Chapter 14: Molecules I

14.1 One-Electron Covalence

14.1.1 First Order Perturbation Theory (FOPT)

Unperturbed System: $\mathbf{H}°$, Orb° (Orb = classical orbit or q.m. orbital), E°

Perturbed System: $\mathbf{H} = \mathbf{H}° + \Delta H$, Orb = Orb° + ΔOrb, E = E° + ΔE with $\boxed{\Delta E(\Delta H,\ \text{Orb}°)}$

14.1.2 Qualitative principles of homopolar interaction

Covalence comes mainly from smearing an electron not over one atom, but over more atoms. Heisenberg's uncertainty explains covalence: increased spatial uncertainty yields smaller Δp, $(\Delta p)^2$ is minimal zero-point $\langle p^2 \rangle$. Pauli principle: two electrons can be "filled" into this orbital with quantum mechanically reduced (from 1 atom to several atoms) kinetic energy density; pair bonding dominates; occupation of low energy levels causes 'valence saturation'. Order of increasing covalence: single center (lone pair) – polar valence ('1.5'-centre) – ordinary two center bond – three center bond (aromatic, metallic).

If low energy molecular orbital exists because of Heisenberg uncertainty, then chemical bonding occurs, if there are (1), 2, (3) electrons available: electron-pair bond is most stable; 1e and 3e bonds are usually less stable. Electron pairing is the result of the existence of a covalently bonding orbital, not vice versa. Sharing, not pairing is the origin of covalence.

TABLE I (simplest example - two nuclei and one electron)

$H + H^+$	H_2^+ (class. FO)	H_2^+ (q.m. FO)	H_2^+ (real mol.)
two separated atoms A, B	two classically superposed atoms	two q. m. superposed atoms	two really interacting atoms
ρ_A, ρ_B	$\rho_A + \rho_B$	$N(\sqrt{\rho_A} \pm \sqrt{\rho_B})^2 =$ $\rho_A + \rho_B \pm \Delta\rho = \rho^{LCAO}$	$\rho^{LCAO} + \delta\rho$
T_o $V = -2T_o$ $E = -T_o$	T_o $V = -2T_o - \delta$ $E = -T_o - \delta$	$T_o \pm \Delta$ $V \approx -2T_o$ (*) $E \approx -T_o \pm \Delta$	$T = -E_{mol}$ $V = 2E_{mol}$ $E \approx -T_o - \Delta - \delta\Delta$.

δ: two (neutral spherical) atoms with overlapping electron clouds: attraction $\sim Z_1 \cdot Z_2$ (CH_4: no valence saturation; H/Pu: no common bond energy; 1He, 2H, 4P: no valence number; no directionality)

$\pm\Delta\rho$: $\pm[2 \cdot \sqrt{(\rho_A(r) \cdot \rho_B(r))} - (\rho_A(r) + \rho_B(r)) \cdot \langle\sqrt{\rho_A(r)}\sqrt{\rho_B(r)}\rangle] / (1 \pm S_{AB})$
      $\langle\Delta\rho\rangle = 0$; because of the denominator, $\Delta\rho$ and its effects are more pronounced for the "−" case (antibinding). Interference transfers density from atoms to bond center (does not change potential energies significantly)*

Δ: reduced kinetic energy, if molecular wavefunction is *rather* flat: Heisenberg uncertainty effect for electrons in a *group* of atoms

(*)   small potential energy change because a) $\Delta\rho > 0$ *in the overlap region*: quantum wave interference shifts electronic charge into the overlap region, where it is attracted from both nuclei; b) $\Delta\rho < 0$ *in the region of high atomic charge density*, where the electrons are attracted most strongly

$\delta\rho$:   molecular density deformation of atoms: a) radial *contraction* towards highest valence electron attraction in the outer *core* region ("n $\to$ (n+1)" orbital mixing, radial hybridization); b) angular *polarization* towards molecular axis ("$l \to (l+1)$ orbital mixing") – so that T increases to $-E_{mol}$ and V decreases to $-2E_{mol}$.

$\delta\Delta$:   T and V change a lot, E decreases only a little by $\delta\Delta$ (variational principle)

14.2 Principles of interatomic interactions

TABLE II

Three basic mechanisms of chemical bonding

H =	T_n +	t_e +	V_{n-e} +	V_{e-e} +	V_{n-n}
	small at room or low temperatures	*relatively* small, if electrons belong to several nuclei (sharing)	*relatively* low, if electrons transferred to more electronegative atom	*relatively* small, if electron correlation keeps r_{e-e} large	repulsion at short n–n distance
	neglect for the moment	$\left\{\begin{array}{l} 2c - 2e \\ 2c - 1e^{a)} \\ 2c - 3e \\ 3c - 2e \\ 3c - 4e \\ \text{etc.} \end{array}\right.$	(ionic valence, polar valence)	(valence bonding, London dispersion force)	

a) Is sensitve against electronegativity difference, in contrast to 2c-2e bond.

There is no pure bonding of a) t_e kinetic-covalence/MO-valence sharing type, b) of V_{ne} ionic/polar, charge transfer type, c) of V_{ee} VB-valence/dispersion/correlation type.

14.3 VB and MO approximations

A●——●B   two atoms with orbitals φ_A, φ_B and two electrons (1+1 "pairing bond" or 2+0 "dative bond")

One electron is described by a spin-orbital function. Probabilities of independent events are multiplicative. Wavefunctions of many–independent electrons–systems are (sums of) spin-orbital products (symmetry-adapted; Pauli exclusion): configuration functions.

Two-electron molecule: Wave function Ψ must be of two-center permutation-antisymmetric product type $\varphi\varphi$ (electrons are smeared and indistinguishable). Approximation: construct Ψ from atomic orbitals (LCAO-approximation, minimal or extended basis). Two different approximation strategies:

14.3.1 *First delocalize, second multiply (MO approach)*

Invented and developed by the spectroscopists and chemical physicists Hund[1], Mulliken[2], Hückel[3], Slater[4]

Molecular function = product of molecular one-electron functions

(so-called MO-configuration = which orbitals are occupied. Graphical symbol for such a model Ψ is an orbital level scheme with electron dots • or arrows ➤).

φ_A and $\varphi_B \rightarrow \varphi_A + \varphi_B = \varphi_g$, $\varphi_A - \varphi_B = \varphi_u$ (note: g/u only for i-symmetric systems)

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[1] Hund, 1896-1997, Germany : physicist - atomic and molecular states and spectroscopy, MO concept (1928), tunnel effect, history of physics

[2] Mulliken, 1896-1986, USA – Germany – USA, American of Austrian origin : theoretician - molecular spectra, MO approach of molecular electronic structure and spectroscopy, electronegativity, charge distribution in molecules. Nobel price 1966

[3] Hückel, 1896-1980, Germany, brother of organic chemist : physicist - theory of strong electrolytes (with Debye and Onsager), quantum mechanics of chemical bonding, σ- and π-bonding, aromatic conjugation (1931).

[4] Slater, 1900-1976, USA : physicist - quantum mechanics of atoms, molecules, solids; several influential monographs

Multiply so that Pauli principle becomes fulfilled   (Fig. 14.18)

$(\varphi_{g,1}\cdot\varphi_{g,2})*(\alpha_1\beta_2-\beta_1\alpha_2)$ or $(\varphi_{g,1}\cdot\varphi_{u,2}+\varphi_{u,1}\cdot\varphi_{g,2})*(\alpha_1\beta_2-\beta_1\alpha_2)$ or $(\varphi_{g,1}\cdot\varphi_{u,2}-\varphi_{u,1}\cdot\varphi_{g,2})*(\alpha_1\cdot\alpha_2)$ ...

Subscripts $_1$, $_2$ mean position and spin coordinates of electrons 1,2. Convention: delete the coordiantes or indices - first/second functinal factor refers to coordinates of the first/second particle.

g-g (or **u-u**): only spin-singlet possible, $E = 2\,(t+V_n)_g + \frac{1}{2}\,J_{AA} + \frac{1}{2}\quad J_{AB} - \delta + (\text{or} -)\,K_{AB}$

two times t-lowering ; (incorrectly) high e-e repulsion (because of J_{AA}: homopolar MO-bond is too 'ionic') ; "physically small, chemically big" exchange&correlation correction δ (of order $10^2\,kJ/mol$).

g-u: both spin-singlet/triplet are possible, $E = (t+V_n)_g + (t+V_n)_u + J_{AA}/J_{AB} - K_{AB} - \delta$

no t-lowering; J is Coulomb repulsion between atomic charge clouds, especially large/small for that charge position distribution, which is Pauli-compatible with spin singlet/triplet; K-'exchange' is Coulomb repulsion in the overlap cloud). – Often not good for large R, "ionic MO-error".

There is a very elegant and simple mathematical-computational procedure for the MO-approach.

The result of a calculation of a MO-configuration can be symbolized by one or more Lewis formulae.

14.3.2 *First multiply, second delocalize (VB approach)*

Invented by the physicists Heitler[5] and London[6], developed and propagated by Pauling[7] and Slater[4]

Molecular function = symmetrized product of atomic electron functions   (Fig. 14.13)

(so-called VB-structure = which atomic orbitals are used for each pair of electrons. Graphical symbol for such a model Ψ is a Lewis formula, which allows only for one-center and two-center pairs) – especially good for large R.

Either $\varphi_{A,1}\alpha_1 \cdot \varphi_{B,2}\alpha_2 \rightarrow \varphi_{A,1}\alpha_1 \cdot \varphi_{B,2}\alpha_2 - \varphi_{B,1}\alpha_1 \cdot \varphi_{A,2}\alpha_2 = (\varphi_{A,1}\cdot\varphi_{B,2}-\varphi_{B,1}\cdot\varphi_{A,2})(\alpha_1\cdot\alpha_2)$

spin-triplet, $E = (t+V)_A + (t+V)_B + J_{AB} + K$ (no evident t-lowering, repulsive K-term)

Or $\varphi_{A,1}\alpha_1 \cdot \varphi_{B,2}\beta_2 \rightarrow \varphi_{A,1}\alpha_1 \cdot \varphi_{B,2}\beta_2 \mp \varphi_{A,1}\beta_1 \cdot \varphi_{B,2}\alpha_2 - \varphi_{B,1}\beta_1 \cdot \varphi_{A,2}\alpha_2 \pm \varphi_{B,1}\alpha_1 \cdot \varphi_{A,2}\beta_2 =$

$$(\varphi_{A,1}\cdot\varphi_{B,2} \pm \varphi_{B,1}\cdot\varphi_{A,2}) \cdot (\alpha_1\cdot\beta_2 \mp \beta_1\cdot\alpha_2).$$

spin-singlet/triplet, $E = (t+V)_A + (t+V)_B + J_{AB} \pm K$ (no evident t-lowering (incorrect), attractive (or repulsive) K-term: low (high) e-e repulsion (good/bad left-right correlation))

Understanding the physics is possible, but quite involved. Instead of explaining, one mentions Lewis formula. This is very appealing to the ordinary chemist.

There is a very elegant, very sophisticated mathematical-computational procedure.

[5] Heitler, 1904-1981, Germany – Ireland – Schweiz : covalent bond (1927), radiation physics, nuclear theory

[6] London, 1900-1954, Germany – England – France – USA : covalent bond, supraconduction, suprafluidity

[7] Pauling, 1901-1994, USA – (Germany) – USA : pioneer of quantum chemistry, promoter of VB approach, electronegativity, x- and e-ray structure-determination, protein structure, several influential text books. Nobel prices 1954 and 1962

Note: Some MO-functions correspond to a single Lewis formula. If a single MO-configuration does not correspond to any single Lewis formula, the VB approach needs several structures already at the lowest level of approximation.

14.3.3 Better approximations

Wavefunctions of real many-particle-systems are sums of many (∞) such products (configurations or structures). Either 'mix' many MO-configurations (Configuration mixing or 'Interaction': CI, 'interaction' is not a good phrase); or mix many VB-structures ('structure resonance', nothing oscillates here in time)

14.3.4 Slater determinant law

A configuration function does not change, if the occupied orbitals are arbitrarily uniformly transformed, 'rotated' mixed, (hybridized). Nothing changes thereby. Example:

$\Psi = (a_1 \cdot b_2 + b_1 \cdot a_2) = (a_1' \cdot b_2' + b_1' \cdot a_2')$; also $\rho = |a|^2 + |b|^2 = |a'|^2 + |b'|^2$

for $a \rightarrow a' = c \cdot a + s \cdot b,$ $b \rightarrow b' = c \cdot b - s \cdot a$ with constants c, s $c^2 + s^2 = 1$.

14.4 Electronic Orbitals and Nuclear Structures

14.4.1 Electrons and Orbitals

Orbitals correspond to some arbitrary partitioning of the measurable N-electron total charge density ρ into arbitrarily eligible one-electron pieces φ_i^2, with $\sum \varphi_i^2 \equiv \rho$.

Therefore one can *choose* the occupied orbitals as orthogonal, ‹ab› = 0. In this case the expectation value formulae become very simple, e.g.

$E_{\text{n electrons}} = \Sigma_{\text{n occupied orbitals}}$(kinetic + nuclear attraction energies) +   ("Not" Fig. 14.7)

  $+ \Sigma_{\text{n(n-1)/2 occupied orbital pairs}}$(Coulomb repulsion of orbital clouds – that of overlap clouds)
A quantum electronic system behaves nearly like a system of quasi-classical orbital clouds. The MO approximation allows a nearly classical picture,
except that the orbitals must be 'occupied' according to the Pauli principle, except that the kinetic energy is quantum mechanical,
except that there is the Coulomb overlap ('exchange') correction, and
except that the orbitals must be orthogonal
(i.e. dominantly in different regions of space if chosen localized – 'Pauli pseudo-repulsion',
or strongly wavy if chosen canonical-delocalized – high kinetic energy-pseudo repulsion).

14.4.2 The meaning of 'existence'

The World exists (1), Ψ^{world}. Think of a piece of the world: a molecule "exists" (2) in the sense that our thinking of an isolated piece makes sense within the context of the problem under discussion.

The complete representation of this molecule is its many-particle (set of) wavefuction(s): this mathematical object " "exists" " (3), $\Psi^{\text{world}} = \Psi^{\text{rest of world}} \cdot \Psi^{\text{molecule}}$, in the sense that the mathematical structure corresponds to the processes in the real world at any level of experimental accuracy.

In many cases, though not always, one nuclear-electronic state function is a reasonable approximation: (only) then a 'smeared geometric structure', and/or the 'occupied orbital set' or 'electron orbital configuration', " " "exist" " " (4), $\Psi^{\text{molecule}} = N^{\text{nuc}} \cdot \eta^{\text{el}}$.

Sometimes the geometric structure is only slightly smeared, then its Eukleidean (molecular, crystal) structure " " " "exists" " " " (5) only, but indeed, in this meaning.

The Hilbert space of occupied orbitals can be represented in different ways by delocalized or localized or hybridized orbitals. Occupied orbitals " " " ""exist" " " " " (6) only, but indeed, in this meaning: $\eta^{el} = \mathcal{A}\Pi\varphi = \mathcal{A}\Pi\varphi'$.

Any object exists in the sense that *nature* allows *us* to construct this abstraction at a given level of accuracy. In this same sense, the geometric structure of nuclei or the electronic orbitals *may* exist for a chosen molecule, depending on the type of molecule and the type of context of our question.

14.4.3 Born-Oppenheimer approximation

If the molecule exists (e.g. H_3O^+ in vacuum, though not in water), it can often be approximated as a system of nuclei "distributed quantum mechanically" or "slowly moving semi-classically or classically" in the field of the "fast smeared quantum electrons":

$$\Psi(nuc,el) \approx N(nuc) \cdot \eta(el) \quad \text{(N is nuclear wavefunction, or trajectory) with}$$

$$[\mathbf{t}_{el} + V_{nuc\text{-}el} + V_{el\text{-}el} + V_{nuc\text{-}nuc}] \circ \eta_{nuc}(el) = \eta_{nuc}(el) \cdot E^{el}_{nuc}$$

$$[\mathbf{T}_{nuc} + E^{el}_{nuc}] \circ N(nuc) = N(nuc) \cdot E \quad \text{(total constant energy)}$$

(E^{el}_{nuc} is the electronic BO-PES, 'potential energy surface', it is a function of the nuclear coordinates, it contains the nuclear-electronic potential energies and the electronic kinetic energy)

14.5 Qualitative diatomic MO schemes

General rules: (Figs. 14.20, 27, 28, 35)

1) Sketch the atomic occupied valence orbital levels on a vertical energy scale. The HOAO of the less electronegative atom should be higher than the HOAO of the more electronegative atom, but lower than its LUAO.

2) Occupy with electrons. Classify the AOs according to the molecular symmetry (rotation axis: σ, (π_x, π_y) equivalent to (π_+, π_-)

3) n AOs yield n MOs. AOs of same symmetry mix to yield MOs of this symmetry. AOs strongly mix, **if** they overlap and **if** their energy is similar. Note that the overlap of different AOs at the *same* atom vanishes, e.g. $\langle s_A| p_A \rangle = 0$.

4) The lowest MO is lower than the lowest AO; the highest MO is *much* higher than the highest AO. Usually the highest MO is unbound (i.e. above the ionization limit).

5) σ-AOs usually mix (overlap) stronger than π-AOs.

6) An $s(p_\sigma)$ AO on atom A overlaps with both s and p_σ (and d_σ) AOs of atom B. Thus s and p_σ of an atom become indirectly mixed in a molecule because of perturbation. This holds especially for 2s/2p of C, B, N (other atoms show only little promotional hybridization in molecules). Constructive/destructive interference with higher energy orbitals reduces / increases the MO energy.

7) An energetically stabilized/(unchanged)/destabilized MO (with respect to its AO components) acts bonding / (nonbonding) / antibonding. An MO with flat behavior between the atoms is bonding (comparatively low kinetic energy).

8) The lower energy AOs contribute more/less in the case of constructive/destructive interference, thereby resulting in polar MOs.

9) Occupy the MOs, energetically distant ones according to Aufbau rule, energetically adjacent ones according to Hund's rule.

10) Generate the localized MOs from the occupied canonical orbitals, as far as possible, and draw the respective Lewis formula, give the term symbol, discuss magnetism. – This is a "minimal basis" model; orbital contraction (e.g. 2s – 3s; …) and orbital polarization (1s + 2p; 2p + 3d; …) are not yet accounted for.

14.6 Localized Orbitals, Triatomics

In the first step, one-electron delocalized canonical orbitals are generated in the MO approximation. They are then occupied according to Aufbau und Hund rules. The occupied delocal MOs are then equivalence-transformed to more localized MOs – as far as possible; then one gets, from the 'spectroscopic' canonical orbital picture, the localized 'chemical' picture more common to the ordinary chemist.

A single three-center MO is of strongly bonding three-center type.

A bonding and an antibonding two-center MO together are equivalent to a left and a right one-center local nonbonding MO (atomic orbitals). "Lone pairs" have more s-character, "two center bonds" have more p-character. A linear three-center system with $1\sigma/1\sigma/1\sigma$ basis-AO per atom (or $1\pi/1\pi/1\pi$) yields a single strong 3c-2e bond, or for 4 electrons a 3c-bond & a 3c-nonbond = 3c – 4e bonding = two polar weak bonds. A 3-center system with $1\sigma/2\sigma$(e.g. s & p_σ)/1σ basis has two bonding and two antibonding orbitals: 4e yield two 2c-2e bonds; 6e yield two lone pairs, and a strong 3c bond which corresponds to two weak bonding interactions between the central and the two terminal atoms. Examples: CO_2, XeF_2, linear H_2O.

Atomic hybridization (mixing) of occupied orbitals does not change the observabel atomic properties (sum over occupied orbitals). Hybrids overlap and interact differently with neighbor-atoms. p_σ-orbitals overlap better than s-AOs. Promotion (s→p) costs energy; "atoms in molecules" are no longer "atoms"; it may be energetically favorable for a molecule to have partial s→p AO promotion.

Polycentric molecules: Examples

H_2O: Symmetries are C_2-rotation (state function symmetric: a, antisymmetric: b) and mirror-plane(s) (symmetric: index 1, antisymmetric: index 2)
AOs: O2s = a_1, O2p=a_1, b_1, b_2, ($b_{1,2}$ indices depend on the convention!); both H1s together = a_1, b_2 (or b_1, depending on the chosen convention)
Canonical orbitals: 4 IPs, 2 different bonding and 2 different nonbonding orbitals.
Localized orbitals: 2 equivalent O-H bonds, 2 equivalent O-lone pairs

CH_4: symmetries are C_3-rotation, S_4-mirror rotation, σ-planes. Symmetry species are a, e (doubly degenerate) and t (triply degenerate)
Canonical orbitals: 2 IPs, one *a*-bonding orbital, a triple of *t*-bonding orbitals
Localized orbitals: 4 equivalent C-H bonds.