CONSTRUCTION OF APPROXIMATELY N-REPRESENTABLE DENSITY MATRICES. COMMENTS ON NON-ORTHOGONAL SPIN GEMINALS, BASIS AUGMENTATION, AND ERROR BOUNDS

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It is shown that although non-orthogonal spin geminals and variation of the spin geminals can be incorporated into our method for constructing optimally N-representable density matrices, they offer no practical advantages. A technique for predicting the effects of basis augmentation is presented and the role of error bounds in our theory is briefly discussed.

1. Introduction

Recently we proposed a method for constructing optimally N-representable 2-matrices which are expressible in terms of any *given* set of spin geminals [1]. A measure of N-representability was introduced and error bounds which allow us to estimate the consequences of approximate N-representability were derived. In this letter we consider the use of non-orthonormal spin geminals and possible variations of these spin geminals chosen to improve the N-representability of the resulting 2-matrices. One conclusion is that non-orthogonal spin geminals can be used in our method but they offer no advantages over orthonormal functions. In fact, while carrying out a calculation one would eventually be faced with the task of orthogonalizing the chosen set of spin geminals. Thus one might as well perform the orthogonalization as the initial step.

We also conclude that no improvement in N-representability can be made by varying the spin geminals within the space spanned by the original set of functions. Only augmentation of the basis gives the possibility for improvement. A scheme for estimating the effects of augmentation is presented.

Lastly we make some brief remarks aimed at clarifying the role of error bounds in our proposed method for constructing optimally N-representable density matrices. These error bounds are an essential component of our modified variational technique which allows the optimization of variational parameters appearing in the resultant 2-matrices.

2. Non-orthonormal spin geminals

We assume that we have available a set of antisymmetric, but not necessarily orthonormal, spin geminals ‡‡ $\{\phi_i(1,2), i = 1,2, ..., M\}$. The development presented in our earlier paper (hereafter referred to as I) can be carried through directly with only the following modification: the normalization condition on $\Psi(1,2, ..., N)$ becomes

$$1 = \sum_{i,j=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}^{*} \int \phi_i^{*}(1,2)\, \phi_j(1,2)\, d\tau_1\, d\tau_2\, C_{j\alpha} \tag{1a}$$

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‡‡ The reader is referred to ref. [1] for notation and details of the discussion.

or

$$\equiv \sum_{i,j=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} C^*_{i\alpha} S_{ij} C_{j\alpha} , \tag{1b}$$

where the second equality serves to define the overlap matrix **S**.

The problem of choosing the coefficients $\{C_{i\alpha}\}$ to maximize the N-representability, subject to the constraint given in eq. (1), leads to the following matrix equation:

$$\sum_{j=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} \hat{T}_{i\alpha, j\beta} C_{j\beta} = \lambda \sum_{j=1}^{M} S_{ij} C_{j\alpha} . \tag{2}$$

To convert this to a conventional matrix eigenvalue problem we first form the matrix **M** whose entries are given by

$$M_{i\alpha, j\beta} = \delta_{\alpha\beta} N_{ij} , \tag{3}$$

where the elements N_{ij} are related to the eigenvectors ‡ V_{ij} and eigenvalues s_j of **S** by

$$N_{ij} = s_j^{-1/2} V_{ij} . \tag{4}$$

If we now define coefficients $\{Q_{i\alpha}\}$ by

$$C_{i\alpha} = \sum_{j=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} M_{i\alpha, j\beta} Q_{j\beta} , \tag{5}$$

we can premultiply eq. (2) by the transpose of **M** to obtain the desired eigenvalue relation

$$\sum_{j=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} (\mathbf{M}^{\mathrm{T}} \hat{\mathbf{T}} \mathbf{M})_{i\alpha, j\beta} Q_{j\beta} = \lambda Q_{i\alpha} , \tag{6}$$

with

$$(\mathbf{M}^{\mathrm{T}} \hat{\mathbf{T}} \mathbf{M})_{i\alpha, j\beta} = \sum_{k,l=1}^{M} N_{ki} \hat{T}_{k\alpha, l\beta} N_{lj} . \tag{7}$$

Once eq. (6) has been solved for the largest eigenvalue of the matrix $(\mathbf{M}^{\mathrm{T}} \hat{\mathbf{T}} \mathbf{M})$ and its associated eigenvectors, the optimum coefficients $\{C_{i\alpha}\}$ are immediately given in terms of the $Q_{i\alpha}$ as

$$C_{i\alpha} = \sum_{j=1}^{M} N_{ij} Q_{j\alpha} . \tag{8}$$

From this discussion it is clear that the only added complexity encountered in treating non-orthonormal spin geminals is the problem of finding the eigenvalues and eigenvectors of the M-dimensional overlap matrix **S**. Forming the matrix $\mathbf{M}^{\mathrm{T}} \hat{\mathbf{T}} \mathbf{M}$ involves simple matrix multiplications over indices which run from 1 to M, cf. eq. (7). However, the problem of finding the eigenvalues and eigenvectors of **S** is *exactly* equivalent to orthogonalizing the original set of spin geminals and then carrying out the calculation using this new orthonormal set. We therefore conclude that the most expeditious route to take when working with non-orthonormal spin geminals is to orthogonalize the geminals by finding the eigenvectors of **S** and to then use the results presented in I for orthonormal spin geminals. We gain no convenience by using the non-orthogonal functions directly.

3. Variations of the spin geminals

Let us suppose that the scheme proposed in I has been successfully completed so that we know the optimum (for the initially chosen $\{\phi_i\}$) functions $\{\chi_i(3,4, ..., N)\}$ in the expansion of $\Psi(1,2, ..., N)$:

$$\Psi(1,2, ..., N) = \sum_{i=1}^{M} \phi_i(1,2)\, \chi_i(3,4, ..., N) . \tag{9}$$

With the $\{\chi_i\}$ considered *fixed* we now investigate the possibility of varying the $\{\phi_i\}$ to further increase the N-representability of the resulting 2-matrix. This procedure would then lead to an iterative scheme for im-

‡ Notice that the subscript j labels the eigenvalue and i is the running index within the jth eigenvector.

proving N-representability in which the $\{\phi_i\}$ and the $\{\chi_i\}$ are successively varied.

Let us first consider the situation in which we restrict the new spin geminals $\{\widetilde{\phi}_i\}$ to lie within the space spanned by the original $\{\phi_i\}$:

$$\widetilde{\phi}_i(1,2) = \sum_{j=1}^{M} U_{ij}\phi_j(1,2)\,, \tag{10}$$

where $\mathbf{U}$ is some non-singular matrix ‡. The new function $\widetilde{\Psi}(1,2,...,N)$ constructed with the *known* $\{\chi_i\}$ and the *variable* $\{\widetilde{\phi}_i\}$ is then given by

$$\widetilde{\Psi}(1,2,...,N) = \sum_{i=1}^{M} \widetilde{\phi}_i(1,2)\,\chi_i(3,4,...,N)$$

$$= \sum_{i,j=1}^{M} \phi_j(1,2)\,U_{ij}\,\chi_i(3,4,...,N)\,. \tag{11}$$

The answer to the problem of varying $\mathbf{U}$ to maximize N-representability is immediately seen to be

$$\mathbf{U} = \mathbf{I}\,, \tag{12}$$

the identity matrix. To show this result in more detail, let us define the *variable* $\{\widetilde{\chi}_i\}$ in terms of the *fixed* $\{\chi_i\}$ as

$$\widetilde{\chi}_j = \sum_{i=1}^{M} U_{ij}\chi_i(3,4,...,N)\,. \tag{13}$$

The function $\widetilde{\Psi}$ can then be written as

$$\widetilde{\Psi}(1,2,...,N) = \sum_{j=1}^{M} \phi_j(1,2)\,\widetilde{\chi}_j(3,...,N)\,. \tag{14}$$

We now inquire as to what choice of the $\{\widetilde{\chi}_i\}$ (or equivalently what choice of the U_{ij}) will, for fixed $\{\phi_i\}$, maximize N-representability. By assumption this problem has already been solved and the answer was to choose

$$\widetilde{\chi}_i(3,...,N) = \chi_i(3,...,N)\,, \tag{15}$$

which immediately implies eq. (12).

‡ We wish to preserve the number of independent spin geminals.

This discussion therefore tells us that once the optimum $\{\chi_i\}$ have been found for a *given* set of spin geminals, nothing can be gained by varying the spin geminals within the space of the original $\{\phi_i\}$. To improve N-representability we *must* either augment the basis of spin geminals or replace some of the $\{\phi_i\}$ by new functions. One scheme for augmenting the basis to improve N-representability and reduce possible errors in calculated expectation values was presented in I. There still remains a need for specific criteria in choosing which spin geminals are most essential in any augmentation.

We now turn our attention to considering the effects of basis set augmentation on the N-representability of resulting 2-matrices. Let us assume that the method in I has been carried through using a basis of M spin geminals $\{\phi_i\}$ and $\binom{R}{N-2}$ Slater determinants $\{[\alpha]\}$ (see I for notation). The $\mathbf{T}$-matrix for this initial calculation will be denoted by $\mathbf{T}^{(0)}$, with (largest) eigenvalue $\lambda^{(0)}$ and eigenvector $\{C_{i\alpha}^{(0)}\}$. If we now add $(M'-M)$ orthonormal spin geminals to the original basis, the dimension of the new $\mathbf{T}$-matrix will be $M'\binom{R'}{N-2} \times M'\binom{R'}{N-2}$. The eigenvalue equation for the augmented $\mathbf{T}$-matrix

$$\mathbf{T}C = \lambda C\,, \tag{16}$$

can be decomposed into two matrix equations

$$\mathbf{T}_{11}C_1 + \mathbf{T}_{12}C_2 = \lambda C_1\,, \tag{17}$$

$$\mathbf{T}_{21}C_1 + \mathbf{T}_{22}C_2 = \lambda C_2\,, \tag{18}$$

by partitioning $\mathbf{T}$ and C into contributions due to the original spin geminals and contributions which arise when the basis is augmented. It should be apparent that we are to identify $\mathbf{T}_{11}$ with $\mathbf{T}^{(0)}$.

Rearranging eqs. (17) and (18) leads to the following equations for C_1 and C_2:

$$[\mathbf{T}_{11} + \mathbf{T}_{12}(\lambda \mathbf{I}_{22} - \mathbf{T}_{22})^{-1}\mathbf{T}_{21}]\,C_1 = \lambda C_1\,, \tag{19}$$

and

$$C_2 = (\lambda \mathbf{I}_{22} - \mathbf{T}_{22})^{-1}\mathbf{T}_{21}C_1\,, \tag{20}$$

where $\mathbf{I}_{22}$ is a unit matrix whose dimension is equal to the dimension of $\mathbf{T}_{22}$. Once eq. (19) is solved for C_1 eq. (20) immediately gives C_2.

Because eq. (19) contains the unknown eigenvalue λ in a complicated fashion it is probably necessary to attempt some approximate solution, perhaps an iteration approach or a perturbation expansion. If, in a perturbation-theoretic sense, we approximate λ by $\lambda^{(0)}$ and C_1 by $C^{(0)}$, eqs. (19) and (20) can be used to write the first-order correction $\lambda^{(1)}$ to the eigenvalue λ as

$$\lambda^{(1)} = C^{(0)\dagger}\,\Upsilon_{12}(\lambda^{(0)}\,\mathrm{I}_{22}-\Upsilon_{22})^{-1}\,\Upsilon_{21}\,C^{(0)} \tag{21}$$

and the first approximation to C_2 as

$$C_2^{(1)} = (\lambda^{(0)}\,\mathrm{I}_{22}-\Upsilon_{22})^{-1}\,\Upsilon_{21}\,C^{(0)}\,. \tag{22}$$

Of course the resulting approximation $\{C^{(0)}, C_2^{(1)}\}$ to C would then have to be renormalized to maintain consistency with the statements in I.

Although this partitioning scheme requires the inversion of the $(\lambda^{(0)}\,\mathrm{I}_{22}-\Upsilon_{22})$ matrix, it does not cause any major computational difficulty because we have in mind a situation in which the number of added spin geminals is quite small, i.e., the dimension of Υ_{22} will usually be *much* smaller than the dimension of Υ_{11}. Evaluation of the elements Υ_{12}, Υ_{21}, and Υ_{22} is easily accomplished by using the results given in I. Eqs. (21) and (22) then give closed (approximate) expressions for the contributions to λ and C due to any basis augmentation.

This procedure not only allows us to estimate the consequences of specific augmentations but it also introduces the possibility of developing rules for determining which spin geminals are most important to add to the original basis. Hopefully we shall have more constructive contributions along these lines in the near future.

4. Error bounds

In I we obtained a bound on the quantity $|\hat{E}-\mu\widetilde{E}|$ involving the measure of N-representability μ. $\hat{E}$ is the expectation value of the hamiltonian with respect to a certain *antisymmetric* wave function while $\widetilde{E}$ is the energy calculated as the trace of the reduced hamiltonian times a 2-matrix obtained by our procedure. The boundary equation

$$|\hat{E}-\mu\widetilde{E}| \leqslant f(\mu) \tag{23}$$

clearly implies

$$\hat{E}-f \leqslant \mu\widetilde{E} \leqslant \hat{E}+f\,. \tag{24}$$

Because $\hat{E}$ is an upper bound to the true ground-state energy E_{T}

$$\hat{E} \geqslant E_{\mathrm{T}}\,, \tag{25}$$

eq. (24) can be used to write

$$\mu\widetilde{E} \geqslant \hat{E}-f \geqslant E_{\mathrm{T}}-f\,. \tag{26}$$

This relation is easily rearranged ‡ to give the final result

$$\widetilde{E} \geqslant E_{\mathrm{T}} + \mu^{-1}\,[E_{\mathrm{T}}(1-\mu)-f(\mu)]\,. \tag{27}$$

Because $f(\mu)$, μ, and $(1-\mu)$ are non-negative quantities and, for bound-state problems, E_{T} is negative, eq. (27) allows us to state that the calculated $\widetilde{E}$ will not be more than $\mu^{-1}|E_{\mathrm{T}}(1-\mu)-f|$ below the true ground-state energy E_{T}. If we know a *lower* bound to E_{T} (say E_{L}), we can replace eq. (27) by

$$\widetilde{E} \geqslant E_{\mathrm{T}} + \mu^{-1}\,[E_{\mathrm{L}}(1-\mu)-f(\mu)]\,, \tag{28}$$

which says that $\widetilde{E}$ cannot be more than $\mu^{-1}|E_{\mathrm{L}}(1-\mu)-f(\mu)|$ below E_{T}.

The importance of this bound lies in the fact that $\widetilde{E}$ is usually obtained as the minimum energy in a variational calculation involving the 2-matrix. For such a variational approach to have any validity we must be able to predict a *lower* bound to *any* calculated energy (as in the common variational method), i.e., there must be some value below which no energy calculated with our 2-matrix can fall.

5. Conclusion

In this letter we showed how non-orthonormal spin geminals can be used in our scheme for constructing optimally N-representable 2-matrices. We concluded that the most direct approach seems to be the best: orthogonalize the spin geminals and then carry out the calculation in terms of these orthonormal functions. It was also demonstrated that nothing can be gained by varying the spin geminals within the space

‡ This step is valid for positive μ. From I we know that $0 \leqslant \mu \leqslant 1$ so $\mu = 0$ is the only possibility for trouble. The $\mu = 0$ case is of no interest to us because $\mu = 0$ implies that the resulting 2-matrix is not at all N-representable.

of the original $\{\phi_i\}$; augmentation of the basis is necessary to improve the N-representability. A method for estimating the effects of spin geminal augmentation was also presented. Finally, we discussed in somewhat more detail than in I the meaning of the error bounds contained in our method.

Reference

[1] J. Simons and J.E. Harriman, Phys. Rev. A2 (1970) 1034.