

## Koopman's Theorem:

The “MO Energy for orbital  $i$ ” = minus the ionization potential for removing an electron from the  $i^{\text{th}}$  MO

**Example:**

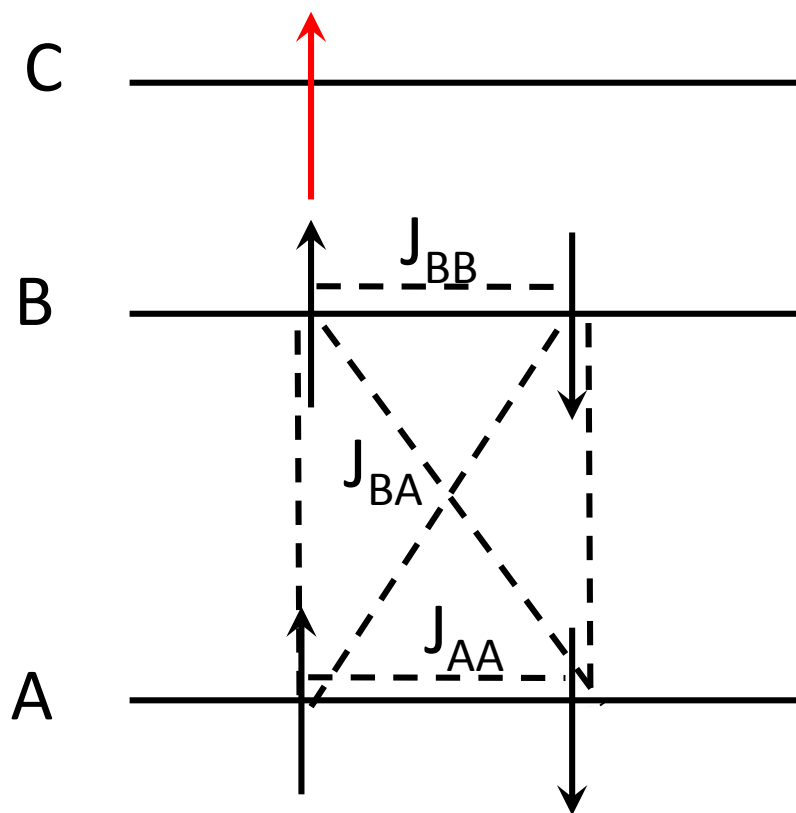
**Remove one of the electrons in MO A**

$$E_{\text{neutral}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA}$$

$$E_{\text{cation}} = h_{AA} + 2h_{BB} + J_{BB} + 2J_{BA} - K_{BA}$$

$$E_{\text{difference}} = h_{AA} + J_{AA} + 2J_{BA} - K_{BA} = \epsilon_A = \text{the orbital energy} = \text{The ionization energy}$$

If no relaxation due to changed electron density



Virtual (i.e., unoccupied orbitals are different!

Add an electron to MO C

any "MO Energy" is for an electron that "sees" ALL of the occupied MO electrons

$$E_{\text{neutral}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA}$$

$$E_{\text{anion}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA} + h_{CC} + 2J_{CA} - K_{CA} + 2J_{CB} - K_{CB}$$

$$E_{\text{difference}} = h_{CC} + 2J_{CA} - K_{CA} + 2J_{CB} - K_{CB} = \epsilon_C$$

**= minus the Electron Affinity**

If no relaxation due to changed electron density

# HF-SCF with LCAO MOs

Build the MOs from AOs:

$$MO = \varphi_i = \sum_{\mu}^{n/2} \chi_{\mu} c_{\mu i}$$

$$AO = \chi_{\mu}$$

one-electron density of an MO =  $\phi_i \phi_i^*$

$$\begin{aligned} \phi_i \phi_i^* &= \sum_{\mu}^{n/2} \chi_{\mu} c_{\mu i} \sum_{\nu}^{n/2} \chi_{\nu} c_{\nu i} \\ &= \sum_{\mu, \nu}^{n/2} c_{\mu i} c_{\nu i} \chi_{\mu} \chi_{\nu} = \sum_{\mu, \nu}^{n/2} D_{\mu\nu}^{ii} \chi_{\mu} \chi_{\nu} \end{aligned}$$

i.e., a linear combination of AO products (transition densities)

and where  $D_{\mu\nu}^{ii} = c_{\mu i} c_{\nu i}$

Note that this defines the MO density matrix as the elements :  $D_{\mu\nu}^{ii} = c_{\mu i}c_{\nu i}$

Now, examine the one-electron density of an MO and write it as a matrix product:

$$\phi_i \phi_i^* = \sum_{\mu,\nu}^{n/2} \chi_{\mu} D_{\mu\nu}^{ii} \chi_{\nu}$$

$$\sum_{\mu,\nu}^{n/2} c_{\mu i} c_{\nu i} \chi_{\mu} \chi_{\nu} = \sum_{\mu,\nu}^{n/2} D_{\mu\nu}^{ii} \chi_{\mu} \chi_{\nu} = \sum_{\mu,\nu}^{n/2} \chi_{\mu} D_{\mu\nu}^{ii} \chi_{\nu}$$

i.e., a linear combination of AO products  
(transition densities)

$$\sum_{\mu, \nu}^{n/2} \chi_{\mu} D_{\mu\nu}^{ii} \chi_{\nu}$$

Is explicitly the matrix multiplication:

$$(\chi_1 \quad \chi_2 \quad \chi_3) \begin{pmatrix} D_{11}^{ii} & D_{12}^{ii} & D_{13}^{ii} \\ D_{21}^{ii} & D_{22}^{ii} & D_{23}^{ii} \\ D_{31}^{ii} & D_{32}^{ii} & D_{33}^{ii} \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \end{pmatrix}$$

i.e., the characteristic summing over repeated indices, suggesting a **1 x N row times an N x N square matrix, times N x1 column**

**Total one-electron density comes from summing over all occupied MOs**

$$\begin{aligned} D(1) &= 2 \sum_{i, occ}^{n/2} \sum_{\mu, \nu} D_{\mu\nu}^{ii} \chi_{\mu} \chi_{\nu}^* \\ &= \sum_{\mu, \nu} \sum_{i, occ}^{n/2} (2D_{\mu\nu}^{ii}) \chi_{\mu} \chi_{\nu}^* \quad (2 \text{ because closed shell}) \\ &= \sum_{\mu, \nu} \sum_{i, occ}^{n/2} 2\chi_{\mu} D_{\mu\nu}^{ii} \chi_{\nu}^* \end{aligned}$$

which is also a linear combination of AO products

**$D_{\mu\nu}$  is the  $\mu\nu^{\text{th}}$  element of the density matrix in the AO basis**

Convenient notation from Robert G. Parr lecture notes:  
*Quantum Theory of Molecular Electronic Structure,*  
*Benjamin 1964*

And used by Jean Standard in the pdf I posted.

$$(ab | cd) \equiv \iint a(1)c(2) \frac{1}{r_{12}} b(1)d(2) d\tau_1 d\tau_2$$
$$= \iint a(1)b(1) \frac{1}{r_{12}} c(2)d(2) d\tau_1 d\tau_2$$

In words:

(ab | cd) simply means the electron-electron repulsion of the generalized density due to the product of **orbital a** times **orbital b** repelling that of **orbital c** times **orbital d**

# The Fock matrix in the AO basis

$$\begin{aligned} F_{\mu\nu} &= \langle \chi_\mu | \hat{F} | \chi_\nu \rangle \equiv \langle \mu | \hat{F} | \nu \rangle \\ &= \langle \mu | \hat{h} | \nu \rangle + \sum_j \left( 2 \langle \mu | \hat{J}_j | \nu \rangle - \langle \mu | \hat{K}_j | \nu \rangle \right) \\ &= \langle \mu | \hat{h} | \nu \rangle + \sum_j \left[ 2(\mu\nu | \varphi_j^* \varphi_j) - (\mu\varphi_j | \nu \varphi_j^*) \right] \end{aligned}$$

The  $J_j$  part is repulsion of the  $\chi_\mu\chi_\nu$  product charge cloud with the  $j^{\text{th}}$  MO cloud of electron charge. This is easy to understand because after summing, it is just the repulsion of the  $\chi_\mu\chi_\nu$  product with the entire electron cloud, D

The  $K_j$  part is repulsion of the product  $\chi_\mu\varphi_j$  charge distribution with the  $\chi_\nu\varphi_j$  electron charge distribution.



We eventually want to express J,K in terms of the D matrix and entirely with AOs

At present it is partly MO

J part is easy

$$F_{\mu\nu} = \langle \mu | \hat{h} | \nu \rangle + \sum_j \left[ 2(\mu\nu | \varphi_j^* \varphi_j) - (\mu\varphi_j | \nu \varphi_j^*) \right]$$

$$\sum_j 2\varphi_j^* \varphi_j = \sum_j 2 \sum_{\lambda\sigma} c_{\sigma j} \chi_\sigma c_{\lambda j} \chi_\lambda$$

$$\sum_j 2\varphi_j^* \varphi_j = \sum_j 2 \sum_{\lambda\sigma} c_{\lambda j} c_{\sigma j} \chi_\lambda \chi_\sigma$$

$$\sum_j 2\varphi_j^* \varphi_j = \sum_j \sum_{\lambda\sigma} 2D_{\lambda\sigma}^{jj} \chi_\lambda \chi_\sigma = \sum_{\lambda\sigma} 2D_{\lambda\sigma} \chi_\lambda \chi_\sigma = D$$

$$\hat{J} = (\mu\nu | D)$$

$$\hat{J} = (\mu\nu | D) = \sum_{\lambda\sigma} D_{\lambda\sigma} (\mu\nu | \lambda\sigma)$$

$\hat{J} = (\mu\nu | D)$  is just the repulsion of a "charge distribution defined as the function  $\chi_\mu\chi_\nu$  repelling the entire electronic density, which is the same thing as:

the sum of all repulsions between the  $N^2$  products of the  $N$  AOs of the basis set,  $\sum_{\lambda\sigma} D_{\lambda\sigma} (\mu\nu | \lambda\sigma)$

Consider H<sub>2</sub> molecule

LCAO-MO method

$$\Psi = N[a(1) + b(1)]N[a(2) + b(2)]$$

where a , b = 1s orbitals and N is the normalization constant

$$(ab | cd) \equiv \iint a(1)c(2) \frac{1}{r_{12}} b(1)d(2) d\tau_1 d\tau_2$$

$$\Psi = N[a(1) + b(1)]N[a(2) + b(2)]$$

where a , b = identical 1s orbitals and N is the normalization constant

$$E = N^4 \langle [a(1) + b(1)][a(2) + b(2) | H | [a(1) + b(1)][a(2) + b(2) \rangle$$

$$(ab | cd) \equiv \iint a(1)c(2) \frac{1}{r_{12}} b(1)d(2) d\tau_1 d\tau_2$$

The  $K$  part keeps the  $\chi_\mu\chi_\nu$  product of AOs from repelling itself and other electrons with the same  $m_s$ . Again, using

$$\begin{aligned}\varphi_j &= \sum_{\sigma} c_{\sigma j} \chi_{\sigma} = \sum_{\lambda} c_{\lambda j} \chi_{\lambda} \\ \sum_j \mu |K_j | \nu \rangle &= \sum_j (\mu \varphi_j | \nu \varphi_j) = \sum_j (\mu \varphi_j | \nu \varphi_j) \\ &= \sum_j \sum_{\lambda \sigma} c_{\lambda j} c_{\sigma j} (\mu \lambda | \nu \sigma) = 1/2 \sum_{\lambda \sigma} D_{\lambda \sigma} (\mu \lambda | \nu \sigma)\end{aligned}$$

**Thus, the Fock matrix elements are:**

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

In words, the Fock matrix elements between AOs  $\chi_\mu$  and  $\chi_\nu$  are:

- 1) The kinetic energy matrix elements:
- 2) The integral over nuclear attraction
- 3) Electrostatic repulsion between all AO products pairs minus  $\frac{1}{2}$  the repulsion of the exchanged pairs

Examine actual HF-SCF output from Gaussian 09 computation for water. (pdf from Jean Standard course website, Illinois State

Chemistry 460 Spring 2015 Dr. Jean M. Standard April 22, 2015

## A Hartree-Fock Calculation of the Water Molecule

Introduction An example Hartree-Fock calculation of the water molecule will be presented. In this case, the water molecule will have its geometry fixed at the experimental values of bond lengths ( $R(\text{O-H})=0.95 \text{ \AA}$ ) and bond angle ( $\angle\text{H-O-H}= 104.5^\circ$ ). Thus, the electronic energy and wavefunction will be computed for fixed nuclear positions; this is known as a single-point energy calculation. A minimal basis set of atomic orbital functions will be employed.

Gaussian input file Jean-h2o.gjf  
(job input file)

All input files must have .gjf

-----

```
%chk=C:\564-17\Jean-h20.chk  
# opt hf/sto-3g pop=full
```

water from Jean Standard pdf, ordered to  
match output

callis

```
0 1  
8 0.000000 0.000000 0.116321  
1 0 .000000 0.751155 -0.465285  
1 0.000000 -0.751155 -0.465285
```

### Atomic orbital basis functions

The water molecule has a total of 10 electrons, eight from the oxygen atom and one each from the hydrogen atoms. Therefore, for a closed shell molecular system like water in its ground state with 10 total electrons, the wavefunction in the form of a Slater Determinant is

$$\Psi_{\text{H}_2\text{O}} = \frac{1}{\sqrt{10!}} \left| \phi_1 \bar{\phi}_1 \ \phi_2 \bar{\phi}_2 \ \phi_3 \bar{\phi}_3 \ \phi_4 \bar{\phi}_4 \ \phi_5 \bar{\phi}_5 \right|. \quad (1)$$

The functions  $\phi_i$  for water are molecular orbitals defined using the LCAO-MO approximation,

$$\phi_i(1) = \sum_{\mu=1}^K c_{\mu i} f_{\mu}(1). \quad (2)$$



**Table 2.** Basis functions for the HF/STO-3G calculation of the water molecule.

Basis function #	Basis function type
1	1s O
2	2s O
3	2p <sub>x</sub> O
4	2p <sub>y</sub> O
5	2p <sub>z</sub> O
6	1s H <sub>a</sub>
7	1s H <sub>b</sub>

Explain qualitatively the sign and magnitude of the overlap integral values in the matrix below with the aid of the input geometry, which gives the signs of the lobes of the p orbitals.

For the STO-3G basis set with the basis functions specified in the order given in Table 2, the overlap matrix  $\mathbf{S}$  is shown in Figure 1. Note that only the lower portion is shown because the upper portion is related by symmetry since  $S_{\mu\nu} = S_{\nu\mu}$ .

$$\mathbf{S} = \begin{bmatrix} 1.000 & & & & & & & \\ 0.237 & 1.000 & & & & & & \\ 0.000 & 0.000 & 1.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 & \end{bmatrix}$$

**Figure 1.** Overlap matrix  $\mathbf{S}$  for HF/STO-3G calculation of water.

## Fock integrals

The Fock integrals  $F_{\mu\nu}$  in Equation (3) are defined as

$$F_{\mu\nu} = H_{\mu\nu}^{\circ} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right]$$

The terms  $H_{\mu\nu}^{\circ}$  correspond to the one-electron Hamiltonian integrals,

$$H_{\mu\nu}^{\circ} = \left\langle f_{\mu}(1) \left| -\frac{1}{2} \hat{\nabla}_1^2 - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{r_{\alpha 1}} \right| f_{\nu}(1) \right\rangle.$$

Explain qualitatively the sign and magnitude of the KE integral values in the matrix below with the aid of the input geometry, which gives the signs of the lobes of the p orbitals.

$$T_{\mu\nu} = \left\langle f_{\mu}(1) \left| -\frac{1}{2} \hat{\nabla}_1^2 \right| f_{\nu}(1) \right\rangle$$

$$\mathbf{T} = \begin{bmatrix} 29.003 & & & & & & & \\ -0.168 & 0.808 & & & & & & \\ 0.000 & 0.000 & 2.529 & & & & & \\ 0.000 & 0.000 & 0.000 & 2.529 & & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & & \\ -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & & \\ -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 & \end{bmatrix}$$

**Figure 2.** Kinetic energy matrix  $\mathbf{T}$  for HF/STO-3G calculation of water.



$$H_{\mu\nu}^{\circ} = T_{\mu\nu} + V_{\mu\nu}$$

$$\mathbf{H}^{\circ} = \begin{bmatrix} -32.730 & & & & & & & & \\ -7.615 & -9.343 & & & & & & & \\ 0.000 & 0.000 & -7.397 & & & & & & \\ 0.000 & 0.000 & 0.000 & -7.623 & & & & & \\ 0.019 & 0.226 & 0.000 & 0.000 & -7.559 & & & & \\ -1.780 & -3.788 & 0.000 & 0.001 & 0.007 & -5.107 & & & \\ -1.780 & -3.788 & 0.000 & -0.001 & 0.007 & -1.643 & -5.107 & & \end{bmatrix}$$

**Figure 4.** One-electron Hamiltonian matrix  $\mathbf{H}^{\circ}$  for HF/STO-3G calculation of water.

## Two-electron integrals

The next step is to compute the two-electron integrals from Equation (5). The terms  $(\mu\nu|\lambda\sigma)$  and  $(\mu\lambda|\nu\sigma)$  represent two-electron repulsion integrals from the Coulomb and Exchange terms in the Fock operator,

$$\begin{aligned}(\mu\nu|\lambda\sigma) &= \left\langle f_\mu(1)f_\lambda(2) \left| \frac{1}{r_{12}} \right| f_\nu(1)f_\sigma(2) \right\rangle \\(\mu\lambda|\nu\sigma) &= \left\langle f_\mu(1)f_\nu(2) \left| \frac{1}{r_{12}} \right| f_\lambda(1)f_\sigma(2) \right\rangle.\end{aligned}\tag{10}$$

The number of two-electron integrals that must be computed is  $K^4$ , where  $K$  is the number of basis functions. For the HF/STO-3G calculation of water,  $K=7$ , so the number of two-electron integrals to be computed is 2401. Because of the symmetry of the water molecule, this number is reduced to a mere 406 integrals. Even that many would take a lot of space to list on a page, so their numerical values will not be included here.

**Table 3.** Coefficients  $c_{\mu i}$  of the initial guess for the occupied molecular orbitals of water.

---

	MO:	1	2	3	4	5
1	O 1S	0.99431	-0.23246	0.00000	-0.10725	0.00000
2	O 2S	0.02551	0.83359	0.00000	0.55664	0.00000
3	O 2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	O 2PY	0.00000	0.00000	0.60718	0.00000	0.00000
5	O 2PZ	-0.00291	-0.14086	0.00000	0.76655	0.00000
6	Ha 1S	-0.00515	0.15562	0.44418	-0.28592	0.00000
7	Hb 1S	-0.00515	0.15562	-0.44418	-0.28592	0.00000

---



$P_{\lambda\sigma}$  = **Density matrix element from AOs  $\lambda\sigma$**

$$P_{\lambda\sigma} = 2 \sum_{i=1}^n c_{\lambda i}^* c_{\sigma i}$$

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & & \\ -0.456 & 2.010 & & & & & & \\ 0.000 & 0.000 & 2.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 & \end{bmatrix}$$

**Figure 5.** Initial density matrix  $\mathbf{P}$  for HF/STO-3G calculation of water based on extended Hückel guess.

Explain qualitatively the sign and magnitude of the overlap integral values in the matrix below with the aid of the input geometry, which gives the signs of the lobes of the p orbitals.

$$F_{\mu\nu} = H_{\mu\nu}^0 + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right]$$

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & & & \\ -5.163 & -2.453 & & & & & & & \\ 0.000 & 0.000 & -0.395 & & & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & & & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 & & \end{bmatrix}$$

**Figure 6.** Initial Fock matrix  $\mathbf{F}$  for HF/STO-3G calculation of water.

**Table 6.** Converged MO eigenvalues  $\varepsilon_i$  and coefficients  $c_{\mu i}$  for the occupied (1-5) and virtual (6, 7) molecular orbitals of water at the HF/STO-3G level of theory.

---

MO:		1	2	3	4	5
Eigenvalues:	(a.u.)	-20.24094	-1.27218	-0.62173	-0.45392	-0.39176
1	O 1S	0.99411	-0.23251	0.00000	-0.10356	0.00000
2	O 2S	0.02672	0.83085	0.00000	0.53920	0.00000
3	O 2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4	O 2PY	0.00000	0.00000	0.60677	0.00000	0.00000
5	O 2PZ	-0.00442	-0.13216	0.00000	0.77828	0.00000
6	Ha 1S	-0.00605	0.15919	0.44453	-0.27494	0.00000
7	Hb 1S	-0.00605	0.15919	-0.44478	-0.27494	0.00000

MO:		6	7
Eigenvalues:	(a.u.)	0.61293	0.75095
1	O 1S	-0.13340	0.00000
2	O 2S	0.89746	0.00000
3	O 2PX	0.00000	0.00000
4	O 2PY	0.00000	0.99474
5	O 2PZ	-0.74288	0.00000
6	Ha 1S	-0.80246	-0.84542
7	Hb 1S	-0.80246	0.84542

---

Qualitatively draw the MOs depicted by the columns, getting relative magnitude and signs correct