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A Simple Illustration of the SCF-LCAO-MO Method

Roothaan's method *(1)* is the most important method currently used to obtain wave functions for atoms and molecules. His equations are derived and discussed in several textbooks on elementary quantum chemistry *(2)*. In their recent paper on the application of the self-consistent field-linear combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) method to the H_2 molecule, Dewar and Kelemen *(3)* pointed out the paucity of simple illustrations of the Roothaan approach. In this paper, SCF-LCAO equations for the helium atom are derived and are used to obtain the $1s$ orbital and the energy of the ground state of helium. Several features of the problem recommend it as an introduction to the SCF-LCAO-MO method. These features are: (1) only one-center integrals are necessary; (2) the iteration procedure is simple but illustrative of the process for more complex systems; (3) the results are very nearly equal to the best SCF results; and (4) a student can carry out the computation on a desk calculator or program the calculation as an exercise in the use of an electronic computer.

SCF-LCAO Equations for Helium

We assume that the wave function for the ground state of the helium atom has the form

$$\psi = \phi(1)\phi(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{1}$$

where $\phi(i)$ is the orbital for electron i and $\alpha(i)$ and $\beta(i)$ are spin functions for electron i. The problem to be considered is the determination of the orbital ϕ which gives the best ground-state energy. If we assume that

$$\phi = \sum_{p=1}^{m} c_p \chi_p \tag{2}$$

where the basis functions χ_p are Slater-type atomic orbitals and the c_p are constants to be determined, then the SCF-LCAO equations give the solution.

These equations for helium are derived as follows: The Hamiltonian operator in atomic units for helium is

$$H_{op} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{1}{r_{12}}$$

Then

$$E = \frac{\int \psi^* H_{op}\psi d\tau_1 d\tau_2}{\int \psi^*\psi d\tau_1 d\tau_2}$$

$$= \frac{\int \phi(1)^*\phi(2)^* H_{op}\phi(1)\phi(2)d\tau_1 d\tau_2}{\int \phi^*(1)\phi(1)d\tau_1 \int \phi^*(2)\phi(2)d\tau_2}$$

$$= \frac{2\int \phi^*(1)\left(-\frac{1}{2}\nabla_1^2 - \frac{z}{r_1}\right)\phi(1)d\tau_1}{\int \phi^*(1)\phi(1)d\tau_1} +$$

$$\frac{\int\int \phi^*(1)\phi^*(2)\frac{1}{r_{12}}\phi(1)\phi(2)d\tau_1 d\tau_2}{\int \phi^*(1)\phi(1)d\tau_1 \int \phi^*(2)\phi(2)d\tau_2}$$

If we define

$$g = \frac{\int \phi^*(2)\frac{1}{r_{12}}\phi(2)d\tau_2}{\int \phi^*(2)\phi(2)d\tau_2} \tag{3}$$

and

$$h = -\frac{1}{2}\nabla_1^2 - \frac{z}{r_1} \tag{4}$$

then

$$E = \frac{2\langle\phi|h|\phi\rangle}{\langle\phi|\phi\rangle} + \frac{\langle\phi|g|\phi\rangle}{\langle\phi|\phi\rangle} \tag{5}$$

where

$$\langle\phi|\text{operator}|\phi\rangle = \int \phi^*(1)(\text{operator})\phi(1)d\tau_1$$

$$\langle\phi|\phi\rangle = \int \phi(1)^*\phi(1)d\tau_1 \tag{6}$$

Substituting eqn. (2) into eqns. (3), (5), and (6), we obtain

$$g = \frac{\sum c_r c_s \int \chi_r(2)\frac{1}{r_{12}}\chi_s(2)d\tau_2}{\sum c_r c_s \int \chi_r(2)\chi_s(2)d\tau_2} \tag{7}$$

$$E = \frac{2\sum c_p c_q \langle\chi_p|h|\chi_q\rangle}{\sum c_p c_q \langle\chi_p|\chi_q\rangle} + \frac{\sum c_p c_q \langle\chi_p|g|\chi_q\rangle}{\sum c_p c_q \langle\chi_p|\chi_q\rangle}$$

$$= \frac{\sum c_p c_q (2h_{pq} + g_{pq})}{\sum c_p c_q \Delta_{pq}} \tag{8}$$

$$\int \phi^*(1)\phi(1)d\tau_1 = \sum c_p c_q \langle\chi_p|\chi_q\rangle$$

where for simplicity the c_p are assumed to be real and the sums are over all possible values of the indices of the c_p. In eqn. (8)

$$h_{pq} = \langle\chi_p|h|\chi_q\rangle$$
$$\Delta_{pq} = \langle\chi_p|\chi_q\rangle$$
$$g_{pq} = \langle\chi_p|g|\chi_q\rangle \tag{9}$$

The matrices which correspond to these matrix elements are **h**, Δ, and **g**. Using eqn. (7), we write eqn. (9) explicitly as

$$g_{pq} = \frac{\sum c_r c_s \left\langle \chi_p(1)\chi_r(2)\left|\frac{1}{r_{12}}\right|\chi_s(2)\chi_q(1)\right\rangle}{\sum c_r c_s \langle\chi_r|\chi_s\rangle} \tag{10}$$

where the integrals in the numerator are over both electrons. If we use minimum energy as the criterion to choose the best ϕ in eqn. (1), we must find the minimum of E in eqn. (8) by varying the coefficients c_p. To avoid quotients in the differentiation we multiply eqn. (8) by $\sum c_p c_q \Delta_{pq}$ obtaining

$$\left(\sum c_p c_q \Delta_{pq}\right)E = 2\sum c_p c_q h_{pq} + \sum c_p c_q g_{pq} \tag{11}$$

We then differentiate eqn. (11) with respect to c_t and find

$$\left(\sum c_p c_q \Delta_{pq}\right)\frac{\partial E}{\partial c_t} + E\frac{\partial}{\partial c_t}\sum c_p c_q \Delta_{pq} = 2\frac{\partial}{\partial c_t}\sum c_p c_q h_{pq} + \frac{\partial}{\partial c_t}\sum c_p c_q g_{pq} \tag{12}$$

The various terms in eqn. (12) are evaluated separately by using the symmetric character of the matrices **h**, Δ, and **g**. A necessary condition for the minimum is

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

Therefore

$$\left(\sum c_p c_q \Delta_{pq}\right)\frac{\partial E}{\partial c_t} = 0 \tag{13}$$

Furthermore

$$E\frac{\partial}{\partial c_t}\sum c_p c_q \Delta_{pq} = 2E\sum c_q \Delta_{tq} \tag{14}$$

$$2\frac{\partial}{\partial c_t}\sum c_p c_q h_{pq} = 4\sum c_q h_{tq} \tag{15}$$

and

$$\frac{\partial}{\partial c_t}\sum c_p c_q g_{pq} = \sum g_{pq}\frac{\partial}{\partial c_t}c_p c_q + \sum c_p c_q \frac{\partial}{\partial c_t}g_{pq}$$
$$= 2\sum c_q g_{tq} + \sum c_p c_q \frac{\partial}{\partial c_t}g_{pq} \tag{16}$$

Now

$$\frac{\partial}{\partial c_t}g_{pq} = \frac{\partial}{\partial c_t}\left(\frac{\sum c_r c_s \left\langle \chi_p(1)\chi_r(2)\left|\frac{1}{r_{12}}\right|\chi_s(2)\chi_q(1)\right\rangle}{\sum c_r c_s \Delta_{rs}}\right)$$

$$= \frac{1}{\sum c_r c_s \Delta_{rs}}\frac{\partial}{\partial c_t}\sum c_r c_s \left\langle \chi_p(1)\chi_r(2)\left|\frac{1}{r_{12}}\right|\chi_s(2)\chi_q(1)\right\rangle -$$

$$\frac{\sum c_r c_s \left\langle \chi_p(1)\chi_r(2)\left|\frac{1}{r_{12}}\right|\chi_s(2)\chi_q(1)\right\rangle}{(\sum c_r c_s \Delta_{rs})^2}\frac{\partial}{\partial c_t}\sum c_r c_s \Delta_{rs}$$

$$= \frac{1}{\sum c_r c_s \Delta_{rs}}\left(\sum c_s \left\langle \chi_p(1)\chi_t(2)\left|\frac{1}{r_{12}}\right|\chi_s(2)\chi_q(1)\right\rangle + \sum c_r \left\langle \chi_p(1)\chi_r(2)\left|\frac{1}{r_{12}}\right|\chi_t(2)\chi_q(1)\right\rangle\right) -$$

$$\frac{1}{\sum c_r c_s \Delta_{rs}}g_{pq}\left(2\sum c_q \Delta_{tq}\right)$$

Then the last term in eqn. (16) is

$$\sum c_p c_q \frac{\partial}{\partial c_t}g_{pq} = 2\sum c_q g_{tq} - \frac{(\sum c_p c_q g_{pq})(2\sum c_q \Delta_{tq})}{\sum c_r c_s \Delta_{rs}}$$

Collecting terms from eqns. (13)–(16) and inserting into eqn. (12) we obtain

$$2E\sum c_q \Delta_{tq} = 4\sum c_q h_{tq} + 4\sum c_q g_{tq} - 2\frac{(\sum c_p c_q g_{pq})(\sum c_q \Delta_{tq})}{\sum c_p c_q \Delta_{pq}}$$

This equation can be rearranged to the form

$$\sum c_q(h_{tq} + g_{tq} - \epsilon\Delta_{tq}) = 0 \tag{17}$$

where

$$\epsilon = \frac{1}{2}\left(E + \frac{\sum c_p c_q g_{pq}}{\sum c_p c_q \Delta_{pq}}\right) \tag{18}$$

Equation (17) for $t = 1, m$ is a system of linear homogeneous equations which allow computation of the c_q from h_{tq}, g_{tq}, and $\Delta_{t'q}$ for allowed values of the parameter ϵ. The matrix elements g_{tq} contain the c_q; hence the solution of eqn. (17) must be repeated until the coefficients which are obtained are the same as those used to calculate the g_{tq} (hence the name SCF-LCAO).

If we let

$$F_{tq} = h_{tq} + g_{tq}$$

eqn. (17) becomes

$$\sum c_q(F_{tq} - \epsilon\Delta_{tq}) = 0 \qquad t = 1,2,...,m$$

or in matrix form

$$(\mathbf{F} - \epsilon\Delta)\mathbf{C} = 0 \tag{19}$$

where $\mathbf{F}$ is called the Fock matrix and

$$\mathbf{C} = \begin{pmatrix} c_1 \\ \vdots \\ c_m \end{pmatrix}$$

Equation (19) is the matrix form of Roothaan's equations[1] and has a nontrivial solution for $\mathbf{C}$ only when $|\mathbf{F} - \epsilon\Delta| = 0$.

The parameter ϵ is called the orbital energy, and using eqns. (8) and (18) we see that

$$\epsilon = \frac{1}{2}\left(\frac{2\sum c_p c_q h_{pq}}{\sum c_p c_q \Delta_{pq}} + \frac{\sum c_p c_q g_{pq}}{\sum c_p c_q \Delta_{pq}} + \frac{\sum c_p c_q g_{pq}}{\sum c_p c_q \Delta_{pq}}\right)$$

$$= \frac{\sum c_p c_q h_{pq} + \sum c_p c_q g_{pq}}{\sum c_p c_q \Delta_{pq}}$$

$$= \frac{\langle\phi|h|\phi\rangle + \langle\phi|g|\phi\rangle}{\langle\phi|\phi\rangle}$$

Calculation of Matrix Elements for Helium

For simplicity let us use a normalized orbital containing just two basis functions. Then

$$\phi = c_1\chi_1 + c_2\chi_2$$

and

$$\langle\phi|\phi\rangle = \sum c_p c_q \Delta_{pq} = 1$$

where

$$\chi_i = 1s(\zeta_i) = \left(\frac{\zeta_i^3}{\pi}\right)^{1/2}e^{-\zeta_i r}$$

The parameters ζ_1 and ζ_2 may be varied to give the best energy, but the coefficients c_1 and c_2 must be optimized for each set of values of ζ_1 and ζ_2. The integrals in the matrix elements can be easily evaluated or found in published tables of integrals *(4)*.

The elements of $\mathbf{h}$ and Δ are

$$h_{11} = \frac{1}{2}\zeta_1^2 - z\zeta_1$$

$$h_{22} = \frac{1}{2}\zeta_2^2 - z\zeta_2$$

$$h_{12} = \frac{1}{2}(\zeta_1 + \zeta_2)(1 - \tau^2)^{3/2}\left[\frac{1}{4}(\zeta_1 + \zeta_2)(1 - \tau^2) - z\right]$$

$$\Delta_{11} = \Delta_{22} = 1$$

$$\Delta_{12} = (1 - \tau^2)^{3/2}$$

where $z = 2$ and

$$\tau = \frac{\zeta_1 - \zeta_2}{\zeta_1 + \zeta_2}$$

From eqn. (10) the g_{pq} are

$$g_{11} = c_1^2\langle\chi_1\chi_1|\chi_1\chi_1\rangle + 2c_1 c_2\langle\chi_1\chi_1|\chi_1\chi_2\rangle + c_2^2\langle\chi_1\chi_1|\chi_2\chi_2\rangle$$
$$g_{22} = c_1^2\langle\chi_1\chi_1|\chi_2\chi_2\rangle + 2c_1 c_2\langle\chi_1\chi_2|\chi_2\chi_2\rangle + c_2^2\langle\chi_2\chi_2|\chi_2\chi_2\rangle \quad (20)$$
$$g_{12} = c_1^2\langle\chi_1\chi_1|\chi_1\chi_2\rangle + 2c_1 c_2\langle\chi_1\chi_2|\chi_1\chi_2\rangle + c_2^2\langle\chi_1\chi_2|\chi_2\chi_2\rangle$$

The integrals in eqn. (20) are given by the formulas

$$\langle\chi_1\chi_1|\chi_1\chi_1\rangle = (5/8)\zeta_1$$

$$\langle\chi_2\chi_2|\chi_2\chi_2\rangle = (5/8)\zeta_2$$

$$\langle\chi_1\chi_1|\chi_2\chi_2\rangle = (1/16)(1 - \tau^2)(5 - \tau^2)(\zeta_1 + \zeta_2)$$

$$\langle\chi_1\chi_2|\chi_1\chi_2\rangle = (5/16)(1 - \tau^2)^3(\zeta_1 + \zeta_2)$$

$$\langle\chi_1\chi_1|\chi_1\chi_2\rangle = (1/32)(1 - \tau^2)^{3/2}(1 - \tau'^2)(5 - \tau'^2)(3\zeta_1 + \zeta_2)$$

$$\langle\chi_1\chi_2|\chi_2\chi_2\rangle = (1/32)(1 - \tau^2)^{3/2}(1 - \tau''^2)(5 - \tau''^2)(\zeta_1 + 3\zeta_2)$$

where

$$\tau = \frac{\zeta_1 - \zeta_2}{\zeta_1 + \zeta_2}$$

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[1] Although eqns. (17) have the same form as Roothaan's equations, his equations differ in that they include exchange terms. If the general Roothaan's equations are applied to the helium atom, the matrix elements g_{pq} include negative terms which arise from the exchange operator. The appendix gives a summary of how eqns. (17) must be modified to include exchange, and shows that both sets of equations give the same energy for the ground state of helium.

$$\tau' = \frac{\zeta_1 - \zeta_2}{3\zeta_1 + \zeta_2}$$

$$\tau'' = \frac{\zeta_1 - \zeta_2}{\zeta_1 + 3\zeta_2}$$

Values of the parameters which give the minimum energy for the helium atom using two basis functions are $\zeta_1 = 1.45$ and $\zeta_2 = 2.90$ (5). The energy is improved only slightly when more than two basis functions are used (6). For the above values of the parameters the two-electron integrals and matrix elements h_{pq} and Δ_{pq} are

$$\langle \chi_1\chi_1 | \chi_1\chi_1 \rangle = 0.906250$$

$$\langle \chi_2\chi_2 | \chi_2\chi_2 \rangle = 1.812500$$

$$\langle \chi_1\chi_2 | \chi_1\chi_2 \rangle = 0.954732$$

$$\langle \chi_1\chi_1 | \chi_2\chi_2 \rangle = 1.181482$$

$$\langle \chi_1\chi_1 | \chi_1\chi_2 \rangle = 0.904091$$

$$\langle \chi_1\chi_2 | \chi_2\chi_2 \rangle = 1.296660$$

$$h_{11} = -1.848750$$

$$h_{12} = -1.883523$$

$$h_{22} = -1.595000$$

$$\Delta_{11} = \Delta_{22} = 1.000000$$

$$\Delta_{12} = 0.838052$$

In order to find the SCF orbitals we guess an initial set of coefficients c_q. When a single basis function is used, the orbital that gives the best energy is $1s$ (1.6875) (7). Since 1.6875 is closer to ζ_1 than to ζ_2, we expect c_1 to be larger than c_2. We therefore take $c_1 = 1.00$ and $c_2 = 0.00$ as our initial values. For these values of the coefficients we obtain

$$g_{11} = 0.906250$$

$$g_{22} = 1.181482$$

$$g_{12} = 0.904091$$

and

$$F_{11} = h_{11} + g_{11} = -0.942500$$

$$F_{22} = h_{22} + g_{22} = -0.413518$$

$$F_{12} = h_{12} + g_{12} = -0.979432$$

The output coefficients are found for the lower value of ϵ which satisfies the following equation, called the secular equation (see eqn. (19)).

$$\begin{vmatrix} F_{11} - \epsilon & F_{12} - \Delta_{12}\epsilon \\ F_{21} - \Delta_{21}\epsilon & F_{22} - \epsilon \end{vmatrix} = 0 \qquad (21)$$

The lower root (corresponding to the ground state) is given by

$$\epsilon = \frac{-[2F_{12}\Delta_{12} - (F_{11} + F_{22})]}{2(1 - \Delta_{12}^2)}$$

$$- \frac{\sqrt{[2F_{12}\Delta_{12} - (F_{11} + F_{22})]^2 - 4(1 - \Delta_{12}^2)(F_{11}F_{22} - F_{12}^2)}}{2(1 - \Delta_{12}^2)}$$

Evaluating ϵ using the matrix elements given above, we obtain $\epsilon = -0.984326$.

The coefficients c_1 and c_2 are obtained from

$$(F_{11} - \epsilon)c_1 + (F_{12} - \epsilon\Delta_{12})c_2 = 0$$

and the normalization condition

$$c_1^2 + 2c_1c_2\Delta_{12} + c_2^2 = 1$$

For $\epsilon = -0.984326$ we find

$$c_1 = \frac{(F_{12} - \epsilon\Delta_{12})}{(F_{11} - \epsilon)}c_2$$

$$c_1 = 3.6942c_2$$

$$(3.6942c_2)^2 + 2(3.6942)(0.838052)c_2^2 + c_2^2 = 1$$

$$c_2 = 0.219059$$

$$c_1 = 0.809249$$

In order to ensure normalization of ϕ, more figures are retained in the coefficients than are actually significant.

The table gives the results for nine iterations of the procedure illustrated. The energy is seen to converge to a constant value in four iterations. The coefficients are stable after eight iterations.

The negative of the orbital energy, $-\epsilon$, is an approximation to the ionization potential, as was shown by Koopmans (8). From eqns. (5) and (18) we see that if ϕ is normalized

$$E = 2\epsilon - \langle \phi | g | \phi \rangle$$

and

$$\epsilon = \langle \phi | h | \phi \rangle + \langle \phi | g | \phi \rangle$$

The wave function for the helium ion He^+ is given approximately by

$$\psi_{\text{ion}} = \phi(1)$$

and

$$E_{\text{ion}} = \int \phi \left(-\frac{1}{2}\nabla^2 - \frac{z}{r} \right) \phi d\tau = \langle \phi | h | \phi \rangle$$

Then if I is the ionization energy of helium

$$I = E_{\text{ion}} - E = \langle \phi | h | \phi \rangle - 2\langle \phi | h | \phi \rangle - \langle \phi | g | \phi \rangle$$

$$= -\langle \phi | h | \phi \rangle - \langle \phi | g | \phi \rangle$$

$$= -\epsilon$$

The SCF value of $-\epsilon$ is 0.918. The experimental ionization energy is 0.904 au. The agreement here is better than usual; errors of several percent are common for predictions of this sort (9).

The SCF-LCAO-MO treatment of polyatomic molecules differs from the above treatment of helium in the following ways.

1) The matrix elements g_{pq} include exchange terms. (As shown in the appendix, an exchange term can also be included in the treatment of helium.)
2) All types of integrals are increased in number and in difficulty of evaluation. For a molecule with m basis orbitals, the number of integrals is roughly proportional to m^4 (10). Many of the integrals involve orbitals centered on different atoms. These multicenter integrals are more difficult to evaluate than the one-center integrals of helium. In approximate MO treatments, many of the integrals are approximated or neglected (11).

Input Coefficients,[a] Matrix Elements, and Eigenvalues for Helium

Iteration	c_1	c_2	F_{11}	F_{12}	F_{22}	ϵ	E
1	1.00	0.00	−0.942500	−0.979432	−0.413518	−0.984326	−2.83308
2	0.809249	0.219060	−0.878023	−0.890728	−0.274563	−0.905561	−2.86061
3	0.847034	0.176952	−0.890534	−0.890068	−0.301876	−0.920652	−2.86163
4	0.839638	0.185241	−0.888073	−0.904663	−0.296517	−0.917676	−2.86167
5	0.841091	0.183615	−0.888556	−0.905331	−0.297569	−0.918259	−2.86167
6	0.840806	0.183934	−0.888461	−0.905200	−0.297363	−0.918145	−2.86167
7	0.840862	0.183871	−0.888480	−0.905226	−0.297403	−0.918167	−2.86167
8	0.840851	0.183884	−0.888476	−0.905221	−0.297395	−0.918163	−2.86167
9	0.840853	0.183881	−0.888477	−0.905222	−0.297397	−0.918164	−2.86167

[a]The output coefficients of iteration n are the input coefficients for iteration $n + 1$.

3) The dimension of the determinant in the secular equation (21) equals m, the number of AO's in the basis set. A computer is required for efficient solution of secular equations of higher order than three, although the equation can often be factored with the aid of group theory (12). Either way, m orbital energies are obtained as roots of the equation, and the electrons are assigned in pairs to the orbitals of lowest energy.

4) In symmetric molecules, some of the coefficients are determined by symmetry, and need not be found iteratively (3, 12).

In spite of these complexities, the SCF-LCAO-MO method has contributed greatly to our understanding of the electronic structure of molecules. With the new generation of computers and more efficient programs, we can expect to see the method extended to moderately large and complex molecules.

Appendix

Equation (17) can be transformed to Roothaan's equations for helium as follows

$$\sum_q c_q(h_{rq} + g_{rq} - \epsilon\Delta_{rq})$$

$$= \sum_q c_q(h_{rq} - \epsilon\Delta_{rq}) + \sum_{q,p,s} c_q c_p c_s \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_q(1)\chi_s(2) \right\rangle$$

$$= \sum_q c_q(h_{rq} - \epsilon\Delta_{rq}) + \sum_{q,p,s} 2 c_q c_p c_s \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_q(1)\chi_s(2) \right\rangle -$$

$$\sum_{q,p,s} c_q c_p c_s \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_s(1)\chi_q(2) \right\rangle$$

The last equation is true because

$$\sum_{q,p,s} c_q c_p c_s \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_q(1)\chi_s(2) \right\rangle =$$

$$\sum_{q,p,s} c_q c_p c_s \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_s(1)\chi_q(2) \right\rangle$$

which follows from the fact that the sum is over all values of q, p, and s.

We may thus write

$$\sum_q c_q(h_{rq} + g'_{rq} - \epsilon\Delta_{rq}) = 0 \qquad (22)$$

where

$$g'_{rq} = \sum_{p,s} c_p c_s \left(2 \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_q(1)\chi_s(2) \right\rangle - \right.$$

$$\left. \left\langle \chi_r(1)\chi_p(2)\left|\frac{1}{r_{12}}\right|\chi_s(1)\chi_q(2) \right\rangle \right)$$

This is the form of the g_{rq} in Roothaan's equations [see Pilar, reference (2a)]. The negative terms are present because for a general closed-shell system the energy is given by

$$E = 2\sum_i^{occ} \langle \phi_i|h|\phi_i \rangle + \sum_{i,j}^{occ} \left(2 \left\langle \phi_i(1)\phi_j(2)\left|\frac{1}{r_{12}}\right|\phi_i(1)\phi_j(2) \right\rangle - \right.$$

$$\left. \left\langle \phi_i(1)\phi_j(2)\left|\frac{1}{r_{12}}\right|\phi_j(1)\phi_i(2) \right\rangle \right).$$

Since in the helium atom there is only one occupied molecular orbital the double sum becomes

$$2 \left\langle \phi_1(1)\phi_1(2)\left|\frac{1}{r_{12}}\right|\phi_1(1)\phi_1(2) \right\rangle - \left\langle \phi_1(1)\phi_1(2)\left|\frac{1}{r_{12}}\right|\phi_1(1)\phi_1(2) \right\rangle =$$

$$\left\langle \phi_1(1)\phi_1(2)\left|\frac{1}{r_{12}}\right|\phi_1(1)\phi_1(2) \right\rangle \equiv \left\langle \phi(1)\phi(2)\left|\frac{1}{r_{12}}\right|\phi(1)\phi(2) \right\rangle$$

as used in eqn. (5) of the text. Consequently, the g_{rq} in eqn. (17) have no negative exchange terms. However, when helium is treated with eqn. (22), the g_{rq}' do have negative exchange terms. Then the values of $F_{rq}' = h_{rq} + g_{rq}'$ differ from those of F_{rq}, but the same SCF values are obtained for c_p, ϵ (lower), and E.

Literature Cited

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