C. Molecular Orbital Theory

Now what we’ve seen are transitions to electronic states of certain symmetry

Problem – how do we determine symmetries of the excited states (or ground state)

Idea – follow same procedure as other quantum mechanical problems of multi dimensions

Try to separate \( H \) into sum over \( h_i(q_i) \) -- where \( h_i(q_i) \) is a single particle Hamiltonian’s

Problem - electron repulsion: \( \sum_{ij} \frac{e^2}{r_{ij}} \) – never really separable,

Solution: effectively treat as a correction in a perturbation or variation sense

For sake of discussion -- let \( H^0 = \sum_i h_i(q_i) \)

where

\[ h_i(r_i) = \frac{-\hbar^2}{2m} \nabla_i^2 + V(r_i) \]

i.e. assume \( V(r_i) \) separable

How? Let \( V(r_i) = -\frac{Ze^2}{r_i} + \langle \text{average repulsion} \rangle \) of all other electrons

{Misses electron correlation}

then \( H^0 \psi^0 = E^0 \psi^0 \)

\( \psi^0 = \prod_{i=1}^{n} \phi_i^0 (r_i) \) – multi electron state

\( h_i \phi_i^0 = \varepsilon \phi_i^0 (r_i) \) – one electron - Hamiltonian

\( \phi_i^0 \rightarrow \text{orbital} \) – one electron w/f solution to molecular potential

so must correspond to representation of group

if \( \phi_i \)'s are functional representation of group

then \( \psi = \prod_{i=1}^{3n} \phi_i \) will be a direct product representation called configuration

when specify occupied \( \phi_i \) -- completely analogous to AOs and atomic state/configuration

For high symmetry -- Due to large number electrons

This would be a real mess if did not have the Pauli principle

Lowest energy wave functions will have electrons paired up

\( \phi_i = \phi_j \) but \( m_s = \pm 1/2 \) -- orbital part is “square” so “\( A_{1g} \)”

These give rise to only \( A_{1g} \) – i.e. only one way to put \( 2e^- \) in one orbital or so - no degeneracy

\( \Gamma_i \otimes \Gamma_i = A_{1g} + \ldots \) \( \rightarrow \) get added representations if degenerate

Issue is choices of ways to arrange the particle--electrons
Recipe to determine symmetry of \( \psi \rightarrow \) the multi-electron state: \( ^{2S+1} \Gamma \)

Only need to consider unpaired electrons
a) if all electrons paired, typically ground (A) state
   \( \psi \) symmetry – total symmetry representation \( ^1A_{1g} \)

b) if only one electron unpaired (radical)
   \( \psi \) symmetry = \( \phi_i \) symmetry for unpaired electron \( i \)
   \( \rightarrow \) orbital sym. = state sym.:

   \[ \Gamma \]

   \( \psi \) symmetry = \( \Gamma \phi_i \otimes \Gamma_j \)…

   i) if all representations non-degenerate
      \( \rightarrow \) multiply out reps, will have unique \( \psi \) & sym

   ii) if representations degenerate and 1e/orbital then
       \( \Gamma \psi = \) direct product

   iii) if multi electron in degenerate orbital - must count possibilities, since elect. identical

   example 1--all orbitals non-degenerate:
   \( \text{H}_2\text{O} \) ground state – all paired: \( (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (b_1)^2 \) -- \( ^1A_1 \)
   \( \text{H}_2\text{O}^+ \) ion state – one unpaired: \( (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (b_1)^1 \) -- \( ^2B_1 \)
   \( \text{H}_2\text{O}^* \) excited state – two unpaired: \( (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (b_1)^1 (2b_2)^1 \) -- \( ^3A_2, ^1A_2 \)

   [c,iii.--last case is like -- for overtones: \( e \times e = a_1 + e \) (no \( a_2 \)) \( t \times t = a_1 + e + t_2 \) (no \( t_1 \))]
   perfect analogy to \( p^2 \rightarrow ^1S, ^3P, ^1D, -- \) only choices due to Pauli Principle

example 2 – some degeneracy issues:
   \( \text{NH}_3 \) ground state – all paired: \( (1a_1)^2 (2a_1)^2 (1e)^4 (3a_1)^2 \) -- \( ^1A_1 \)
   \( \text{NH}_3^* \) excited state – two un-paired: \( (1a_1)^2 (2a_1)^2 (1e)^4 (3a_1)^1 (2e)^1 \) -- \( ^1E - 2+6=8 \) states
   \( \text{NH}_3^* \) doubly excited state – two un-paired: \( (1a_1)^2 (2a_1)^2 (1e)^4 (3a_1)^0 (2e)^2 \) -- \( ^1E, ^1A_1, ^3A_1 \)
   In this case consider possibilities for arranging the identical electrons:

   \[ \downarrow \downarrow , \uparrow \uparrow , \downarrow \uparrow , \uparrow \downarrow \rightarrow ^1A_1, ^3A_1 \) and \[ \uparrow \uparrow , \downarrow \downarrow \rightarrow ^1E, \]

Problem \( \rightarrow \) now need to focus on symmetry of \( \phi_i \)’s
   i.e. How to get \( a_1, b_1 \) etc. orbital symmetries above
   can solve equations and see what symmetries develop for \( 1e^- \) w/f (like in computer demo)

But – know that \( H \rightarrow A_{1g} \) blocks mixing of representations
   so no energy terms between states different symmetry
Choose AO’s to make MO’s \( \rightarrow \) make linear combination of AO’s to form representation
   Symmetry adapted AOs\( \rightarrow \) from reduce representation of exchange of equivalent AOs
   or from projection operator on one of them

Advantage \( \rightarrow \) choose a basis set of functions that have symmetry of molecule
   \( \rightarrow \) will block diagonal \( H \), simplify calculation

Energy Matrix \( \rightarrow \) solve Secular Determinant: \( \mid H_{ij} - E S_{ij} \mid = 0 \)

Diagonalization \( \rightarrow \) maintains symmetry; just makes “unitary transform” of one basis \( \rightarrow \)
   To a new one (diagonal) best solution to one electron \( h_i \) – i.e. still big approximation
Last time looked at H$_2$O
AO’s can be symmetry adapted—minimal basis
“reduce” O(1s) → $a_1$
O(2s) → $a_1$
O(2p) → $a_1^z + b_1^y + b_2^x$
2H(1s) → $a_1 + b_2$

# of MO = # of AO  this is just a coordinate transformation
add more AOs get more MOs – but they will be empty

representations repeat so
convention is to just number them low to high energy

again total number of AO = number of MO for each symmetry
fill them with 2e$^-$ each ⇒ Pauli Principle

MO diagram →
bonding orbital (b) → decrease in energy → attract atom
non bonding orbital (n) → different symmetry (b$_1$) → no mix
anti bonding (*) → increase in energy—node between atoms
# * = # b  for those that mix in large excursion from AO

This is all group theory → reduce representations or projection

Energies for using this determined with Hamiltonian
$$\psi = \prod_{i=1}^{10} \phi_i (r_i)$$  state (configuration) is product of filled orbital
$$\langle \varepsilon \rangle = \langle \psi | H | \psi \rangle = \langle \prod \phi_i | \sum h_i \prod \phi_i \rangle$$
$$= \sum_i \langle \phi_i | h_i | \phi_i \rangle \langle \prod_{j \neq i} \phi_j | \prod_{j \neq i} \phi_j \rangle = \sum_i \varepsilon_i$$

Energy is sum of filled (occupied) orbital energies—count electrons for E
State representation is product of orbital representation

Optimize mix (SCF)→diagonalize $\langle \phi_i | h_i | \phi_i \rangle$  {symmetry representations form block diagonal}

Can choose any basis, but traditional LCAO-MO idea, use as a basis linear combination AO
whose energies are similar and symmetry LCAO → symmetry molecule

Now choose more AO’s → get more MO’s    just a coordinate (basis) transform
these are 1-e$^-$ solutions  the lowest E ones will be occupied: have e$^-$

Identical orbital move into each other by symmetry operator → Project

Minimal Basis:  $\phi_1 = (1S^0_1) - a_1$  $\phi_5 = (2p^0_{x_1}) - b_1$
$\phi_2 = (2S^0_2) - a_1$  $\phi_6 = (2p^0_{y_2}) - b_2$
$\phi_3 = (2p^0_{z_1}) - a_1$
$\phi_4 = (1s^1_H + 1s^1_H) - a_1$  $\phi_7 = (1s^1_H - 1s^2_H) - b_2$
Basis functions: AO's
\[ a_1 \phi_1 = (1s_0) \quad b_1 \phi_5 = (2p_x) \]
\[ \phi_2 = (2s_0) \quad b_2 \phi_6 = (2p_y) \]
\[ \phi_3 = (2p_z) \quad \phi_7 = (1s_{H1} - 1s_{H2}) \]
\[ \phi_4 = (1s_{H1} + 1s_{H2}) \]

Note: sym. adapt. Linear Combination

<table>
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<th>C_2</th>
<th>\sigma_{xz}</th>
<th>\sigma'_{yz}</th>
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<td>1</td>
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<tr>
<td>B_1</td>
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</tr>
<tr>
<td>B_2</td>
<td>1</td>
<td>-1</td>
<td>1</td>
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Secular Determinant: \( \rightarrow \) block diagonal

\[
0 = \begin{pmatrix}
(h_{11} - \varepsilon S_{11}) & (h_{21} - \varepsilon S_{21}) & (h_{31} - \varepsilon S_{31}) & (h_{41} - \varepsilon S_{41}) \\
(h_{22} - \varepsilon S_{22}) & (h_{32} - \varepsilon S_{32}) & (h_{42} - \varepsilon S_{42}) \\
(h_{33} - \varepsilon S_{33}) & (h_{43} - \varepsilon S_{43}) \\
(h_{44} - \varepsilon S_{44}) \\
(h_{55} - \varepsilon S_{55}) & (h_{66} - \varepsilon S_{66}) & (h_{76} - \varepsilon S_{76}) \\
(h_{67} - \varepsilon S_{67}) & (h_{77} - \varepsilon S_{77})
\end{pmatrix}
\]

MO energies -- (orbital diagram)

- ground state configuration: \((1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2\)
  \(\Rightarrow 1^1A_1\) state
  \(1b_1\) may be reversed

- excited configuration: \((1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^1 (2b_1)^1\)
  \(1^1A_2\) or \(^3A_2\) state

MO approach gives symmetrization of AO basis to simplify secular equation
This leads to rough interpretation of energy levels \(\rightarrow\) configurations

Block diagonal due to symmetry basis
To get energies (eigen values) solve Secular Determinant:
Now solution of this would demand evaluating the actual integrals. Group Theory tells which bases mix.

10e⁻ problem fill lowest to highest – ground state

\[
E = \sum_{i=1}^{n} \varepsilon_i \\
\psi = \prod_{i=1}^{n} \phi_i(q_i) = \prod_{i=1}^{n} \left( \sum_{k=1}^{n} C_{ik} \eta_k(q_i) \right)
\]

↑

ground state above to be anti symmetry
note each solution 2-\( \phi_i \)'s express as determinant w/f
ex. \( \phi_{1a_1}^{\uparrow} + \phi_{1a_1}^{\downarrow} \ldots \rightarrow \) determinant w/f

excited states – any other filling mechanism
ex: \( (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^1 (2b_2)^1 \)

\( b_1 \rightarrow b_2 \) excitation
\( E_{\text{ex}} - E_{\text{grd}} = \varepsilon_{\text{ex}} - \varepsilon_{\text{grd}} = \varepsilon_{2b_2} - \varepsilon_{1b_1} \)

These are called \textit{configurations}, since potential is angular of all other states, simple addition not very exact – configuration interact \( \left( \frac{e^2}{r_{ij}} \right) \leftrightarrow \) interact ground and excited configuration, only work for 2 electron excitations (since symmetry of \( H - A_{1g} \))

Actual spectroscopic (i.e. excited state) calculation must then include \textit{configuration interaction} to be accurate – leads to shifts

1) \textbf{Note} only configuration of same symmetry interact due to \( \frac{e^2}{r_{ij}} \sim A_{1g} \)

2) \textbf{Note} use only orbitals as a basis –
    h \rightarrow orbitals with MO properties as bonding anti bonding
    E lower (same symmetry) bond / E up – anti/no charge
    Analogous to result from \( H_2^+ \) ion but have not biased by selection

3) If include more orbitals \( \rightarrow \) get more MO’s
    state depends on which ones filled