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Chapter 15

Molecular Electronic Structure

AB INITIO, DENSITY-FUNCTIONAL, SEMIEMPIRICAL, AND MOLECULAR-MECHANICS METHODS

Diatomic molecules: electronic wave function is a function of only one parameter (the internuclear distance)

Polyatomic molecule: electronic wave function depends on several parameters (bond distances, bond angles, and dihedral angles)

The equilibrium bond distances and angles are found as those values that minimize ($U = E_{\text{el}} + V_{\text{NN}}$)

Four **main methods**

(to calculating molecular properties):

ab initio

semiempirical

density-functional

Molecular mechanics

Semiempirical methods:

- ✓ use a simpler Hamiltonian than the correct \hat{H}
- ✓ use parameters (are adjusted to fit experimental data or the results of ab initio calculations)
- ✓ Example: is the Hückel MO treatment (uses a one-electron Hamiltonian and takes the bond integrals as adjustable parameters rather than quantities to be calculated theoretically)

ab initio (or first principles) method:

- ✓ uses the correct Hamiltonian
- ✓ does not use experimental data (only fundamental physical constants)
- ✓ HF SCF calculation is an ab initio calculation (seeks the antisymmetrized product Φ of one-electron functions that minimizes $\int \Phi^* \hat{H} \Phi d\tau$; $\hat{H} \equiv$ true Hamiltonian)
- ✓ Ab initio \equiv from the beginning (not 100% correct)
- ✓ An ab initio SCF MO calculation: taking ψ as an antisymmetrized product of spin-orbitals and uses a finite (and hence incomplete) basis set.

Density-functional method:

- ✓ does not attempt to calculate the molecular wave function
- ✓ calculates $\rho \rightarrow$ molecular electronic energy from ρ

Molecular-mechanics method:

- ✓ is not a QM method
- ✓ does not use a molecular Hamiltonian operator or wave function
- ✓ molecule \equiv a collection of atoms held together by bonds
- ✓ molecular energy is expressed in terms of force constants for bond bending and stretching and other parameters.

ELECTRONIC TERMS OF POLYATOMIC MOLECULES

Polyatomic molecules:

$[\hat{S}^2, \hat{H}_{el}] = 0$ (when spin-orbit interaction is omitted from the Hamiltonian; spin-orbit interaction is considerable for molecules with heavy atoms; herein S is not a good quantum number.)

Thus, the electronic terms of polyatomic molecules are classified as singlets, doublets, triplets, and so on, (according to $2S + 1$)

linear polyatomic molecules:

$$[\hat{L}_z, \hat{H}_{el}] = 0$$

same term classifications are used as for diatomic molecules (possibilities as $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$, $^1\Pi$, and so on (g or u when there is a center of symmetry)).

nonlinear polyatomic molecules:

$[\hat{L}_z, \hat{H}_{el}] \neq 0 \rightarrow$ the angular-momentum classification of electronic terms cannot be used.

$[\hat{O}_R, \hat{H}_{el}] = 0$ ($\hat{O}_R \equiv$ symmetry operators; electronic states are classified according to the behavior of the electronic wave function on application of these operators).

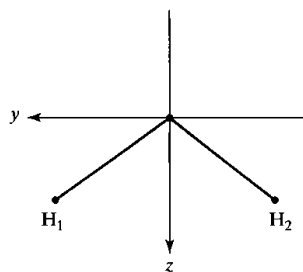
Example: H_2O (C_{2v})

symmetry operations of C_{2v} \hat{E} $\hat{C}_2(z)$ $\hat{\sigma}_v(xz)$ $\hat{\sigma}_v(yz)$

each of the symmetry operations commutes with the other three.
electronic wave functions can be chosen as simultaneous eigenfunctions of all four symmetry operators.

$$\hat{O}_E \psi_{el} = \psi_{el} \quad \text{eigenvalue} + 1$$

$$\hat{O}_R^2 = \hat{1} \quad \text{eigenvalues} + 1 \text{ or } -1$$



Coordinate axes for the H_2O molecule. The standard convention takes the molecular plane as the yz plane

different combinations of symmetry eigenvalues:

Are there $(1)(2)(2)(2) = 8$ possible sets? No

Let $\hat{R}\hat{S} = \hat{T}$ and ψ_{el} be an eigenfunction of them with eigenvalues r , s , and t . Since the symmetry operators multiply the same way the symmetry operations do, we have $\hat{O}_R\hat{O}_S = \hat{O}_T$

$$t\psi_{\text{el}} = \hat{O}_T\psi_{\text{el}} = \hat{O}_R(\hat{O}_S\psi_{\text{el}}) = s\hat{O}_R\psi_{\text{el}} = rs\psi_{\text{el}} \rightarrow rs = t \text{ if } \hat{R}\hat{S} = \hat{T}$$

Hence the eigenvalues of the symmetry operators must multiply in the same way the symmetry operations do.

consider H_2O :

\hat{E}	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$	
1	-1	-1	-1	must be discarded
		\downarrow		
		$\hat{C}_2(z)\hat{\sigma}_v(xz) = \hat{\sigma}_v(yz)$		
1	-1	-1	1	

only these sets are found to multiply properly:

	\hat{E}	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$	
A_1	1	1	1	1	totally symmetric species
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	irreducible representation
B_2	1	-1	-1	1	

Each possible set : symmetry species (or symmetry type)

A or B indicates whether the symmetry eigenvalue for the highest-order C_n or S_n operation of the molecule is +1 or -1.

molecular electronic term : is designated by giving the symmetry species of the electronic wave functions of the term, with the spin multiplicity $2S + 1$ as a left superscript.

Example:

an electronic state with two electrons unpaired and with the electronic wave function unchanged by all four symmetry operators belongs to a 3A_1 term

Orbital degeneracy of molecular electronic terms:

degeneracy connected with the electrons' spatial (orbital) motion

Thus $^1\Pi$ and $^3\Pi$ terms of linear molecules are orbitally degenerate, while

$^1\Sigma$ and $^3\Sigma$ terms are orbitally nondegenerate.

Consider: $[\hat{F}, \hat{H}_{el}] = 0$ and \hat{F} does not involve spin

$$\begin{aligned}\hat{F}\hat{H}_{el}\psi_{el,i} &= \hat{F}E_{el}\psi_{el,i} \\ \hat{H}_{el}(\hat{F}\psi_{el,i}) &= E_{el}(\hat{F}\psi_{el,i})\end{aligned}$$

↓

an eigenfunction of H_{el} with eigenvalue E_{el}

Let: the orbital degeneracy of the term = n.

Thus: $\hat{F}\psi_{el,i}$ is some linear combination of the n orbitally degenerate wave functions of the term that have the same value of S_z as $\psi_{el,i}$

$$\hat{F}\psi_{el,i} = \sum_{j=1}^n c_{ij} \psi_{el,j}$$

certain constants

if $n = 1$ (not orbitally degenerate):

$$\hat{F}\psi_{el,i} = c_F\psi_{el,i}$$

must be an eigenfunction of \hat{F} .

For $n > 1$: n linear combinations of

$$\hat{F}\psi_{el,i} = \sum_{j=1}^n c_{ij,i} \psi_{el,j}$$

is no necessity to be eigenfunctions of \hat{F}

If $[\hat{P}, \hat{H}_{el}] = 0$, $[\hat{G}, \hat{H}_{el}] = 0$, and $[\hat{P}, \hat{G}] \neq 0$

we can pick the linear combinations to be eigenfunctions of \hat{P} or of \hat{G} , but not in general of both \hat{P} and \hat{G} simultaneously.

- ✓ For H_2O all the symmetry operators commute among themselves, and so each ψ_{el} is simultaneously an eigenfunction of all the symmetry operators.
- ✓ Electronic wave functions of H_2O are all orbitally non-degenerate.
- ✓ A and B : symmetry species of orbitally nondegenerate electronic terms.
- ✓ When all symmetry operators commute with one another, ψ_{el} s are each simultaneous eigenfunctions of all symmetry operators, and the only symmetry species are nondegenerate A and B.

For some point groups, the symmetry operators do not all commute (O_h)

Herein, some of the electronic terms are orbitally degenerate.

A symmetry operator applied to an electronic wave function:

$$\hat{F}\psi_{el,i} = \sum_{j=1}^n c_{ij,F} \psi_{el,j}$$

symmetry operator
↑
wave functions of the term

of an orbitally degenerate term

The effect of \hat{O}_R on the wfs of an n -fold orbitally degenerate electronic term

$c_{ij,R}$, $i = 1, \dots, n$, $j = 1, \dots, n$ n^2 numbers; an $n \times n$ square matrix

h symmetry operations \rightarrow h matrices of coefficients \rightarrow constitute the symmetry species of the degenerate-term wave functions

orbital degeneracy:	n	1	2	3	4	5
labels for the symmetry species:	Letter	A, B	E	T	G	H

For a D_{6h} molecule:

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



For molecules with a center of symmetry,

For eigenvalue +1 or -1 for inversion of all electronic spatial coordinates

A_{1g} is the totally symmetric symmetry species, with all c's equal to 1.

An empirical fact: for most molecules in electronic GSs the electronic wave function belongs to the (nondegenerate) totally symmetric species. (spins are usually all paired in the ground state)

small departures from equilibrium geometry \rightarrow symmetry species = those of equilibrium-geometry point group.

Excited states sometimes differ in their eq point group from the GS.

a molecular term \rightarrow several electronic states.

split by spin and orbital (electronic) motion and between electronic and nuclear motions (splittings are usually small)

THE SCF MO TREATMENT OF POLYATOMIC MOLECULES

purely electronic nonrelativistic Hamiltonian:

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

... is the same as diatomic molecules

The best possible variation function that has the form of an antisymmetrized product of spin-orbitals is the Hartree-Fock SCF function. [Improvements beyond the HF stage require some method to allow for electron correlation.]

How are MOs classified?

- ✓ MOs show the same kinds of symmetry behavior as the overall electronic wave function does.
- ✓ MOs are classified according to the symmetry species of the molecular point group.

symmetry species of the MOs of H₂O: a₁, a₂, b₁, and b₂

To distinguish MOs of the same symmetry species: 1a₁, 2a₁, and 3a₁.

- ✓ Each MO holds 2 electrons.
- ✓ Shell: MOs having the same energy.
- ✓ A shell with a single MO (symmetry species a or b) holds two electrons
- ✓ A shell with two e MOs holds four electrons
- ✓ electronic configuration: specification of the number of electrons in each shell
- ✓ electron configuration → one or more terms
Example: (e_{1g})² of a D_{6h} molecule → ¹A_{1g}, ¹E_{2g}, and ³A_{2g}
- ✓ A closed-shell configuration → a single nondegenerate term; multiplicity = 1; totally symmetric symmetry species
- ✓ a closed-shell GS → MO wave function is a single Slater determinant.
- ✓ open-shell configurations → MO wave function may require a linear combination of a few Slater determinants.

SCF MO Wave Functions for Open-Shell States

A HF wave function in which electrons whose spins are paired occupy the same spatial orbital is called a restricted HF (RHF) wave function.

- ✓ **RHF wave function** is generally used for closed-shell states
- ✓ **unrestricted HF** (UHF) and **restricted open-shell HF** (ROHF) are widely used for open-shell states.
- ✓ In ROHF method, paired electrons are given the same spatial orbital function
- ✓ $|1s\overline{1s}2s|$ for the ROHF wave function of the Li ground state
- ✓ $|1s1s'2s|$ for UHF wave function, where $1s \neq 1s'$.
- ✓ the interaction between the $2s\alpha$ and $1s\alpha$ electrons differs from the interaction between the $2s\alpha$ and $1s\beta$ electrons (spatial orbitals, $1s$ and $1s'$).

- ✓ UHF wf gives a slightly lower E than the ROHF wf
- ✓ UHF wf is more useful in predicting ESR spectra
- ✓ main problem with the UHF wf: is not an eigenfunction of \hat{S}^2 (nor a linear combination of a few UHF functions)
- ✓ true wf and the ROHF wf are eigenfunctions of \hat{S}^2 .
- ✓ for the UHF wf, one have to check the deviation of $\langle S^2 \rangle$ from $S(S + 1)\hbar^2$

BASIS FUNCTIONS

Most QM methods begin with the choice of a set of BFs.

For diatomic molecules, the BFs are usually taken as AOs, (centered on a or b)
each AO \equiv a linear combination of one or more STOs.
has the form

$$\text{An STO centered on atom } \underline{a} \quad N r_a^{n-1} e^{-\zeta r_a} Y_l^m(\theta_a, \phi_a)$$

For nonlinear molecules, the real form of the STOs is used (Y_l^m is replaced
by $(Y_l^{m*} \pm Y_l^m)/2^{1/2}$)

$$\phi_i = \sum_r c_{ri} \chi_r$$

← STO basis function

LC-STO MOs

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.

For a triatomic molecule: three-center, two-center, and one-center integrals.

For a molecule with four or more atoms: one also has four-center integrals

Solution of the Roothaan equations:

(rs|tu): is four-center If the BFs centered on different nucleus

H_{rs}^{core} integrals: involve either one or two centers

Number of BFs = b



b different possibilities for each BF in (rs|tu)
(rs|tu) = (sr|tu) = ...

number of different electron-repulsion integrals $\approx b^4/8$

$$b = 20 \text{ to } 400 \rightarrow b^4/8 = 20000 \text{ to } 3 \times 10^9$$

Computer evaluation of three- and four-center integrals over STO basis functions is very time consuming.

To speed up integral evaluation, Boys proposed the use of Gaussian-type functions (GTFs) instead of STOs for the AOs in an LCAO wf.

$$g_{ijk} = N x_b^i y_b^j z_b^k e^{-\alpha r_b^2} \quad \text{A Cartesian Gaussian centered on } b$$

i, j, and k are nonnegative integers,

α is a positive orbital exponent,

x_b, y_b, z_b are Cartesian coordinates with the origin at nucleus b.

$$N = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(8\alpha)^{i+j+k} i! j! k!}{(2i)!(2j)!(2k)!} \right]^{1/2} \quad \text{normalization constant}$$

$i + j + k = 0$ (that is, $i = 0, j = 0, k = 0$) : s-type Gaussian

$i + j + k = 1$: p-type Gaussian

$i + j + k = 2$: d-type Gaussian

Six d-type Gaussians: $x_b^2, y_b^2, z_b^2, x_b y_b, x_b z_b,$ and $y_b z_b$.

five linear combinations ($x_b y_b, x_b z_b,$ and $y_b z_b, x_b^2 - y_b^2, 3z_b^2 - r_b^2$) have the same angular behavior as the five real 3d AOs; sixth ($x_b^2 + y_b^2 + z_b^2 = r_b^2$) is like a 3s function; sometimes omitted from the basis set.

there are ten f-type Gaussians, and these could be combined to have the angular behavior of the seven real 4f AOs.

The form of linear combinations $N r_b^l e^{-\alpha r_b^2} (Y_l^{m*} \pm Y_l^m) / 2^{1/2}$

the principal quantum number n is absent:

s AO (1s or 2s or ...) \equiv a LC of several Gaussians with different α , each Gaussian having the form $\exp(-\alpha r_b^2)$

p_x orbital \equiv a LC of Gaussians, each of the form $x_b \exp(-\alpha r_b^2)$ and so on.

The Cartesian Gaussians form a complete set.

spherical Gaussians:

$$N r_b^{n-1} e^{-\alpha r_b^2} (Y_l^{m*} \pm Y_l^m) / 2^{1/2}$$

A GF does not have the desired cusp at the nucleus (a poor representation of AO for small r_b)

represent an AO as a LC of several GFs.

an LC-GTF SCF MO calculation involves many more integrals than the corresponding LC-STO SCF MO calculation

the number of two-electron integrals $\propto b^4$.

integral evaluation : much less computer time (by G)

Why? the product of two GFs centered at two different points is equal to a single GF centered at a third point (three- and four-center two-electron repulsion integrals are reduced to two-center integrals).

STO basis sets:

minimal (or minimum) basis set : one STO for each inner-shell and valence-shell AO of each atom

C_2H_2 : 1s, 2s, 2p_x, 2p_y, and 2p_z AOs on each C and a 1s STO on each H; five STOs on each C and one on each H = a total of 12 basis functions. two s-type STOs and one set of p-type STOs on each carbon and one s-type STO on each hydrogen; is denoted (2s1p) for the C functions and (1s) for the H functions; notation (2s1p/1s),

minimal STO set for first part of the periodic table:

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

A **double-zeta (DZ) basis set** : replaces each STO of a minimal basis set by two STOs that differ in ζ

C₂H₂ : 2 1s STOs on each H, 2 1s STOs, 2 2s STOs, 2 2p_x, 2 2p_y, and 2 2p_z STOs on each carbon (24 basis functions; (4s2p/2s))

the number of variational parameters c_{ri} in a DZ-BS wf is twice that in a M-BS wf.

A **triple-zeta (TZ) basis set** : replaces each STO of a M-BS by three STOs that differ in ζ .

A **split-valence (SV) basis set** : two (or more) STOs for each valence AO but only one STO for each inner-shell (core) AO.

An SV-BS is minimal for inner-shell AOs and DZ (or TZ or ...) for the valence AOs (VDZ, VTZ,...)

AOs are distorted in shape upon molecule formation (polarization)

Thus, one adds BF STOs whose $\ell > \ell_{\max}$ of the valence shell of the GS atom (polarized (P) basis set)

double-zeta plus polarization set (DZ + P or DZP) :

DZ set + five 3d functions on each "first- and second-row" atoms + three 2p functions (2p_x, 2p_y, 2p_z) on each H atom. (In QC, Li-Ne are called the first-row)

C₂H₅OSiH₃ : is designated as (6s4p1d/4s2p1d/2s1p)

Si C, O H

To increase accuracy, higher- ℓ polarization functions can be added.

Gaussian-basis-sets

Instead of using the individual GFs as BFs, take each BF as a normalized LC of a few Gaussians:

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

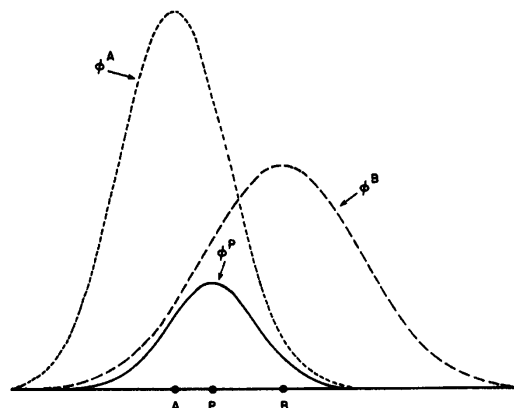
g_u 's : normalized Cartesian Gaussians centered on the same atom and having the same i, j, k, but different α 's.

d_{ur} : contraction coefficients (constants)

χ_r : contracted CGTF

g_u 's : primitive Gaussians.

using CG \Rightarrow number of variational coefficients $\downarrow \Rightarrow$ computational time \downarrow
(little loss in accuracy if d_{ur} s are well chosen)



The product of two 1s Gaussians is a third 1s Gaussian.

The classifications given for STO BSs also apply to CGTF BSs

A minimal basis set : consists of one CGF for each inner-shell AO and for each valence-shell AO

A DZ basis set : two CGTFs for each such AO

A DZP set : adds CGs with higher ℓ to the DZ set, where $\ell = i + j + k$

α s and d_{ur} s of the BFs are kept fixed at the predetermined values

CGTF M-BS : no way for the BFs to adjust their sizes to differing molecular environments.

DZ BS : allow the AO sizes to vary from one molecule to another.

Example:

$1s'$ and $1s''$ be two 1s CGTFs centered on a certain H atom

$1s'$ (and $1s''$) be a linear combination of a few s-type PGs

Let for α in the primitives $1s' > 1s''$. $1s'$ is spread out over a much larger region of space than $1s''$.

expression for a given MO contains $c_1 1s' + c_2 1s''$; c_1 and c_2 are found by the SCF process. The size of the function will increase as the ratio c_2/c_1 increases.

polarization functions vary the AO shapes, shifting charge density away from the nuclei and into the bonding regions in the molecule.

Example

adding 2p functions to a 1s on H

$$c_1 1s + c_2 2p_x + c_3 2p_y + c_4 2p_z$$

AO will be polarized in a direction determined by c_2 , c_3 , and c_4 .

$c_3 = 0$, $c_4 = 0$, $c_1 > 0$, $c_2 > 0$. $c_2 2p_x$ will cancel some of the probability density of the $c_1 1s$ term on one side of the H atom and will augment it on the other side, thereby polarizing the 1s function in the positive x direction.

p-type AOs can be polarized by mixing in d-type AOs.

methods to form CG sets:

1) Minimal CGTF sets are often formed by fitting STOs.

a) one STO per AO, b) Each STO is approximated as a linear combination of N GFs, (coefficients and exponents)

$N = 3 \rightarrow$ **STO-3G** (H through Xe) is not quite as good as a **MBS STO**
(6s3p/3s) contracted to [2s1p/1s] **(2s1p/1s)**

parentheses for primitive Gaussians

brackets for contracted Gaussians.

1s STO having $\zeta = 1$

$$S(r; 1) = \pi^{-1/2} e^{-r}$$

normalized s-type Gaussian $(2\alpha/\pi)^{3/4} e^{-\alpha r^2}$

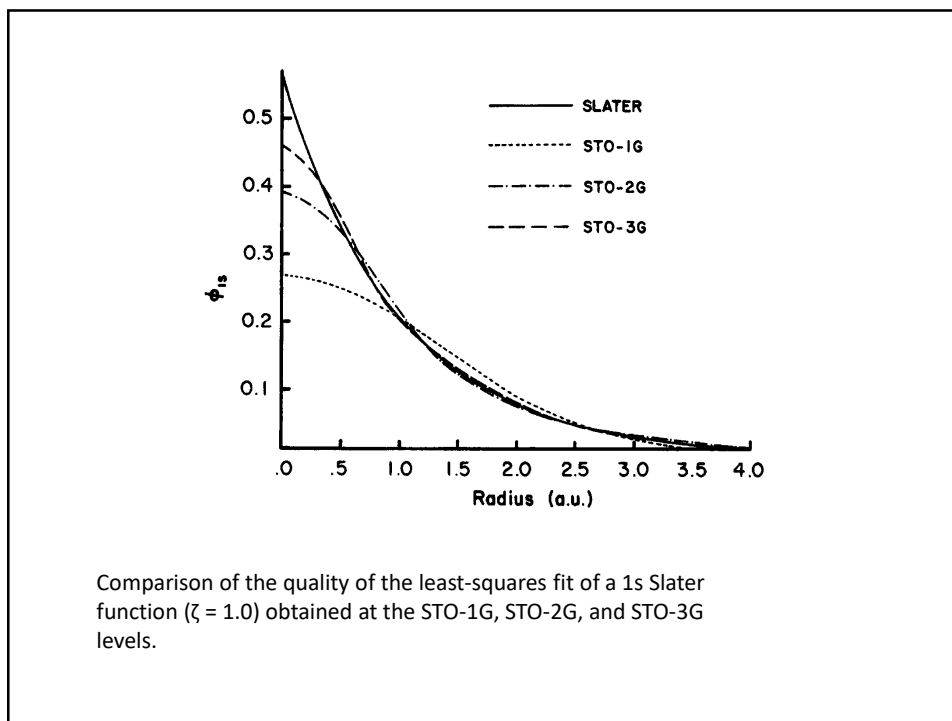
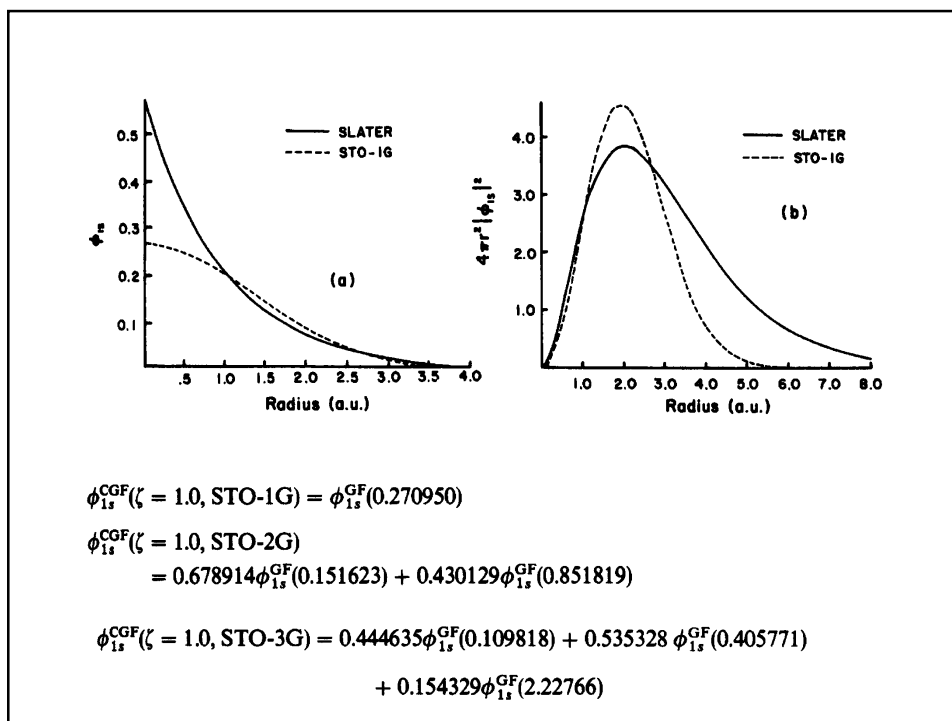
$$G_{3N}(r; 1) = c_1 (2\alpha_1/\pi)^{3/4} e^{-\alpha_1 r^2} + c_2 (2\alpha_2/\pi)^{3/4} e^{-\alpha_2 r^2} + c_3 (2\alpha_3/\pi)^{3/4} e^{-\alpha_3 r^2}$$

$$c_1 = 0.444615, c_2 = 0.535336, c_3 = 0.154340, \alpha_1 = 0.109814, \alpha_2 = 0.40575, \alpha_3 = 2.22746$$

to fit a 1s STO with orbital exponent ζ

For $G_{3N}(r; 1)$, replacing each orbital exponent α_i by $\zeta^2 \alpha_i$

ζ is called a scale factor.



2) start with atomic GTF SCF calculations

Huzinaga used a (9s5p) basis set of uncontracted Gaussians to do SCF calculations on the atoms Li-Ne.

Example: the ground state of the O atom for the nine s-type basis GTFs:

orbital exponents:

g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	g_9
7817	1176	273.2	81.2	27.2	9.53	3.41	0.940	0.285

diffuse function

expansion coefficients for the 1s SCF AO

g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	g_9
0.0012	0.009	0.043	0.144	0.356	0.461	0.140	-0.0006	0.001

expansion coefficients for the 2s SCF AO

g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	g_9
-0.0003	-0.002	-0.010	-0.036	-0.095	-0.196	-0.037	0.596	0.526

a split-valence [3s2p] set of contracted GTFs for O:

1s:

the g_1, g_2, g_3, g_4, g_5 , and g_7 coefficients: 1s AO \gg 2s AO,

g_8 and g_9 coefficients 2s AO \gg 1s AO,

g_6 : substantial contributions to both 1s and 2s.

$$1s = N(0.0012g_1 + 0.009g_2 + 0.043g_3 + 0.144g_4 + 0.356g_5 + 0.461g_6 + 0.140g_7)$$

↑
because g_8 and g_9 have been omitted

2s:

we need two BFs for the 2s AO (from g_6, g_8 , and g_9)

g_9 is called a diffuse function

The outer region of an AO changes the most upon molecule formation (take g_9 as one of the basis)

$$2s = N'(-0.196g_6 + 0.596g_8), \quad 2s' = g_9$$

The 2p and 2p' CGTFs can be formed similarly

3-21G set (H - Xe) and 6-31G set (H - Zn) :

SV basis sets of CGTFs.

3-21G:

inner-shell AO: (1s for Li-Ne; 1s, 2s, 2p_x, 2p_y, 2p_z for Na-Ar; and so on) → single CGTF (a LC of three PGs)

valence-shell AO: (1s for H; 2s and the 2p's for Li-Ne;...; 4s and the 4p's for K, Ca, Ga-Kr; 4s, the 4p's, and the five 3d's for Sc-Zn) → two basis functions (one CGTF that is a LC of two GP and one which is a single diffuse Gaussian).

6-31G:

inner-shell CGTF → six primitives

valence-shell AO → one CGTF (with 3 primitives) + one Gaussian (with one primitive)

α and d_{ur} were determined to minimize the SCF energies of atoms.

in 3-21G, α for H in an atomic calculation are increased using a scale factor

in 6-31G, valence orbital exponents of H and of Li through O are scaled to be more appropriate for molecular calculations.

6-31G* and 6-31G [or 6-31G(d) and 6-31G(d,p)] (H - Zn)****VDZ polarized basis sets:**

6-31G* = 6-31G + six d-type Cartesian-Gaussian polarization functions on Li - Ca and ten f-type Car-GPFs on Sc - Zn.

6-31G** = 6-31G* + three p-type GPFs on H & He.

α of PFs were determined as the average of the optimum values found in calculations on small molecules.

P atom:

6-31G* : 19 BFs centered on it (1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3s', 3p_x, 3p_y, 3p_z, 3p'_x, 3p'_y, 3p'_z, and six d's) and is [4s3p1d] for P.

3-21G(*) (H - Ar)

For second-row atoms, d orbitals contribute significantly to the bonding.

3-21G(*) (H - Ar) = 3-21G + six d-type GFs on each second-row atom.

For H-Ne, 3-21G(*) = 3-21G .

3-21+G, 6-31+G*, 3-21++G and 6-31++G*

Anions, compounds with lone pairs, and hydrogen-bonded dimers have significant electron density at large distances from the nuclei.

3-21+G (and 6-31+G*) = 3-21G (and 6-31G*) + four highly diffuse functions (s, p_x, p_y, p_z) on each non-hydrogen atom; very small α (0.01 to 0.1)

3-21++G (and 6-31++G*) = 3-21+G (and 6-31+G*) + a highly diffuse s function on each H atom.

cc-pVXZ basis sets (a CGTF BS; Dunning and co-workers):

(cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z)

for use in methods (such as CI) that include ec.

cc-pVDZ (correlation consistent, polarized VDZ).

first-row atoms: cc-pVDZ is [3s2p1d]; cc-pVTZ is [4s3p2d1f].

cc-pCVXZ = cc-pVXZ + certain primitive Gaussians (CV stands for core/valence).

for calculations that include correlation effects involving the core electrons.

augmented sets aug-cc-pVDZ = cc-pVXZ + diffuse nonpolarization for correlation calculations on anions and H-bonded species.

Example:

On the basis-set order form, choose the 3-21G basis set and enter O in the Elements box (Gaussian 94)

oxygen atom				
s-type CGTF consisting of 3 PGs	O	0	1.00	
	S	3	0.05923940	large [inner-shell (core) 1s AO]
		322.03700000	0.35150000	
s-type and p-type CGTFs		48.43080000	0.70765800	
	SP	2	1.00	
		7.40294000	-0.40445300	0.24458600
		1.57620000	1.22156000	0.85395500
	SP	1	1.00	
valence 2s and 2p AOs		0.37368400	1.00000000	1.00000000
		α	d_{ur}	d_{ur}
			assures us that the primitive Gaussians are normalized	

1s CGTO

$$1s = 0.0592394g_s(322.037) + 0.3515g_s(48.4308) + 0.707658g_s(10.4206)$$

a normalized primitive s-type GTF with $\alpha = 322.037$

The 3-21G set uses the same orbital exponents for the 2s and 2p AOs, so as to speed up calculations.

the valence CGTFs

$$2s' = -0.404453g_s(7.40294) + 1.22156g_s(1.5762)$$

$$2p'_x = 0.244586g_{p_x}(7.40294) + 0.853955g_{p_x}(1.5762), \dots,$$

$$2s'' = g_s(0.373684)$$

$$2p''_x = g_{p_x}(0.373684), \dots,$$

```

https://bse.pnl.gov/bse/portal  ! 6-311++G(2d,2p) EMSL Basis Set Exchange Library 11/11/27 0:56
! Elements                      References
! -----
! H, Li - Ne: R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople,
!               J. Chem. Phys. 72, 650 (1980)
! Na - Ar:      A.D. McLean and G.S. Chandler J. Chem. Phys. 72, 5639, (1980).
! K - Ca:       J-P. Blandeau, M. P. McGrath, L.A. Curtiss and L. Radom,
!               J. Chem. Phys. 107, 5016 (1997).
! Ga - Kr:      L. A. Curtiss, M. P. McGrath, J-P. Blandeau, M. E. Davis,
!               R. C. Binning, Jr. L. Radom, J. Chem. Phys. 103, 6104 (1995).
! I             : M.N. Glukhovstev, A. Pross, M.P. McGrath, L. Radom, J. Chem. Phys
!               103, 1878 (1995)
!
! Elements                      References
! -----
! H-Ne: M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80, 3265 (1984)
!
! Elements                      Reference
! -----
! H, Li-Cl: T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer,
!               J. Comp. Chem. 4, 294 (1983).
!
!
! ****
! O      0
! S      6 1.00
!         8588.5000000          0.00189515
!         1297.2300000          0.0143859
!         299.2960000           0.0707320
!         87.3771000            0.2400010
!         25.6789000            0.5947970
!         3.7400400             0.2808020
! SP     3 1.00
!         42.1175000            0.1138890          0.0365114
!         9.6283700             0.9208110          0.2371530
!         2.8533200             -0.00327447         0.8197020
! SP     1 1.00
!         0.9056610             1.0000000          1.0000000
! SP     1 1.00
!         0.2556110             1.0000000          1.0000000
! SP     1 1.00

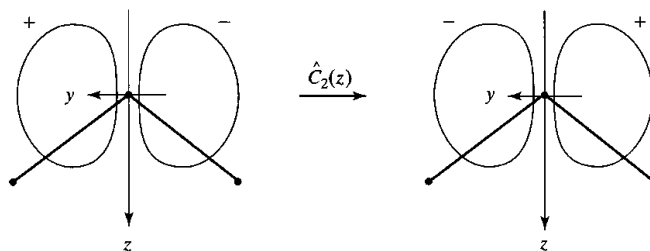
```

6-311++G(2d,2p)

```

O  0
S  6  1.00
    8588.5000000    0.00189515
    1297.2300000    0.0143859
    299.2960000    0.0707320
    87.3771000    0.2400010
    25.6789000    0.5947970
    3.7400400    0.2808020
SP  3  1.00
    42.1175000    0.1138890    0.0365114
    9.6283700    0.9208110    0.2371530
    2.8533200   -0.00327447    0.8197020
SP  1  1.00
    0.9056610    1.0000000    1.0000000
SP  1  1.00
    0.2556110    1.0000000    1.0000000
SP  1  1.00
    0.0845000    1.0000000    1.0000000
D  1  1.00
    2.5840000    1.0000000
D  1  1.00
    0.6460000    1.0000000

```

THE SCF MO TREATMENT OF H₂O

Population Analysis and Bond Orders

SCF wave functions can be analysed by population analysis, introduced by Mulliken [**Mulliken population analysis (MPA)**]

n -electrons $\rightarrow n_r + n_{r-s}$

n_r : net populations in the basis functions χ_r

n_{r-s} : overlap populations for all possible pairs of basis functions

basis set $\{\chi_i\}$

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

For simplicity: c_{si} 's and χ_{si} 's are real

The probability density associated with one electron in ϕ_i is

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

Integrating (ϕ_i and χ_s 's are normalized)

$$1 = c_{1i}^2 + c_{2i}^2 + \cdots + 2c_{1i}c_{2i}S_{12} + 2c_{1i}c_{3i}S_{13} + 2c_{2i}c_{3i}S_{23} + \cdots$$

overlap integrals

Mulliken proposed:

$c_{1,i}^2$: contribution of one electron (in ϕ_i) to the net population in χ_1

$c_{2,i}^2$: contribution of one electron (in ϕ_i) to the net population in χ_2

...

$2c_{1i}c_{2i}S_{12}$: contribution of one electron (in ϕ_i) to the overlap population between χ_1 and χ_2

$2c_{1i}c_{3i}S_{13}$: contribution of one electron (in ϕ_i) to the overlap population between χ_1 and χ_3

For n_i electrons in the MO ϕ_i ($n_i = 0, 1, 2$):

Let,

$n_{ri} \equiv$ contribution of electrons (in ϕ_i) to the net population in χ_r

$n_{r-si} \equiv$ contribution of electrons (in ϕ_i) to the overlap population between χ_r and χ_s

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



summing over the occupied MOs,

$$n_r = \sum_i n_{ri} \quad \text{and} \quad n_{r-s} = \sum_i n_{r-s,i}$$

$$\sum_r n_r + \sum_{r>s} \sum_s n_{r-s} = n \quad \text{total number of electrons}$$

Example:

calculate the net and overlap population contributions for the H_2O

$$2a_1 = -0.027(O1s) + 0.820(O2s_{\perp}) + 0.132(O2p_z) + 0.152(H_11s + H_21s)$$

find n_r for each basis function. Use H_11s and H_21s as basis functions, rather than the symmetry-adapted basis functions.

Overlap integrals between basis STOs centered on different atoms can be found by interpolation in the tables of R. S. Mulliken et al., J. Chem. Phys., 11, 1248

(1949). (see Problem 15.21)

$$\begin{aligned}\langle H_11s|O1s \rangle &= \langle H_21s|O1s \rangle = 0.054, & \langle H_11s|O2s_{\perp} \rangle &= \langle H_21s|O2s_{\perp} \rangle = 0.471 \\ \langle H_11s|O2p_y \rangle &= -\langle H_21s|O2p_y \rangle = 0.319, & \langle H_11s|O2p_z \rangle &= \langle H_21s|O2p_z \rangle = 0.247 \\ \langle H_11s|H_21s \rangle &= 0.238\end{aligned}$$

net populations:

$$\begin{aligned}n_{O1s,2a_1} &= 2(-0.027)^2 = 0.0015, & n_{O2s_{\perp},2a_1} &= 2(0.820)^2 = 1.345, \\ n_{O2p_z,2a_1} &= 0.035, & n_{H_11s,2a_1} &= 2(0.152)^2 = 0.046, \\ n_{H_21s,2a_1} &= 0.046\end{aligned}$$

The five lowest SCF MOs found by Pitzer and Merrifield at the experimental geometry are

$$\begin{aligned}1a_1 &= 1.000(O1s) + 0.015(O2s_{\perp}) + 0.003(O2p_z) - 0.004(H_11s + H_21s) \\ 2a_1 &= -0.027(O1s) + 0.820(O2s_{\perp}) + 0.132(O2p_z) + 0.152(H_11s + H_21s) \\ 1b_2 &= 0.624(O2p_y) + 0.424(H_11s - H_21s) \\ 3a_1 &= -0.026(O1s) - 0.502(O2s_{\perp}) + 0.787(O2p_z) + 0.264(H_11s + H_21s) \\ 1b_1 &= O2p_x\end{aligned}$$

The $O_{2s_{\perp}}$ orbital is an orthogonalized orbital

$$O2s_{\perp} = 1.028[O2s - 0.2313(O1s)]$$

overlap populations

$$n_{O1s-H_11s,2a_1} = 2(2)(-0.027)(0.152)(0.054) = -0.0009 = n_{O1s-H_21s,2a_1}$$

$$n_{O2s_{\perp}-H_11s,2a_1} = 0.235 = n_{O2s_{\perp}-H_21s,2a_1}$$

$$n_{O2p_z-H_11s,2a_1} = 0.020 = n_{O2p_z-H_21s,2a_1}, \quad n_{H_11s-H_21s,2a_1} = 0.022$$

net population of O1s:

$$n_{O1s} = 2(1.000)^2 + 2(-0.027)^2 + 2(-0.026)^2 = 2.00$$

$$n_{O2s_{\perp}} = 1.85$$

$$n_{O2p_z} = 2.00$$

$$n_{O2p_y} = 0.78$$

$$n_{O2p_z} = 1.27, \quad n_{H_11s} = 0.545, \quad n_{H_21s} = 0.545.$$

The MO ϕ_i in a covalent molecule:

$$S = \sum n_{r-s,i} (\chi_r \text{ and } \chi_s \text{ lie on different atoms})$$

$S > 0$ (substantially), the MO is bonding

$S < 0$ (substantially), the MO is antibonding

$S \approx 0$, the MO is nonbonding

for the $3a_1$ MO

overlap of,

$$O1s \text{ with } H_11s : 2(2)(-0.026)(0.264)(0.054) = -0.0015$$

$$O2s_{\perp} \text{ with } H_21s : 2(2)(-0.502) \times (0.264)(0.471) = -0.250,$$

$$O2p_z \text{ with } H_11s : 0.205$$

$$O2p_z \text{ with } H_21s : 0.205$$

$$H_11s \text{ with } H_21s : 2(2)(0.264)(0.238) = 0.066$$

$$\Sigma = -0.03 \text{ for the } 3a_1 \text{ MO} \approx \text{zero} \rightarrow \text{a nonbonding (lone-pair) MO}$$

$$\Sigma = 0.53 \text{ for the } 2a_1 \rightarrow \text{bonding}$$

$$\Sigma = 0.50 \text{ for the } 1b_2 \rightarrow \text{bonding}$$

$$\Sigma = 0.00 \text{ for } 1a_1 \text{ (inner-shell)}$$

- 1) apportioning the electrons into net populations in BFs and overlap populations for pairs of BFs,
- 2) apportioning the electrons among the basis functions only, with no overlap populations. Mulliken proposed : splitting n_{r-s} equally between the BFs χ_r and χ_s .

$$N_r = n_r + \frac{1}{2} \sum_{s \neq r} n_{r-s} \quad \text{gross population}$$

$$\sum_{r=1}^b N_r = n \quad \text{number of electrons in the molecule}$$

Example:

the contribution to the gross population of $O2s_{\perp}$ from the $2a_1$ MO

$$N_{O2s_{\perp}, 2a_1} = 2[(0.820)^2 + (0.820)(0.152)(0.471) + (0.820)(0.152)(0.471)] = 1.58$$

$$N_{O2s2s_{\perp}, 1a_1} = 0.00 \quad N_{O2s2s_{\perp}, 3a_1} = 0.25 \quad N_{O2s2s_{\perp}, 1b_1} = 0.00$$

$$N_{O2s2s_{\perp}, 1b_2} = 0.00$$

$$N_{O2s2s_{\perp}} = 1.83$$

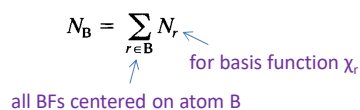
$$N_{O1s} = 2.00 + 0.00 + 0 + 0.00 + 0 = 2.00 \quad N_{O2s_{\perp}} = 1.83; N_{O2p_z} = 0 + 0 + 0 + 0 + 2 = 2$$

$$N_{O2p_y} = 0 + 0 + 1.12 + 0 + 0 = 1.12; N_{O2p_x} = 0 + 0.055 + 0 + 1.445 + 0 = 1.50$$

$$N_{H_{1s}} = 0.00 + 0.184 + 0.442 + 0.150 + 0 = 0.776; N_{H_{2s}} = 0.776$$

gross atomic population N_B for atom B:

$$N_B = \sum_{r \in B} N_r$$



number of electrons in the molecule

$$\sum N_B = n$$

net atomic charge q_B on atom B :

$$q_B = Z_B - N_B$$

One should not put too much reliance on numbers calculated by population analysis.

- 1) assignment of $\frac{1}{2} n_{rs}$ to each basis function is arbitrary and sometimes leads to unphysical results
- 2) a small change in BS can produce a large change in the calculated net charges.

For example:

net atomic charges on each H atom:

	CH ₄	NH ₃	H ₂ O	HF	
STO-3G	0.06	0.16	0.18	0.21	} Comparison ?
3-21G	0.20	0.28	0.36	0.45	
	} Comparison				

An improvement on MPA is **natural population analysis (NPA)**

uses ideas related to natural orbitals

- 1) one calculates a set of orthonormal natural atomic orbitals (NAOs) from $\{\chi_r\}$
- 2) NAOs \rightarrow a set of orthonormal natural bond orbitals (NBOs), (core, lone pair, or bond orbital)
- 3) population analysis by NBOs. q_{NPA} s show less BS dependence than q_{MPA} s.

Other methods of assigning net atomic charges are discussed in the next section.

in view of the existence of improved methods, MPA should no longer be used [S. M. Bachrach in K. Lipkowitz and D. B. Boyd (eds.), Reviews in Computational Chemistry, vol. 5, VCH (1994), Chapter 3.]

bond Orders