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ABSTRACT

A simple perturbation theory has been developed for reduced density matrices which are known to be N-representable as functions of some set of independent parameters. Formulas are presented for single and double perturbations through second order. Extension to higher order would be possible, but involved. The results do not depend explicitly on the order of the density matrix, and when the N-particle density matrix is used, the formulas can be reduced to those of conventional Rayleigh-Schrödinger theory.

Details are given for the special cases of spin-unrestricted or extended SCF density matrices and CI or optimized multiconfiguration density matrices which are known to be N-representable.

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I. INTRODUCTION

Most of the physically interesting properties of a quantum mechanical system can be calculated from the 2-particle reduced density matrix for the system, without reference to the full wave function.[1,2] On the other hand, one often wishes to use knowledge about one problem to get information about closely related problems via the techniques of perturbation theory. It would thus be desirable to have a perturbation theory for reduced density matrices directly, without intermediate appeal to the wave function. The major difficulty in such a development is that of retaining N-representability of the density matrix, i.e., assuring that there does exist an antisymmetric wave function from which the density matrix could be derived, as it is modified under the influence of the perturbation.[3,4] One way of satisfying this requirement is by restricting the density matrix to be of a particular form known to be N-representable. Conventional Hartree-Fock perturbation theory, for example, can be expressed in terms of the Fock-Dirac density matrix.[5] A somewhat more general approach will be used here, in which the density matrix is assumed to be a function of some set of independent parameters.

In Section II the general formulas for the density matrix perturbation theory are developed and it is shown that if the N-particle density matrix is used they can be made equivalent to the usual Rayleigh-Schrödinger formulas. In Section III the cases of spin-unrestricted, spin-extended,[6,7] and configuration interaction or optimized multiconfiguration[8] density matrices are discussed. Some

specific results for these cases are given in the appendices. Results and possible applications are discussed in Section IV.

II. DEVELOPMENT OF THE THEORY

A reduced density matrix, $\underset{\sim}{\Gamma}$, is assumed to depend on a set of parameters θ_i,

$$\underset{\sim}{\Gamma} = \Gamma(\theta_i) \tag{1}$$

with the form of the dependence being such that the N-representability of $\underset{\sim}{\Gamma}$ is retained as the parameters are independently varied. Several such parametrizations are known,[6-8] and others will presumably be found in the future.

Corresponding to the reduced density matrix is a reduced Hamiltonian, $\underset{\sim}{H}$, such that the energy of the system is given by

$$E = \mathrm{tr}\{\underset{\sim}{\Gamma}\cdot\underset{\sim}{H}\} \tag{2}$$

If, as is usual, the full Hamiltonian of the system contains only one- and two-electron operators, then $\underset{\sim}{\Gamma}$ must be at least the two-particle density matrix (the 2-matrix). Higher density matrices can of course be used, but the 1-matrix will not be sufficient. The form of the reduced Hamiltonian depends on the normalization of the density matrix as well as on the full Hamiltonian.

Since the N-representability of $\underset{\sim}{\Gamma}$ is assured, it can be optimized, at least for the ground state, by the variation principle, and thus

$$\left(\frac{\partial E}{\partial \theta_i}\right)_o = \mathrm{tr}\left\{\left(\frac{\partial \underset{\sim}{\Gamma}}{\partial \theta_i}\right)_o \underset{\sim}{H}\right\} = 0 \text{ , all } i. \tag{3}$$

The subscript o refers to the fact that the derivative is to be evaluated at the set of parameter values which lead to a minimum of the energy. It should be noted that the derivatives of $\underset{\sim}{\Gamma}$ are still matrices. It is convenient to define

$$\partial_i \underset{\sim}{\Gamma} = \left(\frac{\partial \underset{\sim}{\Gamma}}{\partial \theta_i}\right)_o$$
$$\partial_i \partial_j \underset{\sim}{\Gamma} = \left(\frac{\partial^2 \underset{\sim}{\Gamma}}{\partial \theta_i \partial \theta_j}\right)_o \tag{4}$$

The form of Eqn. (3) also implies that the basis set used in evaluating the trace is fixed, i.e., does not depend on the θ_i. Part of the dependence of $\underset{\sim}{\Gamma}$ on the parameters may represent a transformation from some other basis to the fixed basis in terms of which $\underset{\sim}{H}$ is expressed.

The perturbation problem can now be considered. If the reduced Hamiltonian is of the form

$$H = H_o + \lambda V \tag{5}$$

then it is natural in the usual perturbation theory approach to assume an expansion of $\underset{\sim}{\Gamma}$ as a power series in λ . The assumptions above require that the only changes in $\underset{\sim}{\Gamma}$ are as consequences of changes in the parameter values, so a series expansion is assumed for each of them:

$$\theta_i = \theta_i^{(o)} + \lambda\theta_i^{(1)} + \lambda^2\ \theta_i^{(2)} + \ldots \tag{6}$$

The dependence of $\underset{\sim}{\Gamma}$ on the parameters, and thus on λ, may be quite complicated. It is reasonable, however, to make a Taylor series expansion about the values $\{\theta_i^{(o)}\}$ which minimize the energy in the absence of the perturbation. Then

$$\underset{\sim}{\Gamma}(\lambda) = \Gamma_o + \lambda\Sigma_i\theta_i^{(1)}\partial_i\underset{\sim}{\Gamma} + \lambda^2\left[\Sigma_i\theta_i^{(2)}\partial_i\underset{\sim}{\Gamma} + \tfrac{1}{2}\Sigma_{ij}\,\theta_i^{(1)}\theta_j^{(1)}\,\partial_i\partial_j\underset{\sim}{\Gamma}\right] + \ldots . \quad (7)$$

A similar expansion for the energy then follows

$$\begin{aligned} E &= \mathrm{tr}\,\{\underset{\sim}{\Gamma}(\underset{\sim}{H}_o + \lambda\underset{\sim}{V})\} \\ &= \mathrm{tr}\{\underset{\sim}{\Gamma}_o\,\underset{\sim}{H}_o\} + \lambda[\mathrm{tr}\{\underset{\sim}{\Gamma}_o\underset{\sim}{V}\} + \Sigma_i\theta_i^{(1)}\,\mathrm{tr}\{\partial_i\underset{\sim}{\Gamma}\underset{\sim}{H}_o\}] \\ &+ \lambda^2[\,\Sigma_i(\theta_i^{(2)}\mathrm{tr}\{\partial_i\underset{\sim}{\Gamma}\underset{\sim}{H}_o\} + \theta_i^{(1)}\mathrm{tr}\{\partial_i\underset{\sim}{\Gamma}\}) \\ &+ \tfrac{1}{2}\Sigma_{ij}\theta_2^{(1)}\theta_j^{(1)}\mathrm{tr}\{\partial_i\partial_j\underset{\sim}{\Gamma}\underset{\sim}{H}_o\}] + \ldots . \end{aligned} \quad (8)$$

The various $\theta_i^{(m)}$ are to be so chosen that the energy is minimized for any value of λ,

$$\frac{\partial E}{\partial\theta_k^{(m)}} \equiv 0 \qquad \text{for each k and m,} \quad (9)$$

and thus the coefficient of each power of λ in the expansion of this expression must vanish separately. This leads to a set of equations, many of which occur more than once, which can be used to obtain the $\theta_i^{(m)}$. The unique equations are

$$\mathrm{tr}\{\partial_k\underset{\sim}{\Gamma}\underset{\sim}{H}_o\} = 0 \quad (10)$$

$$\mathrm{tr}\{\partial_k \underset{\sim}{\Gamma} \underset{\sim}{V}\} + \sum_i \theta_i^{(1)} \mathrm{tr}\{\partial_i \partial_k \underset{\sim}{\Gamma} \underset{\sim}{H}_o\} = 0 \tag{10}$$

$$\sum_i (\theta_i^{(1)} \mathrm{tr}\{\partial_i \partial_k \underset{\sim}{\Gamma} \underset{\sim}{V}\} + \theta_i^{(2)} \mathrm{tr}\{\partial_i \partial_k \underset{\sim}{\Gamma} \underset{\sim}{H}_o\}) \tag{11}$$

$$+ \tfrac{1}{2} \sum_{ij} \theta_i^{(1)} \theta_j^{(1)} \mathrm{tr}\{\partial_i \partial_j \partial_k \underset{\sim}{\Gamma} \underset{\sim}{H}_o\} = 0 \tag{12}$$

etc.

Equation (10), it is to be recalled, implies that

$$\mathrm{tr}\left\{\left(\frac{\partial \underset{\sim}{\Gamma}}{\partial \theta_i}\right)_{\theta=\theta^{(o)}} \underset{\sim}{H}_o\right\} = 0 \qquad \text{all } i$$

and can thus, in principle, be solved for the $\theta_i^{(o)}$. Alternatively, a scheme can be empolyed in which the $\theta_i^{(o)}$ are determined by some direct minimization of the energy in the zero-order problem.[9-11] Eqn. (10) will then be satisfied by this parameter choice. It will be assumed that the $\theta_i^{(o)}$ have been determined in one way or another in the solution of the zero order problem. All derivatives of $\underset{\sim}{\Gamma}$ are understood to be evaluated at $\theta_i = \theta_i^{(o)}$. The functional form of the dependence of $\underset{\sim}{\Gamma}$ on the θ_i is assumed to be known, so that the derivatives are then also known.

A commonly occuring term in the equation is $\mathrm{tr}\{\partial_i \partial_k \underset{\sim}{\Gamma} \underset{\sim}{H}_o\}$. This can be considered to be the i, k element of a matrix $\underset{\sim}{F}$. It is also convenient to define the inverse matrix $\underset{\sim}{G} = \underset{\sim}{F}^{-1}$.

Since the parameters are chosen to minimize the energy, the determinant of the second derivative matrix is positive and the inverse exists. The equations for the first order changes in the parameters and the energy corrections through second order can then be written

$$\theta_i^{(1)} = -\sum_j G_{ij} \, \mathrm{tr}\{\partial_j \underset{\sim}{\Gamma} \underset{\sim}{V}\} \tag{13}$$

and

$$E^{(o)} = \mathrm{tr}\{\underset{\sim}{\Gamma}_o \underset{\sim}{H}_o\} \tag{14}$$

$$E^{(1)} = \mathrm{tr}\{\underset{\sim}{\Gamma}_o \underset{\sim}{V}\} \tag{15}$$

$$E^{(2)} = -\tfrac{1}{2} \sum_{ij} \mathrm{tr}\{\partial_i \underset{\sim}{\Gamma} \underset{\sim}{V}\} \, G_{ij} \, \mathrm{tr}\{\partial_j \underset{\sim}{\Gamma} \underset{\sim}{V}\} \, . \tag{16}$$

These results are readily extended to treat multiple perturbations. For double perturbation

$$H = H_o + \kappa V_1 + \lambda V_2 \, , \tag{17}$$

The first order parameter changes $\theta_i^{(1,0)}$ and $\theta_i^{(0,1)}$ are given by Eqn. (13) with $\underset{\sim}{V}$ replaced by $\underset{\sim}{V}_1$ or $\underset{\sim}{V}_2$. The zero order energy, now $E^{(0,0)}$, is still given by Eqn. (14), and the first order energies $E^{(1,0)}$ and $E^{(0,1)}$ are given by Eqn. (15) with $\underset{\sim}{V}$ replaced by $\underset{\sim}{V}_1$ or $\underset{\sim}{V}_2$. The second order energies are given by expressions similar to Eqn. (16)

$$\begin{aligned} E^{(2,0)} &= -\tfrac{1}{2} \sum_{i,j} \mathrm{tr}\{\partial_i \underset{\sim}{\Gamma} \underset{\sim}{V}_1\} G_{ij} \, \mathrm{tr}\{\partial_j \underset{\sim}{\Gamma} \underset{\sim}{V}_1\} \\ E^{(1,1)} &= -\sum_{i,j} \mathrm{tr}\{\partial_i \underset{\sim}{\Gamma} \underset{\sim}{V}_1\} G_{ij} \, \mathrm{tr}\{\partial_j \underset{\sim}{\Gamma} \underset{\sim}{V}_2\} \\ E^{(0,2)} &= -\tfrac{1}{2} \sum_{i,j} \mathrm{tr}\{\partial_i \underset{\sim}{\Gamma} \underset{\sim}{V}_2\} G_{ij} \, \mathrm{tr}\{\partial_j \underset{\sim}{\Gamma} \underset{\sim}{V}_2\}. \end{aligned} \tag{18}$$

The "interchange theorem" is evident in this expression for $E^{(1,1)}$. It should be noted that the matrix G is symmetric, since it is the inverse of a symmetric matrix.

The relationship between this method and the usual Rayleigh-Schrödinger perturbation theory can be obtained by treatment of a special case. Let $\underset{\sim}{\Gamma}$ be the full, N-particle density matrix

$$\underset{\sim}{\Gamma} = \Psi\Psi^* \tag{19}$$

and introduce as a basis the eigenfunctions of H_o

$$H_o\Phi_k = \varepsilon_k \Phi_k. \tag{20}$$

An arbitrary, normalized function can be expanded in this basis as

$$\Psi = \sum_k B_k\Phi_k \ . \tag{21}$$

It will be assumed, for convenience, that all expansion coefficients and matrix elements are real. The coefficients can be expressed in terms of independent parameters ξ_j, $j>o$, as

$$B_o = (1+\sum_j \xi_j^2)^{-1/2}$$

$$B_i = \xi_i B_o \quad i>o. \tag{22}$$

The unique coefficient B_o will be taken to be that of the ground state zero-order function, although this is not essential. This parametrization and the evaluation of derivatives will be discussed in the next section and in Appendix 2.

The matrices $\underset{\sim}{\Gamma}$ and $\underset{\sim}{H}_o$ are given in this basis by

$$\Gamma_{kl} = B_k B_l$$

$$H_{o,kl} = \epsilon_k \delta_{kl} \tag{23}$$

and thus

$$E = tr\{\underset{\sim}{\Gamma}\underset{\sim}{H}_o\} = \sum_k \Gamma_{kk} \epsilon_k \tag{24}$$

It is found that

$$\frac{\partial \Gamma_{kk}}{\partial \xi_j} = 2B_o B_k (\delta_{jk} - B_j B_k) \tag{25}$$

so that

$$\frac{\partial E}{\partial \xi_j} = 2B_o B_j (\epsilon_j - \sum_k B_k^2 \epsilon_k). \tag{26}$$

The parameter values corresponding to solutions of the zero-order problem are $\xi_j = 0$, all j, for the ground state or some $\xi_j = \infty$ and all other $\xi_i = 0$, for an excited state. Then all of the first derivatives do vanish since all but one of the B_k's will be zero. Only the ground state will be considered here. For another state it would be more convenient to pick the unique B to correspond to the state of interest.

The density matrix derivatives required are

$$\partial_j \Gamma_{kl} = \delta_{jk}\delta_{lo} + \delta_{jl}\delta_{ko} \tag{27}$$

and

$$\partial_i \partial_j \Gamma_{kk} = 2\delta_{ik}\delta_{jk} - 2\delta_{ij}\delta_{ko}. \tag{28}$$

Then

$$F_{ij} = \Sigma_k (\delta_{ik}\delta_{jk} - 2\delta_{ij}\delta_{ko})\,\varepsilon_k$$

$$= 2\delta_{ij}\,(\varepsilon_j - \varepsilon_o) \tag{29}$$

and

$$G_{ij} = \tfrac{1}{2}(\varepsilon_j - \varepsilon_o)^{-1}\delta_{ij}. \tag{30}$$

(Note that i, j >0). The resultant energies through the second order in this case are

$$E^{(0)} = \Sigma_k \delta_{ko}\ \varepsilon_k = \varepsilon_o \tag{31}$$

$$E^{(1)} = \Sigma_{k,l}\delta_{ko}\delta_{lo}V_{kl} = V_{oo} \tag{32}$$

$$E^{(2)} = -\tfrac{1}{2}\Sigma_{i,j>o}[\Sigma_{k,l}(\delta_{ik}\delta_{lo} + \delta_{il}\delta_{ko})\,V_{lk}]$$

$$\times\ \tfrac{1}{2}(\varepsilon_j - \varepsilon_o)^{-1}\delta_{ij}[\Sigma_{mn}(\delta_{jm}\delta_{no} + \delta_{jn}\delta_{mo})V_{nm}]$$

$$= \Sigma_{j>o}\ V_{jo}^{\,2}/(\varepsilon_o - \varepsilon_j). \tag{33}$$

These expressions are just those which occur in the usual Rayleigh-Schrödinger theory.

III. SOME SPECIFIC CASES

In working with density matrices in actual calculations it is usually convenient to deal with their spin components, it being assumed that the wavefunction is an eigenfunction of $\mathcal{S}_z$.[2,14-17] The components to be considered here will include the charge density, or spinless component, γ^o, and the spin density component, γ^z, of the 1-matrix, and the charge density component $\underset{\sim}{\Gamma}^o$ of the 2-matrix. Other components of the 2-matrix which might be of interest in particular problems can be treated in a similar way.

The components of the 1-matrix can be expanded in terms of a set of orbitals $\{\phi_k\}$ which are assumed to be orthonormal

$$\gamma^o(\underset{\sim}{r}_1,\underset{\sim}{r}_i) = \sum_{k1} \gamma^o_{k1}\phi_k(\underset{\sim}{r}_i)\phi_1^*(\underset{\sim}{r}_i)$$

$$\gamma^z(\underset{\sim}{r}_1,\underset{\sim}{r}_i) = \sum_{k1}\gamma^z_{k1}\phi_k(\underset{\sim}{r}_i)\phi_1^*(\underset{\sim}{r}_i). \tag{34}$$

The components of the 2-matrix can be expanded in terms of products of these orbitals. In the case of $\underset{\sim}{\Gamma}^o$, both symmetrized and antisymmetrized products occur[18].

$$s_{ij}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = (2^{-1/2})^{1+\delta_{ij}}[\phi_i(\underset{\sim}{r}_1)\phi_j(\underset{\sim}{r}_2) + \phi_j(\underset{\sim}{r}_1)\phi_i(\underset{\sim}{r}_2)] \tag{35}$$

$$a_{ij}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = 2^{-1/2}[\phi_i(\underset{\sim}{r}_1)\phi_j(\underset{\sim}{r}_2) - \phi_j(\underset{\sim}{r}_1)\phi_i(\underset{\sim}{r}_2)]. \tag{36}$$

Cross terms do not occur and $\underset{\sim}{\Gamma}^o$ can be expressed as a sum of two parts[19,20]

$$\underset{\sim}{\Gamma}^o = \underset{\sim}{\Gamma}^s + \underset{\sim}{\Gamma}^a \tag{37}$$

with

$$\Gamma^{s}(\underset{\sim}{r}_1,\underset{\sim}{r}_2;\underset{\sim}{r}_1',\underset{\sim}{r}_2') = \sum_{i>j}\sum_{k<l} \Gamma^{s}{}_{ij\ kl}\ \ s_{ij}(r_1,r_2)\ s^{*}_{kl}(r_1',r_2')$$

$$\Gamma^{a}(\underset{\sim}{r}_1,\underset{\sim}{r}_2;\underset{\sim}{r}_1'\underset{\sim}{r}_2') = \sum_{i<j}\ \sum_{k<l}\Gamma^{a}{}_{ijkl}\ \ a_{ij}(r_1,r_2)\ a^{*}_{kl}(r_1',r_2'). \qquad (38)$$

A large class of density matrices are known to be N-representable for any choice of the orbitals $\{\phi_k\}$ provided that the coefficients $\gamma^{o}{}_{kl}, \gamma^{z}{}_{kl}, \Gamma^{s}{}_{ij\ kl}$ and $\Gamma^{a}{}_{ij\ kl}$ are properly chosen.[8,9,21] The set of parameters $\{\phi_i\}$ characterizing the density matrix can thus be divided into two subsets:

1) those in terms of which the matrix expansion coefficients are expressed, to be denoted here by $\{\xi_i\}$, and

2) those characterizing a unitary transformation from a fixed orthonormal basis set of orbitals $\{\chi_K\}$ to the orbital set $\{\phi_k\}$.

The choice of the $\{\xi_i\}$ and the dependence of the density matrix components on them will be different for different types of density matrices, SCF, multiconfiguration, etc. Possible choices of the parameters characterizing the orbital transformation and the dependence of the density matrix components on them will be largely independent of the density matrix type involved. This dependence will therefore be considered first.

The $\{\phi_k\}$ can be expressed in terms of a fixed, orthonormal basis $\{\chi_K\}$

$$\phi_k = \sum_K C_{kK}\chi_K \qquad (39)$$

The matrix $\underset{\sim}{C}$ must be unitary. It will be taken here to be real, and is thus orthogonal. This restriction is usually made in actual calculations and is thus not severe. There are many ways of choosing independent parameters characterizing an orthogonal matrix. One which is useful for present purposes is to write $\underset{\sim}{C}$ as the product of a reference orthogonal matrix $\underset{\sim}{C}^{o}$ and the exponential of an antisymmetric matrix $\underset{\sim}{A}$:

$$\underset{\sim}{C} = \underset{\sim}{C}^{o} \exp \{\underset{\sim}{A}\} \quad . \tag{40}$$

The parameters are then taken to be the independent elements $A_{k1}, k>1$, of $\underset{\sim}{A}$. In the present application there are clearly advantages in taking $\underset{\sim}{C}^{o}$ to be the $\underset{\sim}{C}$ matrix of the zero-order problem. The zero order values of the parameters A_{k1} are then all zero. Certain problems arise when the size of the set $\{\chi_\kappa\}$ is much larger than that of the orbital set $\{\phi_k\}$ used. These problems will not be considered here, however.

The derivatives of the density matrix components depend on the derivatives of $\underset{\sim}{C}$, which are

$$\left(\frac{\partial C_{k\kappa}}{\partial A_{ij}}\right)_o = C_{ki}\delta_{\kappa j} - C_{kj}\delta_{\kappa i} \tag{41}$$

evaluated at A =0), as implied by the subscript o. This parameterization has been discussed previously[9-11]. Some of the density matrix and energy derivatives of convenience in the present formulation are summarized in Appendix 1.

If there is symmetry assoicated with the problem it is natural

to take the orbitals $\{\phi_k\}$ to be symmetry adapted. If the basis set is also symmetry adapted, then $\underset{\sim}{C}$ and $\underset{\sim}{A}$ will be block diagonal and the number of parameters is reduced. Some of the symmetry aspects of this parametrization have also been discussed elsewhere.[9,11] In a perturbation problem $\underset{\sim}{H}_0$ is often higher symmetry then the perturbation. In that case $\underset{\sim}{C}^0$ may have a block structure but elements of $\underset{\sim}{A}$ which mix different blocks must be included.

An alternative parametrization of $\underset{\sim}{C}$ in terms of generalized Euler angles has been treated by Raffenetti and Ruedenberg.[22] They have given expressions for first derivatives.

The other set of parameters entering the problem are the $\{\xi_i\}$ characterizing the elements or expansion coefficients of the density matrix components in the $\{\phi_k\}$ basis. A completely general characterization of this parametrization would require a solution of the N-representability problem of reduced density matrix theory. A parametrization is known in at least two cases, however. These are for density matrices corresponding to spin-unrestricted or spin extended SCF functions[6,7] and for those corresponding to optimized multiconfiguration or CI wave functions.[8,23]

The expansion coefficients for all components of the 1-matrix and the 2-matrix corresponding to a spin-unrestricted SCF function (i.e. a spin-polarized or different-orbitals-for-different-spins function) and corresponding to a spin-extended function can all be expressed in terms of a small number of parameters which are closely related to the eigenvalues of γ^0 for the unrestricted function. It is convenient

in this case to require the $\{\phi_k\}$ to be the eigenfunctions of γ^o. These expressions have been presented elsewhere,[6,7] and the way in which derivatives are evaluated have been discussed.[9,11]

For density matrices of configuration interaction or optimized multiconfiguration type the elements of the density matrices are quadratic forms in the CI expansion coefficients.[24] If Φ_i is a single determinant made up of the Φ_k and spin functions, or a linear combination of such determinants taken to have appropriate symmetry properties, and the total wave function is

$$\Psi = \sum_i B_i \Phi_i . \tag{42}$$

The components of $\underset{\sim}{\Gamma}$ are given, for example, by

$$\Gamma^x_{ijkl} = \sum_{tu} P^x_{ijkl,\,tu} B_t B_u^* , \quad x = a \text{ or } s \tag{43}$$

The coupling array $\underset{\sim}{P}$ contains information characterizing the numbering scheme chosen for the orbitals and configurations, and also factors associated with the symmetry, e.g. the choice of spin eigenfunctions. It is, however, independent of any of the variational parameters of the problem.

Derivatives would seem to be trivial in this case if the parameters are taken to be just the expansion coefficients. It must be recalled however, that the development has assumed independent parameters while the expansion coefficients are subject to the normalization constraint

$$\sum_k |B_k|^2 = 1 . \tag{44}$$

Rather than to attempt to introduce constraints at this point it is convenient to define the expansion coefficients in terms of a set of independent variables $\{\xi_j\}$, $j>o$, as considered in the expansion of the previous section; Eqn. (28). The unique coefficient B_o can be taken to multiply the first configuration, which is presumably the most important, but this is not necessary. The only essential feature in the selection of the coefficient taken to be B_o is that it must always be non-zero. The derivatives which result from this parametrization are summarized in Appendix 2.

DISCUSSION

Expressions have been developed here giving first and second order energies in terms of parametrized, reduced density matrices, and it has been indicated that such parametrization and the required derivatives are available in some cases.

To express the first order energy in density matrix terms is essentially trivial, since it is just an expectation value and reduced density matrices are designed to facilitate the evaluation of expectation values. The second order energy expressions are of more interest. They are also somewhat puzzling when compared with usual perturbations in that apparently only the ground state is involved. That this appearance is deceptive is evident in the comparison with Rayleigh-Schrödinger theory. The essential feature is that degrees of freedom which do not figure significantly in the ground state can still occur in the second derivative matrix and thus in $\underset{\sim}{G}$. The basis set and

parametrization must be capable of giving an adequate description of excited states if good results are to be obtained for perturbations for which those states are significant. Despite this requirement for the capability of describing excited states, some advantage is gained in the present method in that these states need never be considered explicitly. The effect of other states is contained in the second derivative matrix which can be evaluated in a straightforward although lengthy process. The inverse second derivative matrix is in effect a resolvent operator. The evaluation of some or all of the elements of the second derivative matrix may be a part of the zero order problem.[9-11]

In cases of highly flexible density matrices with many parameters, the size of the second derivative matrix may be prohibitively large. Frequently, however, flexibility is limited by other considerations. In particular, in small basis set calculations the present method provides a convenient organization. Once $\underset{\sim}{G}$ has been determined any number of perturbations can be easily treated. For particular perturbations, not only are first derivatives sufficient, but they can often be obtained from the 1-matrix.

Suppose, for example, that a spin-extended SCF calculation has been done for a free radical,[10] and $\underset{\sim}{G}$ evaluated. The effects of electrostatic perturbations such as those due to solvation can then be estimated from $\underset{\sim}{G}$ and the first derivatives of γ^0 and γ^z. Determination of the effect of each new perturbation requires only the evaluation of the elements of $\underset{\sim}{V}$ in the fixed basis. One could also consider a double perturbation with orbital Zeeman and spin-orbit terms to estimate the g-tensor. We expect to make such calculations in the near future.

APPENDIX 1. Parametrization and derivatives associated with orbital transformations.

Let $\underset{\sim}{\gamma}$ be a component of the 1-matrix expressed in the $\{\phi_k\}$ basis (again assuming for convenience everything to be real)

$$\gamma(1,1') = \sum_{k,l} \gamma_{kl}\phi_k(1)\phi_l(1'). \tag{A1}$$

The expansion coefficients are the matrix elements of $\underset{\sim}{\gamma}$, and are assumed known as a function of the $\{\xi_i\}$. Let $\underset{\sim}{\omega}$ be the matrix of a one-electron operator in the $\{\chi_K\}$ basis:

$$\omega_{K\lambda} = \int \chi_K(1)\ \omega_1 \chi_\lambda(1) d\tau_1. \tag{A2}$$

In order to compute $\langle\omega\rangle$ as a trace it is necessary to express $\underset{\sim}{\omega}$ and $\underset{\sim}{\gamma}$ in the same basis. Let $\hat{\underset{\sim}{\gamma}}$ be the equivalent of $\underset{\sim}{\gamma}$ in the $\{\chi_K\}$ basis. Since (from Eqn. 45))

$$\begin{aligned}\gamma(1,1') &= \sum_{k,l} \sum_{K\lambda} \gamma_{Kl}\ C_{kK}\chi_K(1)C_{l\lambda}\chi_\lambda(1') \\ &= \sum_{K\lambda} \hat{\gamma}_{K\lambda}\ \chi_K(1)\chi_\lambda(1')\end{aligned} \tag{A3}$$

it is seen that

$$\begin{aligned}\hat{\gamma}_{K\lambda} &= \sum_{kl} \gamma_{kl}C_{kK}C_{l\lambda} \\ &= \sum_{k,l} C^T_{Kk}\ \gamma_{kl}\ C_{l\lambda} = (C^T\gamma C)_{K\lambda}\end{aligned} \tag{A4}$$

and then

$$\langle\omega\rangle = \mathrm{tr}\,\{\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega}\}.$$

It is convenient to relate $\hat{\underset{\sim}{\gamma}}$ for general parameter values not to $\underset{\sim}{\gamma}$ but to $\hat{\underset{\sim}{\gamma}}^{(o)}$, the zero-order transformed matrix:

$$\hat{\underset{\sim}{\gamma}} = \underset{\sim}{C}^{T}\underset{\sim}{\gamma}\underset{\sim}{C} = \underset{\sim}{C}^{T}\underset{\sim}{C}^{o}\underset{\sim}{C}^{oT}\underset{\sim}{\gamma}\underset{\sim}{C}^{o}\underset{\sim}{C}^{oT}\underset{\sim}{C}$$

$$= \exp\{-\underset{\sim}{A}\}\,\hat{\underset{\sim}{\gamma}}^{(o)}\,\exp\{\underset{\sim}{A}\} \tag{A5}$$

since $\underset{\sim}{C}$ is given by Eqn. (46) and

$$\underset{\sim}{C}^{T} = \exp\{-\underset{\sim}{A}\}\,\underset{\sim}{C}^{oT}. \tag{A6}$$

The insertion of $\underset{\sim}{C}^{o}\,\underset{\sim}{C}^{oT}$ has no effect because $\underset{\sim}{C}^{o}$ is orthogonal.

The parameters are the elements of $\underset{\sim}{A}$, and the derivatives of $\hat{\underset{\sim}{\gamma}}$, for example, are

$$\left[\left(\frac{\partial\hat{\underset{\sim}{\gamma}}}{\partial A_{ij}}\right)_{\underset{\sim}{A}=o}\right]_{\kappa\lambda} = \hat{\underset{\sim}{\gamma}}^{(o)}_{\kappa i}\delta_{\lambda j} + \hat{\underset{\sim}{\gamma}}^{(o)}_{i\lambda}\delta_{\kappa j}$$

$$-\hat{\underset{\sim}{\gamma}}^{(o)}_{\kappa j}\delta_{\lambda i} - \hat{\underset{\sim}{\gamma}}^{(o)}_{j\lambda}\delta_{\kappa i} \quad . \tag{A7}$$

Second derivative expressions become rather lengthy, and it is convenient to deal directly with the expectation-value derivatives which are of interest. It is found that

$$\left(\frac{\partial\langle\omega\rangle}{\partial A_{ij}}\right)_{\underset{\sim}{A}=o} = 2\,[(\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{ij} - (\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{ji}] \tag{A8}$$

and

$$\left(\frac{\partial^2 \langle\omega\rangle}{\partial A_{ij}\partial A_{kl}}\right)_{\underset{\sim}{A}=o} = 2\,[\hat{\gamma}_{jl}\,\omega_{ik} + \hat{\gamma}_{ik}\,\omega_{jl} - \hat{\gamma}_{il}\omega_{kj} - \hat{\gamma}_{kj}\omega_{il}]$$

$$+ \delta_{jk}[(\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{il} + (\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{li}] + \delta_{il}[(\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{jk} + (\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{kj}]$$

$$- \delta_{jl}[(\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{ik} + (\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{ki}] - \delta_{ik}[(\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{jl} + (\hat{\underset{\sim}{\gamma}}\underset{\sim}{\omega})_{lj}] \quad . \tag{A9}$$

Second derivatives involving one of these "θ-parameters" and one of the "ξ parameters" can be obtained by using the first-derivative expression (A8) above with the matrix $(\partial\underset{\sim}{\omega}/\partial\xi)$ substituted for $\underset{\sim}{\omega}$.

It is clear that a change in the one-electron basis will also produce a change in the 2-matrix components. If $\underset{\sim}{\Gamma}^x$ is $\underset{\sim}{\Gamma}^a$ or $\underset{\sim}{\Gamma}^s$, expressed in terms of the ϕ's as in Eqns (44) and (41) or (42), and $\hat{\underset{\sim}{\Gamma}}^x$ is this component in terms of symmetrized or antisymmetrized combinations of χ's, then

$$\hat{\underset{\sim}{\Gamma}}^x = \underset{\sim}{U}^{xT}\underset{\sim}{\Gamma}^x\underset{\sim}{U}^x$$

$$= \underset{\sim}{U}^{xT}\underset{\sim}{U}^x, o\underset{\Gamma}{}^x, o\underset{\sim}{U}^x, o^T\underset{\sim}{U}^x. \tag{A10}$$

The transformation matrix $\underset{\sim}{U}^x$ is orthogonal and is given in terms of $\underset{\sim}{C}$ by

$$U^a{}_{kl,\kappa\lambda} = C_{k\kappa}C_{l\lambda} - C_{k\lambda}C_{l\kappa}$$

$$U^s{}_{kl,\kappa\lambda} = \left(\frac{1}{\sqrt{2}}\right)^{\delta_{kl}+\delta_{\kappa\lambda}} (C_{k\kappa}C_{l\lambda} + C_{k\lambda}C_{l\kappa}) \quad . \tag{A11}$$

It should be noted that if the dimension of $\underset{\sim}{\gamma}$ and $\underset{\sim}{C}$ is M, that that of $\underset{\sim}{\Gamma}^{a}$ and $\underset{\sim}{U}^{s}$ is M(M+1)/2. The pair indices k,l and κ,λ range only over values $k<l$, $\kappa<\lambda$ in the antisymmetric case or $k\leq l$, $\kappa\leq\lambda$ in the symmetric case.

Derivatives with respect to the elements of $\underset{\sim}{A}$ can again be determined. The expressions for derivatives of $\underset{\sim}{\Gamma}$ are quite lengthy but those for expectation values are more compact. If $\underset{\sim}{\Omega}$ is a two-electron operator, which we assume to be symmetric with respect to pair-wise interchanges $\Omega_{12} = \Omega_{21}$ so that it also has no non-zero elements between symmetric and antisymmetric germinals, then

$$\begin{aligned}\langle\Omega\rangle &= \langle\Omega\rangle^{s} + \langle\Omega\rangle^{a} \\ &= \mathrm{tr}\{\underset{\sim}{\Gamma}^{s}\underset{\sim}{\Omega}^{s}\} + \mathrm{tr}\{\underset{\sim}{\Gamma}^{a}\underset{\sim}{\Omega}^{a}\}.\end{aligned} \tag{A12}$$

Expressions involving the symmetric and antisymmetric components can be written together, with the help of notational convention.

$$\left(\frac{\partial\langle\Omega\rangle}{\partial A_{ij}}\right)_{A=o} = 2\sum_{k}[(\overline{\underset{\sim}{\Gamma}\underset{\sim}{\Omega}})_{ki,kj} - (\overline{\underset{\sim}{\Gamma}\underset{\sim}{\Omega}})_{kj,ki}] \tag{A13}$$

$$\overline{\Gamma}_{\kappa\lambda,\mu\nu} = (\sqrt{2})^{\delta_{\kappa\lambda}+\delta_{\mu\nu}}\,\hat{\Gamma}_{\kappa\lambda,\mu\nu} \tag{A14}$$

$$\overline{\Omega}_{\kappa\lambda,\mu\nu} = (\sqrt{2})^{\delta_{\kappa\lambda}+\delta_{\mu\nu}}\,\Omega_{\kappa\lambda,\mu\nu} \tag{A15}$$

In obtaining these expressions it has been assumed that $\underset{\sim}{\Gamma}$ and $\underset{\sim}{\Omega}$ are symmetric matrices with respect to interchange of the two pair indices, and either symmetric or antisymmetric, depending on the component being considered, with respect to interchange of the members of either pair.

It should also be noted that (for the symmetric case)

$$(\overline{\underset{\sim}{\Gamma\Omega}})_{pq,rs} = (\sqrt{2})^{\delta_{pq}+\delta_{rs}} (\hat{\underset{\sim}{\Gamma\Omega}})_{pq,rs}$$

$$= (\sqrt{2})^{\delta_{pq}+\delta_{rs}} \sum_{x \leq y} \Gamma_{pq,xy} \Omega_{xy,rs}$$

$$= (\sqrt{2})^{\delta_{pq}+\delta_{rs}} \tfrac{1}{2} \sum_{x,y} 2^{\delta_{xy}} \Gamma_{pq,xy} \Omega_{xy,rs}$$

$$= \tfrac{1}{2} \sum_{x,y} \overline{\Gamma}_{pq,xy} \overline{\Omega}_{xy,rs} \qquad \text{(A16)}$$

(For the antisymmetric case $\overline{\underset{\sim}{\Gamma\Omega}} = \overline{\underset{\sim}{\Gamma\Omega}} = \overline{\underset{\sim}{\Gamma\Omega}}$.)

For the second derivatives

$$\left(\frac{\partial^2 \langle\Omega\rangle}{\partial A_{ij} \partial A_{kl}}\right)_{A=0} = (\overline{\underset{\sim}{\Gamma\Omega}})_{ikjl} + (\overline{\underset{\sim}{\Gamma\Omega}})_{jlik} - (\overline{\underset{\sim}{\Gamma\Omega}})_{iljk} - (\overline{\underset{\sim}{\Gamma\Omega}})_{jkil}$$

$$+ 2 \sum_{m,n} [\, \overline{\Gamma}_{imkn} \overline{\Omega}_{jmln} + \overline{\Gamma}_{jmln} \overline{\Omega}_{imkn}$$

$$- \overline{\Gamma}_{imln} \overline{\Omega}_{jmkn} - \overline{\Gamma}_{jmkn} \overline{\Omega}_{imln} \,]$$

$$- \delta_{ik} \sum_m \left[(\overline{\Gamma\Omega})_{jmlm} + (\overline{\Gamma\Omega})_{lmjm} \right] - \delta_{jl} \sum_m \left[(\overline{\Gamma\Omega})_{imlm} + (\overline{\Gamma\Omega})_{lmim} \right]$$

$$+ \delta_{il} \sum_m \left[(\overline{\Gamma\Omega})_{jmkm} + (\overline{\Gamma\Omega})_{kmjm} \right] + \delta_{jk} \left[(\overline{\Gamma\Omega})_{imlm} + (\overline{\Gamma\Omega})_{lmim} \right] \tag{A17}$$

The sums extend over all values of the index with appropriate permutations to produce ordered pair indices, and in the antisymmetric case associated sign change.

APPENDIX 2. Parametrization and derivatives associated with configuration expansion coefficients.

The expansion of Eqn. (49) and the parametrization of (51) lead to rather simple derivatives. It is first noted that

$$\frac{\partial B_o}{\partial \xi_k} = -\frac{1}{2}\left(1 + \sum_{i=1}^{Q} \xi_i^2\right)^{-3/2} 2\xi_k$$

$$= -B_o^2 B_k \qquad \text{(A18)}$$

$$\frac{\partial B_j}{\partial \xi_k} = \delta_{jk} B_o + \xi_j \frac{\partial B_o}{\partial \xi_k}$$

$$= B_o\left(\delta_{jk} - B_j B_k\right) . \qquad \text{(A19)}$$

These equations apply for any multiconfiguration expression for wave function as a sum of Q + 1 terms, with the normalization constant reducing the number of independent parameters to Q. If the subscript o is used for an expansion coefficient but not for a parameter, then expression (A19) can be used in all cases, including j = o (since k is never zero.)

If the subscripts on $\underset{\sim}{\Gamma}$ and the corresponding subscripts on $\underset{\sim}{P}$, and the superscripts a or s are suppressed, Eqn.(49) can be written

$$\underset{\sim}{\Gamma} = \sum_{t,u} \underset{\sim}{P}_{tu} \underset{\sim}{B}_t \underset{\sim}{B}_u \quad . \tag{A20}$$

It is then found by direct computation that[25]

$$\frac{\partial \underset{\sim}{\Gamma}}{\partial \xi_k} = 2B_o \left[\sum_t (\underset{\sim}{P}_{kt}) \; B_t - B_k \underset{\sim}{\Gamma} \right] \tag{A21}$$

and

$$\frac{\partial^2 \underset{\sim}{\Gamma}}{\partial \xi_k \partial \xi_l} = 2B_o^2 \left[(4B_k B_l - \delta_{kl}) \underset{\sim}{\Gamma} + (\underset{\sim}{P}_{kl}) \right.$$

$$\left. - 2B_l \sum_t (\underset{\sim}{P}_{kt}) \; B_t - 2B_k \sum_t (P_{lt}) \; B_t \right] \tag{A22}$$

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18. These parts are sometimes referred to as singlet and triplet parts, since when $M_S = 0$ they involve sums of the spatial parts of singlet and triplet natural spin geminals. When $M_S \neq 0$, however, the NSG's are not pure singlet or triplet, so the permutational summetry classification of the geminals is preferable.

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24. This is rather obvious and should be regarded as well known. It is seldom explicitly stated, however. An explicit discussion is given in ref. 8.

25. It has been assumed that $P_{tu} = P_{ut}$, as is normally the case. It is not so, each P_{tu} should be replaced in these expressions by $1/2(P_{tu} + P_{ut})$.