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Symmetry and equivalence restrictions in electronic structure calculations

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Abstract

A simple method for obtaining MCSCF orbitals and CI natural orbitals adapted to degenerate point groups, with full symmetry and equivalence restrictions, is described. Among several advantages accruing from this method are the ability to perform atomic SCF calculations on states for which the SCF energy expression cannot be written in terms of Coulomb and exchange integrals over real orbitals, and the generation of symmetry-adapted atomic natural orbitals for use in a recently proposed method for basis set contraction.

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I. Introduction

For an atom or molecule with point group $\mathcal{G}$, a set of functions (such as atomic or molecular orbitals) is said to be *symmetry adapted* if each function is a basis function for an irreducible representation of $\mathcal{G}$, and the set is said to display *equivalence* if a full set of partner functions is available for each basis function. In general, for an atomic or molecular state that transforms according to a degenerate representation of $\mathcal{G}$, an unrestricted SCF or MCSCF calculation on one component of the state will not yield orbitals which are symmetry adapted or equivalent. For example, SCF optimization of the fluorine atom configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z$$

will produce a $2p_z$ orbital with a different radial function (inequivalent) from $2p_x$ and $2p_y$. In addition, if a spin unrestricted approach is used, the orbitals associated with α or β spin will also differ. An MCSCF optimization of a ^2D state using the two configurations s^2d and sd^2 will produce optimum orbitals which are of neither pure s nor pure d type. Constraining the calculation so that orbitals with all the desired symmetry properties are obtained is referred to as imposing symmetry and equivalence restrictions.

Roothaan and Bagus [1] implicitly imposed symmetry and equivalence restrictions [2] in their atomic SCF calculations by solving for only the radial part of the orbital; the angular part was determined by O(3) symmetry. Even in calculations where each orbital is expanded in the full basis set, the simple structure of SCF energy expressions (or, equivalently, of SCF reduced density matrices) allows the restrictions to be imposed via the vector coupling coefficients used to average degenerate configurations- see Jackels and Davidson [3]. For example, in the F atom ^2P case discussed above, an energy expression corresponding to an average of energy associated with the configurations having the $2p_x$, $2p_y$ and $2p_z$ orbitals successively singly occupied would be used. Jackels and Davidson also noted that if the α and β orbitals were averaged, symmetry and equivalence could be imposed in a spin unrestricted approach. In this way many atomic and molecular states can be treated at the SCF level using a molecular SCF program with little or no facilities for handling symmetry: any atomic term arising from occupations of the form $s^m p^n$ can be treated this way, for example. There are, however, states which cannot be treated in this way, such those arising from certain d^k occupations. The terms d^2 (^3F), d^3 (^4F), d^7 (^4F), d^8 (^3F), for instance, each yield average energy expressions which can be expressed in terms of Coulomb ($[ii|jj]$) and exchange ($[ij|ij]$) integrals alone only when complex orbitals are used. In terms of real orbitals, the average energy expressions contain integrals of the general form $[ij|kl]$, and such expressions cannot be handled by conventional SCF codes. Energy expressions which contain only Coulomb and exchange integrals over real orbitals can be obtained by averaging the F states above with the P states of the same spin from the same d occupation: it is actually vector coupling coefficients for these P/F averages that are given by Poirier *et al* in a recent compendium [4], although it is claimed that the coupling coefficients are for the F states.

More complicated energy expressions can be handled by an MCSCF program. However, very few MCSCF (or CI) programs exploit more than D_{2h} symmetry, and if only one component of, say, the d^2 ^3F state is optimized within D_{2h} symmetry, the final MCSCF orbitals will be symmetry adapted within D_{2h} but will not display atomic symmetry and equivalence. (It is relatively easy to eliminate the mixing of the s and d orbitals, although this will not make the five d orbitals equivalent). Similarly, the natural orbitals from a CI calculation in D_{2h} on such a state would again fail to show symmetry and equivalence. Such problems are not, of course, confined to atomic calculations, but arise in any treatment of a degenerate state within D_{2h} or its subgroups. In molecular systems symmetry and equivalence restrictions could be imposed in the same manner as Roothaan used in his work on atoms, that is, a special code for each symmetry of interest could be developed. While this might be consider an elegant approach, it is impractical since it would lead to the problem of developing and supporting a large number of very complex codes. In the present work, we first show formally how symmetry and equivalence restrictions are imposed, and then describe how these can be implemented computationally. A simple example is given to illustrate the method. This approach to symmetry and equivalence restrictions is a very powerful one, and its implementation is a much simpler task than that of extending codes designed originally for D_{2h} and its subgroups to include higher symmetries. The ability to impose symmetry and equivalence restrictions is of particular current importance in the construction of new atomic natural orbital (ANO) basis sets.

II. Symmetry Adapted Natural Orbitals and Geminals

The symmetry properties of density matrices and natural orbitals have been reviewed extensively by McWeeny and Kutzelnigg [5] and by Davidson [6], and we shall generally follow their treatment. The *kernel* of the electron density operator $\gamma(\tau;\tau')$ (τ denotes both spin and spatial coordinates) is given in terms of an orthonormal one-electron basis $\{\psi\}$ as

$$\gamma(\tau;\tau') = \sum_{pq} \psi_p(\tau)\gamma_{pq}\psi_q^*(\tau'), \qquad (1)$$

where γ_{pq} is an element of the density matrix. This is a Hermitian matrix and can be brought to diagonal form by a unitary transformation, yielding natural spin orbitals (NSOs) $\{\chi\}$:

$$\gamma(\tau;\tau') = \sum_{p} n_p\chi_p(\tau)\chi_p^*(\tau'), \qquad (2)$$

where n_p is the occupation number of natural spin orbital χ_p. The NSOs are of pure α or β spin type if the Hamiltonian contains no spin-dependent operators [5]. That is, a given NSO can be written as a product of a spatial orbital $\phi_p(r)$ (r denotes spatial coordinates) and a spin factor α or β. However, it is *not* generally the case that a given $\phi_p(r)$ will appear with both α and β spin factors: the partner function (within the given irreducible representation of the spin group) of an NSO is generally not itself an NSO. This is, in effect, a loss of equivalence properties under the spin group for the NSO. Only in the case of zero total spin projection ($M_S = 0$) is equivalence obtained. This is obviously a nuisance, as different NSOs will be obtained from density matrices for different M_S values. It is therefore customary [5,6] to define a spin-free density matrix (denoted ρ) as the sum of the α-spin and β-spin blocks of γ. It is this matrix which is normally computed as the "density matrix" in electronic structure codes, and its eigenvectors are termed natural orbitals (NOs). As will be seen, this spin-averaging is exactly analogous to imposing spatial symmetry and equivalence restrictions.

The kernel of the spin-free density operator can be written as

$$\rho(r;r') = \sum_{pq} \varphi_p(r)\rho_{pq}\varphi_q(r')^*. \tag{3}$$

It is convenient to assume that the set of orthonormal orbitals $\{\varphi\}$ possess the desired symmetry and equivalence properties. (This is not a practical restriction, as some such set of orthonormal orbitals can always be generated straightforwardly, say, by diagonalizing the one-electron part of the Hamiltonian (h). See for example Ref. 7, where it is shown that it is also trivial to sort the eigenvectors of h by irreducible representations). We denote by $\varphi_p^{\mu a}$ a basis function for row a of irreducible representation μ; p is simply a counting index. Equation (3) thus becomes

$$\rho(r;r') = \sum_{\mu\nu}\sum_{ab}\sum_{pq} \phi_p^{\mu a}(r)\rho_{pq}^{\mu a,\nu b}\phi_q^{\nu b}(r')^*, \tag{3}$$

where $\rho^{\alpha a,\beta b}$ is a sub-block of ρ. What is now desired is to obtain NOs with full symmetry and equivalence properties from ρ. Unfortunately, the eigenvectors of ρ will only display these properties when the wave function transforms according to a non-degenerate irreducible representation of $\mathcal{G}$ [5,6]. In other cases, it is necessary to project out ρ^0, that component of ρ that transforms according to the totally symmetric irreducible representation of $\mathcal{G}$, and use the eigenvectors of ρ as the NOs. These orbitals display full symmetry and equivalence properties and differ as little as possible (in a least-squares sense [5]) from the eigenvectors of ρ itself. The following projection approach, which is essentially that used by Davidson [6], is easily implemented computationally.

The component of ρ which transforms as a basis function for row a of irreducible representation μ is obtained [6,8] as

$$\rho^{\mu a} = g^{-1}n_\mu \sum_R D_{ab}^{\mu}(R)^* R\rho R^{-1}, R \in \mathcal{G}, \tag{4}$$

where g is the order of $\mathcal{G}$ and $\mathbf{D}^\mu(R)$ is one of a set of unitary irreducible representation matrices for μ, which is of dimension n_μ. A set of basis functions for all rows of irreducible representation μ is obtained by choosing a linearly independent subset of the functions obtained using all possible values of index b in (4). For the totally symmetric irreducible representation we have

$$\rho^0 = g^{-1} \sum_R R\rho R^{-1}. \tag{5}$$

It is simplest to project ρ block by block: for block $(\rho^0)^{\mu a,\nu b}$ we obtain

$$(\rho^0)^{\mu a,\nu b} = g^{-1} \sum_R R\rho^{\mu a,\nu b} R^{-1} = g^{-1} \sum_R \sum_{cd} \rho^{\mu c,\nu d} D^{\mu}_{ac}(R) D^{\nu}_{bd}(R)^*. \tag{6}$$

But

$$g^{-1} \sum_R D^{\mu}_{ac}(R) D^{\nu}_{bd}(R)^* = n_{\mu}^{-1} \delta_{\mu\nu} \delta_{ab} \delta_{cd}, \tag{7}$$

by the great orthogonality theorem [8]. Substituting (7) in (6) gives

$$(\rho^0)^{\mu a,\nu b} = \delta_{\mu\nu} \delta_{ab} n_{\mu}^{-1} \sum_c \rho^{\mu c,\mu c} \tag{8}$$

for the only non-vanishing blocks of ρ^0. This is very simple to implement computationally: after identification of blocks of the density matrix by their transformation properties under $\mathcal{G}$, the diagonal blocks are averaged within representations, while all off-diagonal blocks are discarded. ρ^0 can then be diagonalized, to give NO occupation numbers n_p and NOs $\phi_p^{\mu a}$:

$$\rho^0(r; r') = \sum_{\mu} \sum_a \sum_p n_p \phi_p^{\mu a}(r) \phi_p^{\mu a}(r')^*. \tag{9}$$

It is easily seen that projection of that component of γ that transforms according to the totally symmetric irreducible representation of the spin group (together with a renormalization so that NO occupation numbers lie between zero and two) corresponds exactly to the spin averaging procedure described above.

The above approach is sufficient to allow symmetry and equivalence restricted NOs to be generated from a given density matrix. However, in a general energy expression the second-order reduced density matrix will also appear, and it is therefore desirable, for the purposes of averaging energy expressions, to extend the above approach to the second-order reduced density matrix. The kernel of the second-order reduced density operator [5] is

$$\Gamma(\tau_1, \tau_2; \tau_1', \tau_2') = \sum_{mnpq} \psi_m(\tau_1) \psi_p(\tau_2) \Gamma_{mnpq} \psi_n(\tau_1')^* \psi_q(\tau_2')^*. \tag{10}$$

Here, as in (1) above, $\{\psi\}$ is a set of orthonormal spin-orbitals, and $\mathbf{\Gamma}$ is the second-order reduced density matrix. Note that the indices on $\mathbf{\Gamma}$ have been ordered to correspond to those on two-electron integrals given in charge density notation. Again, in order to avoid obtaining different results for different M_S values it is usual to obtain a spin-free kernel $P(r_1, r_2; r_1', r_2')$ by averaging over spin blocks. Full details are given by McWeeny and Kutzelnigg: P and the associated reduced density matrix $\mathbf{P}$

$$P(r_1, r_2; r_1', r_2') = \sum_{mnpq} \varphi_m(r_1)\varphi_p(r_2)P_{mnpq}\varphi_n(r_1')^*\varphi_q(r_2')^*, \tag{11}$$

are the quantities computed in density matrix-driven MCSCF codes.

In terms of the orthonormal symmetry-adapted basis $\{\varphi_p^{\mu a}\}$ introduced above equation (11) becomes

$$P(r_1, r_2; r_1', r_2') = \sum_{\mu\nu\kappa\lambda}\sum_{abcd}\sum_{mnpq} \varphi_m^{\mu a}(r_1)\varphi_p^{\kappa c}(r_2)P_{mnpq}^{\mu a\nu b\kappa c\lambda d}\varphi_n^{\nu b}(r_1')^*\varphi_q^{\lambda d}(r_2')^*, \tag{12}$$

$\mathbf{P}^0$, the component of $\mathbf{P}$ that transforms according to the totally symmetric irreducible representation, is obtained by projection of symmetry blocks of $\mathbf{P}$. For a given block we have

$$\begin{aligned} g^{-1}\sum_R RRP^{\mu a\nu b\kappa c\lambda d}R^{-1}R^{-1} = g^{-1}&\sum_{ijkl} P^{\mu i\nu j\kappa k\lambda l} \\ &\times \{\sum_R D_{ai}^{\mu}(R)D_{ck}^{\kappa}(R)D_{bj}^{\nu}(R)^* D_{dl}^{\lambda}(R)^*\}. \end{aligned} \tag{13}$$

The factor in braces in (13) can be regarded as a product of elements of unitary *reducible* representations for the direct products $\mu \otimes \kappa$ and $\nu \otimes \lambda$. The unitarity of these reducible representations gives

$$\sum_R D_{ai}^{\mu}(R)D_{ck}^{\kappa}(R)D_{bj}^{\nu}(R)^* D_{dl}^{\lambda}(R)^* = n_{\mu\otimes\kappa}^{-1}\delta_{\mu\otimes\kappa,\nu\otimes\lambda}\delta_{ai,bj}\delta_{ck,dl}. \tag{14}$$

Insertion of (14) into (13) yields the final symmetrization formula, however, it is obvious from inspection of (14) that the final form will be more complicated than for the first-order case (8). In the following section we will show how the symmetrization of $\mathbf{P}$ can be avoided in MCSCF calculations. If natural geminals with symmetry and equivalence restrictions were required [5], this step would have to be performed, of course.

III. Illustration

As a simple example of using equation (8) to obtain symmetry and equivalence restricted NOs from a CI wave function, we consider the excited ${}^2E'$ state of planar $\mathrm{CH_3}$. The molecule has D_{3h} symmetry with SCF occupation

$$1a_1'^2 2a_1'^2 1a_2''^2 1e'^3. \tag{15}$$

In a program which handles only D_{2h} and its subgroups, this system must be treated using C_{2v} symmetry. The two components of the ${}^2E'$ state (15) in C_{2v} symmetry are

$$ {}^2A_1 \quad 1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^2 \tag{16}$$

and

$$ {}^2B_1 \quad 1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^1. \tag{17}$$

First, we note that if the orbitals have full D_{3h} symmetry, a CI calculation which includes all single and double excitations from *both* (16) and (17) will yield the same energy for the ${}^2A_1$ and ${}^2B_1$ states. The first-order reduced density matrices from these two CI wave functions are given in Table 1. The two problems which prevent the eigenvectors of either of these density matrices displaying D_{3h} symmetry are immediately apparent. First, density matrix elements such as $\rho_{mn}^{e'_x e'_x}$ are not equal to $\rho_{mn}^{e'_y e'_y}$ in either matrix. Second, both matrices contain non-zero elements of the form $\rho_{mn}^{a'_1 e'_x}$. It is straightforward to see that the projection procedure defined by equation (8) above eliminates both problems, and the same projected density matrix is obtained from both of the original matrices. At this stage it should be pointed out that in practical calculations it is important to ensure that phase relationships among degenerate orbitals are consistent. That is, applying the shift operator $\mathcal{P}_{ab}^{\mu}$, which generates a basis function for row a of irreducible representation μ from a basis function for row b, must yield

$$\mathcal{P}_{ab}^{\mu}\varphi_p^{\mu b} = A\varphi_p^{\mu a}, \tag{18}$$

where A is the same phase factor, for all values of the counting index p. Although this condition does not affect the computed energy, it is important in averaging to obtain symmetry and equivalence properties.

It can also be seen from Table I that the same averaged density matrix as obtained by projection can be obtained by averaging the density matrices for the two components of the $^2E'$ state, since the two wave functions and the corresponding density matrices are related by a shift operator. However, if the averaged density matrix is obtained from averaging calculations on the individual components, it is of paramount importance in practice that the component wave functions be related via a shift operator. For example, it was specified above that the CH_3 wave functions comprised all single and double excitations out of *both* components, (16) and (17). This condition is sufficient to guarantee that the CI wave functions will be related via a shift operator, even though it means that single and double excitations out of reference configurations of the "wrong" symmetry must be included. If such excitations are excluded, then the wave functions for the two components will not be related by a shift operator. This makes it impossible, for example, to impose first-order interacting space restrictions [9] on the CI wave functions. However, the symmetrization procedure of equation (8) requires only one CI calculation to be performed, and first-order interacting space restrictions can be imposed, as the symmetrization procedure effectively generates the result of applying a shift operator to this CI wave function. It therefore seems preferable to symmetrize a density matrix for a single component of a degenerate state rather than to average density matrices for all components.

The ability to obtain CI NOs with full symmetry and equivalence properties is very important for generating contracted basis sets for molecular calculations using atomic natural orbitals (ANOs) and a general contraction scheme [10]. Because of the shell structure exploited in efficient integral codes [11], it is vital that the contracted basis display full atomic symmetry and equivalence, and it is not always possible to find a suitable non-degenerate state of a given atom for generating such ANOs directly.

Our computational implementation of equation (8) for obtaining symmetry-adapted NOs is very simple and we briefly outline it here. We refer to the full symmetry it is desired to impose as "high symmetry" and the appropriate subgroup of D_{2h} as "low symmetry". Required as input is the number of high symmetry irreducible representations, their degeneracy, and the number of orbitals in each irreducible representation. Then, for each row of each irreducible representation (μa), the sequence numbers of the low symmetry orbitals which transform as basis functions for μa are given. The program loops over distinct pairs of irreducible representations μ and ν. If μ and ν are not equal, $\rho_{pq}^{\mu a,\nu b}$ is set to zero. In the case of $\mu = \nu$, $\rho_{pq}^{\mu a,\mu b}$ is set to zero for all $a \neq b$, while for $a = b$, we average $\rho_{pq}^{\mu a,\mu a}$ over all a. Diagonalization of ρ produces NOs with full symmetry and equivalence restrictions. This implementation only requires the identification of the equivalent (high symmetry) orbitals in the original orbital list.

Imposing symmetry and equivalence and restrictions in the NOs in this manner is similar to the method by used in the SCF Fock matrices, where the equivalent blocks are averaged and the off-diagonal elements set to zero. Also this method is being used in MCSCF treatments based on NOs and the BLB theorem [12].

IV. Symmetry and Equivalence Restrictions in MCSCF Calculations

We now turn to the question of imposing symmetry and equivalence restrictions in second-order MCSCF calculations. In most MCSCF methods [13] the variation of the MCSCF energy with respect to orbital rotations is written in terms of first and second-order reduced density matrices, and the methods of section II could therefore be used to impose symmetry and equivalence restrictions on the MCSCF optimization. It is possible to avoid the more complicated symmetrization of the second-order reduced density matrix, however. The MCSCF energy can be expanded in the orbital rotations as

$$E = E_0 + \sum_{p>q} g_{pq} X_{pq} + \frac{1}{2} \sum_{p>q} \sum_{r>s} H_{pq,rs} X_{pq} X_{rs}, \tag{19}$$

where E_0 is the energy with the current MOs, $\mathbf{g}$ is the gradient vector, $\mathbf{H}$ is the Hessian matrix and the antisymmetric matrix $\mathbf{X}$ is used to parametrize the orbital rotations. Seeking a stationary point of (19) leads to the Newton-Raphson equations

$$\sum_{r>s} H_{pq,rs} X_{rs} = -g_{pq}. \tag{20}$$

Symmetry and equivalence properties will be maintained only if the rotations are restricted to mix orbitals of the same symmetry type, (that is, if the only non-vanishing X_{rs} are those for which r and s transform as basis functions for the same row of the same irreducible representation), so this is the condition that must be imposed on the Newton-Raphson equations (20). Labelling the symmetry blocks in (20) explicitly, we have

$$\sum_{\nu} \sum_{b} \sum_{r>s} H_{pq,rs}^{\mu a \mu a, \nu b \nu b} X_{rs}^{\nu b \nu b} = -g_{pq}^{\mu a \mu a}. \tag{21}$$

The symmetry structure of **H** is clearly much simpler than that of the second-order reduced density matrix in equation (12), as the blocks which transform according to four different symmetry indices do not appear in (21).

For the MCSCF case, our implementation is similar in spirit to that for the first-order density matrix; we wish to specify only the number of high symmetry irreducible representations and, for each irreducible representation, its degeneracy and the list of the low symmetry orbitals associated with each of its rows μa. It is obvious that the gradient vector can be symmetrized using exactly the same scheme as for the first-order reduced density matrix. For the Hessian, it is desirable first to compress the notation somewhat. As we are interested only in rotations within symmetries, we can use a single label μa, and we can represent distinct pairs rs by a compound counting index t. The blocks of **X** of interest are then those with elements $X_t^{\mu a}$. Given the high symmetry irreducible representation and orbital list information, potential orbital mixings which would correspond to symmetry breaking can be identified. It is now possible to generate a list of allowed mixings for each irreducible representation, and to use this rather than the list information about the original orbitals. The elements of the Hessian which correspond to a mixing which breaks symmetry are now set to zero (excluding diagonal elements which can be set to an arbitrary positive value). Note that the elements of g corresponding to rotations which break the desired symmetry are eliminated in the projection of the gradient. The program loops over distinct pairs of irreducible representations μ and ν. For the case of $\mu = \nu$, and $a = b$, the Hessian blocks $H_{t\ w}^{\mu a, \mu a}$ are averaged over all a. This is equivalent to the processing of the gradient or first-order reduced density matrix with the orbital indices replaced by the compound mixing indices. For $a \neq b$, the elements $H_{t\,w}^{\mu a,\mu b} + H_{w\,t}^{\mu a,\mu b}$ are averaged for each value of $t \geq w$ over all $a > b$. Thus for an atom with d orbitals, the ten lower-triangular off-diagonal $d - d$ blocks and their transposes would be averaged. For $\mu \neq \nu$, the elements $H_{t\,w}^{\mu a,\nu b}$ are averaged for all a and b. Thus for an atom, fifteen equivalent $p - d$ blocks would have to be averaged.

In the our implementation, we explicitly store the equivalent blocks of the Hessian, thus retaining its orginal low symmetry dimension. Clearly the dimension of the Hessian could be reduced to the unique orbital mixings in the high symmetry. However, by retaining the full low symmetry Hessian dimension the program modifications are limited to the symmetrization of the Hessian. The described method to maintain orbital symmetry and equivalence during MCSCF optimizations is similar to that used by Ruedenberg, Cheung and Elbert in the ALIS program [12].

With the same techniques it is also straightforward to impose symmetry and equivalence restrictions in MCSCF calculations which include orbital-CI coupling: the CI gradient and CI Hessian can be constructed using one component of a degenerate state, while the CI/orbital coupling Hessian can be symmetrized in the same manner as the orbital gradient.

This approach can be used to obtain SCF solutions for the d occupations discussed in the introduction. For example, for d^3 there are ten determinants with $S = M_S = 3/2$, one ${}^4A_g$ and three ${}^4B_{1g}$, ${}^4B_{2g}$, and ${}^4B_{3g}$ in D_{2h} symmetry. Optimum SCF orbitals for the ${}^4F$ atomic state can be obtained by performing an MCSCF calculation with atomic symmetry and equivalence restrictions imposed, solving for any of the seven possible components: ${}^4A_g$ or the two lowest (degenerate) ${}^4B_{1g}$, ${}^4B_{2g}$, or ${}^4B_{3g}$ solutions. All seven solutions will be exactly degenerate and will yield identical orbitals. The third root in each of the B symmetries corresponds to a component of the $d^3({}^4P)$ state.

It is well known [14] that the orbitals for the lowest state arising from the $3d^n4s^2$ and $3d^{n+1}4s^1$ occupations in transition metals are very different. Using the approach described above, we have recently performed state-averaged CASSCF calculations with symmetry and equivalence restrictions for the ${}^3F$ ($3d^24s^2$) and ${}^5F$ ($3d^34s^1$) states of Ti. These CASSCF calculations were followed by CI calculations, and the CI first-order density matrices for the two states were averaged. Since full symmetry and equivalence restrictions were imposed, these averaged NOs can be used to determine an ANO contraction. As discussed by Shavitt [15] in his review of configuration interaction methods, averaged NOs are expected to be a good way of obtaining an equivalent treatment of two states, and for Ti it is found that the average NOs yield a more equivalent description of $^3F - {}^5F$ separation than either ^3F or ^5F orbitals. A $[5s\ 4p\ 3d\ 1f]$ contracted set yields a $^3F - {}^5F$ separation which agrees to within 0.03 eV with the result obtained using the uncontracted (14s 11p 6d 4f) basis set. One example of the need for methods for performing beyond-SCF calculations in which symmetry and equivalence restrictions are imposed is in the construction of such compact ANO contractions.

While the ANO contractions are one clear example of the need to impose symmetry and equivalence restrictions, it is not always an advantage to use the full molecular symmetry. One example would be the distortion away from an isolated point of high symmetry where the wave function is degenerate. The imposition of symmetry and equivalence at the high symmetry point, but not at the lower symmetry geometries could result in a discontinueous potential surface—see the discussion by Davidson and Borden [16]. One solution is to state-average for the two states, then at the high symmetry point, as discussed above, the density matrix has the full high symmetry, and the potential energy surfaces are smooth. While we have sucessfully used this approach in one application, the question of symmetry breaking is very complex and it is not yet clear how general a solution state-averaging will be.

V. Conclusions

We have presented a simple method of modifying a D_{2h}-based MCSCF/CI program to obtain full symmetry and equivalence restricted MCSCF solutions and CI natural orbitals. Among other advantages, this allows ANO basis sets to be generated using standard program systems, and SCF solutions to be obtained for cases where conventional SCF approaches cannot be used.

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Table I. The MO density matrix for the $^2E'_x$ and $^2E'_y$ components of the $^2E'$ state state of CH_3. The density matrix is blocked and labelled by C_{2v}, the symmetry used in the CI calculation, while the orbitals are labelled using D_{3h}, the symmetry of the molecule, and that used in the SCF calculation.

			a_1		
a_1' [a]	1.987957				
	1.987957				
e_x'	-0.003925	1.002602			
	0.003925	1.988767			
a_1'	0.003455	0.030386	0.010319		
	0.003456	-0.030386	0.010319		
a_1'	0.003404	-0.018831	-0.000721	0.005609	
	0.003404	0.018831	-0.000721	0.005609	
e_x'	-0.009404	0.031865	0.000381	-0.001446	0.006198
	0.009404	-0.043940	-0.000381	0.001446	0.005489
			b_1		
e_y'	1.988767				
	1.002602				
e_y'	-0.043940	0.005489			
	0.031865	0.006198			
			b_2		
a_2''	1.972070				
	1.972070				
a_2''	-0.011975	0.020990			
	-0.011975	0.020990			

[a] The top line is for the $^2E'_x$ component while the bottom line is for the $^2E'_y$ component.