A Density Matrix Approach to Multiconfiguration Calculations[*,+]

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ABSTRACT

Density matrix components are determined for a wave function of multiconfiguration type. The array containing information required to obtain the two-electron change density matrix can also be used to construct the N-electron (spin-free) hamiltonian configuration interaction matrix from the two-electron reduced hamiltonian matrix. This array can be obtained in several ways and suggests a useful conceptual organization.

N71-19137

NASA CR-116885

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[*] Research supported by the National Aeronautics and Space Administration Grant NGL 50-002-001 and the National Science Foundation Grant GP-12832.

[+] Paper given at the International Symposium on Atomic, Molecular and Solid State Theory and Quantum Biology at Sanibel Island, Florida, January, 1970.

Introduction

It is well known that reduced density matrices[1-3] provide a good way of interpreting many-electron wavefunctions. This may be a specific wavefunction for a particular system or a general wavefunction of some type. The density matrix (DM) is particularly useful in comparing functions of different types. It may be possible on the basis of a density matrix analysis to make rather general statements about the description any wavefunction of a particular type can make, as in the case of a spin-projected different orbitals for different spins single determinant.[4,5]

The density matrix formulation may also facilitate calculation by suggesting an organization which is not apparent from the wavefunction itself.[6,7] In fact, it would be desirable to work with the density matrix directly, without involving an N-electron wave function. To do so would require a solution of the N-representability problem,[4] a goal which has thus far remained ellusive. One possibility is to construct an N-representable density matrix, containing variational parameters, from a wavefunction of some type, and to work with it. The function is of course implicitly determined, but need not appear explicitly at any time.

Experience with two-electron calculations shows that it is desirable to include r_{12} explicitly in a variational function. One would thus wish to use r_{12}-containing geminals in expanding the 2-matrix. Obviously, however, only a finite number of geminals will be used and thus the rank of the 2-matrix will be finite. It can be proven for all odd $N>1$ [9] and is conjected for even $N>2$, with no known counter examples but as yet no proof, that the rank of the 1-matrix is finite if and only if the rank of the 2 matrix is finite. Introduction of r_{12} geminals into the 2-matrix produces a 1-matrix of infinte rank. It thus seems necessary either to be satisfied with approximate N-representability[10,11] or to use geminals leading to a 1-matrix of finite rank.

When the one-rank is finite, an expansion of the wave function in terms of a finite number determinants is possible. One is thus lead to consider a configuration-interaction (CI) or optimized multiconfiguration (OMC) function.[12] The conventional CI treatment is straightforward, but very many terms are required to give good results. It is hoped that by optimizing orbitals as will a relatively small number of configurations will suffice.

Density Matrix Components

The one- and two-electron reduced density matrices are given in the Löwden normalization by[2]

$$\gamma(x_1, x_1') = N\int\Psi(x_1 x_2 \ldots x_N)\Psi^*(x_1' x_2 \ldots x_N)\,dx_2 \ldots dx_N \qquad (1)$$

$$\Gamma(x_1 x_2, x_1' x_2') = \binom{N}{2}\int\Psi(x_1 x_2 x_3 \ldots x_N)\Psi^*(x_1' x_2' x_3 \ldots x_N)\,dx_3 \ldots dx_N \qquad (2)$$

where as usual x_i stands for the space and spin coordinates of electron i. These density matrices can be resolved into spin components.[3,13-16] For example, if Ψ is an eigenfunction of S_z

$$\gamma(x,x') = \gamma^{++}(\underline{r},\underline{r}')\alpha(\sigma)\alpha^*(\sigma') + \gamma^{--}(\underline{r},\underline{r}')\beta(\sigma)\beta^*(\sigma')$$

$$= \gamma^c(\underline{r},\underline{r}')\ \frac{1}{2}\ \mathbb{1}^{(1)}_{\sigma} + \gamma^z(\underline{r},\underline{r}')\ \mathfrak{s}^{(1)}_z \tag{3}$$

where $\mathbb{1}^{(1)}_{\sigma} = \alpha(\sigma)\alpha^*(\sigma') + \beta(\sigma)\beta^*(\sigma')$ is the unit operator in the one-electron spin space and $\mathfrak{s}^{(1)}_z = \frac{1}{2}[\alpha(\sigma)\alpha^*(\sigma') - \beta(\sigma)\beta^*(\sigma')]$ is equivalent to the usual one electron $\mathfrak{s}_z$ when γ is considered as an operator or matrix.

The change density matrix

$$\gamma^{\circ} = \gamma^{++} + \gamma^{--} \tag{4}$$

and the spin density matrix

$$\gamma^z = \gamma^{++} - \gamma^{--}, \tag{5}$$

which vanishes identically if $M_S = 0$, are the irreducible spin-tensoral components of γ.[14]

A similar resolution of Γ is possible,

$$\begin{aligned}\Gamma(x_1x_2,x_1'x_2') = {} & \Gamma^{++++}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\alpha(\sigma_1)\alpha(\sigma_2)\alpha^*(\sigma_1')\alpha^*(\sigma_2') \\ & +\Gamma^{+-+-}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\alpha(\sigma_1)\beta(\sigma_2)\alpha^*(\sigma_1')\beta^*(\sigma_2') \\ & +\Gamma^{+--+}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\alpha(\sigma_1)\beta(\sigma_2)\beta^*(\sigma_1')\alpha^*(\sigma_2') \\ & +\Gamma^{-++-}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\beta(\sigma_1)\alpha(\sigma_2)\alpha^*(\sigma_1')\beta^*(\sigma_2') \\ & +\Gamma^{-+-+}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\beta(\sigma_1)\alpha(\sigma_2)\beta^*(\sigma_1')\alpha^*(\sigma_2') \\ & +\Gamma^{----}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2')\beta(\sigma_1)\beta(\sigma_2)\beta^*(\sigma_1')\beta^*(\sigma_2')\ .\end{aligned} \tag{6}$$

The only component with which we need be particularly concerned is the two-electron change density matrix

$$\Gamma^{\circ} = \Gamma^{++++} + \Gamma^{+-+-} + \Gamma^{-+-+} + \Gamma^{----}\ . \tag{7}$$

The integral operator of which Γ^o is the kernal acts on two-electron spatial functions or geminals and commutes with P_{12}. Thus Γ^o will have zero matrix elements between symmetric and anti symmetric geminals.[17]

It is convenient to introduce a set of ortho normal orbitals $\{\phi_i\}$ in terms of which the wave function and density matrix components can be expanded. Symmetric and antisymmetric geminals are then formed as

$$s_{ii}(\underline{r}_1,\underline{r}_2) = \phi_i(\underline{r}_1)\phi_i(\underline{r}_2)$$

$$s_{ij}(\underline{r}_1,\underline{r}_2) = 2^{-1/2}[\phi_i(\underline{r}_1)\phi_j(\underline{r}_2) + \phi_j(\underline{r}_1)\phi_i(\underline{r}_2)] \quad i<j$$

$$a_{ij}(\underline{r}_1,\underline{r}_2) = 2^{-1/2}[\phi_i(\underline{r}_1)\phi_j(\underline{r}_2) - \phi_j(\underline{r}_1)\phi_i(\underline{r}_2)] \quad i<j \tag{8}$$

In this basis Γ^o can be expressed

$$\Gamma^o = \Gamma^s + \Gamma^a \tag{9}$$

with

$$\Gamma^s(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') = \sum_{i\leq j}\sum_{k\leq l}\Gamma^s_{ij,kl}\, s_{ij}(\underline{r}_1\underline{r}_2)s^*_{kl}(\underline{r}_1'\underline{r}_2')$$

$$\Gamma^a(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') = \sum_{i<j}\sum_{k<l}\Gamma^a_{ij,kl}\, a_{ij}(\underline{r}_1\underline{r}_2)a^*_{kl}(\underline{r}_1'\underline{r}_2') \tag{10}$$

This decomposition is of course independent of the particular basis chosen.

If the hamiltonian for the N-electron system is made up of one- and two-electron terms

$$H = \sum_i f(i) + \sum_{i<j} g(ij) \tag{11}$$

Then a reduced hamiltonian H_r can be defined as

$$H_r = \frac{1}{N-1}\left[f(1) + f(2)\right] + g(12)$$

with the property that the energy of the system is given by

$$\underline{E} = \mathrm{tr}\{\underline{H}_r \underline{\Gamma}\} \tag{12}$$

If H and thus H_r are spin free, Γ can be replaced by Γ°. The reduced hamiltonian is a symmetric two-particle operator commuting with P_{12} also, and thus

$$E = \mathrm{tr}\{\underline{H}_r \underline{\Gamma}^{\circ}\} = \mathrm{tr}\{\underline{H}_r{}^{s} \underline{\Gamma}^{s}\} + \mathrm{tr}\{\underline{H}_r{}^{a} \underline{\Gamma}^{a}\} \tag{13}$$

This separation of E into contributions from symmetric and antisymmetric components is clearly related to D. W. Smith's separation into $E^{\parallel}$ and $E^{\perp}$.[18] In the present case, it is clear that the antisymmetric geminals involve a symmetry-induced correlation-like effect corresponding to the Fermi hole, while no such effect is essentially present for the symmetric geminals. In fact the two decompositions are related by

$$\begin{aligned}
\Gamma^{s}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') &= \tfrac{1}{2}\,\Gamma^{\perp}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') + \Gamma^{\perp}(\underline{r}_1\underline{r}_2,\underline{r}_2'\underline{r}_1') \\
\Gamma^{a}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') &= \Gamma^{\parallel}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') + \tfrac{1}{2}\Gamma^{\perp}(\underline{r}_1\underline{r}_2,\underline{r}_1'\underline{r}_2') \\
&\quad - \tfrac{1}{2}\,\Gamma^{\perp}(\underline{r}_1\underline{r}_2,\underline{r}_2'\underline{r}_1')\,.
\end{aligned} \tag{14}$$

If one is concerned with computational aspects, further advantage can be taken of the fact that $\underline{\Gamma}^{s}$ and $\underline{\Gamma}^{a}$, as well as $\underline{H}_r$ are symmetric matrices.

(In general they are hermitian, but in practice they will normally be real)

$$\Gamma^{x}_{ij,kl} = \Gamma^{x}_{kl,ij} \qquad x = a \text{ or } s \tag{15}$$

$$H^{x}_{ij,kl} = H^{x}_{kl,ij}$$

The arrays and trace operation can also be linearized to give expressions of the form.

$$E = \sum_{\mu} H_{\mu}\Gamma_{\mu} \tag{16}$$

This process is straightforward and well-known, so we will not give details here.

Multiconfiguration Functions.

A multiconfiguration (MC) wavefunction of the type being considered here can be written as

$$\Psi = \sum_{i} C_i\Phi_i \tag{17}$$

where the single index i stands for a set of indices $i \rightarrow (KLj)$, and

$$\Phi_i = AT_{KL}\theta_{jK} \tag{18}$$

is the antisymmetrized product of a spatial part T_{KL} and a spin part. We will not consider explicitly any symmetries other than spin and permutational, but of course orbital angular momentum or molecular point group symmetry can be treated.

The spatial function involves κ doubly occupied orbitals with indices $k_1 \ldots k_{\kappa}$, and λ singly occupied orbitals with indices $l_1 \ldots l_{\lambda}$. clearly $2\kappa + \lambda = N$. The indices K and L stand for the sets $\{k_i\}$ and $\{l_i\}$ respectively:

$$T_{KL} = \phi_{k_1}\phi_{k_1} \ldots \phi_{k_K}\phi_{k_K}\phi_{l_1} \ldots \phi_{l_\lambda} . \tag{19}$$

The spin function is then taken as

$$\Theta_{jK} = (\alpha\beta)^K \; \theta_j^{(\lambda)} \tag{20}$$

where $\theta_j^{(\lambda)}$ is the jth spin eigenfunction for the last λ electrons with the desired S and M_S values. The antisymmetrized product Φ_i is then a spin eigenfunction with the same quantum numbers. The results are essentially independent of how the spin eigenfunctions are chosen, so long as a complete set is used. It is convenient for some purposes if they are chosen orthonormal.

A large number of different types of wave functions can be written in this form. Clearly included are the conventional CI functions, in which the orbitals are fixed and only the coefficients C_i are optimized in a variational calculation and OMC functions, in which both coefficients and orbitals are optimized. It is also of interest that a variety of "Extended Hartree Fock" functions can be expressed in this form by transformation to an appropriate set of orthogonalized orbitals, such as the eigenfunctions of the charge density matrix γ°.[4] For spin-polarized HF, spin projected or spin extended HF, and even spin-optimized HF functions, the rank of γ° does not exceed N, and thus the wave function can be expanded in configurations involving not more than N orthonormal orbitals.[19] A CI function in which all singly excited configurations are included (sometimes called the polarization function) can also be cast in OMC terms in which case it too has a γ^o of rank about N so that only N optimized orbitals will suffice.[20] It will be of interest to compare these different types of functions when they are expressed in a common form.

Density Matrix Components of Multi-Configuration Functions

It is clear from expressions (1), (2) and (17) that the density matrix components for these MC functions must be expressable as

$$\Gamma^x_{ij,kl} = \sum_{t,u} P^x_{ij,kl;tu} C_t C_u^* \qquad (21)$$

$$x = s \text{ or } a$$

or

$$\gamma^y_{ij} = \sum_{t,u} P^y_{ij;tu} C_t C_u^* \qquad (22)$$

$$y = o \text{ or } z \, .$$

These equations can be taken to *define* the arrays $\underline{P}^x$, $\underline{P}^y$.

With the reintroduction of μ in place of ij,kl for convenience, the energy can now be written

$$E = \sum_{\mu} \sum_{t,u} H_\mu P_{\mu,tu} C_t C_u^* \quad . \qquad (23)$$

Two interpretations of this expression are possible. One is that suggested by the discussion above, namely that the sum over t and u is done first (at least conceptually) to give a density matrix which has been explicitly constructed from an antisymmetric wave function and is thus N-representable. The sum over μ is then done to give the energy according to Eqns (13) or (16). An alternative interpretation arises if the sum over μ is done first to give

$$E = \sum_{t,u} H^{CI}_{ut} C_t C_u^* \qquad (24)$$

$$H^{CI}_{ut} = \sum_{\mu} H_\mu P_{\mu,tu} \qquad (25)$$

Eqn (24) is the usual CI energy expression and $\underline{H}^{CI}$ is the matrix of the (N-electron) hamiltonian in the basis of the configurations Φ_i. The array $\underline{P}$ thus also provides a way of constructing the CI matrix from the elements of the reduced hamiltonian matrix.

The information which is contained in the array $\underline{P}$ is implicitly present in any CI or MC calculation. If each configuration is taken simply as an antisymmetrized product of spin orbitals with no restriction to produce S^2 eigenfunctions, then $\underline{P}$ is purely combinatorial. It elements are 0, ±1, 2 and are completely determined once a numbering scheme is decided for the configurations. If the function is a CI involving only doubly occupied orbitals, essentially the same is true. For functions involving non-trivial spin coupling, the determination of $\underline{P}$ is more difficult.

Particular elements will have different values depending on how the spin eigenfunctions are chosen. It is possible to construct $\underline{P}$'s corresponding to the use of spin projection operators of various sorts, geneologically constructed spin eigenfunctions, or even the "spin free" approach of Matsen and Poshusta.

Dr. Janet Del Bene has written a program to construct $\underline{P}$ for any choice of orthogonal spin eigenfunctions. This work and some conclusions based on it will be reported elsewhere.

We have seen that it does not matter, except possibly from a standpoint of convenience, if non-orthogonal spin eigenfunctions are used. It has been assumed throughout, however, that the orbitals are orthogonal. The use of non-orthogonal orbitals essentially invalidates the approach being presented here, since $\underline{P}$ then depends on orbital overlaps and will change as the orbital set is transformed.

When elements of the CI matrix have been constructed in practice, it has not usually been in terms of a reduced hamiltonian matrix. It is of interest to note, however, that the number of potentially independent elements in $\underline{H}^s$ plus $\underline{H}^a$ is the same as the number of potentially independent coulomb plus exchange integrals in the same basis. In defining the reduced hamiltonian all the one-electron integrals can be absorbed and need not be considered explicitly.

Thus far only permutational and spin symmetry have been considered. Other symmetries, L^2 behavior for an atom or point group symmetry for a molecule, are also of interest. The configurations can be limited, or single orbital products replaced by small, fixed linear combinations of products to give the desired behavior. There will be additional symmetry factorings of H_r and Γ°. These features can also be dealt with by appropriate constructions of P.

Discussion

As has been pointed out above, the information necessary to construct the array P exists implicitly in any MC or CI calculational scheme. The novel feature of the present approach is to separate and consider explicitly various aspects of these approaches. Such a separation is very useful conceptually, and may be of some aid in computation.

The fundamental expression, on which discussion can be based, is Eqn (23). In this equation the three aspects of the MC approach are apparent:

1) The dependence of the energy on the expansion coefficients C_i, as in any CI or MC expression.

2) The dependence on the orbitals involved, which appears here in the reduced hamiltonian matrix. Any transformation of orbitals will induce a transformation of this matrix.

3) The combinatorial and symmetry aspects which are contained in the coupling array $\underline{P}$.

The determination of $\underline{P}$ and those relationships which depend on it can be done independently of the "dynamics" of a particular variationally optimized function. It is thus more convenient to examine separately and explicitly the structural aspects of the problem. In particular, the examination of these aspects in density matrix terms represents a great simiplification over implicit consideration of complicated MC wave functions.

This approach also represents what might be called an avoidance (rather than a solution) of the N-representability problem. By formally constructing a density matrix from a wave function, N-representability is assured. Certain features which will be present if the N-representability problem can be solved then become apparent. It is still necessary to do a variational calculation. One kind of variation is the optionization of the orbital set. One can, for example, parametrize the orthogonal transformation from a fundamental basis set to the orbital set in terms of the exponential of an antisymmetric matrix. The best ways of dealing with this transformation, particularly when the size of the basis set is much larger than the number of orbitals actually used, is a difficult one and needs much more attention. This need becomes apparent in the present formulation.

Notes and References

1. It is clearly beyond the scope of the present paper to provide a survey of the density matrix literature. Early work with application to quantum chemistry is found in references 2 and 3. Surveys are available, for example, in Queen's Papers in Pure and Applied Mathematics No. 11, A. J. Coleman and R. M. Erdahl, eds., (Queen's University Press, Kingston, Ontario, 1968) or in the Ph.D. Thesis of M. B. Ruskai (University of Wisconsin, Madison, 1969).
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10. An example of the use of approximately N-representable density matrices may be found in the work of Garrod and Rosina, since they impose necessary but not sufficient conditions for N-representability and proceed with variational calculations.
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12. This is an extensive field which will not be surveyed here.

13. R. McWeeny, Proc. Roy. Soc. A253, 242 (1959).

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15. W. A. Bingel, J. Chem. Phys. 32, 1522 (1960.

16. W. A. Bingel, J. Chem. Phys. 34, 1066 (1961).

17. W. Kutzelnigg, Z. für Naturforsch. 18a, 1058 (1963).

18. D. W. Smith, Internation. J. Quantum Chem. Sanibel Proceedings 1970, to be published.

19. Each of these methods involves a single orbital product. The orbitals are in general non orthogonal, but the eigenfunctions of γ^0 provide an orthogonal basis for the space spanned, which can certainly not be greater than N in dimension.

20. The rank of γ for such a function is 2N (cf. Ruskai, ref. 1). Since the orbital parts of the α and β spin spinorbitals normally span essentially the same space, the rank of γ^0 will be about N.