the atoms



→ σ_u^* is more antibonding than σ_u is bonding when $S \neq 0$

→ He_2 not stables



not stable since σ_u^* more antibonding than σ_u bonding

bondorder $= \frac{1}{2}$(bonding e^- - antibonding e^-) $= \frac{1}{2}(2-2) = 0$

VB for more complex molecules

in actual calculations MO method works better

but VB better for visualization

The covalent bond

HCl: similar to H_2 when concentrating on $1e^-$ at H, $1e^-$ at Cl

$\psi_1 = \psi_H(1)\,\psi_{Cl}(2)$ $\qquad$ $\psi_2 = \psi_H(2)\,\psi_{Cl}(1)$

$H\overset{1}{\cdot}\ \overset{2}{\cdot}Cl$ $\qquad$ $H\overset{2}{\cdot}\ \overset{1}{\cdot}Cl$

→ symmetric bonding orbital:

$$\psi_s = N_s'(\psi_1 + \psi_2')$$

$$1 = N_s^2 \int \left[\psi_H(1)\,\psi_{Cl}(2) + \psi_H(2)\,\psi_{Cl}(1)\right]^2 d\tau_1\, d\tau_2$$

$$= N_s^2\Big[\underbrace{\int \psi_H^2(1)\, d\tau_1}_{1} \cdot \underbrace{\int \psi_{Cl}^2(2)\, d\tau_2}_{1} + \underbrace{\int \psi_H^2(2)\, d\tau_2}_{1} \underbrace{\int \psi_{Cl}^2(1)\, d\tau_1}_{1} + 2\underbrace{\int \psi_H(1)\,\psi_{Cl}(1)\, d\tau_1}_{S} \underbrace{\int \psi_{Cl}(2)\,\psi_H(2)\, d\tau_2}_{S}\Big]$$

$$= N_s^2\, 2(1+S^2)$$

$$S = \int \psi_H\, \psi_{Cl}\, d\tau$$

$$N_s = \frac{1}{\sqrt{2(1+S^2)}}$$

$$\psi_s = \frac{\psi_1 + \psi_2}{\sqrt{2(1+S^2)}}$$

$\psi_s \to E_b(R_{HCl})$ with mimum → bond

Resonance energy: $E_R = E_{\psi_s} - E_{\psi_1} = E_{\psi_s} - E_{\psi_2}$

Introduction of different structures, covalent like ψ_1, ψ_2 and ionic ones

→ larger E_R → bond more stable

→ closer to reality

<u>structures</u>: all possible ones with

1) all atoms in the same positions

2) same no. of electrons

$E_{\psi_1} = E_{\psi_2}$ (only exchange of the electron coordinates in 1 and 2)

→ large contribution to E_R

ionic structures:

$\psi_3 = \psi_{Cl}(1)\,\psi_{Cl}(2)$ $\qquad$ $\psi_4 = \psi_H(1)\,\psi_H(2)$

$\underline{Cl^- H^+}$ $\qquad$ $Cl^+ H^-$

more important

generally:

1 structure predominant

but in large molecules many can exist

$\psi = (\psi_1 + \psi_2)_{cov} + \lambda \psi_{3\,ionic}$ resonance hybrid

contribution to E_R (variation for λ)

$26\%\ \psi_1$, $26\%\ \psi_2$, $\underline{48\%\ \psi_3}$

even in H_2: 3% from the ionic structures

Electronegativity

HCl as in H_2: bonding by increased e^- density between nuclei

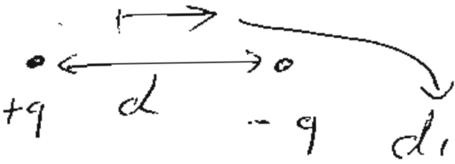
e^--piling up:

H_2: symmetric in exact center

HCl: asymmetric, more e-density closer to Cl

$$\overset{\delta-}{Cl} - H^{\delta+}$$

EN: tendency of an atom to attract e^- to itself in a chemical bond



dipole moment $\vec{\mu}$, $\underline{\mu}$

$\overset{\delta+}{H}\overset{\delta-}{Cl}$ has a dipole moment

$$\mu = q \cdot d$$

$e = 4.8 \cdot 10^{-10}$ esu (electrostatic units)

$= 1.602 \cdot 10^{-19}$ C (As)

$\mu = 1.602 \cdot 10^{-19}\,\text{C} \cdot \underset{(1Å)}{1 \cdot 10^{-10}\,\text{m}} = 1.602 \cdot 10^{-29}$ Cm

$\mu = 4.8 \cdot 10^{-10}\,\text{esu} \cdot \underset{1Å}{1 \cdot 10^{-8}\,\text{cm}} = 4.8 \cdot 10^{-18}$ esu cm

$= 4.8$ D (Debye)

1 D = 10^{-18} esu cm = $3.336 \cdot 10^{-30}$ Cm

assume that we have full ions H^+Cl^- in a HCl molecule

→ ionic dipole moment $\mu_{ionic} = e \cdot d$

$\mu_{exp} < \mu_{ionic}$ because $\overset{\delta+}{H} - \overset{\delta-}{Cl}$, not H^+Cl^-

% ionic character of a bond = $\frac{\mu_{exp}}{\mu_{ionic}} \cdot 100\%$

in $\psi = \left[(\psi_1 + \psi_2)_{cov} + \lambda \psi_{3\,ionic}\right] \cdot N$

Variation of $\int \psi \hat{H} \psi \, d\tau$

→ optimum λ

ψ_3 contributes a part ~ λ^2 to the total energy, which is ~ $(1+\lambda^2)$

1: contribution from $\psi_1 + \psi_2$

→ % ionic character $= \frac{\lambda^2}{1+\lambda^2} \cdot 100\%$

Pauling: reaction

$$AA + BB \longrightarrow 2AB$$

A_2, B_2 symmetric: $\mu = 0$

AB asymmetric: $\mu \neq 0$ ionic character

looking at experimentally know cases, Pauling found: covalent diss. energy:

$$E_{cov}^{AB} = \sqrt{D(AA)\,D(BB)}$$

experimental: $D(AB) > E_{cov}^{AB}$

because of ionic structures in the wave function

→ ionic energy of the bond:

$$E^{AB}_{ionic} = D(AB) - \sqrt{D(AA)\,D(BB)}$$

experimentally known

From the numbers, Pauling found that $\sqrt{E^{AB}_{ionic}}$ is proportional to numbers χ_A and χ_B (electronegativity):
EN

$$\sqrt{E^{AB}_{ionic}} = K\,|\chi_A - \chi_B|$$

when E is in kJ, then with K = 10 kJ

$$\rightarrow \mu = |\chi_A - \chi_B|\ D$$

μ oriented from + to −

<u>means</u> χ such, that with K = 10 kJ $\sqrt{E^{AB}_{ionic}}$ results in kJ

then $\mu = |\chi_A - \chi_B|\ D$

With the χ values given in the table in the book estimates of dipole moments are possible:

$\chi_H = 2.1$, $\chi_{Cl} = 3.0 \rightarrow \mu_{HCl} = (3.0 - 2.1)\ D = 0.9\ D$

oriented from Cl^- to H^+

other method from Mulliken with similar results

ability of element X to attract e⁻ in a bond ~ average of

1) attraction of X^+ for e: ionization potential I

2) attraction of X for e ($\rightarrow X^-$) electron affinity A

if I and A in eV, then

$$\chi_X = \frac{(I+A)/eV}{5.6}$$

example $d_{HF} = 92\ pm$, $\chi_H = 2.1$, $\chi_F = 4.0$

$$\mu_{exp}(HF) = 1.91\ D$$

% ionic character ?

$\mu = (4.0 - 2.1)\ D = 1.9\ D$ (close to experiment)

$1.9D = 1.9 \cdot 3.336 \cdot 10^{-30}\ Cm = 6.34 \cdot 10^{-30}\ Cm$

⑰ - 8

$H^+ \overset{d}{----} F^-$

$$\rightarrow \mu_{ionic} = e \cdot d$$

$$= 1{,}602 \cdot 10^{-19}\,C \cdot 92 \cdot 10^{-12}\,m$$

$$= 1.474 \cdot 10^{-29}\,Cm$$

$$\%\ \text{ionic character} = \frac{\mu_{exp}}{\mu_{ionic}} \cdot 100\%$$

$$= \frac{6{,}34 \cdot 10^{-30}\,Cm}{1{,}474 \cdot 10^{-29}\,Cm} = \underline{43\%}$$

Orbital hybridization

H_2: 1s AO from each H

mostly more AO from 1 atom are needed to form all its bonds

→ hybrids

simplest hybrid: sp

$$\frac{1}{\sqrt{2}}(s \pm p)$$

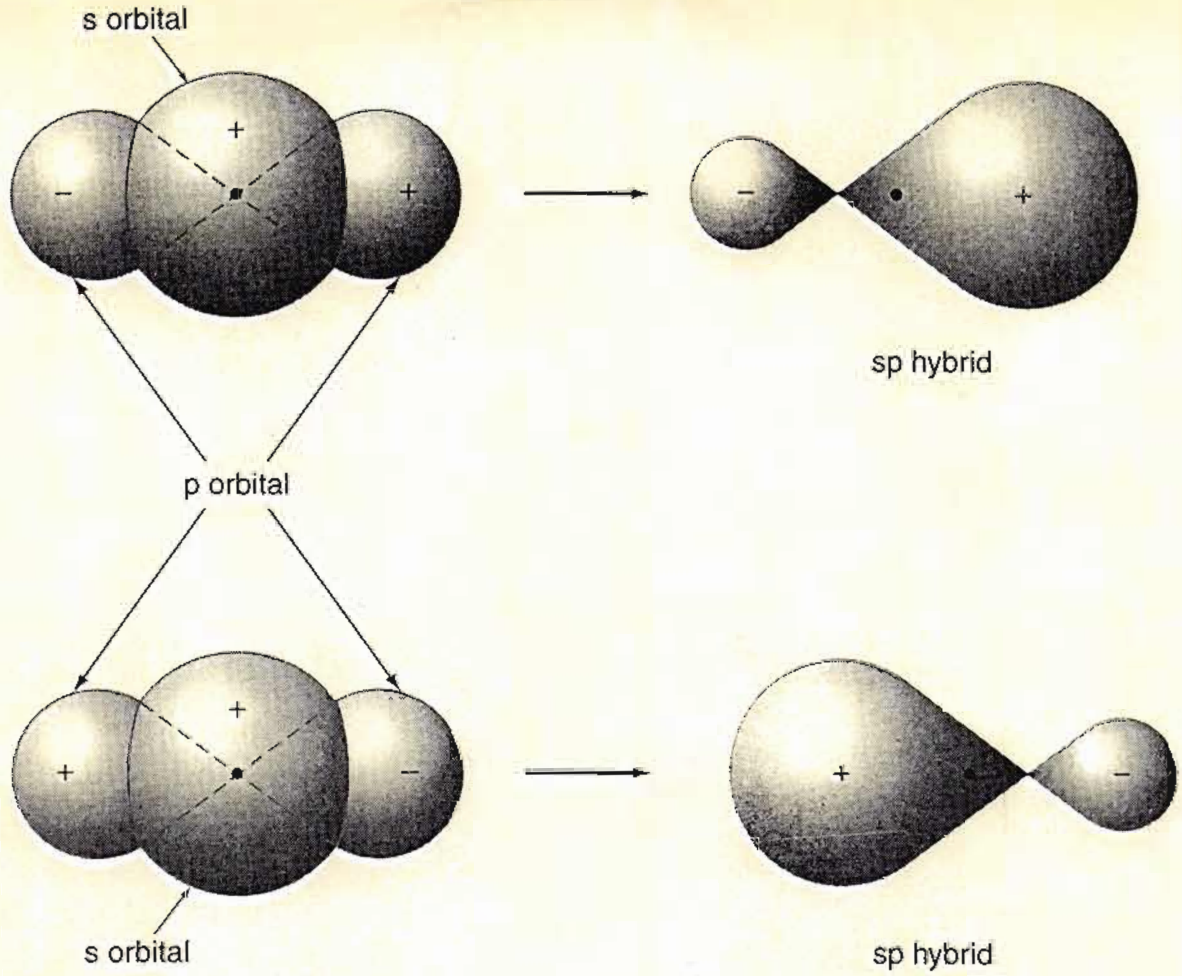
sp^3-hybrid on C: s+ 3 p-AO-s

→ tetrahedral lobes that can lead to bonds when overlapped with $1s_H$ e.g. or can be filled with lone pairs

CH_4 4 C–H σ bonds

$\underline{\dot{O}}H_2$ 2 OH σ bonds + 2 lone pairs

$|NH_3$ 3 NH σ bonds + 1 lone pair



ybrids
bital.

Their extension in space is as large as possible, so that when bonds are formed, the overlap is a maximum. This condition embodies *Pauling's principle of maximum overlap*. These four new orbitals are directed to the apices of a tetrahedron, and the individual bonds are formed by combining one of these hybrid orbitals and a 1s orbital from the hydrogen atom. This can be visualized as the overlapping of the electron clouds, as shown in Figure 12.9a. Obviously the maximum overlap is

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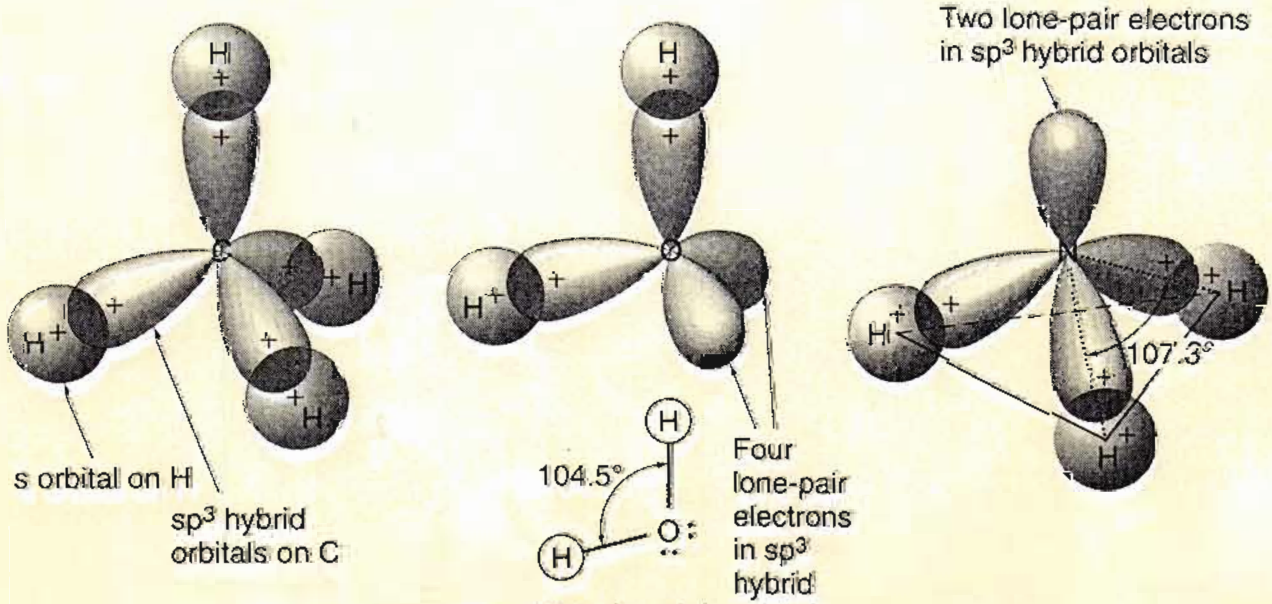


<u>CH_4</u> C: $1s^2 2s^2 2p^2$

↙ 2 overlaps, only 2 bonds possible ?

⇅ ↑ ↑ _

$2s^2$ $2p^2$ (Hund's rule)

<u>no</u> 1. step: promotion:

e^- excited that there are as many unpaired electrons in the outer shell as needed: excited state

only n → n promotion!

C^*: $1s^2 2s^1 2p^3$ ↑ ↑ ↑ ↑

$2s^1$ $2p^3$

4 overlaps, 4 bonds possible

2. with 3 bonds from the 2p AO and 1 bond from the 2s AO

→ 1 bond different from the other 3

experiment: all 4 bonds are equal

hybridization:

formation of 4 identical sp^3 hybrid orbitals from $2s, 2p_x, 2p_y, 2p_z$ different only in direction:

$$t_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

$$t_2 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$t_3 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

$$t_4 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

all 4 like in figure abve:

centered on the atom and pointing into the corners of a tetrahedron

<u>normalization</u>

$N_i^2 \int t_i^2 \, d\tau = 1 = N^2 \int (\cdots)_i^2 \, d\tau$ multiply

→ gives a series of $\int AO_i \cdot AO_j \, d\tau$ integrals

then $\int (\text{same } AO)^2 d\tau = 1$

$\int (AO) \cdot (\text{different } AO) \, d\tau = 0$

orthogonality:

$$N_1N_2\int t_1 t_2\,d\tau = N_1N_2\int(2s+2p_x+2p_y+2p_z)\cdot$$

$$\cdot(2s+2p_x-2p_y-2p_z)\,d\tau$$

$$= N_1N_2\Big[\underset{+1}{\int(2s)^2 d\tau} + \underset{0}{\int 2s\,2p_x\,d\tau} - \underset{0}{\int 2s\,2p_y\,d\tau}$$

$$- \underset{0}{\int 2s\,2p_z\,d\tau} + \int 2p_x\,(\underset{0}{2s} + \overset{+1}{2p_x} - \underset{0}{2p_y} - \underset{0}{2p_z})\,d\tau$$

$$+ \int 2p_y\,(\underset{0}{2s} + \underset{0}{2p_x} - \overset{-1}{2p_y} - \underset{0}{2p_z})\,d\tau$$

$$+ \int 2p_z\,(\underset{0}{2s} + \underset{0}{2p_x} - \underset{0}{2p_y} - \overset{-1}{2p_z})\,d\tau\Big]$$

$$= N_1N_2\left[1+1-1-1\right] = 0$$

Then 1 C–H bond:

$$\frac{1}{\sqrt{2(1+S^2)}}\left(1s_H(1)\,t_{1C}(2) + 1s_H(2)\,t_{1C}(1)\right)$$

+ ionic terms

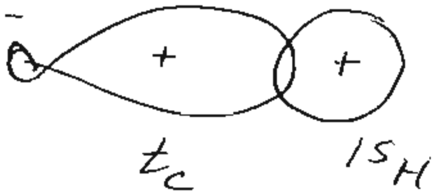
$1s_H$ in direction ~~the~~ of the tetrahedron corner round C into which t_{1C} points

remember figure above

$S = \int 1s_H \, t_{1C} \, d\tau$

$t_1 - t_4$: the 4 e^- clouds are as far away from each other as possible

→ maximum overlap with the 4 $1s_H$ orbitals

- 

→ $t_1 - t_4$ point into tetrahedron corners around C and each 1 overlaps with a $1s_H$ - AO

- H-atoms along tetrahedron axes

→ shape (tetrahedral) from maximum overlap for CH_4

H_2O : O : $1s^2 2s^2 2p^4$

overlaps

$$\underbrace{\underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p}{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}}_{sp^3 \text{ hybrid}}$$

largest distance of clouds

if no hybrid: $2\ 2p-1s$ bonds

→ 90° ∢ HOH

∢ $(P_y, P_z) = 90°$

real ∢ HOH = 104.5°

ideal tetrahedron: 109.7°

(like ∢ HCH in CH_4)

⇒ only partial hybridization

2 corners: lone pairs more extended clouds than bonds

2 corners: O-H bonds compressed by the bigger lone pairs

<u>NH_3</u> 1 corner: bigger lone pair

3 corners: N-H bonds, smaller

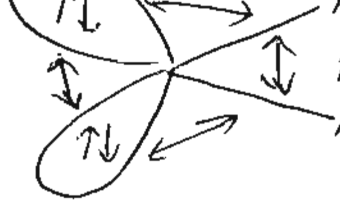
→ bonds compressed by 1 lone pair only: ∡ HNH = 107.3°

Valence shell electron pair repulsion concept: VSEPR

e-pairs in valence shell form an arrangement to be maximal apart from each other,
where lone-pairs need more space than bond pairs

e⁻-pairs repel each other

→ compression of bond angles by lone pairs



weak repulsion

Strong repulsion

→ bond angle compressed

types of hybrids from

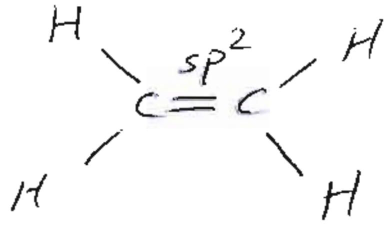
s and p AO: sp, sp^2, sp^3

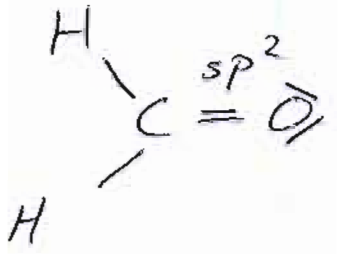
sp: linear lobes BeH_2
∡ 180°

sp^2: planar trigonal ~~lop~~ lobes: BH_3
∡ 120°

also for C in double (sp^2) and

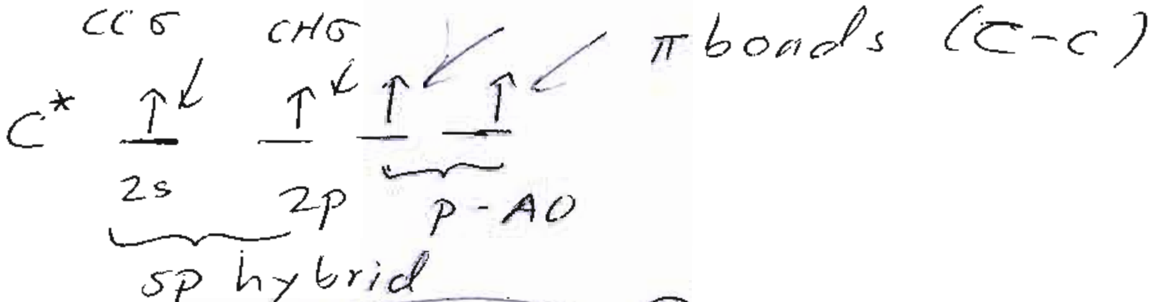
triple (sp) bonds between C atoms

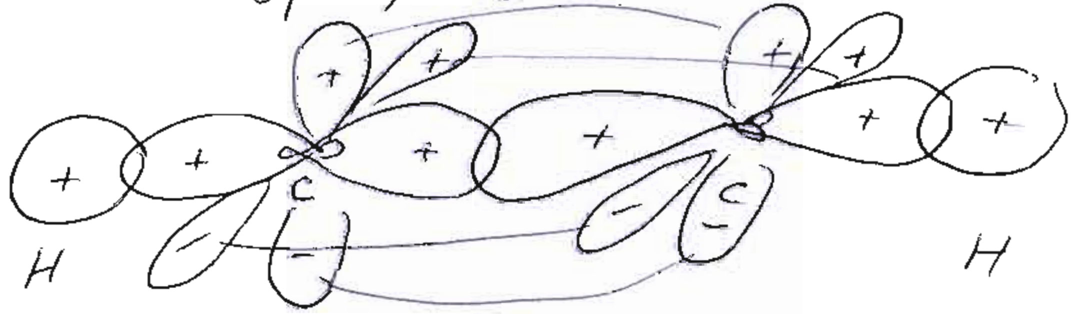




$$\overset{sp}{H-C\equiv C-H}$$

sp: $\psi_{1,2} = \frac{1}{\sqrt{2}}(2s \pm 2p_x)$

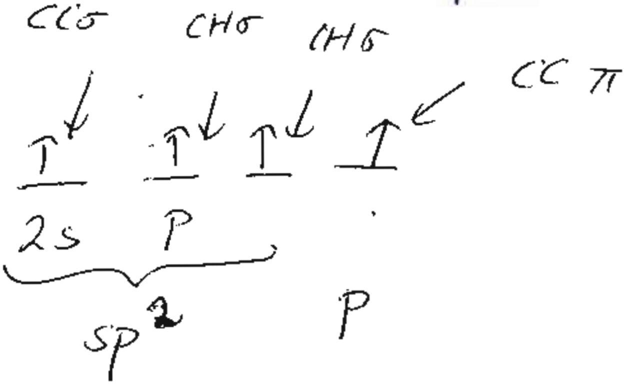


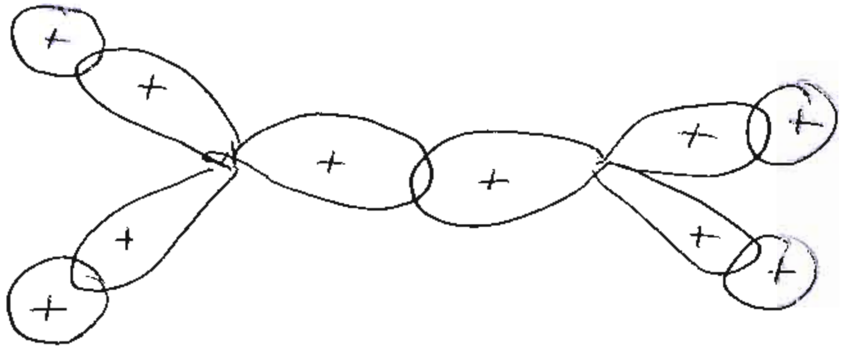


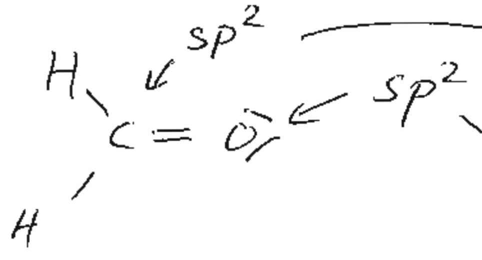
sp^2 $\quad t_1 = \frac{1}{\sqrt{3}}(2s) + \sqrt{\frac{2}{3}}(2p_x)$ ⑱-12

$$t_2 = \frac{1}{\sqrt{3}}(2s) - \frac{1}{\sqrt{6}}(2p_x) + \frac{1}{\sqrt{2}}(2p_y)$$

$$t_3 = \frac{1}{\sqrt{3}}(2s) + \frac{1}{\sqrt{6}}(2p_x) - \frac{1}{\sqrt{2}}(2p_y)$$







→ 2 C-H, 1 C-O σ bond

→ 1 C-O σ-bond, 2 lone pairs

+ 1 C-O π bond

ethylene formaldehyde actylene

The existence of such molecules is explained in valence-bond theory in terms of two different kinds of hybridization, sp^2 and sp, which are illustrated in Figure 12.10b and c. In sp^2 hybridization, the bonding orbitals involve a linear combination of an s orbital and two p orbitals (e.g., p_x and p_y) as follows:

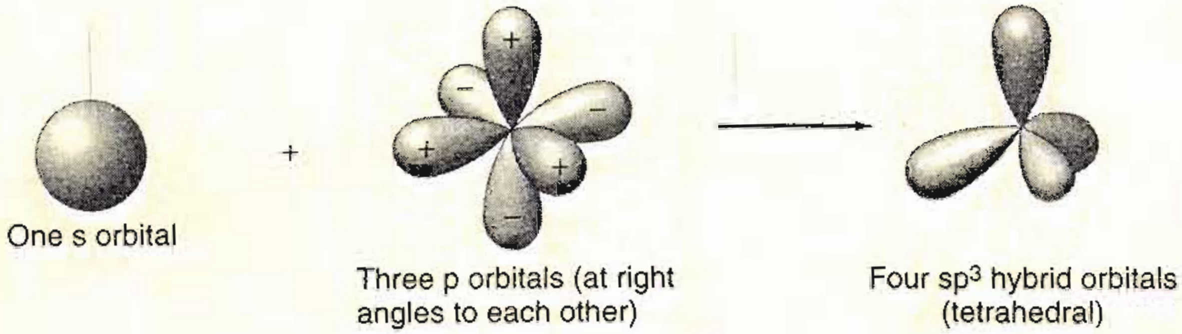
$$\psi_1 = \frac{1}{\sqrt{3}}\psi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\psi_{2p_x} \tag{12.59}$$

$$\psi_2 = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_x} + \frac{1}{\sqrt{2}}\psi_{2p_y} \tag{12.60}$$

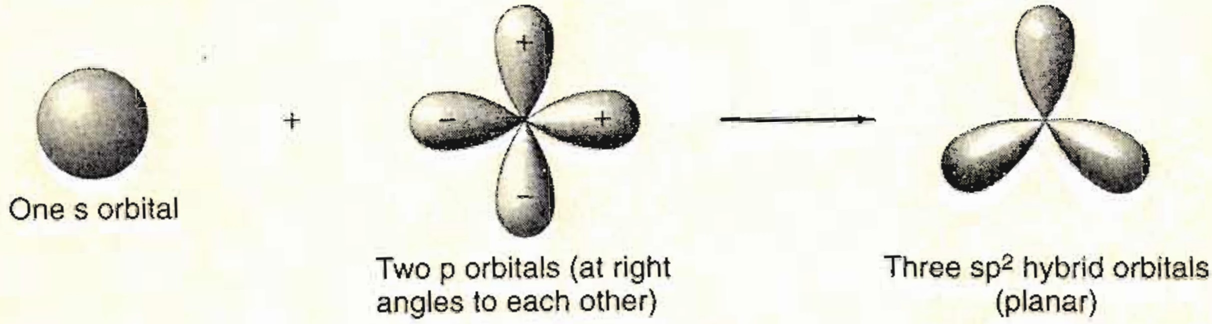
$$\psi_3 = \frac{1}{\sqrt{3}}\psi_{2s} = \frac{1}{\sqrt{6}}\psi_{2p_x} - \frac{1}{\sqrt{2}}\psi_{2p_y} \tag{12.61}$$

As shown in Figure 12.11b, these orbitals lie symmetrically in the XY plane; the angle between orbitals is 120°. In sp hybridization, we combine the s orbital with one

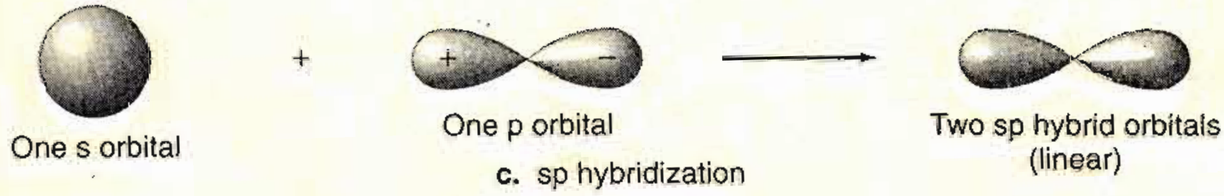
ormed



a. sp^3 hybridization



b. sp^2 hybridization



c. sp hybridization

1) double bond cannot rotate ⑱-13

(single σ bond can)

or $P_z - P_z$ overlap gets lost

2) π bonds are weaker than σ-bonds

because smaller overlap in π

$\rightarrow$ π bonds are more reactiv

than σ-bonds

sp normalization:

$$\psi_{1,2} = N(2s \pm 2p_x)$$

$$\int \psi_1^2 \, d\tau = N_1^2 \Big[\underbrace{\int (2s)^2 d\tau}_{1} + \underbrace{\int (2p_x)^2 d\tau}_{1} + 2 \underbrace{\int (2s)(2p_x) \, d\tau}_{0} \Big]$$

$$= N_1^2 (1 + 1 + 2 \cdot 0) = 2 N_1^2 \quad N_1 = \frac{1}{\sqrt{2}}$$

here no $\sqrt{2(1+S)}$ appears because here the AO-s are on the same atom and orthogonal!

for $S \neq 0$ AO-s must be on different atoms

$$\int \psi_2^2\, d\tau = N_2^2\Big[\underset{1}{\int (2s)^2\, d\tau} + \underset{1}{\int (2p_x)^2\, d\tau} - 2\underset{0}{\int (2s)(2p_x)\, d\tau}\Big]$$

$$= 2N^2 = 1 \Rightarrow N_2 = \frac{1}{\sqrt{2}}$$

$$N_1 = N_2 = N = \frac{1}{\sqrt{2}}$$

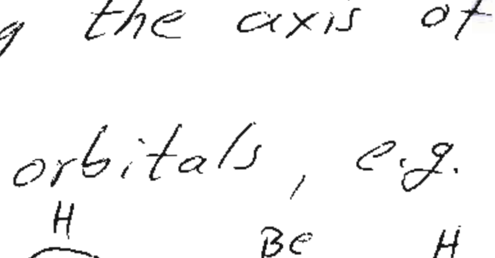
$$\int \psi_1 \psi_2\, d\tau = N^2 \int (2s + 2p_x)(2s - 2p_x)\, d\tau$$

$$= \frac{1}{2}\Big[\underset{1}{\int (2s)^2\, d\tau} - \underset{0}{\int (2s)(2p_x)\, d\tau} + \underset{0}{\int (2p_x)(2s)\, d\tau} - \underset{1}{\int (2p_x)^2\, d\tau}\Big]$$

$$= \frac{1}{2}(1 + 0 + 0 - 1) = 0$$

ψ_1, ψ_2 orthogonal!

$1s_H$ along the axis of one of the hybrid orbitals, e.g. BeH_2

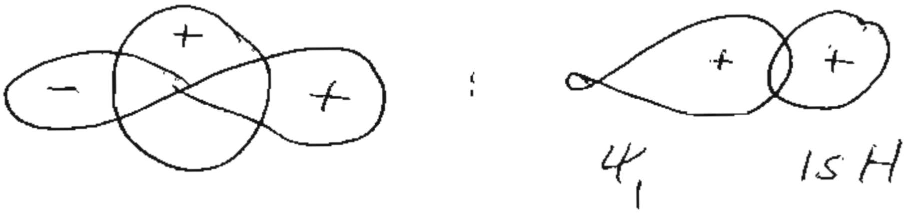


set up the un-normalized VB bond wave function for one of the Be–H bonds covalent part of the Be-H bond (for example with ψ_1 of sp hybrid)

$$\psi_{cov} = \underset{Be(1)}{\psi_1(1)}\ \underset{H(2)}{1s_H(2)} + \underset{Be(2)}{\psi_1(2)}\ \underset{H(1)}{1s_H(1)}$$

symmetric to electron exchange

$$\psi_1 = \frac{1}{\sqrt{2}}\left(2s_{Be} + 2p_{x\,Be}\right)$$ 1 sp lobe



ionic terms:

$\underset{Be^{-}}{\psi_1(1)}\ \underset{H^{+}}{\psi_1(2)}$ less important

$\underset{Be^{+}}{1s_H(1)}\ \underset{H^{\cancel{+}-}}{1s_H(2)}$ more important

all terms symmetric to electron exchange

$$\psi_b = c_1\left[\psi_1(1)\,1s_H(2) + \psi_1(2)\,1s_H(1)\right] \quad \text{Be} - \text{H}$$

$$+ c_2\left[\psi_1(1)\,\psi_1(2)\right] \quad \text{Be}^-\text{H}^+$$

$$+ c_3\left[1s_H(1)\,1s_H(2)\right] \quad \text{Be}^+\text{H}^-$$

c_1, c_2, c_3 from variation

ψ_b: symmetric to e^- exchange

→ antisymmetric spin function

→ wave function of the bond:

$$\psi_b\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

can also be done for an sp^2 or an sp^3 lobe + a $1s_H$ to set up the wave function for a more general A-H bond.

Obj Molecular Orbitals ⑲ -1

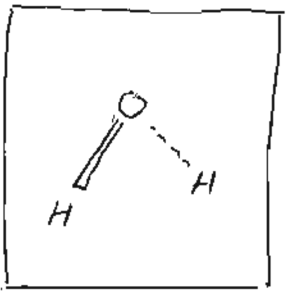
Homonuclear Diatomics, A_2 and ions

Molecular Orbitals (MO-s)

The electron density ψ^2 (total) must have the same symmetry as the molecule

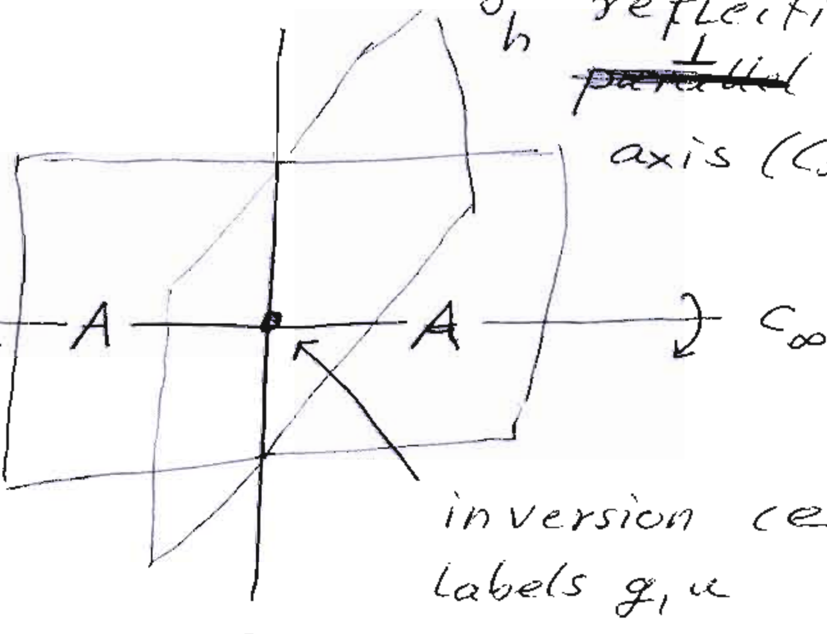
→ also each MO alone

H_2O



reflection symmetry also at molecular plane

Homonuclear Diatomic



σ_h reflection plane ~~parallel~~ ⊥ to main axis (C_∞) ⇒ h

all angles possible

σ_v
∞ number of them
every plane that contains C_∞ is σ_v
∥ to C_∞
containing it)

inversion center i
labels g, u

only 180° rotations
⇒ 2 times possible for 1 time round 360°
→ C_2 (infinite number of them)

⇒ $D_{\infty h}$

if no σ_h (no i): $C_{\infty v}$ A − B

$\underline{H_2}$: $\sigma_g = 1s_A + 1s_B$

symmetry label: capital greek

Σ_g^+ ← symmetric to σ_h

in A_2 also AO-s are in the name:

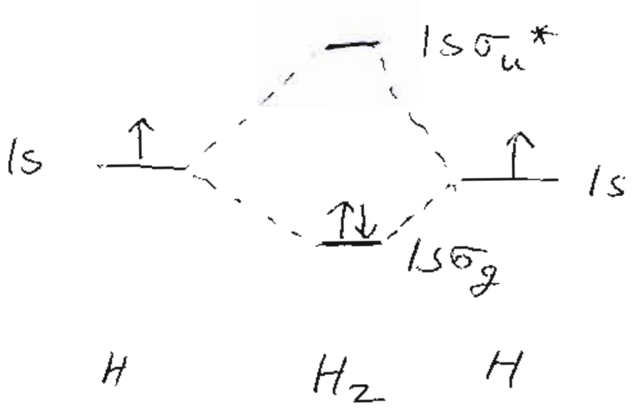
$1s\sigma_g = 1s_A + 1s_B$

$1s\sigma_g$ rotationally (around bond) symmetric orbital (σ) which does not change sign when inverted bi (σ_g) and is made with 1s orbitals ($1s\sigma_g$)

← antibonding, repulsive state

$1s\sigma_u^* = 1s_A - 1s_B$

+ ⇔ − ⇒ u



bond order:

$bo = \frac{1}{2}$(# binding e⁻ − # antibonding e⁻)

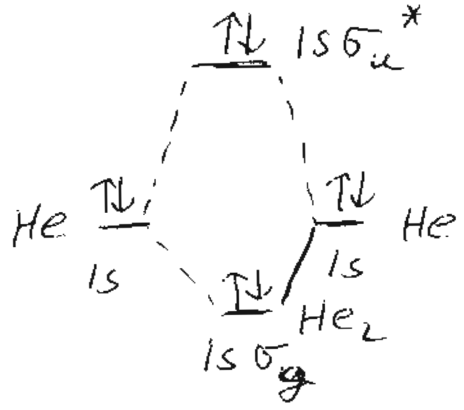
H_2: $bo = \frac{1}{2}(\overset{\sigma_g}{2} - \overset{\sigma_u^*}{0}) = 1$

≙ 1 bond

ground state config.: $1s\sigma_g^2$

next in periodic Table: He_2

Same MO-s as in H_2, but 4 e^-



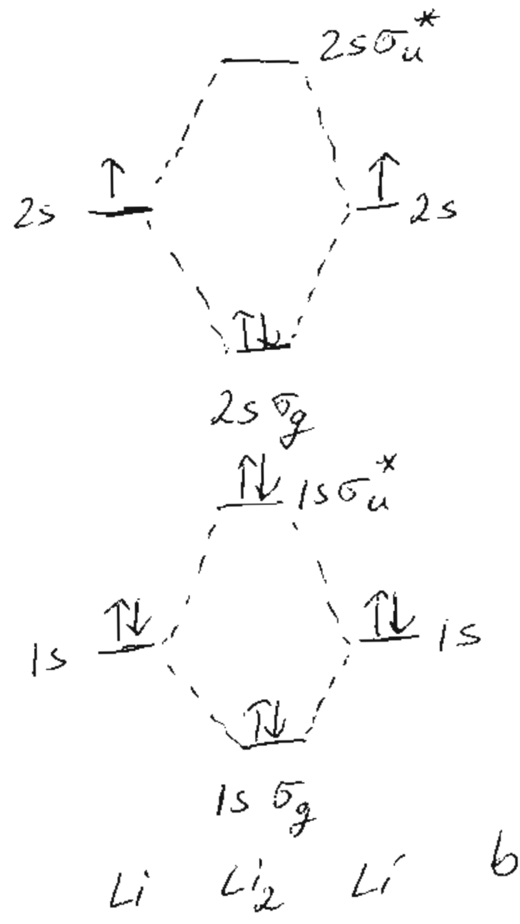
$bo = \frac{1}{2}(\overset{\sigma_g}{2}-\overset{\sigma_u^*}{2}) = 0$

should have no bond

but it can exist with a very weak bond (the weakest one known)

ground state config.: $1s\sigma_g^2 1s\sigma_u^{*2}$

<u>Li_2</u>: each Li: $1s^2 2s^1$



exists in the gas phase

$bo = \frac{1}{2}(\underset{\substack{1s\sigma_g \\ 2s\sigma_g}}{4} - \underset{1s\sigma_u^*}{2})$

bond from 2s electrons

$1s\sigma_g^2 1s\sigma_u^{*2} 2s\sigma_g^2$

bond weakend a little because in $1s\sigma$-s bonding in $1s\sigma_g$ $\left(\frac{J+K}{1+S}\right)$ a little less than antibonding in $1s\sigma_u^*$ $\left(\frac{J-K}{1-S}\right)$

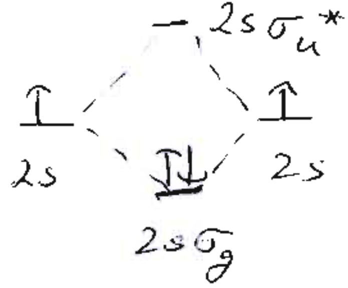
inner shell repulsion

S is quite small, because the 1s AO-s are rather small and more far away from each other than 2s, because Li-Li longer than H-H distance

→ inner shell repulsion can be neglected mostly

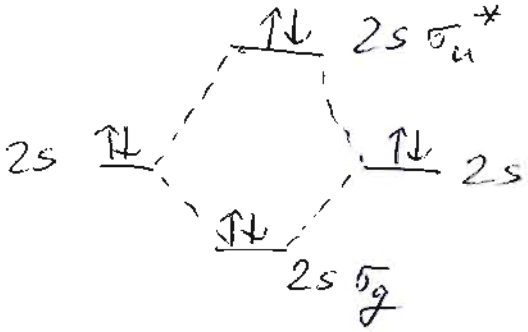
→ for an MO diagram one can usually concentrate on valence e^-:

Li_2:



same bo = 1

Be_2 : Be: $1s^2 2s^2$



$bo = \frac{1}{2}(2-2) = 0$

($1s\sigma_g$, $1s\sigma_u^*$ also 0)

Be_2 not yet experimentally found but large calculations including many AO-s and e-e interactions indicate: Be_2 might be stable with very weak bond

$\underline{B_2}$: B $1s^2 2s^2 2p^1$

⇒ p-AO-s must be considered

P_z along B-B axis assumed ⇒ σ overlap

B_1 ~~label~~ given label A

B_2 given label B:

$$2p\sigma_g = 2p_{zA} + 2p_{zB}$$

$$2p\sigma_u^* = 2p_{zA} - 2p_{zB}$$

rotation symmetry → still σ-MO

the other 2 ~~gar~~ pairs can overlap side ways to form π-MO which are not rotational symmetric, but symmetric to a plane

exactly like π bond formation in VB theory

$2p_y$: $2p\pi_u = 2p_{yA} + 2p_{yB}$

$$2p\pi_g^* = 2p_{yA} - 2p_{yB}$$

Now the bonding orbital changes sign when reflected at i ⇒ π_u bonding, π_g^* antibonding

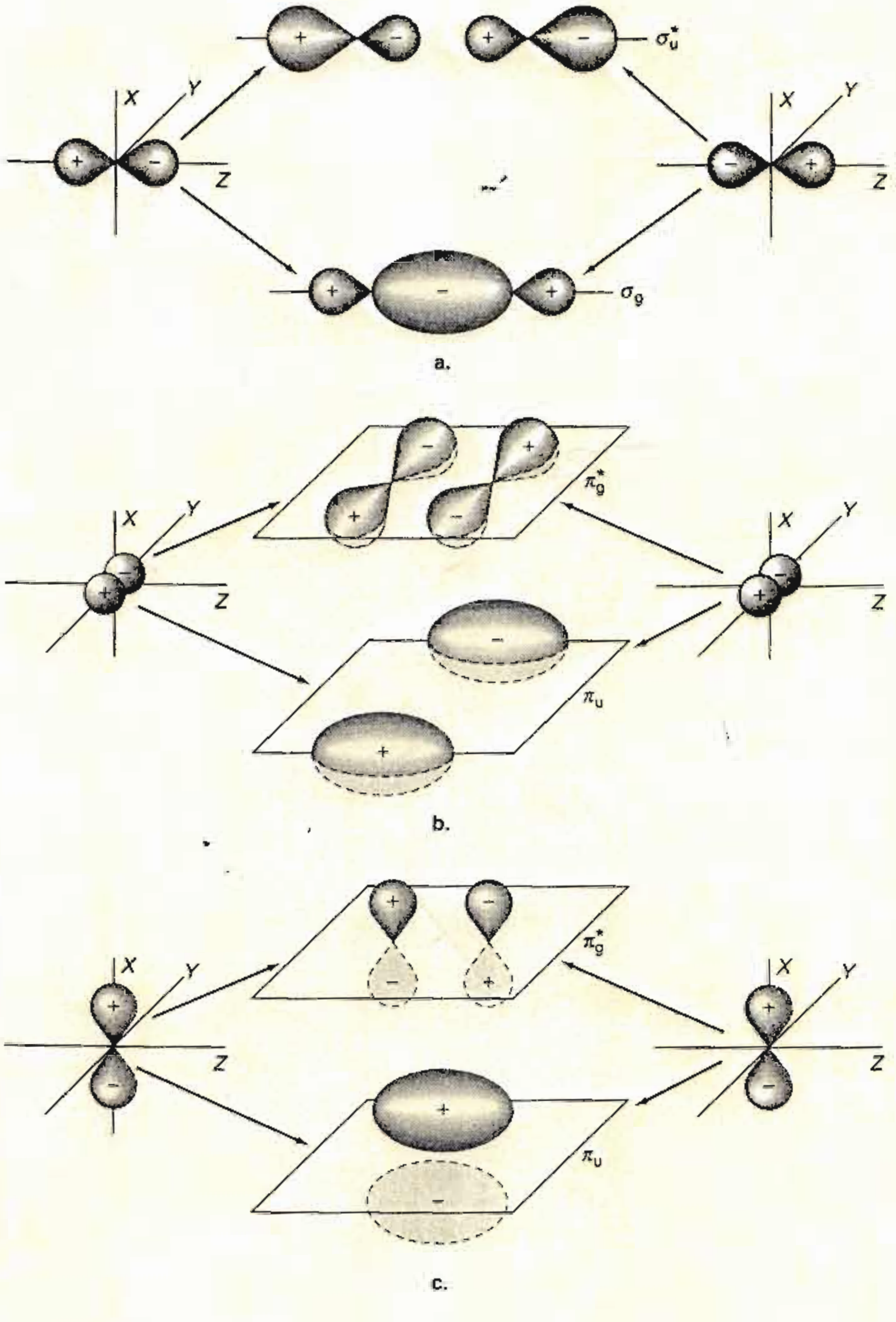


FIGURE 12.20
Combination of p atomic orbitals to give molecular orbitals. (a) σ orbitals formed from two p_z orbitals, which lie along the axis of the molecule (the Z axis). (b) π orbitals formed from p_y orbitals. (c) π orbitals formed from p_x orbitals.

same for $2p_x$:

$$2p\pi_u = 2p_{xA} + 2p_{xB}$$

$$2p\pi_g^* = 2p_{xA} - 2p_{xB}$$

The 2 sets of π-orbitals are equivalent → same energy for the 2 $2p\pi_u$-MO-s and also same energy (higher) for the 2 $2p\pi_g^*$-MO-s

→ two $2p\pi_u$ MO-s are degenerate and two $2p\pi_g^*$-MO-s are degenerate

no combinations of p_x with p_y:

1) overlap p_x - p_y = 0

2) symmetry different from molecule symmetry if p_{xA} is combined p_{yB}

B_2, C_2, N_2: $2p\pi_u$ below $2p\sigma_g$ but not much

O_2, F_2: $2p\pi_u$ above $2p\sigma_g$

no difference for antibonding ones:

$2p\sigma_u^*$ above $2p\pi_g^*$ in all 5 cases

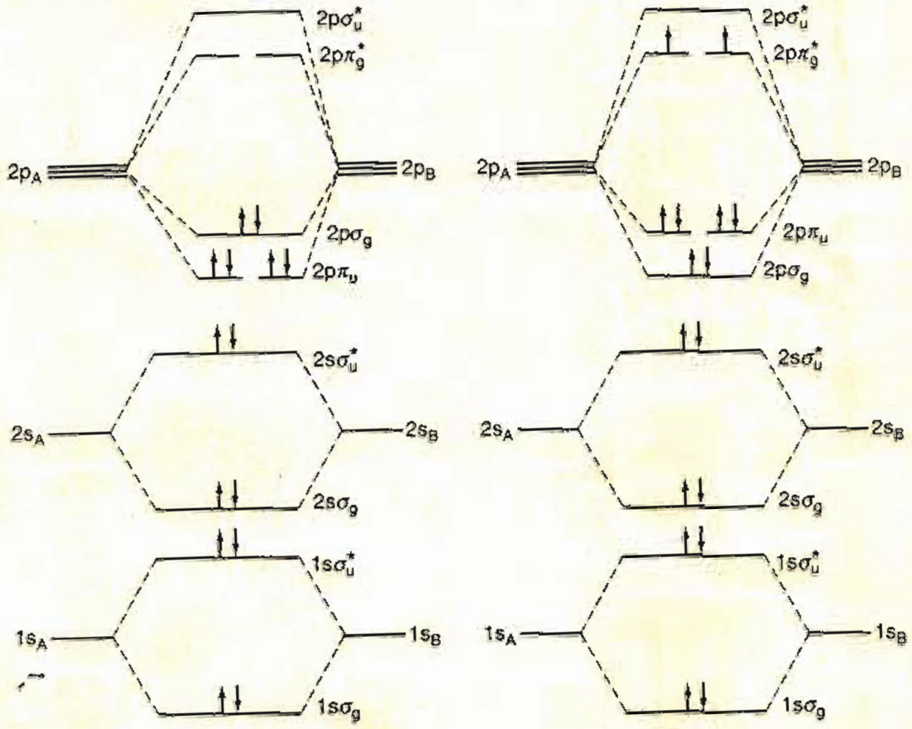
Note that we cannot combine, for example, p_x and p_z orbitals, since the resulting MO would be inconsistent with the symmetry of the molecule.

The electronic configurations in molecules like N_2, O_2, and F_2 depend on the order of the energy levels. Calculations by the self-consistent field method have shown that the $2p\sigma_g$ and $2p\pi_u$ levels have much the same energy, but photoelectron spectroscopy has shown that for N_2 and F_2 the order is as indicated in Figure 12.21a, which gives the assignment of electrons in N_2. The first four electrons go into the $1s\sigma_g$ and $1s\sigma_u^*$ orbitals. The high nuclear charge draws these electrons close to the nuclei, and there is virtually no overlap for the 1s AO's. The next four electrons fill the $2s\sigma_g$ and $2s\sigma_u^*$ MOs. The next level, $2p\pi_u$, shown as two lines, is degenerate and can accommodate four electrons. The remaining two electrons go into the $2p\sigma_g$ orbital. There are therefore six bonding electrons, and the bond order is three. The configuration of N_2 can be written as

$$1s\sigma_g^2 1s\sigma_u^{*2} 2s\sigma_g^2 2s\sigma_u^{*2} 2p\pi_u^4 2p\sigma_g^2$$

For O_2, however, the order of filling is different, as shown in Figure 12.21b.

A valuable feature of MO theory is that it provides a very simple interpretation of molecular magnetism. In Section 11.9 we saw that an electron in any orbital has a magnetic moment. If all such electrons in an atom or molecule are paired, there is no resultant magnetic moment, and there is no interaction with a magnetic field;



a. Bond order = 3

b. Bond order = 2

N_2

O_2

FIGURE 12.21
Molecular-orbital energy diagrams for homonuclear diatomic molecules. (a) The order of energy levels for N_2, showing the assignment of the 14 electrons; the order is the same for F_2. (b) The order of levels for O_2, showing the electrons.

N_2 : N : $1s^2 2s^2 2p^3$ ⑲ - 7

⇒ groundstate has 6 e^- in ~~π~~ $p\sigma$ and $p\pi$ orbitals

$$1s\sigma_g^{2}\, 1s\sigma_u^{*2}\, 2s\sigma_g^{2}\, 2s\sigma_u^{*2}\, 2p\pi_u^{4}\, 2p\sigma_g^{2}$$

$$bo = \frac{1}{2}(\underbrace{10}_{\text{in orbitals without *}} - \underbrace{4}_{\text{in orbitals with *}}) = \frac{6}{2} = 3$$

→ strong triple bond

$N\equiv N$: $941.4\ \frac{kJ}{mol}$ dissociation energy

110 pm bond length

O_2 : Hund's rule for degenerate π-sets

O: $1s^2 2s^2 2p^4$

−2 +2 −6 +2

$$1s\sigma_g^{2}\, 1s\sigma_u^{*2}\, 2s\sigma_g^{2}\, 2s\sigma_u^{*2}\, 2p\sigma_g^{2}\, 2p\pi_u^{4}\, 2\pi\pi_g^{*2}$$

↑ Hund's rule unpaired!

2 + 2 + 2 + 4

$$bo = \frac{1}{2}(\underbrace{10}_{\text{in bonding orbitals (no star)}} - \underbrace{6}_{\text{in antibonding orbitals (*)}}) = \frac{4}{2} = 2$$

O=O : 498.7 $\frac{kJ}{mol}$ dissociation energy

121 pm bond length

F_2 F: $1s^2 2s^2 2p^5$

→ $2e^-$ more which fill $2p\pi_g^*$ ~~wit~~ to $4e^-$

$1s\sigma_g^2 1s\sigma_u^{*2} 2s\sigma_g^2 2s\sigma_u^{*2} 2p\sigma_g^2 2p\pi_u^4 2p\pi_g^{*4}$

2 more in π_g^*

→ bo $= \frac{1}{2}(10-8) = 1$

less strong single bond

F-F : 156.9 $\frac{kJ}{mol}$ dissociation energy

142 pm bond length again longer

$R_{N_2} < R_{O_2} < R_{F_2}$

all electrons paired (N_2, F_2): no net resultant magnetic moment, no interactions with magnetic fields (slight repulsion): dia magnetic

2 unpaired electrons (B_2, O_2); net magnetic moment, interaction (attraction) with magnetic fields: paramagnetic

Table 10.5 Properties of homonuclear diatomic molecules of the second-period elements*

	Li_2	B_2	C_2	N_2	O_2	F_2
$\sigma^\star_{2p_x}$	☐	☐	☐	☐	☐	☐
$\pi^\star_{2p_y}$, $\pi^\star_{2p_z}$	☐☐	☐☐	☐☐	☐☐	↑ ↑	↑↓ ↑↓
σ_{2p_x}	☐	☐	☐	↑↓	↑↓	↑↓
π_{2p_y}, π_{2p_z}	☐☐	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
$\sigma^\star_{2s}$	☐	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Bond order	1	1	2	3	2	1
Bond length (pm)	267	159	131	110	121	142
Bond dissociation energy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic

*For simplicity the σ_{1s} and $\sigma^\star_{1s}$ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that the order of π_{2p_y}, π_{2p_z}, and σ_{2p_x} is reversed for O_2 and F_2.

Example 10.7 shows how MO theory can help predict molecular properties of ions.

EXAMPLE 10.7 The N_2^+ ion can be prepared by bombarding the N_2 molecule with fast-moving electrons. Predict the following properties of N_2^+: (a) electron configurathe magnetic predictions agrees completely with experiment

magnetic moment ~~could have~~ is not associated with angular momentum:

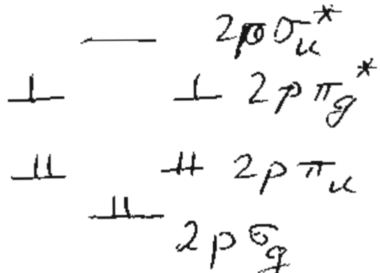
no angular momentum in σ-MO-s

the orbital momenta of π-MO-s cancel if the degenerate π_u set is occupied by 2 or 4 electrons

→ no angular momentum from orbitals no matter if π-e paired or not

⇒ only spin-momenta of unpaired electrons are important for magnetism (paired e-s: spin momenta cancel in each pair)

O_2: ~~π~~ $p\sigma$, $p\pi$ orbitals: ⑲-10

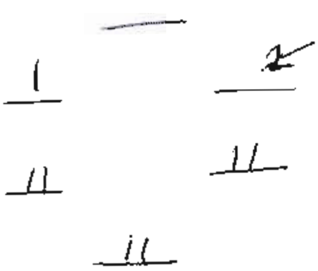


$bo = \frac{1}{2}(6-2) = \frac{4}{2} = 2$

$1s\sigma_g, 1s\sigma_u^*$ and $2s\sigma_g, 2s\sigma_u^*$ cancel in bo

paramagnetic

$\underline{O_2^+}$



1 electron gone → + charge

$bo = \frac{1}{2}(6-1) = 2.5$

paramagnetic

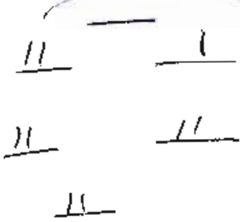
$\underline{O_2^{2+}}$

2 electrons gone → 2+ charge

$bo = \frac{1}{2}(6-0) = 3$

diamagnetic

$\underline{O_2^-}$

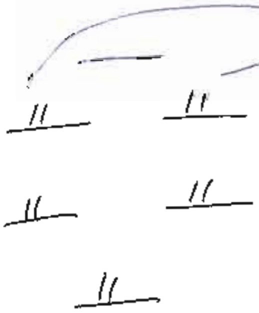


1 electron added → − charge

$bo = \frac{1}{2}(6-3) = 1.5$

paramagnetic

$\underline{O_2^{2-}}$



2 electrons added → 2− charge

$bo = \frac{1}{2}(6-4) = 1$

diamagnetic

obj.: He_2 the weakest bond
hetero nuclear diatomics (AB)
H_2O: triatomic

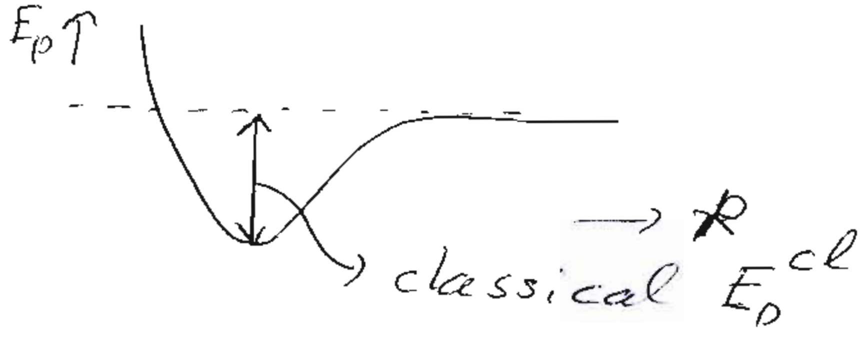
The weakest known bond : He_2

He_2: bo = 0 ⇒ if it exists, it must have a very weak bond

Slater (1928) :

Dissociation energy : $E_D^{cl} = -\left[\overset{\text{well depth}}{\overset{\Downarrow}{E(He_2)}} - 2E(He)\right]$

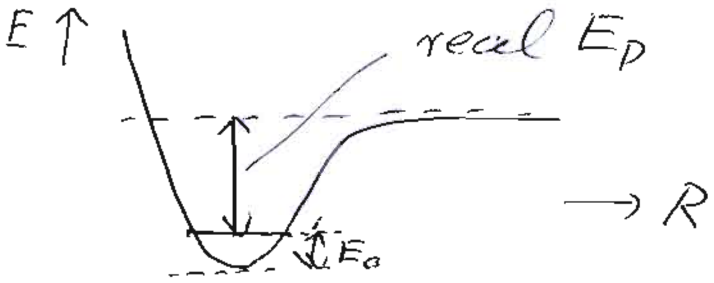
classical E_D: well depth



Slater found : $E_D^{cl} = 1,23 \cdot 10^{23}$ J
$= 74.0$ J/mol

H_2: $E_D = 435.0$ kJ/mol more than 1000 times stronger bond

real dissociation energy E_D : zero-point energy must be added (E_0)



$$E_D = -\left[\underset{\displaystyle\overset{\downarrow}{E_D^{el}}}{E(He_2)} + E_0 - 2E(He)\right]$$

$E_D > 0$ He_2 exists

$E_D < 0$ He_2 does not exist:
2 isolated He atoms are more stable than He_2

here we use energies E_D/k_B
unit is K

Slater's well depth: 8,9 K
if this would be E_D it means that if $T > 8{,}9\,K$ He_2 bond would break and no He_2 exists at $T > 8{,}9\,K$

<u>very</u> exact calculations:
well depth = 10,9 K
R = 297 pm

real diss. energy with E_0 included : $E_D = 10^{-3}\,K = 1\,mK$

$\Rightarrow He_2$ exists <u>only</u> if $T < 1\,mK$

rapid expansion of He gas leads to $T < mK$

in discharge He_2^+ found which could only come from

$$He_2 \rightarrow He_2^+ + e^-$$

He_2 formed from

$$3\,He \longrightarrow He_2 + He$$

at $T < 1\,mK$

the free He atom carries the energy from formation of He_2 away

other hand, there are
(i.e., *odd* electrons),
ien interacts with an
ee of paramagnetism

6 electrons in O_2 are
hand, are in the $2p\pi_g^*$
by Hund's rule they
d to have a resultant
ient with experiment.
but four additional
$2p\pi_g^*$ orbitals in Fig-
cel the bonding from
pair of electrons; the
s the bonding, there
itional valence-bond

but decreasing bond
ord [illegible] N_2, O_2, and F_2.
ed by the decreasing
, and 153.0 kJ mol^{-1},
0 pm for N_2, 121 pm

doubt as to whether
(Figure 12.18) shows
ons. If a bond can be
chanical calculations
led that the classical
ell depth**) is 1.23 ×
han a thousand than,
mol^{-1}. Furthermore,
ecule is very close to
gy, the molecule can
temperatures. If it is

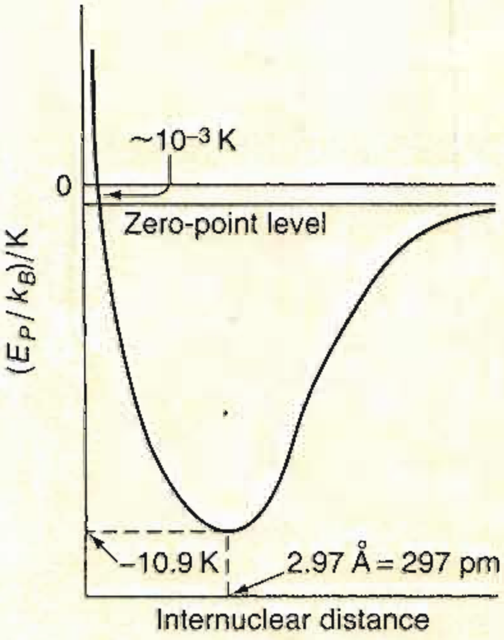


FIGURE 12.22
A schematic diagram of potential energy divided by the Boltzmann constant (E_p/k_B) for the He_2 dimer. It is not possible to draw this diagram to scale, since the zero-point level is in fact extremely close to the line corresponding to dissociation. Note that the zero-point line meets the curve at very high separations, so that the dimer has a large internuclear separation.

internuclear separation
level lies about 10^{-3} K
are shown schematicall
would only survive for

In February, 1993,
University of Minneso
evidence for the existen
1 mK could be achieve
they were able to detect
only be formed by loss
collision between three

At the time of writ
known molecule. The c
larger by several power

Heteronuclear Di

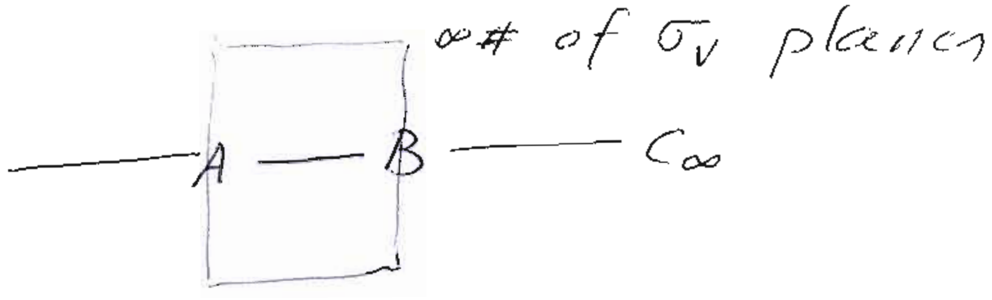
Every heteronuclear di
the molecule is a C_∞ a
symmetry, designated
In particular, a heteron
differs from a homonu

The wave functio
one of the symmetry s
to this chapter. Subscr
of inversion, but for so
the former to indicate
indicate a change of si

Lowercase Greek
individual molecular o
orbitals is called a 1s
orbital. Since the gera
distinguished simply
orbital is formed by
$1s_A + 2s_B$ or $1s_A - 2s$

On this basis we
and two of these may

heteronuclear diatomics AB



but no σ_h plane, no C_2 axes, no i $\Rightarrow$ $C_{\infty v}$ → g and u cannot be used (no i)

→ $1s_A + 1s_B = 1s\sigma$ no g

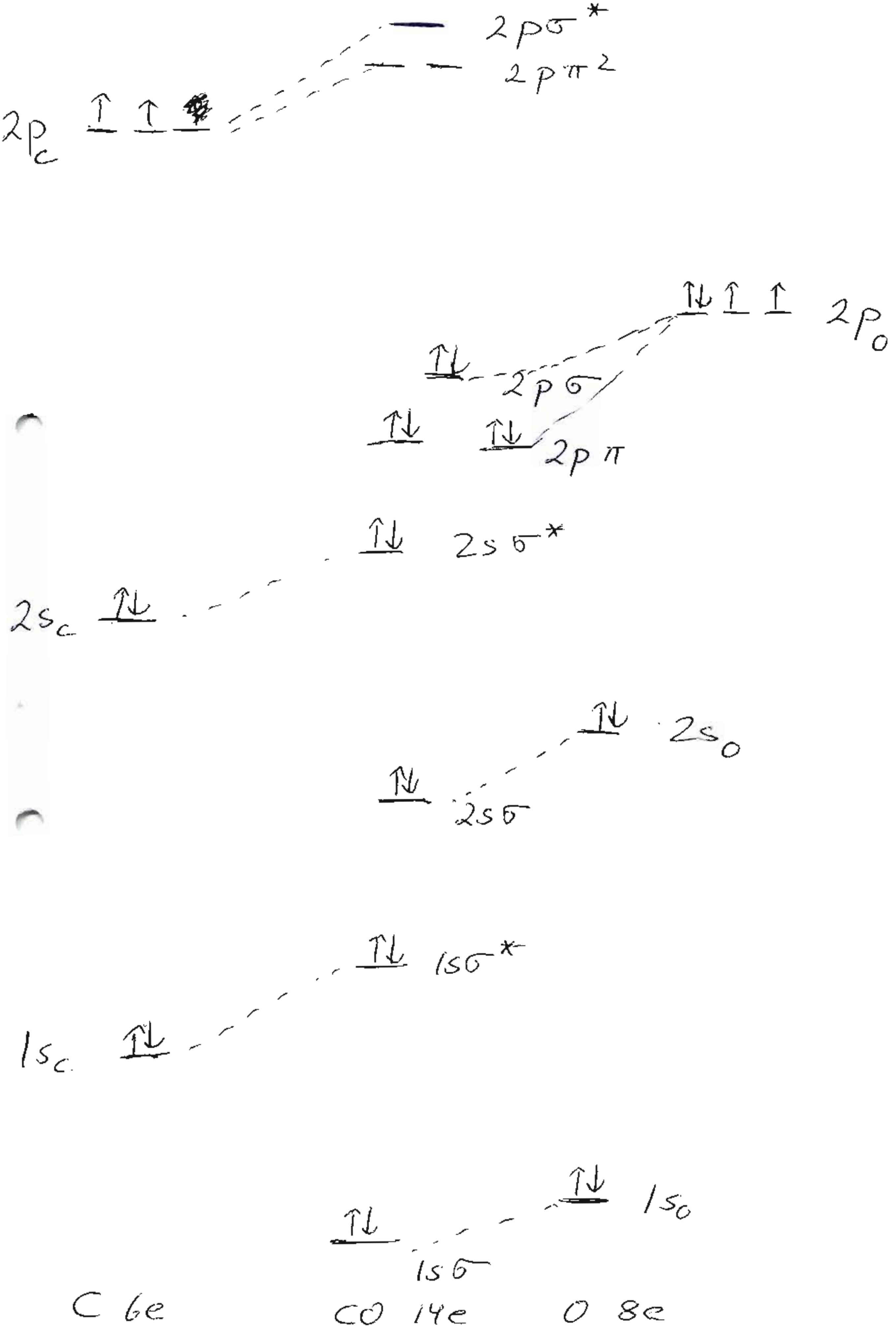
$1s_A - 1s_B = 1s\sigma^*$ no u

MO diagrams are similar but unsymmetric:

the atom, A or B, that has the larger electronegativity has the lower energy AO-s

such similar, only a little unsymm. diagrams appear when e.g. atoms with $n=2$ valence e^- are combined with other $n=2$ atoms

CO


$2p\sigma^*$
$2p\pi^2$
$2p_c$
$2p\sigma$
$2p\pi$
$2p_O$
$2s\sigma^*$
$2s_c$
$2s_O$
$2s\sigma$
$1s\sigma^*$
$1s_c$
$1s_O$
$1s\sigma$
C 6e
CO 14e
O 8e

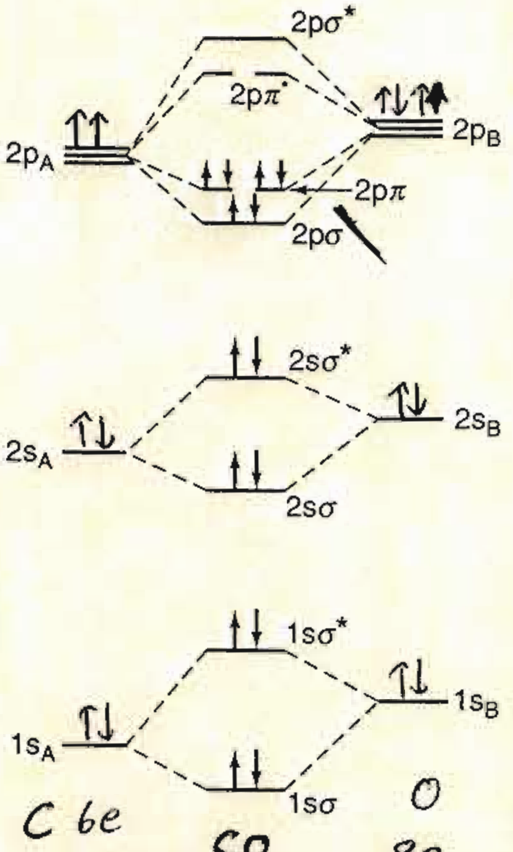


FIGURE 12.23 14e
Molecular-orbital diagram for a heteronuclear diatomic molecule. As an example, the 14 electrons of carbon monoxide are shown as arrows.

Figure 12.23 shows a schematic MO diagran
As an example, carbon monoxide has 14 el
Principle we have

$$(1s\sigma)^2(1s\sigma^*)^2(2s\sigma)^2(2s$$

The two pairs of $\sigma-\sigma^*$ orbitals will cancel a
results from the six electrons in the 2pπ a
three.

The Water Molecule

The procedures for constructing molecular o
may be exemplified by a brief treatment of the
for which are shown in Figure 12.14a. The
symmetry elements, and in Figure 12.24a w
relation to these elements. Since the 1s and
none of the symmetry operations brings ab
therefore of A_1 symmetry. The 2p$_z$ orbital h
the Z axis and a negative lobe in the other. T
no change in this orbital, which is therefore

The 2p$_x$ and 2p$_y$ orbitals, however, be
orbital in the σ_v' plane interchanges the + and
and the same happens with a C_2 rotation. Re
change. The 2p$_x$ orbital is therefore of B_1 sy
that the 2p$_y$ orbital is of B_2 symmetry.

The situation with the orbitals on the hy
a little more complicated, since these atoms
of the molecule; they only lie in the σ_v' p
which we will write as 1s$_A$, therefore does
molecule, and the same is true of the 1s$_B$ or
we can construct orbitals that do have the righ
orbitals, 1s$_A$ + 1s$_B$, is unchanged when any o
and it is therefore of A_1 symmetry. The differ
the C_2 operation is performed and when the σ
unchanged when σ_v' is performed. It is theref

The symmetry properties of the variou
summarized in Figure 12.24b. The complete

CO

$bo = \frac{1}{2}(10-4) = 3$

$(1s\sigma)^2(1s\sigma^*)^2(2s\sigma)^2(2s\sigma^*)^2(2p\sigma)^2(2p\pi)^4$

$\sigma - \sigma^*$ electrons cancel in bo

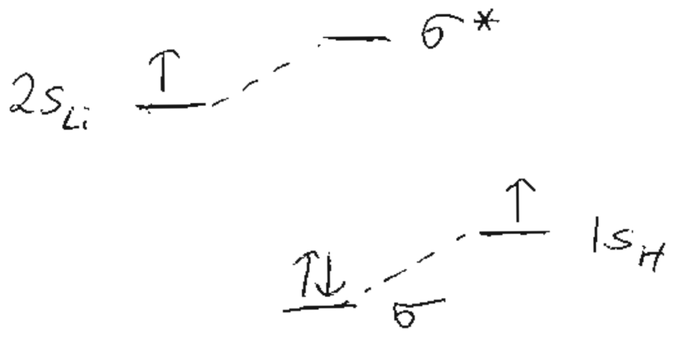
bonding from $p\sigma$ and $p\pi$

bonding orbitals have larger density on O than on C because they are closer in energy to O-AO-s

antibonding ones opposite

if $n=1$ is combined with $n=2$ then the 1s of $n=1$ atom is closer in energy to the 2s valence electrons of the other one.

⇒ bond in LiH from $\sigma = 2s_{Li} + 1s_H$



$bo = \frac{1}{2} \cdot (2-0) = 1$

groundstate:

$1s_{Li}^2 \sigma^2$

$1s_{Li}$ ⇅ .... ⇅ non-bonding

does not count in bo!

H_2O molecule

First: check the symmetry of the AO-s involved according to the molecular symmetry

H_2O: O atom is in the C_2 axis

group: C_{2v}: C_2, σ_v, $\sigma_v'(\perp\sigma_v)$, E

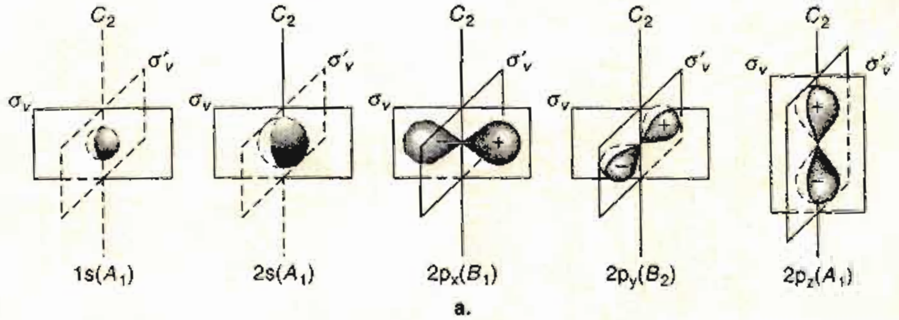
E from "Einheit", unity: does nothing

character tables of a symmetry class give the sign changes of an AO when acted with that symmetry operation on it which is under consideration:

+1 no sign change

−1 sign of the AO changes

the +1, −1 pattern fits only, if the AO belongs to that symmetry class



	E	C_2	σ_v	σ'_v	Atomic Orbitals
A_1	+1	+1	+1	+1	$1s(O)$, $2s(O)$, $2p_z(O)$, $1s_A + 1s_B$
A_2	+1	+1	−1	−1	—
B_1	+1	−1	+1	−1	$2p_x(O)$
B_2	+1	−1	−1	+1	$2p_y(O)$, $1s_A - 1s_B$

b.

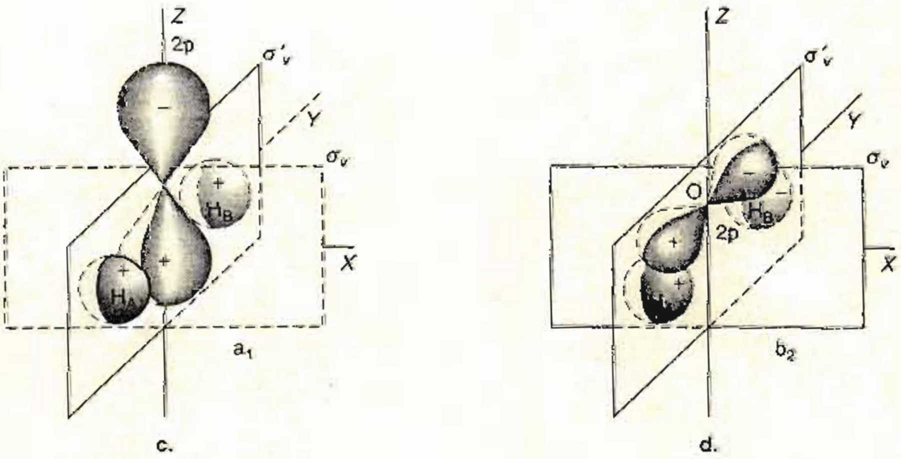


FIGURE 12.24
Orbitals for the water molecule. (a) The atomic orbitals and their symmetry species. The σ'_v plane is the plane of the molecule. (b) The C_{2v} character table showing the symmetries of the atomic orbitals and the symmetry-adapted orbitals. (c) and (d) The bonding molecular orbitals a_1 and b_2.

We can also construct the orbital

$$b_2 = 1s_A - 1s_B + \lambda 2p_y \qquad (12.72)$$

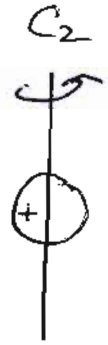
in which orbitals of B_2 symmetry are combined. This orbital is represented in Figure 12.24d.

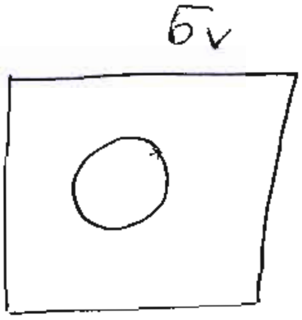
Both of these orbitals are bonding, since the atomic orbitals have been added together, and there is a piling up of charge between the nuclei. For each bonding molecular orbital there is an antibonding one, of the same symmetry, formed by subtracting the atomic orbitals. These are indicated by an asterisk. The antibonding molecular orbital corresponding to a_1 is

$$a_1^* = 1s_A + 1s_B - \lambda'_1 2s - \lambda'_2 2p_z \qquad (12.73)$$

O is in the C_2 axis

$1s_O$, $2s_O$ spherically symmetric and because O is inside the C_2 axis they do not change sign when C_2 acts on them





~~σ_v intersects~~ the center of the ~~st~~ sphere is in both σ_v and σ_v' so they reflect ~~the~~ a positive half ~~the~~ sphege on the other which is the same. E does nothing

$$\rightarrow C_2 s_O = \sigma_v s_O = \sigma_v' s_O = E s_O = s_O$$

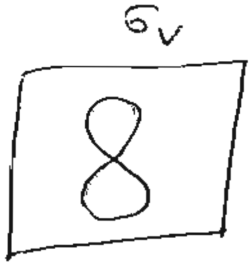
sequence for O:

E	C_2	σ_v	σ_v'
+1	+1	+1	+1

that is the Same as A_1

the same is true for p_z
which is also in the C_2 axis:

no change



same parts of $2p_z$
above and below σ_v

and same for σ_v'

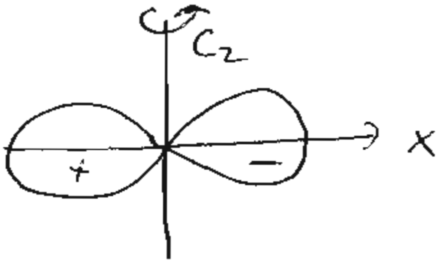
→ for $2p_z$:

E	C_2	σ_v	σ_v'
+1	+1	+1	+1

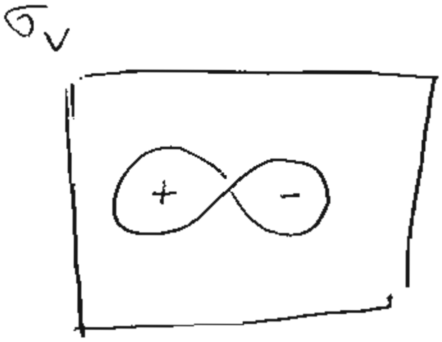
→ of O $1s_O$, $2s_O$, $2p_z$ all have

A_1 symmetry

$E\,2p_{xO} = 2p_{xO}$ +1



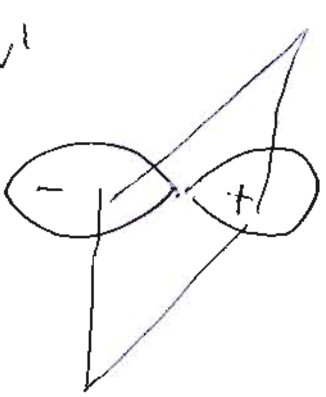
$C_2 2p_{xO} = -2p_{xO}$ −1



reflects half the
orbital on the
corresponding half

→ $\sigma_v 2p_{xO} = 2p_{xO}$ +1

$2p_x$ is perpendicular to $\sigma_v{}'$



so $\sigma_v{}'$ reflect the positive half on the negative one

$\sigma_v{}' 2p_{x0} = -2p_{x0}$ -1

so the sequence of symmetries is

E C_2 σ_v $\sigma_v{}'$

$+1$ -1 $+1$ -1 for $2p_{x0}$

this is the B_1 sequence in the character table

for $2p_{y0}$ the same holds as for $2p_{x0}$, only the roles of σ_v and $\sigma_v{}'$ are interchanged: $\sigma_v 2p_{y0} = -2p_{y0}$

$\sigma_v{}' 2p_{y0} = 2p_{y0}$

so the sequence for $2p_{y0}$ is

E C_2 σ_v $\sigma_v{}'$

$+1$ -1 -1 $+1$ thus $2p_{y0}$ is B_2

H_A is above σ_v,

H_B is below σ_v

$\rightarrow \quad E\,1s_A = 1s_A$

$E\,1s_B = 1s_B$

C_2 rotates H_A into H_B

$\rightarrow \quad C_2\,1s_A = 1s_B$

$C_2\,1s_B = 1s_A$

σ_v reflects the upper H_A into the lower H_B:

$\sigma_v\,1s_A = 1s_B$

$\sigma_v\,1s_B = 1s_A$

σ_v' reflects the upper half of each 1s sphere into the ~~lowe~~ identical one:

$\rightarrow \quad \sigma_v'\,1s_A = 1s_A$

$\sigma_v'\,1s_B = 1s_B$

$\rightarrow$ $1s_A$ and $1s_B$ alone do not molecular symmetry (C_{2v})

they do not belong to any symmetry of the molecule

<u>but</u> the linear combinations

$1s_A + 1s_B$ and $1s_A - 1s_B$ do!

E is always +1, because it does nothing

$$C_2(1s_A + 1s_B) = C_2\,1s_A + C_2\,1s_B = 1s_B + 1s_A$$
$$= 1s_A + 1s_B \ : +1$$

$$\sigma_v(1s_A + 1s_B) = \sigma_v\,1s_A + \sigma_v\,1s_B = 1s_B + 1s_A \ : +1$$

$$\sigma_v'(1s_A + 1s_B) = \sigma_v'\,1s_A + \sigma_v'\,1s_B = 1s_A + 1s_B \ : +1$$

$$\Rightarrow 1s_A + 1s_B : \quad \begin{array}{cccc} E & C_2 & \sigma_v & \sigma_v' \\ +1 & +1 & +1 & +1 \end{array} \quad \Rightarrow A_1$$

$$C_2(1s_A - 1s_B) = 1s_B - 1s_A = -(1s_A - 1s_B) \ : -1$$

$$\sigma_v(1s_A - 1s_B) = 1s_B - 1s_A = -(1s_A - 1s_B) \ : -1$$

$$\sigma_v'(1s_A - 1s_B) = 1s_A - 1s_B \ : +1$$

$$\Rightarrow 1s_A - 1s_B : \quad \begin{array}{cccc} E & C_2 & \sigma_v & \sigma_v' \\ +1 & -1 & -1 & +1 \end{array} \quad \Rightarrow B_2$$

We can only form MO-s where ψ^2 has the same symmetry as the molecule

$\Rightarrow$ only those can be combined which belong to the same symmetry class:

	E	C_2	σ_v	σ_v'	
A_1	+1	+1	+1	+1	$1s_O$, $2s_O$, $2p_{zO}$, $1s_A + 1s_B$
A_2	+1	+1	−1	−1	—
B_1	+1	−1	+1	−1	$2p_{xO}$
B_2	+1	−1	−1	+1	$2p_{yO}$, $1s_A - 1s_B$

$2p_{xO}$ cannot form an MO because it is the only function of B_1 symmetry however from the B_2 orbitals $2p_{yO}$ and $1s_A - 1s_B$ we can form an MO:

$$b_2 = 1s_A - 1s_B + \lambda\, 2p_{yO} \quad \text{bonding}$$

$$b_2^* = 1s_A - 1s_B - \underset{\nearrow}{\lambda'}\, 2p_{yO} \quad \text{antibonding}$$

from variation

in A_1 ; $1s_0$ is too low to form a bond → 1s is an innershell, non bonding orbital and does not change ~~orbitals~~ energy

$2s_0$, $2p_{z0}$ and $1s_A + 1s_B$ can in ~~prnc~~ principle be combined all together

but variation shows that $2s_0$ is not in the MO, does not change energy and is therefore the second lone pair at O

→ lone pairs at O : $2s_0$, $2p_{x0}'$

the other MO is then

$$a_1 = 1s_A + 1s_B + \lambda_2 2p_{y0}$$

$$a_1^* = 1s_A + 1s_B \underset{\substack{\uparrow \\ \text{variation}}}{-\lambda_2} 2p_{y0}$$

⑳-15

$a_1' = 2s_0$

$b_1' = 2p_{xo}$

groundstate: $\overset{\text{non-bonding innershell AO}}{(1s_0)^2}\,\overbrace{(a_1)^2(b_2)^2}^{2\,\text{OH}\ \sigma\ \text{bonds}}\,\overbrace{(a_1')^2(b_1)^2}^{2\,\text{O-lp-s}}$

order in energy: SCF calculation

electrons are in each of the a_1 and b_2 orbitals, and these four electrons are responsible for the two O—H bonds. The remaining four electrons are in the a_1' and b_1 orbitals and constitute the two lone pairs.

This chapter has dealt almost entirely with the general principles relating to the nature of the chemical bond. Much of the modern work being done in this field is concerned with making accurate *ab initio* calculations, by which is meant that no empirical quantities are employed aside from the masses and charges of the electrons and nuclei, and the fundamental physical constants.

Many of the accurate calculations now being made are of energies of molecules. With the aid of supercomputers it is now possible to obtain results that agree with experiment within the experimental error, even for quite complicated molecules. One example already mentioned, on the helium dimer, was particularly challenging,

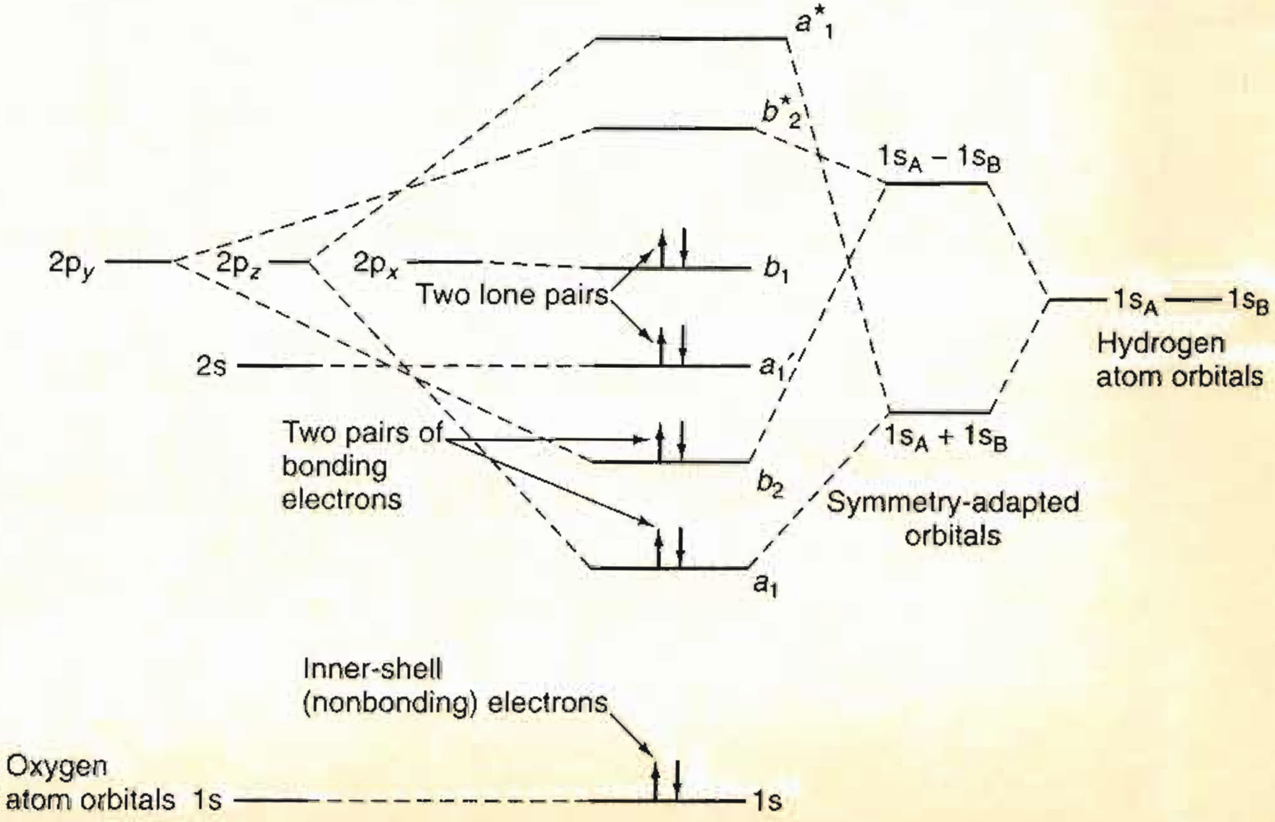


FIGURE 12.25
The energy levels corresponding to the molecular orbitals for water, showing how they are derived from the atomic orbitals of oxygen and hydrogen (not to scale).

general principles of bonds were discussed

physical understanding based on approximations mainly from 1930-s

today: very large, vere accurate ab ~~init ami~~ initio calculations

no experimental numbers used only fundamental physical constants

1) energies within experimental errors even for large molecules and polymers
2) very large, accurate calculations are needed for small bond energies like He_2
3) E_p(all coordinates) → potential hypersurfaces → prediction of reaction mechanisms
4) Testing of QM: compare calculated with experimental results

But

1) The complicated calculations and methods give no further physical understanding of chem. bonding

2) Calculations with more than a million term in the wave function are difficult even on modern supercomputers

→ go over to spectroscopy and we will try to understand spectra with the help of QM

Hückel Molecular Orbital (HMO) Theory

MO method easier, better for large molecules than VB

But also MO gets soon too big and complex

1930 – Hückel: approximations to make it more easy to apply

σ-bonds: e⁻-build up between 2 atoms single bonds

π-bonds: delocalization of electrons over the molecule in conjugated systems

σ/π bonds separated in energy

→ Hückel: seperate treatment of π electrons only

Approximations

overlap integrals: $S_{ij} = \int \psi_i^* \psi_j \, d\tau = \delta_{ij}$

$$= \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases}$$

ψ_i : orbital (p) on atom i

→ ψ_i, ψ_j independent orbitals

S_{ij} : measures the overlap between ψ_i, ψ_j in the real integral

here: $\int \psi_i^* \psi_i \, d\tau = \int \psi_j^* \psi_j \, d\tau = 1$

$$\int \psi_i^* \psi_j \, d\tau = 0$$

→ error, but much more simple calculations

Coulomb integrals on ~~diff~~ atoms:

$$H_{11} = \int \psi_1^* \hat{H} \psi_1 \, d\tau = \langle \psi_1 | \hat{H} | \psi_1 \rangle = \alpha$$

same α for same atoms (e.g. C)

$\alpha = f$(nuclear charge, orbital-type)

exchange, or resonance integrals have a value for bonded atoms i, j, but are 0 for all non-neighboring atoms

$$\underset{\text{neighbors}}{H_{i,i+1}} = \int \psi_i^* \hat{H} \psi_{i+1} \, d\tau = \langle \psi_i | \hat{H} | \psi_{i+1} \rangle = \beta$$

general: $H_{ij} = \beta$

if i, j neighboring atoms: bonded

β has same value if the same 2 atoms bond

$\beta = f$(distance, angles of orbitals)

$\psi_1 = 1s_A(1)\,1s_B(2)$, $\psi_2 = 1s_A(2)\,1s_B(2)$

H_2 : ~~ψ_1 on H_1, ψ_2 on H_2~~

$$\text{MO}: \psi = c_1\psi_1 + c_2\psi_2$$

$$S_{11} = \langle\psi_1|\psi_1\rangle \quad \langle\psi_2|\psi_2\rangle = S_{22}$$

$$\langle\psi_1|\psi_2\rangle = S_{12}$$

$$\hat{H}\psi = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 = E\psi = c_1E\psi_1 + c_2E\psi_2$$

$$\frac{\int\psi^*\hat{H}\psi\,d\tau_1 d\tau_2}{\int\psi^*\psi\,d\tau_1 d\tau_2} = E$$ real wave function:

$$= \frac{\int(c_1^2\psi_1\hat{H}\psi_1 + c_1c_2\psi_1\hat{H}\psi_2 + c_2c_1\psi_2\hat{H}\psi_1 + c_2^2\psi_2\hat{H}\psi_2)\,d\tau_1 d\tau_2}{\int(c_1\psi_1 + c_2\psi_2)^2\,d\tau_1 d\tau_2}$$

$$\int\psi_1\hat{H}\psi_2\,d\tau_1 d\tau_2 = \int\psi_2\hat{H}\psi_1\,d\tau_1 d\tau_2$$

Hermitian, real functions

$$H_{ij} = \int\psi_i\hat{H}\psi_j\,d\tau_1 d\tau_2 = H_{ji}$$

$$S_{ij} = \int\psi_i\psi_j\,d\tau_1 d\tau_2 = S_{ji}$$

$$\rightarrow E = \frac{c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}}{c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}$$

$$\frac{\partial E}{\partial c_1} = \frac{(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2 S_{22})(2c_1 H_{11} + 2c_2 H_{12})}{(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})^2}$$

①

$$- \frac{(c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22})(2c_1 S_{11} + 2c_2 S_{12})}{(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})^2} = 0$$

②

for minimum

$$① = \frac{2c_1 H_{11} + 2c_2 H_{12}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$(① + ②) \cdot (c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})$:

$$(2c_1 H_{11} + 2c_2 H_{12}) = \frac{(c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22})(2c_1 S_{11} + 2c_2 S_{12})}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$2(c_1 H_{11} + c_2 H_{12}) = 2E(c_1 S_{11} + c_2 S_{12})$$

$$\Rightarrow c_1 (H_{11} - E S_{11}) + c_2 (H_{12} - E S_{12}) = 0$$

similar for $\frac{\partial E}{\partial c_2} = 0$

$$\longrightarrow c_1 (\underset{\overset{\uparrow}{= H_{12}}}{H_{21}} - E \underset{\overset{\uparrow}{= S_{12}}}{S_{21}}) + c_2 (H_{22} - E S_{22}) = 0$$

→ secular equations in matrix form:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

homogeneous system of equations for c_1, c_2 and E

→ solution only exists when the coefficient determinant is 0:

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} = 0 \Rightarrow E$$

if $S_{11} = S_{22} = 1$ and $S_{12} = S_{21}$

$$S = \int \overset{1s_A(1)\ 1s_B(1)}{\cancel{\psi_1(1)\,\psi_2(1)}}\, d\tau_1$$

$$S_{12} = \int \overset{1s_A}{\cancel{\psi}}(1)\, \overset{1s_B}{\cancel{\psi}}(2)\, \overset{1s_B}{\cancel{\psi}}(1)\, \overset{1s_{\cancel{B}A}}{\cancel{\psi}}(2)\, d\tau_1\, d\tau_2$$

$$= \int \overset{1s_A}{\cancel{\psi}}(1)\, \overset{1s_B}{\cancel{\psi}}(1)\, d\tau_1 \int \overset{1s_A}{\cancel{\psi}}(2)\, \overset{1s_B}{\cancel{\psi}}(2)\, d\tau_2 = S^2$$

$$\rightarrow \begin{vmatrix} H_{11}-E & H_{12}-ES^2 \\ H_{21}-ES^2 & H_{22}-E \end{vmatrix} = 0$$

HMO : $S = 0$ $\quad (H_2 : \underset{\psi_1}{\bigcirc} - \underset{\psi_2}{\bigcirc})$

$$H_{12} = H_{21} = \beta$$

$$H_{11} = H_{22} = \alpha$$

HMO for H_2: $\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$

$$\rightarrow (\alpha - E)^2 - \beta^2 = 0$$

$$\alpha - E = \pm \beta$$

$$E = \alpha \pm \beta \quad \text{2 levels}$$

$\beta < 0 \Rightarrow E = \alpha + \beta$ bonding $(< \alpha)$

$E = \alpha - \beta$ anti bonding (> 0)

secular equ.: $c_1(\alpha - E) + c_2\beta = 0$

$c_1\beta + c_2(\alpha - E) = 0$

$E = \alpha + \beta$: [illegible] $\beta(-c_1 + c_2) = 0$

$$\beta(c_1 - c_2) = 0$$

$$\hookrightarrow \beta c_1 = \beta c_2$$

$$\frac{c_1}{c_2} = \frac{\beta}{\beta} = 1$$

$\Rightarrow E = \alpha + \beta$: $\psi = N(\psi_1 + \psi_2)$

$$\int \psi^2 d\tau = N^2 \int (\psi_1 + \psi_2)^2 d\tau = N^2 \left[\overbrace{\int \psi_1^2 d\tau}^{1} + \overbrace{\int \psi_2^2 d\tau}^{1} + 2 \overbrace{\int \psi_1 \psi_2 d\tau}^{0} \right]$$

ψ_1, ψ_2 normalized and orthogonal

$\rightarrow 2N^2 = 1 \rightarrow N = \frac{1}{\sqrt{2}}$

$\psi_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ bonding

general: $\frac{c_1}{c_2} = -\frac{\beta}{\alpha - E}$

$E_2 = \alpha - \beta \Rightarrow \frac{c_1}{c_2} = -\frac{\beta}{\alpha - \alpha + \beta} = -1$

$\rightarrow \psi_2 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$ antibonding

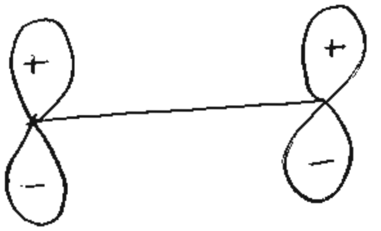
organics: localized σ electrons seperate

ethylene: sp^2 hybrid orbitals on each C form C-H and C-C σ-bonds

$\rightarrow 2p_z$ at each C for π formation

HMO just as above $\psi_{1,2} = \frac{1}{\sqrt{2}}(p_z(C_1) \pm p_z(C_2))$

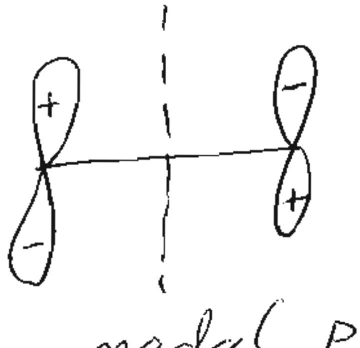
$E_{1,2} = \alpha \pm \beta$



$\psi_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$

$E_1 = \alpha + \beta$

bonding



$\psi_2 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$

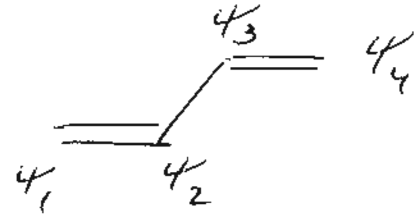
$E_2 = \alpha - \beta$

antibonding

2e in E_1

→ resonance energy $2(\alpha+\beta)$

Butadiene



secular determinant:

each diagonal element $\alpha - E$

off diagonal:

between directly bonded atoms

C_1C_2, C_2C_3, C_3C_4 : β

all other : 0

$$\begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & \alpha-E & \beta & 0 & 0 \\ 2 & \beta & \alpha-E & \beta & 0 \\ 3 & 0 & \beta & \alpha-E & \beta \\ 4 & 0 & 0 & \beta & \alpha-E \end{array} = 0$$

expansion e.g. according to the first line (2 0-s):

$$(-1)^{1+1} H_{11} \begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} + (-1)^{1+2} H_{12} \begin{vmatrix} \beta & \beta & 0 \\ 0 & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$$

1. row, 1. column out

1. row 2. column out

=0

13 and 14 have 0 as factor

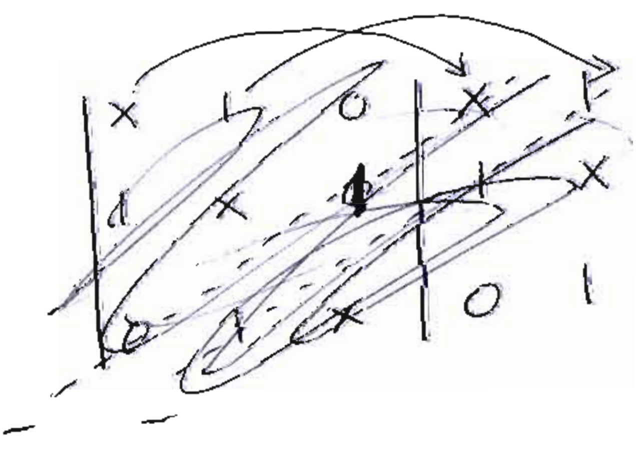
$$(\alpha-E)\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$$

$$-\beta\begin{vmatrix} \beta & \beta & 0 \\ 0 & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$$ mistake in book

also possible: divide equation by β and set $x = \frac{\alpha-E}{\beta}$

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & \frac{\beta}{\beta} & 0 & 0 \\ \frac{\beta}{\beta} & \frac{\alpha-E}{\beta} & \frac{\beta}{\beta} & 0 \\ 0 & \frac{\beta}{\beta} & \frac{\alpha-E}{\beta} & \frac{\beta}{\beta} \\ 0 & 0 & \frac{\beta}{\beta} & \frac{\alpha-E}{\beta} \end{vmatrix} = 0 = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

or: $$x\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$



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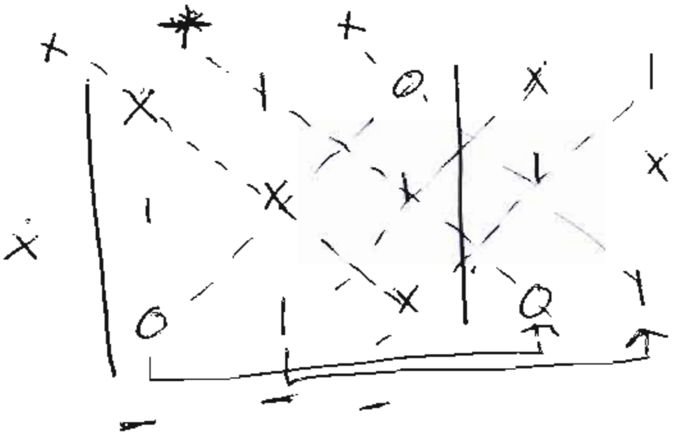
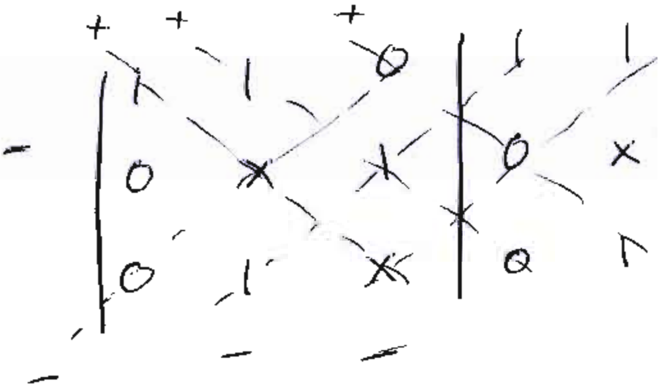


$$\left|\begin{array}{ccc|cc} x & 1 & 0 & x & 1 \\ 1 & x & 1 & 1 & x \\ 0 & 1 & x & 0 & 1 \end{array}\right.$$

$= x\left(x^3 + 1\cdot1\cdot0 + 0\cdot1\cdot1 - 0\cdot x\cdot0 - 1\cdot1\cdot x - x\cdot1\cdot1\right)$

$= x^4 - 2x^2$

$-$ 

$$\left|\begin{array}{ccc|cc} 1 & 1 & 0 & 1 & 1 \\ 0 & x & 1 & 0 & x \\ 0 & 1 & x & 0 & 1 \end{array}\right.$$

$= -\left(x^2 + 1\cdot1\cdot0 + 0\cdot0\cdot1 - 0\cdot x\cdot0 - 1\cdot1\cdot1 - x\cdot0\cdot1\right)$

$= -x^2 + 1$

$x^4 - 2x^2 - x^2 + 1 = 0$

$x^4 - 3x^2 + 1 = 0$

$(x^2)^2 - 3x^2 + 1 = 0$

$X^2 = \frac{1}{2}\left(3 \pm \sqrt{3^2 - 4\cdot1}\right)$

$= \frac{1}{2}\left(3 \pm \underset{\overset{\downarrow}{9-4}}{\sqrt{5}}\right)$

$\longrightarrow x_{1\text{-}4} = \pm\sqrt{\frac{1}{2}(3 \pm \sqrt{5})} = \pm 1{,}6180;\ \pm 0{,}6180$

$\beta < 0$

$\_\_\_\_$ $\alpha - 1.6180\beta$ } antibonding

$\_\_\_\_$ $\alpha - 0.6180\beta$

$- - - - - - - - - - - - - \alpha$

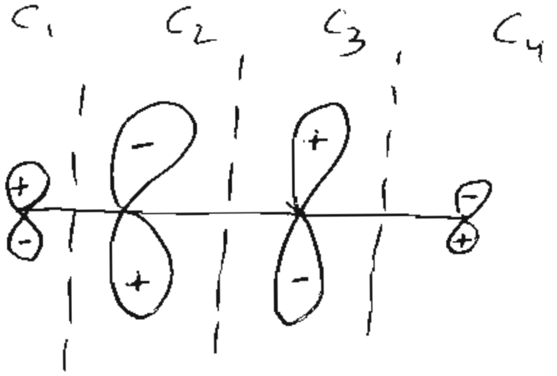
$\underline{\uparrow\downarrow}$ $\alpha + 0.6180\beta$ } bonding

$4\pi e^-$

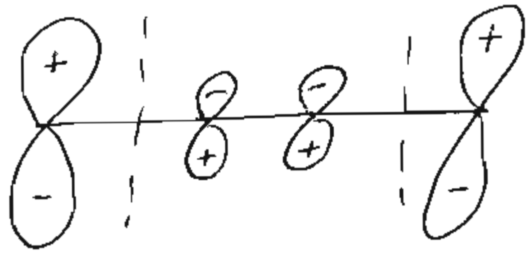
$\underline{\uparrow\downarrow}$ $\alpha + 1.6180\beta$

orbitals: solve for each E_i for the 4 coefficient

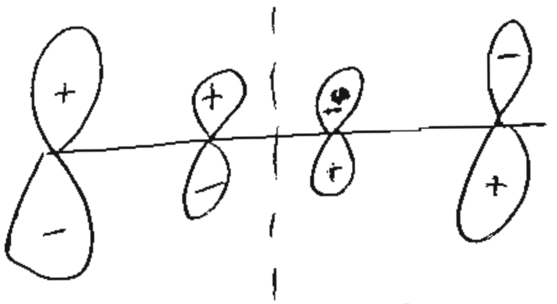
the more nodal plane the higher the energy



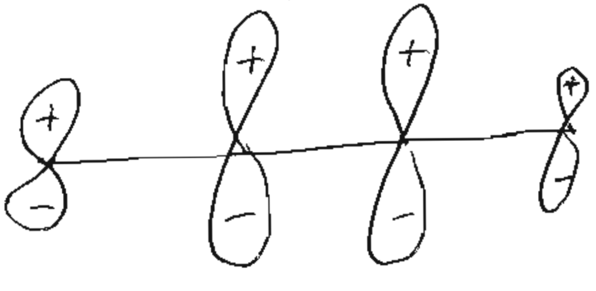
ψ_4 : 3 nodes



ψ_3 : 2 nodes



ψ_2 : 1 node



ψ_1 : no node

ethylene: $E_{eth} = 2(\alpha+\beta)$

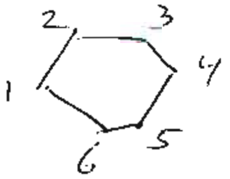
resonance stabilization of butadiene vs 2 ethylene:

$$E_{but} = 2(\alpha + 1.6180\beta) + 2(\alpha + 0.6180\beta)$$

$$= 4\alpha + 4.4720\beta$$

$$\Delta E = 4\overset{\checkmark}{\alpha} + 4.4720\beta - 2\cdot 2(\overset{\checkmark}{\alpha}+\beta)$$

$$= 0.4720\beta$$



benzene C_6H_6

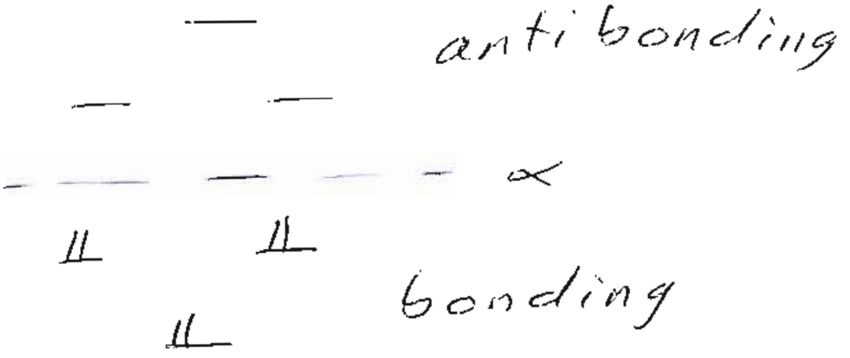
$$\begin{array}{c|cccccc|}
 & 1 & 2 & 3 & 4 & 5 & 6 \\
1 & \alpha-E & \beta & 0 & 0 & 0 & \beta \\
2 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\
3 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\
4 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\
5 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\
6 & \beta & 0 & 0 & 0 & \beta & \alpha-E
\end{array} = 0$$

expansion by 1. column
→ 3 5×5 det.

then again → 4×4 ...

6 eigenvalues, 6 π electrons
into the 3 lowest states

$\rightarrow E_{\pi}(C_6H_6) = 6\alpha + 8\beta$



$$\Delta E = E_{\pi}(C_6H_6) - 3E_{eth}$$
$$= 6\alpha + 8\beta - 6(\alpha + \beta)$$
$$= 2\beta$$

conjugated aromatic molecules

best value: $\beta = -75 \frac{kJ}{mol}$

$\rightarrow \Delta E(\text{benzene}) = 2\beta = -150 \frac{kJ}{mol}$

experimental: $\Delta E = -150 \frac{kJ}{mol}$

yields also bond orders and charge distributions quite reliably

Review Chap. 12 for 2. Major

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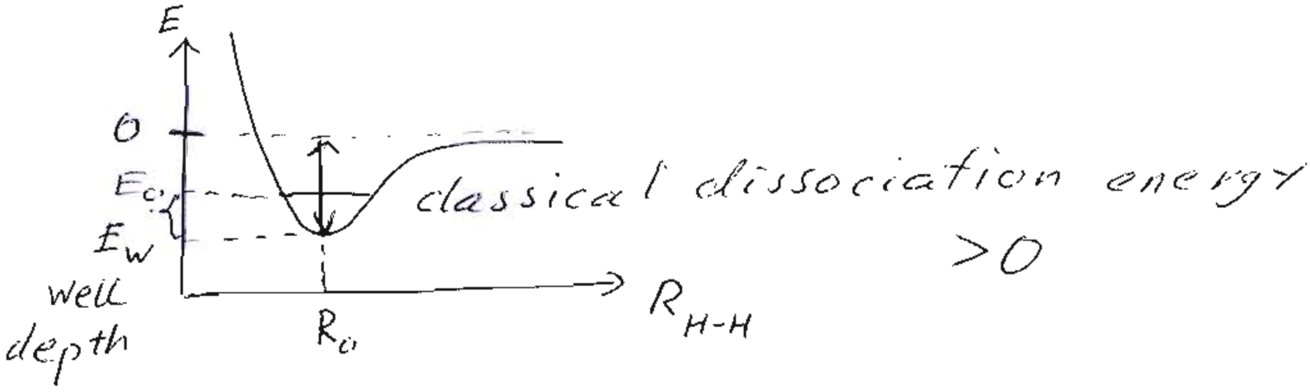
Chemical bond: simplest one H_2^+



$$E_d^{cl.} = E(H) + E(H^+) - E(H_2^+) = E_W$$

$E_W > 0$ well depth

quantum: 0-point energy $E_0 = \frac{1}{2}\hbar\omega_0$

$$E_d^{qu} = E_d^{exp.} = E_d^{class} - E_0$$

$$= \cancel{E_H + E_{H^+}} (E_W - E_0)$$

~~$H_2: 2E_H - (E_W + E_0)$~~

bonding by a pile up of e^- density between the nuclei

σ: orbital wave function has rotational symmetry

$$\sigma = \frac{1}{\sqrt{2(1+S)}} (\psi_{1s_A} + \psi_{1s_B}) \quad \underline{LCAO}$$

$S = \int \psi_{1sA} \psi_{1sB} \, d\tau$

$$\sigma^* = \frac{1}{\sqrt{2(1+S)}} (\psi_{1s_A} - \psi_{1s_B}) \text{ anti bonding}$$

total energy

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_{exp}$$

learn: Hamiltonian terms in elliptical coordinates

Improvement: variation parameter in exponent

adding of more AO-s with variational coefficients

$\underline{H_2}$ learn: coordinates
terms in Hamiltonian $\hat{H}$

<u>and</u> no longer exact solution possible
because $\frac{1}{r_{12}}$

$\psi_{1sA}(1) + \psi_{1sB}(2)$ not good, because electrons can be distinguished

Heitler - London: VB

$$\psi = N\left[\psi_{1sA}(1)\,\psi_{1sB}(2) \overset{\nearrow\ \text{symmetric: S, bond}}{\underset{\downarrow}{\pm}} \psi_{1sA}(2)\,\psi_{1sB}(1)\right]$$

antisymmetric: A
antibonding

maximum overlap →

maximum bonding

$E \sim J$: classical electrostatic energy

≈ 10% of bond energy

and K: quantum exchange energy

≈ 90% of bond energy

Improvement: ionic terms

$$\psi = c_1 \overset{\psi_1}{\left[\psi_{1sA}(1)\,\psi_{1sB}(2) + \psi_{1sA}(2)\,\psi_{1sA}(1)\right]} \text{ covalent}$$

$$+\ c_2 \left[\psi_{1sA}(1)\,\psi_{1sA}(2) + \psi_{1sB}(1)\,\psi_{1sB}(1)\right] \approx 3\%$$

$$\underbrace{H_A^-\,H_B^+ \qquad \cancel{H}H_A^+\,H_B^-}_{}$$

here seem important

not in LiH e.g.

c_1, c_2 determined by variation

$E_R = \cancel{E_{\psi_{1s}}}\ E(\psi_1) - E(\psi_s)$ resonance

stabilization energy

Pauli principle: <u>total</u> wavefunction (including spins) must be antisymmetric to electron exchange

→ spatial orbital ψ_s must be multiplied with an antisymmetric spinfunction

bonding $\psi_s[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

only 1 function singlet or singulet

spatial ψ_A: symmetric spinfunction

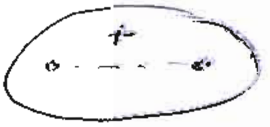
three possible with same energy: triplet

$$\psi_A: \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{cases}$$

<u>MO</u> formation of MO-s for single electrons as LCAO:

$$\begin{array}{llll} \lambda = 0, & 1, & 2, & \ldots \\ \sigma & \pi & \delta & \end{array} \quad L_z \text{ eigenvalues}$$

bonding: $\sigma = \psi_{1sA} + \psi_{1sB}$



antibonding: $\sigma^* = \psi_{1sA} - \psi_{1sB}$

learn how to calculate normalization factors

$\sigma(1)$, $\sigma(2)$

$\rightarrow \psi = \sigma(1)\,\sigma(2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$

$$\sigma(1) = \frac{1}{\sqrt{2(1+S)}}\left[\psi_{1sA}(1) + \psi_{1sB}(1)\right]$$

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$\rightarrow \quad E(\sigma_g) = \frac{J+K}{1+S} \approx J+K$$

$$E(\sigma_u^*) = \frac{J-K}{1-S} \approx J-K$$

with S: σ_u^* more antibonding than σ_g is bonding (energy)

<u>VB</u> HCl:

$$\psi_S = \frac{1}{\sqrt{2(1+S^2)}}\left[\psi_H(1)\,\psi_{Cl}(2) + \psi_H(2)\,\psi_{Cl}(1)\right]$$

covalent

simplest possibility

more correct:

$$\Psi_s = c_1[\overset{\psi_1}{\psi_H(1)\psi_{Cl}(2)} + \overset{\psi_2}{\psi_H(2)\psi_{Cl}(1)}] \quad H\ H$$

$$+\ c_2[\overset{\psi_3}{\psi_{Cl}(1)\psi_{Cl}(2)}] \quad H^+Cl^-$$

$$+\ c_3[\overset{\psi_4}{\psi_H(1)\psi_H(2)}] \quad H^-Cl^+$$

total: $\Psi_s[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

c_3 small, because H^-Cl^+ not important

→ Approximation: $\psi = [\psi_1 + \psi_2]_{cov.} + \lambda[\psi_3]_{ionic}$

Electronegativity

dipole moment $\mu = q \cdot d$

$$+q \bullet \overset{d}{\underset{\xrightarrow[\mu]{}}{\rule{3cm}{0.4pt}}} \bullet -q$$

unit: Cm = Asm or Debye D

$1D = 3.336 \cdot 10^{-30}$ Cm

molecule AB as $\overset{+}{A} \overset{}{\underset{d}{\text{——}}} B^-$

$\mu_{ionic} = q \cdot d$ $\quad$ q: 1 electronic charge

full, in μ_{ionic}

$$\% \text{ ionic character} = \frac{\mu_{exp}}{\mu_{ionic}} \cdot 100\%$$

$$= \frac{\lambda^2}{1+\lambda^2} \cdot 100\%$$

$$x = \frac{\% \text{ ionic character}}{100\%}$$

$$x = \frac{\lambda^2}{1+\lambda^2} \quad ; \quad x(1+\lambda^2) = \lambda^2$$

$$(1-x)\lambda^2 = x$$

$$\lambda = \sqrt{\frac{x}{1-x}} = \sqrt{\frac{\% \text{ ionic char}/100\%}{1 - \frac{\% \text{ ionic char.}}{100\%}}}$$

Pauling EN :

$$AA + BB \longrightarrow 2AB$$

$$E_{cov} = \sqrt{D(AA)\,D(BB)} \quad \text{if fully covalent}$$

$\uparrow$

dissociation energy

$$E_{ionic} = D(AB) - \sqrt{D(AA)\,D(BB)}$$

EN: χ $\quad \sqrt{E_{ionic}} = K|\chi_A - \chi_B|$

$$K = 10\sqrt{kJ/mol}$$

$$\Rightarrow \mu_{exp} \approx |\chi_A - \chi_B| \quad \text{in D}$$

$$\% \text{ ionic char.} = \frac{\mu_{exp}}{\mu_{ionic}} \cdot 100\%$$

$$= \frac{|\chi_A - \chi_B|}{q \cdot d} \cdot 100\%$$

$$\uparrow$$

$$A^+ \overset{d}{\text{———}} B^-$$

full charges at bond distance

$\rightarrow \lambda$!

LiI : $d = 239 \text{ pm}$ $\mu_{exp} = 2.09 \cdot 10^{-29} \text{ Cm}$

$$\mu_{ionic} = \underset{Li^+,\, I^-,\, e}{1.602 \cdot 10^{-19} \text{ C}} \cdot 239 \cdot 10^{-12} \text{ m}$$

$$= 383 \cdot 10^{-31} \text{ Cm} = 3.83 \cdot 10^{-29} \text{ Cm}$$

$$\rightarrow \% \text{ ionic char.} = \frac{2.09}{3.83} \cdot 100\% = 55\%$$

$$\lambda = \sqrt{\frac{0.55}{1-0.55}} = 1.11$$

$$\rightarrow \psi = \psi_{cov} + 1.11\, \psi_{Li^+ I^-}$$

$D(LI_2) = 113 \text{ kJ/mol}$ $D(H_2) = 435 \text{ kJ/mol}$

$D(LiH) = 243 \text{ kJ/mol}$

$$E_{ionic} = \left[243 - \sqrt{113 \cdot 435}\right] \frac{kJ}{mol}$$

$$= 21.3 \ kJ/mol$$

$$|\chi_H - \chi_{Li}| = \frac{\sqrt{E_{ionic}}}{K}$$

$$= \frac{\sqrt{21.3 \ kJ/mol}}{10 \sqrt{kJ/mol}} = 0.46$$

$$\Rightarrow \mu_{exp} \approx 0.46 \ D$$

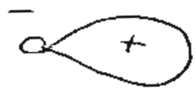
learn to form hybrids sp, sp^2, sp^3

sp → linear, sp^2 → trigonal planar, sp^3 → tetrahedral

how to normalize

how to proof orthogonality

sketches: all lobes like



in sp: 2 orbitals like that

linear, in opposite directions

how to set up spatial orbitals,

like in our BeH_2 example

what spin function for an antisym. orbital: must be antisymmetric for a symmetric bonding orbital learn VB multiple bond orbitals ㉑-10

σ-bonds from hybrids

π-bonds from unhybridized p-AO

MO theory: series of MO diagrams for homonuclear diatomics, A_2

properties of ions from molecules

shapes of orbitals,

symmetry, bond orders $\frac{1}{2}(n_b - n_a)$

n_b: # electrons in ~~[illegible]~~ no-star bonding MO

n_a: # electrons in star antib. MO

magnetism

stability sequence $N_2 > O_2 > F_2$

AB molecules: unsymmetric MO diagrams

H_2O molecule: use of symmetry to set up MO diagram

He_2: ~~[illegible]~~ weakest known bond