3. **Linear Variation Method Boot Camp**

For a case of 3 basis functions it looks like this:

$$(H_{11} - S_{11}E)c_1 + (H_{12} - S_{12}E)c_2 + (H_{13} - S_{13}E)c_3 = 0$$

$$(H_{21} - S_{21}E)c_1 + (H_{22} - S_{22}E)c_2 + (H_{23} - S_{23}E)c_3 = 0$$

$$(H_{31} - S_{31})c_1 + (H_{32} - S_{32}E)c_2 + (H_{33} - S_{33}E)c_3 = 0$$

H_{ij} = Hamiltonian matrix

S_{ij} = Overlap matrix

Linear Variation with 2 orthonormal, real, basis functions

$$\Psi = c_1\,\Phi_1 + c_2\,\Phi_2$$

$$(H_{11} - E)\,c_1 + H_{12}\,c_2 = 0$$
$$H_{21}c_2 + (H_{22} - E)\,c_2 = 0$$

where $H_{12} = <\Phi_1|H|\Phi_2>$, the "interaction" of the two basis functions,
$H_{11} = <\Phi_1|H|\Phi_1>$, the "energy" of Φ_1,
$H_{22} = <\Phi_2|H|\Phi_2>$, the "energy" of Φ_2,
and $E = <\Psi|H|\Psi>$. the expectation value of the energy using the trial function.

For a non-trivial solution (c_1 and c_2 not both zero), the **determinant** of the matrix of numbers multiplying the coefficients c_1 and c_2 must vanish, i.e.,

$(H_{11} - \mathbf{E})\,(H_{22} - \mathbf{E}) - H_{21}\,H_{12} = 0$ quadratic equation; Solve for **E**

$E^2 - E(H_{11} + H_{22}) + (H_{11}H_{22} - H_{21}\,H_{12}) = 0$ quadratic

$$E_{\pm} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{21}H_{12}}}{2}$$

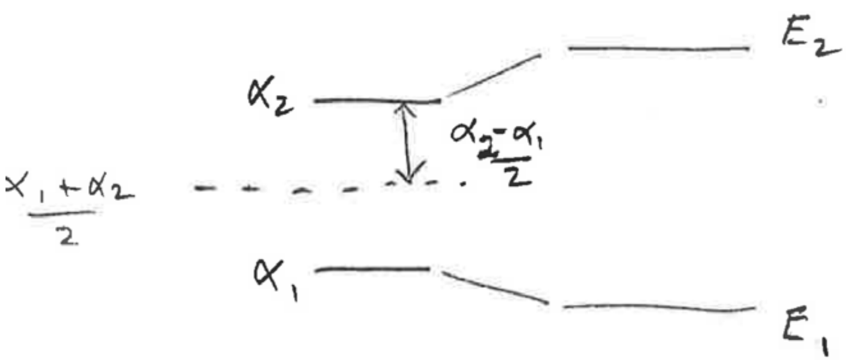
$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2}$$

Because H_{12} is real

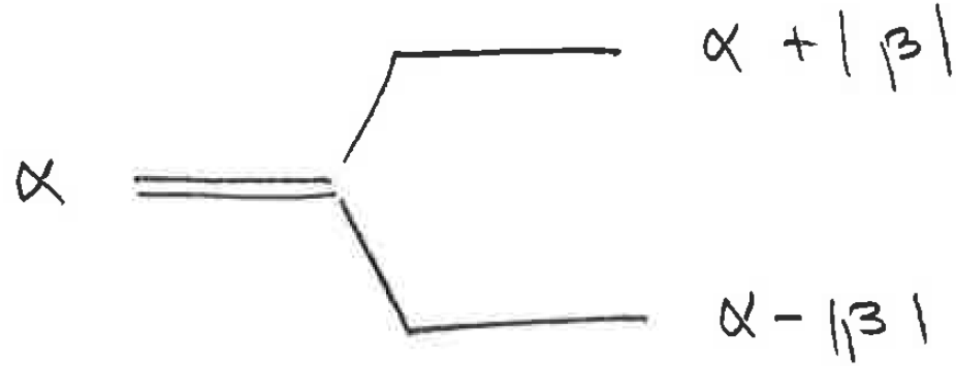
$$H=\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}$$

$$E = \frac{(\alpha_1+\alpha_2)}{2} \pm \sqrt{\frac{(\alpha_1-\alpha_2)^2}{2} + |\beta|^2}$$

Thus, we can already see that E must be either more positive than either α_1 and α_2 or more negative than both α_1 and α_2. That is



This is ALWAYS the case. Now, back to the quadratic formula, you can see how it says the same thing and also that the splitting is symmetrical and increases as β increases - - independent of the sign of β. Also note that if ϕ_1 and ϕ_2 are degenerate, i.e., if $\alpha_1 = \alpha_2$, then the splitting is just 2β and $E = \alpha \pm \beta$.



Case of Two Orthonormal Functions

Solving for $\Psi = c_1\,\Phi_1 + c_2\,\Phi_2$ means solving for $\mathbf{c_1}$ and $\mathbf{c_2}$

$$\begin{aligned}(H_{11} - E)c_1 &+ (H_{12})c_2 = 0 \\ (H_{21})c_1 &+ (H_{22} - E)c_2 = 0\end{aligned} \quad = \quad \begin{aligned}(\alpha_1 - E)c_1 &+ \beta c_2 = 0 \\ \beta c_1 &+ (\alpha_2 - E)c_2 = 0\end{aligned}$$

Solving for c_1 and c_2

You might think that, with two equations and two unknowns, you could solve for both c_1 and c_2; not so. There are actually three equations since $c_1^2 + c_2^2 = 1$ for normalization. The other two are not independent. From them you can only get the ratio of c_1/c_2. You may use either equation and you will get the same result for c_1/c_2, even though it doesn't "look" like you would.

$$\frac{c_1}{c_2} = \frac{-\beta}{\alpha_1 - E} = \frac{\alpha_2 - E}{-\beta}$$

The determinant from the N simultaneous homogeneous equations = 0 is a constraint that means that you can only solve for the *ratio* of the coefficients.

Case of Two Orthonormal Functions

$$(\alpha_1 - E)c_1 \quad + \quad \beta c_2 \quad = 0$$

$$\beta c_1 \quad + \quad (\alpha_2 - E)c_2 \quad = 0$$

The determinant from the N simultaneous homogeneous equations = 0 is a constraint that means that you can only solve for the *ratio* of the coefficients.

First Eq.: $(\alpha_1 - E)c_1 = -\beta c_2$

$$\frac{c_1}{c_2} = \frac{-\beta}{(\alpha_1 - E)}$$

Second Eq.: $\beta c_1 = -(\alpha_2 - E)c_2$

$$\frac{c_1}{c_2} = \frac{-(\alpha_2 - E)}{\beta}$$

$$\frac{c_1}{c_2} = \frac{-\beta}{(\alpha_1 - E)} = \frac{-(\alpha_2 - E)}{\beta} \quad \text{because:}$$

Why must these be equal?

$$(\alpha_1 - E)(\alpha_2 - E) - \beta\beta = 0 = \text{determinant} = 0$$

2) ***If the interaction is negative, i.e..***

If H_{12} is ***negative*** the **lower-energy** eigenvector coefficients have ***same*** signs and those for
the **higher energy** are ***opposite*** in sign. Vice versa if the interaction is positive.

If H_{12} ***POSITIVE, then*** **lower-energy** eigenvector coefficients have ***opposite*** signs

$$\frac{c_1}{c_2} = \frac{-\beta}{(\alpha_1 - E)}$$

Denominator is + for lower state

$$\frac{c_1}{c_2} = \frac{-(\alpha_2 - E)}{\beta}$$

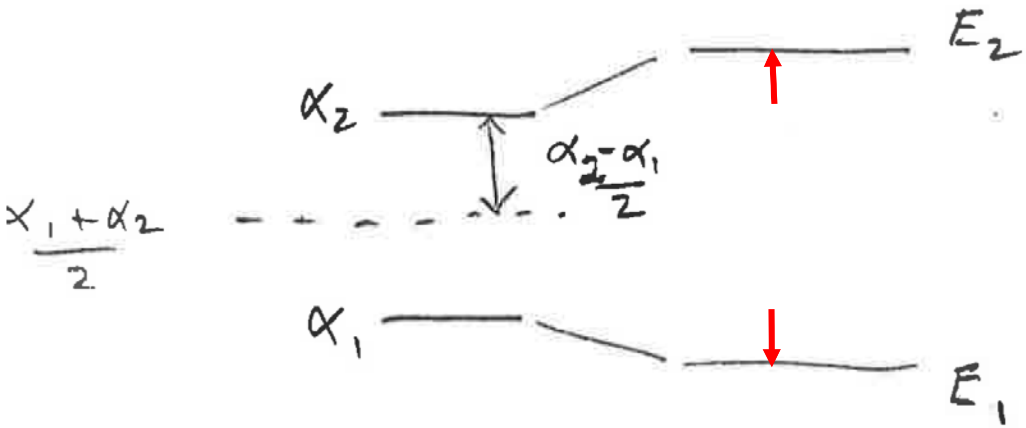
Numerator is + for upper state higher E > α_2

The sign of β depends only on the phases chosen arbitrarily for the basis set, because:

the Hamiltonian is **ALWAYS NEGATIVE** in quantum chemistry, due to Coulomb's Law and electrons seeking to be near positive nuclear charge.

4) **If the energies of the basis functions (the diagonal elements) are not equal,**

the lowest-energy eigenvector will be mostly the lower-energy basis function and the higher energy eigenvector will be mostly the higher energy basis function.



$$E = \frac{(\alpha_1 + \alpha_2)}{2} \pm \sqrt{\frac{(\alpha_1 - \alpha_2)^2}{2} + |\beta|^2}$$

$$E_2 - \alpha_2 = \frac{(\alpha_1 + \alpha_2)}{2} - \alpha_2 \pm \sqrt{\frac{(\alpha_1 - \alpha_2)^2}{2} + |\beta|^2}$$

$$E_2 - \alpha_2 = \frac{(\alpha_1 - \alpha_2)}{2} \pm \sqrt{\frac{(\alpha_1 - \alpha_2)^2}{2} + |\beta|^2}$$

Raising: $E_2 - \alpha_2$

Lowering: $\alpha_1 - E_2$

are NEVER larger than $|\beta|$ as shown by

$$\frac{c_1}{c_2} = \frac{-\beta}{(\alpha_1 - E)}$$

$$\frac{c_1}{c_2} = \frac{-(\alpha_2 - E)}{\beta}$$

$c_{low}{}^2 \geq c_{high}{}^2$ for lower energy state

$c_{high}{}^2 \geq c_{low}{}^2$ for higher energy state

3. **Linear Variation Method**

(c) Demonstrate the following general facts concerning linear variation calculations for two orthogonal basis functions. Give at least ***two*** numerical examples for each case.

1) ***One of the eigenvalues is <u>always</u> lower than the lowest diagonal element; the other is <u>always</u> higher than the highest diagonal element, no matter what the sign of the interaction (off-diagonal element). In other words, mixing always pushes the two states apart.***

2) ***If the interaction is negative, the lower-energy eigenvector coefficients are the same sign and those for the higher energy are opposite in sign. Vice versa if the interaction is positive.***

3) ***When the diagonal elements are equal (degenerate) the two basis functions are mixed equally, no matter what the interaction is (provided it is not zero) and the eigenvalues are equal to the diagonal element $\pm$ the off diagonal element.***

4) ***If the energies of the basis functions (the diagonal elements) are not equal, the lowest-energy eigenvector will be mostly the lower-energy basis function and the higher energy eigenvector will be mostly the higher energy basis function.***

5) ***The farther apart in energy the two basis functions are, the less they mix (assuming a constant interaction).***

6) ***The larger the magnitude of the interaction, the more the mixing (assuming a constant diagonal energy difference).***

7) ***Adding a constant to both diagonal element shifts the eigenvalues by this constant and has no effect on the eigenvectors. (This is known as shifting the zero of energy.)***

To find the eigenvalues and eigenvectors either use the equation in part 1 or use a computer program, e.g. from the internet:

http://www.colby.edu/chemistry/PChem/eigen.html,

http://www.bluebit.gr/matrix-calculator/ , etc.

0 1 0 0 0 1
1 0 1 0 0 0
0 1 0 1 0 0
0 0 1 0 1 0
0 0 0 1 0 1
1 0 0 0 1 0

8) **Perturbation limit:**

$$\begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}$$

For the matrix above , where $\alpha_1 < \alpha_2$ and $|\beta| << (\alpha_2 - \alpha_1)$, and where

$\psi_1 = c_{11}\Phi_1 + c_{21}\Phi_2$, and $\psi_2 = c_{12}\Phi_1 + c_{22}\Phi_2$, show that:

$$E_1 = \alpha_1 - \frac{\beta^2}{\alpha_2 - \alpha_1}; c_{11} \approx 1, c_{21} \approx \frac{-\beta}{\alpha_2 - \alpha_1}$$

$$E_2 = \alpha_2 + \frac{\beta^2}{\alpha_2 - \alpha_1}; \quad c_{12} \approx \frac{\beta}{\alpha_2 - \alpha_1}, \quad c_{22} \approx 1$$

From this point on we will DIAGONALIZE the H matrix to get the eigenvalues and eigenvectors (coefficients)

From this point on we will DIAGONALIZE the H matrix to get the eigenvalues and eigenvectors (coefficients)

Matrices

It is virtually impossibe to deal with these problems without using matrices. Consider the matrix

$$\mathbb{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix}$$

Note how the subscripts say row - column. The 1st subscript tells you which row the element is in; the 2nd tells which column. Now we want to restate the set of equations

$$(H_{11}-E)c_1 + H_{12}c_2 + H_{13}c_3 = 0$$

$$H_{21}c_1 + (H_{22}-E)c_2 + H_{23}c_3 = 0$$

$$H_{31}c_1 + H_{32}-c_2 + (H_{33}-E)c_3 = 0$$

as $H_{11}c_1 + H_{12}c_2 + H_{13}c_3 = Ec_1$

$$H_{21}c_1 + H_{22}c_2 + H_{23}c_3 = Ec_2$$

$$H_{31}c_1 + H_{32}c_2 + H_{33}c_3 = Ec_3$$

as $$H_{11}c_1 + H_{12}c_2 + H_{13}c_3 = Ec_1$$

$$H_{21}c_1 + H_{22}c_2 + H_{23}c_3 = Ec_2$$

$$H_{31}c_1 + H_{32}c_2 + H_{33}c_3 = Ec_3$$

or $$\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

This results from the rule for matrix multiplication $\mathbf{A}\,\mathbf{B} = \mathbf{C}$ which says, for example: the element in the 2nd row and 3rd column of **C**, (C_{23}), is determined by the dot product (also called inner product and scalar product) of the 2nd <u>row</u> of **A** and the 3rd <u>column</u> of **B**.

$$C_{23} = (A_{21}\ A_{22}\ A_{23}) \begin{pmatrix} B_{13} \\ B_{23} \\ B_{33} \end{pmatrix} = A_{21}B_{13} + A_{22}B_{23} + A_{23}B_{33}$$

Notice how the outside indices are always 2 3 and the inside ones are always the same and range from 1 to N (the dimension of the matrix). In a more compact notation:

$$C_{ij} = \sum_{k=1}^{N} A_{ik}B_{kj}$$

At any rate the matrix equation

$$\mathbb{H} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = E_1 \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = \begin{pmatrix} c_{11}E_1 \\ c_{21}E_1 \end{pmatrix}$$

says that the column of coefficients is the eigenvector of the Hamiltonian matrix, $\mathbb{H}$, with eigenvalue, E_1. Likewise $\mathbb{H} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} = \begin{pmatrix} c_{12}E_2 \\ c_{22}E_2 \end{pmatrix}$

Putting them together gives

$$\mathbb{H} \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

$$\mathbf{H\,C = C\,E}$$

We will be seeing computer output in which the molecular orbitals are given as a "C" matrix; the columns of the matrix, the eigenvectors, are the coefficients of the AO's. The MO, ψ, is given as

$$\psi = c_1 \Phi_1 + c_2 \Phi_2 + \ldots . c_N \Phi_N.$$

Diagonalizing a matrix to get eigenvalues and eigenvectors

$$\mathbb{H}\mathbb{C} = \mathbb{C}\ \mathbb{E}$$

$$\mathbb{C}^{-1}\mathbb{H}\mathbb{C} = \mathbb{C}^{-1}\ \mathbb{C}\ \mathbb{E} = \mathbb{I}\mathbb{E} = \mathbb{E}$$

where, $\mathbb{E}$ is a diagonal matrix that has the eigenvalues on the diagonal.

$\mathbb{E} =$ E_1 0 0 0...

0 E_2 0 0 ...

0 0 E_3 0 ...

For a real, symmetric matrix: $\mathbb{C}^{-1} = \mathbb{C}^{\mathrm{TRANSPOSE}}$

For a Hermitian matrix: $\mathbb{C}^{-1} = \mathbb{C}^{\mathrm{ADJOINT}} = [\mathbb{C}^{\mathrm{TRANSPOSE}}]^*$