

Polyatomic bonding -2014, Notes (13) – Atkins Ch.10(p.395-407),  
Engel 16-17, House (Ch. 9.6, 11)



**Balance:**

nuclear repulsion, positive  $R_{\alpha\beta} \rightarrow 0, V \rightarrow \infty$   
with e-n attract, neg.  $\rightarrow$  united atom AO  $\epsilon_i$

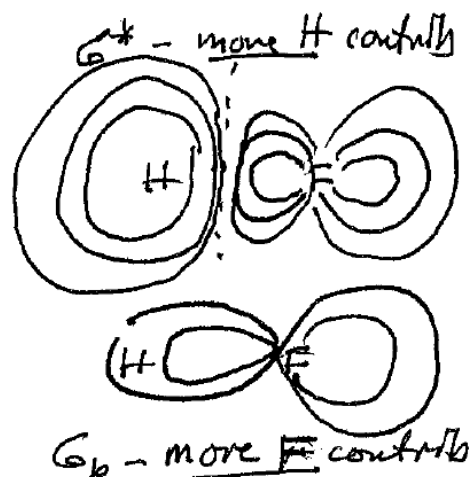
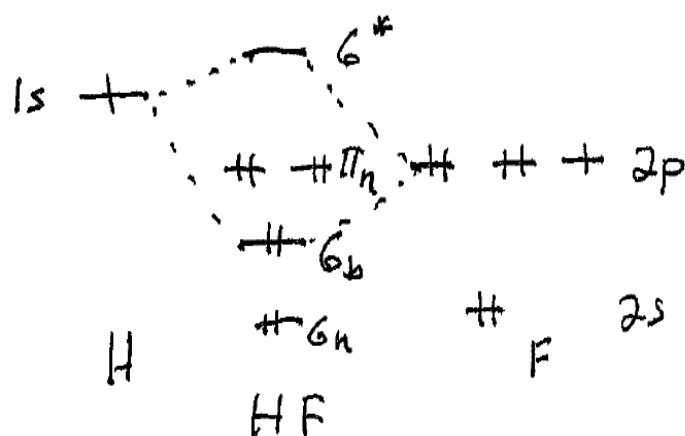
applies to all bonding, just more nuclei in polyatomic  
repulsion and attract maximum at low separation, repulsion dominate --  
get balance – **minimum total (e & n) energy**

Extend LCAO-MO for Simple Polyatomics,

1<sup>st</sup> - Hetero atom diatomic bonding – Atkins, p.384-86,  
requires adjustment to homonuclear diatomic picture

Consider H-F - F more electronegative, *higher IP* than H  
(If ionize, electron goes to vacuum, free to fly away)  
bigger IP means *more negative energy*

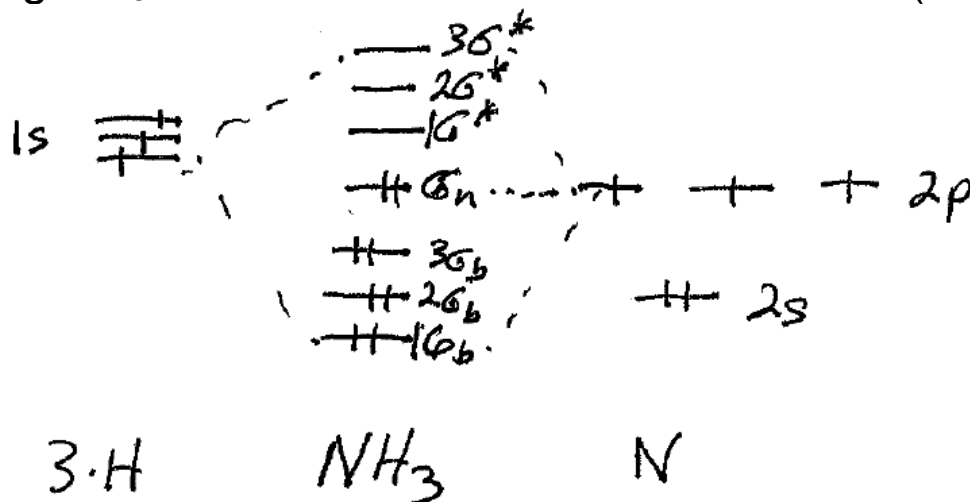
**Ex. HF bonding**



Result: *bonding MO* is closer in energy to F 2p than H 1s,  
 $\sigma_b$  will look more like F-2p<sub>z</sub>, and with 2 electrons, will have  
more *electron density closer to F* than to H  
 $\rightarrow$  create a *dipole moment* by displace e<sup>-</sup>

$\rightarrow 2p_{x,y}^F$  are *non-bonding* in HF,  $\perp$  to  $\sigma$ -bond, no overlap  $1s^H$   
these are then effectively  $\pi$ -lone pairs, but if used hybrids one  
 $sp^3$  would form bond overlap, other three  $sp^3$  would be lone pairs

Same idea for **polyatomics**, keep track of identical atom  
 e.g.  $\text{NH}_3$  – VB--consider **valence electrons**:  $\text{F}(2s,2p)+3\text{H}(1s)$



**split of bonding from non bond is large**, since  $\sigma$ -bonds are strong

**Valence bond (VB) model, local (like diatomic) bonds all  $\sigma$ , in  $\text{NH}_3$**

easiest way for chemist – **hybrid idea**

- bonding interaction bigger energy than s-p split
- “promote” s equivalent to p
- treat s, p as virtually degenerate—can mix

$sp^3 \rightarrow 4$  orbitals point at apex tetrahedral

$sp^2 \rightarrow 3$  orbitals –  $120^\circ$  apart (leaves  $p_z \rightarrow \pi$ ) double bond

$sp \rightarrow 2$  orbitals –  $180^\circ$  apart ( $p_{x,y}$  orbital  $\rightarrow 2\pi$ ) triple bond

linear combinations again, like  $p_x = p_1 - p_{-1}$ , but not degenerate

$$sp^3_1 = s + p_z + p_x + p_y$$

$$sp^2_1 = s + p_x + p_y$$

$$sp^3_2 = s + p_z - p_x - p_y$$

$$sp^2_2 = 2s - p_x - p_y$$

$$sp^3_3 = s - p_z + p_x - p_y$$

$$sp^2_3 = p_x - p_y$$

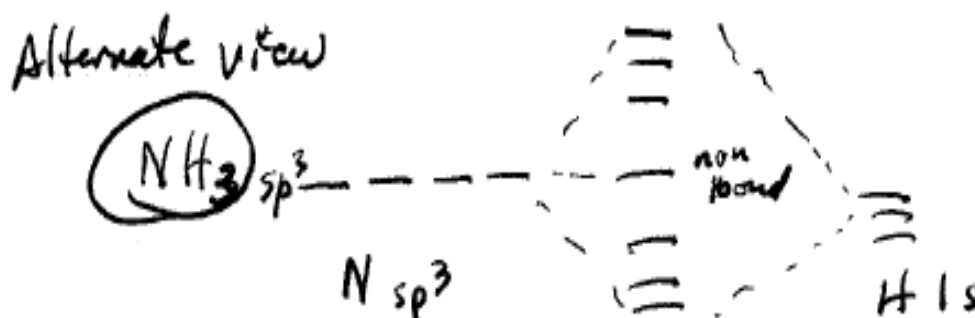
$$sp^3_4 = s - p_z - p_x + p_y$$

$$sp_1 = s + p_z \quad sp_1 = s - p_z$$

**(these coefficients not normalized)**

$\text{NH}_3$  – pyramidal, use  $sp^3$  hybrids, **one orbital non bonding**

$\text{BH}_3$  – planar,  $sp^2$ :  $2p^F_x$ ,  $2p^F_y$  with  $2s^F$ , **empty  $\pi - 2p^F_z$  no overlap  $1s^H$**



These take chemical intuition (scheme assume  $sp^3$  degenerate) balance electronegativity and how molecules form C<sub>2</sub>H<sub>2</sub> –linear, C<sub>2</sub>H<sub>4</sub> –planar, {NH<sub>3</sub> non planar, BH<sub>3</sub> planar}

### A little more depth

We took simplistic separation approach

How do we evaluate energies / realistic wave/fct

imagine AO's as a basis set of orbitals – “guesses”

$$\langle H \rangle = \int \phi^*_i H \phi_i / \int \phi^*_i \phi_i = H_{ii}/S_{ii} \quad \text{expectation value (i,i)-diagonal}$$

$$\langle H \rangle = \int \phi^*_i H \phi_j / \int \phi^*_i \phi_j = H_{ij}/S_{ij} \quad \text{interaction value (i,j)-off-diagonal}$$

These are called **Coulomb integrals** ( $H_{ij}$ ) – energy operator which are normalized to **overlap integrals** ( $S_{ij}$ )

So if  $\psi = \sum c_i \phi_i$  i.e. if MO made of AOs, then want to **optimize**  $c_i$  -- use **variation principle**:  $\partial \langle H \rangle / \partial c_i = 0$

e.g. let:  $\psi = c_A \phi_A + c_B \phi_B$  (as in  $\sigma_b$ ) then -- **demonstrate**

$$E = [c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}] / [c_A^2 + 2c_A c_B S_{AB} + c_B^2]$$

set  $\partial E / \partial c_A = 0$ ,  $\partial E / \partial c_B = 0 \Rightarrow 2$  equations, 2 unknowns

easiest differentiate both sides  $\rightarrow$  **secular equations**,

$$\partial \{E[c_A^2 + 2c_A c_B S_{AB} + c_B^2]\} / \partial c_A = \partial \{c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}\} / \partial c_A$$

$$\partial E / \partial c_A [c_A^2 + 2c_A c_B S_{AB} + c_B^2] + E [2c_A + 2c_B S_{AB}] = [2c_A H_{AA} + 2c_B H_{AB}]$$

First term = 0 (min), rest:  $0 = 2c_A(H_{AA} - E) + 2c_B(H_{AB} - ES_{AB})$   
same for  $H_{BB}$

**Solution:** energies obtained from secular determinant:

(polynomial, quadratic  
2 solution –  $E_1, E_2$ )

$$0 = \begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix}$$

**general wave function** (LCAO-MO):  $\psi = \sum c_i \phi_i$

“Secular Determinant”  $n$ -AOs give  $n$ -MOs  $\rightarrow n - E_K$  values

$$0 = \begin{vmatrix} H_{11} - E & H_{21} - ES_{21} & \dots & \dots & H_{n1} - ES_{n1} \\ H_{12} - ES_{12} & H_{22} - E & & & \vdots \\ H_{13} - ES_{13} & & \ddots & & \vdots \\ \vdots & & & \ddots & \vdots \\ H_{1n} - ES_{1n} & \dots & \dots & \dots & H_{nn} - E \end{vmatrix}$$

Then insert  $E_K$ 's into secular equations ( $n$  - equations)

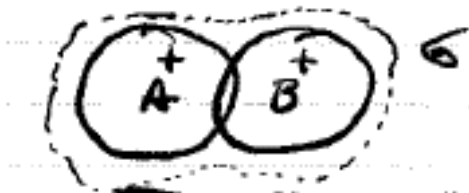
$$\sum_{ij} (H_{ij} - E_K S_{ij}) c_j^K = 0 \quad n - E_K \text{ makes } n \text{ separate sol'n}$$

solve set of **simultaneous equations** for coefficients  
 $\rightarrow$  get a **set of  $n - c_i^K$**  – for **each** ( $n$ -values)  $E_K$

**Delocalization**—major aspect of MO model, see above,  
all MOs are solutions to **secular determinant (energies)** and  
associated set of **secular equations (wave functions)**,  
 $\rightarrow$  so each has **contributions from all the AOs** - delocalized

**Valence Bond method, localized view, chemical appeal**

Idea, AOs on one atom overlap those on another  
and share and electron pair  $\rightarrow$  bond



$$H_2: \psi_{VB}(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$$

electrons identical, need both forms,  
bonding - increase  $e^-$  density between

## Contrast this with the MO picture

$$\begin{aligned}\psi_{\text{MO}}(1,2) &= \sigma_b(1) \sigma_b(2) = [\phi_A + \phi_B](1) [\phi_A + \phi_B](2) \\ &= \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)\end{aligned}$$

*VB 2 e<sup>-</sup> covalent state*
*ionic states (excited)*

Difference, MO too much emphasis on ionic states,  
 VB too much bond strength (e<sup>-</sup> all between nuclei)

Bring them together

VB add excited state (ionic) contribution (e<sup>-</sup> promoted)

$$\psi_{\text{VB}}(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \lambda[\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)]$$

MO add excited configuration,  $\sigma^*(1) \sigma^*(2)$

$$\begin{aligned}\sigma_b(1) \sigma_b(2) - \lambda'[\sigma^*(1) \sigma^*(2)] = \\ \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + (1-\lambda')[\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)]\end{aligned}$$

Adjusting  $\lambda, \lambda'$  will bring these to the same functional form

*Can use variation method to optimize  $\lambda, \lambda'$*

**Poly atomic VB** → select AOs with valence e<sup>-</sup> to mix,  
 share e<sup>-</sup>, form 2e<sup>-</sup> bond, promote e<sup>-</sup> to get hybrids  
 $\text{C } (2s)^2(2p)^2 \rightarrow \text{C } (2s)^1(2p)^3 \rightarrow \text{C } (sp^3)^4$

Then can form local bonds: C-H:  $\phi = \text{C } (sp^3)^1 + \text{H}(1s)^1$

And C-C:  $\phi = \text{C}_a(sp^3)^1 + \text{C}_b(sp^3)^1$  etc.

**Problem:** VB completely **local**, so misses out on delocalized systems like  $\pi$  and interactions between bond networks

VSEPR model — describe molecular geometry

based on  $e^-$  pair repulsion, in VB – bonds, lone pairs

Minimize energy by distance, spread, open angles

Diatomic – linear, trivial, one bond

Triatomic – linear or bent, depend on lone pairs

O=C=O - two bonds around C, both double, linear

H-O-H - two bonds and two lone pairs around O

Approx. tetrahedral, pairs more space

- Rules:
1. bonds to ligands and lone pairs repel
  2. lone pairs require more angular space than bonds
  3. More electronegative ligand—increase space,  
more electronegative central atom, decrease space
  4. multiple bond needs more space than single bond

Ex.  $\text{CH}_4$  –tetrahedral, angle between C-H bonds,  $109^\circ$

$\text{NH}_3$  – pyramidal, lone pair 4<sup>th</sup> position, angle  $\sim 107^\circ$

$\text{H}_2\text{O}$  – bent, two lone pairs other positions, angle  $\sim 105^\circ$

$\text{CO}_2$  – linear,  $\text{SO}_2$  – bent (lone pair)

$\text{C}_2\text{H}_2$  – linear,  $\text{C}_2\text{H}_4$  – planar,  $\text{C}_2\text{H}_6$  – each  $\sim$  tetrahedral

## Solving MO problem for real systems:

Clearly all of this gets complex for large molecules –  
most quantum chemistry problems solved using computers

$$\psi \sim \sum_i c_i \phi_i^{\text{AO}} \quad \phi_i^{\text{AO}} \sim \sum_k a_k f_k \quad f_k - \text{functions, e.g. STO} \rightarrow e^{-\alpha r},$$

Gaussian  $\rightarrow e^{-\alpha' r^2}$

sometimes fix  $a_k$ 's by some optimization (solve for atomic  $E_{\text{min}}$ )

always optimize  $c_i$  by minimizing energy

can also vary geometry to optimize energy

$\Rightarrow$  structure determination

## Hückel Model of $\pi$ -systems -- a little different

$\pi$ -bonds – weaker – so usually highest E filled MO - HOMO

symmetry – out of the plane – not mix with  $\sigma$ -orbital

## Hückel Theory – empirical approximation

— solve  $\pi$ -system separately, idea is  $\pi$  not mix with  $\sigma$

$\psi = \sum_i c_i \phi_i \quad \phi_i = 2p_z^i$  just sum over  $p^z$  orbital on atoms  $i$   
this ignores the  $\sigma_b$  orbitals - lower in energy ( $\sigma^*$  higher)

Ex. Butadiene



normal secular determinant of just  $C 2p_z$  or  $\pi$  electrons:

$$0 = \begin{vmatrix} H_{11} - \epsilon & H_{12} - \epsilon S_{12} & H_{13} - \epsilon S_{13} & H_{14} - \epsilon S_{14} \\ H_{21} - \epsilon S_{21} & H_{22} - \epsilon & H_{23} - \epsilon S_{23} & H_{24} - \epsilon S_{24} \\ H_{31} - \epsilon S_{31} & H_{32} - \epsilon S_{32} & H_{33} - \epsilon & H_{34} - \epsilon S_{34} \\ H_{41} - \epsilon S_{41} & H_{42} - \epsilon S_{42} & H_{43} - \epsilon S_{43} & H_{44} - \epsilon \end{vmatrix}$$

**Rules:** 1. Let  $S_{ij} = 0 \quad i \neq j$  -- no overlap between atoms

2. let  $H_{ii} = \alpha \quad (i = j)$  -- All the same, diagonal,  $S_{ii} = 1$

3. let  $H_{ij} = \beta \quad i = j \pm 1$ , near neighbor interact

4. let  $H_{ij} = 0$  non-near neighbor do not interact

### Hückel secular determinant:

$$0 = \begin{vmatrix} \alpha - \epsilon & \beta & 0 & 0 \\ \beta & \alpha - \epsilon & \beta & 0 \\ 0 & \beta & \alpha - \epsilon & \beta \\ 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix}$$

solution – divide entire matrix (determinant) by  $\beta$  then let  $x = (\alpha - \epsilon)/\beta$

$$0 = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \Rightarrow x^4 - 3x^2 + 1 = 0$$

det - expand by minors (show):  
 solution (just quadratic eq. let  $y=x^2$ ):  
 $x = \pm 0.618, \pm 1.618$

Plug into:  $x = (\alpha - \epsilon)/\beta$  to get expressions for  $\epsilon$

$$\epsilon_1^\pm = \alpha \pm 1.618 \beta$$

$$\epsilon_2^\pm = \alpha \pm 0.618 \beta$$

$$\begin{array}{l} 4\pi \text{ ————— } \epsilon_1^- \quad \alpha - 1.618\beta \\ 3\pi \text{ ————— } \epsilon_2^- \quad \alpha - 0.618\beta \\ 2\pi \text{ ————— } \epsilon_2^+ \quad \alpha + 0.618\beta \\ 1\pi \text{ ————— } \epsilon_1^+ \quad \alpha + 1.618\beta \end{array}$$

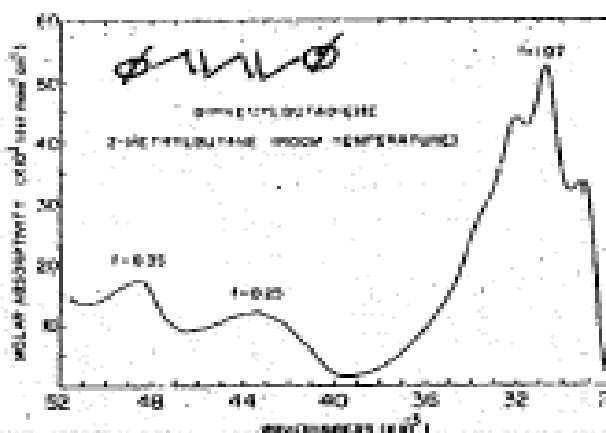
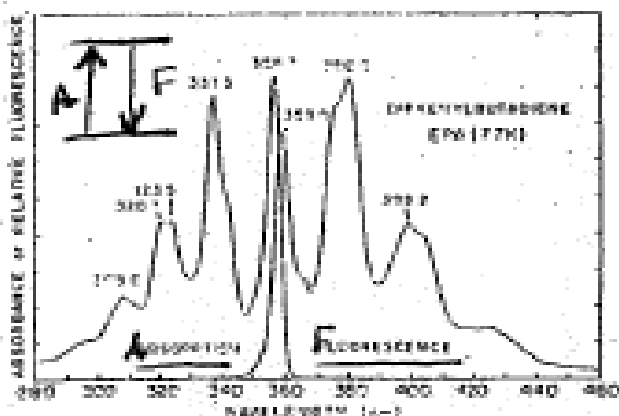
$$\alpha, \beta \text{ — neg}$$

Butadiene has 4  $\pi$ -electrons, could have 2 in each orbital:

$$E_g = 2\epsilon_1^+ + 2\epsilon_2^+ = 4\alpha + 4.472\beta \quad \text{— ground state: } (1\pi)^2 (2\pi)^2$$

$$E_{ex} = 2\epsilon_1^+ + \epsilon_2^+ + \epsilon_2^- = 4\alpha + 3.236\beta \quad \text{— excited state: } (1\pi)^2 (2\pi)^1 (3\pi)^1$$

$$\Delta E = 1.236\beta \quad \text{— transition in uv:}$$





Plug  $\varepsilon^k$  into:  $\sum_{i=1}^4 (H_{ij} - \varepsilon_k \delta_{ij}) c_j^k = 0$  for  $j = 1 - 4$  ( $\delta_{ij}$  - no  $S_{ij}$ )

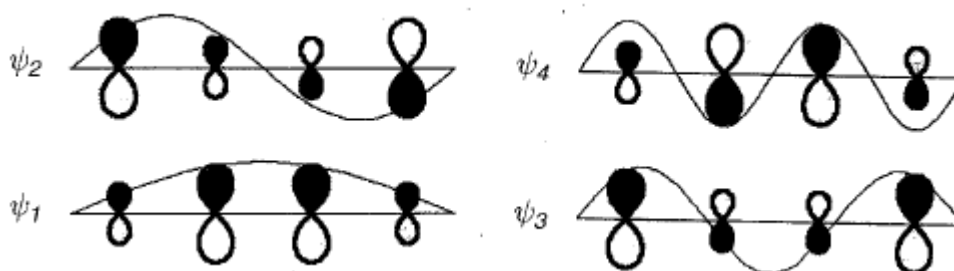
Ex:

$$\begin{aligned} (\alpha - \varepsilon_k) c_1 + \beta c_2 &= 0 \\ \beta c_1 + (\alpha - \varepsilon_k) c_2 + \beta c_3 &= 0 \\ \beta c_2 + (\alpha - \varepsilon_k) c_3 + \beta c_4 &= 0 \\ \beta c_3 + (\alpha - \varepsilon_k) c_4 &= 0 \end{aligned}$$

4 equations (j) solve simultaneously for  $c_j$ , repeat each  $\varepsilon^k$

$$\begin{aligned} \Psi_{1\pi} &= 0.37 p_1 + 0.60 p_2 + 0.60 p_3 + 0.37 p_4 && (0 \text{ nodes}) \\ \Psi_{2\pi} &= 0.60 p_1 + 0.37 p_2 - 0.37 p_3 - 0.60 p_4 && (1 \text{ node}) \\ \Psi_{3\pi} &= 0.60 p_1 - 0.37 p_2 - 0.37 p_3 + 0.60 p_4 && (2 \text{ nodes}) \\ \Psi_{4\pi} &= 0.37 p_1 - 0.60 p_2 + 0.60 p_3 - 0.37 p_4 && (3 \text{ nodes}) \end{aligned}$$

Hückel MO's (phasing, shapes - side view) for butadiene:



# nodes  $\rightarrow$  E

Hückel MO's for benzene very similar, but since cyclic get an extra term in determinant, i.e.  $H_{16}$  and  $H_{61} \neq 0 \rightarrow$  try it!

What if system not  $\pi$ -system?

QM calculational Complexity builds-up  
– semi empirical—extend the idea above

Extended Hückel – let atoms differ, calculate  $S_{ij}$

but valence electrons interaction – empirical parameter  
(i.e. include  $\sigma + \pi$  but parameterize  $H_{ij}$ )

CNDO – MNDO – INDO

– basically variations of neglecting overlap (NDO)  
and including parameters for  $H_{ij}$

*ab initio* → Compute solution to Schrödinger Equation –  
no parameters but many approximations –

**SCF** {typically **Hartree-Fock** – set up w/f and  
use to calculate potential ( $V(r_i)$ ) and  
re-solve -- keep cycling until no change in  $V(r_i)$ }

*Being a little more precise—add spin:*

*Multielectron wave function* - obey Pauli (anti-symmetric w/r/t  
exchange of electrons) -- use determinant form:

$$\psi(r_1, r_2, r_3, \dots, r_N) = \begin{vmatrix} \phi_A(r_1) & \phi_B(r_1) & \phi_C(r_1) & \dots & \phi_N \\ \phi_A(r_2) & \phi_B(r_2) & & \dots & \\ \vdots & & & \dots & \\ \phi_A(r_4) & & & & \phi_N(r_n) \end{vmatrix}$$

This will be anti-symmetric w/r/t exchange of electron

i.e.  $\psi(r_1, r_2, r_3, \dots) = -\psi(r_1, r_3, r_2, \dots)$  etc.

since **exchange electron** → **exchange rows in determinant**

**Still product of one-electron functions (MO) – average  $V(r_{ij})$**

Solving *ab-initio* problem involves 1-2-3-4 center integrals

**example of what this means:**  $\int \phi_A^*(1) \phi_B^*(2) \phi_C(1) \phi_D(2) d\tau$

big problem with 3 + 4 center ⇒ **sol'n: often neglect some**

Gaussian orbitals  $g_k(r) = (\beta r^k) e^{-\alpha r^2}$

make integrals simpler, rep. AOs as:  $STO = \sum c_n g_n(r)$

Calculations get very big – tend to scale like  $n^4 - n^5$

$n$  = number basis functions (the  $g_n(r)$  above)

so small molecules very quick (do on PC)

big molecules (e.g. proteins) become almost impossible

Methods work well for molecules up to ~100 atoms

(or ~1000 basis functions → represent AO's)

multi center integrals ⇒ need large memory / disk

⇒ takes time (now dedicated PC's or **clusters**)

## Alternate approach: Density Functional Theory (DFT)

Hohenberg-Kohn  $\rightarrow$   $\rho(r)$  electron density for grd state  
 in principle can determine w/f:  $\psi(r_1, \dots, r_n)$

Advantage – calculations become easier / bigger system

Disadvantage – involves parameters / approximations  
 (variation works differently)

[now part of standard Quantum Chemistry programs]

Solution – density  $\rightarrow$  orbital  $\rightarrow$  density etc. (self-consist)

QM Goals in Chemistry:

1. molecular properties  $\rightarrow$  *structure*, bonding, charge distribution, dipole moments  
*spectral transitions* – IR(vibration) - grd st property  
 UV (electronic) - more difficult, excited state
2. Structure – optimize geometry – minimum E
3. Kinetics – reaction surface – E as fct geometry

Very large molecules  $\rightarrow$  e.g. proteins / nucleic

Use results of Quantum Mechanics  $\rightarrow$  create  $U_{el}(R)$

an energy function that varies with nuclear position

$\Rightarrow$  minimize geometries: molecular mechanic model

$\Rightarrow$  *dynamics / trajectories: molecular dynamics*