The calculation of resonant states of atoms and molecules by quasi-stationary methods

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THE CALCULATION OF RESONANT STATES OF ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS
THE CALCULATION OF RESONANT STATES OF
ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS

by

James Kendree Williams, Jr.

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James Kendree Williams, Jr.

under the direction of has Dissertation Committee, and approved by all its members, has been presented to and accepted by the Graduate School, in partial fulfillment of requirements for the degree of

DOCTOR OF PHILOSOPHY
DEDICATION

To my wife, Ann,
for patience, forbearance,
and silence beyond that expected of any wife.
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CHAPTER I

INTRODUCTION

An important development in recent collision experiments has been the evidence of autoionizing compound negative ion states with lifetimes from $10^{-14}$ to $10^{-12}$ seconds; considerably shorter than the lifetimes of electronically excited states ($\sim 10^{-8}$ sec.). These compound states have been used to explain resonances in elastic scattering cross sections (Simpson and Fano, 1963), the onset of inelastic processes where no states of the target exist (Schulz and Philbrick, 1964; Chamberlain, 1965), forbidden transitions (Baranger and Guerjoy, 1957), and dissociative attachment (Schulz, 1958).

Most of the states observed in electron scattering experiments have energies lying slightly (0.1 - 1.0 eV) below known excited states of the target and the usual decay process is autoionization. Some specific examples of targets are hydrogen, helium, and the hydrogen molecule.

In hydrogen, the first excited state is $^2S$ 2s or $^2P$ 2p at 10.204 eV above the $^2S$ 1s ground state. A resonance has been observed by Schulz (1964) at 9.75 ± .15 eV, just below the 2s or 2p energy.

At 19.3 eV above the ground state of the helium atom there is a sharp He$^-$ resonance which is so well known that it is used for energy
scale calibration (Schulz, 1964; Simpson, Kuyatt, et al., 1965a; and many others). This is just below the $^1S^1_s$, $^3S^1$ ls2s states of helium at an average energy of 20.2 eV. Fano and Cooper (1965) have also discussed higher He⁺ resonances, such as the $^2P^0$ (2s)$^2$2p at 57.1 eV and $^2D^0$ 2s(sp)$^2$ at 58.2 eV. These lie just below the $^1S^1_s$ (2s)$^2$ and $^3P^0$ 2s2p states at 57.9 and 58.4 eV respectively.

The pre-ionization states of helium can be considered as resonances of He⁺ plus an electron. Madden and Codling (1964) have observed a set of these autoionizing levels, and Cooper, Fano and Prats (1963) have shown that they correspond to a series (2snp+ns2p)$^1P^0$, n = 2, 3, ... which converges to He⁺ 2p (or 2s) at 65.395 eV.

Kuyatt, Simpson and Mielczarek (1965b, 1966) have observed pairs of resonances starting about .9 eV below the $^3P^1^u$ states of the hydrogen molecule, and studied the isotope effect in HD and D₂. In these experiments, spacings of levels were observed which correspond closely to the vibrational levels of the excited $H_2^+$ (HD,D₂) states, which seems to indicate that the third electron in the compound state became trapped in the field of the excited target state, but far enough away that it had little effect on the nuclear motion. Golden and Bendel (1965) report substantially the same result.

Various methods have been proposed and used for calculating the energies and wave functions of these compound states, particularly for scattering of electrons off atoms. The problem is that the normal variation method is inapplicable, as an infinity of states of the same symmetry and equal or lower energy exist for each resonance.
consisting of the ground state of the target plus a free electron with the proper angular momentum and a continuum of energy values.

Fano (1961) and Burke and Schey (1962) have developed methods which actually deal with the scattering cross section. The Fano theory is particularly useful for analysis of line shape, while Burke and Schey use a close-coupling technique to calculate the cross section and study resonances as part of the total scattering problem.

HolŒien (1958a,b), HolŒien and Midtal (1965, 1966) Mandl and Herzenberg (1963, series), O'Malley and Geltman (1965), Taylor and this author (1965), and Lipsky and Russek (1966) have devised quasi-stationary methods for calculation of the energy and wave function of resonant states without predicting any of the features of the cross section except the approximate position of the resonance. Of the above, Taylor and Williams (1965, hereinafter denoted as TW) were the first to do calculations on systems other than two-electron atoms. The Taylor-Williams calculation was on the diatomic molecule \( \text{H}_2 \) plus an electron, and the results compared quite well with the experiments of Kuyatt, et al. (1965) and Golden and Bandel (1965). Since that time, Mandl and Herzenberg (1965) have done a parametrized calculation on the \( \frac{3\Sigma^+}{\Omega} \) state of \( \text{H}_2 \) plus an electron with their modified Kapur-Peierls technique.

Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted as TNG), with the aid of the author, have presented a formal justification of the physical quasi-variation method of TW, and presented a complete quasi-stationary method for calculating the energy of resonances
which includes the TW method as a special case. This work also lists and classifies three types of resonances, including the examples above and two other types which will be discussed later.

Therefore, one of the aims of this work is to present the Taylor-Williams quasivariation method with its original physical arguments, and the formal justification of it as presented by TNG. This is done in Chapter II.

The second aim is to apply these methods to small diatomic molecules (in particular, $H_2$), calculating resonant states and comparing to electron scattering experiments (Chapter III, ff.).

Finally, in conjunction with the second aim, the diatomic molecule calculation methods of Harris (1960) Taylor and Harris (1963, series), and Taylor (1964) for bound states of six electrons or less have been revised to include the quasi-stationary methods, and have been extended to allow both bound and quasi-stationary calculations of energies and wave functions of larger diatomic systems. The latest revision, presented and discussed in the Appendices, can do calculations on up to twenty electrons.
CHAPTER II

THEORY

The formation, lifetime, and decay of the compound states mentioned above can only be described rigorously by wave packets composed of combinations of bound and continuum states of the N+1 electron system. The resonance is simply a highly localized wave packet which remains so for $10^{-14}$ to $10^{-12}$ seconds, so that with the proper restrictions, it can be treated as stationary during this time. This is similar to the treatment of electronically excited states as stationary by ignoring the light field interactions, where inclusion of the light field leads to decay in approximately $10^{-8}$ seconds.

Without any restrictions, a carefully executed variational calculation will lead to the conclusion that no compound states exist, since one can construct an infinite number of states of the same symmetry and equal or lower energy. Thus, even to apply the Hylleraas-Undheim procedure, treating the resonance as the $m$th excited state, one would have to diagonalize an infinite secular determinant, taking the uppermost root as the resonance energy.

The original work of Taylor and Williams (TW, 1965) presented a quasi-variation method based on physical arguments for selecting the
proper restrictions so that valid results could still be obtained.

Briefly the method stated that if an N+1 electron bound state function could be guessed such that it nearly represented the physical situation, it would also closely resemble the proper linear combination of wave packets, and the matrix elements of interaction of this bound function with the infinite number of continuum functions would be so small compared to the bound-bound interactions that the infinite Hamiltonian matrix would be nearly numerically block diagonalized, separating the bound state in the continuum from its adjacent continuum.

The rules given for selecting these N+1 electron functions were that they must be doubly excited, autoionizing configurations, but with small autoionization probability in order to obtain long lifetimes. The small autoionization probability could be assured by selecting "weakly correlated" orbitals (i.e., orbitals having small \(1/r_{ij}\) matrix elements) for the trial wave function. This choice of functions causes both the Hamiltonian and overlap matrices to be nearly block diagonal in the prescribed manner, since the double excitation produces an excited core which is orthogonal to the ground state of the target. Integration over the inner electrons will make the bound-continuum matrix elements small. Hence the total secular determinant is approximately block diagonalized into a finite part mixing multiply excited configurations of the compound state and an infinite part which can be ignored.

These arguments work quite well for certain types of resonances,
but considerable experimental evidence has appeared that there are other resonances which the quasi-variation method would not be able to calculate. Taylor, Nazaroff, and Golebiewski (TNG, 1966) analyzed the experimental data and proposed that it could be explained by three types of resonance, which they classified as Type I Core-Excited, Type II Core-Excited, and Single Particle (hereinafter denoted by CE1, CE2, and SP, respectively).

The resonances of He, H, and H₂ discussed above, which lie 0.1 to 1.0 eV below excited states of the target, are CE1. They could be formed by the virtual process of the impinging electron exciting one of the electrons of the target and becoming trapped in the slight potential well left when the excited electron moves out of its way, with a resultant binding energy of 0.1 - 1.0 eV. The CE1 resonances are the ones which can be handled by the quasi-variation method, and the excitation of one of the target electrons explains the classification Core-Excited.

The potential well can be considered as being formed by additional amount of nuclear charge that the impinging electron sees when the excited core electron moves away.

One of the examples in many textbooks (for instance Messiah, 1961, Vol. I, p. 88) is the case of virtual levels of the square well potential, in which it is shown that if the walls of the finite \( V_0 = \infty \) well were made finite, "long-lived" localized wave packets (bound states in the continuum) can be formed only at those energies in the continuum of the well \( E > V_0 \) at which bound states would have
existed had $V_o$ not been reduced to a finite value.

Based on this argument, TNG proposed the existence of CE2 resonances as virtual states of the potential well caused by core excitation. These resonances should be quite broad (short lived - width is inversely proportional to lifetime) compared to CE1, since they are adjacent to the continua of both the ground state of the target and the excited state of the target, and have no binding energy to provide stability. Experimental examples cited as indicative that CE2 resonances exist were the Hg$^-$ $(5d^{10}6s6p^2)\,^4P_{5/2}$ seen by Kuyatt, Simpson, and Mielczarek (1965) at 4.89 eV, and an elusive peak seen by the same experimenters in the elastic scattering of electrons from helium at 21.4 to 21.6 eV, just above the $n = 2$ levels. Schulz and Philbrick (1965) and Chamberlain and Heideman (1965) observed a stronger peak in the inelastic cross section of He corresponding to nearly the same energy. TNG attribute this resonance to a CE2 above the $n = 2$ level of He, rather than a CE1 below the $n = 3$ level, as the necessary binding energy below the $n = 3$ level would indicate a longer lived resonance and therefore a narrower peak than that observed, and an electron affinity of 2 eV for the $n = 3$ level as opposed to .1 to .6 for the $n = 2$ level.

In the same spirit, it is argued that if an excited target state can support virtual levels, it should be possible for the ground state to do so also. Several experimental observations exist which cannot be explained except by postulating such states, which TNG classified as Single Particle since the physical model assumed is the
nearly unperturbed ground state plus an orbiting planetary electron. These states are also expected to be quite broad.

The experiments leading to these conclusions are the \( N_2 \) - electron scattering experiments of Schulz (1962, 1964, 1966), the \( H_2 \) - electron dissociative attachment experiment of Schulz and Asundi (1966), and structure in the elastic He - electron scattering cross section at about 0.45 eV observed by Schulz (1965).

The introduction of the CE2 and SP resonances requires a more effective procedure for calculating the energy of resonances.

TNG, with the assistance of the author, presented a stabilization method which generalizes the quasi-stationary methods mentioned above (page 3), and incorporates a way of handling CE2 and SP as well as CEL resonances.

The methods of calculating the resonant energies are basically refinement methods. The wave function of the resonant state is written as a superposition of configurations selected on the basis of experimental results and intuition. The refinement method is used to improve the wave function by calculating correction terms. Even though this method is an approximate method, it will be justified below on formal grounds. The most direct justification of the method, however, is the fact that it allows one to calculate \textit{ab-initio} very good approximations to the experimentally observed resonant energies.

In order to gain perspective it is well to consider for the moment how one might calculate an approximate wave function and energy of an excited bound state of an atom or molecule. If the state in
question is the $M$th excited state of a given symmetry one might choose a large number of properly symmetrized basis functions (greater than $M$), diagonalize the Hamiltonian of the system and optimize the $M$th root according to the Hylleraas-Undheim procedure. However, if the state is very highly excited such a procedure will in general not give a good result. One is thus forced to try other methods. There are two possible alternative approaches: a variation-perturbation method or a quasi-variation technique. In a variation-perturbation method one chooses a zero-order wave function and then corrects it by variational versions of perturbation techniques. Such perturbation methods include the inverse nuclear charge method (Knight and Scherr, 1963), the method of Kirtmann and Decious (1966) and the methods of Hirschfelder et al. (1965) and Eyers Brown et al. (1966). These methods are convenient to apply if the system is not too large. For larger systems one is forced to use quasi-variational approaches in which a limited number of configurations is selected on intuitive grounds. These configurations are then optimized variationally by means of linear and non-linear parameters. In such methods one must be careful that the final wave function does have dominant those configurations which one feels on intuitive grounds should be dominant. One adds other configurations to the wave function to see if the mixing is appreciable and constantly checks whether the energy is stabilized. In other words, in practice one must use intuition to a large degree to guide the variational method towards the desired result.

All of the methods mentioned above depend for their success on
the choice of trial functions. The Hylleraas-Undheim method will give poor results if the basis set is chosen poorly; the perturbation methods will give poor or entirely wrong results if the zero-order function is not chosen properly; the quasi-variation of linear and non-linear parameters will also give poor or incorrect results if the configurations chosen do not fit the physics. In the following discussion it will be shown that the situation is much the same in resonant-state calculations.

In order to discuss resonances let us consider a scattering experiment in which a projectile is scattered by a target. The target might be a nucleus and the projectile a neutron or proton as in nuclear physics, or the target might be an atom or molecule and the projectile an electron as in electron-impact spectroscopy. Let us consider an experiment in which a beam of projectiles is fired from a gun at the target, scattered by the target and then detected in a detector. The entrance channel is thus an incoming projectile with the target in the ground state. If the energy of the projectile is insufficient to excite the target, the scattering is elastic and the exit channel will be an outgoing projectile with the target in the ground state. Far from the scattering center (i.e. in the detector) the wave function for the total system is thus a product of the ground-state target wave function and a sum of incoming projectile waves and outgoing spherical projectile waves.

A traditional way of describing an elastic resonance in nuclear physics (Blatt and Weisskopf, 1952) is to say that at certain kinetic
energies the incoming projectile penetrates the target and forms a compound system. The compound system exists for a short time and then decays back into a target in the original state and an elastically scattered electron. The presence of the compound state is evidenced by a sharp and narrow resonance in the elastic scattering cross section at the so-called resonant energy. The possible resonant energies, i.e. the energies of the possible resonant states, are obtained by excluding the incoming and outgoing waves and solving for the energy levels of the compound projectile-target system as if it were a bound system.

One possible way of excluding the incoming and outgoing continuum contributions to the resonant wave function is to put the compound system in a box. In nuclear physics this is a reasonable procedure. The surface of the box would be the surface of the compound nucleus. Since nuclear forces are short-ranged, one can meaningfully define a nuclear surface and can partition physical space into inside the compound nucleus and outside the compound nucleus. However, in the case of electron-atom or electron-molecule scattering it is difficult to define a box because of the long-range Coulombic electron-electron forces. One achieves the effect of putting the compound system in a box by partitioning the Hilbert space of the compound-system Hamiltonian instead of physical space. The Hilbert space is partitioned into P-space which contains all functions expandable in terms of the asymptotic exit channels and into Q-space which contains all functions having no projection on the asymptotic exit channels. Hence, one
diagonalizes the compound-state Hamiltonian in Q-space. The solutions so obtained can have meaning only in the situation in which the electron is confined to the vicinity of the target. The electron has thus been put in a box whose radius is the range of the effective scattering potential without even specifying that radius. It will be shown formally below that diagonalizing the Hamiltonian in Q-space is equivalent to diagonalizing the pseudo-Hamiltonian \( QHQ = H_Q \) in the full Hilbert space. The operator \( Q \) is a projection operator which selects Q-space. The method of calculating resonances thus reduces to diagonalizing the compound-system projectile-target Hamiltonian with as large a basis set as is possible which does not include the asymptotic exit channels.

Let us consider the case of electron-atom scattering. The projectile is an electron and the target is an N-electron atom presumed to be in its ground state. The total energy of the system is the kinetic energy of the incoming electron and the ground-state energy of the atom. In order to obtain the resonant states (and energies) of the \((N + 1)\)-electron atom one looks for apparent bound states of the \((N + 1)\)-electron Hamiltonian in the vicinity of the experimental energy. Therefore, in order to calculate the resonant energies of the electron-atom system, one must diagonalize the full \((N + 1)\)-electron Hamiltonian of the total system as mentioned above.

The problem which is encountered is that as mentioned above the energy of the resonant state will not in general correspond to the lowest root of the \((N + 1)\)-electron Hamiltonian. The situation is
thus similar to that encountered in solving for the energy of a very highly excited bound state, hence one can use either perturbation-variation or quasi-variation methods to zero in on and stabilize the desired root. In order for a root-stabilization method to work the energy of the intuitively-guessed wave function must be close to the actual resonant energy. It is only in such a case that one can safely discard any configuration which seriously alters the energy. One expects a root-stabilization method to work because the electrons most involved in the resonances cannot be highly correlated. If they were highly correlated, the resonant state would not possess a long enough lifetime to be observed experimentally. The low correlation indicates that a one-electron picture (i.e., trial function as product of one electron orbitals, or small linear combination of products) is meaningful. One therefore expects the energy of the resonant state to have essentially settled down to its final value, i.e. to have become stabilized, after mixing a few configurations with the intuitively guessed one(s).

A word of caution is necessary on the use of a stabilization method. If a root cannot be stabilized with a small number of configurations either an incorrect wave function has been chosen to start with or the basis set is not a good one. If very closely-spaced roots begin to occur, then the concept of root-stabilization becomes meaningless and the method is inapplicable. This would be the case if the resonant state belonged to a group of very closely-spaced resonant states. The desired state would be a member of a group of almost
degenerate resonant states in this case. In such a case one would have to consider all of the almost degenerate resonant states as a unit.

The quasi-variation method of Taylor and Williams (1965) and the equivalent method of O'Malley and Geltman (1965) can now be seen to be incomplete. In these methods the Q-space was constructed by eliminating from the basis set all configurations containing those target states included in the exit channels, i.e. they eliminated all parent target states lying below the resonant state. Therefore, these methods could not be used to calculate single-particle or type II core-excited resonant states because they lie above their parent target states. These methods do give results for core-excited type I resonant states comparable with experiment since the core-excited resonant states do not involve to a large degree the lower lying parent target states. Because of the small correlation between the extra electron and the target, the ground target states do not mix very strongly. In other words, the quasi-variation method is a way of zeroing in on the root for those resonant states in which the wave function does not include appreciable overlap with the initial target states (i.e. those target states occurring in the exit channels). The Q-space of the quasi-variation method is a subspace of the more general Q-space of the stabilization method.

The obvious fault of the stabilization methods is that they do not calculate lifetimes. One could stabilize, especially in the case of a single-particle or type II core-excited resonant state, on a root corresponding to a resonant state which is too short-lived to be
observed experimentally. The perturbation method will definitely calculate such short-lived resonant states if the choice of zero-order wave function forces it to do so. In the case of type I core-excited resonant states we are confident that the lifetimes are of the order of $10^{-14}$ to $10^{-13}$ seconds. For single-particle of type II core-excited resonant states experience and intuition are not well enough developed to allow even rough estimates.

Now that the quasi-stationary methods have been described, it remains to show that the eigenfunctions and eigenvalues they yield do correspond to resonant states. In this section the Feshbach theory of resonant reactions (1956, 1962) will be used to establish this correspondence by showing that eigenfunctions of $QH \Psi = H \Psi$ do lead to a Breit-Wigner form in the cross section and correspond to a decaying bound state.

The equation to be solved is the $(N + 1)$-electron Schrödinger equation for the projectile-target system

$$H \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+1}) = E \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+1})$$

for a given energy $E$. The operator $H$ is the full Hamiltonian of the system and $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+1})$ is the total wave function. The procedure used by Feshbach (1962) is to partition space with two projection operators $P$ and $Q$ such that they satisfy the relationships

$$P \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+1}) \xrightarrow{\tau_1 \to \infty} \nu(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+1})$$

for $1 \leq i \leq N+1$.\n
and

\[ P + Q = 1 \]
\[ P^2 = P, \quad Q^2 = Q \]
\[ PQ = QP = 0 \]

(3)

The projection operator \( P \) projects out of the wave function all components on the available asymptotic exit channels at the given energy \( E \).

The Schrödinger equation, Eq. (1) can now be solved formally in a way which will show the resonances explicitly. Writing

\[ \psi = \psi_P + \psi_Q \]

Feshbach partitioned Eq. (1) into a set of two coupled equations

\[
\left( H_{PP} - E \right) \psi_P = -H_{PQ} \psi_Q
\]

(4a)

and

\[
\left( H_{QQ} - E \right) \psi_Q = -H_{QP} \psi_P
\]

(4b)

where \( H_{PP} = \Phi P, \) etc. Solving Eq. (4b) for \( \psi_Q \) and inserting the result into Eq. (4a) yields

\[
\left( H_{PP} + H_{PQ} \frac{1}{E - H_{QQ}} H_{QP} \right) \psi_P = E \psi_P
\]

(5a)

or

\[
\left( H_{PP} + V_{opt} \right) \psi_P = E \psi_P
\]

(5b)

where \( V_{opt} \) is the optical potential. In order explicitly to introduce the resonances into the picture one must consider the equation

\[
\left( H_{QQ} - \epsilon_n \right) \phi_n = 0
\]

(6a)
If this equation has eigensolutions, they must be eigenfunctions of $Q$ with eigenvalue unity, i.e., $Q \varphi_n = \varphi_n$, and $Q$ can be expanded in terms of its eigenfunctions as

$$Q = \sum_n |\varphi_n \rangle \langle \varphi_n | \tag{6b}$$

where the summation includes the integral over the continuum if necessary. Inserting this expression into $V_{\text{opt}}$ yields

$$\left( H_{PP} + \sum_n \frac{H_{PQ}|\varphi_n \rangle \langle \varphi_n |H_{QP}}{E - \epsilon_n} \right) \psi = E \psi \tag{7}$$

Therefore, the optical potential has poles at energies equal to the eigenvalues of Eq. (6). In the case of well-separated resonances one can break up the optical potential into two parts when $E$ is near one of the $\epsilon_n$, say $\epsilon_s$. Thus, Eq. (7) may be rewritten as

$$\left( H_{PP} + \sum_{n \neq s} \frac{H_{PQ}|\varphi_n \rangle \langle \varphi_n |H_{QP}}{E - \epsilon_n} - E \right) \psi = - \left( \frac{H_{PQ}|\varphi_s \rangle \langle \varphi_s |H_{QP}}{E - \epsilon_s} \right) \psi \tag{8a}$$

or, by definition of $H'$,

$$(H' - E) \psi = - \left( \frac{H_{PQ}|\varphi_s \rangle \langle \varphi_s |H_{QP}}{E - \epsilon_s} \right) \psi \tag{8b}$$

The operator $H'$ is that part of the Hamiltonian which varies slowly with the energy $E$ and gives rise to non-resonant scattering while the operator $H_{PQ}|\varphi_s \rangle \langle \varphi_s |H_{QP}/E-\epsilon_s$ gives the rapidly changing, or resonant, contribution to the scattering.

The first step in solving Eq. (8b) is to solve the homogeneous portion $(H' - E)\psi^+ = 0$, where the $+$ indicates that the solution
satisfies outgoing boundary conditions and minus indicates that the solution satisfies incoming boundary conditions. The functions $\Phi^+_O$ describe non-resonant scattering since they are associated with $H'$. It is assumed that $\Phi^+_O$ exist and are known. Given the set of $\Theta_n$ from Eq. (6) and $\Phi^+_O$ one can investigate the T matrix (see Goldberger and Watson, 1964) and thus the scattering cross section. From the outgoing homogeneous solution $\Phi^+_O$ a Green's function can be constructed and an integral equation for the total outgoing solution $\Phi^+_T$ can be derived, namely

$$\Phi^+_T = \Phi^+_O + \frac{1}{E^+ - H'} \frac{H_{QP}}{E - \epsilon_S} \Theta_S \langle \Theta_S | H_{QP} | \Phi^+_T \rangle$$

Operating on the left with $\langle \Theta_S | H_{QP}$ on both sides of Eq. (9) one finds the relation between $\langle \Theta_S | H_{QP} | \Phi^+_T \rangle$ and $\langle \Theta_S | H_{QP} | \Phi^+_O \rangle$ which, after substitution back into Eq. (9), allows one to write $\Phi^+_T$ as

$$\Phi^+_T = \Phi^+_O + \frac{1}{E^+ - H'} \frac{H_{QP}}{E - (\epsilon_S + \Delta(S))} \frac{1}{2} \Gamma(S)$$

where, using Feshbach's notation,

$$\Delta(S) - \frac{1}{2} \Gamma(S) = \langle \Theta_S | H_{QP} \frac{1}{E^+ - H'} H_{QP} | \Theta_S \rangle$$

Since the inverse operator $1/(E^+ - H')$ can be written as

$$\frac{1}{E^+ - H'} = \mathcal{G} \left( \frac{1}{E - H'} \right) - \text{in} \delta (E - H')$$

the explicit definitions of the energy shift $\Delta(S)$ and the level width $\Gamma(S)$ are

$$\Delta(S) = \langle \Theta_S | H_{QP} \mathcal{G} \left( \frac{1}{E - H'} \right) H_{QP} | \Theta_S \rangle$$

$$\Gamma(S) = \frac{1}{2} \left[ \langle \Theta_S | H_{QP} \mathcal{G} \left( \frac{1}{E - H'} \right) H_{QP} | \Theta_S \rangle \right]$$
The \( T \) matrix for the effective Schrödinger equation (8b) is

\[
\langle X_0 | T | X_0 \rangle = \langle X_0 | V | P^+_\text{res} \rangle
\]

where \( X_0 \) is the eigenfunction of that part of \( H' \), called \( H'_{\text{res}} \), which describes unperturbed motion of the incident particle and target system, that is \( H'_{\text{pp}} \), and where according to Eq. (8) \( V \) is given by

\[
V = V_{\text{non-resonant}} + \left( \frac{\langle H'_{\text{QP}} | \phi_s \rangle \langle \phi_s | H'_{\text{QP}} \rangle}{E - \varepsilon_s} \right)_{\text{resonant potential}}
\]

Inserting \( P^+_\text{res} \) from Eq. (10) into Eq. (15) and recalling that \( P^+_\text{res} \) is the outgoing non-resonant scattering solution of \((H' - E)P^+_\text{res} = 0\) and therefore satisfies

\[
P^+_\text{res} = X_0 + \frac{1}{E' - H_0} (H' - H_0) P^+_\text{res} = \left[ 1 + \frac{1}{E' - H'_{\text{res}}} (H' - T_0) \right] X_0
\]

it is seen after some manipulation (see Goldberger and Watson, 1964, sec. 5.4)

\[
\langle X_0 | T | X_0 \rangle = \langle X_0 | H' - H_0 | P^+_\text{res} \rangle_{\text{non-resonant}}
\]

\[+ \left( \frac{\langle P^+_\text{res} | H'_{\text{QP}} | \phi_s \rangle \langle \phi_s | H'_{\text{QP}} | P^+_\text{res} \rangle}{E - (\varepsilon_s + \Delta(s)) + \frac{1}{2} \Gamma(s)} \right)_{\text{resonant}}
\]
Since the cross section is proportional to the square of the T matrix, it will show a Breit-Wigner form and will change rapidly at $E \approx E_s + \Delta(s)$ with a half-width of $\Gamma(s)$. When $E$ is not near $E_s + \Delta(s)$ the non-resonant term will dominate and the cross section will vary smoothly with the energy.

Thus with a rigorous formalism applicable to both atomic and molecular cases it has been shown that the eigenfunctions of the effective Hamiltonian $H_{QQ'}$, Eq. (6), do indeed lead to rapid changes of the Breit-Wigner type in the scattering cross section when the energy $E$ is near an eigenvalue of $H_{QQ'}$. It is assumed that $H_{QQ'}$ does have bound-state solutions in the vicinity of the energy $E$. If this is not the case, the resonant term will obviously vanish at that energy.

In order to interpret what is happening physically when a resonance occurs it is necessary to form a wave packet centered about the energy $E$. To determine with good precision the time at which the particle enters the "internal region," where $Q^\Psi$ is non-zero, a sharp wave packet involving a broad range of energies $\Delta E$ must be constructed with the assumption that $\Delta E \gg \Gamma$. Choosing $t = 0$ as the time at which the incident particle enters the internal region, the part of the packet due to the $Q^\Psi$ part of $\Psi^+$ at $t = 0$ may be written as

$$Q^\Psi(x, t) = \int_{\Delta E} C(E) Q^\Psi(E) e^{-iEt} dE$$

(19)

where $C(E)$ is a slowly varying function of energy. From the
expression

$$Q\Psi = \frac{1}{E^+ - H_{QP}} H_{QP} \Psi^+$$  \hspace{1cm} (20)

it can be shown that, for $E$ near $\epsilon_s$, one has

$$Q\Psi(r) \approx \frac{1}{2} \sqrt{\frac{2}{\pi T(s)}} \frac{\Gamma(s)}{E - (\epsilon_s + \Delta(s)) - \frac{1}{2} i\Gamma(s)} \varphi_s(r)$$ \hspace{1cm} (21)

To see this one has to introduce the operator $Q$ (in Eq. (6b)) before
the $H_{QP}$ operator in Eq. (20) and the expression (10) for $\Psi^+$, and
select all resonant terms of the resulting expression which have the
factor $1/E^+ - \epsilon_s$. In the final step one has to replace $\langle \varphi_s | H_{QP} | \Psi^+_0 \rangle$ by its absolute value (changing in this way only the phase factor of
$\varphi_s$) and to realize that according to Eq. (14b) $|\langle \varphi_s | H_{QP} | \Psi^+_0 \rangle| = \Gamma(s)/2\pi$.

Therefore at $t = 0$, $E \approx \epsilon_s$

$$Q\Psi(r,0) \approx \int_{\Delta E} C(E) \frac{1}{2} \sqrt{\frac{2}{\pi T(s)}} \frac{\Gamma(s)}{(\epsilon_s + \Delta(s)) - E - \frac{1}{2} i\Gamma(s)} \varphi_s(r) \, dE .$$ \hspace{1cm} (22)

At time $t$ this internal wave function becomes (since $\Psi^+(E)$ are eigenfunctions of $H$)

$$Q\Psi(r,t) \approx C(\epsilon_s + \Delta(s)) \varphi_s(r) \int_{\Delta E} \frac{1}{2} \sqrt{\frac{2}{\pi T(s)}} \frac{\Gamma(s)e^{-iE/t}}{(\epsilon_s + \Delta(s)) - E - \frac{1}{2} i\Gamma(s)} \, dE \hspace{1cm} (23)$$

the assumption being made that $\Delta E$ is broad compared to the resonance
at $\epsilon_s + \Delta(s)$, but small compared with the distance between successive
resonances. With the usual approximations for sharply peaked integrands, the integration limits may be extended to \(-\infty\) and \(+\infty\) yielding

\[
Q\Psi(r, t) \approx \frac{1}{2} \sqrt{\frac{2}{\pi \Gamma(s)}} \Psi(r) \left( \epsilon_s + \Delta(s) \right) \varphi_s(r) \\
\times \int_{-\infty}^{\infty} dw \left[ \frac{e^{-i\omega t}}{\left( \epsilon_s + \Delta(s) - \frac{1}{2} i\Gamma(s) \right)} - \gamma_d \right]
\]

This familiar integral (in time-dependent perturbation theory) can be evaluated to give (see Goldberger and Watson, chapter 8)

\[
Q\Psi(r, t) = \begin{cases} \\
\sqrt{\frac{2}{\pi \Gamma(s)}} \pi i\Gamma(s) C\left( \epsilon_s + \Delta(s) \right) \varphi_s(r) \\
\times e^{-1/\hbar(\epsilon_s+\Delta(s))}t \ e^{-r^2/2\hbar t} \\
0 & \text{if } t < 0 \\
t > 0
\end{cases}
\]

The \(Q\Psi\) part of the wave packet thus comes into effect as the particle comes into the region of the target. In this region the \(Q\Psi\) part of the packet and thus the \(N+1\) electron system resembles a stationary eigenfunction of \(H_{QQ}\) except for the fact that this "stationary" state is modulated and decreased in time by an exponential decay factor with mean lifetime \(\tau = \hbar/\Gamma(s)\). It has therefore been shown that the \(N+1\) particle system does exist as a quasi-stationary localized state for an average time \(\tau\). If one looks at Messiah's development of radiation theory, (1963) where projection operators are used to separate the light field from the matter states, one sees that the use of the word
"stationary" in describing the states of negative ions is either rigorous or approximate in the same sense that one calls "stationary" any excited state of an atom or molecule that has a finite spontaneous emission probability.

The beauty of the projection operator formalism is its generality. It does not depend on the choice of $H$, and $Q$ and $P$ are only required to satisfy $P\Psi = \Psi$ at large distances, so that the formalism can be applied to any decaying state problem. Note, however, that both the formal theory and the quasi-stationary methods require that the physical situation be inserted, either by chemical intuition or by proper choice of the projection operators $P$ and $Q$. This is the price which must be paid for not being able to integrate the Schrödinger equation exactly.
CHAPTER III

RESONANT STATES OF H₂⁺

Introduction

In this paper the quasivariation method developed simultaneously by Taylor and Williams (1965, hereinafter denoted by TW) and O'Malley and Geltman (1965), and the stabilization method discussed in the work of Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted by TNG) are applied to the ab initio calculation of quasi-stationary states of H₂⁺. Results are compared quantitatively and qualitatively to dissociative attachment, vibrational excitation and electron scattering experiments.

For the definitions of, and distinctions between the three types of resonance calculated here (Single Particle and Core-Excited Types I and II, hereinafter denoted by SP, CEL, and CEP, respectively); the usefulness of these definitions and a discussion and derivation of the variational principles used in the present work, see the paper of TNG.

*This chapter is to be submitted verbatim to the Journal of Chemical Physics for publication under the joint authorship of James K. Williams and H. S. Taylor.
Experiments and Results

The experiments simplest to explain with the calculations presented here are those in which resonances are seen in the total and inelastic electron-hydrogen cross section. Such observations have been made by Kuyatt, Simpson and Mielczarek (1964, 1965b, 1966) in transmission experiments, by Golden and Bandel (1965) with a modified Ramsauer technique and by Heidemann, Kuyatt, and Chamberlain (1966) in inelastic scattering experiments. These resonances are attributed to the formation of two short-lived states of \( \text{H}_2^- \), and the individual peaks in the cross section correspond to definite vibrational levels of the resonant molecular state. The well-developed vibrational structure indicates a lifetime sufficiently long for molecular vibrations of the order of \( 10^{-13} \) sec.\(^1\)

As was noted in all publications on these resonances, there is a striking resemblance of the vibrational spacings of the two resonances themselves, and also of the spacings of the resonances and the spacings of the four \( \text{H}_2^- \) states \( c^3\Pi_u, a^3\Sigma_g, C^1\Pi_u \) and \( E^1\Sigma_g \).

\(^1\)In the earliest of their publications, Kuyatt et al. report only one resonant state. They later refined the experiment to observe two close-lying states. In TW, a rough calculation was carried out which agreed with the one resonance observed at that time. The general results of TW are still valid but are superseded by the more detailed calculations and analysis of this work. In this work, comparisons will be made with the later experiments of Kuyatt et al., which differ somewhat in energy scale from those of Golden and Bandel. This is admittedly done because of better agreement of the calculations with the Kuyatt work.
This indicates, as discussed in TNG, that the observed resonances are CEl, an electron in the field of a mixture of the four \( H_2 \) states above. Based on physical arguments, TW correctly credited the first resonance to \( \Sigma_g \sigma_{ls} \pi_{u} 2p_{1+1} \pi_{u} 2p'_{-1} \) configuration of \( H^- \), i.e., an electron in the field of the \( 3\Pi_u \) state.\(^2\)

The possible configurations that result from addition of an excited orbital to the four \( H_2 \) states and could cause resonances are listed in Table 1. Non-autoionizing configurations are omitted. In the third section, the details of the mixing of those configurations with the same symmetry in both the quasivariation and stabilization methods are reported.\(^3\)

\(^2\)Since we are using open shell calculations, a prime is used to indicate an orbital of slightly larger average radius than the unprimed orbital. The orbital notation is the standard Mulliken LCAO notation and is used for simplicity of presentation. Any particular Mulliken orbital can be thought of as the dominant term in an expansion of the molecular orbitals, used in this paper and explained in a later section, upon a complete set of Mulliken orbitals.

\(^3\)Only the two \( \sigma_{ls} \pi_{u} 2p_{1+1} \pi_{u} 2p'_{-1} \) resonances and a portion of curve D of Fig. 1 were calculated with the quasivariation method as well as the stabilization method. The latter was used for all other \( H_2 \) states. The reason for this is the difficulty encountered in orthogonalization of the wavefunction of the resonance to the wavefunctions of the states of \( H_2 \) of lower energy whenever the main configuration(s) has two orbitals which are not of \( \pi \) type. This orthogonalization is a requirement of the quasivariation method, but is not required when the stabilization method is used. The difficult orthogonality requirement will probably mean that most future calculations will be done by the stabilization method. Added to this difficulty in the quasivariation method is the fact that CE2 and SP resonances can only be calculated by the stabilization method, as discussed in TNG.
TABLE 1

SOME POSSIBLE $H_2^-$ RESONANT STATES

<table>
<thead>
<tr>
<th>$H_2^-$</th>
<th>Parent $H_2$ States</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\Sigma_g$ g 1s $\pi_2p_1\pi_u np_{-1}$</td>
<td>$3\Pi_u$, $1\Pi_u$</td>
</tr>
<tr>
<td>$2\Pi_u$ g 1s $\pi_2p_1\sigma_2s$</td>
<td>$3\Pi_u$, $a3\Sigma_g^+$, $3\Pi_u$, $E^1\Sigma_g$</td>
</tr>
<tr>
<td>$2\Sigma_g$ g 1s $(\sigma_2s)^2$</td>
<td>$3\Sigma_g^+$, $E^1\Sigma_g$</td>
</tr>
<tr>
<td>$2\Delta_g$ g 1s $(\pi_u 2p)^2$</td>
<td>$3\Pi_u$, $3\Pi_u$</td>
</tr>
</tbody>
</table>
Fig. 1. -- Potential curves for $H_2^-$ resonances and some associated $H_2$ states.

A - $H_2^-$ $2\Sigma^+$ consisting of $^1\Pi_u \cdot \pi_u \ 2p'$

B - $H_2^-$ $2\Sigma^+$ consisting of $^3\Pi_u \cdot \pi_u \ 2p'$

C - $H_2^-$ $2\Sigma^+$ consisting of $^1\Sigma_u^+ \cdot \sigma_u \ 1s'$

D - $H_2^-$ $2\Sigma^+$ consisting of $^3\Sigma_u^+ \cdot \sigma_u \ 1s'$

E - $H_2^-$ $2\Sigma^+$ consisting of $^1\Sigma_u^+ \cdot \sigma_u \ 1s$

F - $H_2^-$ $X^1\Sigma^+_g$ (Kolos and Wolniewicz, 1965).

G - One configuration result for $H_2^-$ $^3\Sigma^+_u \ 1\sigma \ 1\sigma_u$. This curve lies about 0.32 eV above the "exact" $^3\Sigma^+_u$ curve (Kolos and Wolniewicz, 1965), but is used as a comparison with the $H_2^-$ calculation consisting of this configuration plus an extra electron.

H - Two configuration result for $H_2^-$ $^3\Pi_u$ ($1\sigma \ 1\pi_u + 1\sigma \ 1\pi_g$). The minimum of this curve lies about 0.14 eV above the experimental minimum. The $H_2^-$ $a^3\Sigma^+_g$ curve lies so close to this one that they are indistinguishable on this scale.

I - Same as H for $^1\Pi_u$ and $^1\Sigma^+_g$

J - $H_2^-$ $^3\Pi_u$
The outstanding result of the present calculation for these two resonances was that the lower resonance is almost exclusively
\[ ^3\Pi_u + e, \quad 2\Sigma^+ \quad g_1 s_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \] while the next resonance is \[ ^1\Pi_u + e, \quad 2\Sigma^+ \quad g_1 s_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \]. In Table 2, the vibrational levels of these two states are compared to the observed levels of Kuyatt et al., and good agreement is obtained. The calculation also demonstrated a number of physical effects which were discussed in TNG. First, it was found that even though the two CEl \( g_1 s_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \) states were mixed with themselves, with all the states of the same symmetry \( 2\Sigma^+ \) in Table 1, and with many configurations of non-stable \( H_2^- \) states of lower energy, the ratios of the off-diagonal elements of the Hamiltonian matrix to the diagonal elements were \( O(10^{-6}) \) or less between the two spin doublets themselves, and between each of the spin doublets and the large number of other \( H_2^- \) configurations. This indicates the expected extremely weak interactions (low correlation) between electrons in the compound state.

The electron affinity of the lower CEl resonance is 0.8488 eV relative to its parent \( ^3\Pi_u \) state, and the higher CEl resonance has 0.8435 eV binding relative to its \( ^1\Pi_u \) parent, or 0.276 eV relative to the \( ^3\Pi_u \).

CEl resonances were not attainable from configurations representing an electron in the field of the other \( H_2^- \) states in Table 1. No extensive search was made in this work for CEl2 resonances belonging to the states of Table 1, although to check for their existence, one good stabilization calculation was done at the equilibrium internuclear separation of the four parent states \( (R = 1.95 \text{ au}, 1 \text{ au} = 0.52917 \text{ Å}) \), for the configuration an electron in the field of \( ^3\Sigma^+; \quad 2\Sigma^+ \quad g_1 s_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \pi_1 \).


<table>
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<th>Obs. Level</th>
<th>Lower Resonance</th>
<th>Upper Resonance</th>
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</tbody>
</table>

COMPARISON OF EXPERIMENTAL AND CALCULATED VIBRATIONAL LEVELS (energies in eV)
This root stabilized at an energy of -.7291 au (1 au = 27.21 eV), 0.24 eV above $3\Pi_u$, .3 eV below $1\Pi_u$, .13 eV above $3\Sigma_g^-$, and 11.85 eV above the ground vibrational level of H$_2X^1\Sigma_g^+$, the reference zero level for all the calculated and experimental results. This root strongly indicates the existence of a CE2 resonance with this configuration which parallels its $3\Sigma_g^+$ parent with a slightly higher energy in the Franck-Condon region.

Again this $\sigma_{ls\sigma,2s\sigma,2s'}$ configuration does not mix with any of the $\sigma_{ls\pi,2p\pi,2p'}$ types and the resonance is expected to be quite broad relative to the CE1 resonances as discussed in TNG. It is likely that this resonance will only be observable in inelastic scattering experiments leading to its parent, however it is possible that threshold structure will obscure the observation. Because the two CE1 resonances are made from excited H$_2$ orbitals, it is to be expected that these resonant states are more strongly coupled to excited state exit channels of H$_2$, and this accounts for the enhanced signal due to these resonances in elastic scattering (see Heidemann, Kuyatt, and Chamberlain, 1966). 4

4In the next section, an even more tentative CE2 resonance, with the configuration of an electron in the field of $1\Sigma_g^+$, $2\Gamma_d$ $ls\sigma_2s\sigma_2s$ is reported. The uncertainty of this resonance causes us to discuss it only in the next section, but it is mentioned here in the realization that many readers may not be interested in the detailed discussion of the calculations. Work is now in progress on this and other CE2 resonances expected to lie in this energy region. We emphasize that the two CE1 resonances and the single point at 11.85 eV are definitively stabilized and therefore represent final results.
In Fig. 2 the two CE1 resonances and the four aforementioned states of H₂ are shown, as well as the single point for the CE2 resonance (denoted by a cross). The solid lines represent the H⁺ CE1 resonances, the dashed lines the H₂ states, and the dotted line through the cross is the postulated potential curve of the CE2 resonance.

The next type of experiment to be discussed is dissociative attachment. The measured cross sections for the formation of the H⁻ ion in the process

\[ e + H₂ \rightarrow (H⁺_2) \rightarrow \begin{cases} H & + H^- \\ H^* & + H^- \end{cases} \]

are given in Figs. 3 and 4. In an as yet unpublished private communication, Dowell and Sharp have reported finding additional structure in the 8-12 eV peak. Besides the general Gaussian shape and the dip in the cross section at 11.2 eV, they have found a new series of dips on the high energy side of the peak, which have the feature of being spaced analogously to the spacings of the vibrational levels Kuyatt et al. found in their lower CE1 resonance. In TNG, it was shown how these experiments could be used to completely and definitively predict the position of the resonance potential curve causing such structural features as contained in the 8-12 eV peak. First, the general Gaussian shape, kinetic energy analysis, and isotope effect could be caused, as a result of Franck-Condon factors, by any repulsive resonant state with a potential curve which enters the Franck-Condon region of the ground vibrational level of the H₂ ground state at about 8 eV on the right, leaves it at about 13 eV on the left, and goes to the known
Fig. 2.--Comparison of the upper core-excited resonances to $H_2$.

A - $H_2 \, ^3\Pi_u$

B - $H_2 \, ^1\Pi_u$ and $E^1\Sigma_g^+$

C - $H_2 \, a^3\Sigma_g^+$

D - $H_2 \, ^2\Sigma_g^+ \, \sigma \, l\sigma \, l\sigma \, l\sigma \, l\sigma'$

E - $H_2 \, ^2\Sigma_g^+ \, \sigma \, l\sigma \, 2p\pi \, 2p'$ ($^3\Pi_u$ + electron)

F - $H_2 \, ^2\Sigma_g^+ \, \sigma \, l\sigma \, 2p\pi \, 2p'$ ($^1\Pi_u$ + electron)

G - $H_2 \, ^2\Sigma_g^+ \, \sigma \, l\sigma \, 2s\sigma \, 2s'$ ($^3\Sigma_g^+$ + electron)
Fig. 3.--The dissociative attachment cross section of Schulz (1964).
Fig. 4. -- The dissociative attachment cross section of Rapp, Sharp, and Briglia (1965).
stable separated atoms H and H\(^-\) at an energy of 3.75 eV. The dip at 11.2 eV was most easily explained by assuming that this repulsive resonance potential curve could cross the repulsive H\(_2\) \(3\Sigma^+_u\) state at 11.2 eV,\(^5\) thereby changing from a CE1 to a CE2 resonance, and opening a new exit channel H + H + e to the system. Since, from the work of Kolos and Wolniewicz (1965), it is known that the H\(_2\) \(3\Sigma^+_u\) state has a relative energy of 11.2 eV at \(R \sim 1.29\) au, it can be concluded that the H\(_2\)\(^-\) has the same energy at this \(R\).\(^5\) The opening of the new exit channel causes more of the H\(_2\)\(^-\) resonances formed at this energy to decay in channels other than that measured by dissociative attachment, and therefore causes a decrease in the cross section exactly at 11.2 eV. The reason that the cross section recovers its Gaussian envelope is illustrated in Fig. 5, where it is seen that only at the crossing point are the Franck-Condon factors of sufficient magnitude to make possible curve jumping to the \(3\Sigma^+_u + e\) channel.

The Dowell and Sharp result could most simply be explained by assuming that the resonance curve proceeds upward in energy until it approaches the lower \(2\Sigma^+_{2g\ '}\) CE1 resonance of Kuyatt et al. tangentially from the left. As shown in Fig. 6, if this were to occur, since both states are \(2\Sigma^+_{2g\ '}\), one could get an inverse pre-dissociation from the repulsive H\(_2\)\(^-\) state to the bound H\(_2\)\(^-\) state at energies equal to

\(^5\)Actually, in order to have the maxima of the nuclear wave functions coincide, the crossing would occur at a slightly lower energy, as shown in Fig. 5. As a consequence, the \(R\) value for the crossing point predicted by the dip will be slightly smaller than the actual \(R\) value at crossing.
Fig. 5.—Comparison of Franck-Condon Factors.
Fig. 6.--Schematic diagram for inverse pre-dissociation between resonances.
the vibrational levels of the upper resonance. Because of Franck-Condon factors (see Fig. 6) the postulated inverse pre-dissociation could only occur at vibrational levels of the upper resonance, and this could cause exactly the dips in the $H^-$ formation cross section observed by Dowell and Sharp.

Since from experiment one knows the vibrational constants of the Kuyatt state, its potential curve can be determined empirically and the vibrational levels drawn in. By noting the energies and positions at which the vibrational levels and the empirical potential curve intersect, and by ignoring those points which do not correspond to dips in the Dowell and Sharp experiment, one is left with a set of points (denoted by crosses in Fig. 6) through which the repulsive resonance potential curve must pass. If one now smoothly connects the "cross" points of Fig. 6; the point on the $H_2^+ 3 \Sigma_u^+$ curve; the point at which the 8 eV constant energy line intersects the large $R$, vertical Franck-Condon line; and the point at infinite $R$ for the known $H + H^-$ energy, a curve (such as curve D of Fig. 1) is obtained with little ambiguity. In TNG, a conglomeration of tentative calculational, group theoretical, curve crossing and physical arguments were given to predict the curve, which, it was then pointed out, could explain the experiments. The opposite point of view is now being stressed, that once the type of phenomena that can occur in quasi-stationary molecular resonances are understood, and these are quite closely analogous to normal spectroscopic phenomena (i.e., dissociation, inverse pre-dissociation, pre-dissociation, etc.), one can predict where the resonant
state lies completely from experiment.

As also explained in TNG, simple Mulliken type arguments can be combined with the core-excited model to predict a configuration for the resonance of $\Sigma^+_u \sigma_u \sigma_u \sigma_u \sigma_u$. In this work, using the stabilization method, the energy of such a configuration was calculated, and the results which are presented in Fig. 1, curve D and in Table 3 are in perfect agreement with the curve one would anticipate from the application of spectroscopic ideas to the experimental results. As will be shown in detail in the following section, this state also had extremely low correlation, since it did not mix appreciably with any configurations which would normally be regarded as correlating configurations in the configuration interaction picture. Some mixing did occur with the stabilizing configurations, particularly in the CE2 portion of the curve, indicating that the CE2 will have a larger width (be less stable) than the CE1 part. Again it is stressed that it is the lack of correlation in the resonance complex that enables the wavefunctions determined by quasi-stationary methods to give such good agreement for the energies at which resonant phenomena occur.

Work is presently in progress which will use the wavefunctions determined in this work for the $\Sigma^+_u \sigma_u \sigma_u \sigma_u \sigma_u$ state in conjunction with the formal theory of dissociative attachment and vibrational excitation as developed by O'Malley (1966) and Bardsley, Herzenberg, and Mandl (1966a, b) in the hope that this will lead to quantitative agreement with experiment for dissociative attachment and will explain why Schulz is unable to observe any evidence of the $\Sigma^+_u \sigma_u \sigma_u \sigma_u \sigma_u$. 
TABLE 3

POTENTIAL CURVES OF H₂ RESONANCES

<table>
<thead>
<tr>
<th>R(au)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>2.15/3.72</td>
<td>14.4560</td>
<td>--</td>
<td>15.0315</td>
<td>15.0777</td>
<td>--</td>
</tr>
<tr>
<td>1.1</td>
<td>--</td>
<td>13.6693</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.2</td>
<td>1.41/3.22</td>
<td>12.5762</td>
<td>--</td>
<td>13.5694</td>
<td>13.6108</td>
<td>(17.15)</td>
</tr>
<tr>
<td>1.3</td>
<td>--</td>
<td>11.6103</td>
<td>--</td>
<td>12.8656</td>
<td>12.9403</td>
<td>(16.15)</td>
</tr>
<tr>
<td>1.4</td>
<td>1.22/3.04</td>
<td>10.6805</td>
<td>--</td>
<td>12.3197</td>
<td>12.4764</td>
<td>(15.88)</td>
</tr>
<tr>
<td>1.5</td>
<td>--</td>
<td>9.9254</td>
<td>12.742</td>
<td>11.8956</td>
<td>12.0944</td>
<td>--</td>
</tr>
<tr>
<td>1.65</td>
<td>1.3⁷/3.03</td>
<td>9.0085</td>
<td>--</td>
<td>11.1802</td>
<td>11.6621</td>
<td>(14.49)</td>
</tr>
<tr>
<td>1.8</td>
<td>--</td>
<td>7.9560</td>
<td>11.896</td>
<td>11.0513</td>
<td>11.5439</td>
<td>(14.14)</td>
</tr>
<tr>
<td>1.95</td>
<td>--</td>
<td>7.0404</td>
<td>11.735</td>
<td>10.9090</td>
<td>11.4084</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>--</td>
<td>6.9013</td>
<td>--</td>
<td>11.0405</td>
<td>11.4489</td>
<td></td>
</tr>
<tr>
<td>2.25</td>
<td>--</td>
<td>6.3362</td>
<td>11.651</td>
<td>11.1115</td>
<td>11.6084</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>--</td>
<td>5.8157</td>
<td>11.577</td>
<td>11.3615</td>
<td>11.8119</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>--</td>
<td>5.4015</td>
<td>11.901</td>
<td>11.6609</td>
<td>12.1744</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>3.87/4.90</td>
<td>4.8494</td>
<td>--</td>
<td>11.9949</td>
<td>12.4990</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.12</td>
<td>14.12</td>
<td>(13.92)</td>
</tr>
</tbody>
</table>

\[
a - 2\Sigma^+_g \left( X^1\Sigma^+_g + e, \sigma g \sigma' g u \right) \\
b - 2\Sigma^+_g \left( 3\Sigma^+_u + e, \sigma g \sigma' g u \right) \\
c - 2\Sigma^+_g \left( B^3\Sigma^+_g + e, \sigma g \sigma' g u \right) \\
d - 2\Sigma^+_g \left( c^3\Pi^+_u + e, \sigma g \sigma' g u \right) \\
e - 2\Sigma^+_g \left( c^3\Pi^+_u + e, \sigma g \sigma' g u \right) \\
f - 2\Sigma^+_u \left( E^1\Sigma^+_g + e?, \sigma g \sigma' g u \right) \\
g - energies relative to ground vibrational level of H₂ X^1\Sigma^+_g\]
resonance in electron impact experiments where the cross section for excitation from the ground vibrational level of \( H_2 \) to excited vibrational levels is measured. Since the resonance potential curve does cross and go above the \( ^3\Sigma_u^+ \) channel in the Franck-Condon region, and thus lies very close to the \( H_2 \) state in the center of the Franck-Condon region, it is unlikely in any case that transitions through this resonance would make significant contributions to the vibrational excitation cross section to the lower \( H_2 \) vibrational levels.

The shape, isotope effect, and kinetic energy analysis of the 14.2 eV peak were explained in detail in TNG, and credited to transition to the dissociation limit of the two CEI \( 2\Sigma^+_g \) \( 1s\pi \) \( 2p\pi \) \( 2p' \) resonances discussed above. The calculations presented here reinforce and are in complete agreement with the TNG arguments hence the arguments will not be repeated here. In a future paper, the wavefunctions calculated for these states as a function of internuclear distance will also be used in conjunction with the formal theories of dissociative attachment mentioned above.

It was postulated in TNG that the vibrational excitation results of Schulz (1964) and the dissociative attachment cross section, kinetic energy distribution, and sudden onset for the peak occurring at 3.75 eV (Schulz and Asundi, 1966) could be explained by the existence of what must be a quite broad SP resonance with the configuration \( ^2\Sigma_u^+ \) \( g \) \( gs \) \( ls' \) \( as \) \( ls \) electron in the field of \( H,X^1\Sigma_u^+ \).

---

6 The reader is referred to TNG for a discussion of why this configuration was chosen; why it is expected to be broad; why the resonance is difficult to observe in transmission, modified Ramsauer, and
The stabilization method has been applied for this state. A good ground state $H_2$ function was chosen, i.e., a three configuration, well correlated function which gave an energy at the minimum of the potential curve of $-31.76$ eV as compared to the experimental energy of $-31.975$ eV. The three configurations used were $\sigma_g lso ls'$; $\sigma_u ls' c ls'$; and $\pi_u ^{2p+1} \pi_u ^{2p-1}$. The first configuration gives the main contribution around equilibrium nuclear separation $R_e$. The second is an axially correlating configuration near $R_e$ and ensures proper breakup into two H atoms as $R \rightarrow \infty$, where it becomes as important as the $\sigma_g lso ls'$ configuration. The $\pi_u ^{2p+} \pi_u ^{2p-}$ is an angular correlation configuration. The superscript c is added to these orbitals to indicate that they have the same average radial extent as the $\sigma_g ls$ orbital, and are specially optimized to produce the best $H_2$ ground state, as opposed to the $\sigma_u ls$ and $\pi_u 2p$ orbitals of the previous discussion which are similar to large excited orbitals of $H_2$.

For the $\Sigma_u ^+ H_2^-$ calculation a third electron $\sigma_u ls$ was added to these configurations to give three three-electron configurations of symmetry $\Sigma_u ^+$. This was then stabilized as discussed in the next section and resulted in the curve $E$ of Fig. 1, as shown in detail in Fig. 7 and tabulated in Table 3. It is notable that even though one needs at least three configurations to represent this resonance well it is only because one must represent the target $H_2$ state to a high degree of accuracy. This type of configuration mixing does not

$^6$ Total cross section experiments; and the general physics of the situation.
Fig. 7.—The single particle $H_2^- \Sigma_u^+$ states.
indicate strong correlation between the new electron and the original $H_2$ electrons. On the other hand, it was found that some configuration mixing was necessary before the root stabilized. This situation is analogous to that of the CE2 portion of the $2\Sigma^+_g \rightarrow \Sigma^+_g$ repulsive resonance, and again the extra mixing with the stabilizing configurations indicates that this resonance is quite broad. In any case, one finds a wavefunction with a small number of configurations whose eigenvalue was unaffected by further variations of the wavefunction. How much of this configuration interaction is due to width, and how much is due to a limited orbital functional form is impossible to tell.

The interesting features of this resonance are:

1) That at large $R$ it connects smoothly to the $H + H^-$ $2\Sigma^+_u$ state calculated by Taylor and Harris (1963) using a true variation method since at large $R$ $H + H^-$ is the bound, lowest state of $2\Sigma^+_u$ symmetry.

ii) That the potential curve for this state, once inside the curve for $H_2 X \Sigma^+_g$, essentially parallels the $H_2$ curve from above, and turns up sharply at $R \sim 1.0$ au. Since its shape is like that of $H_2$ its harmonic vibrational constant will be similar to $H_2$, and thus the lower vibrational levels will be at $\sim 1.5$ and 2.0 eV above the ground vibrational level of $H_2 X \Sigma^+_g$.

The calculated state could well account for the dissociative attachment result of Schulz and Asundi (1966), but it should be pointed out that the dissociative attachment experiment in this case
gives no information about the position of the potential curve for the resonance inside the target $H_2$ potential curve.

From the vibrational excitation experiment, Schulz (1964) postulated the existence of a very broad resonance about 2.3 eV above the ground level of $H_2 \times ^1\Sigma^+$. The result presented here is certainly lower than this. The only significant test of the calculated state that could be carried out, but for physical reasons, one which might not be extremely sensitive to the detailed form of the wavefunction, is to put the wavefunction calculated here into the formulae for the vibrational excitation cross section as presented by Bardsley, Herzenberg, and Mandl (1966a,b). This has been done by the latter authors using a wavefunction of significantly poorer quality than the one presented here and nevertheless resulted in a calculated cross section which is in quite acceptable agreement with the observed one.

7To demonstrate this point, one need only note that the Herzenberg et al. wavefunction gives rise to an $H_2$ energy of -30.44 eV and an equilibrium internuclear separation of 1.68 au. The wavefunction used in this work, gives an energy of -31.76 eV and an equilibrium separation of 1.4 au. The "experimental" values are -31.975 eV at 1.4011 au (Kolos and Wolniewicz, 1965). Because of the different qualities of the wavefunction and the wide variations in $R_e$, it is meaningless to try to compare the results of the present $H_2^+$ SP calculation with that of Herzenberg et al. Although one does not have a variation principle which says the lower the energy the better the function in these calculations, it is reasonable to assume that the more extensive and better functions used here will lead to more reliable results. The agreement with experiment in the Kuyatt et al. resonances, and the ability to explain the fine structure due to the repulsive resonance, which is completely lacking in the Herzenberg et al. results, seem to substantiate these claims.
In this laboratory the Herzenberg et al. calculations for the vibrational excitation cross section are being repeated with improved wave functions to see how sensitive the calculation is to the quality of the function.

The qualitative comparison of this state to the energy of Schulz is quite difficult since the SP state is so broad. In fact, in the vibrational excitation experiments, since the resonance is so broad, the nuclei do not have time to make definitive molecular vibrations, and Schulz was not able to distinguish any meaningful energies to determine the empirical potential curve for this state.

When the \( \frac{2}{2} \Sigma_u^+ (H_2 \times 1 \Sigma_g) \sigma_u \) ls root was being stabilized, it was noted that a second root stabilized equally as well. The curve for this is \( E' \) in Fig. 1, and the upper \( H^- \) curve of Fig. 7. It seems to dissociate to \( H + H^- \) where \( H^- \) is probably the very broad \( H^- \) resonance ls 2s calculated by Herzenberg and Mandl (1963) to have an energy between 2.0 and 4.0 eV and a width of about 2 eV. This \( H^- \) state, again, will be very broad, and cannot be seen in a dissociative attachment experiment since a long-lived negative ion is necessary. As discussed in TNG, because of its breadth it also might be extremely difficult to detect in the total scattering cross section. Since it occurs at about 3 eV it could possibly contribute to vibrational excitation. One might speculate that both the 1.2 eV and 3.0 eV SP resonances contribute to give the broad vibrational excitation peak estimated by Schulz to be centered at 2.3 eV. Nothing definitive can be until calculations of widths and the vibrational excitation cross section have been made.
An interesting effect observed in these SP calculations was that the extra electron of the higher stable root had a smaller effective orbital radius than that of the lower root at small $R (\sim R_e)$, but at large $R$ the situation became reversed.

When stabilizing the repulsive $^2\Sigma_u^+ \sigma \Sigma_u^+ \sigma \Sigma_u^+ \bar{\sigma} \sigma \Sigma_u^+$ state, in the calculations reported here, because of the open shell methods in which two spin doublets are used, a configuration $^2\Sigma_u^+ \sigma \Sigma_u^+ \sigma \Sigma_u^+ \bar{\sigma} \sigma \Sigma_u^+$ (electron in the field of $B^1\Sigma_u^+$) was automatically included. During the stabilization process, a second root corresponding to this configuration also stabilized, and it was clearly a broad, CE2 resonance. This resonance, as in the other CE1 and CE2 cases, was well stabilized and highly uncorrelated and fits the rules given in TW and TNG for a resonance in the field of the $B$ state. It should be difficult to observe for a number of reasons. As discussed in TNG, the breadth of this resonance favors its being looked for in inelastic experiments to vibrational levels of its parent $B$ state. However, besides its breadth, the large $R_e$ of $\sim 2.45$ au and the small $\omega_e$ of $\sim 0.13$ eV indicate that the resonance potential curve will be in such a position relative to the potential curve of the $H_2$ ground state that Franck-Condon factors will allow transitions only to the highly excited vibrational levels of the resonance ($v \sim 14$) and any structure may be obscured by the closeness of the spacings. It is impossible to tell from the published curves of Heideman, et al. (1966) whether there is any structure just above the excitation threshold, and since the width is not known, it is impossible to really argue whether or not such structure should indeed be observable.
The stabilization of this root, which fits the CE model of TW and TNG, brings up a very interesting and unanswered question; it seems that in the case of core-excited resonances a well stabilized root appears fastest whenever a configuration is used which puts the extra electron into the same type of orbital as the excited $H_2$ orbital \([\sigma_u, \sigma_u^2 \text{ and } \pi_u^2]\). Other configurations do not stabilize rapidly. Why this is so, we do not know, and it is freely admitted that the extent of calculational experience so far is not sufficient to say definitely that these other configurations do not stabilize, but there are strong indications that this is the case. Another strange effect arises when one adds many configurations solely for the purpose of testing the stability of a particular root. If the root under investigation is one which is truly stable, two or three stabilizing configurations are usually sufficient. On the other hand, other roots of the secular equation do eventually become constant after large numbers of configurations have been added, simply because the configurations made of orbitals which can mix with the configurations corresponding to these roots have been exhausted. A subject of future research, especially when reliable widths can be produced, will be a study of the significance of these more slowly stabilizing states. The authors stress that the states reported in the present work stabilized rapidly, and the confusion exists only about other less stable roots which were noted in the calculations.

In the tables and graphs the energies are reported in electron volts relative to the experimental ground vibrational level of $H_2$ in the ground state. When energies of resonances relative to energies of
H₂ are reported, the H₂ energies are those obtained with the same wave function as for H⁻ with the exception that the linear coefficients are re-optimized and the third electron is allowed to go to infinity. This is the only way to get a true comparison and does not yield misleading results since the wavefunctions used in the H₂ case give well over 99% of the total energy and an appreciable fraction of the correlation energy. In view of the experimental errors reported, improving the calculation of resonance and target energies to a degree of sophistication comparable to that of Kolos and Wolniewicz (1965), would do little to improve our understanding of the basic physics, and therefore would not justify the many man-hours and computer expenses involved.

A point of great interest arises when discussing the non-crossing rule of quantum chemistry. As noted by Bardsley et al. (1966), and the present authors, many unstable potential curves cross the stable potential curves. This would seem inadmissible by group theoretical arguments which say that the correct potential curves must be drawn by connecting the nᵗʰ lowest root at all R. These arguments have meaning in the variation method, but not, however, in the quasi-stationary methods used here. Bardsley et al. show this by reference to the work of Mandl (1966) in which it was proven that for resonant states calculated by the quasi-stationary complex energy Siegert method, the real part of the energy can cross (and this is what is calculated here) but that there is no crossing in the complex plane. While the authors have no argument with this correct interpretation, we prefer to present a more physically based model. To be specific, consider the
$2\Sigma^+_g \text{ls} \sigma \text{ls} \sigma \text{ls}'$ repulsive resonant state, which at large $R$ dissociates to $H$ and $H^-$. This separated atom pair in turn lie about 1.0 eV below a pair $H$ and $H^-$, where the $H^-$ represents a SP resonance of $H^-$ discussed by Herzenberg et al. The upper pair also has the symmetry $2\Sigma^+_g$, but is $\sigma \text{ls} \sigma \text{ls}' \sigma 2s$.

In the united atom limit, the $2\Sigma^+_g \text{ls} \sigma \text{ls} \sigma \text{ls}'$ state goes to an obviously core excited state of $\text{He}^-$, while the $H$ and $H^-$ pair goes to $\text{He}^- 2S(1s)^2 2s$. The latter is clearly a very broad SP state of $\text{He}^-$ and lies significantly lower than the core-excited state (about 19 eV). This means that the rapidly stabilizing $\sigma \text{ls} \sigma \text{ls} \sigma \text{ls}'$ root and the unstable $\sigma \text{ls} \sigma \text{ls}' \sigma 2s$ root, which are mixed to test the stabilization of the former, should cross at a reasonably large internuclear distance. This is exactly what was observed in the calculation. The solution to this dilemma is to realize that curve crossing is a dynamical as well as a group theoretical problem, and that the nuclear motion will thus follow the diabatic curve (wave function envelope) as opposed to the adiabatic curve (energy envelope) whenever the velocity of the nuclei is significant and the electronic interactions between the two wave-functions corresponding to the crossing curves is insignificant. In the case of core-excited resonances, it has already been pointed out several times that the mixing between the stable and added stabilizing configurations is 5-10 orders of magnitude smaller than the diagonal energy elements. (As discussed in TNG this fact is physically obvious and fundamentally the reason for the success of the quasi-stationary methods.) This means that in the problems considered here, the
diabatic curves are the ones which must be compared to experiment. The general procedure, therefore, is to follow the diabatic curves which can easily be chosen by studying the smooth change of wavefunction as a function of R, and then by looking to see if there is any significant mixing when two diabatic curves cross. A note of caution is in order — in processes like dissociative recombination and associative ionization, which are basically resonance processes, but where the relative kinetic energy of the nuclei is never more than $\sim 0.03\, \text{eV}$ at 300$^\circ\text{K}$, one should follow the adiabatic curves. (A simplification is introduced in these problems, since the SP states are no longer resonances, but singly excited states of the system formed when an electron is added to the positive molecular ion, and therefore amenable to the quasivariation or variation methods.) In borderline cases, one will have to either refer to the theory of curve crossing, use Mandl's complex energy theorems, or hopefully, resolve the question unambiguously by comparison to experiment (one of the choices, diabatic or adiabatic, should give conspicuously poor agreement).

In this section any discussion of widths has been knowingly omitted. For the $^2\Sigma^+_u^g \, l_s \sigma \, l_s' \sigma \, l_s \, \text{SP}$ and $^2\Sigma^+_g^g \, l_s \sigma \, l_s \sigma \, l_s' \, \text{repulsive state}$, the widths have been calculated by Herzenberg et al., but for reasons that will be discussed in a future publication, the authors
reserve judgment as to their validity. 8

It is clear for CE1 resonances that narrowness of width greatly favors the simplification introduced by using quasi-stationary methods, as opposed to pure close-coupled scattering calculations, when one only wishes to have information about the resonances' energy, width, and assignments. For CE2 and SP, which are quite broad [lifetimes of \( O(10^{-14}) \) sec or less] 9 some authors would prefer to treat the phenomena associated with these states by pure scattering methods, especially the method of distorted waves. Herzenberg et al., in their calculation of the vibrational excitation cross section, stress that they obtain results with quasi-stationary methods for SP resonances 10 which are in as good agreement with experiment as the result of Takayanagi (1965) which was achieved with a distorted wave method.

---

8 The widths of resonances as calculated by complex energy methods similar to those used by Herzenberg et al. will be discussed in a publication in preparation by H. Taylor and A. Golebiewski. It will be shown there that the calculation of widths gives ambiguous results when the boundary enclosure (see Herzenberg et al.) is varied unless extremely large basis sets are used in the inside region. No calculations have ever been done using the complex energy method for widths in which extensive basis sets were used. Such calculations are in progress at this laboratory, and will be the subject of future communications.

9 Single Particle resonances are expected to be even broader because of the relatively lower polarizability of the ground state.

10 Various authors use the following names for what are denoted here by CE2 and SP: Shape resonances, virtual resonances, potential resonances, direct resonances, etc.
As pointed out by Herzenberg et al., this indicates that the two alternate models approach the true situation, that of a distorted target and an interacting passing electron, from two different limiting points of view.

The resonance formulation envisions a quasi-stationary state which must be coupled with outgoing waves, while the distorted wave method envisions a polarized target and a distorted orbit for the passing electron. Both of these approximations, if refined, will of course give the same result.

One can certainly say that the resonance formulation allows one to carry over the chemical concepts that are well known in spectroscopy and quantum chemistry. The authors freely admit that in molecular resonances which live $10^{-14}$ sec or less, there is perhaps a quantitative danger in drawing potential curves which depend on strict adherence to the Born-Oppenheimer approximation. For such short lifetimes it is dangerous to talk about potential curves, vibrational levels, etc. On the other hand, as a first approximation in quantitative calculations (as shown by Herzenberg et al.), and in qualitative explanations and predictions of experiment as shown above and in TNG, the usefulness of the quasi-stationary approach and chemical intuitive ideas cannot be denied.
Calculations

Calculations were done on CE1, CE2, and SP resonances. For CE1, the quasivariation method of TW is adequate, as evidenced by the results published in TW. However, to calculate the CE2 and SP resonances, the stabilization method must be used. Hence a basis set for use in the stabilization method must be constructed which is physically reasonable and insures convergence (stabilization) with as few functions as possible.

The calculations were done with the diatomic molecule program of Harris (1960) and Taylor and Harris (1963, series), modified to include the quasivariation and stabilization methods. In this program, trial functions are composed of linear combinations of products of one electron orbitals, so the one electron orbital basis is what is sought for the stabilization method, as used here.

For a homonuclear diatomic molecule, suitable molecular orbitals are defined as

\[ \zeta_r(\delta, \eta; nmvp) = \exp[-\delta\xi + iv\phi] \xi^n[(\xi^2-\eta^2)(1-\eta^2)]^{v/2} \cdot \eta^m \left\{ \exp[-\alpha\eta] + (-1)^k \exp[\alpha\eta] \right\} \]

(1)

where \( \xi, \eta, \phi \) are the prolate spheroidal coordinates; \( \delta, \alpha \) are non-linear variable parameters; \( n, m \) are integer exponents; \( v \) is the
azimuthal quantum number; \( p \) defines *gerade* or *ungerade* symmetry of the orbital; \( r \) indexes the root of the chosen symmetry which most corresponds to the particular orbital \( \phi_r \). The exponent \( k \) is used to produce the \( g \) or \( u \) symmetry defined by \( p \) through the relation

\[
k = m + p + |v|
\]

where \( p \) is even for \( g \) and odd for \( u \). A complete discussion may be found in the theses of either of the authors.

A more compact notation

\[
r^k_p = \phi_r(\delta,\alpha;nmvp)
\]

is now possible, and will be used in the following discussion. As example,

\[
l^1_g = \phi_1(\delta,\alpha;0000), \quad l^1_u = \phi_1(\delta,\alpha;0001), \quad l_{ou} = \phi_1(\delta,\alpha;00\pm l).
\]

Note that (1) is a highly flexible function with two variable non-linear parameters.

One possible choice of basis would be a set of orbitals as near \( H_2^+ \) orbitals as possible, and the functions (1) can be selected to give an excellent representation of these orbitals. For example, at \( R = 2.0 \) au (1 au = .52917 \( \AA \)), the equilibrium separation for the ground state of \( H_2^+ \), a \( l^1_g \) orbital of the type (1) gives an energy only 0.00002 Hartree above the exact energy as determined by Bates, Ledsham, and Stewart (1953). A basis of this type would be ideal for electron-\( H_2^+ \) scattering calculations, but for the target \( H_2 \) and calculations on CE resonances a slight modification causes faster stabilization. The basis was actually chosen by the following steps:

1. For a particular internuclear separation \( R \), the best \( l^1_g \_2^+ \) orbital is found. As is known, this gives an
excellent representation of the innermost orbital of the excited \( H_2 \) states which is desirable since core-excited resonances are in the field of the excited \( H_2 \) states are to be studied.

2. A \( 1 \sigma_g' \) orbital is then added and holding \( 1 \sigma_g \) fixed, is minimized to make the best one term ground state of \( H_2 \). Due to the fixed \( H_2^+ \) orbital, this one configuration \( H_2 \) result is not the best that could be achieved with the diatomic program.

3. \( 1 \sigma_u \) and \( 1 \pi_u \) orbitals are found by minimization in the field of the \( 1 \sigma_g \) \( H_2^+ \) orbital to make the best one term \( 3,1 \Sigma_u^+ \) and \( 3,1 \Pi_u \) states of \( H_2 \).

4. Higher orbitals \( 2 \sigma_g', 3 \sigma_g \ldots ; 2 \sigma_u', 3 \sigma_u \ldots ; 2 \pi_u, 3 \pi_u \ldots \) are constructed by minimization of higher roots of the secular equation with the trial function

\[
C_1 1 \sigma_g' 1 \lambda_p + \sum_{n=2}^{r} C_n 1 \sigma_u' n \lambda_p
\]

holding the \( 1,2,\ldots r-1 \) orbitals fixed.

The sets of orbitals of \( \sigma_g', \sigma_u', \pi_u \) symmetry for various values of \( R \) which were used in the CE calculations are listed in Tables 4-6.

Products of three of these orbitals are used as a basis for the \( H_2 \) calculations, and in the major configurations representing the CEI resonances the parameters of the outermost orbital were also varied to minimize the energies of the roots which were being stabilized. As all resonance energies (even those obtained by the quasivariation method) were checked for stabilization, this introduced no difficulties.
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<td>F24</td>
<td>F25</td>
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</tbody>
</table>
\begin{table}
\centering
\caption{$\sigma_u$ BASIS ORBITALS}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{R} & $1\sigma_u$ -000 & $2\sigma_u$ -010 & $3\sigma_u$ -210 & $4\sigma_u$ -310 & $5\sigma_u$ -330 & $6\sigma_u$ -430 \\
\hline
1.05 & .21729, .58879 & .25995, .32588 & .180 & .129 & .110 & .06042 \\
1.1 & .23619, .62400 & .27103, .35050 & .189 & .139 & .111 & .06092 \\
1.2 & .27958, .41937 & .29978, .24054 & .205 & .153 & .111 & .06241 \\
1.3 & .33152, .58000 & .29499, .34278 & .222 & .166 & .112 & .06389 \\
1.4 & .38369, .57554 & .32389, .34177 & .238 & .185 & .114 & .06537 \\
1.5 & .42942, .64413 & .34634, .38552 & .258 & .196 & .116 & .06320 \\
1.65 & .51134, .76701 & .37185, .46725 & .283 & .214 & .117 & .06320 \\
1.8 & .60518, .87655 & .39148, .54299 & .313 & .236 & .118 & .060014 \\
1.95 & .68580, .94750 & .40800, .59700 & .337 & .258 & .119 & .060022 \\
2.1 & .79160, 1.02830 & .43431, .64647 & .365 & .277 & .120 & .063204 \\
2.25 & .88569, 1.10406 & .45595, .68393 & .390 & .300 & .121 & .063200 \\
2.4 & .97944, 1.17610 & .47770, .71655 & .414 & .327 & .122 & .063198 \\
2.7 & 1.16486, 1.33033 & .52035, .78053 & .462 & .366 & .123 & .063167 \\
3.0 & 1.34665, 1.47984 & .58694, .85341 & .507 & .404 & .126 & .062900 \\
\hline
\end{tabular}
\end{table}

*as minimized in quasivariation method.
### TABLE 6

**πₜ BASIS ORBITALS**

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<tr>
<th>R</th>
<th>1πᵤ -001ᵇ</th>
<th>No.-nmv</th>
<th>1πᵤ ′-001ᵇ</th>
<th>2πᵤ -201</th>
<th>3πᵤ -121ᶜ</th>
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<td>.27877, .28377</td>
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<tr>
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<td>.29700, .30400</td>
<td>.49924</td>
<td>.030601</td>
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<td>.31723, .32423</td>
<td>.52305</td>
<td>.030586</td>
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</tr>
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<td>.33737, .34642</td>
<td>.55802</td>
<td>.030600</td>
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<tr>
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<td>.088043</td>
<td></td>
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</tbody>
</table>

---

**a** - πₜ orbitals are made by taking the g counterpart of these.

**b** - The orbital 1πᵤ was used to form the c₃Πᵤ state of H₂, and the 1πᵤ ′ to form the c¹Πᵤ state.

**c** - As minimized in quasivariation method.

**d** - nmv changed to 42-1 for all R values below here.
No parameters were varied in CE2 or SP calculations once the basis was obtained, as this could lead to disastrous results.

The spin eigenfunctions used were the two three-electron doublets

\[
\frac{1}{\sqrt{6}} (2\alpha\beta - \alpha\alpha - \beta\alpha)
\]

and

\[
\frac{1}{\sqrt{2}} (\alpha\beta\alpha - \beta\alpha\alpha)
\]

which can be seen to be \( C_1 \alpha\alpha\beta + C_2 (\alpha\beta + \beta\alpha)\cdot\alpha \) and \( C_1 (\alpha\beta - \beta\alpha)\cdot\alpha \) respectively, or therefore one doublet composed of the two electron triplet plus an electron, and one composed of the singlet plus an electron. In the complete open shell treatment (different orbitals for different electrons), both spin doublets are used, and the coefficients corresponding to a particular combination of a spatial configuration (product of three one-electron molecular orbitals) and spin doublet gives an indication of the two electron target state to which the third electron became attached.

The first problem considered was the attempt to improve the results of TW, and to see if two CE1 resonances could be found, rather than the one reported in TW.

Hence the first calculational step was to do a calculation in which \( 3,^1\Pi_u \cdot n\pi_u \) and \( 3,^1\Sigma^+_g \cdot n\sigma_g \) were mixed and the ground state of \( H_2 \) projected out in accordance with the quasivariation method as discussed in TW. The singlet and triplet were automatically mixed by the use of both doublets, so that only two spatial configurations were necessary.
The result was that even though the two electron spatial configurations of the two triplet states were quite close in energy, the three electron states did not mix to six orders of magnitude, and the singlet and triplet parent spin doublets also did not mix. The two-electron Π states have considerably more electron affinity than the Σ states, and both CE1 resonances can thus be formed from $3,^1\Pi_u$ plus an electron, with the $3,^1\Sigma_g^+$ plus an electron yielding CE2 resonances.

The results presented are actually two-configuration results, because the parent target states $^3\Pi_u$ and $^1\Pi_u$ were determined with two configurations, $(C_1 \sigma g \pi_u + C_2 \sigma u \pi_g)$. In the singlet Π state, the orbitals $1\pi_u'$, $1\pi'_g$ of Table 6 were used instead of $1\pi_u', 1\pi_g$. $C_1$ was ~.99 and $C_2$ ~.02 at all internuclear distances. For the three electron calculation, the $3\pi_u$ orbital was added, and its non-linear parameters varied to minimize the energy. The linear coefficients were unchanged.11

The agreement with experiment demonstrates the efficacy of the one-electron model (product of one-electron functions with small number of configurations). At several $R$ values, additional configurations were added, including higher $\pi_u$ orbitals, but no additional

---

11Actually, in a two spatial configuration three electron doublet calculation there are four roots, and four linear coefficients. Since the roots corresponding to the triplet and singlet spin parents do not mix, equivalent results are obtained by using only the doublet $1/\sqrt{6} (2\sigma_{\alpha\beta} - \sigma_{\alpha\alpha} - \sigma_{\beta\beta})$ with the lower CE1 resonance, and the doublet $1/\sqrt{2} (\sigma_{\alpha\alpha} - \sigma_{\beta\beta})$ with the upper. Then the linear coefficients are unchanged from the two electron calculations. This provides a useful simplification if the wave functions are to be used for further calculations, such as widths, etc.
binding to the $^{3,1}_{2n} \Pi_u$ states was obtained. The energy did improve, but
only to the extent that the energy of the two-electron states them-
selves improved. In the interest of computer time, and since the
necessary quantitative information for comparison to experiment has
been obtained, the two configuration results are considered adequate.

Stabilization was checked by adding configurations of the type
e-\text{H}_2(X^1\Sigma^+_g)^2\Sigma^+_g$, i.e. 
$$\left\{C_{1g} \sigma \gamma + C_{2g} \sigma \gamma ' + C_{2u} \pi \gamma \right\} \cdot n \sigma , \ n = 2, 3, \text{ etc.}$$
The roots corresponding to the CE1 resonances were immediately stable
to six figures, the matrix elements between the CE1 resonances and the
stabilizing configurations were completely negligible (10^{-8} or less)
and the corresponding coefficients in the eigenvector matrix therefore
were also negligible. Addition of more no \text{g} orbitals only served to
slightly lower the lowest root to an energy nearer the correct energy
of the ground state of H_2, and inserted unstable roots between the
lowest root and the root corresponding to the CE1 resonance (plus
meaningless roots above the expected range of the CE2 resonances).

The next step was a quasivariation calculation of the resonance
corresponding to e-3\Sigma^+_u for comparison to the dissociative attachment
experiment.

At large R values, no difficulties were observed, but as R was
decreased into the Franck-Condon region, the amount of binding for the
third electron also decreased. Somewhere between 1.4 and 1.3 au (R)
the binding for the third electron became negligible (0.07 eV or less),
and as R was decreased further, the potential curves for the CE1 $^2\Sigma^+_g$
resonances and the $^{3}\Sigma^+_u$ repulsive state of H_2 were coincident for all
practical purposes. This result is consistent with the model of crossing to form a CE2 resonance in the Franck-Condon region. The stabilization method was applied next. When the roots for R greater than or equal 1.5 au were checked, no change was observed, and the mixing of the stable resonance configurations and the stabilizing configurations was negligible.

However, for smaller R values, the mixing is not negligible, and the roots corresponding mainly to the resonance configurations began to move to higher energy values. Stabilizing configurations of the type $1\Sigma^+_g \cdot n\sigma_g$ were used, for n from two to seven. The roots corresponding to the resonance usually stabilized once the three stabilizing configurations $1\Sigma^+_g \cdot \{C_1 2\sigma_g + C_2 3\sigma_g + C_3 4\sigma_g\}$ had been added, however three additional configurations were added at each R as a precautionary check.

The final result obtained was that for the smallest R considered, 1.05 au, the $2\Sigma^+_g$ resonances was 0.2 eV above the $3\Sigma^+_u$ state of $H_2$, and that the resonance changed from CE1 to CE2 between 1.4 and 1.5 au.

In these calculations, simple products of one-electron orbitals were again used, with the $3\Sigma^+_u$ of $1\sigma \, 1\sigma_g \, u$ and $2\Sigma^+_g$ of $1\sigma \, 1\sigma \, 6\sigma$ from Tables 4-6. For $R \geq 1.5$ au only the one-configuration result and considerably easier to apply for any further calculations. For $R < 1.5$ the CE2 resonance mixes with the stabilizing configurations, so the entire eigenvector is presented for the stable CE2 root at each R in Table 7. The numbers to the left of the table indicate the space-spin configuration, with eleven spatial configurations and the two spin
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<th>Configuration</th>
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<tr>
<td>2</td>
<td>$l\sigma g\sigma l\sigma 5\sigma u\sigma u$</td>
</tr>
<tr>
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<td>$l\sigma g\sigma 'l\sigma 5\sigma u\sigma u$</td>
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<td>10</td>
<td>$l\sigma g\sigma '3\sigma 3\sigma g\sigma g$</td>
</tr>
<tr>
<td>11</td>
<td>$l\sigma g\sigma '6\sigma 6\sigma g\sigma g$</td>
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### Table 7

**Eigenvectors for Stabilization of $\sum_{e}^{2}$ CE2 Roots**

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<tr>
<th>No.</th>
<th>$R = 1.05$</th>
<th>$R = 1.1$</th>
<th>$R = 1.2$</th>
<th>$R = 1.3$</th>
<th>$R = 1.4$</th>
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<td>$-0.7024906E-00$</td>
<td>$-0.7379915E-00$</td>
<td>$-0.7721574E-00$</td>
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<td>$0.1977099E-01$</td>
<td>$-0.538126E-02$</td>
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<tr>
<td>2</td>
<td>$-0.2056712E-02$</td>
<td>$-0.3541176E-04$</td>
<td>$-0.322728E-03$</td>
<td>$-0.2535066E-03$</td>
<td>$0.9700729E-04$</td>
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<tr>
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<td>$0.1691520E-00$</td>
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<td>$0.2490221E-00$</td>
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</tr>
<tr>
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<tr>
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<td>$-0.5640836E-02$</td>
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<td>$-0.5276437E-02$</td>
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doublets. The odd indices correspond to the combination of a particular spatial configuration and the triplet spin parent $1/\sqrt{6}$ ($2\alpha\beta-\alpha\beta-\beta\alpha$), while the even indices correspond to the combinations with the singlet spin parent $1/\sqrt{2}$ ($\alpha\beta-\beta\alpha$). The orbitals from Tables 4-6 which make up the eleven configurations are denoted in Table 7. The eigenvectors for the largest, eleven configuration, stabilizing calculation are given rather than a smaller calculation with the same stable root in order to show the relative mixing of the different stabilizing configurations.

These results, and the results of the upper CE1 calculations are presented graphically in Fig. 1. The solid lines correspond to resonances of $H_2^+$, and the dashed lines to one-electron model calculations of the parent $H_2$ states. Note that as a result of using a $1g_u$ orbital as one of the major elements of the basis set in order to get rapid stabilization of the core-excited resonances, the single configuration calculations for the excited $H_2$ states are quite good. The CE1 to CE2 crossing point is determined relative to the $3\Sigma^+_u H_2$ curve calculated with the same basis.

It is also to be noted that the $2\Sigma^+_g$ repulsive curve and the $2\Sigma^+_g$ curve of $e \cdot 3\Pi_u$ do become nearly tangent at small $R$ values. In fact, from the slopes in Fig. 2, it is possible that they may intersect. Therefore, at two small $R$ values, 1.05 and 1.2 au, the $g_u g_u g_u$ and $g_u u u u$ configurations were mixed again as a check. The off-diagonal elements were $\sim 10^{-3}$ smaller than the diagonal elements in both cases, indicating that whether the non-crossing rule holds or not, the mixing of the two states is so small that if the nuclei possess any kinetic
energy at all, they will follow the diabatic curve rather than the adiabatic, as discussed in the preceding section.

For the stabilization of the two SP resonances of symmetry $2\Sigma^+_u$ an entirely different procedure was used. Since the SP resonances are physically considered to be a $\sigma_u$ electron in the field of the slightly polarized ground state, the first step was a full three-configuration variation treatment of the ground state of $H_2$. The $\sigma_g^c ls$ and $\sigma_g^c ls'$ are thus not the same as those listed in Table 4, but those which make the best ground state $H_2$ one term calculation. $\sigma_u^c ls$ and $\sigma_u^c ls'$ were chosen as were $\pi_u^c$ and $\pi_u^c$ as correlating orbitals which minimized the ground state energy. This had to be done at each R point. In general, the orbitals with superscripts $c$ are much more concentrated about the nuclei than the orbitals of Tables 4-6.

The first three-electron wave function was

$$\begin{align*}
&\left\{ C_1 \sigma_g^c ls \sigma_g^c ls' + \\
& C_2 \sigma_u^c ls \sigma_u^c ls' + C_3 \pi_u^c 2p_u \pi_u^c 2p_u' \right\} \times \left\{ \sigma_u^c ls + \sigma_u^c ls' \right\}
\end{align*}$$

and the roots obtained with this calculation were checked for stabilization by adding the $\sigma_u$ orbitals from Table 5 one at a time to the $H_2$ ground state function in the first bracket. The trial function above mixed strongly with the first three of these stabilizing configurations, and the roots only began to settle down after the fourth excited $\sigma_u$ orbital had been added.

This was a very extensive calculation involving a maximum of twelve one-electron orbitals and as many as twenty-one spatial configurations, which with the two spin doublets made a $42 \times 42$ secular equation. For this reason, only the energies and qualitative features of the wave functions have been presented. The parameters of all the
orbitals, the eigenvectors, etc. will be furnished upon request.

As in the CE2 cases, addition of stabilizing configurations tended to drive the root corresponding to the SP resonance configuration up, inserting spurious and unstable roots between it and the ground state and improving the ground state root. In contrast, CE1 resonances calculated by the quasivariation method, when stabilizing configurations were added, tended to have their energies slightly lowered, if any energy change occurred at all.

It is interesting to note that another root in the $2\Sigma^+_u$ sequence became approximately stable, at energies about 1.5 - 2.0 eV above the region of the four states $3^1\Pi_u$ and $3^1\Sigma^+_g$ discussed previously. This probably corresponds to a poor calculation of the $2\Sigma^+_u (\sigma_u \cdot E\Sigma^+_g)$ mentioned above as a possible core-excited resonance. The singlet spin parent was definitely more important in the configuration, so it is also possible that the root could correspond to $e \cdot B\Sigma^+_u$, however this is felt to be less likely, since the stabilizing configurations tend to push the root up, not down. Further study is necessary to resolve this point, since no configurations other than $2\Sigma_u (X\Sigma^+_g) \cdot n\sigma_u$ were included in the trial function, and these cannot be expected to give a good calculation for a CE state, even if a stable root should occur. At present, there is no way of knowing whether the upper root would even remain stabilized upon addition of core-excited configurations, as it did not seem to stabilize as rapidly as the SP root. The semi-stable roots are given in column (f) of Table 3, and the parentheses are used to indicate that they are not considered final or completely
stabilized, but do indicate the possible presence of a CE type resonance near that energy region.

Finally, it should be mentioned that calculations of resonance energies, particularly by the quasivariation method, are fraught with unforeseen and hidden difficulties not encountered in stationary state calculations. First, in every resonance calculated, if the energy was plotted as a function of the "screening parameter" $\delta$ of the outermost added orbital, pseudo-minima were encountered, a situation which had not occurred in the case of stationary state calculations with the diatomic molecule program used here. This is probably because variation of $\delta$ shifts the maximum electron density of the orbital so that it coincides with the maximum density of higher orbitals, even though the orbital exponents $n$ and $m$ are fixed and do not represent the nodal properties of the higher orbital properly. Each coincidence of electron density maxima would then produce a pseudo-minimum. An example of this is the quasivariation calculation of the $e \cdot 3\Pi_u$ resonance. At $R = 3.0$ au, essentially the same energy can be obtained with $\Theta_3(.03056, .0; 12-11)$ or $\Theta_3(.0632, .0; 42-11)$ and fixed $\Theta_1 = \log$ and $\Theta_2 = 1\pi_u$. Both $\Theta_3$ orbitals exhibit false minima for larger $\delta$ values.

The second difficulty is with convergence of the two-electron integrals $(ij|l/r|kl)$ when very small $\delta$ values are used, particularly in the higher orbitals. Within the limitations set by the program, this problem is purely numerical, caused by the loss of significant figures upon subtraction of large numbers and exponent overflow, underflow and wraparound, and can be surmounted by the use of scaling and/or double precision arithmetic.
Third, there is the amount of physical and chemical intuition required to obtain good results. A poor guess of the major resonance configurations, or a poor trial function for them, may either greatly increase the amount of work necessary to get agreement with experiment, or yield completely meaningless results. The ability to calculate widths and energy shifts would greatly aid in the problem.

The consequence of these difficulties is that each resonance calculation must be approached as a completely separate problem requiring special, individual handling. There can be no doubt of the fact that the quasivariation and stabilization methods work, as the agreement with experiment reported here shows, but for these and any other calculations of resonant states, extreme caution is necessary. With a well determined basis set, and based on our experience with both methods the stabilization method appears to be preferable for reasons of both flexibility and safety.

The calculations were performed on the Honeywell 800 computer of the University of Southern California Computer Science Laboratory, and the LBM 7094/7044 DCOS equipment of the Jet Propulsion Laboratory. The authors would like to express their appreciation to both institutions for making available the large amounts of computer time which were necessary for these calculations.
CHAPTER IV

SUMMARY

Quasi-stationary methods of calculating the energy of core-excited and single particle resonances and autoionizing states of atoms and molecules are presented both from an intuitive, physical approach and from a formal, rigorous standpoint.

The methods are applied to resonant states of $H_2^-$, and in the process, a general computer program for calculating the energies and wave functions of diatomic molecules which incorporates both the normal variation method of quantum chemistry for bound states and quasi-stationary methods for resonances has been developed.

The results of the $H_2^-$ calculations are compared to electron scattering experiments.

The diatomic molecule program developed is a modernization of previous methods including several new options, and extended so that calculations can be done for up to twenty electrons. It is fully discussed in a set of Appendices, and a sample calculation on NO$^+$ is presented as an illustration of the applicability of the program to calculations on large diatomic systems.
APPENDIX I. MATHEMATICAL DETAILS

Wave Function and Coordinate System

The diatomic molecule program discussed in these appendices is a generalized program for calculating the energy of a diatomic molecule within the Born-Oppenheimer approximation, using the variation method with optimization of both linear and non-linear parameters to improve the energy. The mathematical procedures used are an extension and generalization of the programs of Harris (1960), and Taylor and Harris (1963, etc.), and extensive use will be made of these references. The inclusion of the full mathematical treatment, rather than only the outline of its departures from the above methods, is for the purpose of completeness, so that these appendices will contain all the information necessary to understand and to use the diatomic program.

The total wave function is composed of linear combinations of products of one-electron molecular orbitals. These orbitals, \( \phi_i \), are expressed in prolate spheroidal coordinates, therefore the discussion will begin with the coordinate system and definition of the \( \phi_i \), and proceed stepwise to the definition of the total wave function.

The prolate spheroidal coordinate system is based on two foci, A and B, where the two nuclei are located. The foci are separated by the internuclear distance \( R \). The coordinates of a point \( P_i \) are
The quantity \( \rho_i \), the distance of \( \mathbf{P}_i \) from the internuclear axis, is also useful, and is expressed as

\[
\rho_i = \frac{1}{2} R \left[ (\xi^2 - 1)(1 - \eta^2) \right]^{\frac{1}{2}}.
\]

The volume element and some differential forms in this system are

\[
dr = \frac{1}{8} R^3 (\xi^2 - \eta^2) \, d\xi \, d\eta \, d\phi
\]

\[
\nabla^2 f = \frac{l_i}{R^2 (\xi^2 - \eta^2)} \left[ \frac{\partial}{\partial \xi} \left\{ (\xi^2 - 1) \frac{\partial f}{\partial \xi} \right\} + \frac{\partial}{\partial \eta} \left\{ (1 - \eta^2) \frac{\partial f}{\partial \eta} \right\} \right]
\]

\[
+ \frac{\left( \xi^2 - \eta^2 \right) \frac{\partial^2 f}{\partial \phi^2}}{(\xi^2 - 1)(1 - \eta^2)}
\]

\[
\nabla f \cdot \nabla g = \frac{l_i}{R^2 (\xi^2 - \eta^2)} \left[ (\xi^2 - 1) \frac{\partial f \partial g}{\partial \xi \partial \xi} + (1 - \eta^2) \frac{\partial f \partial g}{\partial \eta \partial \eta} \right]
\]

\[
+ \frac{(\xi^2 - \eta^2) \frac{\partial f \partial g}{\partial \phi \partial \phi}}{(\xi^2 - 1)(1 - \eta^2)}
\]

with the limits \( 1 \leq \xi \leq \infty, -1 \leq \eta \leq 1, 0 \leq \phi \leq 2\pi \).
FIGURE 8

PROLATE SPHEROIDAL COORDINATE SYSTEM
The one electron spatial function $\phi_i$ is chosen in terms of these coordinates as

$$
\phi_i(\vec{r}_j) = \exp\left[-\delta_i \xi_j - \alpha_i \eta_j + iv_i \phi_j\right] \xi_j^{n_i} \eta_j^{m_i} \cdot \frac{(2\rho_i/R)^{|v_i|}}{v_i}
$$

where $\delta_i, \alpha_i$ are adjustable non-linear parameters which will be determined by the variation method. The $\delta$ parameter is a measure of the extent of an ellipse of electron charge density about the two nuclei, and must be positive to assure that the function goes to zero as $\xi$ goes to infinity. The ratio $\alpha/\delta$ gives a measure of polarization along the internuclear axis since $\alpha = \delta$ centers the electronic charge on the nucleus at A and $\alpha = -\delta$ centers the charge on the nucleus at B. Intermediate $\alpha$ values allow improvement of the molecular orbital by allowing unsymmetrical, polarized charge distributions.

The exponents $n_i, m_i$, are restricted to positive integers or zero, and are used to form higher orbitals. Non-zero $m_i$ introduce a node in the perpendicular bisector plane of the internuclear axis. $v_i$ is the azimuthal quantum number, and can assume any integer value, including zero. The $(2\rho_i/R)^{|v_i|}$ factor has been included to provide regularity on the internuclear axis, and because it provides simplifying cancellations in some of the integral expressions to be introduced later.

Atomic orbitals, in particular Slater type orbitals, can be expressed as linear combinations of the elliptical functions $\phi_i$ without considerable difficulty, although the number of terms necessary in
the combination goes up quite rapidly as \( n \) increases. For example

\[
ls_a = \mathcal{A}(\delta,\delta;000), \quad ls_b = \mathcal{A}(\delta,-\delta;000)
\]

\[
2s_a = \frac{1}{2} R \left[ \mathcal{A}(\delta,\delta;100) + \mathcal{A}(\delta,\delta;010) \right]
\]

\[
2s_b = \frac{1}{2} R \left[ \mathcal{A}(\delta,-\delta;100) - \mathcal{A}(\delta,-\delta;010) \right]
\]

The remainder of the series can be generated using the fact that from (1) one can express

\[
r_a = \frac{1}{2} R(\xi + \eta)
\]

\[
r_b = \frac{1}{2} R(\xi - \eta)
\]

In the homonuclear case, the problem of obtaining gerade or ungerade symmetry of the electronic wave function also presents itself. There are two methods of accomplishing this. One is the passing of the total molecular wave function through the center of inversion, taking the proper linear combination of the function and its inverted counterpart. This method will be discussed later, after introduction of the total wave function. The other is to symmetrize the individual molecular orbitals \( \mathcal{A}_i \), actually defining them as \( \sigma_g, \sigma_u, \pi_u \), etc.

The symmetrization of the molecular orbital \( \mathcal{A}_i \) is accomplished by inverting it, and taking \( \mathcal{A} \pm \mathcal{A} \) with the plus sign for gerade and the minus sign for the ungerade case. The \( \mathcal{A} \) represents the inversion operation, which is equivalent to a reflection in the perpendicular bisector plane of the internuclear axis (interchange of A and B), followed by a rotation of \( \pi \) radians (\( \varphi \to \varphi + \pi \)).
Examination of the function $\mathcal{A}$ (Eq. 6) shows that this inversion is accomplished by replacing $\eta$ by $-\eta$ and $\varphi$ by $\varphi + \pi$, and therefore

$$\mathcal{A}_{\xi,u} = \left\{ \mathcal{A}(\delta,\alpha;\eta \mu \nu) + (-1)^k \mathcal{A}(\delta,-\alpha;\eta \mu \nu) \right\} \frac{\sqrt{2}}{2} \tag{8}$$

where $k = p + m + |\nu|$; $p$ representing the parity $\xi$ or $\mu$ desired, with $p$ even for $\xi$ and odd for $\mu$.

Since only certain portions of the function are affected by this operation, it is convenient to rewrite the symmetrized orbitals as

$$\Phi_{\xi,u}^{\delta,\alpha;\eta \mu \nu} = e^{-i \frac{e}{\xi} \mu} \sum_{\nu=0}^{m} e^{i \eta \mu} \left\{ e^{-i \alpha \eta} + (-1)^k e^{i \alpha \eta} \right\} \eta \tag{6'}$$

to eliminate excessive computational labor in the actual calculation of the spatial matrix elements.

Now let us define a primitive function $\phi_j(\vec{r})$

$$\phi_j(\vec{r}) = \prod_{i=1}^{N} \phi_i(\vec{r}_i) \tag{9}$$

where $N$ is the number of electrons in the system, $\vec{r}_i$ is the position vector of the $i^{th}$ electron, $\vec{r}$ symbolizes collectively the coordinates of all $N$ electrons. The index $j$ will be used to denote a particular spatial configuration after configuration interaction has been introduced.

A single spatial configuration is the antisymmetrized primitive function. Combining it with a spin function $\theta$, one obtains the expression for a single configuration

$$\psi_{j\mu}(\vec{r}, \sigma) = \mathcal{A}_n(\phi_j \theta_{\mu}) \tag{10}$$
where $\theta_\mu$ is the $\mu$th eigenfunction of $\hat{s}^2$ and $\vec{\sigma}$ represents the spin coordinates. Usually in this program one spatial configuration is combined with several spin eigenfunctions comprising a complete spin basis, but depending on the number of closed shell electrons selected in the problem. A more limited spin basis may be used, or a specific spin eigenfunction may be selected which most corresponds to the physical situation. Once a specific problem has been selected (i.e., lowest lying $^3\Sigma$ state of the molecule AB), the number of spin eigenfunctions will be fixed, so for simplicity the word configuration will be used to refer to a spatial configuration, realizing that this spatial configuration may be combined with one or several spin functions.

Defining $d$ as the number of spin functions chosen for a particular problem and $m$ as the number of configurations, the total trial wave function for the $i$th state of the system becomes

$$\psi_i(r, \vec{\sigma}) = \sum_{i=1}^{m} \sum_{\mu=1}^{d} c_{i\mu}^i \psi_{\mu}(r, \vec{\sigma})$$

(11)

where the $c_{i\mu}^i$ are the components of the $i$th column of the eigenvector matrix determined by diagonalization of the secular equation.

It is now possible to show the method of producing $g$ or $u$ symmetry by inversion of the entire molecule through the inversion center.

The linear combination

$$c_1 \psi + c_2 \psi$$

(12)
can be considered as a two configuration problem, and the total
secular matrix will be
\[
\begin{pmatrix}
\langle \psi^* \H \psi \rangle & \langle \psi^* \H_1 \psi \rangle \\
\langle i\psi^* \H \psi \rangle & \langle i\psi^* \H_1 \psi \rangle
\end{pmatrix}
\]
(13)
which is a supermatrix of \( m \times d \times d \) blocks, and is of the form
\[
\begin{pmatrix}
A & B \\
B^T & A
\end{pmatrix}
\]
(14)
since the matrix is Hermitian and \( \langle i\psi^* \H \psi \rangle = \langle \psi^* \H \psi \rangle \).

If this is diagonalized for the energy, both \( g \) and \( u \) solutions
will be obtained due to the form of (12), but it is well known that a
matrix of the structure (14) can be diagonalized by the unitary
transformation
\[
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}
\]
(15)
and applying this to the supermatrix (13) we obtain the block diagonal
matrix
\[
\frac{1}{2} \begin{pmatrix}
\langle [\psi + i\psi]^* \H [\psi + i\psi] \rangle & 0 \\
0 & \langle [\psi - i\psi]^* \H [\psi - i\psi] \rangle
\end{pmatrix}
\]
(13')
or, taking advantage of (14) again, its simplified equivalent
\[
\langle \psi^* \H (\psi \pm i\psi) \rangle
\]
(16)
Thus we see that Eq. (16) is equivalent to actually taking
\[
\psi_{gu} = \sqrt{2}/2(\psi \pm i\psi),
\]
but the amount of labor for calculation of
(16) with the proper sign is only about $\frac{3}{4}$ that of calculating and diagonalizing either the $g$ or $u$ block of (13').

The program itself calculates the blocks $A$ and $B$ and then takes the sum or difference as necessary to select the desired symmetry for the molecule.

In the case of $\Sigma$ states, if pi orbitals are included, plus-minus symmetry must also be considered. This can be handled by replacing $v_i$ by $-v_i$ in each pi orbital in a second configuration and repeating the calculation, and a procedure completely analogous to the above for selecting $g$ or $u$ symmetry can be used to select only the plus or minus linear combinations. Also, one could define a $\mathcal{O}_i$ by replacing the $\exp(iv\varphi)$ factor in $\mathcal{O}$ by

$$[\exp(iv\varphi) + \exp(-iv\varphi)]$$

in the pi orbitals of a configuration.

Spin and Antisymmetry

In the original diatomic methods (Harris, 1960; Taylor and Harris, 1963), spin and antisymmetry were handled by the method of representation matrices presented by Kotani, et al. (1963). This is an elegant group-theoretical approach in which a complete set of spin eigenfunctions is used as a basis to construct irreducible representation matrices, suitably antisymmetrized, for the $n^{th}$ order permutation group $\sigma_n$. The method is completely general, and is particularly adaptable to the case of non-orthonormal spatial orbitals in the complete open shell (different orbitals for different spins)
treatment of the diatomic program.

Unfortunately, the number of mathematical operations in the complete open-shell treatment increases astronomically for larger systems, due to the \( n! \) permutations in the group \( \sigma_n \), and the dimension of each of the set of \( n! \) representation matrices. For modern computers, the practical limit appears to be between six and eight electrons. In order to study larger systems, some sort of approximations must be made just to reduce these numbers to something in the realm of manageability.

One possibility is the closing of some or all of the shells (double occupancy). This has the effect of reducing the dimension of the representation matrices to only the invariant part corresponding to the remaining unpaired electrons as is outlined in Kotani, and of reducing the number of permutations necessary, since double occupancy causes linear dependencies in the group \( \sigma_n \). If there are \( r \) paired orbitals, the number of permutations is reduced to \( n!/2^r \). As an interim measure, this is helpful, but as \( n \) continues to increase, even closing of all the shells fails to reduce the problem to one of manageable size. For example, \( 16!/2^8 \) is still of the order \( 14! \), and even though the representation matrices are of dimension \( 1 \times 1 \), it is clear that some other approach is necessary.

Another alternative is to introduce spatial orthogonalities, and by knowledge of where these orthogonalities exist, eliminate those permutations which can make no contribution to the total secular equation. This procedure can be used independently of the shell-closing procedure, or they can be used in conjunction. In the
16 electron case mentioned above, by orthogonalizing ten inner shell orbitals in closed pairs, and leaving six open-shell electrons for bonding, the size of the problem is reduced to somewhere between the seven and eight electron complete open-shell problems. This is still rather large, but well within the capabilities of a modern large scientific computer.

Thus one of the aims of this research has been to revise the spin-antisymmetry routines of the older versions of the diatomic program to include options which allow a range between complete open-shell and complete closed shell spin treatments, using any orthogonalties which are introduced or exist naturally to reduce the problem.

Since the formal treatment is fully presented in Kotani (1963), the remainder of this section will be mainly concerned with the actual mechanics of applying the method with all the options as it is done in the edition of the diatomic program presented here. The notation used is chosen to be as consistent with both Kotani and Taylor-Harris as possible. Unless otherwise noted, arguments of functions have been suppressed, and the coordinate number is indicated by position (i.e., \( \varphi_3(r_1) \varphi_1(r_2) \varphi_2(r_3) = \varphi_3 \varphi_1 \varphi_2 \)).

Let the two eigenfunctions of the one-electron operator \( \mathbf{S}_z \) be denoted as \( \alpha \) and \( \beta \), with eigenvalues 1/2 and -1/2, respectively. Then eigenfunctions of the many-electron operator \( \mathbf{S}_z \) can be represented as simple products of \( \alpha \) and \( \beta \),

\[
\Omega = \alpha \alpha \cdots \beta \beta \beta \cdots .
\]
with eigenvalue $M$. In general, there are

$$n_\Omega = \binom{N}{\frac{1}{2}N + M}$$  \hspace{1cm} (19)

linearly independent simple product functions $\Omega$ for a given $M$ value in an $N$ electron problem; and the desired relation

$$\sum_{M=-N/2}^{N/2} \binom{N}{\frac{1}{2}N + M} = 2^N$$ holds.

The $\Omega$ functions are not generally eigenfunctions of $S^2$ which, like $S_z$, commutes with the Hamiltonian, but a simultaneous eigenfunction of $S^2$ and $S_z$ can be expressed as

$$\theta^{N}_{S,M} = \sum_{i} c_i \Omega_i$$  \hspace{1cm} (20)

There are $r^N_S = (1/2N + S) - (1/2N + S + 1)$ functions

$$\theta^{N}_{S,M,k} = 1, 2, \cdots F^{N}_{S}$$ for given eigenvalues $S(S+1)$ of $S^2$ and $M$ of $S_z$.

In the diatomic program, the coefficients in the above expansion of $\theta^{N}_{S,M,k}$ are those generated by the method of genealogical construction (Kotani, 1963) which uses the vector coupling formula and the functions $\alpha$ and $\beta$ to produce

$$\theta^{N}_{S,M,k} = -\sqrt{\frac{S-M+1}{2S+2}} \theta^{N-1}_{S+\frac{1}{2},M-\frac{1}{2};k} \cdot \alpha \sqrt{\frac{S+M+1}{2S+2}} \theta^{N-1}_{S+\frac{1}{2},M+\frac{1}{2};k} \cdot \beta$$

$$k = 1, 2, \cdots F^{N-1}_{S+\frac{1}{2}}$$  \hspace{1cm} (21)
and
\[ \begin{align*}
\theta_{S,M,k}^N &= \sqrt{\frac{S+M}{2S}} \sqrt{\frac{N-1}{S-\frac{1}{2},M-\frac{1}{2},h}} \cdot \sqrt{\frac{S-M}{2S}} \sqrt{\frac{N-1}{S-\frac{1}{2},M+\frac{1}{2},h}} \cdot f, \\
&= \frac{F_{N-1}}{S-\frac{1}{2}} + h \\
h &= 1, 2, \ldots, F_{N-1}^\frac{1}{2}
\end{align*} \]

(21)

This is not a unique choice of \( \theta_{S,M,k}^N \), but any other choice may be expressed as a unitary transformation of this set. Katsura (1963), has published a set of all \( \theta_{S,M,k}^N \) up to six electrons, and Weltin (1966) has developed a rapid and efficient scheme for generating all \( \theta_{S,M,k}^N \) which is limited only by available storage space in the computer.

For the case of \( d \) and \( m \) both equal to one (one configuration and one spin function), so that the total wave function is represented by Eq. (10). The matrix element of an operator \( Q \), which acts only on spatial coordinates, is

\[ \langle J_n [\phi_1 \theta_1] | Q | J_n [\phi_1 \theta_1] \rangle \]

(22)

and using the Hermitian property of the antisymmetrizer plus the relation \( J_n^2 = \sqrt{n!} J_n^2 = \sum_p (-1)^p p \), (22) becomes

\[ \sum_p (-1)^p \langle \phi_1 \theta_1 | Q | J_n [\phi_1 \theta_1] \rangle \]

(22')

where \( p \) is the even or odd parity of the permutation \( P \). Since \( P = P_r P_o \), Eq. (22') can be separated to obtain

\[ \sum_p \langle \phi(r') | Q | \phi(p_r) \rangle \langle \theta(\vec{r}) | (-1)^P \theta(p_o) \rangle \]

(23)
where the \((-1)^P\) has been included in the spin integral for convenience. Calculation of the spin integrals yields a set of coefficients \(U_{\mu}(P)\), so that the matrix element can be expressed as

\[
\sum_{P} U_{\mu}(P) \langle \phi | \varnothing | P\varnothing \rangle = \sum_{P} U_{\mu}(P) \varnothing(P) \tag{24}
\]

with the definitions

\[
\varnothing(P) = \langle \phi | \varnothing | P\varnothing \rangle \tag{25}
\]

\[
U_{\mu}(P) = (-1)^P \langle \theta | P\theta \rangle
\]

where the permutation is on either the functions or the coordinates in both integrals.

Additional spin functions may be introduced in which case the set \(U_{\mu}(P)\) becomes a matrix of dimension \(d\), where \(d\) is the number of spin eigenfunctions in the basis. Thus for one configuration, the matrix element of the operator \(\varnothing\) becomes a \(d\times d\) matrix of the form

\[
\sum_{P} U(P) \varnothing(P) \tag{26}
\]

where

\[
U(P) = \begin{bmatrix} U_{\mu\nu}(P) \end{bmatrix} = (-1)^P \langle \theta_{\mu} | P\theta_{\nu} \rangle \tag{27}
\]

The secular equation for the energy is then

\[
\sum_{P} U(P) \left[ H(P) - E\varnothing(P) \right] = 0 \tag{29}
\]

If the complete set of spin eigenfunctions is included \((d = F_{S}^{N})\) the matrices \(U(P)\) become unitary, irreducible representations of the permutation group, and are exactly the \(U(P)\) defined in Kotani (1963) and the Taylor-Harris papers (1960, 1963, etc.).
When spatial configuration interaction is included, the definition of $Q(P)$ can be expanded to $O_{jk}(P) = \langle \phi_j | 0 | \phi_k \rangle$, and the total secular matrix (29) becomes an $m \times d$ matrix, composed of $d \times d$ blocks for each $H_{jk}(P), S_{jk}(P); j, k = 1, 2, \ldots m$.

Given the sets $\theta_{S, M, k}^N$, it is now possible to generate the representation matrices $U(P)$ systematically, thus completely separating the spin and space parts of the problem, since once generated, the $U(P)$ are general for any problem with the same $N, S$, and $M$. From Eq. (27)

$$U_{\mu \nu}(P) = (-1)^P \left\langle \theta_{S, M, \mu}^N | P \theta_{S, N, \nu}^N \right\rangle$$

(27')

and therefore for an arbitrary permutation $P$, the associated $U(P)$ may be generated from a single rectangular matrix $C$, which has $n\Omega$ rows and $d$ columns stemming from the expansion of $\theta_{S, M}^N$ in terms of the $\Omega_i$ (Eq. 20).

Thus the $\mu, \nu$ elements

$$U_{\mu \nu}(P) = (-1)^P \left\langle \sum_{i=1}^d C_{i \mu} \Omega_i | P \sum_{j=1}^d C_{j \nu} \Omega_j \right\rangle$$

$$= (-1)^P \sum_{i=1}^d \sum_{j=1}^d C_{i \mu} \cdot C_{j \nu} \left\langle \Omega_i | \Omega_j \right\rangle$$

where $P\Omega_j = \Omega_{Pj}$, which is a member of the complete $\Omega$ set, and due to the orthogonality of the $\Omega$

$$U_{\mu \nu}(P) = (-1)^P \sum_{i=1}^d \sum_{j=1}^d C_{i \mu} C_{Pj \nu} \delta_{i, Pj} \cdot$$

This is repeated for all $\mu, \nu; 1 \leq \mu \leq d, 1 \leq \nu \leq d$ to make the full matrix. The $\alpha$'s and $\beta$'s are easily represented in a digital computer.
as 0's and 1's, making the operation $R_j$ and the checking of $\delta_{i,j}$ relatively simple.

For a truncated $\theta_k$ basis, depending on the functions which are omitted, certain rows in $C$ may have only zero elements ($C_{i\mu} = 0; 1 \leq \mu \leq d$). If so, those rows are omitted, and the multiplication by zero handled implicitly by the Kronecker $\delta$ function for computational convenience.

Since it is now possible to form the matrix $U(P)$ for any arbitrary $P$, the next requirement is a method of generating all the permutations $P$ of the group $\sigma_n$. Harris (1960) devised a simple algorithm for systematically generating all $N!$ permutations of the full group, optimizing mathematical operations and scan time.

Consider the arbitrary permutation $P$. It is desired to generate the succeeding permutation $Q$ in as few operations as possible and such that $Q$ is not a repetition of some permutation generated prior to $P$.

Read the numbers in $P$ from left to right until the first increase occurs (i.e., first number which is larger than the one to its left). The position of this number is called the pivot position. Interchange the number in the pivot position with the largest number to its left which is less than the number itself. Simply copy (leave unchanged) everything to the right of this position. Then arrange all numbers to the left of the pivot position in ascending order. The result is the permutation $Q$. If there was no increase, all permutations have been generated.
For example, consider $P$ represented by $\frac{1}{1} \frac{1}{2} \frac{k}{3} \frac{l}{4} \ldots s/n$, with $i > j < k > l$, and $i > k$. The pivot position is 3, occupied by $k$. By the inequalities, $j$ is the largest number less than $k$, so $j$ and $k$ are interchanged and $l, \ldots s$ are left as they were. Then $i$ is greater than $k$, so they are rearranged in ascending order, and the resulting $Q$ representation is $\frac{k}{1} \frac{j}{2} \frac{j}{3} \frac{l}{4} \ldots s/n$.

The parity is easily determined by inspection of the canonical number of the position immediately to the left of the pivot position, $c_{piv-1}$. If $c_{piv-1} [\text{Mod. } 4]$ is less than two, the parity of $Q$ is opposite to that of $P$, and if it is $\geq 2$, the parity of $Q$ is the same as that of $P$. In the example above $c_{p-1} = 2$, and $2[\text{Mod. } 4] = 2$, therefore $Q$ and $P$ have the same parity.

Table 8 gives a full numerical illustration of the results of the above techniques for the case of a complete open-shell three-electron doublet, with two spin functions $\theta_{\frac{1}{2}, \frac{1}{2}, 1}^3$ and $\theta_{\frac{1}{2}, \frac{1}{2}, 2}^3$, and six permutations in the order they are generated.

The above procedure is general for any number of $\theta$ functions, but if closed shells are introduced and the dimension of the $\theta$ set reduced concomitantly, the $U(P)$ become linearly dependent. (The expression "closed shells" is to be interpreted as strict double occupancy.) It is still possible to generate all the $N!$ permutations and $U(P)$, but a much more favorable computational situation would occur if a way of generating only the linearly independent subset of $P$ and $U(P)$ could be determined.
### TABLE 8

**SPIN-PERMUTATION MATRICES FOR THE OPEN-SHELL THREE ELECTRON DOUBLET**

| Eigenvector matrix $C_n\theta|\Theta$ | $\alpha\alpha\beta$ | $2/\sqrt{6}$ | 0 |
|----------------------------------------|---------------------|-------------|---|
| $\alpha\beta\alpha$                   | $-1/\sqrt{6}$       | $-1/\sqrt{2}$ |
| $\beta\alpha\alpha$                   | $-1/\sqrt{6}$       | $-1/\sqrt{2}$ |

<table>
<thead>
<tr>
<th>$p$</th>
<th>$p$</th>
<th>$U(P)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 3 2 (+)</td>
<td>$\frac{1}{2}$</td>
<td>$\begin{pmatrix} 1 &amp; -\sqrt{3} \ \sqrt{3} &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>3 1 2 (+)</td>
<td>$\frac{1}{2}$</td>
<td>$\begin{pmatrix} 1 &amp; -\sqrt{3} \ -\sqrt{3} &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>2 3 1 (+)</td>
<td>$\frac{1}{2}$</td>
<td>$\begin{pmatrix} 1 &amp; \sqrt{3} \ -\sqrt{3} &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>3 2 1 (-)</td>
<td>$\frac{1}{2}$</td>
<td>$\begin{pmatrix} 1 &amp; \sqrt{3} \ \sqrt{3} &amp; -1 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

For $r$ closed shell pairs of electrons, the $\theta$ basis becomes

$$\theta_{S,M,k}^{N} = \theta_{S,M,k}^{N-2r} (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\cdots(\alpha\beta-\beta\alpha) \left(\frac{\sqrt{2}}{r}\right)^{\tau}$$

$$k = 1, 2, \cdots \tau_{S}^{N-2r}$$

(30)
and there are \( N! \sqrt{2^N} \) linearly independent matrices and permutations in
the subgroup of \( \sigma_N \). The generation of the \( U(P) \) is the same as before,
except using the reduced \( \theta \) basis so the problem becomes one of
generation of only the linearly independent subset of permutations.

The Harris algorithm can easily be adapted to this problem. If
an auxiliary permutation vector \( R \) is introduced, such that the vector
\( P \) contains the actual function (coordinate) numbers, and \( R \) contains a
set of dummy indices in which the closed shells are represented by
duplicated numbers, a linearly independent subset can be generated by
doing the permutation-generating scan over \( R \), performing the same
operations on \( P \), and using \( P \) to generate \( U(P) \) and \( Q(P) \).

For example, a six electron triplet might have the form
\[
\frac{\sqrt{2}}{4} (\alpha \beta + \beta \alpha)(\alpha \beta - \beta \alpha)(\alpha \beta - \beta \alpha)
\]
and the corresponding initial \( P \) and \( R \) would be
\[
P = 1 2 3 4 5 6 \\
R = 1 2 3 3 5 5 
\]
As an even more complete example, consider the three electron doublet
with one closed shell pair, whose spin eigenfunction is \( \theta_{11}' \) and
whose \( P \) and \( U(P) \) can be represented by the \( \text{U}_{2,2} \) elements of the six
permutation matrices of Table 8. Here it is seen that of the set of
six permutations, if electrons one and two are the same, 123-213,
132-231, and 312-321 are equivalent, and moreover, that the 2,2
elements of their matrices are also identical. Thus selection of three
of the non-equivalent permutations with their respective matrices would
only have the effect of multiplying the total secular equation by a constant, in this case $1/2$.

Setting the initial $P$ and $R$ as $123$ and $113$ respectively, the sequence of permutations becomes

$$
P - 123(+) \quad 231(+) \quad 321(-)
$$

$$
R - 113(+) \quad 131(+) \quad 311(-)
$$

so we see that the search over $R$ will produce $3!/2 = 3$ non-equivalent permutations and using $P$ to generate $U(P)$ and $Q(P)$ will produce the desired secular equation.

The preceding techniques can be applied automatically by the present modification of the diatomic program. The case of orthogonal functions is slightly less easy to generalize, and thus requires some planning on the part of the user before proceeding to the computation stage. No modification of the program is necessary, only careful preparation of the input data cards.

A completely orthogonal spatial basis would have non-zero elements only in the case of pairwise interchanges and the identity permutation.

For any other case, one must consider the spatial orthogonalities and the coordinate operators. Clearly, the set of permutations used must include all possibilities of one or two electron operators contributing to the secular equation. Thus, any permutation of a configuration which produces no more than two zero factors in $S(P)$ must be included, and conversely, any permutations which may be seen to include three or more overlap factors which are zero may be excluded.
In a many configuration calculation, the configuration with the minimum number of orthogonalities controls the exclusion of permutations.

This option has been included in the program by allowing the user to generate a set of permutations particular to his problem by hand and instruct the permutation generating routine of the program of the specific limitations placed upon it. The program will generate any additional permutations as required and produce the reduced set of $U(P)$ delineated by the permutations.

As an example, see the NO$^+$ calculation reported elsewhere in this work (page 140ff.) which was included specifically for the purpose of illustrating the use of this option.

A word of caution is necessary here. When a complete spin basis is used, and the full $N'$ set of matrices $U(P)$ is thus generated, the ordering of the one-electron spatial functions in each configuration is energetically immaterial, since re-ordering is a unitary transformation, and the eigenvalues will not be changed. However, the eigenvectors will reflect the re-ordering transformation, and they will be changed accordingly.

On the other hand, if a truncated spin basis is used, whether all $N' U(P)$ are generated or not, the eigenvalues will be dependent on the order, and for best results, the spatial functions must be ordered to correspond physically to the ordering of the $\alpha$ and $\beta$ in the spin functions.

If one takes advantage of the orthogonality options, obviously the functions must be ordered to correspond with the set of hand-
generated permutations, and the ordering must be preserved in all configurations of a multi-configuration problem.

**Matrix Elements**

To produce the secular equation (29), the spatial integrals $H(P)$ and $S(P)$ must be evaluated. From Eq. (25), these are recognized as

$$S_{jk}(P) = \left( \phi_j | P \phi_k \right)$$

and

$$H_{jk}(P) = \left( \phi_j | \mathcal{H} | \phi_k \right)$$

where

$$\mathcal{H} = \frac{Z_A Z_B}{R} + \sum_{i=1}^{n} h_i + \sum_{i<j}^{n} \frac{1}{r_{ij}}$$

and

$$h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{iA}} - \frac{Z_B}{r_{iB}}$$

$Z_A$ and $Z_B$ are the charges of nuclei A and B, separated by the distance $R$. The distances $r_{xy}$ are the distances between particles x and y. Atomic units are used, with energies in Hartrees ($1 \text{ au} = 27.21 \text{ eV}$), and length in Bohrs ($1 \text{ au} = .52917 \text{ Å}$).

Since no term of $\mathcal{H}$ includes the coordinates of more than two electrons, $H(P)$ is reducible to sums of products of one- and two-electron integrals, and obviously $S(P)$ can be expressed as a simple product of one-electron overlap integrals.
Thus the matrices

\[(i|h|j) = \int \phi_i^*(r_1) h_1 \phi_j(r_1) dr_1\]  
\[(i|j) = \int \phi_i^*(r_1) \phi_j(r_1) dr_1\]  

and

\[(ij|1/r|kl) = \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{r_{12}} \phi_k(r_1) \phi_l(r_2) dr_1 dr_2\]  

can be calculated and stored, and the necessary elements combined to make \(H(P)\) and \(S(P)\) for a given \(P\).

Expanding in terms of the coordinates (Eq. 1), the one-electron integral \((i|h|j)\) separates into a kinetic energy integral and two nuclear attraction integrals,

\[(i|h|j) = \left( i - \frac{1}{2} \nabla^2 \right) j - \frac{2}{R} (Z_A + Z_B) \left( i - \frac{\xi}{(\xi^2 - \eta^2)} \right) j + \frac{2}{R} (Z_A - Z_B) \left( i - \frac{\eta}{(\xi^2 - \eta^2)} \right) j .\]

With the form of the wave function (6), all the one-electron integrals may be expressed in closed form in terms of the functions (Kotani, 1963)

\[A_n(\delta) = \int_{-\infty}^{\infty} t^n \exp[-\delta t] dt\]  
\[B_n(\alpha) = \int_{-\infty}^{\infty} t^n \exp[-\alpha t] dt .\]
The integrals for non-zero \( v \) may be compactly handled if the definitions of (38) and (39) are extended to

\[
A_n^v(\delta) = \sum_{k=0}^{\left| v \right|} \binom{\left| v \right|}{k} (-1)^{v-k} A_{n+2k}^v(\delta)
\]  

(38')

\[
B_n^v(\alpha) = \sum_{k=0}^{\left| v \right|} \binom{\left| v \right|}{k} (-1)^{v} B_{n+2k}^v(\alpha)
\]  

(39')

Then, by direct substitution of the function (6), followed by separation of variables and integration over \( \varphi \), it may be found that

\[
(i|j) = \frac{\pi R^3}{4} \delta(v_i, v_j) \left[ A_{n+2}^v(\delta) B_m^v(\alpha) - A_n^v(\delta) B_{m+2}^v(\alpha) \right]
\]  

(40)

\[
\left( i \left| \frac{\kappa}{(\xi^2 - \eta^2)} \right| j \right) = \frac{\pi R^3}{4} \delta(v_i, v_j) A_{n+1}^v(\delta) B_m^v(\alpha)
\]  

(41)

\[
\left( i \left| \frac{\eta}{(\xi^2 - \eta^2)} \right| j \right) = \frac{\pi R^3}{4} \delta(v_i, v_j) A_n^v(\delta) B_{m+1}^v(\alpha)
\]  

(42)

where \( n = n_1 + n_j, \ m = m_1 + m_j, \ \delta = \delta_1 + \delta_j, \ \alpha = \alpha_1 + \alpha_j \) and \( v = v_i = v_j \).

The kinetic energy integral is more tedious, but after some manipulation can be converted to the form

\[
\left( i - \frac{1}{2} \varphi^2 | j \right) = -\frac{1}{6} \delta(v_i, v_j) \int \, dr \left( \frac{2\rho}{R} \right)^2 |v|
\]

\[
\times \left[ \partial_i \varphi \partial_j \varphi + \partial_j \varphi \partial_i \varphi - 2\nabla \partial_i \varphi \cdot \nabla \partial_j \varphi - 4\left( \frac{\nu}{\rho} \right)^2 \partial_i \varphi \partial_j \varphi \right]
\]

where \( \partial_i \varphi = \sum \partial_i \eta_\mu \exp \left[ -(\delta_1 \xi + \alpha_1 \eta) \right] \), and after substitution of (6)
becomes
\[
(i - \frac{1}{2} \sqrt{2}) j\]
\[
= \pi R^3 \beta(v_1, v_j) \times \left[ -\frac{1}{2R^2} \right] \left\{ k'^2 A_{n+2}^v(\delta) - 2(n' + 5) A_{n+1}^v(\delta) + 2\beta' A_{n-2}^v(\delta) \right\} \frac{1}{B_m^v(\delta)}
\]
\[
+ \{n'^2 + n - 2, m'^2 - m - 2\} A_{n}^v(\delta) B_m^v(\delta) - 4v^2 \{ n'^2 + n - 2, m'^2 - m - 2 \}
\]
\[
\{ \frac{1}{B_m^v(\delta)} - (\alpha' + m') B_m^v(\delta) + 2(\alpha' m' + \alpha) B_m^v(\delta) \}
\]
\[
\{ B_m^v(\delta) \}
\]
where \( n' = n_1 - n_j, m' = m_1 - m_j, \delta' = \delta_1 - \delta_j, \) and \( \alpha' = \alpha_1 - \alpha_j. \)

The coefficients of \( A_n^v(\delta) \) and \( B_m^v(\delta) \) vanish when negative indices would be required, and correct results are obtained when these undefined values of \( A_n^v \) and \( B_m^v \) are assumed to be zero.

The symmetrized orbitals \((6')\) are easily included by noting that
\[
\left( i_{\beta, \nu} \right| 0 \right| j_{\beta', \nu'} \right) = (i \left| 0 \right| j) + (-1)^{(k_1 + k_2 (i \left| 0 \right| j') + (-1)^{(k_1 + k_2 (i' \left| 0 \right| j)} + (-1)^{(k_1 (i' \left| 0 \right| j)}
\]
where \( i' \) is the function \( \delta_1, \delta_2; \nu, \mu, \nu'. \) It is clear that
\[
B_m^v(-\alpha) = (-1)^m B_m^v(\alpha)
\]
therefore it is possible by collecting terms to define the auxiliary integral
\[
B_m^v(\alpha, \alpha') = 2\delta \left[ 0, m+k_1, k_2 (\mod 2) \right] \left\{ B_m^v(\alpha) + (-1)^k B_m^v(\alpha') \right\}
\]
and since in each of the integrals (40-43) all terms involving \( m \) are of the same parity, the Kronecker delta function can be factored out, leaving the integrals in exactly the same form, except using
rather than $B_m(\alpha')$. This method is not unique, but it has the advantages that it requires less memory storage, and reduces the amount of actual computation by about one-third.

The $A_n(\delta)$ are obtained by the recursion formula

$$A_n(\delta) = A_0(\delta) + \frac{n}{6} A_{n-1}(\delta)$$

with $A_0(\delta) = \frac{1}{6} e^{-\delta}$. The $B_m(\alpha)$ could also be generated recursively, using the formula (Kotani, 1963)

$$B_m(\alpha) = \frac{1}{\alpha} \left\{ (-1)^m e^{\alpha} - e^{-\alpha} + nB_{n-1}(\alpha) \right\}$$

but Corbato (1956) has developed a method which does not involve subtraction of terms of similar magnitude and therefore is more accurate. The $B_m$ are calculated in conjunction with related functions used in the two-electron integrals.

Because all the orbitals in this problem are of a single parametric form, there is but one type of 2-electron integral in our work, rather than the usual plethora of hybrid, coulomb, exchange, and one-center integrals. To evaluate the 2-electron integral $(i|j|1/r|k\ell)$, we use Neumann's expansion (1878) of $1/r_{12}$,

$$\frac{R}{2r_{12}} = \sum_{\mu=0}^{\infty} \sum_{\sigma=\pm \mu} (-1)^{\sigma} (2\mu + 1) \left[ \frac{(\sigma)}{(\mu+\sigma)} \right]^2$$

$$\times P_{\mu} \frac{|\sigma|}{(\xi_\mu)} Q_{\mu} \frac{|\sigma|}{(\xi_\mu^+)} P_{\mu} \frac{|\sigma|}{(\eta_\mu)} P_{\mu} \frac{|\sigma|}{(\eta_\mu^+)} \exp \left[ i\sigma (\varphi_1 - \varphi_2) \right]$$

where $\xi_\mu$ and $\xi_\mu^+$ mean the larger, and smaller, respectively, of
\( \xi_1 \) and \( \xi_2 \). \( P_\mu^{(\sigma)} \) and \( Q_\mu^{(\sigma)} \) are associated Legendre functions.

On substituting Eq. (45), and introducing the wave functions, Eq. (6), we perform first the integrations over \( \varphi_1 \) and \( \varphi_2 \). If we let

\[
\nu_\kappa - \nu_i = \sigma_1 , \quad \nu_\ell = \nu_j = \sigma_2 \tag{46}
\]

the \( \varphi \) dependence of the integral is \( \exp i(\sigma_1 + \sigma) \varphi_1 + i(\sigma_2 - \sigma) \varphi_2 \), so the integral vanishes unless

\[
\sigma_1 + \sigma_2 = 0 , \tag{47a}
\]

in that case the sum over \( \sigma \) collapses to the single value (or its negative)

\[
\sigma = |\sigma_1| = |\sigma_2| . \tag{47b}
\]

Henceforth we shall use \( \sigma \) to mean the value given by Eqs. (47a)-(47b).

The \( \varphi \) integrations then cause the removal of the \( \sigma \) summation, and the change of the lower limit of the \( \mu \) summation to \( \sigma \), while contributing to \( (ij|1 \, r|k\ell) \) a factor \( 4\pi^2 \delta(\sigma_1, -\sigma_2) \).

We next consider the factors involving \( (\xi^2 - 1) \) and \( (1 - \eta^2) \). When the contributions from all four wave functions are collected, we have

\[
\left[ \xi_1^2 (1 - \eta_1^2) \right]^{1/2} |v_i| \frac{1}{2} |v_i| |v_j| \left[ \xi_2^2 (1 - \eta_2^2) \right]^{1/2} |v_j| \frac{1}{2} |v_j| .
\]

When we do the \( \xi \) and \( \eta \) integrations, we will find it convenient to write this as

\[
\left[ \xi_1^2 (1 - \eta_1^2) \right]^{1/2} |v_i| + \left[ \xi_2^2 (1 - \eta_2^2) \right]^{1/2} |v_j| ,
\]
since the $1/2\sigma$ power can be naturally associated with the Legendre functions. In general, the $\tau$ value to be associated with any two orbitals, say $\phi_u$ and $\phi_v$, will be $\tau = 1/2(|v_u|+|v_v|-|v_u-v_v|)$, and in particular

$$\tau_1 = \frac{1}{2} \left( |v_1|+|v_k|-\sigma \right)$$

$$\tau_2 = \frac{1}{2} \left( |v_j|+|v_\ell|-\sigma \right).$$

Note that these definitions imply that $\tau$ is a positive integer or zero.

We are now prepared to consider the integrations over $\xi_1$ and $\xi_2$. It is evident that the integrand cannot be factored to separate the coordinates $(\xi_1, \eta_1)$ from $(\xi_2, \eta_2)$ because of the presence of the Legendre functions involving $\xi_+$ and $\xi_-$. This situation can be alleviated somewhat by using a slight generalization of a formula published by Ruedenberg (1951). The formula we need can be expressed as

$$(-1)^\sigma(2\mu + 1) \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 P_\mu^{(\xi_+)}Q_\mu^{(\xi_-)}g_\mu^{1(\xi_1)}g_\mu^{2(\xi_2)} = \int_1^\infty dX G_\mu^{1(\xi)}G_\mu^{2(\xi)}$$

where $g^{\gamma}_\mu(\xi)$ and $G^{\gamma}_\mu(x)$, $\gamma = 1$ and 2, are related by

$$G^{\gamma}_\mu(x) = \left\{(2\mu + 1)[(\mu + \sigma)!/(\mu - \sigma)!]\right\}^{1/3} \times \left[ P_\mu^{\sigma}(x)(x^2 - 1)^{1/2} \right]^{-1} \int_1^x d\xi P_\mu^{\sigma}(\xi)g^{\gamma}_\mu(\xi).$$
This transformation may be applied whenever all the operations indicated are meaningful. The exponential dependence of the wave functions is sufficient to guarantee the utility of Eqs. (49) and (50).

Summing both sides of Eq. (49) from \( \mu = \sigma \) to \( \infty \), we have, with suitable definition of \( g_\mu^\gamma (\xi) \), an expression for \( (ij|l/r|kl) \). Examining the result of the substitution of Eqs. (45) and (6) into \( (ij|l/r|kl) \), it may be seen that

\[
g_\mu^\gamma (\xi) = \left[ \frac{(\mu - \sigma)!}{(\mu + \sigma)!} \right] \int_{-1}^{1} d\eta (\xi^2 - \eta^2) \exp (-\delta_\gamma \xi - \alpha \eta)
\]

\[
\times P_\mu^\sigma (\eta) (\xi^2 - 1)^{(\sigma/2) + \gamma} (1 - \eta^2)^{\gamma} (\sigma/2) \quad (51)
\]

Here, \( \delta_1 = \delta_i + \delta_k \), \( \delta_2 = \delta_j + \delta_l \), with corresponding definitions for \( \alpha \), \( \eta \), and \( m \). The \( \eta \) integrations appearing in Eq. (51) are all of the same general form. Define

\[
i \mu^\sigma (m, \alpha, \tau) = \left\{ (2\mu + 1) \left[ \frac{(\mu - \sigma)!}{(\mu + \sigma)!} \right] \right\}^{\frac{1}{8}}
\]

\[
\times \int_{-1}^{1} d\eta P_\mu^\sigma (\eta) \exp (-\alpha \eta) \eta^m (1 - \eta^2)^{\gamma} (\sigma/2) + \tau \quad (52)
\]

and Eq. (51) may be rewritten

\[
\left\{ (2\mu + 1) \left[ \frac{(\mu + \sigma)!}{(\mu + \sigma)!} \right] \right\}^{\frac{1}{8}} g_\mu^\gamma (\xi)
\]

\[
= \exp (-\delta_\gamma \xi) \eta^\gamma (\xi^2 - 1)^{(\sigma/2) + \gamma} \left[ \xi^2 P_\mu^\sigma (m, \alpha, \tau) - 1 \right] \quad (53)
\]

The integrals defined in Eq. (52) are related to spherical Bessel functions, and also to the \( B_n (\alpha) \). The \( B_n \) can be expressed (Corbato, 1956) in terms of the \( i \mu^\sigma \) as
where \( \sigma = 0 \), or if \( \nu \neq 0 \), since \( \sigma \) is necessarily zero for non-zero one-electron integrals, \( \nu_1 = \nu_j = \tau \), so the binomial summation of (39') can be avoided by using the relation

\[
B_n^\nu(\alpha) = \sum_{\mu=0,1}^n \frac{n! \left(\frac{2}{\mu+1}\right)^\frac{1}{2}}{(n-\mu)!!(n+\mu+1)!!} i_{\mu}(0,\alpha,\tau) .
\]

In both expressions the prime on the summation sign indicates taking only every other term such that the highest \( \mu \) value = \( n \), and the double factorial is \( n!! = n(n-2)(n-4)\ldots(2 \text{ or } 1) \).

For the symmetrized one electron orbitals, the \( i_{\mu}^\sigma(m,\alpha,\alpha',\tau) \) become

\[
i_{\mu}^\sigma(m,\alpha,\alpha',\tau) = 2\delta_{[0,\text{mod}_2(m+\kappa_1+\kappa_j+\mu-\sigma)]} i_{\mu}^\sigma(m,\alpha,\tau) + (-1)^{\kappa_3} i_{\mu}^\sigma(m,\alpha',\tau)
\]

since

\[
P^\sigma_\mu(-\eta) = (-)^{\mu-\sigma} P^\sigma_\mu(\eta) .
\]

The next step is to substitute Eq. (53) into Eq. (50), and perform the \( \xi \) integration. When doing so, it is convenient to define another set of integrals

\[
K^\sigma_\mu(n,\delta,\tau,x) = \left[ P^\sigma_\mu(x)(x^2 - 1)^{\frac{3}{2}} \right]^{-1}
\]

\[
\times \int_1^x d\xi P^\sigma_\mu(\xi) \exp(-\delta \xi) \xi^n(\xi^2 - 1)^{\sigma/2 + \tau}
\]
in terms of which Eqs. (53) and (50) yield

\[ G_{\mu}^\gamma(X) = K_{\mu}^\sigma(n_{\gamma} + 2, \delta_{\gamma}, \tau_{\gamma}, X) i_{\mu}^\sigma(m_{\gamma}, \alpha_{\gamma}, \tau_{\gamma}) \]

\[ - K_{\mu}^\sigma(n_{\gamma}, \delta_{\gamma}, \tau_{\gamma}, X) i_{\mu}^\sigma(m_{\gamma} + 2, \alpha_{\gamma}, \tau_{\gamma}). \] (57)

To show more clearly the role of the wave functions in \( G_{\mu}^\gamma(X) \), we shall from now on use the notation \( (u|G_{\mu}(X)|v) \) to mean a form like \( G_{\mu}(X) \), but with \( n_{\gamma} \) replaced by \( n_u + n_v \), etc.

Recapitulating the earlier discussion in more explicit form, we obtain the result that the two-electron integral has been reduced to the form

\[ (ij|1/r|kl) = \left( \frac{\pi R^3}{4} \right)^2 \left( \frac{2}{R} \right)^2 \delta(\sigma_1, -\sigma_2) \int_1^\infty dX \sum_{\mu=\sigma}^\infty (i|G_{\mu}(x)|k)(j|G_{\mu}(x)|l). \] (58)

The integral over \( X \) in Eq. (58) is now to be evaluated numerically.

Using values of the integrand at points \( x_\kappa \), the integral can be written

\[ (ij|1/r|kl) = \left( \frac{\pi R^3}{4} \right)^2 \left( \frac{2}{R} \right)^2 \delta(\sigma_1, -\sigma_2) \sum_{\mu=\sigma}^\infty (i|G_{\mu}(x_\kappa)|k)(j|G_{\mu}(x_\kappa)|l), \]

where \( w_\kappa \) is a weight factor. Defining

\[ (w_{\kappa})^{\frac{1}{2}} (i|G_{\mu}(x_\kappa)|j) = (i|G_{\mu}\kappa|j), \] (59)

Eq. (58) becomes

\[ (ij|1/r|kl) = \left( \frac{\pi R^3}{4} \right)^2 \left( \frac{2}{R} \right)^2 \delta(\sigma_1, -\sigma_2) \sum_{\mu=\sigma}^\infty (i|G_{\mu}\kappa|k)(j|G_{\mu}\kappa|l). \] (60)
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The number of terms one must keep in the sum over \( \mu \) may be estimated by studying the behavior of the \( K \) and \( i \) integrals, Eqs. (52) and (54). By far the most important quantities affecting the convergence of the sum are found to be \( |\alpha_1| \) and \( |\alpha_2| \), larger values of which correspond to slower convergence. In fact, for \( \alpha = 0 \) the series reduces to a finite number of terms. Since the speed of computation depends on the number of terms, we actually compute a number chosen for each integral after examining its \( |\alpha_1| \) and \( |\alpha_2| \). As a rough indication, we use an average of 13 terms for \( |\alpha| = 10 \), and 19 terms for the maximum value, \( |\alpha| = 19.9 \).

Details of the calculation of the integrals \( i_\mu^q(m,\alpha,\tau) \) and \( K_\mu^q(n,\delta,\tau,x) \) can be found in Appendices II and III of the Harris work (1960).

Parameter Variation Scheme

The trial wave function can be improved both by selection of the best set of linear coefficients through diagonalization of the secular equation, and by minimization of the energy with respect to the non-linear parameters \( \delta_i \) and \( \alpha_i \), \( i = 1,2, \ldots N \). In this discussion, the word energy signifies the total electronic energy of the desired root of the secular equation.

In the earlier modifications of the diatomic program, a pure network search was used, because there was no way of knowing at that time whether more sophisticated searching routines would get trapped in false minima.
An analysis of the energy dependence on the non-linear parameters has now become possible since large numbers of calculations on many types of systems have been performed using the stepwise search.

Several representative calculations have been analyzed, including ground states, excited states, heteronuclear and homonuclear molecules, atoms, and resonant states. Some definite features were observed, leading to the following conclusions:

1. In true bound states of atoms or molecules, both ground and excited, the dependence of the energy on the non-linear parameters is smooth. No false or pseudo-minima were found in any of the extensive number of calculations checked.

2. The energy is considerably more sensitive to the choice of the $\delta$ parameter for a given orbital than the choice of the $\alpha$ of the same orbital.

3. The parameters of the orbitals, if originally chosen in a "reasonable" fashion (not such that the maximum density of a $\sigma_2s$ lies inside the maximum density of a $\sigma_1s$, for example), are relatively independent of each other.

4. Resonant states exhibited false minima in the $\delta$ parameter of the added electron (outermost orbital), and the $\alpha$ dependence was nearly flat. The energy is particularly sensitive to very small variations of $\delta$ in the region nearest the minimum.
Thus it is now possible to use a more sophisticated parameter searching routine, as long as some option is retained to avoid the false minima in resonances (or other false minima if they are suspected).

Consider the case of a set of parameters chosen so that the energy is near the minimum value attainable with the trial function being used. Let \( x_i \) represent the non-linear parameters, either \( \delta_i \) or \( \alpha_i \), \( E_0 \) = the energy calculated with the set \( x_i \), and \( y_i \) the set of increments \( (x_i - a_i) \). The energy can be expanded as

\[
E_x = E_0 + \sum_i \left( \frac{\partial E_0}{\partial x_i} \right)_0 y_i + \frac{1}{2} \sum_i \sum_j \left( \frac{\partial^2 E_0}{\partial x_i \partial x_j} \right)_0 y_i y_j + \ldots \quad (61)
\]

and the minimum will be attained if

\[
\frac{\partial E}{\partial x_i} = 0 \quad (62)
\]

Dropping all terms of order greater than two in the expansion and substituting the minimization condition, we obtain the set of equations

\[
\left( \frac{\partial E}{\partial x_i} \right) + \sum_j \left( \frac{\partial^2 E}{dx_i dx_j} \right) y_i = 0 \quad (63)
\]

which can be solved for the revised set of parameters if \( 1/2(n+2)(n+1) \) calculations of the energy are done (\( n \) is the number of parameters in the set \( x_i \)). This can be seen to be the equivalent of assuming the energy dependence on each parameter to be a parabola, and finding the minimum of the set of parabolae which are linked by the cross terms.
$x_i x_j (i = j)$. Ransil (1960) applied a similar procedure to diatomic molecule calculations and found that if the parameters were nearly independent, this method converged in three to five passes through the set of $\frac{1}{2}(n+2)(n+1)$ energy calculations, using the new $\bar{y}_i$ to determine a revised $E_o$.

However, if the parameters are independent, or nearly so, the effect of the cross terms should be negligible, and an equivalent result should be obtained if each of the parameters $\bar{x}_i$ were fitted to a parabola holding the other parameters fixed, and the set $\bar{x}_i$ stepped through one by one. This requires only $3n$ energy calculations per pass through the set $\bar{x}_i$, and as there are two non-linear parameters per orbital, produces a nice reduction in the amount of work necessary to minimize the energy with respect to the non-linear parameters if there are two or more orbitals.

This process, with a slight modification to be described below, is the one used in the present diatomic program. It also converges quite rapidly, with two passes normally minimizing the energy to five or six figures.

The actual scheme works slightly differently for variation of $\bar{\delta}_i$ and of $\bar{\alpha}_i$. Since the initial set of $\delta$ parameters may be quite far from the optimum set, each parameter is stepped with a large step size in the forward or backward direction until there exists an $E_i(\delta_i)$ which is less than both $E_{i-1}(\delta_{i-1})$ and $E_{i+1}(\delta_{i+1})$, where $i$ indexes the number of the calculation. If the energy continues to improve in a certain direction, the step size is increased to hasten finding
the \( \delta_{i+1} \) which causes the energy to turn back upwards. The optimum parameter \( \delta \) is then determined by fitting to the parabola passing through the lowest three points \( E_i, E_{i+1}, \) and \( E_{i-1} \). In this process, more than three energy calculations may be required before fitting, but it has the advantage that the first pass through the \( \delta \) set always produces a revised \( E_o \) which is quite close to the true minimum of the functional.

Since the \( \alpha \) dependence is more flat, the search procedure for the first pass through the \( \alpha \) parameters only makes three calculations per \( \alpha \), at the values \( \alpha_0, 1/2 \alpha_0, \) and \( 3/2 \alpha_0 \). On subsequent passes through the \( \alpha \) set, the method is the same as for \( \delta \).

After one complete pass through all the \( \delta \) and \( \alpha \) which are to be optimized, the step size is reduced to one-third the starting value and the process is repeated.

In the case of resonances, a stepwise search over the parameters of the outermost electron is still necessary in order to avoid becoming trapped in a pseudo-minimum. This option is included in the program by setting a tag which both demands a stepwise search in the forward direction, and determines the number of steps to be taken. As in the previous modifications of the program, the programmer-user must apply his experience and physical intuition to determine the magnitude of the step size and the number of steps which will locate the parameter near the true minimum without becoming trapped. After each of the designated outer orbital parameters has been linearly searched by this method, the optimum set of stepwise parameters is
re-minimized by the parabola search method.

In all of the above procedures, the search may be terminated externally by setting of a sense switch. In the parabolic search, variation of a particular parameter is eliminated in subsequent passes if the program determines that the energy is relatively independent of it. This can also be done externally by proper preparation of the input cards.

If the program is not terminated externally, it proceeds automatically through the list of parameters to be varied, reducing the step size after each pass until it is lower than a preset threshold step size. At this time, a final calculation is made with the optimum set of parameters and the search for the problem is terminated.

In this modification of the program, it is also possible to treat the internuclear distance $R$ as a parameter, in that after completion of a parameter search at one $R$ value, $R$ can be incremented or decremented and the problem restarted. In this case, the non-linear parameters are scaled by $R_{\text{new}}/R_{\text{old}}$ and the $\bar{\alpha}$ search assumes that it has already made one pass.

Thus, if computer time is available, it is possible to calculate the entire potential curve for a particular molecule in one run, stepping through $R$ and minimizing the energy in terms of the non-linear parameters at each desired $R$ value.
APPENDIX II. DETAILS OF THE DIATOMIC MOLECULE PROGRAM

AND INSTRUCTIONS FOR ITS USE

Overall Logic

General Comments

The diatomic molecule program as written is designed for a 32,768 word high-speed computer with at least four peripheral storage units (tape or disc). It is in the FORTRAN IV language, with no machine language programs, in order that maximum machine-to-machine compatibility be achieved. To the same end, no advantage has been taken of special features of some machines, such as reading tapes backward, multiple entries to subroutines, availability of additional peripheral equipment, etc. Variable dimension statements and logical IF statements have been used.

A rather extensive list of options has been included, in order to do the most general diatomic molecule problem without changing the program internally, and still allow some special treatment of specific problems.

The program is designed to calculate the energy and electronic wavefunction of heteronuclear or homonuclear diatomics. In the homonuclear case, gerade or ungerade symmetry can be achieved either through the use of symmetry adapted one-electron orbitals, or by an
option of reflecting the entire molecular function through the inversion center and taking the proper linear combination of the original and inverted functions.

The spin portions are set to handle the complete open-shell (different orbitals for different spins) problem automatically for up to a 28 x 28 set of representation matrices, which includes the full, eight electron case. By a change in the input deck, up to twenty electrons may be handled with partially or completely closed shells. The spin routines are also arranged so that advantage can be taken of the reduction in numbers of permutations which can be introduced through spatial orthogonalities, by never generating those permutations which would make no contribution to the secular equation.

The one-electron spatial functions are two-centered elliptical orbitals. A transformation routine is included which allows linear combinations of these functions prior to diagonalization, so that both fixed and variable linear coefficients are possible. Space is available for up to sixteen functions and a 16 x 16 transformation matrix.

Non-linear parameter search options include a combination network-gradient search and a pure stepwise network search, with the ability to vary one function independently, or two functions simultaneously. Through appropriate tagging, one, both, or neither of the two non-linear parameters of a particular function may be varied, and the search routine has the ability to set these tags internally if the energy is found to be relatively independent of the parameter being varied.
null
Through the use of sense switches, the programmer may also externally terminate the search, skipping immediately to the final output routine with the best set of parameters achieved up to that time.

The internuclear distance may also be varied, with a new calculation of the electronic wave function, including non-linear parameter variation at each R value.

Thus the program presented here is a compromise among generality, speed, efficiency, and size. For selected specific types of problem, some of the options may be removed if desired for further optimization of these factors.

Block Structure

The logic flow of the program is divided into five main branches, which are handled by an input and controlling main program. The function of each of these branches is as follows:

Branch 1 - SETUP Branch

Reads auxiliary tape identifiers, loads permanent data tables for integral calculations, makes spin-permutation tape. Re-entered only if spin problem is changed. All output from this branch is labeled COMMON blocks or on tape (disc).

Branch 2 - INTEGRAL Branch

Controls calculation of all one- and two-electron spatial integrals. Makes integral table tape of indices, parameters, one-electron integrals, and $G_{i,k}(x,\mu)$. Combines all $G_{i,k}$
with $G_{jl}$ to make tape of all two-electron integrals. Upon exit, all one- and two-electron integrals are on tape for subsequent iterations, and in fast memory for combining with spin.

Branch 3 - MATRIX Branch
Applies transformation to spatial integrals if required. Combines spatial integrals with spin matrices from tape to make total secular equation. In homonuclear case with total molecular inversion option, secular equation is block diagonalized in this branch.

Branch 4 - SEARCH Branch
Solves secular equation. Varies non-linear parameters as desired, prints intermediate output. If parameter search not completed, return to INTEGRAL branch, otherwise proceed to OUTPUT branch.

Branch 5 - OUTPUT Branch
Prints final output, including total secular equation, eigenvalues, eigenvectors, converted energies and spatial configurations. If program was cut externally by sense switch, punches new input deck for convenient restart.

Control of Storage and Internal Overlays

Of prime importance is the control of the working space inside fast memory. In the various branches, and inside the branches, data is overlaid when it is no longer needed. In order to prevent destroying information which will be required later in the calculation,
an understanding of the places and times that these overlays occur is mandatory if modifications are to be introduced, if it is desired to use certain routines as "black boxes" for entirely different calculations, or if the program is to be updated.

To facilitate bookkeeping, all fast storage is in four labeled COMMON blocks. A description of the contents of these blocks and the overlays which occur in them follows.

/SFACE/ - 309 words. Contains most problem definition data as described in input deck summary below, plus

ITX - iteration counter. 1-first pass; 2-intermediate passes; 3-final pass

FPARØ - best set of non-linear parameters, stored from FPAR as determined

EØ - best energy, corresponding to calculation with FPARØ

NO - tag for parameter being searched. 1-delta; 2-alpha

MO - function number of parameter being searched, i.e., search over FPAR(NO,MO)

ICTAG - 64 locations available for additional tags as desired.

Data in this block is generally permanent, with the only overlays being resetting of tags, changing parameters, etc.


/CIJ/ - 268 words. Transformation matrix and tags. Matrix is recalculated if NOTRF > Ø, but not overlaid by other data.
/WORK/ - 12,518 words. Main working area. Overlaid by all branches as follows:

1. **SETUP** - overlays controlled by subroutine SPIN. Used to contain all information for generation of spin tape. Completely destroyed upon exit from spin routine.

2. **INTEGRAL** - during making of one-electron tapes and combination to make two-electron tape, /WORK/ is composed of two arrays JTA and JTB, dimensioned 146x4, and the one-electron integrals S1 and H1, singly dimensioned at 136 words each. S1 and H1 are stored as calculated. The two-electron tape is read upon completion, storing the H2 integrals over JTA and JTB. Array JTB is used as temporary storage by the integral routines ONEL, BANDI, and GLIST. 289 locations available in array named DUMBO.

3. **MATRIX** - at entry, contains H2 (9317), SPRI, HPRI (S1, H1 of INTEGRAL branch), transformed one-electron sets renamed S1,H1, one 28x28 spin matrix, one permutation, and room for the total S,H stored triangularly (1866 words). At exit, H2 is overlaid by the total secular equation OVP, HAM which is S,H unpacked and stored as full two dimensioned arrays. Array named DOM has 19 locations available.

4. **SEARCH** - six 42x42 matrices for secular equation and eigenvectors, including two copies of secular equation, one for printing if desired, and one which is destroyed during diagonalization. Several vectors dimensioned 42 for
eigenvalues, etc. Array named FINK has 176\ell locations available.

5. OUTPUT - essentially same as SEARCH, except FINK contains only 1672 locations.

Limitations

The following limitations must be observed to prevent premature termination of the calculation by built-in error checks:

- Maximum number of one-electron functions: 16
- Maximum number of electrons in IPER: 20
- Maximum number of spin eigenfunctions $\theta$: 28
- Maximum number of spin functions $\Omega$: --
- Maximum dimension of secular equation: 42
- Largest $n_i, m_i$: 4
- Largest $\alpha_i$: 19.9
- Smallest $\delta_i$: .01

Error Messages

Error messages may occur during calculation if the internal checks are positive. Some of these errors will not cause premature termination of the program, and others will. The following is a summary of these error messages, their causes, and the action taken by the program:

1. WRONG PERM TAPE xxxxxx xxxxxx

The identification tag on the spin-permutation tape does not agree with the tag required by the formula
JCODE = 1000*N + 10*10SH + MULT

calculated when the problem is defined. This can be due to
a mis-positioned tape or to having mounted the wrong tape.
The program repositions the tape and either continues or
exits, depending on the condition of a recheck. The first
number in the message is the desired number, and the second
is the number read from the tape.

2. SEC EQN TOO BIG    xxxx

The dimension of the secular equation requested by the input
parameters (NCONXND) is larger than 42.

3. INDICES DONT CHECK   xx xx xx xx xx xx

Subroutine INTEG has detected that the indices on tape KR
and the indices in the integral calculation loop do not
correspond. The indices LI, I and J are printed in pairs
with the supposed LI, I, and J read from tape KR.

4. BANDI - NO CONVERGE

The \( \mu \) summation of Eq. (60) did not converge in 36 terms
or less.

5. BANDI - PARAMS OUT   xx xx xx xx

One or more parameters are out of range. The four numbers
printed are \( t, m, |\sigma|, \) and \( M \), where \( t, m, \) and \( |\sigma| \) are defined
in Appendix I and \( M = 28 + |\alpha|/1.95 \), which defines a dimension
and cannot exceed 60.

6. GLIST - GENERAL ERR

Self-explanatory
7. GLIST - PARAMS OUT  xxxxxx  xx  xx

Parameters out of range in subroutine GLIST. The three numbers are 5, n, and \( IM = 14 + n + 2\tau + 2 \), where 5 and n are explained in Appendix I, and \( IM \) is a calculated dimension which cannot exceed 45.

8. ENERGY.LT.MIN

The calculated energy is lower than the experimental or test energy punched on the title card. An exit is made to the OUTPUT branch, after which a new calculation may be started if more input cards are present.

9. GR.SRCH SEEKS MAX

The gradient or parabola search is seeking a maximum rather than a minimum. This is an information message only.

10. END SRCH OF FCN  xx  xx

The energy has been found to be independent of a particular parameter, and the tag has been set to discontinue the search of this parameter. Its indices are printed for information.

11. OVRIAP NOT POS DEF  xxxxxx  xx  xx

The overlap matrix is not positive definite. If it is positive semi-definite, this is an information message only. If the magnitude of the negative diagonal element is less than \( 10^{-7} \), the program assumes that the matrix is numerically positive semi-definite, deletes the row and column corresponding to this element in both the S and H matrices, and
continues. This results in an eigenvalue of $10^{26}$ which can easily be seen. If the negative diagonal element is greater than $10^{-7}$ in magnitude, the program makes an error exit.

Specific Programs and Subroutines

A short summary of the programs follows. Those routines which are marked by asterisks are discussed in detail below the summary. The logic of the unmarked routines can be followed without difficulty in the program listings themselves.

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</tbody>
</table>

*TABLE - FIXES PERMANENT DATA BLOCK, POINTS, WEIGHTS, ETC.* Subroutine TABLE generates $D_1$, $DD_1$, and $DD_2$ for BANDI and GLIST. Their definitions are:

\[
D_{1,ij} = (i-1)! (2j-1)/[(i-j)! (i+j-1)!] \tag{64}
\]

\[
DD_{1,ij} = [(i+j-2)! (2i-1)/(i-j)!]^{1/2} \tag{65}
\]

and

\[
DD_2_{1,ij} = [(i+j-1)(i-j+1)/(4i^2-1)] , \tag{66}
\]

and they are calculated recursively.

The numerical quadrature points and weights are read in this routine. They are read as data rather than loaded as a permanent
BLOCK DATA Subroutine to allow the use of several different quadrature formulae, with different numbers of points. Space is available for up to a forty point integration rule. The integral limits $(1, \infty)$ are transformed to $(0,1)$, so the points are in increments of $1/x$ and the weights are

$$w_k = x_i w_i^2 / (x_i^2 - 1)^{1/2}$$

(67)

where

- $w_k$ is the value punched on the input cards, $WT(K)$
- $x_i$ is the $i^{th}$ point in POINT
- $w_i$ is the tabulated weight from the numerical quadrature rule.

Card decks have been prepared and are available for the original 34-point Newton-Cotes formula used by Harris and Taylor (1963, etc.), and for 16, 20, 24, and 32 point Gaussian formulae. Table 9 gives a comparison of two-electron integrals for various $\delta$ values using these formulae. The 34-point formula should be used in any check calculations which attempt to duplicate the results of the old Taylor-Harris or Taylor calculations.

*SPIN - PREPARES TAPE OF SPIN-PERMUATION MATRICES. Subroutine SPIN applies the methods described in Appendix I, (84 ff.) to generate the permutations IPER, and their $ND \times ND$ representation matrices UMAT(I,J). A given permutation (read or calculated) is applied to the spin product functions ISP, and an ordering vector ISSPM is created such that if the permutation is denoted by $P$, and $P$ on $ISP(I)$ yields $ISP(K)$, then $ISSPM(K) = I$. Using this ordering vector,
TABLE 9

COMPARISON OF ANALYTIC AND NUMERICAL
TWO-ELECTRON INTEGRALS

<table>
<thead>
<tr>
<th>( s )</th>
<th>Analytic</th>
<th>32 Pt Gaussian</th>
<th>24 Pt Gaussian</th>
<th>20 Pt G</th>
<th>16 Pt G</th>
<th>34 Pt Newton-Cotes</th>
</tr>
</thead>
<tbody>
<tr>
<td>.005</td>
<td>( 3.12496 \times 10^{-2} )</td>
<td>( 3.37119 \times 10^{-2} )</td>
<td>( 3.382192 \times 10^{-2} )</td>
<td>( 2.73463 \times 10^{-2} )</td>
<td>( 1.16467 \times 10^{-2} )</td>
<td>( 1.114793 \times 10^{-1} )</td>
</tr>
<tr>
<td>.010</td>
<td>( 6.24967 \times 10^{-2} )</td>
<td>( 5.91432 \times 10^{-2} )</td>
<td>( 6.69905 \times 10^{-2} )</td>
<td>( 7.82367 \times 10^{-2} )</td>
<td>( 7.21512 \times 10^{-2} )</td>
<td>( 1.14921 \times 10^{-1} )</td>
</tr>
<tr>
<td>.02</td>
<td>( 1.24973 \times 10^{-1} )</td>
<td>( 1.26405 \times 10^{-1} )</td>
<td>( 1.20132 \times 10^{-1} )</td>
<td>( 1.19074 \times 10^{-1} )</td>
<td>( 1.140510 \times 10^{-1} )</td>
<td>( 1.18887 \times 10^{-1} )</td>
</tr>
<tr>
<td>.04</td>
<td>( 2.49787 \times 10^{-1} )</td>
<td>( 2.49477 \times 10^{-1} )</td>
<td>( 2.51654 \times 10^{-1} )</td>
<td>( 2.51091 \times 10^{-1} )</td>
<td>( 2.37301 \times 10^{-1} )</td>
<td>( 1.81768 \times 10^{-1} )</td>
</tr>
<tr>
<td>.08</td>
<td>( 4.98302 \times 10^{-1} )</td>
<td>( 4.98276 \times 10^{-1} )</td>
<td>( 4.98209 \times 10^{-1} )</td>
<td>( 4.97302 \times 10^{-1} )</td>
<td>( 5.03481 \times 10^{-1} )</td>
<td>( 5.05149 \times 10^{-1} )</td>
</tr>
<tr>
<td>.16</td>
<td>( 9.86616 \times 10^{-1} )</td>
<td>( 9.86615 \times 10^{-1} )</td>
<td>( 9.86571 \times 10^{-1} )</td>
<td>( 9.86810 \times 10^{-1} )</td>
<td>( 9.85717 \times 10^{-1} )</td>
<td>( 9.96227 \times 10^{-1} )</td>
</tr>
<tr>
<td>.25</td>
<td>( 1.51281 )</td>
<td>( 1.51281 )</td>
<td>( 1.51282 )</td>
<td>( 1.51278 )</td>
<td>( 1.51306 )</td>
<td>( 1.50251 \times 10^{-1} )</td>
</tr>
<tr>
<td>.32</td>
<td>( 1.89865 )</td>
<td>( 1.89865 )</td>
<td>( 1.89864 )</td>
<td>( 1.89866 )</td>
<td>( 1.89852 )</td>
<td>( 1.89674 )</td>
</tr>
<tr>
<td>.5</td>
<td>( 2.77261 )</td>
<td>( 2.77261 )</td>
<td>( 2.77261 )</td>
<td>( 2.77260 )</td>
<td>( 2.77254 )</td>
<td>( 2.77393 )</td>
</tr>
<tr>
<td>.75</td>
<td>( 3.67753 )</td>
<td>( 3.67753 )</td>
<td>( 3.67753 )</td>
<td>( 3.67753 )</td>
<td>( 3.67738 )</td>
<td>( 3.67721 )</td>
</tr>
<tr>
<td>1.0</td>
<td>( 4.25974 )</td>
<td>( 4.25974 )</td>
<td>( 4.25974 )</td>
<td>( 4.25974 )</td>
<td>( 4.25974 )</td>
<td>---</td>
</tr>
<tr>
<td>1.5</td>
<td>( 4.79705 )</td>
<td>( 4.79705 )</td>
<td>( 4.79705 )</td>
<td>( 4.79705 )</td>
<td>( 4.79686 )</td>
<td>---</td>
</tr>
</tbody>
</table>
\[ \text{UMAT}(I,L) = \left[ \sum_{J=1}^{NISP} \text{USET}(I,J) \cdot \text{USET}(L,K) \right] \cdot \text{SIG} \]

where \( \text{USET} \) is the spin eigenvector matrix, \( K = \text{ISSPM}(J) \), and \( \text{SIG} = \pm 1 \), the parity of the permutation \( P \).

**CONFIG - READS CONFIGURATION TABLES INTO LCON.** Subroutine CONFIG is simply a reading routine using variable dimension statements which allows maximum use of the 150 words allocated for the configuration table LCON. LCON is dimensioned as an \( NCON \times N \) matrix rather than with fixed dimensions, so that 75 two-electron, 50 three-electron, etc. configurations are possible. CONFIG reads, prints, or punches LCON in this type of storage. Note, however, that the maximum dimension of the total secular equation is \( 42 \times 42 \), and that \( NCON \times N \) may not exceed this limit.

**INTEG - CONTROLS PRODUCTION OF ALL SPATIAL INTEGRALS.** The second major branch is controlled by subroutine INTEG, which handles the calculation of all spatial integrals. This is done in two steps, the first being the calculation of the one-electron integrals \( S_{ij} \), \( H_{ij} \), and \( G_{ij} \) for all \( i \) and \( J \) \((i \geq j)\), and second, taking all possible combinations of \( G_{ij} \) with \( G_{i'j'} \), to make the two-electron integrals.

To save storage space, and due to the symmetry of the spatial one-electron matrix elements, the \( S_{ij} \) and \( H_{ij} \) sets are stored as vectors containing only the \( l \cdot n(n+1) \) elements of the lower triangle. The \((i,j)\) element of the matrix can be looked up by

\[ \text{INDX}(I,J) = \text{MIN}(I,J) + [(\text{MAX}(I,J) \cdot (\text{MAX}(I,J) - 1))/2] \]

where \( \text{MIN}(I,J) \) is the lesser of \( i \) and \( j \), and \( \text{MAX}(I,J) \) the greater.
By the same token, a double application of this method allows storage of the two-electron integrals in a single vector H2, containing \( \frac{1}{2} m (m+1) \) elements where \( m=\frac{1}{2} n (n+1) \). In this case, the \( \tau \) integrations are done later.

A single \((i,j)\) integral table requires 1460 words — 19 words for indices, parameters, and one-electron integrals, and the \((40\times36)\)
\( G_{ij}(x,\mu) \) matrix (also treated as a one-dimensional vector by INTEG — unpacked only in GLIST and TWOEL).

For optimization of input-output time, since these tables (named JTA, JTB, or ZGl in the routine) must be stored on tape or disc, they are generated in blocks of four, and written on tape KW each time four sets have been completed. One to three blank tables may be written in the last block of four in order to make the total number of tables a multiple of four. If a previous integral tape KR exists (i.e., second and subsequent passes of parameter variation scheme), the pertinent blocks of tables are read from this tape before actual integral calculation begins.

Subroutine ONE is called for generation of each table. Upon return, the \( S_{ij} \) and \( H_{ij} \) are extracted, normalized, and stored in fast memory for subsequent branches.

The second, combination, stage of INTEG uses COMBIN and TWOEL. Every block of four tables must be combined with every other block, making ten or sixteen two-electron integrals depending upon whether a block is combined with itself or another block.
To effect this combination of $G_{1k}$ tables from the tape, the following logic is used to minimize tape-handling time, which experience has shown to be the rate-controlling step in the entire energy calculation.

Let there be NTOT blocks of four tables. The last ($NTOT^{th}$) block is still intact in fast memory. This block is combined with itself while the tape is rewound. The tape is then read forward and blocks 1, 2, 3, ..., NTOT-1, are combined with NTOT. At this point, the $NTOT^{th}$ block has been completely combined, so NTOT is reduced by one. The tape is now read backwards (actually, two BACKSPACEs followed by a read to remain in the FORTRAN IV language), combining the new $NTOT^{th}$ block with all the blocks down to block one. This process is continued back and forth dropping a block each time as it has been fully combined until all the blocks have been eliminated. For example, if there are five blocks of four tables, the logic would produce the following order of block combination:

$$55, 51, 52, 53, 54, 44, 34, 24, 14, 11, 12, 13, 33, 23, 22.$$  

Since the single index of each two-electron integral is calculated from the $i, j, k, l$ indices in the tables and written on the two-electron integral tape $KINT$ along with the integral, this peculiar order of calculation has no effect.

Upon completion of the combinations, the two-electron integrals are read into fast memory for the next branch.

*ONEL - MAKES ONE-ELECTRON INTEGRALS FROM BANDI OUTPUT.* Subroutine ONEL is called by INTEG with a particular $i$ and $j$, and a designated table of 1460 words. ONEL compares the parameters in the
table (if an old table exists) with the current set and either returns if there has been no change, or calculates a new set of one-electron integrals and G vector through calls to BANDI and GLIST.

The layout of each individual table is as follows [Greek symbols as defined in Appendix I (ff.)]:

<table>
<thead>
<tr>
<th>WORD</th>
<th>DEFINITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NLP(1) - $v_i - v_j = \sigma$</td>
</tr>
<tr>
<td>2</td>
<td>NLP(2) - $(</td>
</tr>
<tr>
<td>3</td>
<td>NLP(3) - $m_i + m_j = m$</td>
</tr>
<tr>
<td>4</td>
<td>NLP(4) - number of steps necessary for convergence of I integrals (i.e., upper limit of $\mu$ summation)</td>
</tr>
<tr>
<td>5</td>
<td>NLP(5) - $n_i + n_j = n$</td>
</tr>
<tr>
<td>6</td>
<td>NLP(6) - $m_i - m_j = m'$</td>
</tr>
<tr>
<td>7</td>
<td>NLP(7) - $n_i - n_j = n'$</td>
</tr>
<tr>
<td>8</td>
<td>NOTA(1) - I</td>
</tr>
<tr>
<td>9</td>
<td>NOTA(2) - J</td>
</tr>
<tr>
<td>10</td>
<td>EPOT - potential energy term, independent of $\Omega$</td>
</tr>
<tr>
<td>11</td>
<td>INDX - $J+I(I-1)/2$ ($J \leq I$)</td>
</tr>
<tr>
<td>12</td>
<td>Maximum length of table - $19+JMAX+(NLP)^2$</td>
</tr>
<tr>
<td>13</td>
<td>FLP(1) - $\delta_i + \delta_j = \delta$</td>
</tr>
<tr>
<td>14</td>
<td>FLP(2) - $\delta_i - \delta_j = \delta'$</td>
</tr>
<tr>
<td>15</td>
<td>FLP(3) - $\alpha_i + \alpha_j = \alpha$</td>
</tr>
<tr>
<td>16</td>
<td>FLP(4) - $\alpha_i - \alpha_j = \alpha'$</td>
</tr>
<tr>
<td>17</td>
<td>$S1(I,J)$</td>
</tr>
<tr>
<td>18</td>
<td>EKIN - kinetic energy term, independent of $\Omega$</td>
</tr>
<tr>
<td>WORD</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>19</td>
<td>GINY - point at infinity for $G_{ij}$; zero except in 34-point Newton-Cotes integration (see Harris, 1960 - Eq. 115)</td>
</tr>
<tr>
<td>20</td>
<td>$G_{ij}$ - integral table, of length $\text{JMAX} \cdot (\text{NLP}(4) -</td>
</tr>
</tbody>
</table>

*MATRX - COMBINES SPACE AND SPIN PARTS TO MAKE TOTAL SECULAR EQUATION. Subroutine MATRX calls TXFORM and TRANS to prepare the spatial one-electron integrals in final form.

The spatial integrals and the spin matrices are combined to make the secular equation

$$\sum_{P} U(P) [H(P) - ES(P)] = 0$$

storing $\underline{H}(P)$ and $\underline{S}(P)$ as row vectors of dimension $1/2 \cdot \text{NMAT} \cdot (\text{NMAT}+1)$, where $\text{NMAT}$ is $\text{NCON} \times \text{ND}$.

The routine makes one pass through the spin tape, preparing all contributions of a particular permutation matrix to each matrix element in $H$ and $S$ before reading the next set on IPER and UMAT from the tape.

The function TRX is used to look up the proper two-electron integral and apply any transformations to it, plus doing the $p$ integration. It is called with the indices $i,j,k,l$ and returns the integral $(ij|1/r_{12}|kl)$.

After the secular equation is complete, it is unpacked and stored as two full matrices, $\text{HAM}$ and $\text{OVP}$, for use by the diagonalization and search routines.

In the homonuclear case, if the full molecular inversion option has been selected, the secular equation is pretransformed at this
point into block diagonal form, with two blocks of equal size. The block corresponding to the desired symmetry (g or u) will be in the upper left, and only this block will be carried over into the next branch.

**Input Deck Setup**

The input deck is divided into three sections:

1. Points and weights for numerical quadrature (SETUP branch)
2. Spin information (SETUP branch)
3. Problem definition and electron information (MAIN branch)

Section 1 is common to all calculations in which a specific quadrature rule is desired, and is retained in memory intact throughout the entire run. Section 2 is common to all calculations involving the same number of electrons and a specific spin multiplet. It is used to produce the spin tape, which is retained until subsequent data cards redefine the spin problem. Section 3 is only common to the calculation which is immediately in progress.

One comment is necessary here. This program was designed to be compatible with any machine which accepts a FORTRAN IV language. Due to differences from system to system, all input-output statements involving tapes (common input tape, work tapes, etc.) use symbolic names. The actual numbers can be read from data cards, with one important exception. The symbolic tag of the common input tape for a particular system must be set internally. Therefore, even though this is not part of the input deck, this is included here. In the main program, the variable IN must be set to correspond to the logical tape
number for the system common input tape. (Example - for the Honeywell Automath 800/1800, IN = 2, for IBM 7094/7044 DCOS, IN = 5).

The setup for the input deck proper is as follows:

<table>
<thead>
<tr>
<th>BRANCH</th>
<th>CARD NO.</th>
<th>FORMAT</th>
<th>LIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>SETUP</td>
<td>1</td>
<td>(12I3)</td>
<td>KW, KR, NT, KINT, IOUT, NPCH</td>
</tr>
</tbody>
</table>

KW - Write tape for integral tables
KR - Read tape for integral tables
NT - Spin tape
KINT - Two electron integral tape
IOUT - Logical number of system common output tape
NPCH - Logical number of system common punch tape

SETUP 2 (6X, 2F8, E30.12, 2A6) JMAX, NMINUS, WTINF, RULE

JMAX - Number of points in quadrature formula
NMINUS - Number of points to be accumulated negatively (See WT below)
WTINF - Weight of point at infinity (= 0 for Gaussian quadratures)
RULE - Alphabetic name of quadrature formula (limited to 12 letters)

SETUP 3-12 (6X, 4E18.12) POINT

POINT - Array of quadrature points (Maximum = 40 points)

SETUP 13-22 (6X, 4E18.12) WT

WT - Array of weights corresponding to points. These contain the square root of the weight given by the quadrature formula. Since some may be negative leading to imaginary roots, only absolute values are stored, with the first MINUS weights being the negative ones.

SETUP 1 (12I3) JNT, NEL, NISP, MULT, ND, IOSH, JGEN

JNT - Tag. JNT=0, make new spin tape; JNT=1, spin tape already mounted
NEL - Number of electrons
NISP - Number of spin product functions (eigenvalues of $S_z$)
MULT - Spin multiplicity 2S+1
ND - Number of eigenfunctions of $S^2$ (= dimension of a one-configuration block of the total secular equation)
IOSH - Number of open-shell electrons (See App. I and II)
JGEN - Number of hand-generated permutations (See App. I and II)

**SETUP 2** (deck) (14I5) ISP
ISP - Spin product functions. Read as column vector of dimension NISP

**SETUP 3** (deck) (5F14.10) USET
USET - Coefficient matrix for eigenfunctions of $S^2$. Dimension ND×NISP, read as column vectors.

**SETUP 4** (deck) (F9.4,21I3) SIG,JPRI,KPRI
SIG - Parity of a hand-generated permutation
JPRI - Hand-generated permutation (Example - +1. 3 4 1 2)
KPRI - Aux. permutation with double occupancies noted
Note - if JNT = 1, card decks 2, 3, and 4 are omitted.

**MAIN 1** (8A6,3F10.6) TITLE,A1,A2,EFIN
TITLE - Run identification of 48 characters, to be printed on each output page
A1 - Atomic energy of atom 1
A2 - Atomic energy of atom 2 (A1,A2 used to calculate dissociation energy)
EFIN - Experimental energy. If $E_{\text{calc}} < E_{\text{fin}}$, the program assumes an error exists and stops. If no error test is desired, set EFIN = 0.

**MAIN 2** (7F10.4) ZA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP
ZA - Nuclear charge of atom A
ZB - Nuclear charge of atom B
RMAX - Maximum internuclear separation.
STEP3 - Maximum step size in variation of non-linear parameters
STEP2 - Minimum step size in variation of non-linear parameters
**BRANCH CARD NO. FORMAT LIST**

<table>
<thead>
<tr>
<th>RMIN - Minimum internuclear separation. If blank, only RMAX is used.</th>
<th>RSTEP - Decrement to RMAX until R ≤ RMIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAIN 3 (12I3)</td>
<td>N,NHUG,NCON,NFCN,NE,LSRCH,NOTRF,NU,KOLD,IS</td>
</tr>
</tbody>
</table>

N - Number of electrons (used as check on NEL and spin tape).

NHUG - Tag. 0 = Heteronuclear; ±1 = Homonuclear with symmetrized orbitals; ±2 = Homonuclear with inversion of total molecule; > 0 = gerade, < 0 = ungerade.

NCON - Number of spatial configurations

NFCN - Number of spatial functions

NPC - Number of functions whose parameters are to be varied. For single calculation, set = 0.

NE - Eigenvalue to be minimized. 0 = ground state, 1 = 1st excited state, etc.

LSRCH - Search tag. 0 = standard step and gradient search. > 0 = linear search of LSRCH steps in positive direction.

NOTRF - Spatial transformation tag. < 0, read C. from cards; = 0, no transformation; = 1, project out first NU functions from specified orbitals; = 2, orthonormalize all spatial functions.

NU - See NOTRF. If NOTRF = 0, NU can be used to start parameter search in NU + 1st spatial function.

KOLD - Variation tag. = 0, vary each spatial function independently; = 1, vary i and i + NFCN/2 simultaneously.

IS - Search tag. 0 = search α as 3/2 α, 1/2 α, > 2 search α as 5. (Special note: if an old integral tape KR exists, IS = 2 will set ITX = 2. This provides a convenient restart if the last KW tape has been saved.)

**MAIN 4(deck) (I$,2F10.6,6I3) I,FPAR(1,I),FPAR(2,I),(NFPAR(J,I), J=1,6)**

Spatial function cards

I - Function number

FPAR(1,I) - δ_i

FPAR(2,I) - α_i

NFPAR(1,I) - n_i
<table>
<thead>
<tr>
<th>BRANCH</th>
<th>CARD NO.</th>
<th>FORMAT</th>
<th>LIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPAR(2,I)</td>
<td>m&lt;sub&gt;i&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NFPAR(3,I)</td>
<td>v&lt;sub&gt;i&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NFPAR(4,I)</td>
<td>Parity of symmetrized orbital 0 = gerade, + 1 = ungerade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NFPAR(5,I)</td>
<td>Projection tag. = 0 - no projection; = 1, project out 1&lt;sup&gt;st&lt;/sup&gt; NU functions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NFPAR(6,I)</td>
<td>Variation tag. = 0, search both ( \delta ) and ( \alpha ); = 1, search ( \alpha ) only; = 2, search ( \delta ) only; = 3, no search of this function</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**MAIN 5(deck)**

\[(12I3) \quad I, (LCON(I,J), J=1,N)\]

I - configuration number

LCON - Array of function numbers belonging to the configurations

**MAIN 6(deck)**

\[(6E12.7) \quad ([C(I,J), J=1,N], I=1,N)\]

C - Transformation matrix for spatial functions. No deck unless NOTRF = -1
APPENDIX III. ILLUSTRATIVE EXAMPLES

AND HINTS - THE NO⁺ CALCULATION

Illustrative examples are furnished to allow the reader to see just how an input deck is set up for a particular type of problem, and as calculations which can be used to check that the program is running properly on a particular computer after the minor modifications necessary to make it compatible with that computer have been made.

Three problems are listed in the sample input decks of Table . The first of these is a LiH calculation, illustrating the heteronuclear capability of the program. This is a one-configuration four electron singlet calculation, and the correct results for the lowest root are:

1. Total electronic energy = -9.708228 au
2. Electronic + nuclear (potential curve) = -7.708228 au
3. Dissociation energy = -7.708228 au

The input deck for this run is self-explanatory once the summary in Appendix II is understood.

The second example is an H₂ calculation using the symmetrized one electron orbitals and two configurations, \( C₁^g ls^g ls' + C₂^u ls^u ls' \). This is for the ground state and the calculated energies should be:
1. Total electronic energy = -1.869461 au
2. Electronic + nuclear (potential curve) = -1.155176 au
3. Dissociation energy = -0.155176 au

Note that NHUG = +1 for a *gerade* state with symmetrized orbitals.

Third, the $H_2$ calculation is repeated using the option of total inversion of the molecule through the inversion center, selecting the *gerade* linear combination $\Psi + i\Psi$. Several things should be noted here. The first is that the reflected counterpart of each function (same function with $\alpha$ replaced by $-\alpha$) is included explicitly in the input deck, and that all unreflected functions precede the reflected ones so that if there are $m$ unreflected functions $1,2,...,m$, and each corresponding reflected function is denoted $1',2',...,m'$, the input functions are numbered $1,2,...,m$, $m+1 = 1'$, $m+2 = 2'$, $..., m+m = m'$. The configuration cards are treated similarly, in that each configuration made of unreflected orbitals must be paired with a configuration composed of the corresponding reflected orbitals, with all unreflected configurations. The program combines the reflected configurations with a rotation by $\pi$ and adds or subtracts the paired configurations as necessary for $g$ or $u$. Note that NFCN and NCON are set for the total number of functions and configurations. NHUG = +2 is the tag which instructs the program to perform the rotation and block diagonalize the total secular equation taking only the $g$ block.
The energies in this case are:

1. Total electronic energy = \(-1.791067\) au
2. Electronic + nuclear (potential curve) = \(-1.076781\) au
3. Dissociation energy = \(-0.076781\) au

Note that although the same functions were used in both \(H_2\) calculations, the one with symmetrized orbitals has a slightly lower energy. This is because the symmetrized orbitals allow two linear coefficients, while in the total molecular inversion option there is only one. The total inversion, in effect, gives \(C'_1(\sigma \sigma' \sigma') = C'_1(\sigma \sigma + \sigma \sigma')\), and we see that \(C'_1 = \sqrt{2/2}\). However, the total inversion requires only \(3/2\) to \(3/4\) the work required by the symmetrized orbitals, and if only \(\sigma \sigma\) were used in the symmetrized case, a poorer answer would result.

The \(C_1 \sigma \sigma + C_2 \sigma \sigma\) calculation can be improved by varying the parameters of the \(\sigma_u\) orbitals, since they are not restricted to be equal to the parameters of the \(\sigma_g\) orbitals as is the case of total inversion. They were set equal purely to demonstrate the relative effect of the two options.

Some specific hints are also helpful for actual use of the program on particular computers.

On machines having some type of CHAINing feature, the programs themselves can be overlaid. For example, the IBM 7094/7044 DCOS IBSYS monitor, version 13, was used with three links. The INTEGRAL, MATRIX, and SEARCH branches were included in one link for optimum efficiency, and the SETUP and OUTPUT branches formed the other two links.
An additional space-speed saving can be effected in systems with adjustable input-output buffer sizes, such as the Honeywell Automath 800/1800 monitor, by buffering the two-electron integral tape to the smallest possible size, since only two words are written per logical record; and by buffering the spin-permutation tape to the smallest size which will include \( N + ND \times ND \) words in one logical record. Tapes KW and KR should be buffered with the largest double buffers possible, since tape handling by subroutine INTEG is the time-controlling factor.

On the Honeywell 800/1800 system, a small calling program is necessary to set up the monitor for use with variable tape identifiers. The entire deck setup is as follows:

```vhdl
*JOBID, JOBNAME, IO020305, 08SN0025, 09DB0019, 06DB0200, 07DB0200

* Project number xxx, users name, any special instructions to
* be typed at console for operator. (64 columns/card)

TITLEDIAT --- entire diatomic program deck as presented in App. IV

*DATA
6 7 8 9 3 5 (Tape identifiers, corresponding to *JOBID card above)

*ENDFILE
```

On the other hand, when the IBM 7094/7044 DCOS system is used, the monitor sets up all buffers when variable tape names are used, and
rather than tricking the monitor with the four statements WRITE(n)I
above, one must use a MAP program which deletes the unused buffers.
Copies of this program are available on request, or the following
logic may be used to create the program for a specific installation.
To delete the buffer for peripheral unit nu, the MAP program is

```$IBMAP BUF. NODECK
ENTRY .UNnn.
.UNnn. PZE
END```

The ENTRY and PZE instructions are repeated with different
numbers 01, 02, ... as desired to delete any unnecessary unit.

The format for control cards, accounting cards, etc. can be
found by consulting the appropriate IBM manuals and the notices
published by the particular installation.

In the program listings (App. IV) the reader will note several
comment cards relevant to particular machines, and accompanying
FORTRAN statements. These must be included or pulled as necessary.
The comments are considered self-explanatory.

The NO+ Calculation

As an illustration of the use of the spin-permutation program
options, the following sample calculation on NO+ is presented. The
approximations used were picked more to illustrate the use of the pro-
gram than for their physical validity and thus the calculation is by
no means a definitive one.

To do a complete 14 electron spin problem, 14! 429x429 matrices
U(P) would be required, which is patently impossible. The approxi-
mations used to reduce this number to a manageable one are:

1. The closing of the shells which include the ten inner electrons so that the spatial configuration is approximately represented by

\[ \pi^2p_{+N}\pi^2p_{-O}\pi^2p_{-O}(o1s)^2_{N} (o1s)^2_{O} (c2s)^2_{N} (c2s)^2_{O} (o2p)^2_{ON} \]

and thus requires only two spin functions

\[ \theta_{001}^4[1/\sqrt{2}(o\beta-\beta\alpha)]^5 \text{ and } \theta_{002}^4[1/\sqrt{2}(o\beta-\beta\alpha)]^5. \]

2. Orthogonalization of the closed shell (doubly occupied) orbitals. This results in a spatial configuration of seven shells of two-electron pairs which are pairwise orthogonal.

With the open shell electrons listed first, the auxiliary permutation vector for the identity permutation is

1 2 3 4 55 66 77 88 99

and obviously no permutations are necessary between electrons 55, 66, etc. which reduces the number of permutations necessary for spin reasons to 14! / 2^5. We now take advantage of the spatial orthogonalities which were purposely introduced.

As pointed out in App. I, any permutation which produces three or more integrals (i|j) which are zero can be eliminated, since it cannot contribute to the secular equation. Inspection of the auxiliary permutation vector above shows that only 20 permutations among the first four orbitals can contribute to the secular equation, and that no more than one interchange of the closed shell functions is allowed at a time.
Thus, there are 31 allowed interchanges of the closed shell orbitals with themselves or with the open shell orbitals 1-4.

The twenty allowed permutations of the open shell set result in 620 permutations which can contribute to the secular equation within this particular closed shell and orthogonality system, and the result is 620 $2 \times 2$ matrices $U(P)$ which is obviously a considerable improvement over the complete open shell treatment.

To make the input deck slightly easier to prepare, the orthogonality in the set of four open shell electrons are ignored, and all $4!$ permutations among them are produced in the program. Hence there are $31 \times 4! = 744$ permutations and their corresponding $U(P)$ produced.

The input deck for this calculation is shown in Table 11. Note that the paired orbitals are replaced by their canonical numbers, and that IOSH = 4. Since the permutations among the ten closed shell electrons are explicitly done by hand, no auxiliary permutation vector is needed in the input deck. The tape identifiers and quadrature points have been omitted. Preparation of the spin tape required about two hours on the Honeywell 800 and about eight minutes on an IBM 7094/7044 direct coupled system.

Once the spin tape was prepared, the NO+ calculation itself took about three minutes on the 7094 and about twenty minutes on the H-800. The resulting energy was -105.93 au, which is of the right order of magnitude, but does not even show binding over the separated atom calculations of Clementi (1964). Due to limited time available
TABLE 10
SAMPLE INPUT DECK

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**GAUSSIAN**

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TABLE 11

INPUT DECK FOR NO$^+$ CALCULATION
to the author, no attempt was made to improve this calculation by variation of the non-linear parameters or by making more realistic physical approximations. Upon completion of the single one-shot run it was decided that the original purpose of this study had been achieved, that of demonstrating that a calculation on a large many-electron diatomic molecule is possible and practical with the present modification of the diatomic program.

The short time required for the actual calculation shows that parameter variation and even some configuration mixing are possible in reasonable amounts of computer time, and a much improved energy obtainable even with the limited spin set used.
APPENDIX IV

LISTING OF DIATOMIC PROGRAM

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<td>RMAX = INTERNUCLEAR SEPARATION</td>
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<td>STEP3 = INITIAL STEP SIZE FOR PARAMETER SEARCH</td>
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<td>RMIN = MINIMUM INTERNUCLEAR SEPARATION</td>
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<td>RSTEP = DECREMENT TO R UNTIL REACHES RMIN</td>
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<tr>
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<td>NHUG = HET=HUMD=GERADE=UNGERADE TAG = (0=HET, =UNG, =GER)</td>
<td>DIA 150</td>
<td></td>
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<td></td>
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<td>NPC = NO. OF FUNCTIONS/ORBITALS) TO BE VARIED(PARAM, SRCH</td>
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<td>NE= DESIRED ROOT OF SEC. EQN. (0=GND. STATE, 1=1ST EXCITED ST+Etc.)</td>
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148
KSIM = (ITAG(4)) SIMULTANEOUS VARIATION TAG, IF NON-ZERO, VARIATION TAGS
MO=TH AND NFCN/2-MO=TH FUNCTIONS SIMULTANEOUSLY
IS = IF #2 , TAPE KR IS MOUNTED FROM PREVIOUS RUN, AND PROG.
SETS ITX=2
FUNCTION CARDS -----------
DELTA(I)=FPAR(1,I), ALPH(A(I)=FPAR(2*I)
FPAR = WORKING SET OF DELTA, ALPHA
FPAR0= BEST SET DETERMINED SO FAR
NFPAR= FIXED EXPONENTS
N(I)=NFPAR(1+I), M(I)=NFPAR(2+I), NU(I)=NFPAR(3+I), PARITY(I)=
NFPAR(4+I), (1=U, 0=G, NFPAR(5+I)=NOT USED, NFPAR(6+I)=VARIATION TAG
0=VARY DELT AND ALF, 1=VARY ALF ONLY, 2=VARY DELT ONLY, 3=SKIP BOTH
CONFIGURATION CARDS ARE READ BY SUBROUTINE CONFIG

DIMENSION OF HI, SI, HZ BASED ON 16 FUNCTIONS (NFCN=16)

COMMON/SPACE/ZKZB*RNFHUG*NCN*MULT*KK*KR*KRNT*JNT*JCODE
1NPERMS, ND, NFCN, MMAT, N10, NMAT, NE, NPC, LSMP, MSHARE, ITX, N1, NC1, NC2, DIA
2LSRCH, JKW3, L1AR, STP1, STP2, E0, NO, MO, IS, A1, A2, EFIN, SAVEA(9), MAD(2), DIA
3, FPAR0(2+16), FPAR(2+16), NFPAR(6+16), ITAG(6), ICTAG(64),
4DELT(25), *MAX, RSTEP, *STEP3
COMMON/UTFBS/D1(11, 11), D02(36, 7), D02(43, 7), JMAX, WTINF, POINT(40), DIA
1WT(40), *MINUS, RULE(2)
COMMON/WORK/NEL, NISP, MULT1, ND1, IOSH, JGEN, IDEN(3), KW1, KR1, NT1, KOR1, DIA
1DA(2917), S1(9588)
COMMON/C1J/C16, 16), NOTRF, NU, MU, KRUD(9)
EQUVALENE (KR1*I), (KOR1*I), (10*LSMP)
EQUVALENE (ITAG(1)*IN), (ITAG(2)*KNT)
EQUVALENE (NPH, ITAG(3))
COMMON LCON (150)
100 FORMAT(1213)
101 FORMAT(8A6,3F10.6)
102 FORMAT(7F10.4)
103 FORMAT(15,2F10.6,6), 13)
104 FORMAT(1H020X, 15HSEC EQN TOO BIG16)
105 FORMAT(1H020X,16HWRONG PERM TAPE216)
111 FORMAT(8E10.5)

C
C HONEYWELL
IN=2
C FOR IBM SET IN = 5
MSPARE=42
ITX=1313
LIAR=0
C
26 CALL SETUP(IN)
25 REWIND NT
REWIND KW
REWIND KR
READ(IN,101) (SAVEA(I),I=1,8), A1,A2,EFIN
READ(IN,102) LA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP
IF(RMIN EQ 0.0) RMIN=RMAX
READ(IN,100) N,NHUG,NCON,NFCN,NPC,NE,LSCH,NOTRF,NU,ITAG(4),IS
IF(IS.EQ.0) IS=1
DO 3 N10=1,NFCN
READ(IN,103) N1,FPARO(1,N1),FPARO(2,N1),(NFPAR(JNT,N1),JNT=1,6)
MOD=N1
IF(ABS(FPARO(2,MO)) GT 1.2*FPARO(1,MO)) FPARO(2,MO)=SIGN(1.2*
*FPARO(1,MO)*,FPARO(2,MO))
FPAR(1,N1)=FPARO(1,N1)
FPAR(2,N1)=FPARO(2,N1)
3 CONTINUE
CALL CONFIG (1,LCOM,N,NCON,IN,10)
JCODE=1000*N+10*IDSH+MULT
IF(NOTRF*GE.*0) GO TO 9
49 DO 48 I=1,N
48 READ(IN,111) (C(I,J),J=1,N)
9 REWIND NT
READ(NT) IDEN
IF(JCODE*NE.IDEN(3)) GO TO 8
REWIND NT
ND=IDEN(1)
MMAT=NFCN*(NFCN+1)/2
NMAT=NCON*ND
IF(NMAT*GT*MSPARSE) GO TO 10
IF(NPC*NE*.0) NPC=NPC+NU
IF(IABS(NHUG)*EQ*.2) ITAG(4)=1
5 R=RMAX
MO = 1 + NU
NO=1
ITX=1
IF(IS*EQ.2) ITX=2
STEP1 = STEP3
11 CALL HDG
CALL CONFIG (2,LCON,N,NCON,IN,IO)
7 CALL INTEG
CALL MATRIX(IN,LCON,N,NCON,N)
CALL SEARCH
IF(ITX*NE.0) GO TO 7
CALL OUTPUT(LCON,N,NCON,N)
IF(RMAX*LE*RMIN) GO TO 1
RMAX=RMAX=STEP
R=RMAX/R
DO 22 I=1,2
DO 22 J=1,16
FPAR0(I,J)*FPAR0(I,J)*R
22 FPAR(I,J)*FPAR0(I,J)*R
GO TO 5
8 WRITE(10,105) JCODE, IDEN(3)
CALL EXIT
10 WRITE(10,104) NMAT
CALL EXIT
1 CALL SWITCH(4,MORE)
IF(MORE*NE.1) GO TO 222
REWIND NPCH
WRITE(NPCH,101) (SAVEA(I),I=1,N) A1*A2*EF1
WRITE(NPCH,102)Z1,Z2,STEP3,STEP2,RMIN,RSTEP
MU=NFCN-MO =1
WRITE(NPCH,100) N,NHUG,NCON,NFCN,MU,NE,LSRCH,NOTRF,MO
DO 333 N=1,NFCN
333 WRITE(NPCH,103) N,FPARO(1,N1),FPARO(2,N1),NFPAR(JNT,N1),JNT=1,6
CALL CONFIG(3,NC1,2,N,IN,NPCH)
ENDFILE NPCH
READ(IN,100) JNT,NEL,NISP,MULT,ND,IOSH,JBEN
IF(JNT.EQ.999) CALL EXIT
C
C
C HONEYWELL 800 ONLY - FOR SOME REASON THIS PREVENTS UNDEFINED
C TAPE POSITION ERRORS WHEN STARTING A NEW CALCULATION.
C
C
K=6
KR=7
C
IF(JNT.NE.0) GO TO 25
GO TO 26
END
**  ****  ****  ****  ****  ****  ****  ****  ****  ****  ****  **
SUBROUTINE HDG
PRINTS HEADING LINES IN OUTPUT
COMMON SPACE/ZA,ZB*R+N,NHUG,NCON,MULT,KW,KR,DR,NT,JNT,JCODE
11NPERM5,ND,NFCN,MAT,N1,10,NMAT,NE,NE,NPC,LSPACE,MSPACE,ITX,N1,NC1,NC2P
2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EF1,SAVEA(9),MAD(2)
3,FPARU(2,16),FPARU(2,16),NFPARU(6,16),ITAG(16),ICTAG(6),LCON(6,8),
DEL(125),RMIN,RSTEP,STEP3
COMMON/VATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
1WT(40),NMINUS,RULE(2)
EQUIVALENCE (I,JNT),(TUP,NC2P)
EQUIVALENCE (IC,LSPACE)
EQUIVALENCE (I*BLANK,ICTAG)
DIMENSION HAG(8),BLANK(3)
999 DATA(HAG(1),I=1,8)/SHHETER,SH HOM,5HONUC,5H GER,5H UNG,6HMOL,HDG
* I*6HNVERTD*6H

10 FORMAT(15X*12HCJT W SSWITCH )

303 FORMAT(1H18A6/7X,3HZAF8.2*3X,3HZB=F8.2*3X,3HNF=12.3X,5H2S+1=12.3XHDG )

*2HC=12.3X2HR=F8.3*4H(AU)3X2HR=F8.4*5H(ANG) /

TUP= 2917*R
WRITE(10,303)(SAVEA(1),I=1*8),ZA,ZB,N,MULT,NCON,R,TUP

100 FORMAT(15X*3A5,2A6 )
IF(NHUG*EQ*0) GO TO 2
BLANK(1)=HAG(8)
BLANK(2)=HAG(8)
IF(IABS(NHUG)*NE*2) GO TO 3
BLANK(1)=HAG(6)
BLANK(2)=HAG(7)

3 BLANK(3)=HAG(4)
IF(NHUG*LT*0) BLANK(3)=HAG(5)
WRITE(10,100) HAG(2)*HAG(3)*BLANK(3)*BLANK(1),BLANK(2)
GO TO 7

2 WRITE(10,100) HAG(1)*HAG(3)
7 CONTINUE
IF(LIAR*NE*0) WRITE(10,10)
WRITE(10,107) RULE*JMAX

107 FORMAT(1H0*20X*2A6,21HINTEGRATION, NO. PTS= I4 )
9 RETURN

END
SUBROUTINE CONFIG(NRW,LCON,N,NCON,IN,IO)
C READ OR PRINT CONFIG CARDS
DIMENSION LCON(NCON,N)
100 FORMAT(12I3)
106 FORMAT(5X,4HCONF:17,5X,3HFCN 2X,2013)
GO TO (1+2+3)*NRW
1 DO 4 N10= 1,NCON
READ(IN*100) N1,(LCON(N1+JNT),JNT=1,N)
4 CONTINUE
RETURN
2 DO 20 N1=1,NCON
20 WRITE(IO*106) N1,(LCON(N1+J),J=1,N)
RETURN
3 DO 21 N1=1,NCON
21 WRITE(IO*100) N1,(LCON(N1+J),J=1,N)
RETURN
END

** ***** ***** ***** ***** ***** ***** ***** ***** ***** ***** **
SUBROUTINE SETUP(IN) SET 10
C CONTROLLING PROGRAM OF SETUP BRANCH SET 20
C SETS PERMANENT DATA BLOCK AND MAKES INITIAL SPIN TAPE SET 30
COMMON/SPACE/ZA,ZN,NG,NSHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,NDFCMMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2,P,SET 40
2LSHC,H,K3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2),SET 50
3,FPARU(2,16),FPARU(2,16),NPARU(1,16),ITAG(16),ICTAG(16),LCON(5+8),SET 60
4DELT(25),RMAX,RMIN,RSTEP,STEP3,SET 70
COMMON/WORK/NEL,NISP,MULT1,ND1,IOSH,JGEN,IDEN(3),KW1,KR1,NT1,KOR1,SET 80
IMDA(2917), S1(9588) SET 90
EQUIVALENCE (IOUT,LSPARE) SET 100
EQUIVALENCE (ITAG(2)*KINT),(ITAG(3)*NPCH) SET 110
100 FORMAT(12I3)
IF(ITX*NE,1313) GO TO 1
READ(IN*100) KW,KR,NT,KINT, IOUT,NPCH
CALL TABLE(IN)
READ(IN*100) JNT,NEL,NISP,MULT,ND,IOSH,JGEN
1 IF(JNT.EQ.0) CALL SPIN(NT,NPERMS,IN,NEL,NISP,MULT,ND,IOSH,JGEN, SET 120
** SUBROUTINE TABLE (M) **

C MAKES PERMANENT DATA BLOCK FOR INTEGRAL ROUTINES

COMMON/DATABLES1,D1(11),DD1(36),JMAX,WTINF,POINT(40),
WIDEPOINT, NMINUS, RULE(2)

EQUIVALENCE (WT(1)*1), (WT(2)*J), (WT(3)*K), (WT(4)*A), (WT(5)*B),
*(WT(6)*C)

C APPENDIX II = EQN (64)

DO 1 I=1,9
DO 1 J=1,9
1 DD1(I,J)=0.

DD1(I+1,J)=1.

DO 5 I=2,7
A=2*I-1.

5 DD1(I+1,J)=DD1(I-1,J-1)*SQRT(A*(A-1)).

DO 6 J=1,7
K=J+1.

DO 6 J=1,7
A=I+J-2.
C=I-J.

6 DD1(I,J)=DD1(I-1,J)*SQRT(A/C*B/(B-2)).

C APPENDIX II = EQN (65)

DO 2 I=1,11
DO 2 J=1,11
2 D1(I,J)=0.

D1(I+1,J)=1.

DO 3 I=2,11
A=I-1.

3 D1(I,J)=D1(I-1,J-1)*A/B.

DO 4 J=1,9
K=J+2.
DO 4 I=K+1,11+2  
A=I-1  
C=I-J  
B=I+J-1  
4 D1(I,J)=D1(I-2,J)*A/C*(A-1)/B  
C APPENDIX II - EQN (66)  
DO12 I=1,43  
DO12 J=1,7  
A=I+J-1  
B=I-J+1  
C=4*I*J-1  
12 DD2(I,J)=A*B/C  
READ(M,100) JMAX,NMINUS,WTINF,RULE  
READ(M,101) POINT  
C APPENDIX II - EQN (67)  
READ(M,101) WT  
RETURN  
100 FORMAT(6X,21B*E30.12,2A6)  
101 FORMAT(6X,4E18.12 )  
END  
** **** **** **** **** **** **** **** **** **** ****  **  
SUBROUTINE SPIN (NTNP,IN,N,NISP,MULT,ND,IOSH,JGEN,IDENT,umat,  
     *ISP,ITPR,ISPM,JPRI,I1,USET)  
C MAKES PERM TAPE OF UMAT AND IPER WITH OPTIONS RANGING FROM CLOSED  
C SHELL TO COMPLETE OPEN SHELL  
C  
C SPACE AND DIMENSIONS ARE SUFFICIENT FOR HANDLING THE FULL  
C EIGHT ELECTRON PROBLEM  
C  
C INPUT  
C NEL - NUMBER OF ELECTRONS  
C NISP - NUMBER OF SIMPLE SPIN PRODUCT FUNCTIONS (AABBA...)  
C MULT - MULTIPLICITY (2S+1)  
C ND - DEGENERACY (FNS OF KOTANI)  
C IOSH - NUMBER OF ELECTRONS TO BE INCLUDED IN PERM. SCAN  
C JGEN - NUMBER OF HAND GENERATED PERMUTATIONS  
C  
TBL 330  
TBL 340  
TBL 350  
TBL 360  
TBL 370  
TBL 380  
TBL 390  
TBL 400  
TBL 410  
TBL 420  
TBL 430  
TBL 440  
TBL 450  
TBL 460  
TBL 470  
TBL 480  
TBL 490  
TBL 500  
TBL 510  
TBL 520  
SPN 10  
SPN 20  
SPN 30  
SPN 40  
SPN 50  
SPN 60  
SPN 70  
SPN 80  
SPN 90  
SPN 100  
SPN 110  
SPN 120  
SPN 130  
SPN 140  
SPN 150
C PERMS WHICH PRODUCE ZEROS DUE TO CLOSING OF SHELLS OR SPATIAL ORTHOGONALITIES ARE OMITTED BY PROPER PREPARATION OF JGEN LIST

INPUT (CARDS)
ISP = ACTUAL CODING OF BIT CONFIGURATIONS FOR SPIN PRODUCT FUNCTIONS
USET = COEFFICIENT MATRIX (DIMENSION NDXNISP)
JPRI = UNPAIRED TRUE PERMUTATION VECTOR
KPRI = AUXILIARY PERM VECTOR WITH PAIRS INDICATED

OUTPUT = ON TAPE NT
UMAT = ANTISYMMEITRIZED MATRIX REPRESENTATION OF PERMUTATIONS
IPER = THE ACTUAL PERMUTATIONS (PERMUTED FUNCTION NUMBERS)
NP = THE NUMBER OF SETS (UMAT, IPER) WRITTEN ON TAPE NT

DIMENSION IDEN(3), UMAT(ND, ND), ISP(NISP), ITE(NISP, N), ISSPM(N), *JPRI(N), IP1(N), USET(ND, NISP), KPRI(20)

100 FORMAT(14I5)
101 FORMAT(5F14.10)
102 FORMAT(F9.2, 21I3)
REWIND NT
DO 110 I=1, ND
DO 9 J=1, ND
9 UMAT(I, J)=0.
110 UMAT(I, I)=1.
NP=0
LOCA=0
READ(IN, 100) (ISP(I), I=1, NISP)

C UNPACK ISP INTO ITE
DO 11 I=1, NISP
 IX = ISP(I)
 IZ = 2**(N-1)
 DO 11 J=1, N
 ITE(I, J)=IX/IZ
 IX=IX-IZ*ITE(I, J)
11 IZ = IZ/2
DO812 I=1*ND
READ(IN*101) (USET(I*J),J=1*NISP)
812 USE(T(I*J),J=1*NISP)
     IDEN(1)=ND
     IDEN(2)=N
     IDEN(3)=1000*N+10*IOSH*MULT
WRITE(N1); IDEN
J1PER=1
20 READ(IN*102) (G(J),J=1*N) *(KPR1(K),K=1*N)
     IF(KPRI(1)*NE.0) GO TO 999
     DO 998 K=1*N
998 KPRI(K)=JPRI(K)
     IF(NP*EQ.0) GO TO 27
     GO TO 116
21 K1=IOSH-1
     DO 301 K=1*K1
     IF(KPRI(K+1)*GT.KPRI(K)) GO TO 302
     CONTINUE
     IF(J1PER*GE.JGEN) GO TO 117
     J1PER=J1PER+1
     GO TO 20
301 CONTINUE
     IF(J1PER*EQ.JGEN) GO TO 117
     J1PER=J1PER+1
     GO TO 20
302 IF 303 L=1*K
     ISSPM(L)=KPRI(L)
303 II(L)=JPRI(L)
     DO 304 L=1*K
     K1=L+1
     KPRI(L)=ISSPM(K1)
304 JPRI(L)=II(K1)
     DO 305 L=1*K
     IF(ISSPM(L)*LT.KPRI(K+1)) GO TO 306
     CONTINUE
305 K1=L+1
     JPR1(K1)=JPR1(K+1)
     JPR1(K+1)=II(L)
     KPRI(K1)=KPRI(K+1)
KPRI(K+1) = ISSPM(L)
IF(MOD(K+4) .LT. 2) SIG = -SIG
116 DO 10 I=1,NISP
10 ISSPM(I) = 0
DO 14 I=1,NISP
IX = 0
DO 12 K=1,N
IX = 2*IX
I3=JPRI(K)
12 IX = IX + ITE(I,I3)
DO 13 K=1,NISP
IF(IK .NE. ISP(K)) GO TO 13
ISSPM(K) = 1
GO TO 14
13 CONTINUE
14 CONTINUE
DO 1180 L=1,ND
DO 1180 J=1,ND
UITEM=0
DO 1175 J = 1,NISP
K=ISSPM(J)
IF(K .EQ. 0) GO TO 1175
UITEM=UITEM+USET(I,J)*USET(L*K)
1175 CONTINUE
1180 UMAT(I*L) = UITEM*SIG
27 WRITE(NT) (JPRI(I)*I=1,N),((UMAT(K,J)*K=1,ND)*J=1,ND)
NP = NP+1
GO TO 21
117 ENDFILE NT
REWIND NT
RETURN
END
SUBROUTINE INTEG

C CONTROLLING PROGRAM OF INTEGRAL BRANCH
C GENERATES AND STORES ONE AND TWO ELECTRON INTEGRALS
C kw = WRITE TAPE, kr = READ TAPE WITH BEST SET OF INTEGRALS TO DATE
C JTA AND JTB ARE COMPLETE INTEGRAL TABLES, WITH ALL DATA NECESSARY
C FOR COMBINING TO MAKE THE TWO ELECTRON INTEGRALS
C
C SEE SUBROUTINE ONEI FOR TABLE LAYOUT OF (JTA(I,L),I=1,1460)
C TOTAL INTEGRAL PACKAGE CONSISTS OF BANDI, GLIST, ONEI, TWOEL
C COMB IN AND TAPE
C
COMMON/SPACE/ZA, ZB, R, N, HUG, NCON, MULT, KW, KR, KOR, NT, JNT, JCODE
INPERMS, ND, NFCN, MMT, N10, NMT, NE, NPC, LSPARE, MSPARE, ITX, N1, NCL, NC2P
LSRCH, JK, L, LAR, STEP1, STEP2, E0, NO, MOS, IA1, A2, EFIN, SAVEA(9), MAD(2)
3 FPARU(2,16), FPAR(2,16), NFPAR(6,16), ITAG(16), ICTAG(6), LCON(6,8)
4 DElia, KM, RMIN, RSTEP, STEP3
COMMON/WORK/JTB(1460,4), JTA(1460,4), I, J, L, L1, NT0T, DUMB(289)
1 S1(136), H1(136), REST(272)
COMMON/DTABLE/D1(11,11), DD1(36,7), DD2(43,7), JMAX, WTI NF, POINT(40)
1 W1(40), NMINUS, RULE(2)
COMMON/LI/CL, C(16,16), NOTRF, NU, MU, KRUD(9)
EQUIVALENCE (LSPARE, IO)
EQUIVALENCE (ITAG(2), KINT)
EQUIVALENCE (JTA, ZG1), (JTB, H2)
DIMENSION H2(9317), ZG1(1460,4)
DATA FINAL/6MNO MORE/

C 303 REWIND KW
REWIND KINT
REWIND NT
REWIND KR
NT0T=1
L=0
L1=0
DO 302 I=1,NFCN
DO 302 J=1,I
L1=L1+1
IX=NFCN/2
IF (NOTRF.EQ.1) IX=IX*NU
IF ((IABS(NHUG).EQ.2).AND.(J.GT.IX)) GO TO 301
L=L+1
IF (IX.EQ.1) GO TO 309
IF (L.EQ.1) CALL TAPE(KR+1,JTA)
IF (JTA(11,L).EQ.L1) GO TO 309
358 WRITE(10,399)L1,JTA(11,L),JTA(8,L),JTA(9,L)
CALL EXIT
309 CALL ONEL(I,J,JTA(1,L),JTA(1,L),JMAX)
JTA(11,L)=L1
S1(L1)=ZG1(17,L)
IF (J.NE.1) GO TO 400
REST(I)=SQR(S1(L1))
MERDE=IX+1
IF (IABS(NHUG).EQ.2) REST(MERDE)=REST(I)
400 H1(L1)=(2.*ZG1(10,L)=ZG1(18,L)/(2.*R))/R
IF (L.LT.4) GO TO 302
CALL TAPE(KW+2,JTA)
L=0
NTOT=NTOT+1
301 CONTINUE
302 CONTINUE
L1=L1+1
DO 300 I=L1+4
JTA(11,I)=0
300 JTA(12,I)=20
CALL TAPE(KW+2,JTA)
ENDFILE KW
REWIND KW
L1=0
C NORMALIZE

INT 360
INT 370
INT 380
INT 390
INT 400
INT 410
INT 420
INT 430
INT 440
INT 450
INT 460
INT 470
INT 480
INT 490
INT 500
INT 510
INT 520
INT 530
INT 540
INT 550
INT 560
INT 570
INT 580
INT 590
INT 600
INT 610
INT 620
INT 630
INT 640
INT 650
INT 660
INT 670
INT 680
INT 690
INT 700
DO 304 I=1,NLCN
DO 304 J=1,1
L1=L1+1
X=REST(I)*REST(J)
S1(L1)=S1(L1)/X
H1(L1)=H1(L1)/X
IF(I.EQ.J) S1(L1)=1.
304 CONTINUE
I=L+4*(NTOT=1)
I=1*(I+1)/2+1
310 CALL COMBIN(JTA,JTA,KINT*R,JMAX*REST)
IF(NTOT.EQ.1) GO TO 241
NTOT=NTOT-1
DO 311 L1=1,NTOT
IX=1
CALL TAPE(KW,IX,JTB)
IF(IX.EQ.13) GO TO 303
CALL COMBIN(JTA,JTB,KINT*R,JMAX*REST)
311 CONTINUE
CALL COMBIN(JTB,JTB,KINT*R,JMAX*REST)
IF(NTOT.EQ.1) GO TO 241
NTOT=NTOT-1
DO 312 L1=1,NTOT
BACKSPACE KW
BACKSPACE KW
IX=1
CALL TAPE(KW,IX,JTA)
IF(IX.EQ.13) GO TO 303
CALL COMBIN(JTA,JTB,KINT*R,JMAX*REST)
312 CONTINUE
GO TO 310
241 WRITE(KINT) 1*FINAL
ENDFILE KINT
242 REWIND KINT
REWIND kw
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SUBROUTINE TPE(0,KACT,JT)
C PACKS, READS, AND WRITES INTEGRAL TABLES G(I,K)
DIMENSION JT(1460,4)
GO TO (1,2) KACT
1 READ (NU) L*{(JT(I,J),I=1,L),J=1,4)
RETURN
2 L=MAX0(JT(12,1),JT(12,2),JT(12,3),JT(12,4))
WRITE (NU) L*{(JT(I,J),I=1,L),J=1,4)
RETURN
END

C SUBROUTINE UNEL(J1,J2,TA1,TA2,MAX)
C TAB LAYOUT = 1-7 NLP, 8-J1, 9-J2, 10-EPOT, 11-IND2, 12-NW
C 13-16 FLP, 17-5, 18-KEIN, 19-GINI, 20-1460 GINT
C JTAB=TAB FOR PACKING AND UNPACKING FIXED OR FLOAT WORDS
C COMMON SPACE: ZA>ZB>R>N+HUG>N+C>MUL+K>KR>KO+JNT+JNT+JCODE
C 1NPERM5, ND, NFCN, MMAT, N10, NMAT, NE, NPC, LSPARE, MSPARE, ITX, N1, NC1, NC2, N1, ONE 60
C 2LSRCH, JKW3, LIA, STEP1, STEP2, E0, NO, MO, IS, A1, A2, EFIN, SAVEA(9), MAD(2), ONE 70
C 3, FPAR(1,2), FPAR(2,16), NFPAR(6,16), ITAG(16), ICTAG(6), LCON(6,8), ONE 80
C 4DELT(25) * MAX, RMIN, RSTEP, STEP3
C COMMON WORK: NL(7), NOTA(5), FLP(4), S1, H1, A(7), B(7), BINT(36,2), C(7,2), ONE 100
C 1, DUMM(1326), FL1*C2*C3*C5*C6*C7*KDNEK, EDEL, EZET, EK1, ONE 110
C 2EKZ, EK3, EK4, EK2PK1, EK3PR1, IZG1(1470), RMDR(9588)
DIMENSION TAB(1460), JTAB(1460)
EQUIVALENCE (EPOT, NOTA(3)), (E1, H1)
NOTA(1)=J1
NOTA(2)=J2
NOTA(5)=JTAB(12)
FLP(1)=FPAR(1, J1) * FPAR(1, J2)
FLP(2)=FPAR(1, J1) * FPAR(1, J2)
FLP(3)=FPAR(2, J1) * FPAR(2, J2)
FLP(4)=FPAR(2, J1) * FPAR(2, J2)
IF (ITX.EQ.1) GO TO 31
IF (FLP(1) .NE. TAB(13)) GO TO 31
IF (FLP(2) .NE. TAB(14)) GO TO 31
IF (FLP(3) .NE. TAB(15)) GO TO 31

TAP 10
TAP 20
TAP 30
TAP 40
TAP 50
TAP 60
TAP 70
TAP 80
TAP 90
TAP 100
ONE 10
ONE 20
ONE 30
ONE 40
ONE 50
ONE 60
ONE 70
ONE 80
ONE 90
ONE 100
ONE 110
ONE 120
ONE 130
ONE 140
ONE 150
ONE 160
ONE 170
ONE 180
ONE 190
ONE 200
ONE 210
ONE 220
ONE 230
ONE 240
ONE 250
IF (FLP(4)$NE$TAB(16)) GO TO 31
RETURN
31 NLP(1)$=NFPAR(3$J1)$-NFPAR(3$J2)
NLP(2)$= (IABS(NFPAR(3$J1))$+IABS(NFPAR(3$J2))$-IABS(NLP(1)))/2
NLP(3)$=NFPAR(2$J1)$-NFPAR(2$J2)
C NLP(4) OK L4 TO BE REDETERMINED BY BANDI IF ENTERED
NLP(4)$=JTAB(4)
NLP(5)$=NFPAR(1$J1)$+NFPAR(1$J2)
NLP(6)$= NFPAR(2$J1)$-NFPAR(2$J2)
NLP(7)$=NFPAR(1$J1)$=NFPAR(1$J2)
MMM$=NFPAR(2$J1)$+NFPAR(3$J1)$+NFPAR(4$J1)
NNN$=NFPAR(2$J2)$+NFPAR(3$J2)$+NFPAR(4$J2)
CALL BANDI(NNN,MMM)
CALL GLIST(TAB(20)$+TAB(19)$,JMAX)
C KRONNECK DELTA OVER NU(I)$+NU(J)
IF (NLP(1)$=EQ$.0) GO TO 65
S$=0.$
H1$=0.$
EPOT$=0.$
GO TO 53
C KRONNECK DELTA OVER GERADE$+UGERADE
65 IF (MOD(NHUG,2)$=EQ$.0) GO TO 1331
KRONKE$= MMM$+NNN$+NLP(3)
IF (MOD(KRUNKE,2)$=EQ$.0) GO TO 1331
S$=0.$
H1$=0.$
EPOT$=0.$
GO TO 53
C APPENDIX I$- EQN (40)
1331 S$=A(7)$+$B(5)-A(5)$+$B(7)$
C2$=NLP(2)$
C3$=NLP(3)$
C5$=NLP(5)$
C6$=NLP(6)$
C7$=NLP(7)$
<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>APPENDIX I - EQN (41) EDELT=A(6)<em>B(5)</em>(ZA+ZB)</td>
</tr>
<tr>
<td>C</td>
<td>APPENDIX I - EQN (42) EZETA= A(5)<em>B(6)</em>(ZA+ZB)</td>
</tr>
</tbody>
</table>
| C    | HERE TO STATEMENT 1332 - APPENDIX I - EQN. (43) EK1=B(5)*(FLP(2)*FLP(2)*A(7)=2*(FLP(2)*C7+FLP(1)) 1*A(6)*Z0*FLP(2)*C7*A(4)*(C5=C7*C7)*A(3)) EK4=A(2)*B(1)=A(1)*B(2) EK2=A(5)*(FLP(4)*FLP(4)*C(7:1)=2*(FLP(4)*C6+FLP(3)))*C(6:1) 1*20*FLP(4)*C6*C(4:1)*(C3=C6*C6)*C(3:1) EK3=A(5)*C(5:1)*(C7*C7*C5=FLP(2)*FLP(2)=C6*C6=C3+FLP(4)*FLP(4)) IF(MOD(NHJG+2),EQ.0) GO TO 1332 FL1=1. IF(MOD(NHN+2),NE.0) FL1=FL1 EK2PRI=A(5)*(FLP(3)*FLP(3)*C(7:2)=2*(FLP(3)*C6+FLP(4)))*C(6:2) 1*2*FLP(3)*C6*C(4:2)*(C3=C6*C6)*C(3:2) EK3PRI=A(5)*C(5:2)*(C7*C7*C5=FLP(2)*FLP(2)=C6*C6=C3+FLP(3)*FLP(3)) EK2=EK2+FL1*EK2PRI EK3=EK3+FL1*EK3PRI 1332 EK1=EK1+EK2+EK3+EK4 EPOT=EDELT+EZLTA 53 CONTINUE DO 55 I=1,18 55 JTAB(1)=NLP(1) RETURN END

**Variables:**
- A: Array
- B: Array
- C: Array
- EK1, EK2, EK3, EK4: Constants
- FLP: Functions
- NHJG, NHN: Constants
- ZA, ZB: Constants
- FL1, FL2: Variables
- EDELT, EZLTA, EPOT: Variables
- NLP: Variable

**Constants:**
- A(6), A(5), A(4), A(3), A(2), A(1), B(5), B(6), B(1), B(2): Constants
- C7, C6, C3, C2, C1: Constants

**Functions:**
- FLP(2), FLP(4): Functions
FUNCTION TWOEL (TABA,TABB,G1,G2,NLP1,NLP2,R,NDIM,S)  \hspace{1cm} \text{TWO} \hspace{1cm} 10
C FUNCTION IS H2, OBTAINED BY MERGING THE 2 GINT LISTS, USING SIGMA AND  \hspace{1cm} \text{TWO} \hspace{1cm} 20
C INDEX MAXIMA GIVEN IN NLP1 AND NLP2.  \hspace{1cm} \text{TWO} \hspace{1cm} 30
C JMAX, NUMBER OF INTEGRATION POINTS, AND NMINUS, NUMBER TO BE  \hspace{1cm} \text{TWO} \hspace{1cm} 40
C ACCUMULATED NEGATIVELY AT BEGINNING OF LIST, TO BE SUPPLIED  \hspace{1cm} \text{TWO} \hspace{1cm} 50
C SEPARATELY AS CONSTANT INFORMATION.  \hspace{1cm} \text{TWO} \hspace{1cm} 60
C APPENDIX I = EWN* (60), EXCEPT FOR KRONECKER DELTA OVER  \hspace{1cm} \text{TWO} \hspace{1cm} 70
C SIGMA(1) =SIGMA(2), WHICH IS APPLIED IN FUNCTION TRX  \hspace{1cm} \text{TWO} \hspace{1cm} 80
C COMMON/DATBLS/D1(11,11),D1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),  \hspace{1cm} \text{TWO} \hspace{1cm} 90
C WT(40)*NMINUS*RULE(2)  \hspace{1cm} \text{TWO} \hspace{1cm} 100
C DIMENSION TABA(1460),TABB(1460),NLP1(7),NLP2(7)  \hspace{1cm} \text{TWO} \hspace{1cm} 110
C DIMENSION G1(NDIM,36),G2(NDIM,36),S(16)  \hspace{1cm} \text{TWO} \hspace{1cm} 120
L= MINU (NLP1(4)-IABS (NLP1(1)),NLP2(4)-IABS (NLP2(1)))  \hspace{1cm} \text{TWO} \hspace{1cm} 130
TWOEL=TABA(19)*TABB(19)  \hspace{1cm} \text{TWO} \hspace{1cm} 140
L1 = NMINUS + 1  \hspace{1cm} \text{TWO} \hspace{1cm} 150
DO 15 K=1,L  \hspace{1cm} \text{TWO} \hspace{1cm} 160
IF (NMINUS*EQ.0) GO TO 16  \hspace{1cm} \text{TWO} \hspace{1cm} 170
14 DO 13 K1=1,NMINUS  \hspace{1cm} \text{TWO} \hspace{1cm} 180
13 TWOEL = TWOEL+G1(K1,K)*G2(K1,K)  \hspace{1cm} \text{TWO} \hspace{1cm} 190
16 DO 15 K1 = L1,JMAX  \hspace{1cm} \text{TWO} \hspace{1cm} 200
15 TWOEL = TWOEL+G1(K1,K)*G2(K1,K)  \hspace{1cm} \text{TWO} \hspace{1cm} 210
TWOEL=Z/R*TWOEL  \hspace{1cm} \text{TWO} \hspace{1cm} 220
K=NLP1(8)  \hspace{1cm} \text{TWO} \hspace{1cm} 230
L=NLP1(9)  \hspace{1cm} \text{TWO} \hspace{1cm} 240
K1=NLP2(8)  \hspace{1cm} \text{TWO} \hspace{1cm} 250
L1=NLP2(9)  \hspace{1cm} \text{TWO} \hspace{1cm} 260
TWOEL=TWOEL/(S(K)*S(L)*S(K1)*S(L1))  \hspace{1cm} \text{TWO} \hspace{1cm} 270
RETURN  \hspace{1cm} \text{TWO} \hspace{1cm} 280
END  \hspace{1cm} \text{TWO} \hspace{1cm} 290
SUBROUTINE BAND (MMM,NNN)

GENERATES B AND BINT FOR PARAMETER ZETA
A CONTAINS A INTEGRALS FOR ONE-ELECTRON CALCULATIONS

INPUT L1 = NLP(1)*SIGMA=NU(1)*NJ(J)
L2=TAU
L3=M(I)*M(J)
L5=N(I)*N(J)

OUTPUT B B(1) = B(MS) FOR TAU(1), B(2) = B(MS+2) FOR TAU(1)
B(3) TO B(7) = B(MS+2) TO B(MS+2) FOR NU1=NU2
BINT(K,L) BLOCK - I INTEGRAL, L=1 FOR I(MS), L=2, I(MS+2)
K GIVES LOWER INDEX, VALUE OF I STARTS AT K=MUS.
L4=UPPER LIMIT OF MU SUMMATION IN NEUMANN EXPANSION

D(I,J)=FACT(FLOAT(I-1))*FLOAT(2*I-1)/FACT(FLOAT(I-J))/FACT(FLOAT(I-J))

COMMON/SPACE/IDUM(309)
COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELT(2),ZETA(2),UL(2),
*A(7),F(7),BINT(362),B(72).
95(38+11*2)+R(60).
8 C+Cl+K+L*M*K1*K2*K3*K4*K5*NIXIT*NUTS*I*X+I+Y+IZ+NO+M+PAX
7I+TEMP(426)+ZG(140),KMDR(9588)
COMMON/DAIBLS/D(11,11),DD(367),DD2(437),JMAX,WTINF,POINT(40),
1WT(40)*MINUS*RULE(2)
DIMENSION X(60)

EQUIVALENCE(IDUM(5),NHUG),(X,R),(LL,IX),(DELT,DELT(1))
EQUIVALENCE(IDUM(22),IOUT)
NIXIT = IABS(L1)
NO=1
DO 102 L=1,936
102 A(I)=0.
IF(L3*GT.8)*OR.(L2*GT.3)*OR.(NIXIT*GT.6) GO TO 6
1 IF(ABS(ZETA(NO))<.GE.1.E-5) GO TO 1290
C MAKE I(0,ZETA,U) FOR VERY SMALL ZETA
   K1 = 2*NIXIT
   S(1+1,NO) = 2.
   DO 127 K=2,K1
   C=2*K-1
   127 S(K+1,NO) = -S(K=1,1,NO) / C
   S(K1+1,NO) = S(K1,1,NO)*ZETA(NO)
   K1 = K1+1
   DO1280 K=K138
   1280 S(K+1,NO) = 0.
   GO TO 1311
   1290 M=28.*ABS(ZETA(NO)/1.95)
   IF(M.GT.60) GO TO 6
   C MAKE I FOR M AND TAU ZERO
   1291 R(1) = 0.
   DO 1300 K=2,M
      C=C*(M-K)+3
   1300 R(K) = -ZETA(NO)/(C-ZETA(NO)*R(K-1))
      S(1+1,NO) = 2.*EXP(ABS(ZETA(NO)))*ZETA(NO)**(-NIXIT)/(1.*ABS(ZETA(NO))
      1)) = ZETA(NO)*R(M)
      DO 1310 K=1,37
      L=M-K+1
      1310 S(K+1,NO) = S(K1,1,NO)*R(L)
      1311 IF(MOD(NHUG,2).EQ.0) GO TO 100
      C MAKE I(M,ALFPR1,TAU) + APPENDIX I = EQN.(55)
      NO = NO+1
      IF(NO.EQ.2) GO TO 1
      C MAKE COEFFICIENTS FOR M AND TAU CALCULATION
      100 DO 1315 K=1,36
         C=K*NIXIT
         C1=2*K+1
      1315 R(K)*C/C1
      C ADVANCE TAU AND IF SIGMA ZERO, PREPARE B
      K4=37
      IF(L2.EQ.0) GO TO 1400
1320 K1=L2=1
1325 IF(K1) 1400,1330,1340
1330 IF(L1,NE.0) GO TO 1340
C CALCULATE B FOR NU=1
1332 K2=L3+1
   K3=L3=2*(L3/2)+1
   B(1,1)=0.
   B(1,2)=0.
   DO 1333 K=K3,K2+2
   DO 1333 NU=1,N2
1333 B(1,NO)=B(1,NO)+D(K2,K)*S(K,1,NO)
   K2=K2+2
   B(2,1)=0.
   B(2,2)=0.
   DO 1334 K=K3,K2+2
   DO 1334 NO = 1,N2
1334 B(2,NO)=B(2,NO)+D(K2,K)*S(K,1,NO)
1340 K1=K1--1
C ADVANCE TAU BY 1
1350 DO 1360 J=1,N2
    DO 1360 NO=1,N2
    S(J,NO)=S(J,NO)
    K4=K4--1
    DO 1360 K=1,K4
1360 S(K+1,J+1,NO)=(1.0-R(K))*S(K+2,J,NO)+R(K)*S(K+J,NO)
   K5=K4--1
   DO 1370 K=1,K5
   DO 1370 NO=1,N2
1370 S(K,J+1,NO)=S(K+1,J,NO)+S(K,3,NO)
   GO TO 1325
1400 IF(L1,NE.0) GO TO 1440
C CALCULATE B FOR NU EQUALS NU
   K1=1
   IF(L3,GT.1) K1=L3+1
1410 K2=L3+3
DO 1420 J=K1*K2
DO 1420 NO = 1.2
K5=J=K2+7
K3=J=2*((J-1)/2)
B(K5,NO)=0.
DO 1420 K=K3+J,2
1420 B(K5,NO)=B(K5,NO)+D(J,K)*S(K+1,NO)

C ADVANCE M TO FINAL VALUES
1440 K2=L3+2
DO 1450 J=1,K2
DO 1450 NO = 1.2
S(1,J+1,NO)=S(2,J,NO)
K4=K4=1
DO 1450 K=1,K4)
1450 S(K+1,J+1,NO)=(1+R(K))*S(K+2,J,NO)+R(K)*S(K+J,NO)
IF (MOD(NHUG,2) EQ 0) GO TO 1600
PAX=1.
IF (INT=M(MM/2)*Z)*NE.0) PAX=PAX
DO 1501 IX=1,38
DO 1501 IY=1,11
1501 S(IX,IY,1)= (S(IX,IY,1)+PAX*S(IX,IY,2))
DO 1502 IX=1,7
1502 F(IX)+B(IX+1)*PAX+B(IX+2)
C MULTIPLY BY DD COEFFICIENTS
1500 K5=K4+1
K1=NIXIT + 1
DO 1455 J=K1,K5
S(J,K2=1,1) = DD(J,K1)*S(J,K2=1,1)
1455 S(J,K2+1,1) = DD(J,K1)*S(J,K2+1,1)
C TEST FOR CUT-OFF INDEX VALUE OR NON-CONVERGENCE
C=0.
DO 1460 K=K1,K5
1460 C=AMAX1(C,ABS(S(K,K2=1,1))*ABS(S(K,K2=1,1))
C=1.E=5*C
DO 1463 K=1,K5
172

1463 CONTINUE
1470 IF(L4.EQ.K5) GO TO 1498
C FINAL STORAGE OF INTEGRALS
1471 IF(MOD(NHUG,2).*EQ.0) GO TO 1504
C KRONNEKER DELTA OF EQN. (55)
   MMA=MMA+NNN+L3 = NIXIT
   DO 1505 IX= K1,K5
   NUTS = MMA + IX =1
   NUTS=NUTS= (NUTS/2)*2
   IF(NUTS.EQ.0) GO TO 1505
   S(IX*K2=1)= 0.
   S(IX*K2=1)= 0.
1505 CONTINUE
1504 DO 1480 K=K1,L4
   J=K+1=K1
   BINT(J+1)=S(K*K2=1,
1480 BINT(J+2)=S(K*K2=1,1)
   NOTA(5)=19*JMAX*(L4=NIXIT)
C MAKE A SUB N INTEGRALS = EQNS. (38,38PRIME*44)
   LL=L5+2*L2+2
   IF(NIXIT*NE.0) RETURN
   X(1)=EXP (=DELTA)/DELTA
   DO 1860 K=1,LL
   C=K
1860 X(K+1)=X(1)*C*X(K)/DELTA
   K5=L5+1
   IF(L2.EQ.0) GO TO 1890
1862 K3=L2=1
   K2=LL=1
1863 IF(K3)1890,1864,1870
1864 A(1)=X(K5)
   A(2)=X(K5+2)

BAI 1410
BAI 1420
BAI 1430
BAI 1440
BAI 1450
BAI 1460
BAI 1470
BAI 1480
BAI 1490
BAI 1500
BAI 1510
BAI 1520
BAI 1530
BAI 1540
BAI 1550
BAI 1560
BAI 1570
BAI 1580
BAI 1590
BAI 1600
BAI 1610
BAI 1620
BAI 1630
BAI 1640
BAI 1650
BAI 1660
BAI 1670
BAI 1680
BAI 1690
BAI 1700
BAI 1710
BAI 1720
BAI 1730
BAI 1740
BAI 1750
1870 K3*K3=1
K2*K2=2
DO 1880 K=1,K2
1880 X(K)*X(K+2)=X(K)
GO TO 1863
1890 IF(L5=1) 1893,1892,1891
1891 A(3)*X(K5=2)
1892 A(4)*X(K5=1)
1893 A(5)*X(K5)
A(6)*X(K5+1)
A(7)*X(K5+2)
RETURN
1498 WRITE(IOUT*7)
CALL EXIT
6 WRITE(IOUT*9) L2*L3*NIXIT,M
CALL EXIT
7 FORMAT(1H020X,17HBANDI-NO CONVERGE )
9 FORMAT(1H020X,16HBANDI-PARMS OUT 415)
C B LOOP FOR HETERONUCLEAR CASE
1600 DO 1604 I=1,7
1604 F(I) = B(I)*1)
GO TO 1500
END
SUBROUTINE GLIST(GINT,GT,NDIM)
C
INPUT-- SCRENNING parameter DELTA, MUST BE GREATER THAN +1.E-2.
BINT, LIST OF I INTEGRALS OUTPUT FROM BANDI PROGRAM.
LI=SIGMA ( MAY BE EITHER SIGN), L2=TAU, L5=N,
L4=MAXIMUM INDEX VALUE USED (STARTING FROM SIGMA=0), L4 IS
PRODUCED AS OUTPUT IN BANDI PROGRAM.
OUTPUT-- GINT CONTAINS OUTPUT VALUES FOR TWO-ELECTRON INTEGRALS, IN
A NUMBER DETERMINED BY L4 AND WPTBL (FROM GLIST PROG.);
USES CONSTANT DATA BLOCK DATBL$, ASSEMBLED SEPARATELY
/DATBL$ CONTAINS NO, POINTS, BLOCK FOR 40 POINTS
BLOCK FOR CORRESPONDING 40 WEIGHTS, NO. OF INITIAL POINTS ENTERING
WITH MINUS SIGN IN SCALAR PRODUCT FORMATION.

ARRAY S(I,J)=K(MJ+SIGMA) OF EQN. (56)
ARRAY GINT IS THE ARRAY OF G(I,K) INTEGRALS DEFINED BY
EQNS. (57-59)

D(I,J)=FLOAT(2*I-1)/FLOAT(I+J-1)
DD(I,J)=FLOAT(I+J-1)*FLOAT(I+J)*FLOAT(4*I+I-1)
COMMON/SPACE/ IDUM(309)
COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELTA,ZETA(5),A(7),B(7)
*BI NT(36,2),CX(7,2)
2X(44), FRAT(45,14), S(45,11)
4REST(153),ZG1(1470), RMDR(9588)
COMMON/DATBL$/D1(11,11),D1(36,7),D2(43,7),JMAX,WTINF,POINT(40)
1WT(40),NMINT,RULE(2)
DIMENSION GINT(NDIM,36)
EQUIVALENCE (IOUT,IDUM(22))
DO 1984 J=11,189
1984 X(J)=0.
LL=L5+2*L2+2
LM=L4+LL
LN=LM+1
K1=IABS(L1)

GLI 10
GLI 20
GLI 30
GLI 40
GLI 50
GLI 60
GLI 70
GLI 80
GLI 90
GLI 100
GLI 110
GLI 120
GLI 130
GLI 140
GLI 150
GLI 160
GLI 170
GLI 180
GLI 190
GLI 200
GLI 210
GLI 220
GLI 230
GLI 240
GLI 250
GLI 260
GLI 270
GLI 280
GLI 290
GLI 300
GLI 310
GLI 320
GLI 330
GLI 340
GLI 350
IF((L5*GT.8)*OR.(LM*GE.45)*OR.(DELTA*LT.0.01)) GO TO 11
DO 1862 J=1,JMAX
   R=0.0
   TEE=DELTA*POINT(J)
   IF(TEE*LT.128.0) R=W(T(J)*EXP(-TEE)/DELTA
   TEE=TEE=DELTA
1700 X(I)=POINT(J)
1701 DO 1702 K=2*LM
1702 X(K)=POINT(J)-DD(K=1)+X(K-1)
C LARGE Y*DELTA. K0 AND K1
   S(1+1)=W(T(J)*EXP(-DELTA)/DELTA = R
   S(2+1)=(S(1+1)*(DELTA+1.0)/DELTA+R*(1-POINT(J)))/POINT(J)
C LARGE Y*DELTA. REMAINING K
   DO 1710 K=2*LM
   C=K
1710 S(K+1)=((S(K+1)+R)*C*(POINT(J)=X(K))/(C=1.0)*C*S(K+1)/DELTA)
   IF(K.EQ.0) GO TO 1810
C NON-ZERO SIGMA. LARGE Y*DELTA. MAKE F
1720 K2=K+1
   DO 1721 L=K2+LM
   FRAT(L+1)=1.0
   C=L
1721 FRAT(L+2)=(X(L)*(2.0*C=1.0)/(C=POINT(J)))*DELTA/(C=1.0)
   KK9=K2+2
   IF(KK9) 1741=1741,1730
1730 C=(POINT(J)**2=1.0)*DELTA
   DO 1740 L=K2+LM
   CL=L
   DO 1740 K=1,K9
   C=K
1740 FRAT(L+K+2)=(-2.0*CK*POINT(J)*FRAT(L+K+1)*C*FRAT(L+K))*DELTA/((CL-GLI=670
   1CK=1.0)*(CL+CK))
1741 CONTINUE
C LARGE Y*DELTA. MAKE K SUB SIGMA
GLI 390
DO 1760 K=K2+LM
CC=FRAT(K+2)
IF(K2=2) 1999,1750,1742
1742 DO 1744 L=3,K2
1744 CC=CC+FRAT(K+L)
1750 C=K1
IP = K1
1760 S(K+1)=((SORT(POINT(J)*POINT(J)-1)*)**IP)*S(K+1)*FRAT(K+1)-R*CC)/XFRAT(K+K2)
C SEE IF NEW X COEFFICIENTS ARE NEEDED
IF(K1.EQ.0) GO TO 1810
C NEW X COEFFICIENTS ARE NEEDED
1800 C=K1
X(1)=C*POINT(J)
K2=K1+1
DO 1803 K=2+LN
1803 X(K)=POINT(J)=DD(K-1,K2)/X(K-1)
C ADVANCE M AND TAU
1810 K5=L2
K2=K1+2
K3=LM
K4=K1+1
IF(L2.EQ.0) GO TO 1830
1811 K6=3
1812 DO 1820 L=2,K6
S(K1+1,L)=POINT(J)*S(K2,L-1)
K3=K3+1
DO 1820 K=K2+K3
1820 S(K+L)=X(K)*S(K+1,L-1)+(POINT(J)=X(K))**S(K-1,L-1)
K5=K5+1
IF(K5) 1840,1822,1822
1822 DO 1824 K=K4,K3
1824 S(K+1)=S(K+3)-S(K+1)
IF(K5) 1999,1830,1812
1830 K6=L5+3
GO TO 1812
C COMBINE THESE RESULTS WITH I INTEGRALS
1840 IF(K3.NE.L4) GO TO 1999
1841 DD 1842 K.K4*K3
L=K*K4+1
1842 GINT(J,L)*S(K.K6)*BINT(L+1)-S(K.K6-2)*BINT(L,2)
C POINT AT INFINITY
1844 GT * 0.
IF(K1.EQ.0) GT=WTINF*(A(7)*BINT(L,1)-A(5)*BINT(L,2))
RETURN
1999 WRITE(IOUT,18)
CALL EXIT
11 WRITE(IOUT,19) DELTA,L5,LM
CALL EXIT
18 FORMAT(19020X,17HGLIST-GENERAL ERR )
19 FORMAT(19020X,16HGLIST-PARAMS OUT10.4,214)
END

** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** **** 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EQUIVALENCE (OLP+H2) * (HAM+H2(1765))
EQUIVALENCE (IQ,LSPARE)
DIMENSION OLP(42*42),HAM(42*42), LCON(NUMBR,NEL)
IND2(I*K) = MINO(I*K) + (MAXO(I*K) * (MAXO(I*K) - 1) / 2)

1 FORMAT(8E15.7)
NMAT=NCON*ND
CALL TXFORM(SPRI,UMAT,IPER,DOM,NFPAR,ITX,NFCN,INPT,HPRI)
CALL TRANS(S1,H1,SPRI,HPRI)
IF(ITX+EQ.2) GO TO 1314
L4=(NMAT*(NMAT+1))/2
WRITE(IO+1)(S1(I),I=1*NMAT)
WRITE(IO+1)(H1(I),I=1*NMAT)
WRITE(IO+1)(H2(I),I=1*L4)
IF(NOTRF+EQ.0) GO TO 1314
WRITE(IO+1)(SPRI(I),I=1*NMAT)
WRITE(IO+1)(HPRI(I),I=1*NMAT)

1314 CONTINUE
IZ=0
L1=0
DO 401 L=1*NMAT
DO 401 K=1*L
L1=L1+1
H(L1)=0.
401 S(L1)=0.

401 CONTINUE
READ(NT) IDEN
IF(IDEN(3)+NE. JCODE) GO TO 1999
DO 411 IP=1*NPERMS
READ (NT) (IPER(I),I=1*N),(UMAT(K+J),K=1*ND),J=1*ND)
DO 412 ICON1=1*NCON
II = (ICON1-1)*ND
MU=ICON1
IF((IABS(NHUG)+EQ.2)+AND+(ICON1+GT+(NCON/2))) MU=NCON/2

MTX  190
MTX  200
MTX  210
MTX  220
MTX  230
MTX  240
MTX  250
MTX  260
MTX  270
MTX  280
MTX  290
MTX  300
MTX  310
MTX  320
MTX  330
MTX  340
MTX  350
MTX  360
MTX  370
MTX  380
MTX  390
MTX  400
MTX  410
MTX  420
MTX  430
MTX  440
MTX  450
MTX  460
MTX  470
MTX  480
MTX  490
MTX  500
MTX  510
MTX  520
MTX  530
DO 412 ICON2=1,MU
JJ = (ICON2=1)*ND
406 IZ = 0
ZS1 = 1.
DO 413 IE1 = 1*N
I = LCON(ICON1,IE1)
L1 = IPER(IE1)
K = LCON(ICON2,L1)
L2=IND2(I,K)
IF(S1(L2),EQ,0.) GO TO 414
ZS1 = ZS1*S1(L2)
GO TO 413
414 IZ = IZ+1
IF (IZ=2) 415,416,412
415 K1=I
K2=K
K5=IE1
KIK=L2
GO TO 413
416 K3=I
K4=K
KJL=L2
413 CONTINUE
IF(IZ=1) 420,421,422
C NO OVERLAP WAS ZERO
420 ZH = 0.
DO 423 IE1=1*N
I = LCON(ICON1,IE1)
L1 = IPER(IE1)
K = LCON(ICON2,L1)
L2 = IND2(I,K)
ZH=ZH+H1(L2) /S1(L2)
DO 419 IE2=1*IE1
IF(IE1,EQ,IE2) GO TO 423
J=LCON(ICON1,IE2)
L3 = IPER(IE2)
L = LCON(ICON2+L3)

419 ZH=ZH+TRX(I*J*K*L*H2*S1)
423 CONTINUE
GO TO 426
C ONE OVERLAP INTEGRAL = 0. ELECTRON NO. STORED IN L3
421 ZH=HI(KIK)
DO 425 IE2=1,N
IF(IE2 EQK5) GO TO 425
J=LCON(ICON1+IE2)
L1=IPER(IE2)
L=LCON(ICON2+L1)
ZH=ZH+TRX(K1+J,K2,L,H2+S1)
425 CONTINUE
GO TO 426
C TWO FACTORS WITH ZERO OVERLAP
422 ZH=TRX(K1,K3+K2+K4,H2+S1)
IF(ZH EQ0) GO TO 412
426 ZH=ZH*ZS1
C STORE ZS1,ZH*UMAT(I,J) IN D*D BLOCKS, INDEXED AS A ROW VECTOR
DO 424 I=1,N
L1=II+1
L1=(L1*(L1-1))/2
KJL=ND
IF(IJ EQJJ) KJL=I
DO 424 J=1,KJL
L2=JJ+J+L1
IF(IJ GT0) GO TO 424
S(L2) = S(L2) + UMAT(I,J)*ZS1
424 H(L2) = H(L2) + UMAT(I,J)*ZH
412 CONTINUE
411 CONTINUE
L1=0
DO 500 I=1,NMAT
DO 500 J=1+I
L1=L1+1
HAM(I,J) = H(L1)
OLP(I,J) = S(L1)
OLP(J,I) = S(L1)
500 HAM(J,I) = H(L1)

C INVERT TOTAL MOLECULAR FUNCTION AND PICK G OR U = EQN (16)
IF(IABS(NHUG) .NE.2) RETURN
KIK=NCON/2
KJL=NMAT/2
DO 512 ICON1=1,KIK
II=(ICON1-1)*ND
JJ=II+KJL
IZ=0
DO 513 I=1,N
J=ICON(ICON1,I)
513 IZ=IZ*NFPAR(2,J)*NFPAR(3,J)
IP=ISIGN(1*NHUG)
IF(MOD(IZ+2) .NE.0) IP=IP
ZH=IP
DO 514 I=1,N
L1=I+1
L2=J+1
DO 514 J=1,KJL
514 HAM(L1,J) = HAM(L1,J) + ZH*OLP(L2,J)
512 continue

C HAM,OLP ARE CARRIED OVER INTACT TO SEARCH
RETURN

C FORTRAN TAPE KICKING MACRO TO CORRECT TAPE POSITION ERRORS
C CONSISTENTLY MADE BY HONEYWELL AUTOMATH 1800 MONITOR
1999 IF(IZ.EQ.1313) CALL EXIT
WRITE(IO,105) JCODE,IDEN(3)
IZ=1313
REWIND NT

MTX 1240
MTX 1250
MTX 1260
MTX 1270
MTX 1280
MTX 1290
MTX 1300
MTX 1310
MTX 1320
MTX 1330
MTX 1340
MTX 1350
MTX 1360
MTX 1370
MTX 1380
MTX 1390
MTX 1400
MTX 1410
MTX 1420
MTX 1430
MTX 1440
MTX 1450
MTX 1460
MTX 1470
MTX 1480
MTX 1490
MTX 1500
MTX 1510
MTX 1520
MTX 1530
MTX 1540
MTX 1550
MTX 1560
MTX 1570
MTX 1580
GO TO 410
105 FORMAT(1H020X,15HWRRONG PERM TAPE216)
END

** **** **** **** **** **** **** **** **** ****
SUBROUTINE TXFORM(S1,S,NORD,IORD,NFPAR,ITX,N,IN,H1)
TXF 10
C
PREPARE TRANSFORMATION MATRIX
TXF 20
C
THE TAG NOTRF DETERMINES THE TYPE TRANS.
TXF 30
C
NOTRF*LT*0 = CONSTANT TRANS BY INPUT CARDS
TXF 40
C
NOTRF*EQ*0 = NO TRANSFORMATION
TXF 50
C
NOTRF*GT* ZERO = TRANSFORMATION IS TO BE CALCULATED
TXF 60
COMMON/C1J/C(16,16),NOTRF,NU,MU,I,J,K,L,HH,JUNK(4)
TXF 70
DIMENSION S1(136),S(16,16),NORD(16),IORD(16),NFPAR(6,16)
TXF 80
DIMENSION H1(136)
TXF 90
IND2(I,K)=MINO(I,K)+(MAXO(I,K)*MAXO(I,K)-1)/2
TXF 100
IF(NOTRF*LE*0) RETURN
TXF 110
50 IF(NOTRF*EQ*1) GO TO 54
L=0
DO 55 I=1,N
DO 55 J=1,I
L=L+1
55 S(J,I)=S1(L)
GO TO 63

54 L=0
DO 51 I=1,N
DO 51 J=1,I
L=L+1
S(I,J)=0.
S(J,I)=0.
IF(I*EQ*J) S(I,I)=S1(L)
TXF 170
51 CONTINUE
K=NU+1
DO 52 I=K,N
DO 52 J=1,NU
IF(NFPAR(S1*1)*EQ*0) GO TO 52
L=IND2(I,J)
S(J,I)=S1(L)
TXF 250
52 CONTINUE
52 CONTINUE
63 NORD(I)=1313
   CALL D23CHO(N*S,C,C,C,1ORD,NORD,16)
   DO 64 I=1,N
   DO 64 J=1,N
64   C(I,J)=S(J*1)
   RETURN
   END

**   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****   ****
** SUBROUTINE TRANS (SPRI*HPRI*S1*HI)                 **
C APPLIES A TRANSFORMATION C(I,J) IN /CIJ/ TO H1,S1, STORING
C THE RESULT IN THE LAST 272 WORDS OF /WORK/
C TRANSFORMATION IS SUPPLIED ELSEWHERE BY INPUT CONSTANTS OR CALC.
   COMMON/SPACE/ZA,ZB,RN,NHUG,NCON,MULT,KW,KD,KR,KOR,NT,INT,JCODE*
   INPERMS*ND*NCN,MMAT*N10,MMAT*NE,NPC,LSPARE,MSPARSE,ITX,N1,NC1,NC2P,TRA
   2LSRC,JKW3,LIAR,STEP1,STEP2,ED,NO,MO,IS,A1,A2,EFN,SAVEA(9)*MAD(2)TRA
   3,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),TRA
   4DEL(25),RMAX,RMIN,STEP,STEP3  
   COMMON/CIJ/C(16,16),NOTRF,NU,MU,F10,J,K,L,L1,HH,SS,CO,SAM
   DIMENSION S1(136),HI(136),SPRI(136),HPRI(136)
   INDZ(I*1)*MINO(I*1)+(MAXO(I*1)*MAXO(I*1)-1)/2)
   IF(NOTRF*NE.*0) GO TO 10
   DO 11 I=1,MMAT
   HPRI(I)=HI(I)
11   SPRI(I)=S1(I)
   RETURN
10   L1=0
   SAM=1.E+10
   DO 1 I=1,NFCN
   DO 1 K=1,I
   L1=L1+1
   HH=0.
   SS=0.
   DO 2 J=1,NFCN
   IF(C(I,J)*EQ.0.0) GO TO 2
   DO 3 L=1,NFCN
      TRA 330
   TRA 340
   TRA 350
   TRA 360
   TRA 370
   TRA 380
   TRA 390
   TRA 400
   TRA 10
   TRA 20
   TRA 30
   TRA 40
   TRA 50
   TRA 60
   TRA 70
   TRA 80
   TRA 90
   TRA 100
   TRA 110
   TRA 120
   TRA 130
   TRA 140
   TRA 150
   TRA 160
   TRA 170
   TRA 180
   TRA 190
   TRA 200
   TRA 210
   TRA 220
   TRA 230
   TRA 240
   TRA 250
   TRA 260
   TRA 270
IF(C(K*L)*EQ*0.) GO TO 3
INDX=IND2(J*L)
C0=C(I,J)*C(K*L)
SS=SS*C0*S1(INDX)
HH=HH*C0*H1(INDX)
3 CONTINUE
2 CONTINUE
IF((K*EQ*1.)*AND*(SS*LT*SAM)) SAM=SS
SPRI(L1)=SS
HPRI(L1)=HH
1 CONTINUE
SAM=1.E-7*SAM
DO 4 I=1,MMAT
IF(SPRI(I)*LE*SAM) SPRI(I)=0.*
4 CONTINUE
RETURN
END

** FUNCTION TRX(I,J,K,L,H2,S1) **

C CALCULATES THE TRANSFORMED TWO-ELECTRON INTEGRALS UNDER THE
C TRANSFORM C(I,J) STORED IN /CIJ/
C THE TRANSFORM IS DEFINED AS FOLLOWS X(K)=(SUM(L)) OF C(K,L)*XPRI(L) TRX
COMMON/SPACE/LA,ZBR,NHUG,NCON,MULT,KW,MR,KOR,TNT,NT,JCODE,
INPERMS,NDI,NFCN,MMAT,N10,MMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,TRX
2LSRCH/KW3,LIAR,STEP1,STEP2,EO,NO,MOSIS,A1,A2,EFIN,SAVEA(9),MAD(2) TRX
3,FPAR0(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), TRX
4,DELT2(25),MMAX,RMIN,STEP1,STEP3,TRX
COMMON/CIJ/C(16,16),NOTRF,NMU,HI,J1,K1,L1,IDX1,IDX2,IDX3,M1,M2
DIMENSION H2(9317),S1(136)
IND2(I*K)=MINU(I*K)+(MAXO(I*K)+(MAXO(I*K)-1)/2)
TRX=0.*
M1=IND2(I,K)
M2=IND2(J,L)
IF(NOTRF*NE*0.) GO TO 10
IF((NFPAR(3,I)-NFPAR(3,K)+NFPAR(3,J)-NFPAR(3,L))*NE*0.) RETURN
IDX1=IND2(M1,M2)
185

```
TRX=H2(IDX1)
GO TO 11
10 DO 1 I1=1,NFCN
IF(C(I*I1)=EQ.0.) GO TO 1
DO 2 J1=1,NFCN
IF(C(J*J1)=EQ.0.) GO TO 2
DO 3 K1=1,NFCN
IF(C(K*K1)=EQ.0.) GO TO 3
DO 4 L1=1,NFCN
IF(C(L*L1)=EQ.0.) GO TO 4
IF((NFPAR(I*I1)=NFPAR(3*K1)*NFPAR(3*J1)-NFPAR(3*L1))=NE.0.) GO TO 5
IDX1=IND2(II+K1)
IDX2=IND2(J1+L1)
IDX3=IND2(IDX1+IDX2)
TRX=TRX+C(I+I1)*C(J+J1)*C(K+K1)*C(L+L1)*H2(IDX3)
5 CONTINUE
4 CONTINUE
3 CONTINUE
2 CONTINUE
1 CONTINUE
11 IF(NOTRF.GT.0) RETURN
IF(S1(M1)=NE.0.) TRX=TRX/S1(M1)
IF(S1(M2)=NE.0.) TRX=TRX/S1(M2)
RETURN
END
```
SUBROUTINE SEARCH
CONTROLLING PROGRAM OF SEARCH BRANCH

ENERGY CALCULATION AND PARAMETER SEARCH LINK

COMMON/SPACE/ZAKRomerNHUGNCONMULTKwKORNTJNTJCODE
1NPERMSNDNFCNNMATN10NMTANENPCLSPAREMSPARSEITXN1NC1NC2P
2LSRCHJKW3LIARSTEP1STEP2EONOOMOISAZAEFINSAVEA(9)MAD(2)
3*FPARO(2,16)FPAR(2,16)NFPAR(6,16)ITAG(16)ICTAG(6)LCON(6,8)
4FELT(25)RMAXRMINSTEP3
COMMON/WORK/OVRLAP(42,42)HAMILT(42,42)COET(42,42)COET0(42,42)
*OVP(42,42)HAM(42,42)E(42)E1(42)E2(42)E3(42)KOIO1JTEMPNE1
XFINK(1760)SIG
COMMON/IAIBLS/D1(11,11)DD1(36,7)DD2(43,7)JMAXwTINFPPOINT(40)
1WT(40)XMINUSRULE(2)
COMMON/C1J/C(16,16)NOTRFNUMUVRUD(9)
DIMENSION D(6),Z(6),ENERG(6),X(2),Y(2),A(6)
EQUIVALENCE (D,FELT(1)) (X,E1) (Y,E2) (A,E3) (Z,ENERG) (Z,FELT(7))
EQUIVALENCE (DELT,FELT(25))
EQUIVALENCE (MSPARSE,ID)
EQUIVALENCE (ID,LSPARSE)
EQUIVALENCE (ITAG(5),PA)
DIMENSION AG(2)

1984 DATA (AG(1),AG(2),AG(2)6HOVRLAP6HHAMILT/
109 FORMAT (I3X,5HFPAR(12,1H12,2H)=F10.5/X+4HNC1#15)
104 FORMAT (1H0*10PARAMETERS/)
105 FORMAT (5X,I3*2F12.6,3X613)
106 FORMAT (1H0*13*7E15.7)
107 FORMAT (1H0*10X,3HE=E16.8,7HFCN(I2.1H12,7H)KOR#13,
*8HSTEPS2F14.6)
305 FORMAT (1H0*20X,A6,1X6HMATRIX)
DD 101 I=1*NMAT
DD 101 J=1
OVP(I,J)=OVRLAP(I,J)
OVP(1,J)=OVRLAP(1,J)
SCH 10
SCH 20
SCH 30
SCH 40
SCH 50
SCH 60
SCH 70
SCH 80
SCH 90
SCH 100
SCH 110
SCH 120
SCH 130
SCH 140
SCH 150
SCH 160
SCH 170
SCH 180
SCH 190
SCH 200
SCH 210
SCH 220
SCH 230
SCH 240
SCH 250
SCH 260
SCH 270
SCH 280
SCH 290
SCH 300
SCH 310
SCH 320
SCH 330
SCH 340
SCH 350
OVRLAP(J,I) = OVRLAP(I,J)
HAMILT(J,I) = HAMILT(I,J)
HAMILT(J,I) = HAMILT(I,J)
101 WRITE(10,104)
DO 110 J = 1,NFCN
110 WRITE(10,105) J, FPAR(1,J), FPAR(2,J), (NFPAR(I,J),I=1,6)
E2(I) = 0.
CALL D23CHO(NMAT, OVP, HAM, COET, COET0, E, E2, ID)
NE1 = NE1 + 1
IF(EFIN.EQ.0.) GO TO 1000
IF(E(NE1).GT.EFIN) GO TO 1000
WRITE(10,1003)
1003 FORMAT(1M020X,14HENERGY, LT, MIN.)
GO TO 31
1000 CONTINUE
WRITE(10,106) (E(I), I = 1, NMAT)
WRITE(10,107) (NE1), NO, MO, KOR, STEP1, STEP2
1005 GO TO (200, 400, 262, 200), ITX
200 CONTINUE
IF(KR.NE.0.) GO TO 2
KR = KW
KW = KOR
GO TO 3
2 KD = KR
KR = KW
KW = KO
3 N10 = N
412 E0 = E(NE1)
IF(NPC.EQ.0.) GO TO 53
KD = MO*NFCN/2
IF(NOTRF.EQ.1) KD = MO*(NFCN-NU)/2
WRITE(10,305) AG(1)
CALL PMA(OVRLAP, NMAT, E3, 0, E, ID, IO)
WRITE(10,305) AG(2)
CALL PMA(HAMILT,NMAT,E3,O,E,ID,IO)
ITX=2
KOR=0
GO TO 401

400 KO= MO*NFCN/2
IF(NOTRF*EQ.1) KO=MO*(NFCN=NU)/2
IF(E(NE1)>E(KO)) GO TO 401
MU=KR
KR=KW
KW=MU
FPAR0(NO,KO)=FPAR(NO,KO)
IF(ITAG4*EQ.0) FPAR0(NO,KO)=FPAR(NO,KO)
E0=E(NE1)

401 KOR=KOR+1
CALL SSWITCH(4,IREX)
IF(IREX*EQ.2) GO TO 403
RMAR=RMIN
LIAR=1
GO TO 62

403 IF(LSRCH*EQ.0) GO TO 402
C LINEAR STEP SEARCH ONLY
IF(KOR*EQ.LSRCH) GO TO 804

805 FPAR(NO,KO)=FPAR(NO,KO)*STEP1
GO TO 11

804 FPAR(NO,KO)=FPAR(NO,KO)
GO TO 40

402 CONTINUE
CALL SSWITCH(5,IREX)
IF(IREX*EQ.1) GO TO 998
ENERGY(KOR)=E(NE1)
IF((NO,EQ.2)*AND.(IS,LE.1)) GO TO 500

1500 D(KOR)=FPAR(NO,KO)
GO TO (10,20,31,540), KOR
C DELTA SEARCH
10 PA=1.
21 FPAR (NO,MO) = D(KOR) + PA*STEP1
11 SIG = 1.
   IF (ZA*EQ.ZB) AND (MOD(NHUG,2)*EQ.0)) SIG = 1.
12 IF (FPAR(1,MO) * LT .0.01) FPAR(1,MO) = .01.
   IF (ABS(FPAR(2,MO)) * GT 1.0*FPAR(1,MO)) FPAR(2,MO) = SIGN(1.0*FPAR(1,MO))
   FPAR(1,MO) = FPAR(2,MO)
   IF (ITAG(4) * EQ.0) GO TO 241
   FPAR(1,MO) = FPAR(1,MO)
   FPAR(2,MO) = SIG*FPAR(2,MO)
241 RETURN
20 IF (Z(2) * LT *Z(1)) GO TO 21
   PA = 1.
   FPAR(NO,MO) = D(1)*PA*STEP1
   GO TO 11
31 IF (Z(3) * GT .00) GO TO 30
   IF (ABS(FPAR(1,MO)) * LT .001) GO TO 30
   IF (ABS(FPAR(2,MO)) * GT (1.09*FPAR(1,MO))) GO TO 30
33 Z(1) = Z(2)
   Z(2) = Z(3)
   D(1) = D(2)
   D(2) = D(3)
   KOR = 2
   PA = 1.5*PA
   GO TO 21
30 A(5) = 0.
   DO 131 1 = 1,3
      X(I) = D(I)*D(1)
      Y(I) = D(I)
   131 CONTINUE
      A(1) = Z(1) * Y(2) * Y(3) * Y(1) * (Z(3) = Z(2) + Z(2) * Y(3) - Y(2) * Z(3)
      A(2) = X(1) * (Z(2) = Z(3) + Z(1) * (X(3) = X(2) + X(2) * Z(3) - Z(2) * X(3)
      DELT = 5*A(2)/A(1)
      WRITE(IO,109) NO,MO,DELT,NC1
      IF (A(1)/(D(1) = D(2)) * (D(1) = D(3)) * (D(2) = D(3))) 35*999,32
32 FPAR (NO,MO) = DELT
DO 34 I=1,3
  IF(ABS(DELT-D(I))*LT.1.E-5) GO TO 40
34 CONTINUE
GO TO 11
999 NFPAR(6,MO)=1
  IF(NO.EQ.2) NFPAR(6,MO)=2
40 KOR=1
  PA=1.
  Z(1)=EO
  FPAR(NO+MO)=FPAR0(NO+MO)
  IF(ITAG(4)*NE.0) FPAR(NO+KO )=FPAR0(NO+KO )
41 IF(NO.EQ.2) GO TO 60
  IF(NFPAR(6,MO)*GE.2) GO TO 60
  NO=NO+1
  D(1)=FPAR(NO+MO)
  IF(IS*GT.1) GO TO 10
C INITIAL ALPHA SEARCH
500 GO TO (D10*520, 30*540), KOR
510 D(3)=D(1)/2.
  D(2)=D(1)+D(3)
  FPAR(NO+MO)=D(2)
  GO TO 11
520 FPAR(NO+MO)=U(3)
  GO TO 11
540 NC2P=0
  DO 541 I=1,4
  IF(ABS((Z(I)-Z(4))/Z(4))*LT.1.E-5) NC2P=NC2P+1
541 CONTINUE
C SET TAG IF ENERGY IS INDEPENDENT OF PARAMETER
  IF(NC2P.EQ.4) NFPAR(6,MO)= NO + NFPAR(6,MO)
  GO TO 40
60 IF(MO.EQ.NPC) GO TO 61
  MO=MO+1
  KO=KO+1
  NO =1
IF((NFPAR(6*MO).EQ.1).OR.(NFPAR(6*MO).GE.3)) GO TO 41
D(1)=FPAR(NO*MO)
GO TO 10
61 IF(STEP1.LE.STEP2) GO TO 62
STEP1=3*STEP1
IF(STEP1.LT.STEP2) STEP1=STEP2
LSRCH=0
65 IS=IS+1
64 MO=1
NO = 1
IF(NOTRF.EQ.0) NU=0
MO=MO+NU
KO=(NFCN=NU) /2 +1
D(1)=FPAR(NO*MO)
GO TO 10
62 ITX=3
DO 63 J=1,2
DO 63 J=1,16
63 FPAR(I,J)=FPAR0(I,J)
RETURN
262 CONTINUE
53 CONTINUE
531 ITX=0
RETURN
35 WRITE(10,108)
108 FORMAT(1H020X,17HGR.SRCH SEEKS MAX )
GO TO 40
997 FORMAT(1H010X,15HEND SRCH OF FCN 214/)
998 WRITE(10,997) NO*MO
C THIS CANNOT BE DONE ON IBM 7094
PAUSE 998
NFPAR(6*MO)=NO + NFPAR(6*MO)
GO TO 40
END
SUBROUTINE D23CHO \((n, s, h, p, c, e, n, n, i, d)\)

SOLVES GENERAL SECULAR EQUATION \((h-e) = 0\) WHERE S NEED NOT BE DIAGONAL

AL. BY CHOLESKY-BANACHIEWICZ ALGORITHM

IF \(n(n)\) IS SET TO 1313 PRIOR TO ENTRY, PROGRAM DETERMINES LINEAR

TRANSFORMATION TO ORTHONORMALIZE BASIS SET WHOSE GRAM DETERMINANT

IS STORED IN ARRAY NAMED S

DIMENSION S(I,1), H(I,1), P(I,1), C(I,1), E(I,1), N(I,1)

EQUIVALENCE (N, T, L), (NT, K)

120 FORMAT(1H0Z0X, 1BCOMVRAP NOT POS DEFE15, 7, 214)

IF(N, G, T, 1) GO TO 100

E(1), = H(11)/S(1,1)

P(1,1), = 1.

RETURN

CALCULATE UPPER TRIANGULAR MATRIX

100 DO 10 I=1, N

L = I-1

DO 10 J=1, N

HH = S(I,J)

IF(L, G, T, 0) GO TO 5

3 DO 4 K=1, L

4 HH = HH - S(K, J)*S(K, I)

IF(I, G, T, J) GO TO 7

6 S(I, J), = HH/S(I, I)

GO TO 10

7 IF(HH, G, T, 0, E, 5) GO TO 75

C IBM COMMON/SPACE/KLUTZ(309)

C IBM EQUIVALENCE (IDJT, KLUTZ(22))

C IBM WRITE(1OUT, 120) HH, I, J INSTEAD OF PRINT STATEMENT

PRINT 120, HH, I, J

IF(HH, G, T, 0, E, 0) GO TO 75

IF(N, G, T, 1, E, 1313) CALL EXIT

IF(ABS(HH)+L+1, E, 7) GO TO 74

CALL EXIT

74 DO 30 K=1, N

S(I, K), = 0.

CHO 10

CHO 20

CHO 30

CHO 40

CHO 50

CHO 60

CHO 70

CHO 80

CHO 90

CHO 100

CHO 110

CHO 120

CHO 130

CHO 140

CHO 150

CHO 160

CHO 170

CHO 180

CHO 190

CHO 200

CHO 210

CHO 220

CHO 230

CHO 240

CHO 250

CHO 260

CHO 270

CHO 280

CHO 290

CHO 300

CHO 310

CHO 320

CHO 330

CHO 340

CHO 350

192
S(K*I) = 0.0
H(K*I) = 0.0
30 H(I*K) = 0.0
   S(I*I) = 1.0E-10
   H(I*I) = 1.0E+5
   GO TO 10
75 S(I+J) = SQRT(HH)
10 CONTINUE
C
   INVERSE MATRIX IN UPPER TRIANGLE
   DO 18 J=1,N
      L = J-1
      DO 18 I=1,N
      IF(I=J) 12,11,20
20   S(I+J) = 0.0
      GO TO 18
11   S(J+J) = 1.0 / S(J+J)
      GO TO 18
12   HH = 0.0
13   DO 14 K=1,L
14   HH = HH-5(K+J)*S(I+K)
15   S(I+J) = HH/S(J+J)
18   CONTINUE
   IF(NN(I)*EQ.1313) RETURN
C
   TRANSFORM H-MATRIX
   DO 29 I=1,N
   DO 29 J=1,N
   HH = 0.0
   DO 28 K=1,I
   DO 27 L=1,J
   HH = HH+S(L+J)*S(K+I)*H(K+L)
27  CONTINUE
28  CONTINUE
   P(J+I) = HH
29   P(I+J) = HH
   CALL EIG(N+P+L+J,D)
N1=N
DO 2 I=1,N1
E(I)=P(I,I)
2 NN(I)=1
IF (N1*E(I,1) .GT. 0.0) GOTO 40
NT=N1
1 NT=NT+1
NTA=0
C ORDER EIGENVALUES AND EIGENVECTORS
DO 33 J=1,NT
IF((E(J+1)-E(J)) .GE. 0.0) GOTO 33
HH=E(J+1)
E(J+1)=E(J)
E(J)=HH
I=NN(J+1)
NN(J+1)=NN(J)
NN(J)=1
NTA=1
33 CONTINUE
IF((NTA .EQ. 1)) GOTO 1
C TRANSFORM C TO P
DO 40 J=1,N
NT=NN(J)
DO 21 I=1,N
HH=0.0
DO 22 K=1,N
HH=HH+S(I,K)*C(K,NT)
21 P(I,J) = HH
RETURN
END
SUBROUTINE EIG (N,H,C,ID)
C FINDS EIGENVALUES AND COLUMN EIGENVECTORS BY JACOBI METHOD
C INPUT MATRIX IS H, EIGEN VALUES RETURNED IN H(I,I)
C VECTOR MATRIX IS C, SET TO IDENTITY MATRIX IN THIS ROUTINE
DIMENSION H(ID,ID),C(ID,ID)
IF(N.EQ.1) RETURN
C ENTER UNITY-MATRIX
DO 99 II=1,N
   DO 98 JJ=1,N
      98 C(II,JI)=0.
      99 C(II,II)=1.
      SIG=N *N
      TR=0.*
      DO 1 JJ=2,N
         M=II-1
         DO 1 JI=1,M
            H(JI,II)=H(II,JI)
            TR=TR+ABS(H(II,JI))
         1 IF(TR*EQ.0.*0.) RETURN
            SUM=TR
            THRESH=1.E-15*TR
            TR=SUM/SIG
            LTAG=0.
            SUM=0.*
            M = N-1
            KKK=0
            DO 137 K=1,M
               KKK=KKK+1
               L=K+1
               DO 137 JI=KKK*K
               DO 137 II=L,N
                  SUM=SUM+ABS(H(II,JI))
               137 IF(ABS(H(II,JI))*LE.*TR) GO TO 137
                  LTAG=1.
                  P=1.
                  EIG 10
                  EIG 20
                  EIG 30
                  EIG 40
                  EIG 50
                  EIG 60
                  EIG 70
                  EIG 80
                  EIG 90
                  EIG 100
                  EIG 110
                  EIG 120
                  EIG 130
                  EIG 140
                  EIG 150
                  EIG 160
                  EIG 170
                  EIG 180
                  EIG 190
                  EIG 200
                  EIG 210
                  EIG 220
                  EIG 230
                  EIG 240
                  EIG 250
                  EIG 260
                  EIG 270
                  EIG 280
                  EIG 290
                  EIG 300
                  EIG 310
                  EIG 320
                  EIG 330
                  EIG 340
                  EIG 350
X = H(I1+J1)
CC = 5*(H(I1+I1)-H(J1+J1))
IF (CC LT 0.0) P = P
P = P*X/SURT(X*X*CC*CC)
CC = SQRT(1.0*P*P)
S = P/SQT(2.0*(1.0*CC))
SS = S*S
CC = 1.0*SS
X = SQRT(CC)
S2 = 2.0*X*S
C
TRANSFORM 2X2 BLOCK
P = H(I1+I1)+H(J1+J1)
CC = H(I1+I1)*CC = H(I1+J1)*S2 = H(J1+J1)*SS
SS = P = CC
DO 242 JP = 1+N
P = H(I1+JP)
H(I1+JP) = P*X = H(J1+JP)*S
H(J1+JP) = P*S + H(J1+JP)*X
H(JP+1) = H(I1+JP)
H(JP+J1) = H(J1+JP)
P = C(JP+I1)
C(JP+I1) = P*X = C(JP+J1) * S
C(JP+J1) = P*S = C(JP+J1) * X
242 CONTINUE
H(I1+I1) = CC
H(J1+J1) = SS
H(I1+J1) = 0.0
H(I1+J1) = 0.0
137 CONTINUE
IF (LTA@EQ.1) GO TO 107
IF (SUM.GT.THRESH) GO TO 105
RETURN
END
SUBROUTINE PMA (A,N,NN,NBOOL,E,ID,KU)

C PRINTS MATRICES AND ARRAYS
C
C NBOOL = 0 SYMMETRIC, PRINT LOWER TRIANGLE
C NBOOL = 1 UNSYMMETRIC MATRIX, E(I) IS NOT PRINTED
C NBOOL = 2 UNSYMMETRIC MATRIX, PRINT OF VECTOR E
C KO= IDENT. OF COMMON OUTPUT DEVICE(TAPE,DISC)
C
DIMENSION A(ID,ID),NN(ID),E(ID)

101 FORMAT(1H0,10X,7(I10,5X))
102 FORMAT(17,3X,7E15.7)
103 FORMAT (/)
104 FORMAT (10X,7E15.7)

DO 13 I=1,N
13 NN(I) = I
LPM = 7
DO 8 JA = 1,N,LPM
JE = JA+LPM+1
IF (N*LT*JE) JE = N
3 WRITE(KO,101)(NN(J),J=JA,JE)
WRITE(KO,103)
IF (NBOOL *LT*2) GO TO 15
WRITE(KO,104)(E(J),J=JA,JE)
WRITE(KO,103)
15 L = JA
IF (NBOOL * NE * 0) L=1
DO 7 I=L+1,N
IE = JE
IF (NBOOL * NE * 0) GO TO 6
IF (I*LT*JE) IE=I
6 WRITE(KO,102)(NN(I),8(A(I,J),J=JA,IE))
7 CONTINUE
8 CONTINUE
RETURN
END
SUBROUTINE OUTPJ (LCON, NUMBR, NEL) OUT 10
CONTROLLING PROGRAM OF OUTPUT BRANCH OUT 20
PRINTS FINAL OUTPUT OUT 30
COMMONTSPACE ZA ZB R N NHUG NCON MULT K W KR KOR N T JNT JCODE OUT 40
1NPERMS ND NFCN MMAT N10 NMAT NBE NPC LSPACE MSPACE ITX N1 NC1 NC2 P OUT 50
2LSKCH J W3 LIA STEP1 STEP2 E0 NO M0 IS A1 A2 EFIN SAVEA (9) MAD (2) OUT 60
3 FPARU (1, 16) FPAR (2, 16) NFPAR (6, 16) ITAG (6) ICTAG (64) OUT 70
4DELT (25) RMAX RMIN TSTEP STEP3 OUT 80
COMMONTWORK UVRAP (42, 42) HAMiLT (42, 42) COET (42, 42) COETO (42, 42) OUT 90
*OLP (42, 42) HAM (42, 42) E (42) E4 (42, 6) A1 J K L M L1 L2 I7 I6 I5 OUT 100
IBLANK TAGIT F (1627) OUT 110
COMMONTCIJ C (16, 16) NOTRF EUGEN (11) OUT 120
DIMENSION PROD (30), TAG (6) OUT 130
EQUIVALENCE (PROD,F) OUT 140
EQUIVALENCE (10 LSPACE) OUT 150
DIMENSION LCON (NUMBR, NEL) OUT 160
SORT (X) *SQR T (X) OUT 170

999 DATA (TAG (1), i=1, 16)/1H, 1H+, 1H+, 6H HAMiLT, 6HOVRAP, 6HTRANS. / OUT 180
305 FORMAT (1HO, 20X, 66, 1X, 6H MATRIX) OUT 190
300 FORMAT ( //30H PARAMETERS FOR CONFIGURATION, 13, ) OUT 200
301 FORMAT (12H, ELECTRON, 13, F11. 5, F11. 5, 317, 6X, A1) OUT 210
302 FORMAT (21X, 48HDELTA ZETA, N, M, NU, PARITY) OUT 220
312 FORMAT (14H, ENERGY = 1PE14. 7, 6H, NE = 12, ) OUT 230
314 FORMAT (1HO, 10X, 31HENERGIES (ELECTRONIC + NUCLEAR) 24X, 21H DISSOCIATION OUT 240
10 ENERGIES / 2 (17X, 23HARTREES ELECT, VOLTS6X, 9HKCAL/ MOLE) / OUT 250
315 FORMAT (21, 10X, 3E15.7) OUT 260
320 FORMAT ( // 7X, 23HNORMALIZED COEFFICIENTS ) OUT 270
321 FORMAT ( // 7X, 12H COEFFICIENTS ) OUT 280
1313 FORMAT (1HO, 30X, 55H THE MONSTER - COURTESY OF KEN WILLIAMS AND EUGEN OUT 290
* N WE L T IN ) OUT 300
WRITE (10, 1313) OUT 310
N1 = NMAT OUT 320
N10 = N1 OUT 330
A = ZA * ZB/R OUT 340
DO 500 I = 1, NMAT OUT 350
E4(I+1)=E(I)+A
E4(I+2)=E4(I+1)*270.21
E4(I+3)=E4(I+1)*6270.71
E4(I+4)=E4(I+1)*A1-A2
E4(I+5)=E4(I+4)*270.21
500  E4(I+6)=E4(I+4)*6270.71
DO 54 K=1,N10
54    PROD(K)=0.
      L2 = NMAT=1
      DO 55 K=1,N10
      DO 55 L1 = 1,L2
      L=L1+1
      DO 55 M=L*NMAT
      PROD(K)=PROD(K)+2.*(COET(L1*K)*COET(M*K)*OVRLAP(M,L1))
      DO 56 K=1,N10
      DO 56 L=L*NMAT
      PROD(K)=PROD(K)+COET(L*K)**2*OVRLAP(L,L)
      DO 57 K=1,N10
      DO 57 L=L*NMAT
      IF(OVRLAP(I,L),GE.,0.) GO TO 57
      OVRLAP(I,L)=0.
57    COET0(I,K)=(COET(I,K)/SQRTF(PROD(K)))*SQRTF(OVRLAP(I,I))
C    OUTPUT
    CALL HDG
    WRITE(IO,312) E0*NE
    DO 350 I5=1,NCON
    WRITE(10,300) I5
    WRITE(10,302)
    DO 351 I6=1,N
    I7=LCON(I5,I6)
    BLANK=TAG(I)
    IF(MOD(NHUG,2),EQ.,0.) GO TO 996
    BLANK=TAG(2)
    IF(NFPAR(I,E+17).NE.,0) BLANK=TAG(3)
    996 WRITE(10,301) I7,FPAR (I,17),FPAR (2,17),(NFPAR (L,17),L=1,3)*BLANKOUT
351 CONTINUE
350 CONTINUE
WRITE(10,320)
CALL PMA(COE10,NMAT,F,2,E4(1,1),MSPARE,IO)
CALL HDG
WRITE(10,314)
WRITE(10,315)((E4(I,J),J=1,6),I=1,NMAT)
CALL HDG
WRITE(10,305) TAG(5)
CALL PMA(OVR,LAP,NMAT,F,0,E,MSPARE,IO)
WRITE(10,305) TAG(4)
CALL PMA(HAM1LT,NMAT,F,0,E,MSPARE,IO)
WRITE(10,321)
CALL PMA(COE1,NMAT,F,2,E,MSPARE,IO)
IF(NOTRF.EQ.0) RETURN
WRITE(10,305) TAG(6)
CALL PMA(C,NFCN,F,1,F,16,IO)
RETURN
END

* HAS=0.0*CE
BIBLIOGRAPHY


