

What are you working on?

On what molecule do you want to do quantum chemistry?

Linear Variation

$$\Psi = c_1\phi_1 + c_2\phi_2$$

Wondering how can adding in a higher energy state LOWERS E???

$$E = \int (c_1\phi_1 + c_2\phi_2)H(c_1\phi_1 + c_2\phi_2)d\tau$$

$$= c_1^2 H_{11} + 2c_1c_2 H_{12} + c_2^2 H_{22}$$

$$= \left[c_1^2 H_{11} + c_2^2 H_{22} \right] + 2c_1c_2 H_{12}$$

$$c_1^2 H_{11} + c_2^2 H_{22} \quad \text{This is just the weighted average}$$

$$2c_1c_2 H_{12}$$

If H12 is negative, then c1 and c2 must have the same sign to lower the E

If H12 is positive, then c1 and c2 must have the opposite signs to lower the E

At any rate the matrix equation

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

says that the column of coefficients is the eigenvector of the Hamiltonian

matrix, H , with eigenvalue, E_1 . Likewise $H \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} = \begin{pmatrix} c_{12} E_2 \\ c_{22} E_2 \end{pmatrix}$

Putting them together gives

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

$$H C = C E$$

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

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_N \phi_N$$

Diagonalizing a matrix to get eigenvalues and eigenvectors

$$HC = C E$$

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

For a Hermitian matrix: $C^{-1} = C^{\text{ADJOINT}} = C^{\text{TRANSPOSE} *}$

$$C^{\text{T}} HC = C^{\text{T}} C E = I E = E$$

where, E is a diagonal matrix that has the eigenvalues on the diagonal.

$$E = \begin{matrix} E_1 & 0 & 0 & 0 & \dots \\ 0 & E_2 & 0 & 0 & \dots \\ 0 & 0 & E_3 & 0 & \dots \end{matrix}$$

A symmetric real matrix is Hermitian

$$\begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}^T \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{21} \\ c_{12} & c_{22} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}$$

recall: $c_{11}^2 + c_{21}^2 = 1$, $c_{11}c_{12} + c_{21}c_{22} = 0$

$$\begin{pmatrix} c_{11} & c_{21} \\ c_{12} & c_{22} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I = \text{identity matrix}$$

3. Linear Variation Method **NON-Orthogonal basis**

$$(H_{11} - S_{11}E)C_1 + (H_{12} - S_{12}E)C_2 + (H_{13} - S_{13}E)C_3 = 0$$

$$(H_{21} - S_{21}E)C_1 + (H_{22} - S_{22}E)C_2 + (H_{23} - S_{23}E)C_3 = 0$$

$$(H_{31} - S_{31}E)C_1 + (H_{32} - S_{32}E)C_2 + (H_{33} - S_{33}E)C_3 = 0$$

$$HC = CE \quad \text{Orthonormal}$$

$$HC = SC E \quad \text{NON-Orthogonal}$$

Recall that the columns of the C matrix are the eigenvectors

Let's pause to look at some actual eigenvectors output from a Gaussian 09 output file

Below is an input file for an ab initio calculation of the ground state energy Hartree Fock electronic energy for the hydroxide ion

stands for Hartree-Fock calculation with a basis set of Slater Type Orbital made from 3 Gaussian functions

output all MO eigenvectors

```
# hf/sto-3g pop=full
```

OH- singlet state paired electrons spin $S=0$ multiplicity
= $2S+1 = 1$ with charge = -1

```
-1 1  
8 0. 0. 0.  
1 0 0. 1.
```

Cartesian coordinates , x,y,z, in free format (requires decimal points)

Atomic numbers of the atoms (or type O and H or o and h)

Small part of the output file

SCF Done: E(RHF) = -74.0615732889 A.U. after 7 cycles
Conv = 0.3902D-09 -V/T = 1.9748

Population analysis using the SCF density.

Orbital symmetries:

Occupied (SG) (SG) (SG) (PI) (PI)
Virtual (SG)

The electronic state is 1-SG.

Alpha occ. eigenvalues -- -19.38926 -0.58791 0.07224 0.24593 0.24593
Alpha virt. eigenvalues -- 1.21168

Molecular Orbital Coefficients:

MO energies		coefficients				
		1	2	3	4	5
		O	O	O	O	O
Eigenvalues	--	-19.38926	-0.58791	0.07224	0.24593	0.24593
1	1 O 1S	0.99428	-0.23774	0.11015	0.00000	0.00000
2	2S	0.02449	0.86833	-0.57415	0.00000	0.00000
3	2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	2PY	0.00000	0.00000	0.00000	1.00000	0.00000
5	2PZ	-0.00351	-0.05761	-0.54037	0.00000	0.00000
6	2 H 1S	-0.00644	0.26686	0.67815	0.00000	0.00000

columns are the eigenvectors = LCAO coefficients

MO energies		6
		V
Eigenvalues	--	1.21168
1	1 O 1S	0.08774
2	2S	-0.54857
3	2PX	0.00000
4	2PY	0.00000
5	2PZ	0.96100
6	2 H 1S	0.99946

Note: Because the Slater orbitals have NO RADIAL NODES (spherical), the 1s and 2s become mixed to create the nodes

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

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

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

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

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

\mathbf{C} , (C_{23}), is determined by the dot product (also called inner product

and scalar product) of the 2nd row of \mathbf{A} and the 3rd column of \mathbf{B} .

$$HC = SCE$$

S is diagonalized in the usual way: $SA = AI$; $A^{-1}SA = A^{-1}AI = I$
because the eigenvalues of S are all = 1 if normalized basis

Now insert I cleverly a couple of places:

$$HAA^{-1}C = SAA^{-1}C \quad E$$

$$(A^{-1}HA) (A^{-1}C) = (A^{-1}SA)(A^{-1}C) \quad E$$

$A^{-1}HA$ and $A^{-1}SA$ are examples of similarity transformations, one property of which is they **do not affect eigenvalues**.

thus: $H'C' = I C'E$

H' is diagonalized as usual giving $C' = A^{-1}C$

But we want C so mult. both sides by A

$$AC' = AA^{-1}C = C, \text{ the original matrix of } c_i$$

Effect of Non-orthogonality for two normalized, but **non-orthogonal** basis functions for which $H_{11} = H_{22} = \alpha$ and $H_{12} = \beta$ (degenerate case)

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

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

but $S_{11} = S_{22} = 1$ and $S_{12} = S_{21}$ so call it S

$$(\alpha - E)c_1 + (\beta - SE)c_2 = 0$$

$$(\beta - SE)c_1 + (\alpha - E)c_2 = 0$$

Eigenvalues = ? Determinant = 0: $(\alpha - E)^2 - (\beta - SE)^2 = 0$

$$\text{so } \alpha - E = \pm(\beta - SE)$$

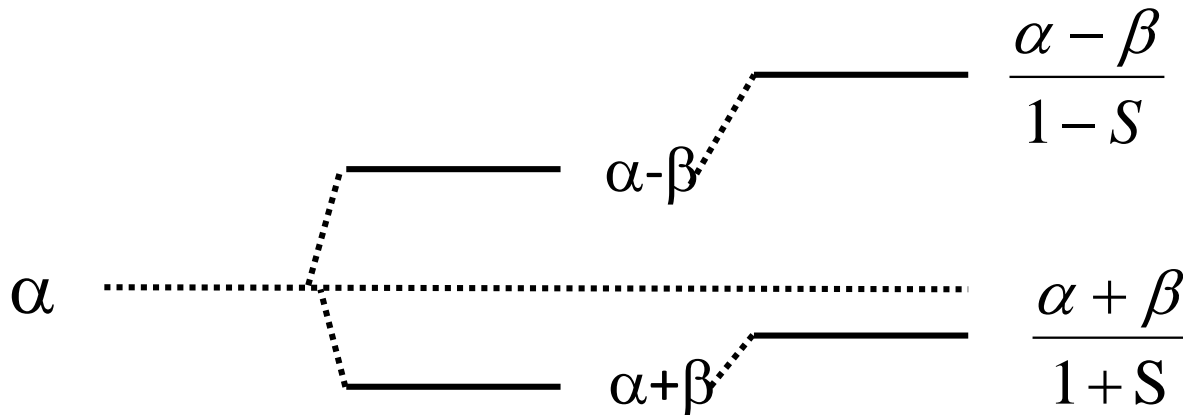
$$\alpha \pm \beta = E(1 \pm SE)$$

$$E = \frac{\alpha \pm \beta}{1 \pm S}$$

when we choose phase so S is positive, β will be negative

$$E_{\text{lowest}} = \frac{\alpha + \beta}{1 + S} \text{ which is less negative than } \alpha + \beta$$

$$E_{\text{highest}} = \frac{\alpha - \beta}{1 - S} \text{ which is more positive than } \alpha - \beta$$



Note that $E_{\text{higher}} - (\alpha - \beta)$ is greater than $E_{\text{lower}} - (\alpha + \beta)$. Therefore, the overlap makes the upper state MORE antibonding than the bonding state is bonding.

Thus, **He₂** does not have a zero bond order, **but a negative bond order**

Electron Spin, Spin Orbitals, and Slater Determinants

Quantization of Angular Momentum:

$$L^2 = L(L+1) (h/2\pi)^2 ;$$

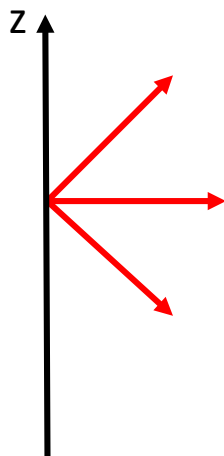
$$L_z = m (h/2\pi)$$

“multiplicity” = degeneracy = $2L+1$ = the number of different m values from $-L$ to $+L$ (z components)

For electrons we use S for total spin angular momentum instead of L

for single electrons $S = s = \frac{1}{2} h/2\pi$, therefore $m = \frac{1}{2}$ and $-\frac{1}{2}$

(Don't say spins are $+$ and $-\frac{1}{2}$; **spin, S , is never negative**, only some of the m values



Example of $S=1$, $m=1,0,-1$
 $2S+1 = 3$

Spin Statistics Theorem

permutation of two identical fermion coordinates changes sign of wavefunction (“antisymmetric”) leads to exclusion principle

permutation of two identical boson coordinates DOES NOT change sign of wavefunction (“symmetric”) leads to inclusion principle

Electron Spin State Functions:

$|\alpha\rangle$ has $m = \frac{1}{2}$

$|\beta\rangle$ has $m = -\frac{1}{2}$

with $\hbar/2\pi = 1$ atomic unit

$$S_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle$$

$$S_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

both have $s = \frac{1}{2}$

therefore

$$S^2 |\alpha\rangle = \frac{1}{2}(\frac{1}{2}+1) |\alpha\rangle$$

$$S^2 |\beta\rangle = \frac{1}{2}(\frac{1}{2}+1) |\beta\rangle$$

Helium ground state, and singlet vs triplet excited state

The notation of spin orbital is often used for compactness:

$$\varphi_{1s}(1) = 1s(1)\alpha(1)$$

$$\bar{\varphi}_{1s}(1) = 1s(1)\beta(1)$$

For example the ground state function for He can be written as:

$$\varphi_{1s}(1)\bar{\varphi}_{1s}(2) - \bar{\varphi}_{1s}(1)\varphi_{1s}(2)$$

or

$$= 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The ***space-spin separated*** form is convenient for understanding the triplet state of a ***2-electron*** system. This factorization, however, cannot be done for 3 or more electrons.

Now consider the lowest excited states of He, $1s2s$, an example of an ***open shell*** system.

Here one must consider that electron exchange is also between the spatial orbitals as well as the spin functions.

Because we may factor into space times spin functions, it is obvious that one may achieve an antisymmetric function two general ways:

- (1) space = sym, spin = antisymmetric** to permutation
- (2) space = antisym, spin = symmetric** to permutation

There is **only 1 way to achieve the (1)**, so it is called a **singlet state**:

$$\Psi_{\text{singlet}} = [1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

There are **3 ways** to have a **symmetric** spin function while having an antisymmetric space function, however:

$$\Psi_{\text{triplet}} =$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\alpha(2)], \quad M_S = 1/2 + 1/2 = 1$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad M_S = 1/2 - 1/2 = 0$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\beta(1)\beta(2)], \quad M_S = -1/2 - 1/2 = -1$$

This obeys the universal rule of quantum angular momentum: $M_S = -S, -S + 1, -S + 2 \dots +S$
i.e., $2S+1$ values.

Notice that the antisymmetric space function vanishes whenever the two electrons are at the same point in space—ENTIRELY because of the wavefunction, meaning that the two electrons with same m_s avoid each other—
NOT because of Coulombic repulsion, but because of the Pauli exclusion principle

This is qualitatively why **TRIPLET STATES have LOWER energy** than the corresponding singlet state.