Exercises on the Hartree-Fock method

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1 If you are interested in carrying out an SCF calculation of the OH- anion using the popular 6-31G** basis set:

a) Number and indicate the type of all the basis functions that will be used for each atom following these rules:

1. List first the basis functions for the H atom, then for the O atom.

2. Within each atom, the order is s-type before p-type, and then d-type.

3. For valence shells, the basis functions described by 3 primitives come before those described by 1 primitive.

4. Polarization functions are last. For oxygen, we use Cartesian d-functions (six of them).

We denote each basis function as ϕ_i, and each primitive Gaussian as $g_{i,\mu}$. The coefficients that form the linear combination of primitives are $c_{i,\mu}^{(\ell)}$, where $\ell \in \{s,\, p,\, d\}$ denotes the orbital type.

Basis Functions on Hydrogen

First valence s (3 primitives):

$$\phi_1(H,s) \;=\; \sum_{\mu=1}^{3} c_{1,\mu}^{(s)}\, g_{1,\mu}^{(s)}\big(\boldsymbol{r}_H\big).$$

Second valence s (1 primitive):

$$\phi_2(H,s) \;=\; c_{2,1}^{(s)}\, g_{2,1}^{(s)}\big(\boldsymbol{r}_H\big).$$

Polarization p orbitals (1 primitive each):

$$\phi_3(H,p_x) \;=\; c_{3,1}^{(p)}\, x\, g_{3,1}^{(p)}\big(\boldsymbol{r}_H\big),$$
$$\phi_4(H,p_y) \;=\; c_{4,1}^{(p)}\, y\, g_{4,1}^{(p)}\big(\boldsymbol{r}_H\big),$$
$$\phi_5(H,p_z) \;=\; c_{5,1}^{(p)}\, z\, g_{5,1}^{(p)}\big(\boldsymbol{r}_H\big).$$

Total on H: 5 basis functions.

Basis Functions on Oxygen

Core $1s$ (6 primitives):

$$\phi_6(O, s) \;=\; \sum_{\mu=1}^{6} c_{6,\mu}^{(s)}\, g_{6,\mu}^{(s)}(\boldsymbol{r}_O).$$

First valence shell: one s + three p (3 primitives each)

$$\phi_7(O, s) \;=\; \sum_{\mu=1}^{3} c_{7,\mu}^{(s)}\, g_{7,\mu}^{(s)}(\boldsymbol{r}_O),$$

$$\phi_8(O, p_x) \;=\; \sum_{\mu=1}^{3} c_{8,\mu}^{(p)}\, x\, g_{8,\mu}^{(p)}(\boldsymbol{r}_O),$$

$$\phi_9(O, p_y) \;=\; \sum_{\mu=1}^{3} c_{9,\mu}^{(p)}\, y\, g_{9,\mu}^{(p)}(\boldsymbol{r}_O),$$

$$\phi_{10}(O, p_z) \;=\; \sum_{\mu=1}^{3} c_{10,\mu}^{(p)}\, z\, g_{10,\mu}^{(p)}(\boldsymbol{r}_O).$$

Second valence shell: one s + three p (1 primitive each)

$$\phi_{11}(O, s) \;=\; c_{11,1}^{(s)}\, g_{11,1}^{(s)}(\boldsymbol{r}_O),$$

$$\phi_{12}(O, p_x) \;=\; c_{12,1}^{(p)}\, x\, g_{12,1}^{(p)}(\boldsymbol{r}_O),$$

$$\phi_{13}(O, p_y) \;=\; c_{13,1}^{(p)}\, y\, g_{13,1}^{(p)}(\boldsymbol{r}_O),$$

$$\phi_{14}(O, p_z) \;=\; c_{14,1}^{(p)}\, z\, g_{14,1}^{(p)}(\boldsymbol{r}_O).$$

Cartesian d-type polarization (6 functions, 1 primitive each):

$$\phi_{15}(O, d_{xx}) \;=\; c_{15,1}^{(d)}\, x^2\, g_{15,1}^{(d)}(\boldsymbol{r}_O),$$

$$\phi_{16}(O, d_{yy}) \;=\; c_{16,1}^{(d)}\, y^2\, g_{16,1}^{(d)}(\boldsymbol{r}_O),$$

$$\phi_{17}(O, d_{zz}) \;=\; c_{17,1}^{(d)}\, z^2\, g_{17,1}^{(d)}(\boldsymbol{r}_O),$$

$$\phi_{18}(O, d_{xy}) \;=\; c_{18,1}^{(d)}\, (x\,y)\, g_{18,1}^{(d)}(\boldsymbol{r}_O),$$

$$\phi_{19}(O, d_{xz}) \;=\; c_{19,1}^{(d)}\, (x\,z)\, g_{19,1}^{(d)}(\boldsymbol{r}_O),$$

$$\phi_{20}(O, d_{yz}) \;=\; c_{20,1}^{(d)}\, (y\,z)\, g_{20,1}^{(d)}(\boldsymbol{r}_O).$$

Total on O: 15 basis functions.

Overall Count

$$\underbrace{5}_{H} \;+\; \underbrace{15}_{O} \;=\; 20 \quad \text{(basis functions in total)}.$$

b) Indicate the size of the core Hamiltonian matrix in the basis function representation

The core Hamiltonian is represented in the same basis set that is used for the molecular orbitals. Hence, its matrix dimension is equal to the total number of basis functions. Therefore, the core Hamiltonian matrix is of size 20×20.

c) Express:

c.1) the overlap integral in basis functions $S_{1,6} = \langle \phi_1 \mid \phi_6 \rangle$ in terms of the overlap integrals between primitive functions.

- ϕ_1 is the first basis function, corresponding to the hydrogen 1s orbital with 3 primitives:

$$\phi_1(H, s) = \sum_{\mu=1}^{3} c_{1,\mu}^{(s)} \, g_{1,\mu}^{(s)}(\mathbf{r}_H),$$

- ϕ_6 is the first basis function for oxygen, corresponding to the 1s core orbital with 6 primitives

$$\phi_6(O, s) = \sum_{\nu=1}^{6} c_{6,\nu}^{(s)} \, g_{6,\nu}^{(s)}(\mathbf{r}_O).$$

Hence, the overlap integral between ϕ_1 and ϕ_6 is:

$$S_{1,6} = \langle \phi_1 \mid \phi_6 \rangle = \int \phi_1^*(\mathbf{r}) \, \phi_6(\mathbf{r}) \, d\mathbf{r}.$$

Substituting:

$$S_{1,6} = \int \left(\sum_{\mu=1}^{3} c_{1,\mu}^{(s)} \, g_{1,\mu}^{(s)}(\mathbf{r}_H) \right) \left(\sum_{\nu=1}^{6} c_{6,\nu}^{(s)} \, g_{6,\nu}^{(s)}(\mathbf{r}_O) \right) d\mathbf{r}.$$

Rearranging the constants:

$$S_{1,6} = \sum_{\mu=1}^{3} \sum_{\nu=1}^{6} c_{1,\mu}^{(s)} \, c_{6,\nu}^{(s)} \underbrace{\int g_{1,\mu}^{(s)}(\mathbf{r}_H) \, g_{6,\nu}^{(s)}(\mathbf{r}_O) \, d\mathbf{r}}_{S\left[g_{1,\mu}^{(s)}(H), \, g_{6,\nu}^{(s)}(O) \right]}.$$

Hence, we express $S_{1,6}$ as a sum of products of the contraction coefficients and the overlap integrals of the primitive Gaussians:

$$\boxed{S_{1,6} = \sum_{\mu=1}^{3} \sum_{\nu=1}^{6} c_{1,\mu}^{(s)} \, c_{6,\nu}^{(s)} \, S\left[g_{1,\mu}^{(s)}(H), \, g_{6,\nu}^{(s)}(O) \right].}$$

Where:

- $c_{1,\mu}^{(s)}$ are the coefficients of the primitives for the H 1s basis function ϕ_1.

$-c_{6,\nu}^{(s)}$ are the coefficients of the primitives for the O 1s basis function ϕ_6.

$-S\left[g_{1,\mu}^{(s)}(H),\, g_{6,\nu}^{(s)}(O)\right]$ are the overlap integrals between primitive Gaussian functions.

This expression shows that the overlap integral between basis functions $S_{1,6}$ is a weighted sum of overlap integrals between individual primitive Gaussians. The weights are determined by the coefficients of the primitives from the 6-31G** basis set.

c2) The kinetic integral $T_{4,9} = \langle \phi_4 | \hat{T} | \phi_9 \rangle$ in terms of the kinetic integrals between primitive functions.

From section a), the basis functions in terms of the integrals between primitive Gaussian functions are:

$$\phi_4(H, p_y) \;=\; c_{4,1}^{(p)} \, y \, g_{4,1}^{(p)}(\mathbf{r}_H),$$

$$\phi_9(O, p_y) \;=\; \sum_{\nu=1}^{3} c_{9,\nu}^{(p)} \left(y \, g_{9,\nu}^{(p)}(\mathbf{r}_O) \right),$$

and $\hat{T}$ is the kinetic-energy operator (in atomic units, $\hat{T} = -\frac{1}{2}\nabla^2$). Therefore:

$$T_{4,9} \;=\; \int \phi_4(\mathbf{r})\, \hat{T}\, \phi_9(\mathbf{r})\, d\mathbf{r}.$$

Substituting the expansions:

$$T_{4,9} \;=\; \int \left(c_{4,1}^{(p)} \, y \, g_{4,1}^{(p)}(\mathbf{r}_H) \right) \hat{T} \left(\sum_{\nu=1}^{3} c_{9,\nu}^{(p)} \, y \, g_{9,\nu}^{(p)}(\mathbf{r}_O) \right) d\mathbf{r}.$$

Rearranging the constants:

$$T_{4,9} \;=\; \sum_{\mu=1}^{1} \sum_{\nu=1}^{3} c_{4,\mu}^{(p)} \, c_{9,\nu}^{(p)} \underbrace{\int \left(y \, g_{4,\mu}^{(p)}(\mathbf{r}_H) \right) \hat{T} \left(y \, g_{9,\nu}^{(p)}(\mathbf{r}_O) \right) d\mathbf{r}}_{T\left[y\, g_{4,\mu}^{(p)}(H),\; y\, g_{9,\nu}^{(p)}(O) \right]}$$

Since there is only one primitive in ϕ_4 (the index for it is $\mu = 1$), the double sum simplifies to a single sum over ν:

$$\boxed{T_{4,9} \;=\; \sum_{\nu=1}^{3} c_{4,1}^{(p)} \, c_{9,\nu}^{(p)} \, T\left[y\, g_{4,1}^{(p)}(H),\; y\, g_{9,\nu}^{(p)}(O) \right]}$$

- $T_{4,9}$: The kinetic integral between the p_y basis function of hydrogen (ϕ_4) and the p_y basis function of oxygen (ϕ_9).

- $\sum_{\nu=1}^{3}$: summation over the three primitive Gaussian functions that form the oxygen basis function (ϕ_9).

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- $c_{4,1}^{(p)}$: contraction coefficient for the hydrogen p_y basis function (ϕ_4), which contains only one primitive Gaussian in the 6-31G** basis set.

- $c_{9,\nu}^{(p)}$: contraction coefficient for the oxygen p_y basis function (ϕ_9), which consists of three primitive Gaussians, indexed by ν.

- $T\left[y\, g_{4,1}^{(p)}(H),\ y\, g_{9,\nu}^{(p)}(O)\right]$: the primitive kinetic-energy integral between the individual Gaussian primitives of hydrogen and oxygen, each multiplied by y, which represents their p_y-orbital character.

This equation describes the kinetic-energy interaction between the p_y atomic orbitals of hydrogen and oxygen in a Gaussian basis set representation.

Está esto bien?:

c.3) The attractive electron-nuclear potential integral $V_{12,18} = \langle \phi_{12} \mid \hat{V}_{Ne} \mid \phi_{18} \rangle$ in terms of the potential integrals between primitive functions.

From section a), the basis functions in terms of the integrals between primitive Gaussian functions are:

$$\phi_{12}(O, p_x) = \sum_{\mu=1}^{1} c_{12,\mu}^{(p)} \left(x\, g_{12,\mu}^{(p)}(\mathbf{r}_O) \right) = c_{12,1}^{(p)}\, x\, g_{12,1}^{(p)}(\mathbf{r}_O),$$

$$\phi_{18}(O, d_{xy}) = \sum_{\nu=1}^{1} c_{18,\nu}^{(d)} \left(x\, y\, g_{18,\nu}^{(d)}(\mathbf{r}_O) \right) = c_{18,1}^{(d)}\, x\, y\, g_{18,1}^{(d)}(\mathbf{r}_O).$$

Since both ϕ_{12} and ϕ_{18} each have only a single primitive in this basis function.

Therefore:
$$V_{12,18} = \int \phi_{12}(\mathbf{r})\, \hat{V}_{\text{nuc}}\, \phi_{18}(\mathbf{r})\, d\mathbf{r}.$$

Substituting:

$$V_{12,18} = c_{12,1}^{(p)}\, c_{18,1}^{(d)} \int \left(x\, g_{12,1}^{(p)}(\mathbf{r}_O) \right) \hat{V}_{\text{nuc}} \left(x\, y\, g_{18,1}^{(d)}(\mathbf{r}_O) \right) d\mathbf{r}.$$

Since both functions depend on x, we rewrite the integral:

$$V_{12,18} = c_{12,1}^{(p)}\, c_{18,1}^{(d)} \int x^2 y\, g_{12,1}^{(p)}(\mathbf{r}_O) \hat{V}_{\text{nuc}} g_{18,1}^{(d)}(\mathbf{r}_O)\, d\mathbf{r}.$$

Using the property of Gaussian integrals, the potential integral can be rewritten as:

$$V_{12,18} = c_{12,1}^{(p)}\, c_{18,1}^{(d)} \underbrace{\int x^2 y\, g_{12,1}^{(p)}(\mathbf{r}_O) \hat{V}_{\text{nuc}} g_{18,1}^{(d)}(\mathbf{r}_O)\, d\mathbf{r}}_{V[x^2 y; g_{12,1}^{(p)}, g_{18,1}^{(d)}]}.$$

Thus, the integral can be expressed as:

$$\boxed{V_{12,18} \;=\; c_{12,1}^{(p)}\, c_{18,1}^{(d)}\, V[x^2 y;\, g_{12,1}^{(p)},\, g_{18,1}^{(d)}].}$$

where:

- $c_{12,1}^{(p)}$ and $c_{18,1}^{(d)}$ are the contraction coefficients for the basis functions.

- $V[x^2 y;\, g_{12,1}^{(p)},\, g_{18,1}^{(d)}]$ is the primitive electron-nuclear potential integral between the Gaussians.

This integral depends on the nuclear position $\mathbf{R}_A$ and the Gaussian exponents.

2 Show that in each SCF iteration, the closed-shell Hartree-Fock energy can be calculated as:

$$E_0 \;=\; \tfrac{1}{2} \sum_{\mu\nu} P_{\mu\nu} \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right)$$

Where $P_{\mu\nu}$ is the one-particle density matrix in the atomic-orbital (AO) basis, $H_{\mu\nu}^{\text{core}}$ is the one-electron (core) Hamiltonian matrix, and $F_{\mu\nu}$ is the Fock matrix.

For a restricted (closed-shell) HF wavefunction, the electronic energy can be written as

$$E_0 \;=\; \underbrace{\sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}}}_{\text{one-electron energy}} + \underbrace{\tfrac{1}{4} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \Big(2 \langle \mu\,\lambda \mid \nu\,\sigma \rangle - \langle \mu\,\lambda \mid \sigma\,\nu \rangle \Big),}_{\text{two-electron energy}}$$

Here,

- $P_{\mu\nu}$ is the one-particle density matrix in the atomic-orbital (AO) basis.

- $H_{\mu\nu}^{\text{core}}$ represents all one-electron terms (kinetic + nuclear attraction).

- $F_{\mu\nu}$ is the Fock matrix in the same AO basis.

- $\langle \mu\,\lambda \mid \nu\,\sigma \rangle$ are the usual two-electron repulsion integrals in the Atomic Orbitals basis

By definition the Fock matrix in the Atomic Orbitals basis is:

$$F_{\mu\nu} \;=\; H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} \Big(\langle \mu\,\lambda \mid \nu\,\sigma \rangle - \tfrac{1}{2} \langle \mu\,\lambda \mid \sigma\,\nu \rangle \Big).$$

- The first term $H_{\mu\nu}^{\text{core}}$ is the same one-electron core Hamiltonian used above.

- The sum over $\lambda\sigma$ multiplies the density $P_{\lambda\sigma}$ by the appropriate two-electron integrals.

- The factor $\tfrac{1}{2}$ in front of the exchange integral $\langle \mu\,\lambda \mid \sigma\,\nu \rangle$ is specific to a closed-shell (restricted) HF system.

Multiplying both sides by $P_{\mu\nu}$ and summing over μ, ν gives:

$$\sum_{\mu\nu} P_{\mu\nu} F_{\mu\nu} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \sum_{\mu\nu}\sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}\left(\langle \mu\lambda \mid \nu\sigma \rangle - \frac{1}{2}\langle \mu\lambda \mid \sigma\nu \rangle\right) \quad (1)$$

$$\sum_{\mu\nu} P_{\mu\nu} F_{\mu\nu} - \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} = \sum_{\mu\nu}\sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}\left(\langle \mu\lambda \mid \nu\sigma \rangle - \frac{1}{2}\langle \mu\lambda \mid \sigma\nu \rangle\right) \quad (2)$$

Now, considering the two-electron term in E_0:

$$\frac{1}{4}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}\left(2\langle \mu\lambda \mid \nu\sigma \rangle - \langle \mu\lambda \mid \sigma\nu \rangle\right). \quad (3)$$

By comparing equation 3 with the expression in equation 2:

$$\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}\left(2\langle \mu\lambda \mid \nu\sigma \rangle - \langle \mu\lambda \mid \sigma\nu \rangle\right) = 2\sum_{\mu\nu} P_{\mu\nu} F_{\mu\nu} - 2\sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}}. \quad (4)$$

Dividing both sides by 4:

$$\frac{1}{4}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}\left(2\langle \mu\lambda \mid \nu\sigma \rangle - \langle \mu\lambda \mid \sigma\nu \rangle\right) = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu} F_{\mu\nu} - \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}}. \quad (5)$$

Substituting the result above in the original expression for E_0:

$$E_0 = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \left[\frac{1}{2}\sum_{\mu\nu} P_{\mu\nu} F_{\mu\nu} - \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}}\right] \quad (6)$$

Grouping terms:

$$\boxed{E_0 = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu}\left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}\right).} \quad (7)$$

This is the formula used at each iteration of the SCF method for computing the closed-shell electronic Hartree-Fock energy.

Typically, the total Hartree–Fock energy E_{HF} also includes the (constant) nuclear–nuclear repulsion term, $E_{\text{nuc}} = \frac{1}{2}\sum_{A\neq B}\dfrac{Z_A Z_B}{R_{AB}}$, so that the total HF energy is given by:

$$E_{\text{HF}} = E_{\text{nuc}} + \tfrac{1}{2}\sum_{\mu\nu} P_{\mu\nu}\left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}\right).$$

Hence, obtaining the complete Hartree–Fock energy of the system.