JOURNAL OF COMPUTATIONAL PHYSICS 6, 142–145 (1970)

Diatomic Molecule Symmetry Eigenfunctions by Direct Diagonalization

INTRODUCTION

Recently we reported a procedure [1] and computer program to obtain atomic L-S eigenfunctions by direct diagonalization of the operator $\mathbf{L}^2 + (1/20)\,\mathbf{S}^2$. Such eigenfunctions are required in order to obtain correlated wave functions for many-electron atoms. This program [1] has made it possible for us to perform configuration interaction (CI) calculations [2] which would not otherwise have been feasible. By using symmetry-adapted configurations, rather than simple Slater determinants, the size matrix to be diagonalized is greatly reduced. A recent neon atom calculation [3] shows the usefulness of this approach. In this calculation [3] 8392 distinct Slater determinants were used, but yielded only 434 ^1S L-S configurations.

It should be noted that most of the previous work [4–8] on the construction of symmetry-adapted functions makes use of projection operators [9]. Reference [1] indicates that, for the atomic case, direct diagonalization compares quite favorably with the use of projection operators. Gershgorn and Shavitt [10] have discussed another method for constructing molecular symmetry-adapted functions.

DIATOMIC MOLECULE SYMMETRY

For the computation of accurate CI wave functions for diatomic molecules, it is helpful to obtain symmetry-adapted functions for diatomic molecules. For a $\sum$ state of a homonuclear diatomic molecule, the nonrelativistic electronic Hamiltonian

$$H = \sum_i \left(-\frac{1}{2} \Delta_i^2 - \frac{Z_a}{r_{ia}} - \frac{Z_b}{r_{ib}} \right) + \sum_{i<j} \frac{1}{r_{ij}} \tag{1}$$

commutes with the operators $\mathbf{S}^2$, S_z, C_ϕ, σ_v, and i where

$$\mathbf{S}^2\psi = S(S+1)\,\psi, \tag{2}$$

$$S_z\psi = M_s\psi, \tag{3}$$

$$C_\phi\psi = e^{i\Lambda\phi}\psi, \tag{4}$$

$$\sigma_v\psi = \pm\psi, \tag{5}$$

$$i\psi = \pm\psi. \tag{6}$$

For heteronuclear diatomics, the operator i does not commute with H. $\sum$ states ($\Lambda = 0$) can be classified as + or −, depending on the effect of the operator σ_v on the wave function. By utilizing this σ_v symmetry, we divide by two the size of the CI matrix to be diagonalized. In addition, this type of partitioning of the Hamiltonian matrix into $\sum^+$ and $\sum^-$ blocks also eliminates the problem (encountered when a number of states of $\sum$ symmetry are being investigated) of differentiating between the + and − states. For states with $| \Lambda | > 0$, however, it is not possible to simultaneously diagonalize C_ϕ and σ_v. And, in fact, all the symmetry of the diatomic molecule is satisfied *without* the use of σ_v.

Therefore, rather than simple single Slater determinants, our configurations should be symmetry-determined linear combinations of Slater determinants. These configurations should have the desired values of the quantum numbers S, M_s, Λ, + or − (if appropriate), and g or u (if appropriate), respectively.

PROCEDURE

The essence of our approach is to diagonalize the matrix of the operator $\mathbf{S}^2 \pm (1/2)\, \sigma_v$, where σ_v is the operator that determines the + or − symmetry. For, Π, Δ,... states, only the operator $\mathbf{S}^2$ is diagonalized. Two FORTRAN IV computer programs [11], to construct symmetry eigenfunctions for homonuclear and heteronuclear diatomics, were written for the CDC 6600. These programs are available from the Quantum Chemistry Program Exchange [11].

Input to the program is the orbital occupancy and the symmetry desired. For a homonuclear case, the O_2 molecule, one might desire all linearly independent ${}^3\Sigma_g^-$ configurations arising from the orbital occupancy $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g\ 3\sigma_u\ 1\pi_g^3\ 1\pi_u^3$. Given the input, the program proceeds in three steps:

(1) All possible Slater determinants D_i with the proper values of M_s, Λ, and g or u are generated for the given orbital occupancy. This step guarantees eigenfunctions of S_z, C_ϕ, and i. For reasons which will be obvious later, we always choose $M_s = S$. In HEDIAG [11] the g or u determination is omitted.

(2) All matrix elements $\langle D_i \mid \mathbf{S}^2 \pm (1/2)\, \sigma_v \mid D_j \rangle$ are computed. The $\mathbf{S}^2$ matrix elements are obtained by the well-known relation

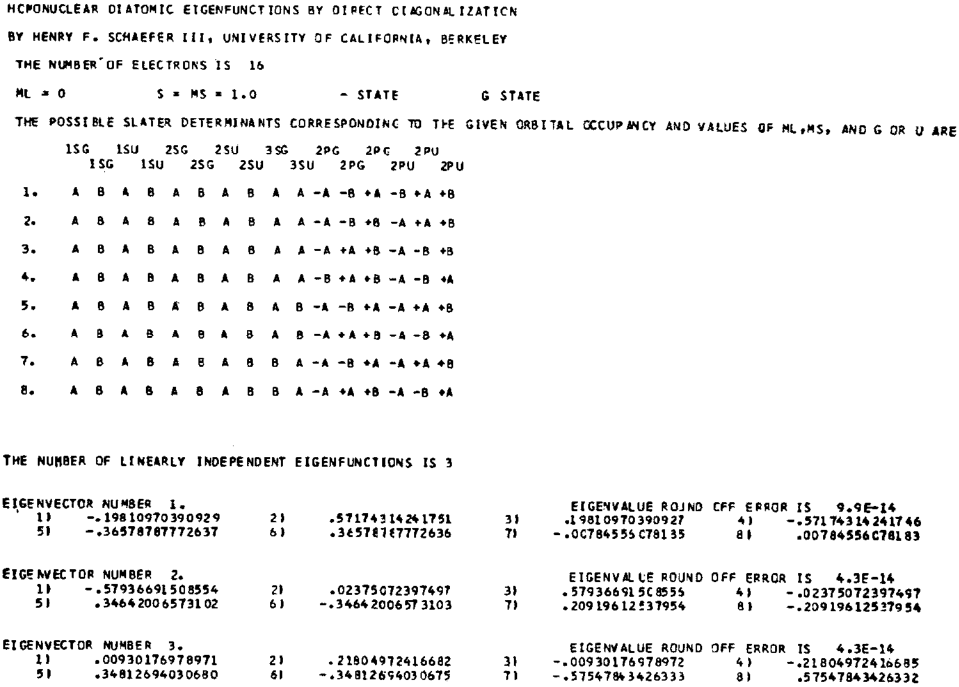
$$\mathbf{S}^2 = S^+S^- + S_z^2 - S_z \tag{7}$$

where S^+ and S^- are the many-electron raising and lowering operators. The matrix element $\langle D_i \mid \sigma_v \mid D_j \rangle$ has the value 0, +1, or −1.

(3) The matrix $\langle D_i \mid \mathbf{S}^2 \pm (1/2)\, \sigma_v \mid D_j \rangle$ is diagonalized, and the eigenvectors corresponding to the lowest eigenvalue are the desired symmetry-adapted con-

figurations. The above useful fact is guaranteed by choosing $M_s = S$ in step 1 and by operating with $S^2 + (1/2)\,\sigma_v$ for $-$ states and $S^2 - (1/2)\,\sigma_v$ for $+$ states.

Output for the above example is given in Fig. 1. For a similar number of Slater determinants and linearly independent configurations, computation times are minimal and comparable to those given in Reference 1.



```
HCPONUCLEAR DIATOMIC EIGENFUNCTIONS BY DIPECT CIAGONALIZATICN

BY HENRY F. SCHAEFER III, UNIVERSITY OF CALIFORNIA, BERKELEY

 THE NUMBER OF ELECTRONS IS  16

 ML = 0          S = MS = 1.0          - STATE          G STATE

 THE POSSIBLE SLATER DETERMINANTS CORRESPONDINC TO THE GIVEN ORBITAL OCCUPANCY AND VALUES OF ML,MS, AND G OR U ARE
         1SG   1SU   2SG   2SU   3SG   2PG   2PG   2PU
            1SG   1SU   2SG   2SU   3SU   2PG   2PU   2PU

  1.     A  B  A  B  A  B  A  B  A  A -A -B +A -B +A +B

  2.     A  B  A  B  A  B  A  B  A  A -A -B +B -A +A +B

  3.     A  B  A  B  A  B  A  B  A  A -A +A +B -A -B +B

  4.     A  B  A  B  A  B  A  B  A  A -B +A +B -A -B +A

  5.     A  B  A  B  A  B  A  B  A  B -A -B +A -A +A +B

  6.     A  B  A  B  A  B  A  B  A  B -A +A +B -A -B +A

  7.     A  B  A  B  A  B  A  B  B  A -A -B +A -A +A +B

  8.     A  B  A  B  A  B  A  B  B  A -A +A +B -A -B +A


THE NUMBER OF LINEARLY INDEPENDENT EIGENFUNCTIONS IS 3

EIGENVECTOR NUMBER  1.                                             EIGENVALUE ROJND CFF ERROR IS   9.9E-14
    1)    -.198109703909 29     2)     .57174314241751      3)   .19810970390927      4)    -.57174314241746
    5)    -.36578787772637      6)     .36578787772636      7)  -.00784556C78135      8)     .00784556C78183

EIGENVECTOR NUMBER  2.                                             EIGENVALUE ROUND OFF ERROR IS   4.3E-14
    1)    -.57936691508554      2)     .02375072397497      3)   .57936691508555      4)    -.02375072397497
    5)     .34642006573102      6)    -.34642006573103      7)   .20919612537954      8)    -.20919612537954

EIGENVECTOR NUMBER  3.                                             EIGENVALUE ROUND OFF ERROR IS   4.3E-14
    1)     .00930176978971      2)     .21804972416682      3)  -.00930176978972      4)    -.21804972416685
    5)     .34812694030680      6)    -.34812694030675      7)  -.57547843426333      8)     .57547843426332
```

FIG. 1. ${}^3\Sigma_g^-$ eigenfunctions for the orbital occupancy $1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g 3\sigma_u 1\pi_g{}^3 1\pi_u{}^3$. In the printout, S means σ, P means π, A means α ($m_s = +1/2$), B means β ($m_s = 1/2$). A minus $(-)$ indicates $m_l = -1$ and a plus $(+)$ indicates $m_l = +1$.

Eigenvector accuracy is 13 or 14 significant figures on the CDC 6600. As written the program requires about 20,000 words of memory. Restrictions on the program are:

(1) No more than 36 electrons outside of closed shells.

(2) No more than 100 determinants of the correct M_s and Λ arising from the given orbital occupancy.

(3) No more than 20 symmetry eigenfunctions arising from the specified orbital occupancy and molecular quantum numbers.

ACKNOWLEDGMENTS

We thank the Nuclear Chemistry Division of the Lawrence Radiation Laboratory, Berkeley, for a grant of computer time. Thanks are also due to the referee, who pointed out an error in the original version of this paper.

REFERENCES

1. H. F. SCHAEFER AND F. E. HARRIS, *J. Comput. Phys.* **3** (1968), 217.
2. H. F. SCHAEFER AND F. E. HARRIS, *Phys. Rev. Lett.* **21** (1968), 1561.
3. J. W. VIERS, F. E. HARRIS, AND H. F. SCHAEFER, *Phys. Rev.* **A1** 24, (1970).
4. R. K. NESBET, *J. Math. Phys.* **6** (1961), 701.
5. A. ROTENBERG, *J. Chem. Phys.* **39** (1963), 512.
6. H. F. SCHAEFER AND F. E. HARRIS, *Chem. Phys. Lett.* **1** (1967), 407.
7. C. F. BUNGE, *Phys. Rev.* **168** (1968), 92.
8. J. KOUBA AND Y. OHRN, *Int. J. Quantum Chem.* **3** (1969), 513.
9. P. O. LOWDIN, *Phys. Rev.* **97** (1955), 1509.
10. Z. GERSHGORN AND I. SHAVITT, *Int. J. Quantum Chem.* **15** (1967), 403.
11. Programs HODIAG and HEDIAG, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana 47401.

RECEIVED: December 4, 1969

HENRY F. SCHAEFER III*

Department of Chemistry,
University of California,
Berkely, California 94720

---

* Supported in part by the Petroleum Research Fund, administered by the American Chemical Society,