

# Semiempirical Molecular Orbital Theory

Slater-determinantal wave functions  
and Hartree-Fock theory

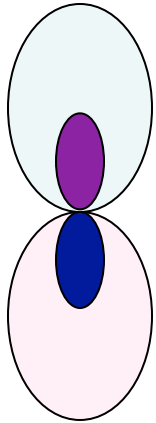
Video III.iv

# Constructing a 1-Electron Wave Function

The units of the wave function are such that its square is electron per volume. As electrons are quantum particles with non-point distributions, sometimes we say “density” or “probability density” instead of electron per volume (especially when there is more than one electron, since they are indistinguishable as quantum particles)

For instance, a valid wave function in cartesian coordinates for one electron might be:

$$\phi(x, y, z; Z) = \underbrace{\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}}_{\text{normalization factor}} \underbrace{\left(6 - Z\sqrt{x^2 + y^2 + z^2}\right)}_{\text{radial phase factor}} \underbrace{ye^{-Z\sqrt{x^2 + y^2 + z^2}/3}}_{\text{cartesian directionality (if any) ensures square integrability}}$$



normalization factor

radial phase factor

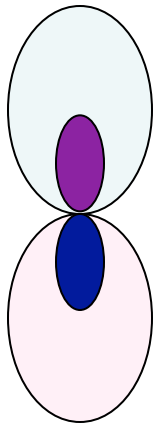
cartesian directionality (if any)

ensures square integrability

# Constructing a 1-Electron Wave Function

*A valid wave function in cartesian coordinates for one electron might be:*

$$\phi(x, y, z; Z) = \underbrace{\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}}_{\text{normalization factor}} \underbrace{\left(6 - Z\sqrt{x^2 + y^2 + z^2}\right)}_{\text{radial phase factor}} \underbrace{y}_{\text{cartesian directionality (if any)}} \underbrace{e^{-Z\sqrt{x^2 + y^2 + z^2}/3}}_{\text{ensures square integrability}}$$



normalization factor

radial phase factor

cartesian directionality (if any)

ensures square integrability

*This permits us to compute the probability of finding the electron within a particular cartesian volume element (normalization factors are determined by requiring that  $P = 1$  when all limits are infinite, i.e., integration over all space)*

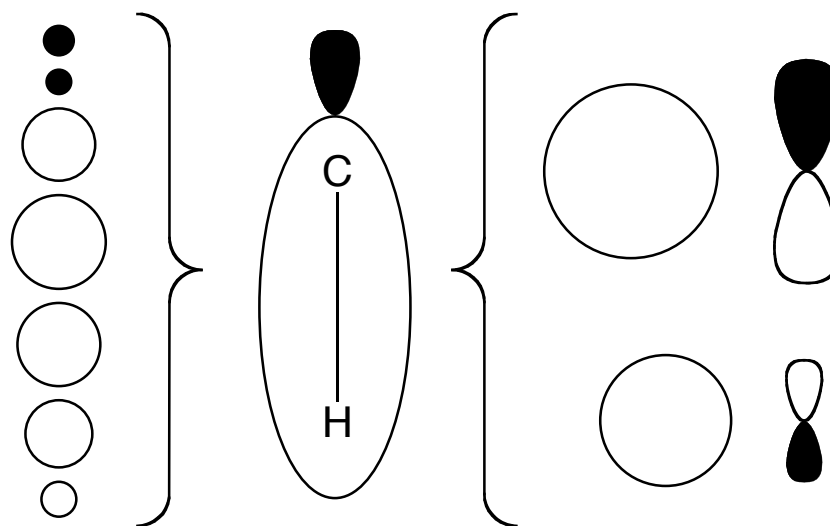
$$P \begin{bmatrix} x_1 \leq x \leq x_2 \\ y_1 \leq y \leq y_2 \\ z_1 \leq z \leq z_2 \end{bmatrix} = \int_{x_1}^{x_2} \int_{y_1}^{y_2} \int_{z_1}^{z_2} |\phi|^2 dx dy dz$$

# Constructing a 1-Electron Wave Function

*To permit additional flexibility, we may take our wave function to be a linear combination of some set of common “basis” functions, e.g., atomic orbitals (LCAO). Thus*

$$\phi(\mathbf{r}) = \sum_{i=1}^N a_i \varphi(\mathbf{r})$$

*For example, consider the wave function for an electron in a C–H bond. It could be represented by s and p functions on the atomic positions, or s functions along the bond axis, or any other fashion convenient.*



# Constructing a 1-Electron Wave Function

To optimize the coefficients in our LCAO expansion, we use the variational principle, which says that

$$E = \frac{\int \left( \sum_i a_i \varphi_i \right) H \left( \sum_j a_j \varphi_j \right) d\mathbf{r}}{\int \left( \sum_i a_i \varphi_i \right) \left( \sum_j a_j \varphi_j \right) d\mathbf{r}} = \frac{\sum_{ij} a_i a_j \int \varphi_i H \varphi_j d\mathbf{r}}{\sum_{ij} a_i a_j \int \varphi_i \varphi_j d\mathbf{r}} = \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}}$$

which is minimized by one root  $E$  of the “secular equation” (the other roots are excited states)—each value of  $E$  that satisfies the secular equation determines all of the  $a_i$  values and thus the shape of the molecular orbital wave function (MO)

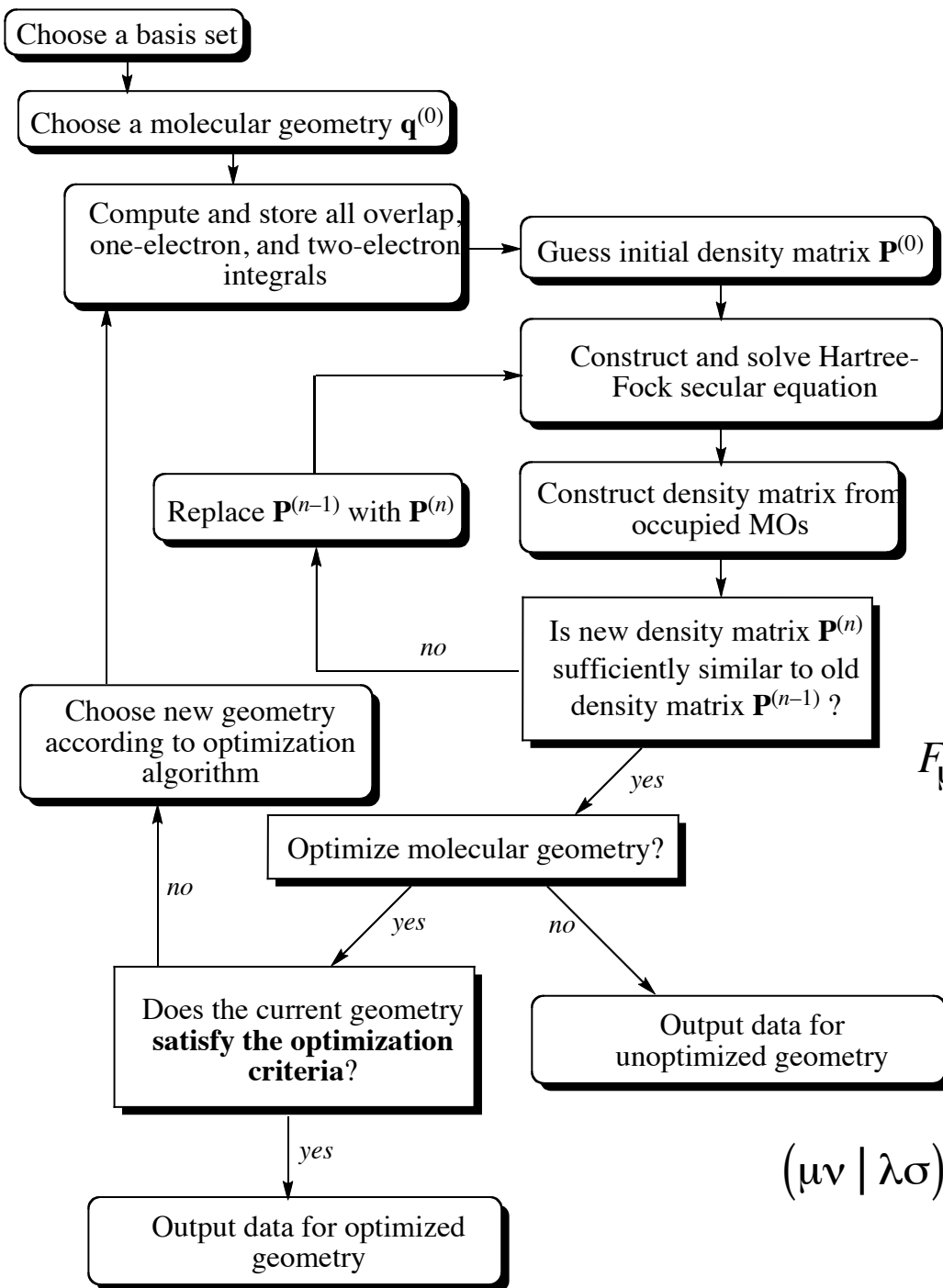
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

# What Are These Integrals $H$ ?

*The electronic Hamiltonian includes kinetic energy, nuclear attraction, and, if there is more than one electron, electron-electron repulsion*

$$H_{ij} = \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_j \right\rangle - \left\langle \varphi_i \left| \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right| \varphi_j \right\rangle + \left\langle \varphi_i \left| \sum_n^{\text{electrons}} \frac{|\phi|^2}{r_n} \right| \varphi_j \right\rangle$$

*The final term is problematic. Solving for all electrons at once is a many-body problem that has not been solved even for classical particles. An approximation is to ignore the correlated motion of the electrons, and treat each electron as independent, but even then, if each MO depends on all of the other MOs, how can we determine even one of them? The Hartree-Fock approach accomplishes this for a many-electron wave function expressed as an antisymmetrized product of one-electron MOs (a so-called Slater determinant)*



# The Hartree-Fock procedure

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\phi_\sigma(2) d\mathbf{r}(1)d\mathbf{r}(2)$$

One MO per root E

# Cement Your Understanding

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

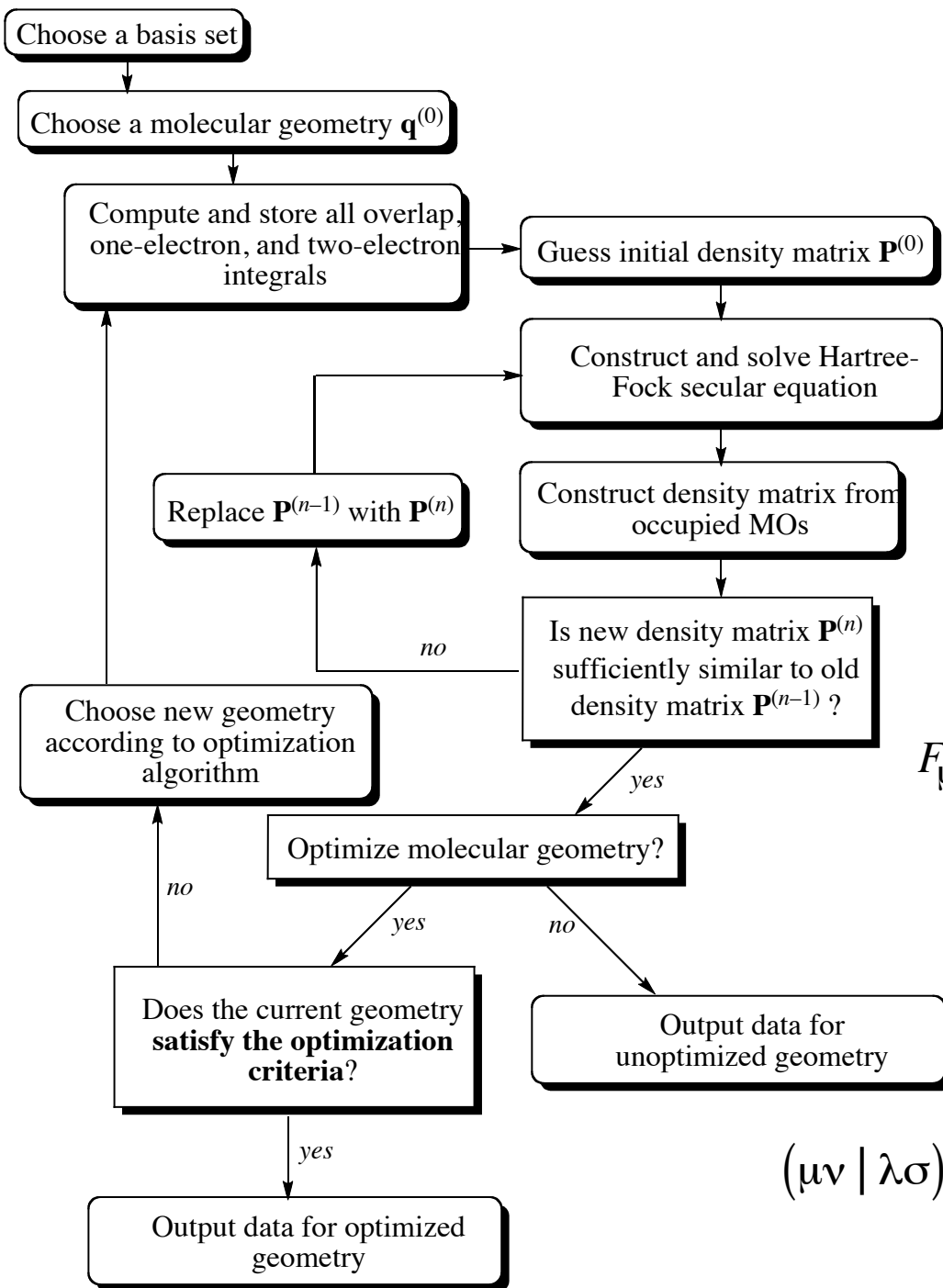
*Try to write out, neatly and carefully, in full mathematical notation, every generic integral in the Fock matrix for Slater-type orbital basis functions with all functions and operators expressed in Cartesian coordinates (which is how they are most typically evaluated in actual practice)*



# Semiempirical Molecular Orbital Theory

Semiempirical simplifications  
of the Fock matrix (early)

Video III.v



# The Hartree-Fock procedure

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\phi_\sigma(2) d\mathbf{r}(1)d\mathbf{r}(2)$$

One MO per root E

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle \quad P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$+ \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] \quad \phi_i = \sum_{\mu} a_{\mu i} \varphi_{\mu}$$

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

Consider only first- and second-row atoms; consider a minimal basis set

$$(\mu\nu | \lambda\sigma) = \int \varphi_{\mu}(1) \varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2) \varphi_{\sigma}(2) dr_1 dr_2$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle \quad P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

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$$(\mu\nu | \lambda\sigma) = \int \varphi_{\mu}(1) \varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2) \varphi_{\sigma}(2) dr_1 dr_2$$

Things to consider in a semiempirical model:

- 1) What shall I choose for a basis set?
- 2) What shall I do for overlap integrals (in the secular determinant)?
- 3) What shall I do for Fock matrix elements?
- 4) As part of (3), what shall I do about electron repulsion integrals?

Essentially all semiempirical models adopt a “minimal” basis set. The AO basis functions cover *only* the valence s, p, d, and f orbitals (p, d, and f only as needed), one function per orbital (so, 1 s, 3 p, 5d, and 7f orbitals). The basis functions themselves are taken to be Slater orbitals.

$$\varphi_{\text{STO}}(r, \theta, \phi; \xi, n, l, m) = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\xi r} Y_l^m(\theta, \phi)$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle \quad P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$+ \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] \quad \phi_i = \sum_{\mu} a_{\mu i} \varphi_{\mu}$$

$$(\mu\nu | \lambda\sigma) = \int \varphi_{\mu}(1) \varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2) \varphi_{\sigma}(2) dr_1 dr_2$$

General choice for overlap integrals,  $S_{\mu\nu}$ :

The overlap between any two STOs can be computed analytically (i.e., it is a simple arithmetic function of position and values of  $\zeta$ ,  $n$ ,  $l$ , and  $m$ ). Overlap integrals find use in computing some *Fock* matrix elements.

However, when forming the secular determinant, the simplification  $S_{\mu\nu} = \delta_{\mu\nu}$  is adopted.

$$\varphi_{\text{STO}}(r, \theta, \phi; \zeta, n, l, m) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$\phi_i = \sum_{\mu} a_{\mu i} \varphi_{\mu}$$

$$(\mu\nu | \lambda\sigma) = \int \varphi_{\mu}(1) \varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2) \varphi_{\sigma}(2) dr_1 dr_2$$

There are 3 types of Fock matrix integrals,  $F_{\mu\nu}$ :

A Fock matrix element can be “diagonal” (i.e.,  $\mu = \nu$ ), or not. When the matrix element is off-diagonal, it can be monatomic (i.e.,  $\mu \neq \nu$ , but  $\mu$  and  $\nu$  are on the same atom), or it can be diatomic (the only remaining possibility)

As every Fock matrix element includes ERIs, first let’s consider the ERIs (we’ll get to one-electron integrals later)

# COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP

Reducing the  $N^4$  scaling problem:

CNDO:  $(\mu\nu | \lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu | \lambda\lambda)$

$$(\mu\mu | \lambda\lambda) = \gamma_{AB}$$

$$\gamma_{AA} = \text{IP}_A - \text{EA}_A$$

$$\gamma_{AB} = \frac{\gamma_{AA} + \gamma_{BB}}{2 + r_{AB}(\gamma_{AA} + \gamma_{BB})}$$

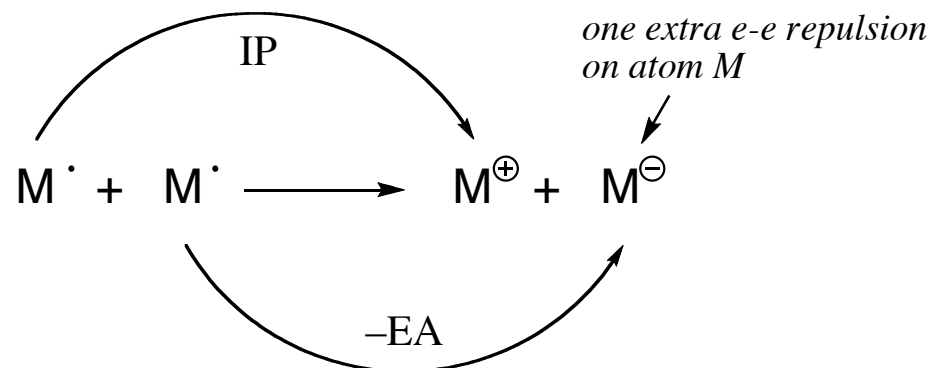
function above has proper limits at  $r_{AB} = 0$  (since then A must be B, the same atom) and at  $r_{AB}$  very large (just  $1/r_{AB}$ , which is Coulomb's law in atomic units)

$$(\mu\nu | \lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

only ERIs not equal to zero are Coulomb integrals between 2 AO basis functions, which may or may not be on the same atom

$\gamma$  is a number or function that depends only on the atoms A and B on which  $\mu$  and  $\lambda$  are found, respectively.

interaction between electrons on same atom taken as difference between ionization potential and electron affinity



# COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP

Reducing the  $N^4$  scaling problem:

$$(\mu\nu|\lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

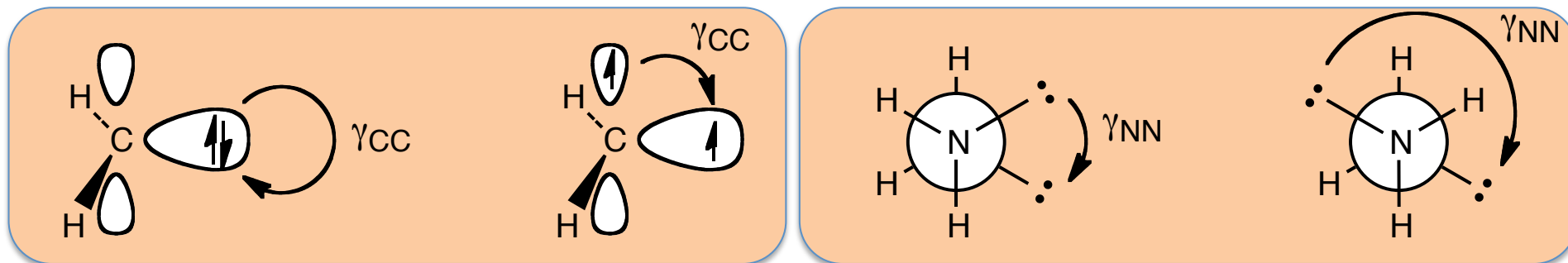
CNDO:  $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu|\lambda\lambda)$

only ERIs not equal to zero are Coulomb integrals between 2 AO basis functions, which may or may not be on the same atom

$$(\mu\mu|\lambda\lambda) = \gamma_{AB}$$

$\gamma$  is a number or function that depends only on the atoms A and B on which  $\mu$  and  $\lambda$  are found, respectively.

*no distinction in 2-electron repulsions:*





# Semiempirical Molecular Orbital Theory

Semiempirical simplifications  
of the Fock matrix (subsequent)

Video III.vi

# COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP

Reducing the  $N^4$  scaling problem:

$$(\mu\nu|\lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

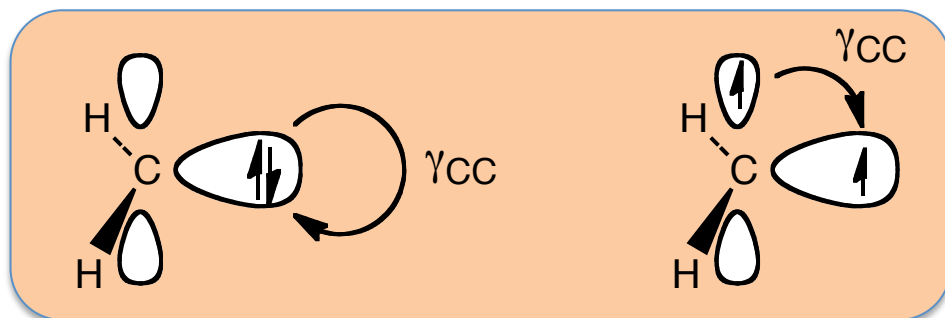
CNDO:  $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu|\lambda\lambda)$

only ERIs not equal to zero are Coulomb integrals between 2 AO basis functions, which may or may not be on the same atom

$$(\mu\mu|\lambda\lambda) = \gamma_{AB}$$

$\gamma$  is a number or function that depends only on the atoms A and B on which  $\mu$  and  $\lambda$  are found, respectively.

*no distinction in 2-electron repulsions:*



# INTERMEDIATE NEGLECT OF DIFFERENTIAL OVERLAP

Reducing the  $N^4$  scaling problem:

$$(\mu\nu|\lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

INDO:  $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu|\lambda\lambda)$

still taken to be true *unless*  $\mu$  and  $\lambda$  are on the same atom

$$(ss|ss) = G_{ss}$$

$$(ss|pp) = G_{sp}$$

$$(pp|pp) = G_{pp}$$

$$(pp|p'p') = G_{pp'}$$

$$(sp|sp) = L_{sp}$$

For an atom with only s and p valence functions, 5 unique integrals are kept (they are simply values, in energy units, that can be determined from spectroscopy or taken as free parameters). Note that  $p'$  refers to a p orbital different from a reference one, e.g.,  $(pp|p'p')$  might be  $(p_x p_x | p_y p_y)$ , i.e., the through-space repulsive interaction between electrons in two perpendicular p orbitals

This extra flexibility in the *atomic* ERIs tends to improve relative energies for electronic states that differ by occupation of orbitals on single-centers. That is, for instance, excited states that are well characterized as one-electron local excitations. INDO still finds substantial use for spectroscopy.

# NEGLECT OF DIATOMIC DIFFERENTIAL OVERLAP

Reducing the  $N^4$  scaling problem:

$$(\mu\nu|\lambda\sigma) = \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2$$

NDDO:  $(\mu\nu|\lambda\sigma) = \delta_{A_\mu X_\nu} \delta_{B_\lambda Y_\sigma} (\mu\nu|\lambda\sigma)$

$$(ss|ss) = G_{ss}$$

$$(ss|pp) = G_{sp}$$

$$(pp|pp) = G_{pp}$$

$$(pp|p'p') = G_{pp'}$$

$$(sp|sp) = L_{sp}$$

so, the only integrals that survive are those where both  $\mu$  and  $\nu$  are on the same atom, and  $\lambda$  and  $\sigma$  are on the same atom, but neither the two atoms need to be the same, nor do the two functions on the individual atoms need to be the same. For monatomic ERIs, the INDO-like values are retained. For diatomic ERIs, there are 100 possible integrals for s and p basis functions (try and verify that...)

The diatomic integrals are not easily evaluated for Slater type orbitals. Instead, NDDO methods model the integrals as classical multipole interactions between the two atoms. Whether the multipole is a point charge (ss), a dipole (sp), or a quadrupole (pp or pp') depends on the nature of the orbitals, and the orientation of the higher multipoles does, too. The magnitudes of the dipoles and quadrupoles depend on the exponents of the Slater basis functions.

# ONE-ELECTRON INTEGRALS

$$\left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle$$

Consider diagonal term,  $\mu = \nu$ :

$$\begin{aligned} \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \mu \right\rangle - Z_{k_\mu} \left\langle \mu \left| \frac{1}{r_{k_\mu}} \right| \mu \right\rangle - \sum_{k \neq k_\mu}^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \mu \right\rangle \\ = U_\mu - \sum_{k \neq k_\mu}^{\text{nuclei}} Z_k (\mu\mu|s_k s_k) \end{aligned}$$

where  $U$  is a parameter that should be nearly equal to the ionization potential of an electron in atomic orbital  $\mu$  and the attraction to a nucleus at the positions of other atoms  $k$  is  $Z_k$  times the repulsion with an electron in an s orbital on the same atom.

# ONE-ELECTRON INTEGRALS

$$\left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle$$

Consider off-diagonal term,  $\mu \neq \nu$ , both on same atom

$$\begin{aligned} \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - Z_{k_\mu} \left\langle \mu \left| \frac{1}{r_{k_\mu}} \right| \nu \right\rangle - \sum_{k \neq k_\mu}^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle \\ = - \sum_{k \neq k_\mu}^{\text{nuclei}} Z_k (\mu\nu | s_k s_k) \end{aligned}$$

where the first two terms are zero for s and p orbitals by symmetry considerations and the attraction to a nucleus at the positions of other atoms  $k$  is  $Z_k$  times the repulsion with an electron in an s orbital on the same atom.

## ONE-ELECTRON INTEGRALS

$$\left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle$$

Consider off-diagonal term,  $\mu \neq \nu$ , each on a different atom

$$= \frac{(\beta_\mu + \beta_\nu)}{2} S_{\mu\nu}$$

where  $\beta$  is our old friend from Hückel theory, the resonance integral (a numerical parameter) and  $S$  is the overlap matrix computed from the Slater type orbitals. Note that the  $\beta$  values depend on both the atomic number *and* the orbital (i.e., carbon has a different  $\beta$  value for an s orbital than for a p orbital)

What would a table of parameters look like for an NDDO model?

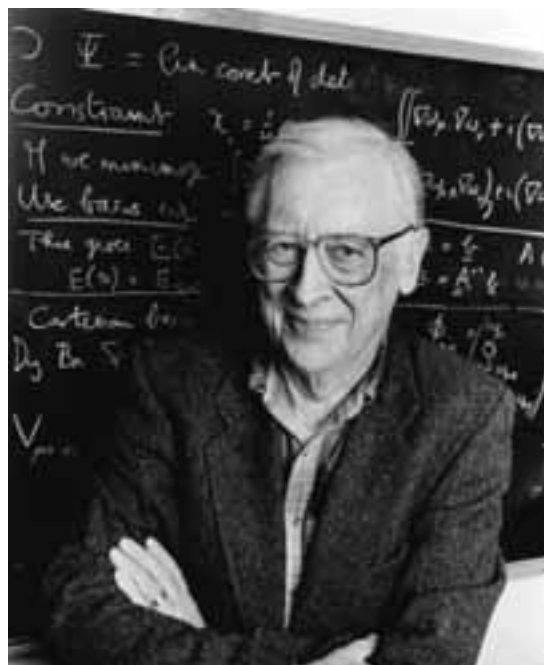
# Semiempirical Molecular Orbital Theory

Semiempirical parameterizations  
and modern usage

Video III.vii



# Big Personalities



John Pople



Michael Dewar

# FINAL MOLECULAR-MECHANICS-LIKE TOUCHUP

First adopted in MNDO, later in AM1 and PM3, etc.

$$V_N(A,B) = Z_A Z_B (s_A s_A | s_B s_B) + \frac{Z_A Z_B}{r_{AB}} \sum_{i=1}^4 \left[ a_{A,i} e^{-b_{A,i} (r_{AB} - c_{A,i})^2} + a_{B,i} e^{-b_{B,i} (r_{AB} - c_{B,i})^2} \right]$$

where the first term says that nuclei repel each other proportional to the degree that their s electrons repel one another, but the following sum effectively creates gaussian shaped ripples, positive or negative, in the potential energy surface surrounding the atoms. Such an approach permits a fine tuning of atomic separations that must be considered rather ad hoc, but not necessarily inconsistent with semiempirical principles. (Later extended by Jorgensen and co-workers using "Pairwise Distance Directed Gaussians" (PDDG) for MNDO and PM3.)

# Chemical Intuition vs Maths

$$Z = \left[ \sum_i^{\text{Observables}} \sum_j^{\text{Occurrences}} \frac{(\text{calc}_{i,j} - \text{expt}_{i,j})^2}{w_i^2} \right]^{1/2}$$



Michael Dewar

MNDO

AM1

AMPAC



Jimmy Stewart

MNDO

AM1

PM3

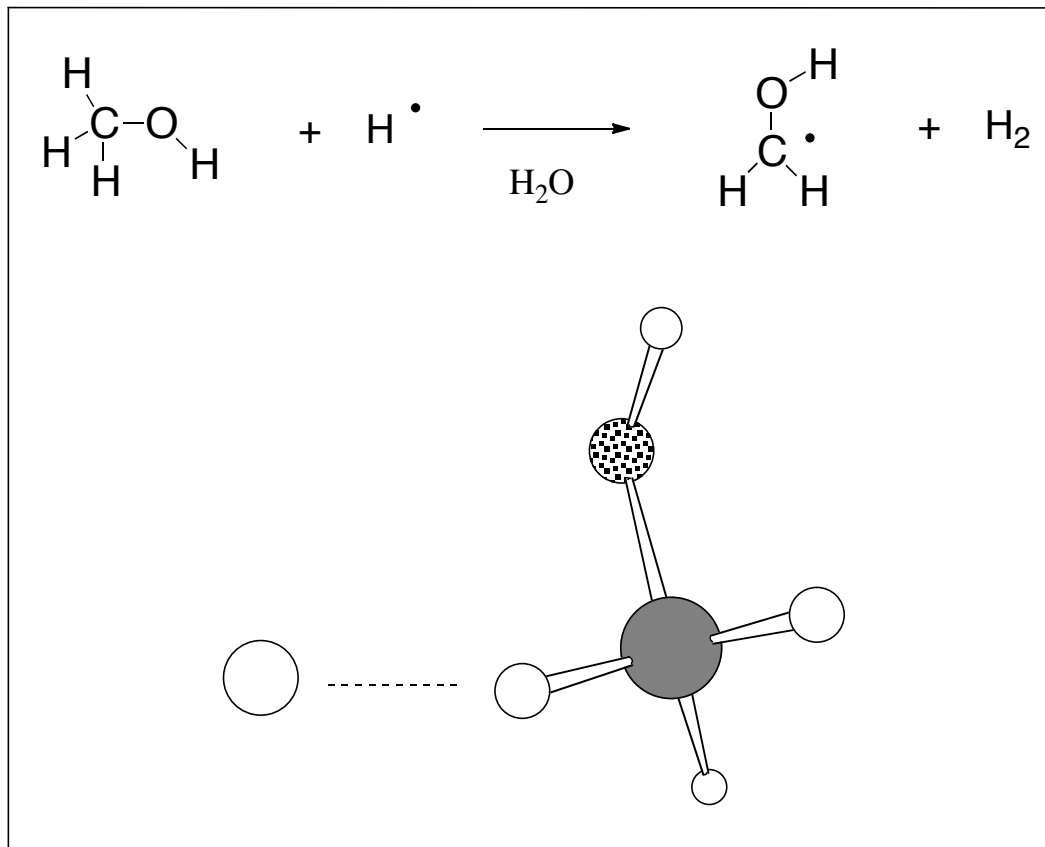
MOPAC

# Errors in Computed Heats of Formation (kcal/mol)

Elements (Number)	Subset (Number)	MNDO	AM1	PM3	MNDO/d
Lighter (181)		7.35	5.80	4.71	
	CH (58)	5.81	4.89	3.79	
	CHN (32)	6.24	4.65	5.02	
	CHNO (48)	7.12	6.79	4.04	
	CHNOF (43)	10.50	6.76	6.45	
	radicals (14)	9.3	8.0	7.4	
Heavier (488)		29.2	15.3	10.0	4.9
	Al (29)	22.1	10.4	16.4	4.9
	Si (84)	12.0	8.5	6.0	6.3
	P (43)	38.7	14.5	17.1	7.6
	S (99)	48.4	10.3	7.5	5.6
	Cl (85)	39.4	29.1	10.4	3.9
	Br (51)	16.2	15.2	8.1	3.4
	I (42)	25.4	21.7	13.4	4.0
	Hg (37)	13.7	9.0	7.7	2.2
	Normal (421)	11.0	8.0	8.4	4.8
	Hypervalent (67)	143.2	61.3	19.9	5.4
Cations (34)		9.55	7.62	9.46	
Anions (13)		11.36	7.11	8.81	

# MODERN USAGE? SPECIFIC RANGE PARAMETERS

Parameter	AM1	AM1-SRP
<u>C</u>		
$U_s$	-52.03	-49.85
$U_p$	-39.61	-40.34
$\beta_s$	-15.72	-16.91
$\beta_p$	-7.72	-9.19
<u>O</u>		
$U_s$	-97.83	-99.18
$U_p$	-78.26	-80.76
$\beta_s$	-29.27	-29.00
$\beta_p$	-29.27	-29.25



Source	$\Delta E_{\text{rxn}}$	$D_e(\text{C-H})$	$D_e(\text{H-H})$
AM1	-28.0	81.4	109.4
AM1-SRP	-4.9	104.4	109.4
Expt.	-5.1	104.4	109.5