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Diatomic Molecule Project at RIAS and Boston University*

R. K. NESBET†

RIAS, 7212 Bellona Avenue, Baltimore 12, Maryland

IN recent years electronic digital computers have become available for use in the theory of quantum chemistry. The introduction of this new technique has had the effect of opening up certain lines of investigation that had previously been closed primarily because of the great complexity and difficulty of quantum mechanical calculations. Concurrently, methods of carrying out such calculations have recently been studied and improved in many points of practical importance.

The project described in this paper is intended to apply some of these recent developments to the particular problem of calculating properties of the electronic wave functions of diatomic molecules. Programs for the IBM 704 computer have been written which incorporate a general procedure for calculating such wave functions, using contemporary methods.

The results of this project to date have been extremely encouraging. It has been found that it is not necessary to sacrifice speed of operation to any great extent in order to achieve generality. These programs carry out matrix self-consistent field calculations by the method of Roothaan[1] with modifications which take full advantage of the molecular symmetry and which allow calculations on arbitrary configurations either by the unrestricted Hartree-Fock method or by the method of symmetry and equivalence restrictions.[2] Molecular self-consistent orbitals are expanded as linear combinations of exponential orbitals on the atoms, with arbitrary powers of r and spherical harmonics. There is essentially no limit on the parameters, such as angular quantum numbers, which can be handled, nor on the number of basis functions, other than the economic problem of finding computer time for lengthy calculations. The programs also carry out the transformation of all integrals to an orthonormal basis (that of the self-consistent orbitals), which is the most laborious stage of a configuration interaction calculation.

The method used for evaluating integrals has been developed by P. Merryman from the exchange integral method of Ruedenberg,[3] based on the earlier work of Kotani.[4] One point of great importance is that economies of scale are realized by the use of an intermediate calculation of certain integrals over charge densities. This reduces the dominant term in the time required for evaluation of all integrals necessary for a diatomic molecular calculation from the fourth power of the number of basis orbitals to the second power. An advantage in speed of a factor between five and ten over times reported for previous programs[5] has been found in preliminary calculations with the present programs. Because of the economies of scale, this factor actually improves for larger calculations.

With these programs, it will be possible to remove some of the more serious restrictions that have affected *ab initio* wave function calculations for diatomic molecules. Most such calculations on molecules other than H_2 have used the minimum number of atomic orbitals which would describe the independent orbitals of the separated atoms. In principle, a complete (and necessarily infinite) set of such orbitals should be used for accurate linear expansion of the molecular wave function. Effects of obvious importance, such as the polarization of atomic orbitals by their molecular environment, can only be described by the inclusion of more basis orbitals than the minimum set, and by including orbitals of higher angular quantum numbers than those occupied in the separated atoms.

Some of the most interesting applications of more accurate molecular electronic wave functions will be in considering the various electric and magnetic properties of a molecule, either in interaction with the moments of its nuclei or with external fields. A program for external moments is presently in use, and a program for internal moments (e.g., the quadrupole coupling constant) will be included in the near future. All such specialized matrix elements can be obtained by modifications of the general integral program.

To illustrate the work being done with these programs, results of a calculation on the electronic ground state of HF are summarized in Table I. Only the result of the Roothaan self-consistent field calculation is reported

TABLE I. Electronic energy of HF in molecular Hartree-Fock approximation.

Total electronic energy	$-105.184971\ e^2/a_0$ (Hartree units)
Nuclear repulsion at $R=1.7328a_0$	5.193906
Energy calculated for separated atoms	-99.829018
Binding energy	0.162047 $=4.409$ ev

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[†] Permanent address: Boston University, Physics Department, Boston 15, Massachusetts.

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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]

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On the Role of the Equivalence Restriction in Molecular Calculations

A. J. FREEMAN

Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, and Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

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

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