

Chemical Bonds

I. TIME-INDEPENDENT PERTURBATION THEORY

We assume that the Hamiltonian of the system is

$$\hat{H} = \hat{H}_0 + V, \quad (1)$$

where \hat{V} is a small addition (perturbation) to the "unperturbed" Hamiltonian \hat{H}_0 . Let us assume that the spectrum of the Hamiltonian \hat{H}_0 is discrete. The corresponding Schrödinger equation is

$$\hat{H}_0 \Psi^{(0)}(q) = E^{(0)} \Psi^{(0)}(q), \quad (2)$$

where $\Psi^{(0)}(q)$ and $E^{(0)}$ are eigenvectors and eigenvalues of the Hamiltonian \hat{H}_0 which are known and q is the set of all coordinates. We seek to find an approximate solution for the Schrödinger equation

$$\hat{H} \Psi(q) = (\hat{H}_0 + \hat{V}) \Psi(q) = E \Psi(q). \quad (3)$$

The wavefunctions $\Psi_m^{(0)}$ are orthogonal to each other and form a complete basis set:

$$\int \Psi_m^{(0)*}(q) \Psi_{m'}^{(0)}(q) dq = \delta_{mm'}. \quad (4)$$

Any unknown wavefunctions Ψ can be expanded over this basis set as

$$\Psi(q) = \sum_m c_m \Psi_m^{(0)}(q), \quad (5)$$

where c_m are expansion coefficients which do not depend on q .

Substituting eq.(5) into (3) one gets

$$\sum_m c_m (\hat{H}_0 + \hat{V}) \Psi_m^{(0)}(q) = E \sum_m c_m \Psi_m^{(0)}(q). \quad (6)$$

Multiplying both sides of eq.(6) from the left by $\Psi_k^{(0)*}(q)$ and integrating over q one gets

$$\begin{aligned} \sum_m c_m \int \Psi_k^{(0)*}(q) (\hat{H}_0 + \hat{V}) \Psi_m^{(0)}(q) dq &= E \sum_m c_m \int \Psi_k^{(0)*}(q) \Psi_m^{(0)}(q) dq, \\ \sum_m c_m (\delta_{km} E_k^{(0)} + \langle k | \hat{V} | m \rangle) &= E \sum_m c_m \delta_{km}, \\ (E - E_k^{(0)}) c_k &= \sum_m c_m \langle k | \hat{V} | m \rangle. \end{aligned} \quad (7)$$

Eq.(7) is still exact and equivalent to the initial Schrödinger equation in eq.(3). Now we seek for its approximate solution presenting the coefficients c_m and the energy E in the form

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots \quad c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots \quad (8)$$

First we assume that the eigenvectors of the Hamiltonian \hat{H}_0 are non-degenerate and will seek for correction to the energy level E_n . Then the zeroth-order expansion coefficients in eq.(7) stands for $c_k^{(0)} = \delta_{kn}$.

First correction to the energy

Substituting $E = E_n \simeq E_n^{(0)} + E_n^{(1)}$ and $c_k \simeq c_k^{(0)} = \delta_{kn}$ into eq.(7) one gets for $k = n$:

$$E_n^{(1)} = \langle n | \hat{V} | n \rangle = \int \Psi_n^{(0)*}(q) \hat{V} \Psi_n^{(0)}(q) dq = V_{nn}. \quad (9)$$

Therefore

$$E_n \simeq E_n^{(0)} + \langle n | \hat{V} | n \rangle. \quad (10)$$

First correction to the expansion coefficient c_k

Substituting $E = E_n \simeq E_n^{(0)}$ and $c_k \simeq \delta_{kn} + c_k^{(1)}$ into eq.(7) one gets for $k \neq n$:

$$c_k^{(1)} = \frac{\langle k | \hat{V} | n \rangle}{E_n^{(0)} - E_k^{(0)}}. \quad (11)$$

Therefore,

$$\Psi_n \simeq \Psi_n^{(0)} + \sum'_k \frac{\langle k | \hat{V} | n \rangle}{E_n^{(0)} - E_k^{(0)}} \Psi_k^{(0)}, \quad (12)$$

where summation is proceeded over all $k \neq n$.

Eq.(12) gives a simple criterium of the approximation used: there must be fulfilled the inequality:

$$|\langle k | \hat{V} | n \rangle| \ll |E_n^{(0)} - E_k^{(0)}|. \quad (13)$$

Second correction to the energy

Substituting $E = E_n \simeq E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$ and $c_k \simeq \delta_{kn} + c_k^{(1)} + c_k^{(2)}$ into eq.(7) one gets for $k = n$:

$$E_n^{(1)} + E_n^{(2)} = \langle n | \hat{V} | n \rangle + \sum'_m c_m^{(1)} \langle n | \hat{V} | m \rangle \quad (14)$$

Having in mind eqs.(9) and (11) we obtain the following expression for the second-order correction to the energy

$$E_n^{(2)} = \sum'_m \frac{|\langle n | \hat{V} | m \rangle|^2}{E_n^{(0)} - E_m^{(0)}}, \quad m \neq n. \quad (15)$$

Note, that if n is the ground state, then the second-order correction to the energy is always negative $E_n^{(2)} \leq 0!$

A. Degenerate case

Let us denote by $\Psi_n^{(0)}, \Psi_{n'}^{(0)} \dots$ the wavefunctions which correspond to the same energy $E_n^{(0)}$. Eq.(7) cannot be solved now as before, because $E_n^{(0)} - E_{n'}^{(0)} = 0$ in the denominator of eq.(11). If the number of the degenerate states l does not exceed 2, or 3 the set of equations (7) can be solved exactly. Otherwise, the wavefunction of the energy state n in the zero approximation can be written as superposition of the wavefunctions $\Psi_n^{(0)}, \Psi_{n'}^{(0)} \dots$:

$$\Psi^{(0)} = c_n^{(0)} \Psi_n^{(0)} + c_{n'}^{(0)} \Psi_{n'}^{(0)} + \dots \quad (16)$$

where the coefficients $c_n^{(0)}, c_{n'}^{(0)}$ should be determined later.

We rewrite (7) for $k = n', n'' \dots$ using there in the first approximation $E_n = E_n^{(0)} + E_n^{(1)}$, while for the coefficients c_k we use their zeroth-order approximation: $c_n \simeq c_n^{(0)}$, $c_{n'} \simeq c_{n'}^{(0)}$, \dots $c_k = 0$ if $k \neq n, n' \dots$. Then eq.(7) can be presented as

$$E_n^{(1)} c_n^{(0)} = \sum_{n'} V_{n,n'} c_{n'}^{(0)}, \quad (17)$$

or

$$\sum_{n'} (V_{n,n'} - E^{(1)} \delta_{nn'}) c_{n'}^{(0)} = 0 \quad (18)$$

which is the system of linear homogeneous equations where the coefficients $c_{n'}^{(0)}$, with $n' = 1, 2, \dots, l$ and the corresponding eigenvalues $E^{(1)}$ have to be determined. As known from the Mathematical Analysis such a set of equations has nonzero solutions only if the following determinant is equal to zero:

$$\begin{vmatrix} V_{1,1} - E^{(1)} & V_{1,2} & \dots & V_{1,l} \\ V_{2,1} & V_{2,2} - E^{(1)} & \dots & V_{2,l} \\ \dots & \dots & \dots & \dots \\ V_{l,1} & V_{l,2} & \dots & V_{l,l} - E^{(1)} \end{vmatrix} = 0, \quad (19)$$

where n, n' take their values from $n = 1$ till $n = l$.

Eq.(19) is known as secular equation, it is an algebraic linear equation of the rang l for variable $E^{(1)}$ and in general has up to l different roots. These roots are the corresponding

corrections to the energy in the first approximation. Substituting these roots one after another into eq.(18) one can determine all coefficients $c_{n'}^{(0)}$ which specify l correct zeroth-order wavefunctions according to eq.(16).

The explained perturbation theory method will be later used for calculation of the wavefunctions and the energy levels of molecular H_2^+ ion.

II. TIME-DEPENDENT PERTURBATION THEORY

Let us consider the Hamiltonian

$$\hat{H} = \hat{H}_0 + V(t), \quad (20)$$

where the perturbation V explicitly depends of time. In this case it is not possible to discuss corrections to the energy, because the energy is simply not preserved and therefore, the stationary states do not exist. Besides, we will calculate the approximate residual wavefunctions starting from the wavefunctions of the initial unperturbed system. Let the wavefunctions $\Psi_k^{(0)}(t)$ are the eigenvectors of the unperturbed system.

$$i\hbar \frac{\partial \Psi_k^{(0)}(t)}{\partial t} = \hat{H}_0 \Psi_k^{(0)}(t) \quad (21)$$

which can be presented as $\Psi_k^{(0)}(t) = e^{-\frac{i}{\hbar} E_0 t} \Psi_k^{(0)}$, where E_0 is the eigenvalue energy of the Hamiltonian H_0 and the wavefunction $\Psi_k^{(0)}$ does not depend on time. We seek for the solution of the perturbed equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = (\hat{H}_0 + \hat{V}(t)) \Psi(t) \quad (22)$$

as an expansion

$$\Psi(t) = \sum_k a_k(t) \Psi_k^{(0)}(t) \quad (23)$$

where the expansion coefficients $a(t)$ are functions of time.

Substituting eq.(23) into eq.(22) and having in mind eq.(21), we get

$$\begin{aligned} i\hbar \sum_k \left(\Psi_k^{(0)}(t) \frac{\partial a_k(t)}{\partial t} + a_k(t) \frac{\partial \Psi_k^{(0)}(t)}{\partial t} \right) &= \sum_k a_k(t) (\hat{H}_0 + \hat{V}(t)) \Psi_k^{(0)}(t) \\ i\hbar \sum_k \Psi_k^{(0)}(t) \frac{\partial a_k(t)}{\partial t} &= \sum_k a_k(t) \hat{V}(t) \Psi_k^{(0)}(t) \end{aligned} \quad (24)$$

Multiplying both sides of eq.(24) from the left by the wavefunction $\Psi_m^{(0)*}$ and integrating over all coordinates q we get the differential equation for the expansion coefficients $a(t)$

$$i\hbar \frac{\partial a_m(t)}{\partial t} = \sum_k a_k(t) \langle m|V(t)|k\rangle, \quad (25)$$

where

$$\langle m|V(t)|k\rangle = \int \Psi_m^{(0)*}(t) \hat{V}(t) \Psi_k^{(0)}(t) dq = V_{mk} e^{i\omega_{mk}t}, \quad \omega_{mk} = \frac{E_m^{(0)} - E_k^{(0)}}{\hbar}. \quad (26)$$

The eq.(25) is still exact and equivalent to the time-dependent Schrödinger equation (22). Now we will find an approximate solution of this equation.

In the zeroth-order approximation we put in eq.(23) $a_0^{(0)}(t) = 1$ and $a_k^{(0)} = 0$ for $k \neq 0$. In the first-order approximation we seek a solution in the form $a_k(t) = a_k^{(0)}(t) + a_k^{(1)}(t)$, however to the right-hand side of eq.(25) we put $a_k(t) = a_k^{(0)}(t)$ because it already contains the small value $V_{mk}(t)$. Thus, for $k \neq 0$ we come to the equation

$$i\hbar \frac{\partial a_k^{(1)}(t)}{\partial t} = \langle k|V(t)|0\rangle. \quad (27)$$

The solution of the eq.(27) is as

$$a_k^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \langle k|V(\tau)|0\rangle d\tau = -\frac{i}{\hbar} \int_0^t V_{k0} e^{i\omega_{k0}\tau} d\tau. \quad (28)$$

the probability that the system will be found in the state k is proportional to the square modulus of the coefficient of the state, $|a_k(t)|^2$. Therefore, the rate of change of population of the state k due to transition from the state 0 is

$$W_{k \leftarrow 0} = \frac{d|a_k(t)|^2}{dt} = a_k(t) \frac{da_k^*(t)}{dt} + a_k^*(t) \frac{da_k(t)}{dt} \quad (29)$$

which can be easily calculated from eqs.(27) and (28). The most important that the rate of change is proportional to the square modulus of the matrix element of the perturbation between two states:

$$W_{k \leftarrow 0} \propto |V_{k0}|^2. \quad (30)$$

For example, the perturbation which correspond to the interaction between the oscillating electromagnetic field and an electric dipole moment $\vec{\mu} = e \sum_i \vec{r}_i$ of the molecule can be written as

$$\hat{V}(t) = -\vec{\mu} \cdot \vec{E} \cos \omega t = -\mu_z E_z \cos \omega t \quad (31)$$

In this case we can conclude that

$$W_{k \leftarrow 0} \propto |\mu_{z, k0}|^2 E_z^2, \quad (32)$$

where μ_{k0} is the matrix element of the **transition dipole moment**:

$$\mu_{z, k0} = \int \Psi_k^{(0)*} \mu_z \Psi_0^{(0)} dq \quad (33)$$

It is seen that the rate of transition is proportional to E_z^2 , and therefore, to the intensity I of the incident radiation which is proportional to E^2 , $I \propto E^2$. This important results is a basis of the most of the molecular spectroscopy discussion we will consider later.

III. THE VARIATION METHOD

Let us consider another method of approximate solution of the time-independent Schrödinger equation

$$\hat{H}\Psi(q) = E\Psi(q), \quad (34)$$

where $\Psi(q)$ and E are unknown wavefunctions and energy states which must be determined.

Multiplying both parts of eq.(34) from the left with $\Psi^*(q)$ and integration over all coordinates q one can clearly see that

$$E = \frac{\int \Psi^*(q) \hat{H} \Psi(q) dq}{\int \Psi(q)^* \Psi(q) dq}, \quad (35)$$

In case of any conceivable wavefunction $\tilde{\Psi}(q)$ we can still build the expectation value of the energy as follows

$$\langle \hat{H} \rangle = \frac{\int \tilde{\Psi}^*(q) \hat{H} \tilde{\Psi}(q) dq}{\int \tilde{\Psi}(q)^* \tilde{\Psi}(q) dq}, \quad (36)$$

The **Variation Theorem** states that for any conceivable wavefunction obeying the same boundary conditions as the correct ground-state energy eigenfunction $\Psi_{gr}(q)$ the corresponding expectation value of the energy $\langle \hat{H} \rangle$ is larger than the correct ground-state energy eigenvalue of the system E_{gr} .

$$\langle \hat{H} \rangle \geq E_{gr} \quad (37)$$

The **variational method** consists of evaluating of the expectation value of the energy $\langle \hat{H} \rangle$ with approximate wavefunctions obeying the same boundary conditions as the correct ground-state energy eigenfunction which depends on a number of parameters and of varying

these parameters until the expectation value gets its minimum ($\delta \langle \hat{H} \rangle = 0$). The result is an upper limit for the ground state energy of the system, which is likely to be close to actual ground state energy if the trial wavefunction resembles the true molecular system eigenvector (for instance, if it has the right number of nodes, etc.).

IV. SUPERPOSITION PRINCIPLE AND WAVE FUNCTION EXPANSION

If two, or more wavefunctions $\phi_1, \phi_2, \dots, \phi_n$ are solutions of the Schrödinger equation $\hat{H}\phi_i = E\phi_i$, then any their linear superposition

$$\phi = \sum_i a_i \phi_i \quad (38)$$

is also a solution of the same Schrödinger equation.

This is a fundamental **Superposition Principle** of quantum mechanics. The eigenvectors ϕ_i can all be made normalized and they are also orthogonal to each other:

$$\int \phi_k^*(q) \phi_i(q) dq = \langle \phi_k | \phi_i \rangle = \delta_{ki}. \quad (39)$$

These wave functions form a **complete basis set**, which means that almost **any** wavefunction of the same variables q can be expanded over the wavefunctions ϕ_i :

$$\psi(q) = \sum_i c_i \phi_i(q). \quad (40)$$

Here c_i are expansion coefficients which can all be determined using the orthogonality relation of the wavefunctions $\phi_i(q)$ in eq.(39). Multiplying both sides of eq.(40) by the wavefunction $\phi_k^*(q)$ and integrating over the variables q we get:

$$c_k = \langle \phi_k | \psi \rangle. \quad (41)$$

Eqs.(40) and (41) represents the very general principle of **Wave Function Expansion** which is of fundamental importance in chemistry. That is because we usually know exact solutions of the Schrödinger equation only for very limited number of simple systems and have to built the approximate wavefunction of the systems of interest as a linear combination of these exact solutions.

V. LINEAR COMBINATIONS OF ATOMIC ORBITALS (LCAO):

H_2^+ MOLECULE

As a simplest example we will discuss the theory of the molecular bonds in the hydrogen molecule-ion H_2^+ . Let us consider two protons A and B which are placed at the distance R from each other and one electron somewhere between them. In case of the infinite separation $R \rightarrow \infty$ the electron can belong either to the proton A , or to the proton B . The corresponding wavefunctions of the isolated ground state hydrogen atoms A and B are $\Psi_A = \Psi_{1S_A}^H(\mathbf{r}_A)$ and $\Psi_B = \Psi_{1S_B}^H(\mathbf{r}_B)$, respectively, where \mathbf{r}_A and \mathbf{r}_B are the electron coordinates calculated from the corresponding proton. As known

$$\Psi_{1S_A}^H(\mathbf{r}) = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}}, \quad (42)$$

where a_0 is the **Bohr radius**, $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 52.9177$ pm.

The Hamiltonian for a single electron in the molecular ion H_2^+ is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V, \quad V = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right). \quad (43)$$

The expressions in eqs.(42), (43) are written in SI units. However, it is often more convenient to proceed calculations in microscopic physics using co-called **atomic units**, where $c = e = m_e = \hbar = 4\pi\epsilon_0 = 1$. The atomic unit of length is the **Bohr radius**, $a_0 = \hbar^2/m_e e^2$. The atomic unit of energy is $me^4/\hbar^3 = 27,21eV$. The atomic units of mass and charge are electron mass m_e and charge e , respectively.

Using the atomic units eqs. (42) and (43) can be rewritten in a somewhat more simpler form

$$\Psi_{1S_A}^H(\mathbf{r}_A) = \frac{e^{-r_A}}{(\pi)^{1/2}}, \quad (44)$$

$$\hat{H} = -\frac{1}{2}\nabla^2 + V, \quad V = -\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right). \quad (45)$$

For finite separations R the electron belongs to both atoms A and B and in the first approximation the corresponding overall molecular wavefunction can be written as superposition of the two atomic orbitals H_2^+ wavefunction

$$\Psi = [c_A\Psi_A(\mathbf{r}_A) + c_B\Psi_B(\mathbf{r}_B)], \quad (46)$$

where c_A and c_B are expansion coefficients and r_A and r_B are the distances from the electron to each of the nucleus A and B .

The wavefunction in eq.(46) is a **linear superposition of atomic orbitals** (LCAO). This is an approximate molecular orbital which has cylindrical symmetry around the internuclear axis and is called a σ **orbital** because it has no angular momentum around the internuclear axis.

The molecular energy levels can be obtained using the perturbation theory method explained in sec. IA. Writing the Schrödinger equation in the form

$$\hat{H}\Psi = E\Psi, \quad (47)$$

where \hat{H} and Ψ are given in eqs.(43) and (46), respectively, we multiply both sides of this equation alternatively by the wavefunctions $\Psi_A^*(\mathbf{r}_{A1})$ and $\Psi_A^*(\mathbf{r}_{B1})$ and integrate over the coordinate of the electron \mathbf{r}

$$\begin{aligned} c_A\langle\Psi_A|\hat{H}|\Psi_A\rangle + c_B\langle\Psi_A|\hat{H}|\Psi_B\rangle &= E(c_A + c_BS) \\ c_A\langle\Psi_B|\hat{H}|\Psi_A\rangle + c_B\langle\Psi_B|\hat{H}|\Psi_B\rangle &= E(c_AS + c_B), \end{aligned} \quad (48)$$

or

$$\begin{aligned} c_A\left(\langle\Psi_A|\hat{H}|\Psi_A\rangle - E\right) + c_B\left(\langle\Psi_A|\hat{H}|\Psi_B\rangle - ES\right) &= 0 \\ c_A\left(\langle\Psi_B|\hat{H}|\Psi_A\rangle - ES\right) + c_B\left(\langle\Psi_B|\hat{H}|\Psi_B\rangle - E\right) &= 0, \end{aligned} \quad (49)$$

where S is so named **overlap** integral:

$$S = \int \Psi_A(\mathbf{r}_A)\Psi_B(\mathbf{r}_B) d\mathbf{r}. \quad (50)$$

The set of two homogeneous equations (49) slightly differ from the **secular equations** explained in sec. (IA) because the basic eigenfunctions $\Psi_A(\mathbf{r}_A)$ and $\Psi_B(\mathbf{r}_B)$ are not orthogonal, as they are centered of different nuclei A and B . Therefore, the the overlap integral S appears in eqs. (49) instead of the Kronecker symbol $\delta_{nn'}$ in eqs.(18). The matrix element $\langle\Psi_A|\hat{H}|\Psi_A\rangle = \alpha_A$ is called a **Coulomb integral**. It can be interpreted as the energy of the electron when it occupies A (for α_A) and it is **negative**. In a homonuclear diatomic molecule $\alpha_A = \alpha_B = \alpha$. The matrix element $\langle\Psi_A|\hat{H}|\Psi_B\rangle = \beta$ is called a **resonance integral**. It is mostly responsible for the molecular bonding. It vanishes when the orbitals do not overlap, and at equilibrium bond length it is normally **negative**. The determinant in the set of two algebraic equations in (49) results in a second order algebraic equation and can easily be

solved. Two corresponding energies are

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}, \quad (51)$$

while the corresponding expansion coefficients c_A and c_B are

$$c_A = N, \quad c_B = \pm N, \quad N = \frac{1}{[2(1 + S)]^{1/2}}, \quad (52)$$

The corresponding molecular wavefunctions

$$\Psi_+(\mathbf{r}) = N [\Psi_A(\mathbf{r}_A) + \Psi_B(\mathbf{r}_B)] \quad (53)$$

and

$$\Psi_-(\mathbf{r}) = N [\Psi_A(\mathbf{r}_A) - \Psi_B(\mathbf{r}_B)] \quad (54)$$

are known as **bonding** and **antibonding** molecular orbitals, respectively.

VI. HOMONUCLEAR DIATOMIC MOLECULES

The above concepts can be applied to homonuclear diatomic molecules in general. For two atomic homonuclear molecules like H_2 , O_2 , N_2 etc, the LCAO expansion represents an especially simple approach. The progress made with the ionic molecule H_2^+ is as well valuable for other homonuclear species. We will treat these molecules in the same way. Of course, we will face some additional points, especially for bonds established by more than one electron. Analogous to atomic orbitals, we introduce molecular orbitals of different energy. The molecular electrons are distributed among them in a way that the orbitals with the lowest energies are occupied first and the Pauli principle is accomplished.

A. General Concepts

Note, that from two atomic orbitals we can build two one-electron molecular orbitals. In general, from N atomic orbitals we can build N one-electron molecular orbitals. A general principle of molecular orbital theory is that **all atomic orbitals of an appropriate symmetry contribute to a molecular orbital**. One-electron molecular orbitals are classified according to the quantum number λ for the angular momentum about the internuclear axis. In general, for an electron in a diatomic molecule the axial angular momentum is given by

$$l_z = \pm \lambda \hbar \quad (55)$$

The value of λ for a one-electron orbital of a diatomic molecule is denoted by a lowercase Greek letter according to

$$\begin{array}{rcccc} \lambda & = & 0 & 1 & 2 & 3 \\ \text{Orbital} & = & \sigma & \pi & \delta & \phi \end{array}$$

This is, of course, analogous to the classification of atomic one-electron orbitals as s , p , d , $f \dots$ according to $l = 0, 1, 2, 3, \dots$

The subscript indices g and u (from the German even/*gerade* and odd/*ungerade*), for instance, σ_g , or π_u refer to the symmetry of the one-electron molecular orbital with respect to the **Inversion** of all electron coordinates in the molecular center of symmetry (the middle of the internuclear distance). The *gerade* MOs which are indicated by the subscript index g remain the same under the Inversion, while the *ungerade* MOs which are indicated by the subscript index u change their sign.

B. Period 1 Diatomic Molecules

In the first approximation, we consider these molecular orbitals (MO) as linear combinations of atomic orbitals. Combining two $1s$ orbitals of the hydrogen atom, we obtain two MOs which already appeared in the previous chapter:

$$\sigma_g = N [\Psi_A(1s) + \Psi_B(1s)] \quad (56)$$

$$\sigma_u = N [\Psi_A(1s) - \Psi_B(1s)] \quad (57)$$

The electron cloud which is related to the σ molecular orbital is axially symmetric over the internuclear axis. Note that the wavefunctions $\Psi_A(1s)$ and $\Psi_B(1s)$ in eqs.(56) and (57) are identical for homonuclear molecules, however centered on different nuclei. Therefore, both wave functions are introduced with the same weight N . Later we will denote them as $\Psi_A(1s) \equiv \Phi_A$ and $\Psi_B(1s) \equiv \Phi_B$.

According to eq.(51) in case where the overlap integral S is small compared with unity, the energy values E_{\pm} which are degenerated at infinite R separation, split symmetrically at a finite R separation into two values above and below the original energy level. The level with the smaller energy is called **bonding MO** as it is below the energy level of the separated atoms. The level with the larger energy is called **antibonding MO** as it is above the energy

level of the separated atoms. Horizontal lines in the following figure represent two atomic and two molecular orbitals and the corresponding electron energy at each orbital.

Using the Pauli Principle we can now we populate the MOs starting with the lowest one. For H_2^+ the only electron can populate either σ_g , or σ_u^* orbital where the former corresponds to the molecular ion ground state. Here the asterix (*) indicates the antibonding orbital.

For H_2 molecule in the first approximation the total molecular wavefunction can be written as product of two one-electron wavefunctions. Assuming that the each electron wavefunctions are $\sigma_g(1)$ and $\sigma_g(2)$, the total ground state wavefunction of the molecule can be written as:

$$\begin{aligned}\Psi_g &= \sigma_g(1) \sigma_g(2) \simeq [\Phi_A(1) + \Phi_B(1)] [\Phi_A(2) + \Phi_B(2)] \\ &= \Phi_A(1)\Phi_B(2) + \Phi_B(1)\Phi_A(2) + \Phi_A(1)\Phi_A(2) + \Phi_B(1)\Phi_B(2)\end{aligned}\quad (58)$$

The first two terms describe two electrons which are located at different protons each. These terms describe so named **covalent bond**. The last two terms describe two electrons which are located at the same nucleus A, or B. These terms describe so named **ionic bond**. In fact the better agreement with experiment can be obtained when the total molecular wavefunction is taken in the form

$$\Psi_g = \Phi_A(1)\Phi_B(2) + \Phi_B(1)\Phi_A(2) + c[\Phi_A(1)\Phi_A(2) + \Phi_B(1)\Phi_B(2)], \quad (59)$$

where the coefficient c can be determined within the variation procedure.

Therefore, the ground state electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital. This is schematically shown in the **molecular orbital energy level diagram**. These are two electrons which can enter the σ_g orbital by pairing their spins. According to the Pauli Principle, no more electrons can enter this bonding orbital. The diagram also contains data for other Period 1 diatomic molecules. Particularly, He_2 molecule contains four electrons which should contribute to both σ_g and σ_u^* orbitals. Although these orbitals differ in detail from those in H_2 , the general shape is the same, and we can use the same qualitative energy level diagram in the discussion. Two from the four electrons enter the σ_g orbital, but then it is full, and the next two must enter the antibonding σ_u^* orbital as shown in figure. The ground electronic configuration of He_2 is therefore $\sigma_g^2\sigma_u^{*2}$. We see that there is one bond and one antibond. Because an antibond is slightly more antibonding than a bond is bonding, the He_2 molecule is unstable having higher energy than the separate atoms.

C. Bonding order

A measure of the net bonding in a diatomic molecule is its **bond order**, b :

$$b = \frac{1}{2}(n - n^*), \quad (60)$$

where n is the number of electrons in bonding orbitals and n^* is the number of electrons in antibonding orbitals. For instance, for H_2 $b = 1$, corresponding to a single bond $H - H$, while for He_2 $b = 0$, corresponding to no bond at all.

D. Period 2 diatomic molecules: σ orbitals

For building σ orbitals we form linear combinations of all atomic orbitals that have **cylindrical symmetry** about the internuclear axis. For instance, in Period 2 atoms the valence atomic orbitals are $2s$ and $2p$. Assuming that \mathbf{Z} axis is parallel to the internuclear axis \mathbf{R} , the general form of the molecular σ orbital can be written as

$$\Psi_\sigma = c_{A2s}\Phi_{A2s} + c_{B2s}\Phi_{B2s} + c_{A2p_z}\Phi_{A2p_z} + c_{B2p_z}\Phi_{B2p_z} \quad (61)$$

Using these four atomic orbitals: $|A2s\rangle$, $|B2s\rangle$, $|A2p_z\rangle$, and $|B2p_z\rangle$ we can form four molecular orbitals of the σ symmetry by an appropriate choice of the coefficients c . A procedure of calculating these coefficients is similar to what was discussed before for H_2^+ and consists of solving the **secular equation**.

Sometimes, $2s$ and $2p_z$ orbitals can be treated separately, because they have distinctly different energies. Then, the $2s$ orbitals of the two atoms overlap with each other giving a bonding (σ_g) and an antibonding (σ_u^*) molecular orbital. The two $2p_z$ atomic orbitals which are directed along the internuclear axis interact strongly. They may interfere with each other giving a bonding (σ_g) and antibonding (σ_u^*) molecular orbital.

Thus, you can see that there are many molecular orbitals of the same symmetry appear from theory. The nomenclature of these orbitals can be done in several different ways. For instance, in some handbooks you will find the notation for the molecular orbitals which explicitly indicates the atomic orbitals involved to a definite molecular orbital, for instance: $\sigma_g 2p$, or $\sigma_u 1s$, where $2p$ and $1s$ are corresponding atomic orbitals. This nomenclature is very clear and useful for didactic. However, in general, **all** atomic orbitals of the same symmetry can contribute to a given molecular orbital as seen from eq.(61). In other handbooks

molecular orbitals are labelled just by their numbers, for instance, $1\sigma_g$, or $3\sigma_u$, where the numbers order the molecular orbitals of the same symmetry with respect to their energy. The higher the number is, the higher is the energy of an electron within this state. This nomenclature, which we use in these lectures is more abstract than the first one, but more appropriate for theoretical analysis.

E. Period 2 diatomic molecules: π orbitals

Considering the $2p_x$ and $2p_y$ orbitals of both atoms we see that they are perpendicular to the internuclear axis. They can overlap only being oriented to the same side, that is $2p_x$ with $2p_x$ and $2p_y$ with $2p_y$. The overlapping can be constructive, or destructive and results in a bonding, or antibonding π **orbital**. The bonding π orbitals are *u* (ungerade) instead of *g* (gerade) because the two lobes of the $2p$ atomic orbitals have opposite signs.

Although the $2p_x$, $2p_y$, $2p_z$, atomic orbitals are at the same energy, the overlap for the $\sigma 2p_z$ molecular orbitals is different from that of the $\pi 2p$ orbitals. Therefore, the $\sigma 2p_z$ energy is not equal to the $\pi 2p_x$ and $\pi 2p_y$ energies, although the $\pi 2p_x$ and $\pi 2p_y$ energies are equal to each other. This leads to additional degeneracy of the π orbitals, each of them can be populated by the maximum four electrons.

F. Period 2 diatomic molecules: Succession of Molecular Orbitals and Aufbau Principles

Now we are able to use the succession of MOs to describe homonuclear two atomic molecules. The electrons are distributed among the orbitals according to energy and the Pauli principle. Due to degeneracy, up to two electrons are allocated to any σ energy level and up to four electrons are allocated to any π energy level.

The sequence of MO energies implies structural properties of molecules in a similar way the energy levels of AOs are used to explain the properties of atoms. The currently available data support the following succession of molecular orbitals for the Period 2 diatomic molecules up to and including N_2 :

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 1\pi_u < 3\sigma_g < 1\pi_g < 3\sigma_u$$

However, for O_2 and F_2 the $3\sigma_g$ orbital becomes lower than the $1\pi_u$ orbital. Therefore, succession of the orbitals for the Period 2 molecules from O_2 till Ne_2 is as follows:

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g < 1\pi_u < 1\pi_g < 3\sigma_u$$

With the orbitals established, we can deduce the ground configuration of the molecules by adding the appropriate number of electrons to the orbitals and following the **Aufbau principles**:

- (i) **Electron occupy different orbitals approximately in the order of their energies**
- (ii) **Only two electrons can occupy any non-degenerate orbital**
- (iii) **An atom, or a molecule in its ground state adopts a configuration with the greatest number of unpaired electrons (Hund's maximum multiplicity rule)**

G. Period 2 diatomic molecules: description of different molecules

The MO description tends to ignore the inner shell electrons and descriptions of electronic configurations just care for the former valence electrons. For example Li_2 with two valence electrons is described with the inner shell electrons as

$$Li_2[(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2], \quad (62)$$

or, shortly by introducing capital letters for complete shells as

$$Li_2[KK(2\sigma_g)^2]. \quad (63)$$

Let us consider N_2 with 10 valence electrons. The electronic configuration can be written as

$$N_2[KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2], \quad (64)$$

where two lowest electron pairs occupy and fill the bonding ($2\sigma_g$) and antibonding ($2\sigma_u$) orbitals, respectively. Six other electrons occupy the bonding ($1\pi_u$) and ($3\sigma_g$) orbitals. Therefore, the bonding order for N_2 is $\frac{1}{2}(8 - 2) = 3$ indicating a very strong triple molecular bond $N \equiv N$ which is consistent with very high dissociation energy of the molecule (942 kJ mol^{-1}).

The ground state electron configuration of O_2 with 12 valence electrons is

$$N_2[KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2], \quad (65)$$

with the bond order 2.

According to the Hund's rule for allocation of electrons in degenerated MOs $1\pi_{gx}^*$ and $1\pi_{gy}^*$ these two electrons will have parallel spins. Therefore, the O_2 molecule has a net spin angular momentum $S = 1$ and its ground state is so called **triplet state**.

In a similar manner, we describe the electronic configuration of fluorine molecule F_2

$$F_2[KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4], \quad (66)$$

where $(1\pi_u)^4$ denotes the degenerated pair of $(1\pi_{xu})^2$ and $(1\pi_{yu})^2$ orbitals. $2\sigma_g$ and $2\sigma_u$ as well as $1\pi_u$ and $1\pi_g$ are pairs of bonding and antibonding MOs. Therefore, of the 14 valence electrons only the pair of electrons in $(3\sigma_g)^2$ are regarded as bonding and this corresponds to the finding of a single bond of the σ -type in the molecule.

VII. HETERONUCLEAR DIATOMIC MOLECULES

As well for a treatment of heteronuclear diatomic molecules, such as CO , or HCl the LCAO method can also be applied. However, now the electron cloud distribution is usually not evenly shared between the atoms because it is energetically favorable for the electron pair to be closer to one atom than the other. This type of covalent bond is called **polar bond**.

If only two atomic orbitals are involved, the one-electron molecular orbital can be written as linear combination of atomic orbitals as

$$\Psi = c_A\Phi_A + c_B\Phi_B, \quad (67)$$

where Φ_A and Φ_B are the atomic orbitals of the atom A and B , respectively and the coefficients c_A and c_B are usually not equal.

The general principles of construction of the polar molecular orbitals are the same as for the non-polar orbitals described above. Particularly:

- (i) The energy levels of the atomic orbitals Φ_A and Φ_B cannot differ too much. Therefore, the valence orbitals of the atoms combine strongly, whereas contribution from the inner shell orbitals can usually be neglected.

- (ii) The atomic orbitals Φ_A and Φ_B should be of the same symmetry.
- (iii) The overlap of the orbitals Φ_A and Φ_B must be high, this is often referred to as "Principle of maximal overlap".

Let us apply the conditions for an effective linear combination of atomic orbitals to the hydrogen fluoride molecule HF and consider only the $1s$ atomic orbital of the H atom and $2p$ valence atomic orbital of the F atom. As discussed above, only the $2p_z$ atomic orbital of F can combine with the $1s$ orbital of H giving a σ and σ^* type molecular orbitals. Note, that the molecule is not symmetric over the Inversion and the subscripts g and u cannot be now used. Therefore, the general form of the molecular orbital is

$$\Psi = c_H \Phi_H(1s) + c_F \Phi_F(2p_z) \quad (68)$$

The $H1s$ orbital lies 13.6 eV below the zero of energy (the separated proton and electron) and the $F2p$ orbital lies at 18.6 eV. Hence, the bonding σ orbital in HF is mainly $F2p$, while the anti-bonding σ^* orbital is mainly $H1s$ orbital in character. Therefore, the two electrons in the molecular ground state are most likely to be found in the $F2p$ orbital and there is a partial **negative** charge on the F atom and a partial **positive** charge on the H atom. The electron configuration of the molecule can be written as

$$(1\sigma)^2(2\sigma)^2(1\pi)^4 : {}^1\Sigma \quad (69)$$

The expansion coefficients c_H and c_F as well as the energies of two corresponding molecular states can be found using the perturbation theory method described in Section I A. The secular determinant for the two-state problem is as:

$$\begin{vmatrix} \alpha_F - E & \beta - ES \\ \beta - ES & \alpha_H - E \end{vmatrix} = 0, \quad (70)$$

where α_F and α_H are Coulomb integrals while β is the resonance integral.

Eq.(70) can be rewritten as a following second-order equation

$$(\alpha_F - E)(\alpha_H - E) - (\beta - ES)^2 = 0 \quad (71)$$

Assuming that the energy of the bonding MO energy E_{bond} differs only slightly from the fluoride atomic orbital energy $\Delta E_1 = E_{bond} - \alpha_F \ll 1$ we reduce eq.(71) to the first order

getting the solution

$$E_{bond} \simeq \alpha_F - \frac{(\beta - \alpha_F S)^2}{\alpha_H - \alpha_F} \quad (72)$$

In the same way assuming that the energy of the anti-bonding MO energy $E_{antibond}$ differs only slightly from the hydrogen atomic orbital energy $\Delta E_2 = E_{antibond} - \alpha_H \ll 1$ we get another solution

$$E_{antibond} \simeq \alpha_H + \frac{(\beta - \alpha_H S)^2}{\alpha_H - \alpha_F} \quad (73)$$

Thus, it is seen from eqs. (72) and (73) that the bonding state energy is lower than the fluoride atomic orbital energy, while the antibonding state energy is higher than the hydrogen atomic orbital energy. More, both bonding and antibonding interactions decrease as the difference $|\alpha_F - \alpha_H|$ increases. Note, that the obtained solutions (72) and (73) can be used only for polar molecule case $\alpha_F \neq \alpha_H$ and are not valid for the homogeneous molecule case $\alpha_F - \alpha_H \simeq 0$.

To obtain the coefficients c_A and c_B that represent the weight of the single atomic orbitals, we introduce the obtained expression for E_{bond} into equation (18):

$$(\alpha_F - E)c_F + (\beta - ES)c_H = 0 \quad (74)$$

Using again the approximation $|E_{bond} - \alpha_F| \ll 1$ we find:

$$\frac{c_F}{c_H} \simeq -\frac{\alpha_H - \alpha_F}{\beta - \alpha_F S}, \quad (75)$$

or

$$\Psi_{bond} \simeq c_F \left(\Phi_F(2p_z) - \frac{\beta - \alpha_F S}{\alpha_H - \alpha_F} \Phi_H(1s) \right) \quad (76)$$

In the similar way using eq. (73) for the $E_{antibond}$ we get

$$\Psi_{antibond} \simeq c_F \left(\Phi_F(2p_z) + \frac{\beta - \alpha_H S}{\alpha_H - \alpha_F} \Phi_H(1s) \right) \quad (77)$$

VIII. HYBRIDIZATION

Now we consider the example of Lithium Hydride (LiH) and discuss the LCAO description of the molecular orbitals. *Ab initio* calculations with a minimal basis of $1s$, $2s$, and $2p$ *Li*-atom orbitals the $1s$ *H*-atom orbital result in (according to Ransil (1960)) the following

molecular orbitals:

$$\begin{aligned} |1\sigma\rangle &\simeq \Phi_{Li}(1s) \\ |2\sigma\rangle &\propto 0,323\Phi_{Li}(2s) + 0,231\Phi_{Li}(2p_z) + 0,685\Phi_H(1s) \end{aligned} \quad (78)$$

and the electron configuration

$$LiH \left[(1\sigma)^2 (2\sigma)^2 \right] \quad (79)$$

Thus, the inner filled molecular orbital of lithium hydride, $(1\sigma)^2$, is almost identical with the Li -atom $1s$ orbital, and the bonding 2σ molecular orbital consists of three atomic orbitals: $\Phi_{Li}(2s)$, $\Phi_{Li}(2p_z)$, and $\Phi_H(1s)$. The $2p$ and $2s$ -AO of lithium contribute almost equally to the 2σ molecular orbital because the first of them is only slightly higher in energy than the other. The wavefunctions in eq.(78) are so named Hartree-Fock orbitals which were obtained using the the self consistent field approach. However, there is a possibility to go back to our previous policy of including only two atomic orbitals in our LCAO-MOs with the only minimal damage of the wave function. We replace the $2s$ and $2p_z$ Li atomic orbitals by two new kind of atomic orbitals:

$$\begin{aligned} \Phi_{sp1} &= \frac{1}{\sqrt{2}}(\Phi_{Li}(2s) + \Phi_{Li}(2p_z)) \\ \Psi_{sp2} &= \frac{1}{\sqrt{2}}(\Phi_{Li}(2s) - \Phi_{Li}(2p_z)), \end{aligned} \quad (80)$$

where the coefficients $1/\sqrt{2}$ are normalization factors.

The new orbitals in eq.(80) are called **(sp) hybrid orbitals** and they can be used instead of the $2s$ and $2p_z$ orbitals. Therefore, eq.(78) can be presented in a somewhat more simple form:

$$\begin{aligned} |1\sigma\rangle &\simeq \Phi_{Li}(1s) \\ |2\sigma\rangle &\simeq 0,501\Phi_{sp1} + 0,865\Phi_H(1s) \end{aligned} \quad (81)$$

The approximate orbitals in eq.(81) are not as good as the exact Hartree-Fock orbitals in eq.(78), however, they can be used for qualitative description of the molecular bonding. In the 2σ LCAO-MO, the coefficient of the $1sH$ orbital is roughly twice as large as the coefficient of the $sp1Li$ orbital. We say that the electron cloud is not equally shared and see again that the bond in LiH is a **polar covalent bond**. Particularly, the H end of the molecule is negatively charged, while the Li end is positively charged. This distribution of the electron cloud gives the molecule an **electric dipole moment**.

A. sp^3 Hybridization

Other type of hybrid orbitals are particularly useful for description of the bonding problem and structure in polyatomic molecules, like methane CH_4 , water H_2O and many others. Let us consider water molecule. Since the molecule is a 10-electron system at least five space orbitals are required for an orbital wavefunction. We will first use unmodified five lowest-energy atomic space orbitals of one oxygen atom two atomic orbitals of the hydrogen atoms. The $1s$ oxygen orbital is far lower in energy than the other orbitals and we will use it as a nonbonding orbital. All of the oxygen second shell orbitals have appropriate energies to be used in bonding LCAO-MOs with the hydrogen $1s$ orbitals.

Since the $2p_z$ orbital is cylindrically symmetric about the Z axis, we place a hydrogen nucleus denoted by A on the Z axis and construct the bonding molecular orbital

$$|1\sigma\rangle = c_O|2p_zO\rangle + c_H|1sA\rangle, \quad (82)$$

where $|1sA\rangle$ is the $1s$ hydrogen orbital centered on hydrogen nucleus A and the coefficients c_O and c_H are constants.

Then, we place another hydrogen atom denoted by B on the Y axis and another construct the LCAO-MO:

$$|2\sigma\rangle = c_O|2p_yO\rangle + c_H|1sB\rangle. \quad (83)$$

The obtained $|1\sigma\rangle$ orbital is a σ orbital because it is a linear combination of two atomic orbitals corresponding to $m = 0$. The $|2\sigma\rangle$ orbital bears the same relationship to the Y axis as the $|1\sigma\rangle$ orbital does to the Z axis, so the projection of the orbital angular momentum on the Y axis for this orbital is also equal to zero.

Since the energy of the oxygen $2p$ orbitals is lower than that of the hydrogen $1s$ orbitals, optimization of the coefficients will give for the bonding orbital

$$|c_O| > |c_H| \quad (84)$$

which means that the electrons occupying the $|1\sigma\rangle$ and $|2\sigma\rangle$ orbital will be more likely found near the oxygen nucleus than near the hydrogen nucleus. According to the Aufbau principle the ground state configuration is thus

$$(1sO)^2(2sO)^2(2p_xO)^2(1\sigma)^2(2\sigma)^2 \quad (85)$$

with two single bonds at a bond angle of 90° .

However, this result disagree with the experimental value of the bond angle of $104,5^\circ$. Also this result disagree with the known fact that the water molecule tends to form two equivalent hydrogen bonds between its oxygen atom and hydrogen atoms of other water molecules, indicating that the two pairs of of nonbonding electrons in the valence shell should occupy equivalent orbitals, instead of occupying the oxygen $2s$ and $2p_x$ orbitals.

A better wave function for the water molecule is obtained by creating a set of hybrid orbitals that are the linear combinations of the $2s$ orbital and all three of the $2p$ orbitals:

$$|2sp^3 1\rangle = \frac{1}{2}(-|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle) \quad (86)$$

$$|2sp^3 2\rangle = \frac{1}{2}(-|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle) \quad (87)$$

$$|2sp^3 3\rangle = \frac{1}{2}(-|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle) \quad (88)$$

$$|2sp^3 4\rangle = \frac{1}{2}(-|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle) \quad (89)$$

The orbital regions of the $2sp^3$ hybrid orbitals are directional. In the figure, vectors are drawn along the positive coordinate axis in the direction of the largest positive values of the $2sp^3$ orbitals. These vectors are axes of the cylindrical symmetry of the corresponding hybrid orbitals. Since connecting the four alternative corners of a cube with line segments constructs a regular **tetrahedron**, the angle between any two of the axes shown is called the **tetrahedral angle** and approximately equal to 109 degrees.

We can now construct an approximate wavefunction for the water molecule using the $2sp^3$ hybrid orbitals. We place the two hydrogen atoms on the symmetry axes of two $2sp^3$ hybrid orbitals: hydrogen A on the axis of the $2sp^3 2$ orbital and hydrogen B on the axis of the $2sp^3 3$ hybrid orbital. Then we form two bonding LCAO molecular orbitals

$$|\sigma A\rangle = c_O |2sp^3 2\rangle + c_H |1s A\rangle \quad (90)$$

$$|\sigma B\rangle = c_O |2sp^3 3\rangle + c_H |1s B\rangle \quad (91)$$

Along with the bonding orbitals $|\sigma A\rangle$ and $|\sigma B\rangle$ there are antibonding orbitals $|\sigma^* A\rangle$ and $|\sigma^* B\rangle$ which are somewhere higher in energy and vacant in the ground state. By the Aufbau principle the electron configuration of the ground state is

$$(1s O)^2 (2sp^3 1)^2 (2sp^3 4)^2 (\sigma A)^2 (\sigma B)^2 \quad (92)$$

As for earlier approximate wavefunction, there are two single bonds and two pairs of valence shell nonbonding electrons which occupy nonbonding sp^3 orbitals. The bond angle is equal to the tetrahedral angle 109° and is in reasonably good agreement with the experimental bond angle of 105° .

Now we qualitatively consider the bonding structure in methane molecule CH_4 using the **electron pair bond** approach where the bond between only two partners is treated. The conditions for the bond formation is as follows:

- (i) Both partners provide one suitable orbital each for building the molecular bond.
- (ii) Two electrons are needed for the bond: each partner can contribute one electron, or both electrons can be contributed by one partner.

The **electron pair bond** approach is closely related to the **valence-bond theory** which was the first quantum mechanical theory of bonding. Although this theory has undergone less much computational development than the **molecular orbital theory** we explained above, it is very useful for qualitative explanation and widely used throughout chemistry.

As seen from the picture of the carbon electron structure, there are at least three different possible ways of building the molecular bonds in CH_4 molecule:

- (a) Bonding of two H atoms to a C atom using two available $2p$ orbitals of carbon. No additional (**promotion**) energy has to be supplied, but only two bonds are formed instead of four.
- (b) Bonding of four H atoms to a C atom using two sp linear hybrid and two $2p$ orbitals of carbon. Thus four bonds can be built, however the energy for the promotion of two hybrid sp orbitals to be supplied is

$$E_H = 2 \cdot \frac{1}{2} = \Delta E \quad (93)$$

- (c) Bonding of four H atoms to a C atom using four sp^3 tetrahedral hybrid orbitals of carbon. Thus four equivalent bonds can be built and the energy for the promotion of four hybrid sp orbitals to be supplied is

$$E_H = 2 \cdot \frac{3}{4} \Delta E - 2 \cdot \frac{1}{4} \Delta E = \Delta E \quad (94)$$

The overlap through hybrid orbitals in case (c) better than in case (b). Therefore, tetrahedral orbitals should be preferred for the bond formation. Indeed a tetrahedral arrangement of four H atoms around the C atom was found experimentally in methane, where the bonding angle is very close to the tetrahedral angle ($109^{\circ}28'$).

B. sp^2 Hybridization

Other important type of hybrid orbitals is sp^2 hybridization. In this case $2s$ orbital and two of the three $2p$ orbitals can be combined as follows

$$|2sp^2_1\rangle = \frac{1}{\sqrt{3}} (|2s\rangle + \sqrt{2}|2p_z\rangle) \quad (95)$$

$$|2sp^2_2\rangle = \frac{1}{\sqrt{3}} \left(|2s\rangle + \sqrt{\frac{3}{2}}|2p_x\rangle - \frac{1}{\sqrt{2}}|2p_z\rangle \right) \quad (96)$$

$$|2sp^2_3\rangle = \frac{1}{\sqrt{3}} \left(|2s\rangle - \sqrt{\frac{3}{2}}|2p_x\rangle - \frac{1}{\sqrt{2}}|2p_z\rangle \right), \quad (97)$$

while the third $2p$ orbital remains the same: $|2sp^2_4\rangle = |2p_y\rangle$.

The combination of the $|2sp^2_1\rangle$, $|2sp^2_2\rangle$, and $|2sp^2_3\rangle$ hybrid orbitals have their maxima shifted by 120° in the XZ plane. These orbitals are called **trigonal planar hybrid orbitals**. These orbitals are particularly important for describing bonding in the planar molecules like ethene C_2H_4 , benzene C_6H_6 and others which are discussed in the next section.

C. Molecules with π electron systems: the Hückel approximation

Chemical bonding in such molecules as H_2 , HCl , LiH , H_2O , and CH_4 described above can be described by σ -type MOs with **single** bonds. Now we will consider another important class of molecules with **double**, or **triple** bonds, where the π molecular orbitals play important role. These are, for instance, Ethene (C_2H_4), Butadiene (C_4H_6), Benzene (C_6H_6), Ethyne (C_2H_2), and many others. These molecules can be viewed as system where π electrons move relatively freely and are extending over the entire molecular skeleton which is formed by the σ electrons. The highest occupied molecular orbitals in such molecules (**HOMO**) is a π orbital and the lowest unfilled molecular orbital (**LUMO**) is a π^* orbital.

These two orbitals jointly forms the **frontier orbitals** of the molecule. The **frontier orbitals** are very important because they are likely response for many of the chemical and spectroscopic properties of the molecule.

Note, that strictly speaking the classification of an orbital as σ and π is valid in linear molecules only. However, it is widely used to denote the local orbital symmetry with respect to a given $A - B$ bond axis. For planar molecules the σ bonds are nodeless with respect to the molecular plane and the π bonds have a node in the molecular plane.

Let us first consider in more detail the electronic structure of a carbon atom and formation of hybrid orbitals discussed above. Two important hybrid orbitals which can fit the symmetry of a planar molecule are the linear sp and the trigonal sp^2 orbitals described above.

The molecular orbital energy level diagram can be constructed using a set of approximations suggested in 1931 by Erich Hückel (German physicist and theoretical chemist, 1896-1980). The Hückel approximations are as follows:

1. Only the frontier π orbitals are calculated, while the lower energy σ orbitals are assumed to form a rigid framework that determines the general shape of the molecule.
2. All the C atoms are treated identically, so all Coulomb integrals α for the atomic orbitals which contribute to the π orbitals are set equal.
3. All overlap integrals S are set equal to zero.
4. Only the resonance integrals between the neighbor C atoms are set nonzero and all equal to β .

Let us consider molecular orbital energy level diagrams for several important molecules

Ethene C_2H_4

Each carbon atom has three neighbors, so the best suitable bonding orbital is a trigonal hybrid orbital. The carbon atoms are kept together by trigonal planar σ bonds. The same bonds keeps two H atoms to each carbon atom. A single π molecular orbital which is built from the rest $2p_z$ orbitals of both C atoms additionally keeps them together producing the double bond.

Quantitatively, the π orbitals in C_2H_4 can be expressed by as LCAOs of two $C2p$ orbitals, which are perpendicular to the molecular plane:

$$\Psi = c_A\phi_A + c_B\phi_B, \quad (98)$$

where ϕ_A and ϕ_B are $2p_Z$ orbitals of the C atoms A and B , respectively. For obtaining the expansion coefficients c_A and c_B and the energies we have to solve the second-order secular determinant:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0, \quad (99)$$

where according to the Hückel approximations the Coulomb integrals α are set the same and where the overlap integral must be set to zero $S = 0$.

Eq. (99) has obvious roots

$$E = \alpha \pm \beta, \quad (100)$$

where the sign (+) corresponds to the bonding orbital (note, that β is negative) and the sign (−) corresponds to the antibonding orbital. The Aufbau principle leads to the configuration $1\pi^2$ where each carbon atom supplies one electron to the π bond.

Butadiene C_4H_6 .

Here again each carbon atom has three neighbors, so the best suitable bonding orbital is a trigonal hybrid orbital. The carbon and hydrogen atoms are kept together by trigonal planar σ bonds. There are four $2p_z$ orbitals from each of the four C atom which form four π molecular orbitals contributing to the double bonds.

Quantitatively, the π orbitals in C_4H_6 can be expressed by as LCAOs of four $C2p$ orbitals:

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4, \quad (101)$$

where ϕ_i , $i = 1 \dots 4$ are four $C2p_Z$ orbitals. The Hamiltonian matrix becomes now four-dimensional. According to the Hückel approximations the corresponding secular determinant can be written as:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (102)$$

Eq. (102) is equivalent to the fourth-order linear algebraic equation and can be easily solved with an appropriate mathematical software. The roots are as follows: Eq. (99) has obvious roots

$$\begin{aligned}
 E_1 &= \alpha + 1,62\beta \\
 E_2 &= \alpha + 0,62\beta \\
 E_3 &= \alpha - 0,62\beta \\
 E_4 &= \alpha - 1,62\beta
 \end{aligned}
 \tag{103}$$

where the energy states E_1 and E_4 corresponds to pure bonding and antibonding orbital, respectively, while the states E_2 and E_3 are mixture of bonding and antibonding orbitals. The Aufbau principle leads to the configuration $1\pi^2 2\pi^2$.

Benzene C_6H_6 .

The most notable example of delocalization π bonding is benzene and the aromatic molecules based on its structure. Six C atoms have three trigonal planar sp^2 hybrid orbitals each and a single 2π orbital which is perpendicular to the molecular plane.

An H atom is bonded by an overlap ($H1s + Csp^2$) σ orbital to a C atom and the remaining hybrid orbitals form a regular hexagon structure of the C atoms. The internal angle of a regular hexagon is 120° which perfectly fits sp^2 hybridization angle.

The rest six $2p$ orbitals, one from each of the C atom form six π molecular orbitals which are spread all round the hexagon ring. These six molecular orbitals and their energies can be calculated within the Hückel approximations by diagonalizing a 6×6 Hamiltonian matrix. Particularly, the π orbitals can be expressed by as LCAOs of six $C2p$ orbitals:

$$\Psi = \sum_{i=1}^6 c_i \phi_i
 \tag{104}$$

where ϕ_i , $i = 1 \dots 6$ are six $C2p_z$ orbitals.

The corresponding secular determinant can be written as:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0, \quad (105)$$

where the non-zero matrix elements β in the right-upper and left-down corners indicate cyclic interaction between the C atoms within the hexagon ring.

The MO energies which are the roots of Eq. (105) are as follows

$$\begin{aligned} E_6 &= \alpha - 2\beta \\ E_{4,5} &= \alpha - \beta \\ E_{2,3} &= \alpha + \beta \\ E_1 &= \alpha + 2\beta \end{aligned} \quad (106)$$

where the lowest energy state E_1 is bonding between all neighboring atoms, the highest energy state E_6 is antibonding between each pair of neighbors, and other four intermediate states are a mixture of the bonding, antibonding, and nonbonding orbitals. It is also seen that the energy level E_2 is degenerate with the level E_3 , and that the level E_4 is degenerate with the level E_5 . According to the Aufbau principle three lowest orbitals are fully occupied giving the ground state configuration $a_{2u}^2 e_{1g}^4$. It is important that the occupied molecular orbitals have net bonding character.

IX. TERM SYMBOLS IN DIATOMIC MOLECULES

A total many-electron molecular wavefunction can be formed as products of one-electron molecular orbitals taking into account indistinguishability of electrons. The modulus of the component of the **total orbital angular momentum** of a diatomic molecule $|L_Z|$ onto the internuclear axis is usually denoted by the capital Greek letter Λ which can take the integer values $\Lambda = 0, 1, 2, \dots$ and the corresponding molecular states are indicated by the capital Greek letters $\Sigma, \Pi, \Delta, \dots$, respectively. More completely, a symbol of a molecular energy state contains also of a preceding superscript multiplicity index $2S+1$, where S is the total electron spin of the molecule and a subscript symmetry index g , or u (for homonuclear molecules), which indicates the symmetry of the electron wavefunction under **Inversion**. The Σ states have also an additional upper index $(+)$, or $(-)$ depending on the symmetry of the electron wavefunction under **Reflection** in the plane containing the internuclear axis.

For example, the notation ${}^2\Pi_u$ describes the molecular state with a total electron spin $S = 1/2$, the modulus of the projection of the total angular momentum onto the internuclear axis $\Lambda = 1$, and negative parity of the molecular wavefunction under Inversion. The notation ${}^3\Sigma_g^+$ describes the state with a total electron spin $S = 1$, the projection of the angular momentum $\Lambda = 0$, positive parity of the molecular wavefunction under Inversion, and positive parity of the molecular wavefunction under Reflection.

Let us now consider relationship between the configuration of one-electron orbitals in a diatomic molecule and the quantum numbers of the corresponding total many-electron molecular wavefunction. For molecules with only one valence electron the projection λ is equal to the corresponding projection Λ . For molecules with several valence electrons, this relationship is not always so simple and depends on whether these electrons are equivalent, or not. If they are equivalent, the Pauli principle must be taken into consideration, while if they are not equivalent, no further restrictions apply. Note, that there is no contribution from any full inner shell molecular orbitals, therefore, only the valence MOs should be taken into consideration.

TABLE I: **Molecular Terms: Equivalent Electrons**

Electron Configuration	Molecular Terms
σ^1	$^2\Sigma$
σ^2	$^1\Sigma$
π^1	$^2\Pi$
π^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Delta$
π^3	$^2\Pi$
π^4	$^1\Sigma^+$
δ^1	$^2\Delta$
δ^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Gamma$
δ^3	$^2\Delta$
δ^4	$^1\Sigma^+$

For example, a σ MO occupied by two electrons forms a $^1\Sigma$ term because the orbital angular momentum of each electron is zero and therefore the electrons must have opposite projections of their spins, which results in zero total spin. For the molecules with one unpaired electron with its spin $s = 1/2$, we always get a duplet ($S = 1/2$) state. With two unpaired electrons, we obtain a triplet state ($S = 1$) if the electron spins are parallel to each other and a singlet state ($S = 0$) if the electron spins are antiparallel to each other.

The order of the molecular states which correspond to the same electron configuration is regulated by the **Hund's maximum multiplicity rule**: the state with the larger number of unpaired electrons usually has the lower energy.

The relationship between different configurations of one-electron molecular orbitals and the corresponding total many-electron molecular wavefunction terms are summarized in Table I and Table I for equivalent and not equivalent electron shells, respectively.

TABLE II: Molecular Terms: Non-Equivalent Electrons

Electron Configuration	Molecular Terms
$\sigma\sigma$	$^1\Sigma, ^3\Sigma$
$\sigma\pi$	$^1\Pi, ^3\Pi$
$\sigma\delta$	$^1\Delta, ^3\Delta$
$\pi\pi$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta$
$\pi\delta$	$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$
$\delta\delta$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Gamma, ^3\Gamma$
$\sigma\sigma\sigma$	$^2\Sigma^+, ^2\Sigma^+, ^4\Sigma^+$
$\sigma\sigma\pi$	$^2\Pi, ^2\Pi, ^4\Pi$
$\sigma\sigma\delta$	$^2\Delta, ^2\Delta, ^4\Delta$
$\sigma\pi\pi$	$^2\Sigma^+, ^2\Sigma^+, ^4\Sigma^+, ^2\Sigma^-, ^2\Sigma^-, ^4\Sigma^-, ^2\Delta, ^2\Delta, ^4\Delta$