Chapter 8 Ab Initio Treatments of Polyatomic Molecules

8.1 Ab Initio Methods and and Semiemprical Methods

Semiempirical and Ab initio Methods

Molecular quantum-mechanical methods are classified as either ab initio or semiempirical.

Semiempirical methods use a simple Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of ab initio calculations.

HMO, EHMO, CNDO, …

An *ab initio* calculation uses the correct Hamiltonian and does not use experimental data other than the values of the fundamental physical constants. (*Ab initio* is Latin for “from the beginning” and indicates a calculation based on fundamental principles.)

Hartree-Fock SCF calculation:

Basis set → Atomic orbital → Molecular orbital → Slater determinant → Iterative solution …

Classification of Electronic Terms of Polyatomic Molecules

Linear Molecules:

The operator $\boldsymbol{L_z}$ for the axial component of the total electronic orbital momentum commutes with the electronic Hamitionian, and the same classifications are used as for diatomic molecules; we have such possibilities as $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$, $^1\Pi$, and so on. For linear polyatomic molecules with a center of symmetry, the g, u classification is added.

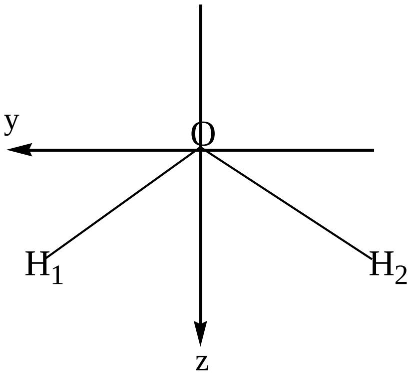
Nonlinear polyatomic molecules:

There is no orbital angular-momentum operator that commutes with the electronic Hamiltonian, and the angular momentum classification of electronic terms cannot be used. Operators that do commute with the electronic Hamiltonian are the symmetry operators O_R of the molecule, and the electronic states of polyatomic molecules are classified according to the behavior of the electronic wave function on application of these operators.

Consider H_2O as an example.

In its equilibrium configuration, water belongs to group C_{2V} with the symmetry operators

$$E \quad C_2(z) \quad \sigma_v(xz) \quad \sigma_v(yz)$$



	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Consider an operator ***R*** that commutes with the molecular Hamiltonian ***H*** that does not involve spin; we have

$$\mathbf{RH} = \mathbf{HR}$$

$$\mathbf{RH}\Psi = \mathbf{R}E\Psi$$

$$\mathbf{H}(\mathbf{R}\Psi) = E(\mathbf{R}\Psi) \qquad (8.1)$$

so that $\mathbf{R}\Psi$ is an eigenfunction of **H** with eigenvalue E. We have

$$\mathbf{R}\Psi = \lambda\Psi \qquad (8.2)$$

Here Ψ must be an eigenfunction of the symmetry operator **R**. Thus, the electronic states of polyatomic molecules can be classified according to the symmetry of the electronic wave function associated with the molecular point group. For the term classification of H_2O, we have such possibilities as ${}^1A_1$, ${}^1A_2$, ${}^1B_1$, ${}^1B_2$, ${}^3A_1$, etc.

As an example, the possible symmetry species of a D_{6h} molecule to be

A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1g}, E_{2g}

A_{1u}, A_{2u}, B_{1u}, B_{2u}, E_{1u}, E_{2u}

8.2 The SCF MO Treatment of Polyatomic Molecules

The purely electronic nonrelativistic Hamiltonian for a polyatomic molecule is (in atomic units):

$$\hat{H}_{el} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \qquad (8.3)$$

Best possible variation function — Hartree-Fock SCF function: The form of an antisymmetrized product of spin-orbitals. The MOs are usually expressed as linear combinations of basis functions, the coefficients being found by solution of the Roothaan equations.
A sufficiently large basis set → Accurate approximations to the Hartree-Fock MO's.
A minimal basis set → only rough approximations to the Hartree-Fock MO's, still referred to as SCF molecular orbitals.

Classification of Molecular Orbitals
As might be expected, the MOs of a polyatomic molecule show the same kinks of possible symmetry behavior as the electronic wavefunction does. The MOs are therefore classified according to the symmetry species of the molecular point group.

For example, the MOs of H_2O have the possible symmetry species a_1, a_2, b_1, and b_2. Lowercase letters are used for MO symmetry species. To distinguish MOs of the same symmetry species, we number them in order of increasing energy. $1a_1$, $2a_1$, $3a_1$, …; $1b_1$, $2b_1$, …

For benzene C_6H_6, there are some doubly degenerate symmetry species, so some of the benzene MOs occur in having the same energy. Specification of the number of electrons in each MO specifies the molecular ***electronic configuration***. For example, an $(e_{1g})^2$ configuration of D_{6h} molecule gives the terms $^1A_{1g}$, $^1E_{2g}$, and $^3A_{2g}$.

*A closed-shell configuration gives rise to a single nondegenerate term whose multiplicity is **1** and whose symmetry species is the totally symmetric.*

SCF-MO Wave Functions for Open-Shell States.

For SCF MO calculations of closed-shell states of molecules and atoms, electrons paired with each other almost given precisely the same spatial orbital function. A Hartree-Fock wave function in which electrons whose spins are paired occupy the same spatial orbital is called a restricted Hartree-Fock (RHF) wave function.

For open-shell states, two different approaches are widely used.

Restricted Open-Shell Hartree-Fock (ROHF) Method

In the ROHF method, electrons that are paired with each other are given the same spatial orbital function. For example, the ROHF wave function of the Li ground state is $|1s\overline{1s}2s|$, where the two 1s electrons occupy the same spatial MO. The 2s electron in this ROHF function has been given spin α.

Restricted Open-Shell Hartree-Fock (ROHF) Method

Since electron with the same spin tend to keep away from each other (Pauli repulsion), the interaction between the 2sα and 1sα electrons differs from the interaction between the 2sα and 1sβ electrons, and it seems reasonable to give the two 1s electrons slightly different spatial orbitals, which we call 1s and 1s′. This gives the unrestricted Hartree-Fock (UHF) wave function for the Li ground state as $|1s\overline{1s'}2s|$, where $1s \neq 1s'$. In a UHF wave function, the spatial orbitals of spin-α electrons are allowed to differ from those of spin-β electrons.

Comparison of ROHF with UHF

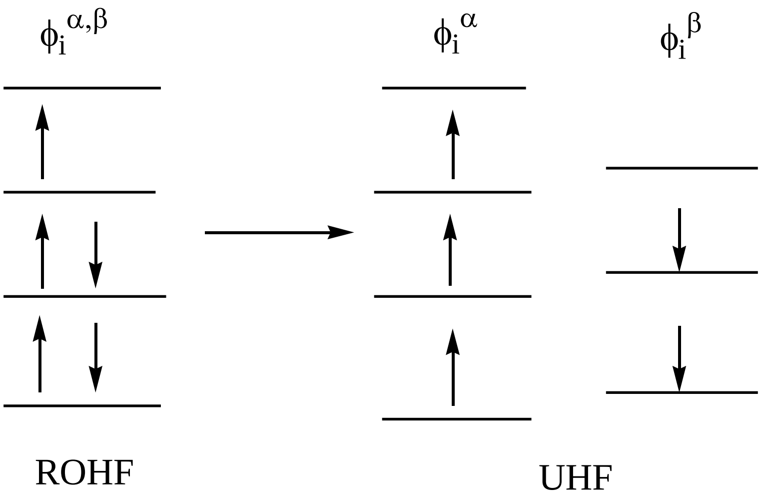
The UHF wave function gives a slightly lower energy than the ROHF wave function and is much more useful in predicting electron-spin-resonance spectra. The main problem with the UHF wave function is that it is not an eigenfunction of the spin operator $\mathbf{S}^2$, whereas the true wave function and the ROHF wave function are eigenfunctions of $\mathbf{S}^2$.

When a UHF wave function is found, one calculate $<S^2>$ for the UHF function; if the deviation of $<S^2>$ from $S(S+1)\hbar^2$ is substantial, the UHF wave function should be viewed with suspicion.

Spin contaminant

The expection value of $<S^2>$ for an unrestricted determinant

$$< S^2 >_{UHF} = S(S+1) + N^{\beta} - \sum_i \sum_j | S_{ij}^{\alpha\beta} |^2 \qquad (8.4)$$



8.3 Basis Functions

Most molecular quantum-mechanical methods, whether SCF, CI, perturbation theory, or coupled cluster, begin the calculation with the choice of a basis set. The use of an adequate basis set is an essential requirement for success of the calculation.

Slater orbitals (STOs)

A Slater function centered on nucleus a has the form

$$\chi_r = N r_a^{n-1} e^{-\xi r_a} Y_l^m(\theta_a, \phi_a) \qquad (8.5)$$

Molecular orbital (MO)

$$\phi_i = \sum_r c_{ri} \chi_r \qquad (8.6)$$

where the χ_r's are the STO basis functions. We have LC-STO MOs.

For polyatomic molecules, the LC-STO method uses STOs centered on each of the atoms. The presence of more than two atoms causes difficulties in evaluating the needed integrals.

Gaussian-type orbitals (GTOs)

Computer evaluation of three- and four-center integrals over STO basis functions is very time consuming. To simplify molecular integral evaluation, Boys proposed in 1950 the use of Gaussian-type functions (GTOs) instead of STOs for the atomic orbitals in an LCAO wave function.

A Cartesian Gaussian centered on nucleus **a** is defined as

$$g_{ijk} = N x_a^i y_a^j z_a^k e^{-\alpha r_a^2} \qquad (8.7)$$

where N is the normalization constant, i, j, and k are nonnegative integers, and α is positive orbital exponent.

i+j+k = 0, s-type Gaussian

i+j+k = 1, p-type Gaussians, p_x, p_y, p_z.

i+j+k = 2, d-type Gaussians, 6 *d*-type Gaussians,

with the factors x^2, y^2, z^2, xy, xz, yz. They can form five linear combinations having the same angular behavior as the five 3d AOs; the sixth combination with the factor

$x^2 + y^2 + z^2 = r^2$ is like a 3s AO.

Spherical Gaussians

$$Nr_a^{n-1}e^{-\alpha r_a^2}(Y_l^{m*} \pm Y_l^m)/\sqrt{2} \tag{8.8}$$

LC-GTO AO

A Gaussian function does not have the desired cusp at the nucleus and hence gives a poor representation of an AO for small values of r_a. To get an accurate representation of an AO, we must use a linear combination of several Gaussians — LC-GTO AOs. *Therefore, an LC-GTO SCF MO calculation involves evaluation of very many more integrals than the corresponding LC-STO SCF MO calulation.*

Gaussian integral evaluation takes much less computer time than Slater integral evaluation. This is because the *product of two Gaussian centered at two different points is equal to a single Gaussian centered at a third point. Thus all three- and four-center two-electron repulsion integrals are reduced to two-center integrals.*

The STO Basis Set Terminology

Minimal (or minimum) basis set: One STO for each inner-shell and valence-shell AO of each atom. For example, for C_2H_2 a minimal basis set consists of 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ AOs on each carbon and 1s STO on each hydrogen; there are five STOs on each C and one on each H, for a total of twelve basis functions; such a set is denoted by (2s1p) for the carbon functions and (1s) for the hydrogen functions, a notation which is further abbreviated to (2s1p/1s).

The numbers of basis functions in a minimal set for the first part of the periodic table are

H, He	Li-Ne	Na-Ar	K, Ca	Sc-Kr
1	5	9	13	18

A Double-Zeta (DZ) basis set: Replacing each STO of a minimal basis set by two STOs that differ in their orbital exponents ζ (zeta).

For example, for C_2H_2 a double-zeta basis set consists of (1s,1s’), (2s,2s’), ($2p_x$,$2p_x$’), ($2p_y$,$2p_y$’), and ($2p_z$,$2p_z$’) AOs on each carbon and

(1s,1s’) STOs on each hydrogen, for a total of twenty-four basis functions; this is (4s2p/2s) basis set.

A Split-valence (SV) basis set: Minimal for the inner-shell and double zeta for the valence AOs.

Polarization functions:

A set of three 2p functions ($2p_x$, $2p_y$, $2p_z$) on each hydrogen atom.

A set of five 3d functions on each “first-row” and “second-row” atom.

A set of seven 4f functions on each “third-row” atom.

……

A double-zeta plus polarization: **DZ+P**

For improved accuracy, higher-***l*** polarization functions can be added.

Contracted Gaussian-type functions

Instead of using the individual Gaussian functions (8.7) as basis functions, the current practice is to take basis function as a linear combination of a small of Gaussians, according to

$$\chi_r = \sum_u d_{ur} g_u \tag{8.9}$$

where the g_u’s are Cartesian Gaussians [Eq.(8.7)] centered on the same atom having the same i, j, k values as one another, but different α’s. The coefficients d_{ur} are constants that are held fixed during the calculation. In (15.12), χ_r called a contracted Gaussian-type function (**CGTF**) and the g_u’s are called primitive Gaussians.

By using contracted Gaussians instead of primitive Gaussians as basis set, the number of variational coefficients to be determined is reduced, which gives large savings in computational time with little loss in accuracy if the contracted coefficients d_{ur} are well chosen.

Several methods exist to form contracted Gaussian sets. Minimal CGTF sets are usually formed by fitting STOs. Each STO is approximated as a linear combination of N Gaussian functions (called STO-NG basis set), where the coefficients in the linear combination and the Gaussian orbital exponents are chosen to give the best least-square-fit to the STO, .

Another way to form contracted Gaussians is to start with atomic CTF SCF calculations. Huzinaga used a (9s5p) basis set of uncontracted Gaussians to do SCF calculations on the atoms Li-Ne. For example, for the ground state of the O atom, the optimized orbital exponents of the nine s-type basis GTFs and the expansion coefficients were found to be

	Exponents	1s Coefficients	2s Coefficients
g_1	7817	0.0012	-0.0003
g_2	1176	0.009	-0.002
g_3	273.2	0.043	-0.010
g_4	81.2	0.144	-0.036
g_5	27.2	0.356	-0.095
g_6	9.53	0.461	-0.196
g_7	3.41	0.140	-0.037
g_8	0.94	-0.0006	0.596
g_9	0.285	0.001	0.526

Suppose we want to form a split-valence [3s2p] set of contracted GTFs for O. We can take following contracted scheme

$$1s = N(0.0012g_1 + 0.009g_2 + 0.043g_3 + 0.144g_4 + 0.356g_5 + 0.461g_6 + 0.14g_7)$$

$$2s = N'(-0.196g_6 + 0.596\, g_8)$$

$$2s' = g_9$$

……

Standard basis sets: (by Pople and coworkers)

STO-3G, 3-21G, 4-31G, 6-31G, 6-311G,…

3-21G*, 6-31G*, …

In the 3-21G set, each inner-shell AO (1s for Li-Ne; 1s, 2s, 2p for Na-Ar; and so on) is represented by a single CGTF that is a linear combination of three primitive Gaussian; for each valence-shell AO (1s for H; 2s and the 2p's for Li-Ne; …), there are two basis functions, one of which is a CGTF that is a linear combination of two Gaussian primitives and one which is a single diffuse Gaussian.

ECP basis sets

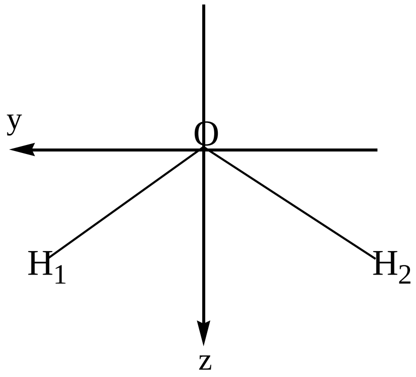
Such basis sets are available in the widely used ab initio programs GAUSSIAN 98, GAMESS, HONDO, etc.

8.4 The SCF MO Treatment of H_2O

A minimal-basis-set MO treatment

Basis functions: O1s, O2s, O2p_x, O2p_y, O2p_z; $H_1$1s, $H_2$1s.
Linear combinations of these 7 basis AOs give LCAO approximations to the seven lowest MOs of water.

Symmetry-adapted basis functions.



	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Each oxygen AO transforms according to one of the symmetry species of water and can serve as a symmetry orbital. However, neither of the two hydrogen 1s AOs belongs to a symmetry species of water, and we must construct two symmetry orbitals from these AOs. Consider the following linear combinations:

$$H_1 1s + H_2 1s \qquad (8.10)$$

$$H_1 1s - H_2 1s \qquad (8.11)$$

Examination of the effects of the other three symmetry operators shows (8.10) and (8.11) to belong to the symmetry species a_1 and b_2, respectively.

The seven basis symmetry functions and their symmetry species are then

χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7
$H_1$1s+$H_2$1s	O1s	O2s	O2p_z	$H_1$1s-$H_2$1s	O2p_y	O2p_x
a_1	a_1	a_1	a_1	b_2	b_2	b_1

Now consider the SCF secular determinant det ($F_{rs} - \varepsilon_i S_{rs}$). We assert that

$$F_{rs} =< \chi_r \,|\, \hat{F} \,|\, \chi_s >= 0 \qquad (8.12)$$

whenever χ_r and χ_s belong to different symmetry species. Moreover, since two eigenfunctions of a Hermitian operator that correspond to different eigenvalues are orthogonal, we have

$$S_{rs} \equiv <\chi_r|\chi_s> = 0 \qquad (8.13)$$

From (8.12) and (8.13) it follows that the use of symmetry orbitals puts the secular determinant of water in block-diagonal form, each block corresponding to a different symmetry species; the blocks are 4×4, 2×2, and 1×1.

The set of Roothaan simultaneous equations (for H_2O), i.e.,

$$\sum_k c_{ik}(H_{jk}^{eff} - \varepsilon_i S_{jk}) = 0, \qquad j = 1,2,3,4,5,6,7 \qquad (8.14)$$

then breaks up into one set of four simultaneous equations (a_1 symmetry), one set of two simultaneous equations(b_2 symmetry), one set of one “simultaneous” equation (b_1 symmetry). Therefore, four of the lowest seven water MOs are linear combinations of the four a_1 symmetry orbitals; these four MOs must have a1 symmetry. Similarly, we have two MOs of b_2 symmetry and one MO of b_1 symmetry.

The forms of the lowest MOs of H_2O are then

$$\begin{aligned}
\phi_1 &= c_{11}\chi_1 + c_{21}\chi_2 + c_{31}\chi_3 + c_{41}\chi_4 \\
\phi_2 &= c_{12}\chi_1 + c_{22}\chi_2 + c_{32}\chi_3 + c_{42}\chi_4 \\
\phi_3 &= c_{13}\chi_1 + c_{23}\chi_2 + c_{33}\chi_3 + c_{43}\chi_4 \\
\phi_4 &= c_{14}\chi_1 + c_{24}\chi_2 + c_{34}\chi_3 + c_{44}\chi_4 \\
\phi_5 &= c_{55}\chi_1 + c_{65}\chi_2 \\
\phi_6 &= c_{56}\chi_1 + c_{66}\chi_2 \\
\phi_7 &= \chi_7
\end{aligned} \qquad (8.15)$$

The next step in SCF MO calculation is to determine the orbital energies and the coefficients of the symmetry orbitals.

Pitzer and Merrifield did an H_2O minimal-basis-set calculation [*J. Chem. Phys*. 1970, 52, 4782].

Orbital energies in hartree:

$1a_1$, -20.56; $2a_1$, -1.28; $1b_2$, -0.62; $3a_1$, -0.47; $1b_1$, -0.40.

The ground-state electronic configuration of this ten-electron molecule is

$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$

The ground state has a closed-subshell configuration and is a ${}^1A_1$ state.

The five lowest SCF MOs at the experimental geometry are

$1a_1$ = 1.000(O1s) +0.015(O2s') + 0.003(O2p_z) - 0.004($H_1$1S+$H_2$1s)

$2a_1$ = -0.027(O1s) +0.820(O2s') + 0.132(O2p_z) + 0.152($H_1$1S+$H_2$1s)

$1b_2$ = 0.624(O2p_y) + 0.424($H_1$1S+$H_2$1s) (8.16)

$3a_1$ = -0.026(O1s) - 0.502(O2s') + 0.787(O2p_z) + 0.264($H_1$1S+$H_2$1s)

$1b_1$ = O2p_x

The O2s' orbital in (8.16) is an orthogonalized orbital:

O2s' = 1.028[(O2s)-0.2313 (O1s)] (8.17)

Bonding in water

The lowest MO, $1a_1$, is essentially a pure nonbonding 1s oxygen AO.

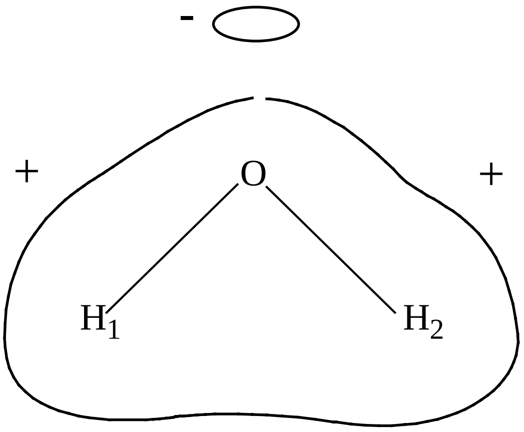
The next MO, $2a_1$, is the combination of the hybridized O2s and O$2p_z$ orbitals with the $H_1$1s and $H_2$1s orbitals, which gives electron probability-density buildup in the region enclosed by the three nuclei. Therefore the $2a_1$ MO contributes to the bonding in water.

Consider the $1b_2$ MO. The $2p_y$ oxygen AO has its positive lobe on the H_1 side of the molecule, so that the positive lobe of O$2p_y$ adds to $H_1$1s in the $1b_2$ MO, giving electron charge buildup between the H_1 and O nuclei. Similarly, the negative lobe of O$2p_y$ adds to –$H_2$1s, giving charge buildup between O and H_2 in this MO. Hence $1b_2$ is a bonding MO.

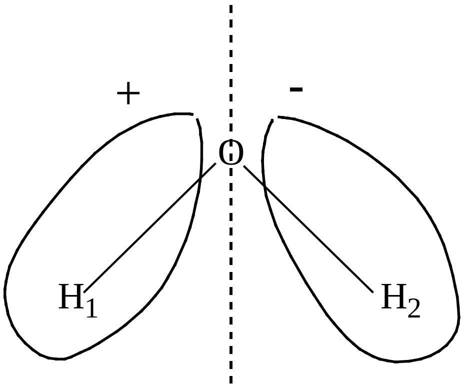
In 3a1 the hybridization of the 2s and $2p_z$ oxygen AOs concentrates electron probability density along the negative z axis, away from the hydrogens; hence, this MO contributes only modestly to the bonding, and is best described as mainly a lone-pair MO with some bonding character.

The $1b_1$ MO is a nonbonding lone-pair $2p_x$ oxygen AO.

The shapes of the bonding MOs $2a_1$ and $1b_2$ in water.



$2a_1$



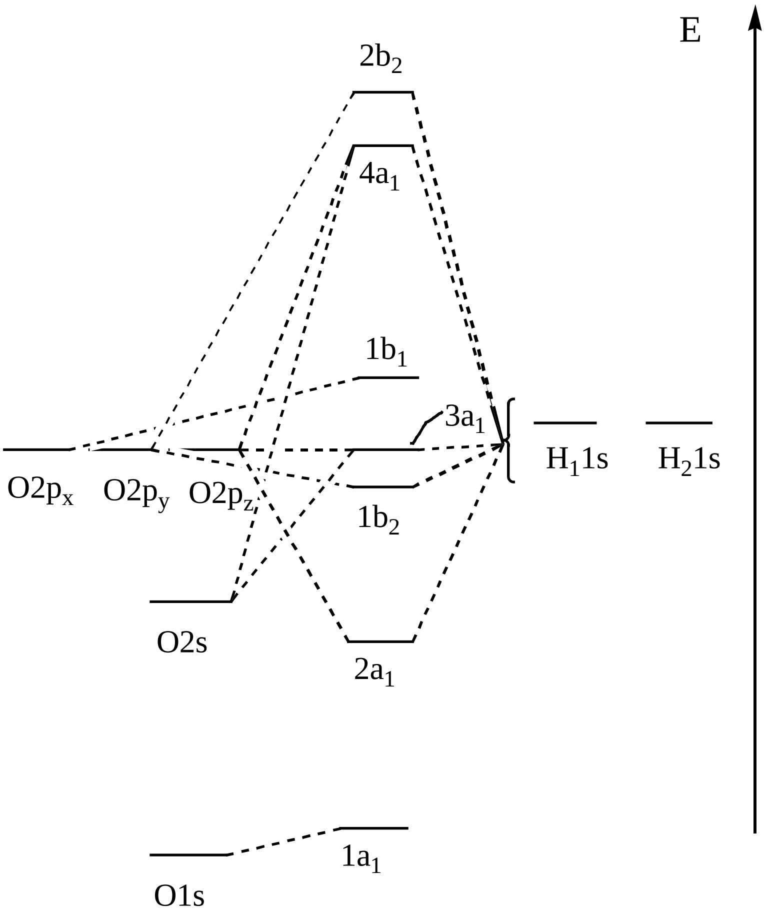
$1b_2$

The unoccupied $4a_1$ and $2b_2$ MOs of water:

$4a_1 = 0.08(\mathrm{O1s}) + 0.84(\mathrm{O2s'}) + 0.70(\mathrm{O2p_z}) - 0.75\ (\mathrm{H_11s} + \mathrm{H_21s})$

$2b_2 = 0.99(\mathrm{O2p_y}) - 0.89(\mathrm{H_11s} - \mathrm{H_21s})$

These MOs are antibonding.



Formation of the H_2O MOs from the minimal basis AOs.

H_2O SCF MO Calculations

Basis Set	Energy/E_b	μ/D	θ	R_{OH}/Å
STO-3G	-74.97	1.69	100.0°	0.990
3-21G	-75.59	2.44	107.6°	0.967
Minimal STO	-75.70	1.92	100.3°	0.990
6-31G*	-76.010	2.19	105.5°	0.947
140CGTFs	-76.0673	1.98		
HF-limit	-76.0675		106.3°	0.940
Nonrelativistic fixed-nuclei energy	-76.440			
Expt. values	-76.480	1.85	104.5°	0.958

Koopman Theorem

The energy required to remove an electron from a closed-shell atom or molecule is reasonably well approximated by minus the orbital energy ε of the AO or MO from which the electron is removed.

$$I_i = -\varepsilon_i \qquad (8.18)$$

Comparison of Hartree-Fock orbital energies (in eV) with the experimentally observed ionization energies for H_2O.

	$1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
Theory:	559.5	36.7	19.5	15.9	13.8
Expt.	539.7	32.2	18.5	14.7	12.6

8.5 Population Analysis

For the set of basis functions χ_1, χ_2, ……, χ_b, each MO ϕ_i has the form

$$\phi_i = \sum_s c_{si}\chi_s = c_{1i}\chi_1 + c_{2i}\chi_2 + \cdots + c_{bi}\chi_b \qquad (8.18)$$

For simplicity, we shall assume that the c_{si}'s and χ_s's are real. The probability density associated with one electron in ϕ_i is

$$|\phi_i|^2 = c_{1i}^2\chi_1^2 + c_{2i}^2\chi_2^2 + \cdots + 2c_{1i}c_{2i}\chi_1\chi_2 + 2c_{1i}c_{3i}\chi_1\chi_3 + \cdots \quad (8.19)$$

Integrating this equation over three-dimensional space and using the fact that ϕ_i and the χ_s's are normalized, we get

$$1 = c_{1i}^2 + c_{2i}^2 + \cdots + 2c_{1i}c_{2i}S_{12} + 2c_{1i}c_{3i}S_{13} + \cdots \qquad (8.20)$$

where the *S*'s are overlap integrals: $S_{12} = \int \chi_1\chi_2 dv_1 dv_2$, and so on.
Mulliken proposed that the terms in (8.20) be apportioned as follows. One electron in the ϕ_i contributes $2c_{1i}^2$ to the net population in χ_1, $2c_{2i}^2$ to the net population in χ_2, and so on, and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between χ_1 and χ_2, and so on.
Let there be n_i electrons in the MO ϕ_i (n_i =0, 1, 2), we have

$$n_{r,i} = n_i c_{ri}^2, \qquad n_{r-s,i} = n_i(2c_{ri}c_{si}S_{rs}) \qquad (8.21)$$

Summing over the occupied MOs, we obtain the ***Mulliken net population*** n_r in χ_r, and the overlap population n_{r-s} for the pair χ_r and χ_s as

$$n_r = \sum_i n_{r,i}, \quad and \quad n_{r-s} = \sum_i n_{r-s,i} \qquad (8.22)$$

The sum of all the net and overlap populations equals the total number of electrons in the molecule:

$$\sum_r n_r + \sum_{r>s} \sum_s n_{r-s} = n. \qquad (8.23)$$

It is convenient for some purposes to apportion the electrons among the basis functions only, with no overlap populations. Mulliken proposed that this be done by splitting each overlap population $n_{r\text{-}s}$ equally between the basis functions χ_r and χ_s. This gives a gross population N_r in χ_r, namely,

$$N_r = n_r + \frac{1}{2}\sum_{s \neq r} n_{r-s} \qquad (8.24)$$

The sum of all the gross populations equals the number of electrons in the molecule: $\sum_{r=1}^{b} N_r = n$.

The ***gross atomic population N_B*** for atom B:

$$N_B = \sum_{r \in B} N_r \qquad (8.25)$$

The notation $r \in B$ denotes all basis functions centered on atom B.

The ***net charge*** q_B on atom B with atomic number Z_B is defined as

$$q_B \equiv Z_B - N_B$$

A small change in basis set can produce a large change in the calculated net charges.

Net charges on each H atom

	CH_4	NH_3	H_2O
STO-3G	0.06	0.16	0.18
3-21G	0.20	0.28	0.36

A comparison of values calculated with the same basis set correctly shows that the charge on each H atom as the electronegativity increases from C to O.

8.6 Localized MOs

Experimentally, molecular properties can be analyzed as the sum of contributions from individual bonds and lone pairs (Localized MOs). For example, the O—H stretching vibrational band occurs at nearly the same frequency no matter whether it is HOH or HOCl or CH_3OH that is observed.

However, the photoelectron spectroscopy of a molecule has no such the localized behavior, in consistent with the MO theory. For example, the ground state of CH_4 has the closed-shell configuration $(1a_1)^2(2a_1)^2(1t_2)^6$ and is a $^1A_1$ state. Calculated MO energies and experimental ionization energies as follows:

Calc.	14.7 eV ($1t_2$)	25.3 eV ($2a_1$)
Expt.	12.7-16 eV	23 eV

In the MO formalism, each of the bonding MOs is delocalized over the entire molecule, and it is seemingly inconsistent with the existence of individual bonds in the molecule. Actually, MO theory can explain the observed near invariance of a given kind of chemical bond, as we now show.

The MO approximation to the ground state of water is a Slater determinant of the form

$$\Psi = |\phi_1\phi_2\cdots\phi_m| = |\Phi| \qquad (8.26)$$

Let

$$\begin{aligned} u_i &= \sum_j \phi_j T_{ji} \\ U &= \Phi T \end{aligned} \qquad (8.27)$$

where T is a unitary matrix. According to (8.27), the delocalized MOs are transformed into the localized MOs.

$$\Psi = |u_1 u_2 \cdots u_m| = |U| = |\Phi T| = |\Phi||T| = |\Phi| \qquad (8.28)$$

Despite the different verbal descriptions, the wave functions (8.26) and (8.28) are identical.

For example, the wave function of the ground state of water:

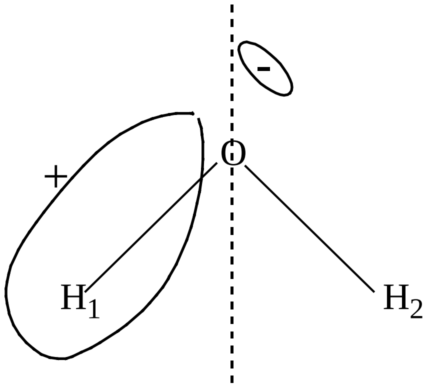
Localized MOs

$$\Psi = | i(O)\overline{i(O)}b(OH_1)\overline{b(OH_1)}b(OH_2)\overline{b(OH_2)}l_1(O)\overline{l_1(O)}l_2(O)\overline{l_2(O)} |$$

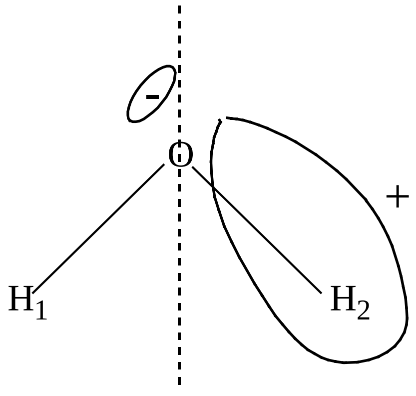
Delocalized MOs

$$\Psi = | 1a_1\overline{1a_1}2a_1\overline{2a_1}1b_2\overline{1b_2}3a_1\overline{3a_1}1b_1\overline{1b_1} |$$

Rough sketches of the localized bonding MOs in H_2O



b(OH_1)



b(OH_2)

8.7 The SCF MO treatment of methane, ethane, and ethylene