Variational Principle

Applied to Diatomics

Variational Principle

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \geq E_o$$

short for <E>

true ground state energy

denominator is just to allow use of an unnormalized ψ (for convenience)

Essential equations for applying the Variational Principle

may be unnormalized

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

MO

$$\psi = \sum c_i \psi_{AO_i} \qquad \text{(LCAO-MO)}$$

$$\frac{\partial E}{\partial c_i} = 0$$

Simplify for purposes of example

Consider diatomic molecule, limit sum to 2 terms, and simplify the notation:

$$\psi = c_A\psi_A + c_B\psi_B = c_A A + c_B B$$

where (A) and (B) indicate wavefunctions centered on nuclei A and B

$$\frac{\partial E}{\partial c_A} = 0 \quad \text{and} \quad \frac{\partial E}{\partial c_B} = 0$$

We will assume that A and B are real AOs (e.g. 1s orbitals) for our example (just to keep the notation simple). The results, though, generalize to complex AOs.

Expand Normalization Integral

$$\int \psi^* \psi d\tau = \int (c_A A + c_B B) \cdot (c_A A + c_B B) d\tau$$

$$= c_A^2 \int A^2 d\tau + c_B^2 \int B^2 d\tau + 2c_A c_B \int AB d\tau$$

$$= c_A^2 + c_B^2 + 2c_A c_B S$$

Note: S is the overlap integral

Expand Hamiltonian Integral

$$\int \psi^* \hat{H} \psi d\tau = \int (c_A A + c_B B)\, \hat{H} (c_A A + c_B B) d\tau$$

$$= c_A^2 \int A\hat{H}A d\tau + c_B^2 \int B\hat{H}B d\tau + c_A c_B \int A\hat{H}B d\tau + c_A c_B \int B\hat{H}A d\tau$$

$$= c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB}$$

$$= c_A^2 \alpha_A + c_B^2 \alpha_B + 2 c_A c_B \beta$$

Notes:

- $\bar{\bar{H}}$ is called the Hamiltonian matrix and its elements are H_{AA}, H_{BB} etc; $H_{AB}=H_{BA}$ by Hermiticity.
- An alternative nomenclature is: $\alpha_A=H_{AA}$, $\alpha_B=H_{BB}$, $\beta=H_{AB}$
- α_A and H_{AA} are called Coulomb integrals
- β and H_{AB} are called Exchange integrals

Put it together and take derivatives

$$E = \frac{c_A^2\alpha_A + c_B^2\alpha_B + 2c_Ac_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS}$$

$$\frac{\partial E}{\partial c_A} = \frac{2c_A\alpha_A + 2c_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS} - (2c_A + 2c_BS)\frac{c_A^2\alpha_A + c_B^2\alpha_B + 2c_Ac_B\beta}{(c_A^2 + c_B^2 + 2c_Ac_BS)^2}$$

E

$$= \frac{2}{c_A^2+c_B^2+2c_Ac_BS}[(\alpha_A - E)c_A + (\beta - ES)c_B] = 0$$

Thus: $\boldsymbol{(\alpha_A - E)c_A + (\beta - ES)c_B}$ **= 0**

Same reasoning for $\frac{\partial E}{\partial c_B}$ yields: $\boldsymbol{(\beta - ES)c_A + (\alpha_B - E)c_B}$ **= 0**

Rewrite as matrix equation

$$\begin{pmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

- Need to solve simultaneously for E, c_A, and c_B
- There will be 2 possible values of E. Each corresponds to a different pair of values for c_A and c_B.

Solving for E, c_A and c_B

The only solutions, other than the trivial solution $c_A = c_B = 0$, are when the **secular determinant** is zero:

$$\begin{vmatrix} \boldsymbol{\alpha_A - E} & \boldsymbol{\beta - SE} \\ \boldsymbol{\beta - SE} & \boldsymbol{\alpha_B - E} \end{vmatrix} = \mathbf{0}$$

Which becomes: $$\boldsymbol{(\alpha_A - E)(\alpha_B - E) - (\beta - SE)^2 = 0}$$

There will be two solutions for E (E_+ and E_-) because the equation is quadratic.

The expressions are complicated in general, but for homonuclear diatomics, $\alpha_A = \alpha_B$ and the expressions simplify to:

$$\boldsymbol{E_+ = \frac{\alpha_A+\beta}{1+S}} \quad \textbf{and} \quad \boldsymbol{E_- = \frac{\alpha_A-\beta}{1-S}}$$

This looks quite different from our earlier expressions for $E_{1\sigma}$ and $E_{2\sigma}$

$$\boldsymbol{E_{1\sigma} = E_{1s} + \frac{j_o}{R} - \frac{j+k}{1+S}} \quad \textbf{and} \quad \boldsymbol{E_{2\sigma} = E_{1s} + \frac{j_o}{R} - \frac{j-k}{1-S}}$$

But actually, they are equivalent when A = B = ψ_{1s} (good homework problem?).

Determining c_A and c_B

Once E_+ and E_- are known, each can be substituted for E in the original equations, which can then be solved for c_A and c_B. Note that E_+ and E_- each give their own values of c_A and c_B.

$$(\alpha_A - E)c_A + (\beta - SE)c_B = 0$$

$$(\beta - SE)c_A + (\alpha_B - E)c_B = 0$$

Remembering that for homonuclear diatomics, $\alpha_A = \alpha_B$, little algebra using either equation above shows:

For $E = E_+$: $\quad c_A = c_B$

To solve for c_A explicitly, we need to make use of the normalization condition:

$c_A^2 + c_B^2 + 2c_Ac_BS = 1$ from which we find: $\quad c_A = c_B = \dfrac{1}{\sqrt{2(1+S)}}$

Likewise, for

$$\boldsymbol{E = E_{-}:} \quad \boldsymbol{c_A = -c_B = \frac{1}{\sqrt{2(1-S)}}}$$

Also just as we found before!

Heteronuclear diatomics

Expressions for E_+ and E_- more complicated than for homonuclear diatomics. Expressions obtained using a simplifying approximation are given in the text. Two important points:

- E_+ is closer to energy of lower-energy AO; E_- is closer to energy of higher-energy AO.
- ψ_+ contains greater contribution lower-energy AO; ψ_- contains greater contribution from higher-energy AO

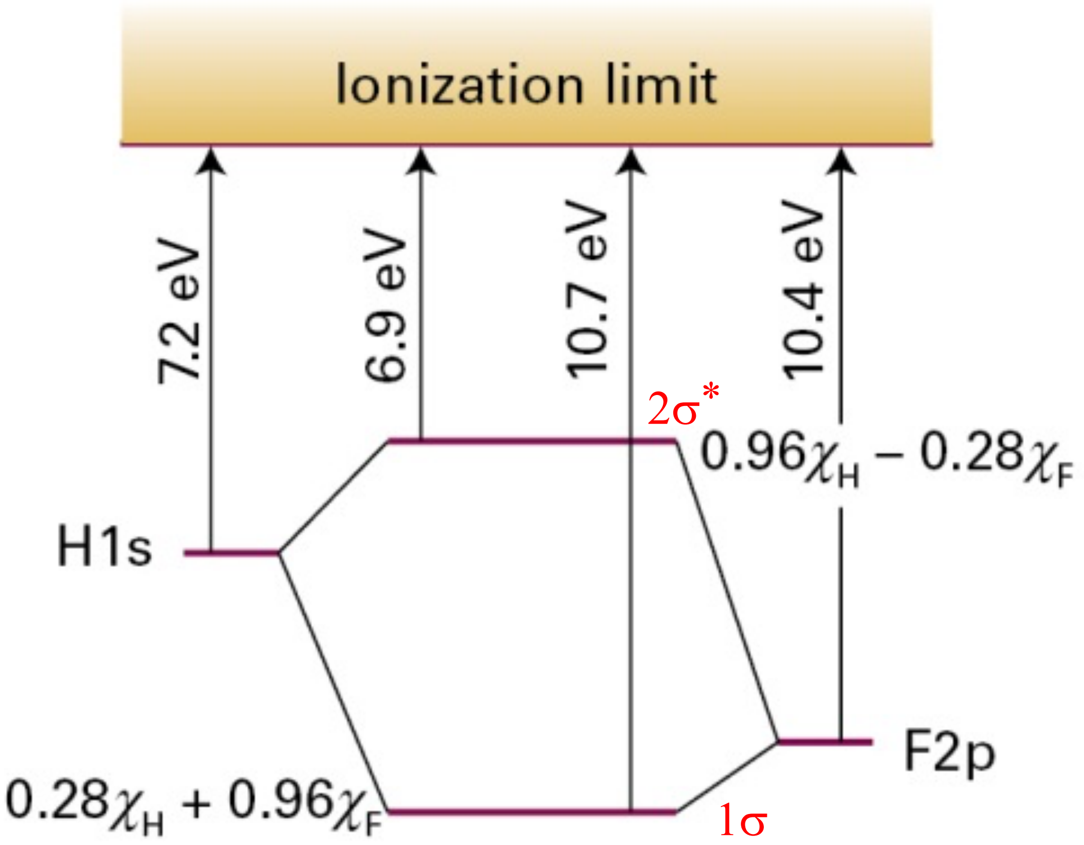

Figure 10D.3 The estimated energies of the atomic orbitals in HF and the molecular orbitals they form.

Generalizing method with matrix notation (not required)

Begin with the equations:

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0$$
$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0$$

And rewrite them in $H_{AA,}$ H_{AB} etc. notation:

$$(H_{AA} - E)c_A + (H_{AB} - ES)c_B = 0$$
$$(H_{BA} - ES)c_A + (H_{BB} - E)c_B = 0$$

This can be re-written in matrix format:

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Repeating:

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This can be rewritten:

$$\left(\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} - E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \right) \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This can be rearranged:

Hamiltonian matrix: $\bar{\bar{H}}$

Overlap matrix: $\bar{\bar{S}}$

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

Vector: $\bar{c}$

The matrix equation can be rewritten compactly:

$$\bar{\bar{\boldsymbol{H}}}\bar{\boldsymbol{c}} = \boldsymbol{E}\bar{\bar{\boldsymbol{S}}}\bar{\boldsymbol{c}}$$

Kind of eigenvalue equation, because it can be rewritten as $\bar{\bar{\boldsymbol{M}}}\bar{\boldsymbol{c}} = \boldsymbol{E}\bar{\boldsymbol{c}}$ where $\bar{\bar{\boldsymbol{M}}} = \bar{\bar{\boldsymbol{S}}}^{-1}\bar{\bar{\boldsymbol{H}}}$.

- Matrix $\bar{\bar{M}}$ is like an operator
- Vector $\bar{c}$ is like an eigenfunction
- Scalar E is like an eigenvalue

There will be as many solutions E_i, $\bar{c}_i$ as there are rows and columns in the matrices. All of these can be combined by defining a matrix $\bar{\bar{c}}$ whose columns are each of the vectors $\bar{c}_i$ and another matrix, $\bar{\bar{E}}$, whose diagonal elements are the scalars E_i (all other elements are zero):

$$\begin{pmatrix} \boldsymbol{E_1} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{E_2} \end{pmatrix}$$

The new equation is:

$$\bar{\bar{\boldsymbol{H}}}\bar{\bar{\boldsymbol{c}}} = \bar{\bar{\boldsymbol{S}}}\bar{\bar{\boldsymbol{c}}}\bar{\bar{\boldsymbol{E}}}$$

Rearrange matrix equation

$$\bar{\bar{\boldsymbol{H}}}\bar{\bar{\boldsymbol{c}}} = \bar{\bar{\boldsymbol{S}}}\bar{\bar{\boldsymbol{c}}}\bar{\bar{\boldsymbol{E}}}$$

Multiply from the left by $\bar{\bar{\boldsymbol{S}}}^{-1}$

$$\bar{\bar{\boldsymbol{S}}}^{-1}\bar{\bar{\boldsymbol{H}}}\bar{\bar{\boldsymbol{c}}} = \bar{\bar{\boldsymbol{S}}}^{-1}\bar{\bar{\boldsymbol{S}}}\bar{\bar{\boldsymbol{c}}}\bar{\bar{\boldsymbol{E}}} = \bar{\bar{\boldsymbol{c}}}\bar{\bar{\boldsymbol{E}}}$$

Multiply from the left by $\bar{\bar{\boldsymbol{c}}}^{-1}$

$$\bar{\bar{\boldsymbol{c}}}^{-1}\bar{\bar{\boldsymbol{S}}}^{-1}\bar{\bar{\boldsymbol{H}}}\bar{\bar{\boldsymbol{c}}} = \bar{\bar{\boldsymbol{c}}}^{-1}\bar{\bar{\boldsymbol{c}}}\bar{\bar{\boldsymbol{E}}} = \bar{\bar{\boldsymbol{E}}}$$

Thus, by finding matrix inverses and multiplying by them, we have:

$$\bar{\bar{c}}^{-1}\bar{\bar{S}}^{-1}\bar{\bar{H}}\bar{\bar{c}} = \bar{\bar{E}}$$

The important things to recognize:

- $\bar{\bar{H}}$ and $\bar{\bar{S}}$ are created from the Hamiltonian and the AOs (all known).
- $\bar{\bar{E}}$ and $\bar{\bar{c}}$ are the unknowns we need to solve for.

Note:

- $\bar{\bar{E}}$ is a diagonal matrix (has nonzero entries only along the diagonal).
- Finding the matrix $\bar{\bar{c}}$ that "diagonalizes" $\bar{\bar{S}}^{-1}\bar{\bar{H}}$ {this product is itself a matrix ($\bar{\bar{M}}$ from earlier slide)} is called "diagonalizing."
- Finding the inverse of a matrix and diagonalizing a matrix are operations that computers are great at.

Why did we go through all this math if the results are the same as we got earlier with our simpler approach?

- Earlier, we *assumed* that $c_B = c_A$ for a homonuclear diatomic bonding orbital. Now we have proven it.
- The earlier approach only applied to homonuclear diatomics. Now we can handle heteronuclear diatomics, too.
- The new approach, based on the variational principle, can be generalized to
  - more than 2 AOs in the sum for a given MO
  - larger molecules.
- We will use a simplified form of this approach for polyatomics in the next section.

→ The variational principle is the foundation for most computer approaches for calculating the electronic structures of molecules.