here. In addition, all integrals were transformed to the orthonormal self-consistent basis and matrix elements of the dipole operator were computed, in a total of approximately forty-five minutes. There were nine independent σ orbitals and five independent π orbitals, including $d\sigma$ and $d\pi$ orbitals. The binding energy obtained in this approximation is twice that reported for a calculation with a basis of the atomic self-consistent orbitals.[6]

[6] A. Karo and L. C. Allen, J. Chem. Phys. **31**, 968 (1959).

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On the Role of the Equivalence Restriction in Molecular Calculations

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IN the treatment of open-shell atoms or molecules[1–3] an effort is being made to retain, as a basis for calculation, techniques relating to single determinantal trial functions composed of one-electron wave functions which were developed in treating closed-shell systems. However, variation of the orbitals in general expressions of the energy leads to equations which imply a parametric dependence on the spin and the magnetic quantum number of the orbital angular momentum. Pairs of orbitals are not necessarily related by the step-up and step-down operators; degenerate sets are not orthonormal transforms of one another. Furthermore, if the total wave function belongs to a degenerate representation, then the one-electron orbitals need not be symmetry orbitals at all. Nesbet[1] has formulated procedures that restrict the spin orbitals to be orthonormal transforms (equivalence restriction) within sets of symmetry orbitals (symmetry restriction). More recently Roothaan[3] has shown that if the total energy is given as the average expectation value for all the degenerate components for any degenerate state under consideration, then the solutions of the variational equations can always be symmetry orbitals. Roothaan also applies equivalence restrictions in computing the energy, and one might refer to this scheme as an average equivalence restriction procedure.

In this note we report and compare the results for two LCAO-SCF treatments of a molecule with a degenerate open shell, OH. The basis set is a set of Slater functions with parameters that have been described previously by Krauss.[4] Both the techniques applied here are variants of the equivalence and symmetry restriction technique.

The procedures employed by Higuchi[5] and Krauss[4] to investigate some diatomic hydrides are obviously simple examples of the general procedure discussed by Roothaan.[3] For the OH radical with a $^2\pi$ ground state, the open-shell orbitals are of a different symmetry, π, than that of the closed shell, σ. Inasmuch as the solution of Roothaan's equations may be taken to be symmetry orbitals, then certain simplifications of Roothaan's equations occur. Roothaan has shown that the Lagrangian multipliers coupling the closed and open shells may be written

$$\theta_{mk}=-f\langle\phi_m|2\alpha J_o-\beta K_o|\phi_k\rangle$$

(see Roothaan[3] for definitions of operators, subscripts, and other coefficients). The J_o and K_o operators are totally symmetric under all group symmetry operations if equivalence restriction holds so that

$$\theta_{mk}=0$$

where ϕ_m belongs to the π open shell and ϕ_k belongs to the σ closed shell. Therefore the usual unitary transformations

$$\phi_c'=\phi_c U_c, \quad \phi_o'=\phi_o U_o,$$

which transform the closed and open shells among themselves, bring the matrix of Lagrangian multipliers

[1] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954); G. Berthier, J. chim. phys. **51**, 363 (1954).
[2] G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).
[3] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), this issue.
[4] M. Krauss, J. Chem. Phys. **28**, 1021 (1958).
[5] J. Higuchi, J. Chem. Phys. **22**, 1339 (1954); **24**, 535 (1956).

TABLE I. LCAO coefficients.

Case I				
$a_{11}=1.0002$	$a_{12}=0.0162$	$a_{13}=0.0031$	$a_{14}=-0.0052$	$\epsilon_1=-20.5084$
$a_{21}=-0.0246$	$a_{22}=0.8712$	$a_{23}=0.1152$	$a_{24}=0.1978$	$\epsilon_2=-1.2259$
$a_{31}=-0.0297$	$a_{32}=-0.5192$	$a_{33}=0.6671$	$a_{34}=0.5662$	$\epsilon_3=-0.5266$
$a_{41}=-0.0613$	$a_{42}=-0.6107$	$a_{43}=-0.8556$	$a_{44}=1.1127$	$\epsilon_4=0.4735$
Case II				
$a_{11}=1.0002$	$a_{12}=0.0174$	$a_{13}=0.0031$	$a_{14}=-0.0055$	$\epsilon_1=-20.5037$
$a_{21}=-0.0238$	$a_{22}=0.8939$	$a_{23}=0.1080$	$a_{24}=0.1662$	$\epsilon_2=-1.2983$
$a_{31}=-0.0298$	$a_{32}=-0.4915$	$a_{33}=0.6741$	$a_{34}=0.5664$	$\epsilon_3=-0.5444$
$a_{41}=-0.0616$	$a_{42}=-0.6007$	$a_{43}=-0.8510$	$a_{44}=1.1178$	$\epsilon_4=0.4609$

to diagonal form, and we obtain the following matrix equations:

$$F_c\phi_k=\phi_k\epsilon_k, \quad F_o\phi_m=\phi_m\epsilon_m,$$

where

$$F_c=H+2J_c-K_c+2J_o-K_o,$$
$$F_o=H+2J_c-K_c+2aJ_o-bK_o.$$

The Coulomb and exchange coupling operators included by Roothaan are deleted from the preceding equations since

$$L_o\phi_k=M_o\phi_k=0, \quad L_c\phi_m=M_c\phi_m=0.$$

Higuchi[5] and Krauss[4] chose an even simpler problem by using a single atomic orbital with a fixed radial function to represent the π orbitals. It is possible, for this situation, to obtain the same matrix equations for the closed-shell case without considering the average expectation value for the energy over all of the degenerate components, since the open shell can be represented by some constant potential term and incorporated into the constant matrix of the one-electron terms in the Fock operator of the SCF equations. This calculation is designated as I and the total energy, LCAO coefficients, and dipole moment are so denoted in the Tables. (See Tables I and II.)

In the other calculation, which we designate II, we follow the prescription of Nesbet as carried out earlier by Freeman[6] who used numerical Hartree-Fock atomic orbitals as basis. As we have noted previously the equations derived from a single determinant for the space orbitals show that the space orbitals for different spins are neither orthogonal nor identical; there is a different equation for functions associated with α spin than those associated with β spin. The matrix of the α coefficients transforms independently of the β coefficients. Nesbet suggested that solutions should consistently be chosen from one equation (α or β) arbitrarily and equivalence restrictions

$$(S_+\phi_\beta=\phi_\alpha)(S_-\phi_\alpha=\phi_\beta)$$

applied both in iterating the equations to a final solution and then to calculate the energy and other properties. In this case the solution of that matrix equation corresponding to the spin which is in excess was chosen.

The calculations were performed on Whirlwind I using a Roothaan SCF LCAO procedure as written by Meckler[7] and Nesbet,[8] only modified in each case to perform the computations according to either procedure I or II. In both calculations the same set of integrals[4] was used as machine input.

The results of the two calculations given in the tables show essential agreement. Even the relatively small energy difference of half an exchange integral between the open- and closed-shell orbitals for the Fock operator of the second procedure over the first one does not reflect itself finally in the total energy. As it is very probable that any attempt to obtain a H-F approximation or better would necessitate a considerable extension of the basis set, it seems evident that the minor differences in these schemes can be ignored and the computationally simplest scheme chosen in any particular case even though the average equivalence restriction procedure and its generalization by Roothaan is more consistent theoretically.

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TABLE II. Total energy and dipole moment.[a]

Case I		Case II	
Energy	Dipole moment	Energy	Dipole moment
−75.0600	0.3608	−75.0596	0.3862

[a] In a.u.

[6] A. J. Freeman, J. Chem. Phys. 28, 230 (1958).

[7] A. Meckler, Quart. Progr. Rep., Solid State and Molecular Theory Group, MIT (January 15, 1955), p. 10.

[8] R. K. Nesbet, Quart. Progr. Rep., Solid State and Molecular Theory Group, MIT (July 15, 1957), p. 27.