Foundations of Molecular Orbital Theory

Variational Principle for Linear Combination of Atomic Orbital Wave Functions

Video III.i

Variational Method: Recap

We can very rarely determine exact wave functions by analytical solution of a relevant Schrödinger (wave) equation

But we can always evaluate expectation values for a guess wave function Φ

Variational principle for Hamiltonian operator (expectation value energy):

$$\frac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0$$

where E_0 is the *true* ground-state energy

Lower-limit condition: convenient way of evaluating the quality of different guesses (lower is better)

It permits us to use the tools of variational calculus if Φ depends on parameters

LCAO

One-electron molecular orbitals φ are built up as linear combinations of atomic orbitals φ according to

$$\phi = \sum_{i=1}^{N} a_i \varphi_i$$

The set of N atomic-orbital basis functions φ_i is called the "basis set" and each "basis function" has associated with it some coefficient a_i for any given MO.

Use the variational principle to find the optimal coefficients.

Many-electron wave functions Φ: antisymmetrized Hartree products—Slater determinants—of occupied one-electron orbitals ϕ_n

LCAO: Energy and Minimization

For a given one-electron orbital we evaluate

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

H_{ij} and S_{ij} "resonance" and "overlap" integrals

Minimization condition

$$\frac{\partial E}{\partial a_k} = 0 \quad \forall \, k$$

N linear equations must be satisfied in order for above to hold true

$$\sum_{i=1}^{N} a_i \left(H_{ki} - E S_{ki}\right) = 0 \quad \forall \, k$$

.

The Secular Equation

$$\sum_{i=1}^{N} a_i \left(H_{ki} - ES_{ki} \right) = 0 \quad \forall \, k$$

These linear equations can be solved for the variables a_i if and only if

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

Secular: or century equations:

corrections required to compensate such inequalities in the celestial motions as occur in the course of one century

The Secular Equation

Polynomial of order N, so N roots (N different satisfactory values of E).

For each E_j there is a *different* set of coefficients, a_{ij} (i runs over basis functions, j runs over molecular orbitals, each having energy E_j)

Solve the set of linear equations using that specific E_j to determine a_{ij} values

Coefficients define an optimal associated one-electron wave function ϕ_j within the given basis set.

Steps in a Calculation

1) Select a set of N basis functions

2) Determine all $N(N-1)/2$ values of both H_{ij} and S_{ij}

3) Form the secular determinant; determine N roots E_j of secular equation

4) For each E_j solve the set of linear eqs. to determine the basis set coefficients a_{ij} for that MO

Food for Thought

In general, what are the upper and lower limits on N? Consider this from a question of physical requirements and also practicality. If it helps to have a specific example to think about, what answer might you offer for the molecule formaldehyde?

Write H_{ij} and S_{ij} in Dirac notation (bras and kets) and in standard mathematical notation. What are the relevant integration variables?

Under what circumstances would you expect the values of H_{ij} or S_{ij} to be zero?

Foundations of Molecular Orbital Theory

Integrals in the Secular Equation and Effective Hamiltonians

Video III.ii

What *Are* Resonance and Overlap Integrals?

Overlap is easy: a value between –1 and 1 (for normalized basis functions) measuring nearness ($|S_{ij}|$ near 1) and phase relationship.

Resonance is trickier. It is helpful to consider diagonal vs. off-diagonal resonance integrals.

Diagonal is

$$H_{ii} = \int \varphi_i^* H \varphi_i d\mathbf{r}$$

and this is the expectation value of the Hamiltonian operator for the "pure" basis function (orbital). That is, the resonance energy is the energy of an electron found in that orbital.

Off-diagonal Resonance Integral

Consider a system of only two basis functions, 1 and 2. Further, let the overlap integral between the two normalized orbitals be zero (i.e., $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = 0$).

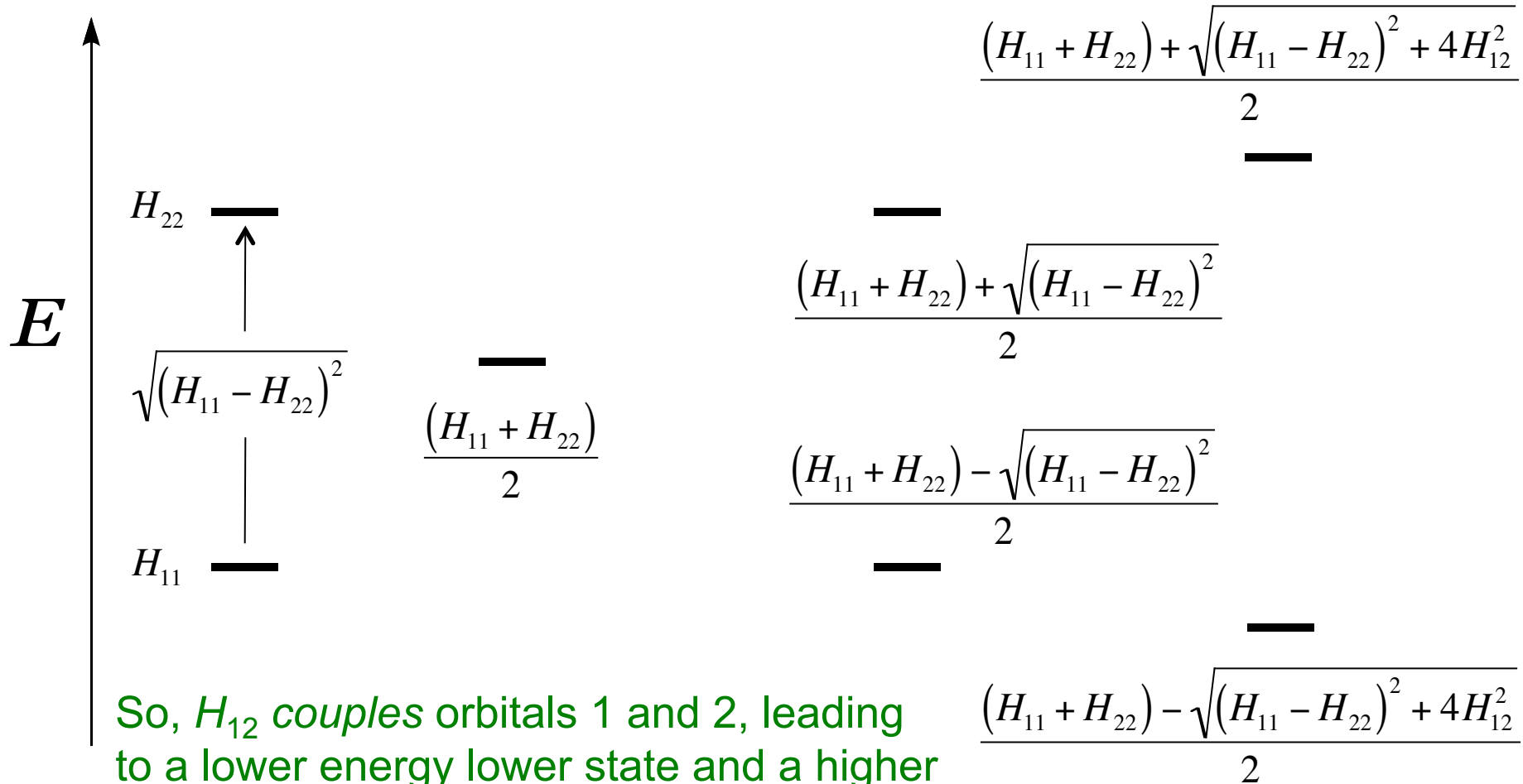In that case, the secular equation is

$$0 = \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix}$$

Solving for E, noting that $H_{12} = H_{21}$ gives

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

Off-diagonal
Resonance
Integral

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

$$\frac{(H_{11} + H_{22}) + \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

E

H_{22}

$\sqrt{(H_{11} - H_{22})^2}$

$$\frac{(H_{11} + H_{22}) + \sqrt{(H_{11} - H_{22})^2}}{2}$$

$$\frac{(H_{11} + H_{22})}{2}$$

$$\frac{(H_{11} + H_{22}) - \sqrt{(H_{11} - H_{22})^2}}{2}$$

H_{11}

So, H_{12} *couples* orbitals 1 and 2, leading to a lower energy lower state and a higher energy higher state (resonance)

$$\frac{(H_{11} + H_{22}) - \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

Effective Hamiltonian or Semiempirical Theories

Knowing the *qualitative* meaning of different resonance and overlap integrals means that we can adopt rational empirical approaches to estimating their quantitative values. This will likely compromise accuracy, but may greatly increase computational speed by avoiding extensive computations (especially of many very small integrals in large molecules)

Hückel Theory

Molecular orbital theory (1930s) developed by Erich Hückel for unsaturated and aromatic hydrocarbons.

Conventions:

a) Basis set is formed from parallel carbon 2p orbitals, one per atom.

b) The overlap matrix

$$S_{ij} = \delta_{ij}$$

c) Matrix elements H_{ii} equal to the negative of the ionization potential of the methyl radical $CH_3^{\bullet}$, i.e., the orbital energy of the singly occupied 2p orbital in the prototypical system defining sp^2 carbon hybridization.

Symbol α ($\alpha = -9.9$ eV from experiment)

Hückel Theory: Energies

(d) Matrix elements H_{ij} between nearest neighbors are also derived from experimental information.

A 90° rotation about the π bond in ethylene removes all of the bonding interaction between the two carbon 2p orbitals: positive cost of the process is

$$\Delta E = 2E_{\text{p}} - E_{\pi}$$

$E = E_{\pi}$ $E = 2E_{\text{p}}$
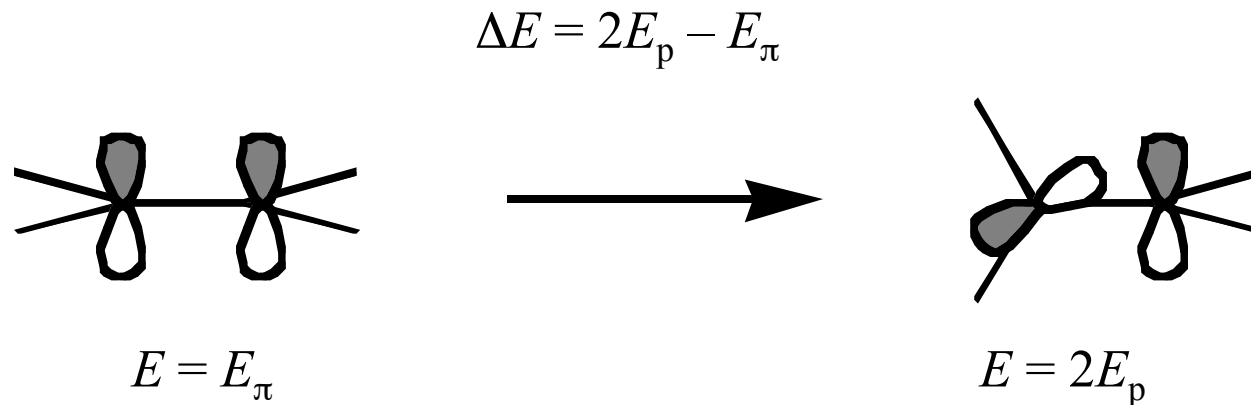
The (negative) stabilization energy for the π bond is distributed equally to the two p orbitals involved (divided in half) :

quantity termed β used for H_{ij} between neighbors

Hückel Theory: Energies

$$\Delta E = 2E_p - E_\pi = -2\beta$$

$$E_p = \alpha$$

$$\text{So } E_\pi = -(\Delta E - 2E_p) = 2\alpha + 2\beta$$

π bond energy in ethylene ca. 60 kcal/mol= 2.6 eV.

Dividing between the two carbon atoms: $\beta = -1.3$ eV.

(e) H_{ij} between 2p more distant than nearest neighbors is zero.

Hückel Theory: Extended?

What steps would be necessary to
extend Hückel theory to include,
say, N and O atoms?

Foundations of
Molecular Orbital Theory

Hückel Theory for the Allyl (C_3H_5) System

Video III.iii

The Allyl π System: C_3H_5

Three carbon atoms: basis set determined from convention (a)

3 2p orbitals, one centered on each atom (1, 2, 3, from left to right)
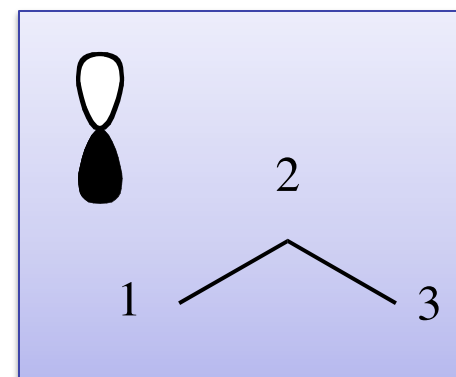
Solve a 3 x 3 secular equation.

Conventions (b)-(e):

$H_{11}=H_{22}=H_{33}=\alpha$ $\qquad$ $H_{12}=H_{21}=H_{23}=H_{32}=\beta$

$H_{13}=H_{31}=0$ $\qquad$ $S_{11}=S_{22}=S_{33}=1$, all other $S=0$

Solve:

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

Energies

Kronecker δ to define the overlap matrix: E appears only in the diagonal elements. Expand the 3 x 3 determinant

$$(\alpha-E)^3+(\beta^2\bullet 0)+(0\bullet\beta^2)-[0\bullet(\alpha-E)\bullet 0]-\beta^2(\alpha-E)-(\alpha-E)\beta^2=0$$

three solutions
$$E_1 = \alpha + \sqrt{2}\beta,$$
$$E_2 = \alpha$$
$$E_3 = \alpha - \sqrt{2}\beta$$

α and β are negative by definition: the *lowest* energy solution is E_1

To find the MO associated with this energy: use linear equations

$$\sum_{i=1}^{N} a_{ij}\left(H_{ki} - E_j S_{ki}\right) = 0 \quad \forall\, k$$

Coefficients

$$\sum_{i=1}^{N} a_{ij}\left(H_{ki} - E_{j}S_{ki}\right) = 0 \quad \forall\, k$$

$$a_1\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_3\left[0 - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] = 0$$

$$a_1\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_2\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] + a_3\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] = 0$$

$$a_1\left[0 - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_3\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] = 0$$

($k = 1$, $k = 2$, $k = 3$)

$$a_2 = \sqrt{2}a_1$$

$$a_3 = a_1$$

Infinitely many values of a_1, a_2, and a_3 which satisfy above 2 equations

Add requirement that the wave function be normalized:

$$\sum_{i=1}^{3}\left|a_i\right|^2 = 1$$

Lowest MO

The unique values satisfying all equalities are then

$$a_{11} = \frac{1}{2}, \quad a_{21} = \frac{\sqrt{2}}{2}, \quad a_{31} = \frac{1}{2}$$

coefficients are specific to the *lowest energy* molecular orbital E_1.

With both the coefficients *and* the basis functions, we may construct the lowest energy molecular orbital

$$\phi_1 = \frac{1}{2} p_1 + \frac{\sqrt{2}}{2} p_2 + \frac{1}{2} p_3$$

By choosing the higher energy roots we can determine the coefficients required to construct ϕ_2 (from $E = \alpha$) and ϕ_3 (from $E = \alpha - \sqrt{2}\beta$).
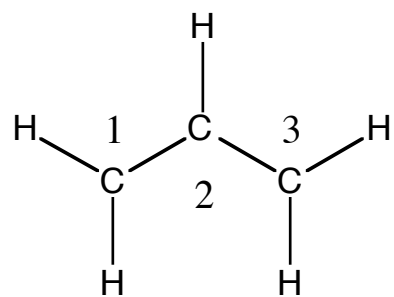
The other two MOs

$$a_{12} = \frac{\sqrt{2}}{2} \ , \quad a_{22} = 0 \ , \quad a_{32} = -\frac{\sqrt{2}}{2}$$

$$a_{13} = \frac{1}{2} \ , \quad a_{23} = -\frac{\sqrt{2}}{2} \ , \quad a_{33} = \frac{1}{2}$$

Three orbitals: bonding, non-bonding, and antibonding

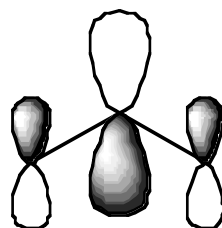Analysis of the so-called resonance energy arising from electronic delocalization in the π system

Delocalization: participation of more than two atoms in a given MO
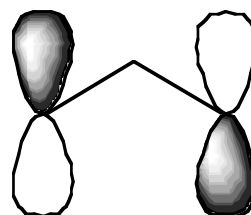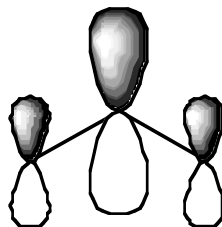
MO energy diagram

$\phi_3 = $ —— $\alpha - \sqrt{2}\beta$

p_C

$\phi_2 = $ —— α

$\phi_1 = $ $\alpha + \sqrt{2}\beta$

E

The Allyl π Cation: $C_3H_5^+$

Molecular aufbau principle of filling lowest energy MOs first:

each electron has the energy of the one-electron MO that it occupies (ϕ_1 in this case) total energy of the allyl cation π system is $2(\alpha + \sqrt{2}\beta)$.

Alternative fully localized structure:

full (doubly-occupied) π bond between two of the carbons

empty, non-interacting p orbital on the remaining carbon atom

π energy: that of a double bond: $2(\alpha + \beta)$.

Hückel resonance energy, $H_{\text{Huckel}} - H_{\text{localized}}$, is 0.83β (β is negative, so resonance is a favorable phenomenon).

Recalling the definition of β, the resonance energy in the allyl cation is about 40% of the rotation barrier in ethylene—ca. 25 kcal mol^{-1}.

Allyl Radical and Anion

Add the energy of ϕ_2 to the cation for each successive electron

$$H_\pi(\text{allyl radical}) = 2(\ \alpha + \sqrt{2}\beta\ ) + \alpha$$

$$H_\pi(\text{allyl anion}) = 2(\ \alpha + \sqrt{2}\beta) + 2\alpha$$

Hypothetical fully-π-localized non-interacting system, each new electron would go into the non-interacting p orbital, also contributing each time a factor of α to the energy (by definition of α).

Resonance energies of the allyl radical and the allyl anion are the same as for the allyl cation, 0.83β.

Neither experiment, (measured rotational barriers), nor more complete levels of quantum theory support the notion that in all three cases the magnitude is the same. (The failure is mostly associated with using a one-electron-like model for a many-electron problem; more to come!)