Matrix Algebra

- A systematic and concise way for managing systems of linear equations

a single equation

$ax = b$ with solution $x = a^{-1}b$

$$a_{11}x + a_{12}y = c_1$$

$$a_{21}x + a_{22}y = c_2$$

- A **matrix** is a rectangular array of elements that obeys certain rules of arithmatic

$$\begin{pmatrix} 1 & 2 \\ 7 & 2 \end{pmatrix} \qquad \begin{pmatrix} 5 \\ 2 \\ 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 & 7 & 4 \end{pmatrix}$$

$2 \times 2\,matrix$ $3 \times 1\,matrix$ $1 \times 4\,matrix$

or

$$\begin{bmatrix} 1 & 2 \\ 7 & 2 \end{bmatrix} \qquad \begin{bmatrix} 5 \\ 2 \\ 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 & 7 & 4 \end{bmatrix}$$

Operator. acts on a function to give a new function

Differentiation operator ***d/dx***

$$\frac{d}{dx}f(x) = \frac{df(x)}{dx} = f'(x)$$

Addition and Subtraction.

Only matrices of the same size can undergo addition and subtraction

$$\begin{pmatrix} 2 & 1 \\ 7 & 4 \end{pmatrix} + \begin{pmatrix} 1 & 3 \\ 5 & 6 \end{pmatrix} = \begin{pmatrix} 2+1 & 1+3 \\ 7+5 & 4+6 \end{pmatrix} = \begin{pmatrix} 3 & 4 \\ 12 & 10 \end{pmatrix}$$

$$\begin{pmatrix} 7 \\ 0 \\ 3 \end{pmatrix} + \begin{pmatrix} 4 \\ 4 \\ 1 \end{pmatrix} = \begin{pmatrix} 7+4 \\ 0+4 \\ 3+1 \end{pmatrix} = \begin{pmatrix} 11 \\ 4 \\ 4 \end{pmatrix}$$

$$\begin{pmatrix} 2 & 1 \\ 7 & 4 \end{pmatrix} - \begin{pmatrix} 1 & 3 \\ 5 & 6 \end{pmatrix} = \begin{pmatrix} 2-1 & 1-3 \\ 7-5 & 4-6 \end{pmatrix} = \begin{pmatrix} 1 & -2 \\ 2 & -2 \end{pmatrix}$$

Scalar Multiplication

$$2\begin{pmatrix} 2 & 1 \\ 7 & 4 \end{pmatrix} = \begin{pmatrix} 2\times 2 & 2\times 1 \\ 2\times 7 & 2\times 4 \end{pmatrix} = \begin{pmatrix} 4 & 2 \\ 14 & 8 \end{pmatrix}$$

Matrix Algebra

Matrix Multiplication

$$\mathbf{AB} = \begin{pmatrix} 1 & 3 \\ 7 & 2 \end{pmatrix}\begin{pmatrix} 2 & 4 \\ 5 & 6 \end{pmatrix} = \begin{pmatrix} 1(2)+3(5) & 1(4)+3(6) \\ 7(2)+2(5) & 7(4)+2(6) \end{pmatrix} = \begin{pmatrix} 17 & 22 \\ 24 & 40 \end{pmatrix}$$

matrix multiplication is not commutative: **AB** $\neq$ **BA**

$$\mathbf{BA} = \begin{pmatrix} 2 & 4 \\ 5 & 6 \end{pmatrix}\begin{pmatrix} 1 & 3 \\ 7 & 2 \end{pmatrix} = \begin{pmatrix} 2(1)+4(7) & 2(3)+4(2) \\ 5(1)+6(7) & 5(3)+6(2) \end{pmatrix} = \begin{pmatrix} 30 & 14 \\ 47 & 27 \end{pmatrix}$$

Managing systems of linear equations

$$a_{11}x + a_{12}y = c_1$$

$$a_{21}x + a_{22}y = c_2$$

Can be represented as

$$\mathbf{AB} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} a_{11}x & a_{12}y \\ a_{21}x & a_{22}y \end{pmatrix}$$

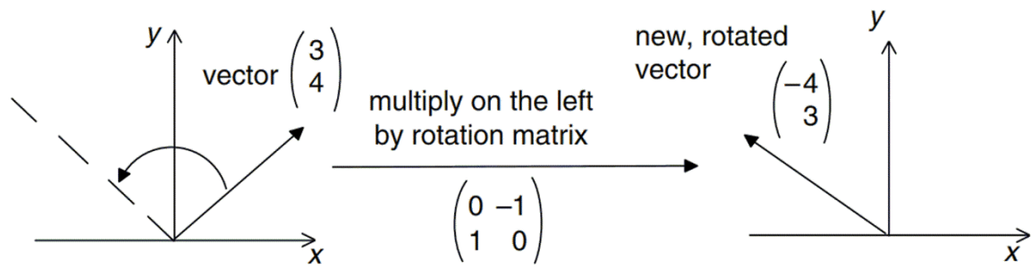
or

$$\mathbf{AB} = \mathbf{C} \qquad \text{where} \qquad \mathbf{C} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\mathbf{A}^{-1}\mathbf{AB} = \mathbf{A}^{-1}\mathbf{C} \qquad \text{i.e.} \quad \mathbf{B} = \mathbf{A}^{-1}\mathbf{C}$$

Matrix acting as an operator

Multiplying a rotation matrix by a column matrix transforms or rotates it into another the column matrix



Some Important Matrices

- **Null matrix**

0 = $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 & 0 \end{pmatrix}$

- **Diagonal matrix.** a square matrix with all of the off-diagonal elements as zero

$\begin{pmatrix} 2 & 0 \\ 0 & 4 \end{pmatrix}$ $\begin{pmatrix} 3 & 0 & 0 \\ 0 & 6 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

- **Identity matrix.** a diagonal matrix with 1 across the diagonal

I = (1) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Matrix Algebra

- **Inverse matrix. $A^{-1}A = AA^{-1} = I$**

$$\text{If } \mathbf{A} = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \quad \text{then} \quad \mathbf{A}^{-1} = \begin{pmatrix} -2 & 1 \\ 3/2 & -1/2 \end{pmatrix}$$

- **Symmetric matrix.** element $a_{ij} = a_{ji}$

$$\begin{pmatrix} 1 & 4 \\ 4 & 3 \end{pmatrix} \; a_{12} = a_{21} = 4 \qquad \begin{pmatrix} 2 & 7 & 1 \\ 7 & 3 & 5 \\ 1 & 5 & 4 \end{pmatrix}$$

- **Transpose. A^T.** Operation that exchanges rows and columns

$$\text{If } \mathbf{A} = \begin{pmatrix} 2 & 3 \\ 4 & 7 \end{pmatrix} \quad \text{then} \quad \mathbf{A}^{\mathrm{T}} = \begin{pmatrix} 2 & 4 \\ 3 & 7 \end{pmatrix}$$

$$\text{If } \mathbf{A} = \begin{pmatrix} 2 & 1 & 6 \\ 1 & 7 & 2 \end{pmatrix} \quad \text{then} \quad \mathbf{A}^{\mathrm{T}} = \begin{pmatrix} 2 & 1 \\ 1 & 7 \\ 6 & 2 \end{pmatrix}$$

- **Orthogonal Matrix. A** is orthogonal if $\mathbf{A}^{-1} = \mathbf{A}^{T}$

$$\mathbf{A}_1 = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \qquad \mathbf{A}_2 = \begin{pmatrix} 1/\sqrt{6} & -1/\sqrt{2} & -1/\sqrt{3} \\ 2/\sqrt{6} & 0 & 1/\sqrt{3} \\ 1/\sqrt{6} & 1/\sqrt{2} & -1/\sqrt{3} \end{pmatrix}$$

Matrix Diagonalization

Matrix diagonalization will be needed for calculating energies (eigenvalues) of molecular orbitals (eigenvectors).

A is diagonalizable if $\mathbf{A} = \mathbf{PDP}^{-1}$

$$\text{if } \mathbf{A} = \begin{pmatrix} 4 & -2 \\ 1 & 1 \end{pmatrix} \text{ then } \mathbf{P} = \begin{pmatrix} 1 & 2 \\ 1 & 1 \end{pmatrix}, \mathbf{D} = \begin{pmatrix} 2 & 0 \\ 0 & 3 \end{pmatrix}, \text{and } \mathbf{P}^{-1} = \begin{pmatrix} -1 & 2 \\ 1 & -2 \end{pmatrix}$$

It can be proven that if **A** is symmetric, then **P** is orthogonal and thus $\mathbf{P}^{-1} = \mathbf{P}^{T}$

$$\text{if } \mathbf{A} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{ then}$$

$$\mathbf{P} = \begin{pmatrix} 0.707 & 0.707 \\ 0.707 & -0.707 \end{pmatrix}, \mathbf{D} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{P}^{-1} = \begin{pmatrix} 0.707 & 0.707 \\ 0.707 & -0.707 \end{pmatrix}$$

Determinants

2x2

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}, \quad \begin{vmatrix} 5 & 2 \\ 4 & 3 \end{vmatrix} = 5(3) - 2(4) = 7$$

3x3

$$\begin{vmatrix} 2 & 1 & 3 & 0 \\ 1 & 7 & 3 & 5 \\ 3 & 4 & 6 & 1 \\ 1 & 8 & 2 & -2 \end{vmatrix} = 2\begin{vmatrix} 7 & 3 & 5 \\ 4 & 6 & 1 \\ 8 & 2 & -2 \end{vmatrix} - 1\begin{vmatrix} 1 & 3 & 5 \\ 3 & 6 & 1 \\ 1 & 2 & -2 \end{vmatrix} + 3\begin{vmatrix} 1 & 7 & 5 \\ 3 & 4 & 1 \\ 1 & 8 & -2 \end{vmatrix}$$

$$- 0\begin{vmatrix} 1 & 7 & 3 \\ 3 & 4 & 6 \\ 1 & 8 & 2 \end{vmatrix}$$

Molecular Mechanics / Intro to Quantum Chemistry

MM Weaknesses

Since MM is oblivious to electronic distributions, universal accuracy in describing molecules should not be expected

–Using force fields that lack appropriate parameterization.

–No transfer of parameters between force fields

–Optimization may not lead to a minimum initially, and slight modifications to the geometry are needed to *guide* the optimization

–Solvent and local electric fields are not typically addressed, but can be corrected

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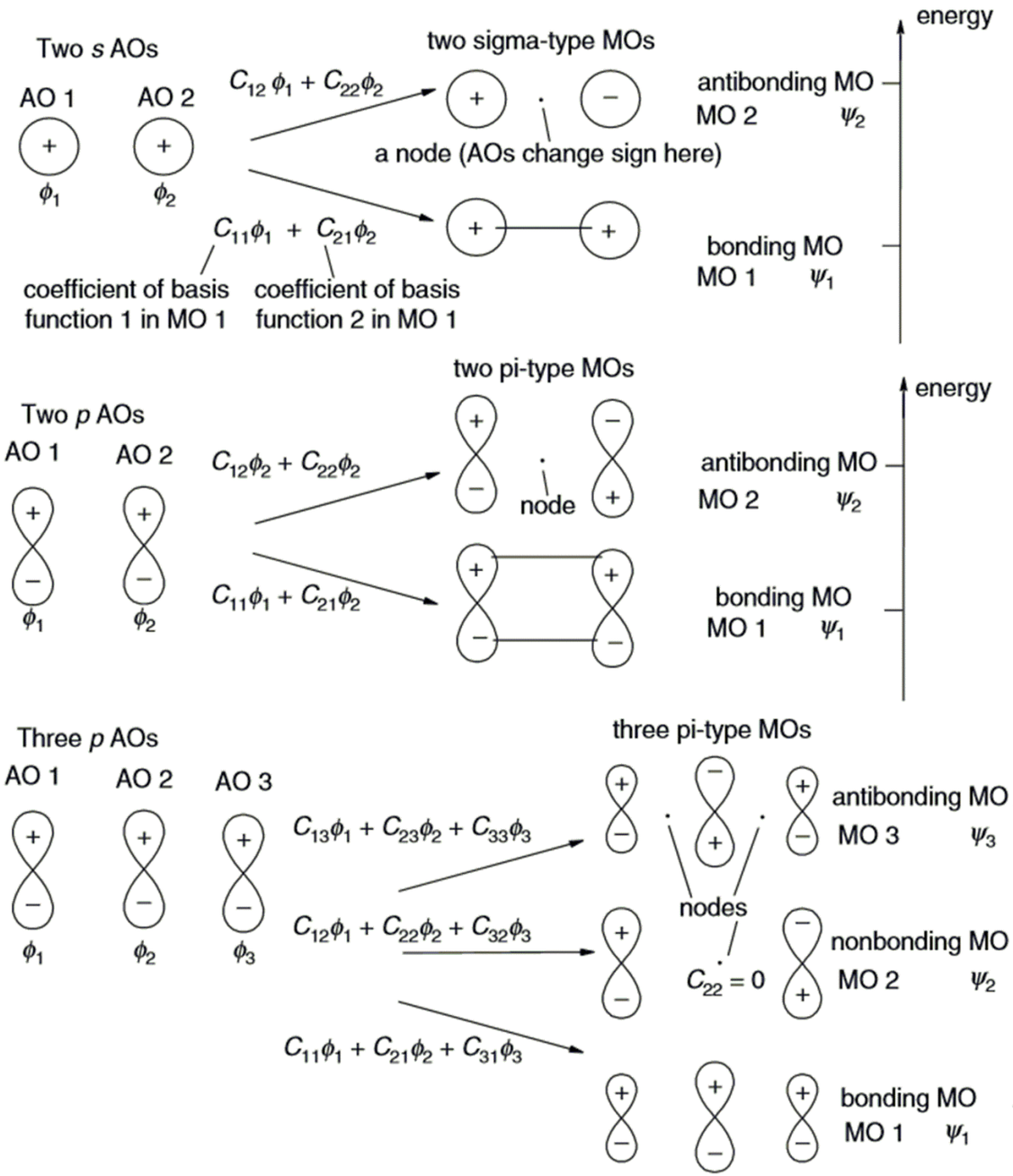
• Introduction to Quantum Chemistry

Reading: Ch 4. pg 118-131
Matrix review: pg. 108-118

Atomic Orbitals, Molecular Orbitals, and Basis Functions



Intro to Quantum Chemistry

Two Orbital Mixing Problem / Hückel Theory

Begin from the Schrodinger equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2$$

After some manipulation

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)\psi = E\psi$$

$$\hat{H} = \left(\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)$$

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian operator. It is the total energy operator from all of the forces acting on the system. This is an eigenvalue equation of the form;

$$\hat{O}f = kf, \quad \hat{O} = \text{operator}$$

f is the eigenfunction and k is the eigenvalue. Eigenvalue equations appear frequently in quantum chemistry.

How do we get the energy?

$$\hat{H}\psi = E\psi$$

Multiply the wavefunction by both sides of the eigenvalue equation

$$\psi\hat{H}\psi = E\psi^2$$

followed be division and integration over the spatial coordinates

$$E = \frac{\int \psi\hat{H}\psi dv}{\int \psi^2 dv}$$

What is the form of the wavefunction?

LCAO Approximation (Linear Combination of Atomic Orbitals)

Two-orbital mixing problem $\psi = c_1\phi_1 + c_2\phi_2$

The coefficients tell us the extent of contribution from each atomic orbital

Substitution in the Energy formula above gives

$$E = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)dv}{\int (c_1\phi_1 + c_2\phi_2)^2 dv}$$

$$E = \frac{c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1c_2S_{12} + c_2^2 S_{22}}$$

How to we get the optimal coefficients?

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

H_{ij} are not operators, but are in units of energy physical nature of which will be covered later.

$$\int \phi_1 \hat{H} \phi_1 dv = H_{11}$$

$$\int \phi_1 \hat{H} \phi_2 dv = H_{12} = \int \phi_2 \hat{H} \phi_1 dv = H_{21}$$

$$\int \phi_2 \hat{H} \phi_2 dv = H_{22}$$

$$\int \phi_1^2 dv = S_{11}$$

$$\int \phi_1 \, \phi_2 dv = S_{12} = \int \phi_2 \, \phi_1 dv = S_{21}$$

$$\int \phi_2^2 dv = S_{22}$$

Obtain coefficients that lead to the lowest energy by minimizing E with respect to the coefficients. The idea is to search for a minimum in coefficient space (aka MO space).

$$\partial E / \partial c_1 = 0$$
$$\partial E / \partial c_2 = 0$$

First rearranging gives;

$$E\left(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}\right) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

followed by differntiation with respect to c_1

$$\left(\frac{\partial E}{\partial c_1}\right)\left(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}\right) + E(2c_1 S_{11} + 2c_2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12}$$

set $\partial E / \partial c_1 = 0$

$$E(2c_1 S_{11} + 2c_2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12}$$

and rearrange

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

doing the same for c_2 gives;

$$(H_{12} - ES_{12})c_1 + (H_{22} - ES_{22})c_2 = 0$$

which is identical to

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0$$

the results can be presented as a system of linear equations;

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0$$

These equations are often referred to as the ***secular equations***

The secular equations can be present in a more concise matrix representation

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\left[\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \right] - \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

and more concisely as; $[\mathbf{H} - \mathbf{S}E]\mathbf{c} = \mathbf{0}$

and rearranged to; $\mathbf{Hc} = \mathbf{S}E\mathbf{c}$

Here **c** is a column matrix and *E* is a scalar. The above can be modified slightly to obey *orbital conservation* (the combination of two atomic orbitals must furnish two molecular orbitals with a distinct energy and coefficients). See the determinant approach to solving the secular equations for a better understanding of the origins of orbital conservation.

$$\mathbf{HC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}$$

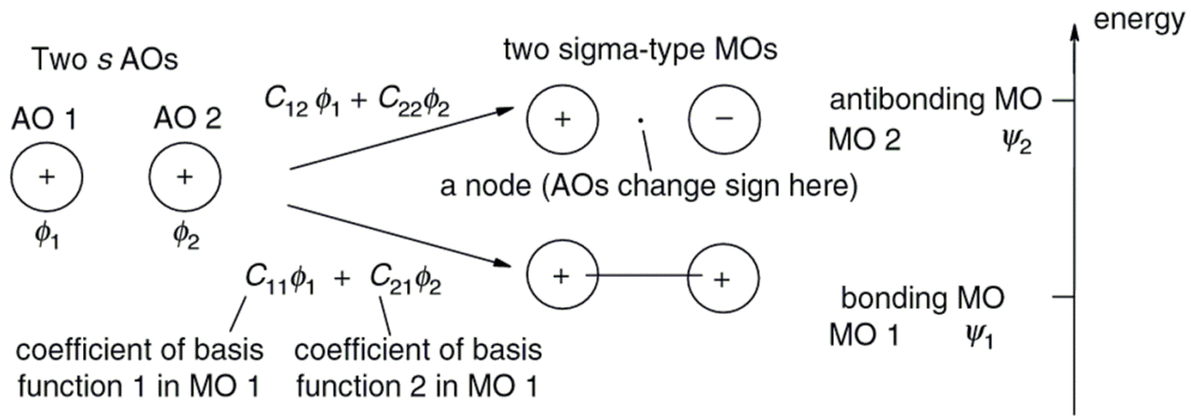
$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$$

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$

Now $\mathbf{C}$ is a square matrix with $\boldsymbol{\varepsilon}$ being a diagonal matrix.

The coefficients c_{11} and c_{21} are the basis function coefficients for ψ_1

The coefficients c_{12} and c_{22} are the basis function coefficients for ψ_2



S is the overlap matrix with matrix elements as overlap integrals S_{ij}

Each S_{ij} measures the extent that basis functions φ_i and φ_j overlap.

$$S_{ii} = S_{jj} = 1 \qquad S_{ij} = S_{ji}$$

$\boldsymbol{\varepsilon}$ is the energy levels matrix with ψ_1 having an orbital energy of ε_1 and ψ_2 having an orbital energy of ε_2

Thus far, this has been an analytical derivation without any approximations. Now we will introduce some approximations in order to reduce complexity. This will be a derivation of so-called **Hückel theory**.

Intro to Quantum Chemistry

Lets make the following approximations (severe approximations);

$$S_{11} = 1$$
$$S_{12} = S_{21} = 0$$
$$S_{22} = 1$$

or $S_{ij} = \delta_{ij}$ where $\delta_{ij} = 1$ if $i = j$ *and* $\delta_{ij} = 0$ if $i \neq j$

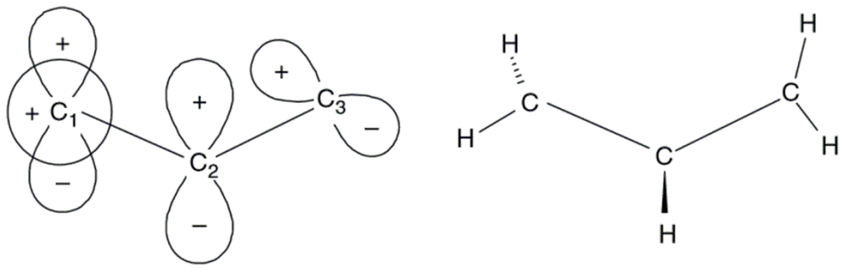
then the overlap matrix reduces to $\mathbf{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

then the matrix equation reduces to $\mathbf{HC} = \mathbf{C}\varepsilon$

and diagonalization of the Fock matrix $\mathbf{H}$ gives the coefficient matrix and the energy level matrix

$$\mathbf{H} = \mathbf{C}\varepsilon\mathbf{C}^{-1}$$

Orthogonal vs Orthonormal



This results here describe the Simple Hückel Model (SHM) and suffers from too severe approximations to be accurate. However it does provide some physical insight regarding orbital interaction and energy levels of simple π systems (only p orbitals are treated).

The energy integrals in SHM are the following

For basis functions on the same atom;

$$\int \phi_i \hat{H} \phi_i dv = H_{ii} = \alpha$$

For p orbitals on adjacent atoms;

$$\int \phi_i \hat{H} \phi_j dv = H_{ij} = \int \phi_j \hat{H} \phi_i dv = H_{ji} = \beta$$

For p orbitals separated by one or more atoms

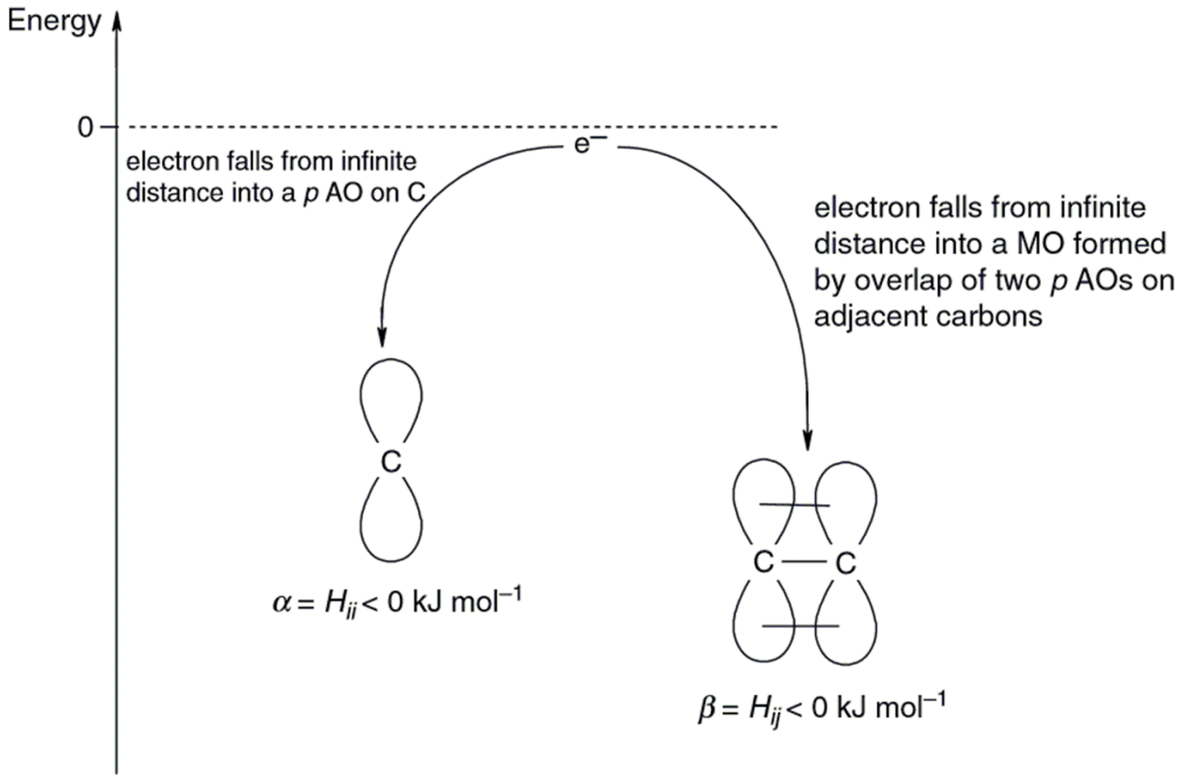
$$\int \phi_i \hat{H} \phi_j dv = H_{ij} = \int \phi_j \hat{H} \phi_i dv = H_{ji} = 0$$

α is defined as the **coulomb integral** which can be interpreted as the ionization energy of the p orbital in question

β is defined as the **resonance integral** which can be interpreted as the energy of an electron occupying the overlapping region between adjacent p orbitals. A rough approximation for β is the average of the coulomb integrals for the adjacent p orbitals.

Intro to Quantum Chemistry

Physical representation of α and β

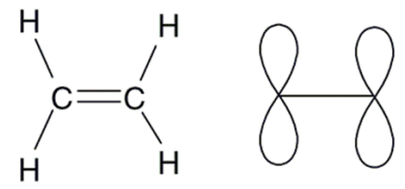


With an understanding of the definitions of α and β, we can write the SHM Fock matrix for systems described by only overlapping p orbitals.

Generic Fock matrix

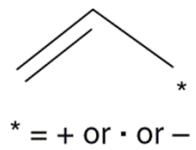
$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \vdots & \vdots & \dots & \vdots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{pmatrix}$$

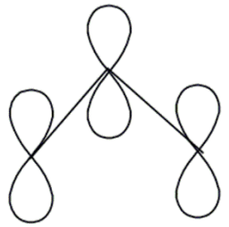
Ethylene

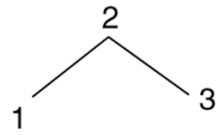


$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

Allyl

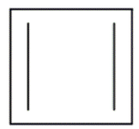


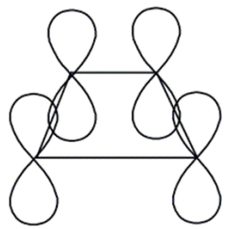


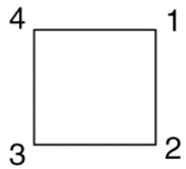


$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix}$$

Cyclobutadiene







$$\begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix}$$

Corresponding Fock matrices

Ethylene

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

Allyl

$$\mathbf{H} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

Cyclobutadiene

$$\mathbf{H} = \begin{pmatrix} 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \end{pmatrix}$$

We can define β relative to α, which is set to zero

Intro to Quantum Chemistry

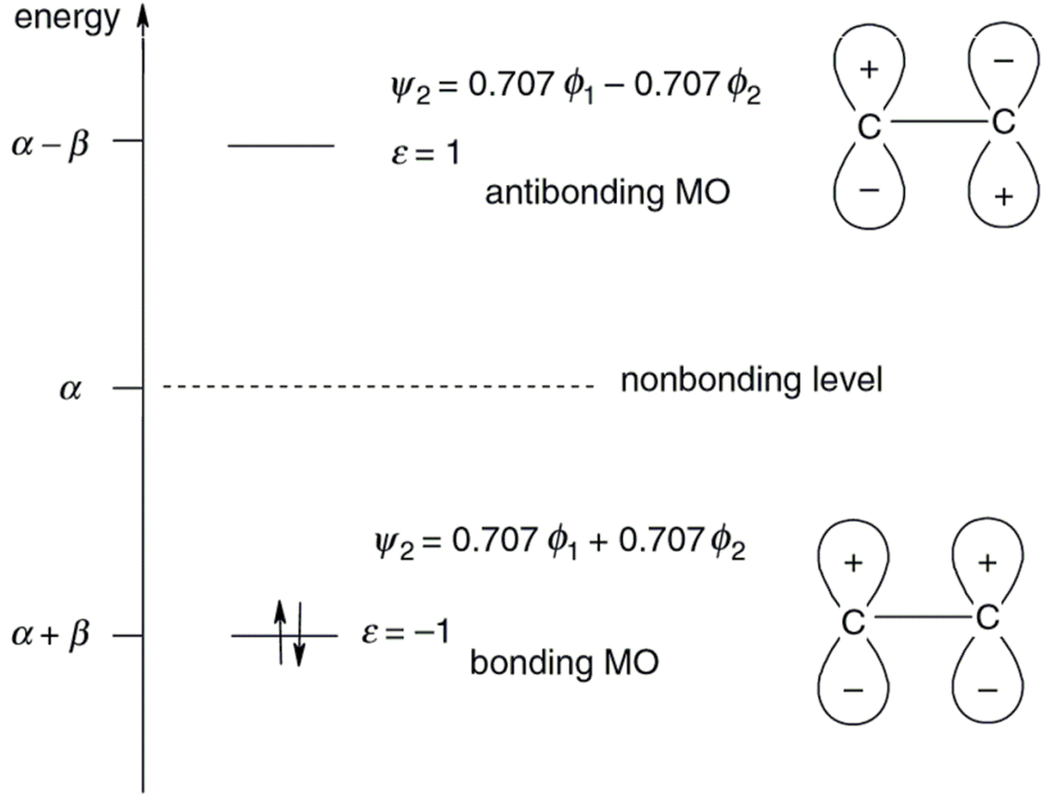
Diagonalize the Fock matrix to get the orbital coefficients and energy levels

$$\mathbf{H} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} = \underset{\mathbf{C}}{\begin{pmatrix} 0.707 & 0.707 \\ 0.707 & -0.707 \end{pmatrix}} \underset{\boldsymbol{\varepsilon}}{\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}} \underset{\mathbf{C}^{-1}}{\begin{pmatrix} 0.707 & 0.707 \\ 0.707 & -0.707 \end{pmatrix}}$$

The eigenvectors below describe the orbital distributions

$$\underset{\mathbf{v}_1}{\begin{pmatrix} 0.707 \\ 0.707 \end{pmatrix}} \equiv -1 \quad \text{and} \quad \underset{\mathbf{v}_2}{\begin{pmatrix} 0.707 \\ -0.707 \end{pmatrix}} \equiv 1$$

Orbital energy diagram for ethylene as determined from SHM

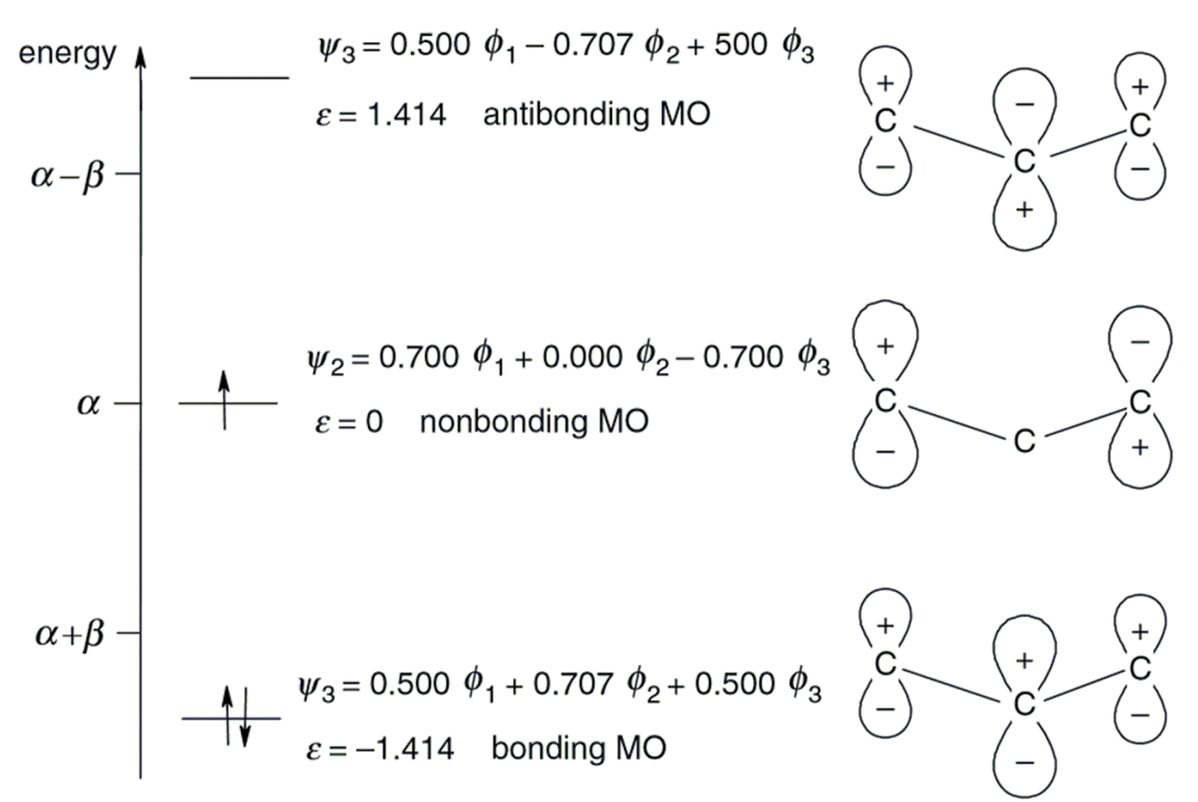


Allyl

$$\mathbf{H} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} =$$

$$\underset{\mathbf{C}}{\begin{pmatrix} 0.500 & 0.707 & 0.500 \\ 0.707 & 0 & -0.707 \\ 0.500 & -0.707 & 0.500 \end{pmatrix}} \underset{\boldsymbol{\varepsilon}}{\begin{pmatrix} -1.414 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1.414 \end{pmatrix}} \underset{\mathbf{C}^{-1}}{\begin{pmatrix} 0.500 & 0.707 & 0.500 \\ 0.707 & 0 & -0.707 \\ 0.500 & -0.707 & 0.500 \end{pmatrix}}$$

$\mathbf{v}_1 \quad \mathbf{v}_2 \quad \mathbf{v}_3$

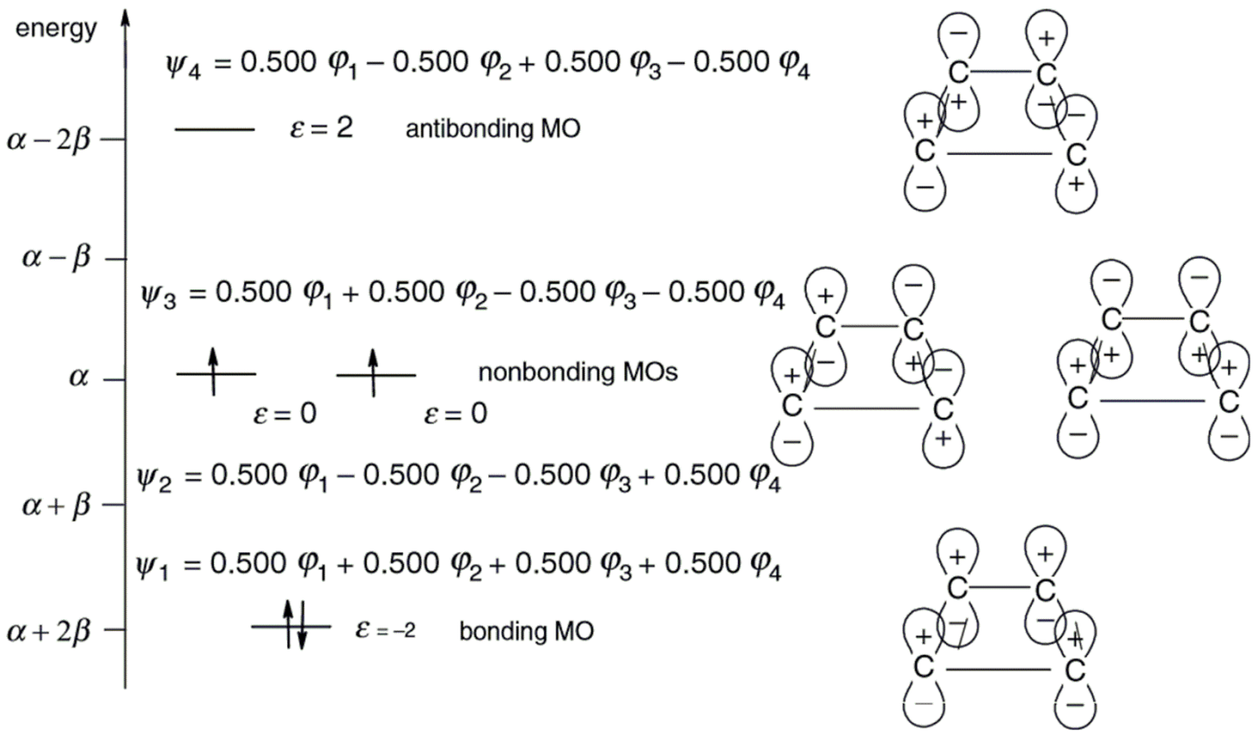


$$\begin{pmatrix} 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \end{pmatrix} =$$

$$\begin{pmatrix} 0.500 & 0.500 & 0.500 & 0.500 \\ 0.500 & -0.500 & 0.500 & -0.500 \\ 0.500 & -0.500 & -0.500 & 0.500 \\ 0.500 & 0.500 & -0.500 & -0.500 \end{pmatrix} \begin{pmatrix} -2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 0.500 & 0.500 & 0.500 & 0.500 \\ 0.500 & -0.500 & -0.500 & 0.500 \\ 0.500 & 0.500 & -0.500 & -0.500 \\ 0.500 & -0.500 & 0.500 & -0.500 \end{pmatrix}$$

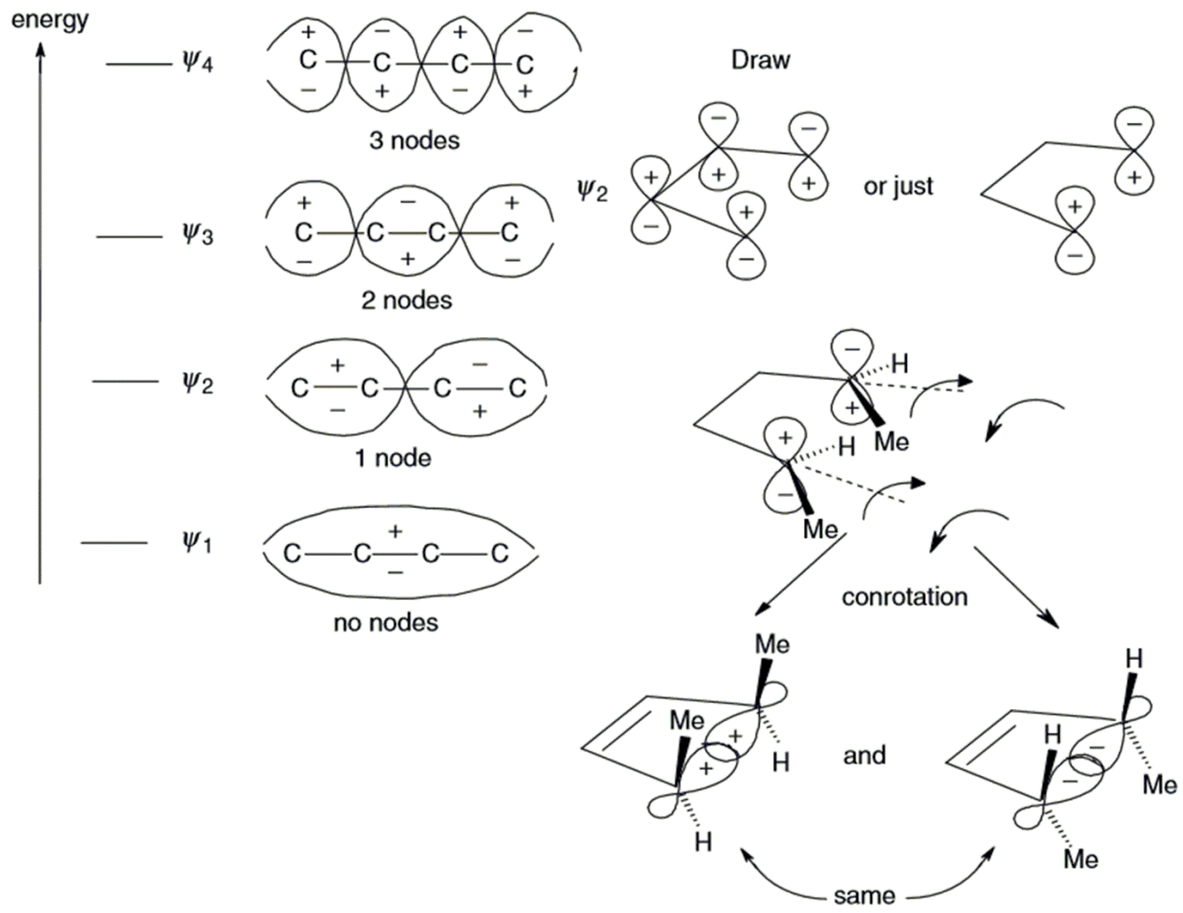
$\mathbf{v}_1 \quad \mathbf{v}_2 \quad \mathbf{v}_3 \quad \mathbf{v}_4$ $\quad \begin{pmatrix} \varepsilon_1 & 0 & 0 & 0 \\ 0 & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \varepsilon_3 & 0 \\ 0 & 0 & 0 & \varepsilon_4 \end{pmatrix}$

$\mathbf{C} \qquad \boldsymbol{\varepsilon} \qquad \mathbf{C}^{-1}$



- Nodal Properties of MOs
  - A plane where the phase of the wavefunction changes
  - The orbital energy increases as the nodal character increases

Butadiene, nodes, and orbital symmetry

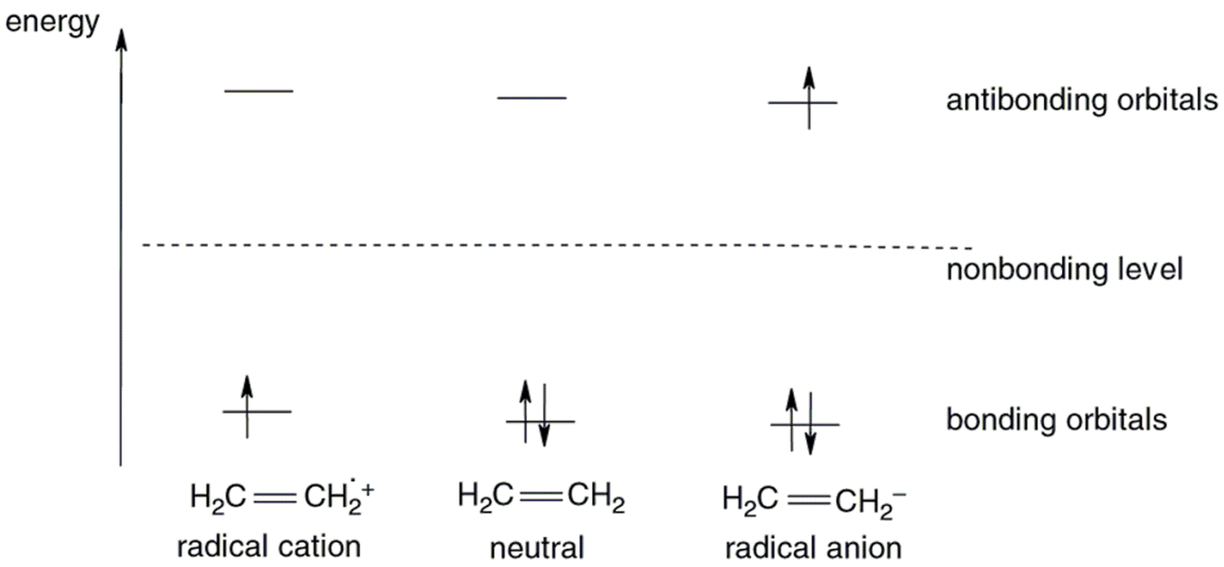


Intro to Quantum Chemistry

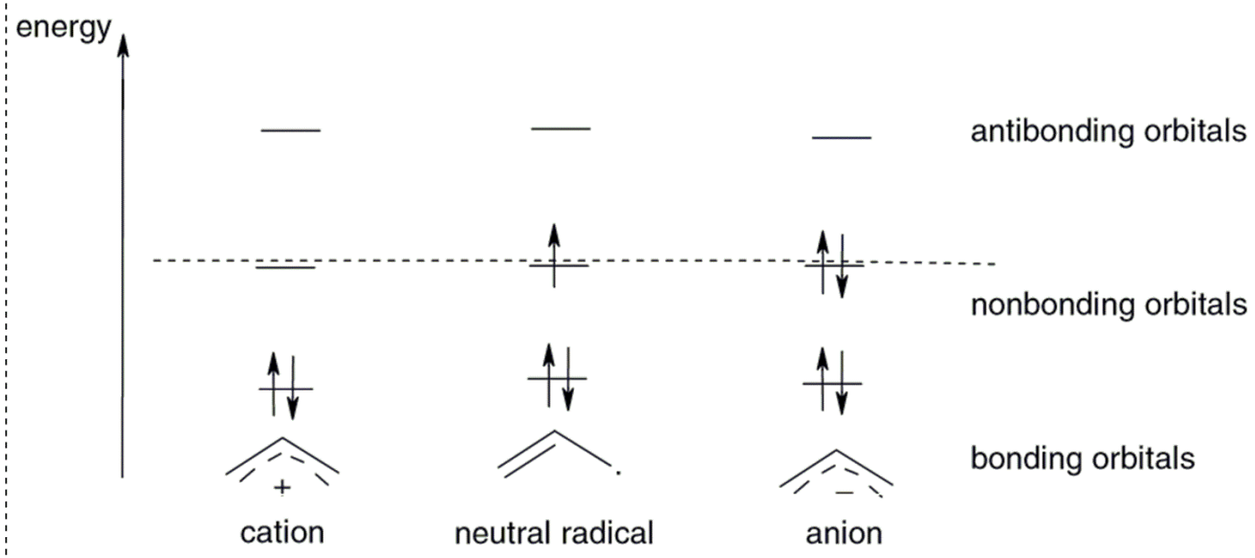
- Stability

– Orbital energy diagrams gives some sense of relative stability

Ethylene orbital energy diagram with differing number of electrons

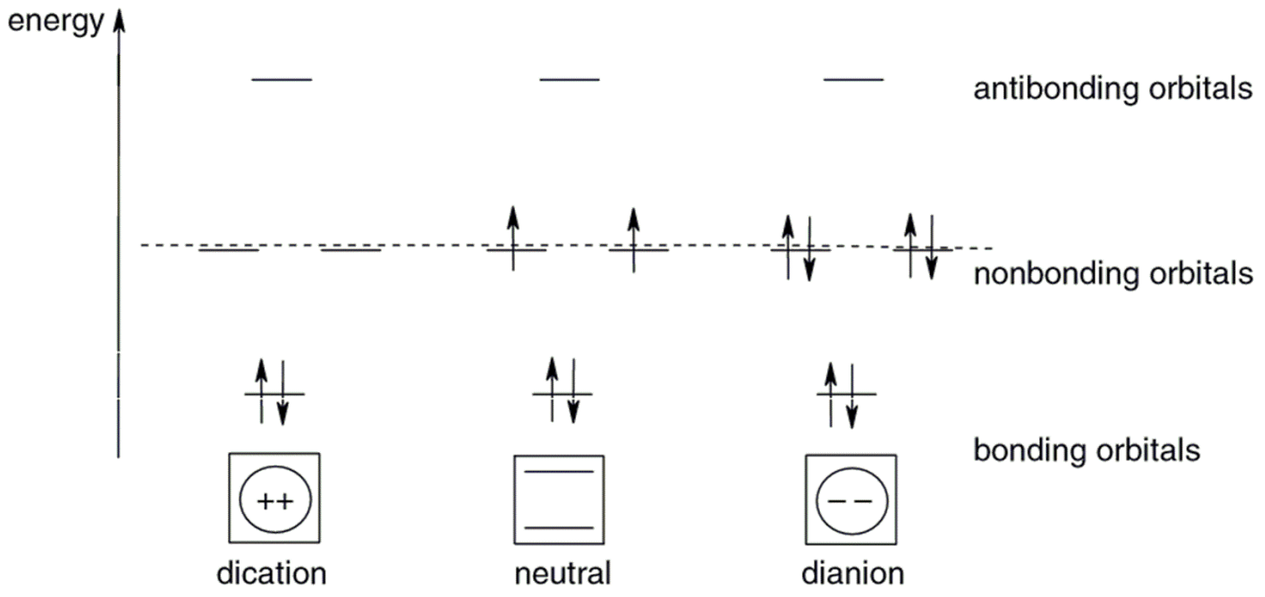


Allyl orbital energy diagram with differing number of electrons



– cation not readily undergoes oxidation
– neutral radical can be more easily oxidized since the electron is in a non-bonding orbital, with the same potential as the cation to be reduced
– anion expected to exhibit similar oxidation potential as the neutral radical, while it should be resistant to reduction.

Cyclobutadiene orbital energy diagram with differing number of electrons



Intro to Quantum Chemistry

Diagram shapes for acyclic systems

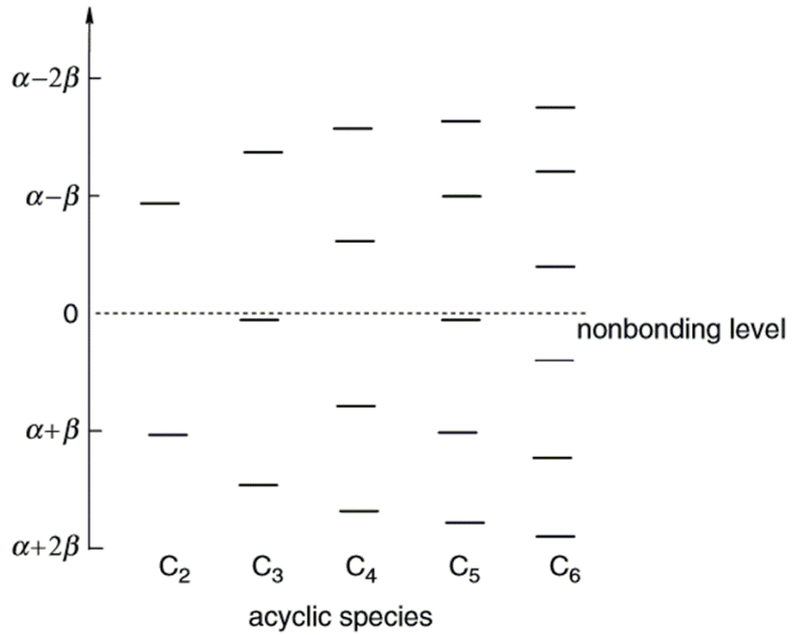
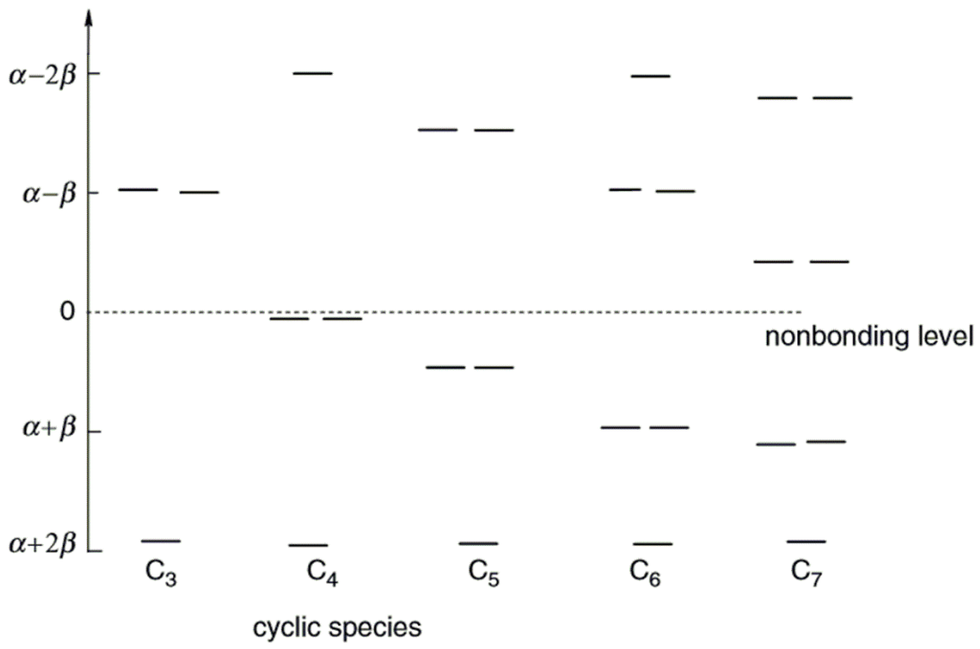
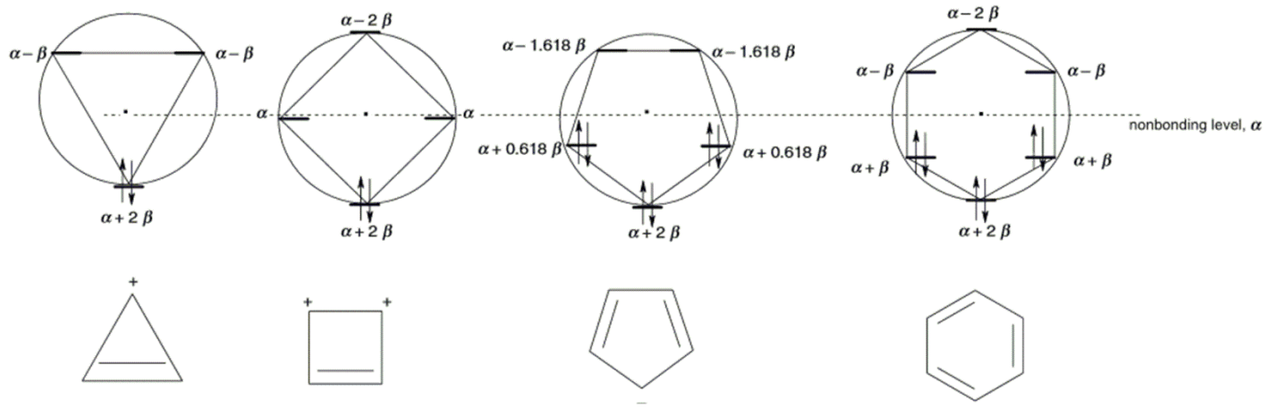


Diagram shapes for cyclic systems

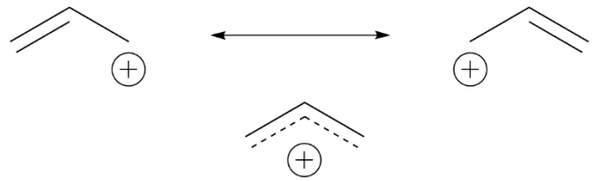


The 4n+2 π electron rule (n=0,1,2, ...) for aromaticity comes from Hückel theory



- Resonance Stabilization Energy

– Allyl cation



π electronic energy may by determined by the sum of the energy levels of the occupied orbitals

$$E_\pi(\text{prop. cation}) = 2(\alpha + 1.414\beta) = 2\alpha + 2.828\beta$$

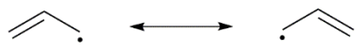
2π electron reference without resonance may be chosen as ethylene

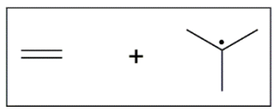
$$E_\pi(\text{reference}) = 2(\alpha + \beta) = 2\alpha + 2\beta$$

Resonance energy is then determined as;

$$\begin{aligned} E(\text{stab, cation}) &= E_\pi(\text{prop. cation}) - E_\pi(\text{reference}) \\ &= (2\alpha + 2.828\,\beta) - (2\alpha + 2\beta) = 0.828\beta \end{aligned}$$

Intro to Quantum Chemistry

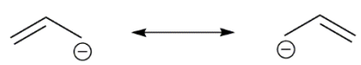
– Allyl (propyl) radical 

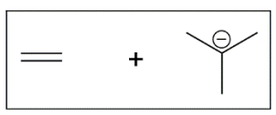
reference 

$$E_\pi(\text{prop. radical}) = 2(\alpha + 1.414\beta) + \alpha = 3\alpha + 2.828\beta$$

$$E_\pi(\text{reference}) = (2\alpha + 2\beta) + \alpha = 3\alpha + 2\beta$$

$$\begin{aligned} E(\text{stab, radical}) &= E_\pi(\text{prop. radical}) - E_\pi(\text{reference}) \\ &= (3\alpha + 2.828\beta) - (3\alpha + 2\beta) = 0.828\beta \end{aligned}$$

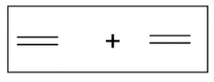
– Allyl (propyl) anion 

reference 

$$\begin{aligned} E(\text{stab anion}) &= E_\pi(\text{prop. anion}) - E_\pi(\text{reference}) \\ &= (4\alpha + 2.828\beta) - (4\alpha + 2\beta) = 0.828\beta \end{aligned}$$

- π allyl radical, cation, and anion all have the same resonance energy. Why?

– Cyclobutadiene 

reference 

$$E_\pi(\text{cyclobutadiene}) = 2(\alpha + 2\beta) + 2\ \alpha = 4\alpha + 4\beta$$

$$\begin{aligned} E(\text{stap, cyclobutadiene}) &= E_\pi(\text{cyclobutadiene}) - E_\pi(\text{reference}) \\ &= (4\alpha + 4\beta) - (4\alpha + 4\beta) = 0 \end{aligned}$$

– Cyclobutadiene dication 

reference 

$$E_\pi(\text{dication}) = 2(\alpha + 2\beta) = 2\alpha + 4\beta$$

$$E_\pi(\text{reference}) = 2\alpha + 2\beta$$

$$\begin{aligned} E(\text{stab, dication}) &= E_\pi(\text{dication}) - E_\pi(\text{reference}) \\ &= (2\alpha + 4\beta) - (2\alpha + 2\beta) = 2\beta \end{aligned}$$

- Cyclobutadiene gains no stabilization from resonance
- Cyclobutadiene dication has additional stabilization from resonance

- Bond Orders (BO)

- Describes number of electrons within bonding region

  $BO_{single} = 1$; $BO_{double} = 1$; $BO_{triple} = 1$;

- SHM Bond Order

  based on the bonded atoms' contributions to the MO's

$$B_{i,j} = 1 + \sum_{\text{all occ}} nc_i c_j$$

Ethene (4 electrons)

$$B_{i,j} = 1 + \sum_{\text{all occ}} nc_i c_j = 1 + 2(0.707)0.707 = 1 + 1.000 = 2.000$$

Ethene radical anion (5 electrons)

$$\begin{aligned} B_{i,j} = 1 + \sum_{\text{all occ}} nc_i c_j &= 1 + 2(0.707)0.707 + 1(0.707)(-0.707) \\ &= 1 + 1 - 0.500 = 1.500 \end{aligned}$$

Intro to Quantum Chemistry

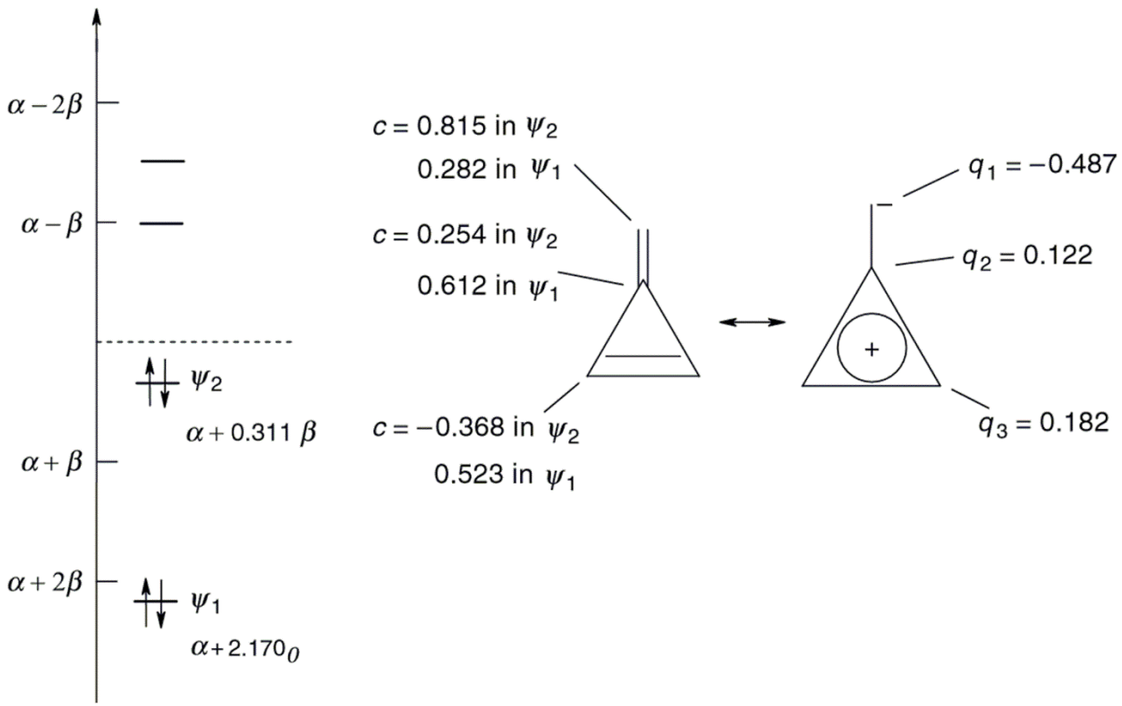
• Atomic Charges

- Describes extent to which a test charge is repelled or attracted to an atom
- Dependent on atomic contributions to the MOs

$$q_i = 1 - \sum_{\text{all occ}} nc_i^2$$

- A carbon with no π electrons would have q_i = +1

Methylenecyclopropane



$$q_1 = 1 - \sum_{\text{all occ}} nc_1^2 = 1 - \left[2(0.282)^2 + 2(0.815)^2\right] = 1 - 1.487 = -0.487$$

$$q_2 = 1 - \sum_{\text{all occ}} nc_2^2 = 1 - \left[2(0.612)^2 + 2(0.254)^2\right] = 1 - 0.878 = 0.122$$

$$q_3 = q_4 = 1 - \sum_{\text{all occ}} nc_3^2 = 1 - \left[2(0.523)^2 + 2(-0.368)^2\right] = 1 - 0.817 = 0.182$$

• SHM Strengths and Weaknesses

– Strengths

- Provides some limited insight into systems of π electrons

– Weaknesses

- Only provides insight into systems of π electrons
- Approximations are too severe to produce desirable accuracy levels

$$\int \phi_i \, \phi_j dv = S_{ij} = 1 \text{ or } 0$$

$$\int \phi_i \hat{H} \phi_j dv = H_{ij} = \alpha, \beta \text{ or } 0$$

– electron-electron repulsion is largely untreated

– electron spin is not considered

• Extended Hückel Theory (EHT)

– In SHM, a Fock matrix is formed and diagonalized to give the MO energies and coefficients

– EHT was formulated to remedy the deficiencies in the Fock matrix from SHM

– SHM Summary

- Basis set consists of only p orbitals which are supported by a sigma framework (sp, sp^2)
- orbital interactions (H_{ij}) are limited to α, β, or 0
- Fock matrix elements are not calculate (H_{ij} are not dependent on location)
- Overlap integrals (S_{ij}) are either 1 (adjacent) or 0 (not adjacent). This gives an overlap matrix of unity (**S** = **1**), which permits direct diagonalization of the Fock matrix (**H**). **HC = SCε = 1 = Cε**

  HC = Cε **H = CεC^{-1}**