Limitation on the density-equation approach to many-electron problems

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The density equation proposed by Nakatsuji assumes a matrix form when a basis set is introduced. The matrix equation is shown to have highly degenerate solutions for almost any value of the energy, and thus to provide little useful information in the absence of N-representability constraints. The imposition of such constraints is also considered, and approximate constraints are predicted to be of little value.

I. INTRODUCTION

In independent developments, Nataksuji[1] and Cohen and Frishberg[2] have shown that the reduced density matrices (RDMs) obtained from a wave function which satisfies the time-independent Schrödinger equation will themselves satisfy a series of "hierarchy" or "density" equations. (A similar approach has also been applied to the investigation of the properties of spin compounds of RDMs.[3,4]) Cohen and Frishberg and Naksuji used the independent article ansatz that the many-electron RDMs are antisymmetrized products of the one-electron RDM[5] to provide a nonvariational derivation of the Hartree-Fock equation. This has been extended by Schlosser[6] to the multiconfiguration self-consistent field case.

Nakatsuji has also shown that if the RDM is N representable[7] by a wave function Ψ and satisfies the density equation, Ψ will be a solution of the Schrödinger equation. Since complete N-representability conditions remain unknown, it is not immediately possible to substitute the density equation for the Schrödinger equation. Nakatsuji suggests, however, that a valuable approach may lie in first solving the density equation with only simple N-representability constraints and then examining the solutions to see which of them satisfy additional N-representability conditions. It was the purpose of the work presented here to consider that approach with no initially imposed constraints. Unfortunately, the conclusion is that in the absence of N-representability constraints the density equation seems to have no practical utility. While no definitive results have been obtained for cases in which some constraints are imposed, plausibility arguments suggest similar conclusions then, as well.

II. MATRIX FORMULATION

The density-hierarchy equation of interest is an intergrodifferential equation for the four-electron RDM. Since even in the simpler case of the Schrödinger equation for a two-electron atom no analytic solution is known, it is apparent that some approximate method of solution will be necessary. The method considered here is a basis set expansion which could become exact as the basis set becomes complete.

We begin with a set of r orthonormal spin orbitals and, for simplicity, neglect all symmetry other than permutational. The n-electron basis can then be taken as $\binom{r}{n}$ orthonormal determinantal functions, and the exact problem is replaced by a model problem requiring the diagonalization of the $\binom{r}{n}\times\binom{r}{n}$ Hamiltonian matrix:

$$\underline{H}^{(n)}\underline{c}_J = E\underline{c}_J \,. \tag{1}$$

This equation can be reduced, by methods described elsewhere,[8] to the discrete analog of the density-hierarchy equation

$$\hat{K}\underline{D}^{(4)} = E\hat{L}\underline{D}^{(4)} \tag{2}$$

where, symbolically,

$$\begin{aligned}\hat{K} = {} & [\hat{f}(1)+\hat{f}(2)+\hat{g}(1,2)]\hat{L}_4^2 \\ & + (n-2)\hat{L}_3^2[\hat{f}(3)+\hat{g}(1,3)+\hat{g}(2,3)]\hat{L}_4^3 \\ & + \frac{(n-2)(n-3)}{2}\hat{L}_4^2\hat{g}(3,4)\,,\end{aligned}$$

$$\hat{L} = \hat{L}_4^2. \tag{3}$$

We need not be concerned here with the precise form taken by $\hat{f}$ and $\hat{g}$ in the matrix formulation. (They are the one- and two-electron operators, respectively, in the Hamiltonian.) The operators $\hat{K}$ and $\hat{L}$ both involve mappings of the space $\mathcal{S}_4$ of Hermitian matrices defined with respect to four-electron functions onto the space $\mathcal{S}_2$ of Hermitian operators defined with respect to two-electron functions. The dimensions of these spaces for the basis we are using are $\binom{r}{4}^2$ and $\binom{r}{2}^2$, respectively. It follows that in the discrete formulation $\hat{K}$ and $\hat{L}$ are replaced by rectangular matrices of $\binom{r}{2}^2$ rows and $\binom{r}{4}^2$ columns, while $\underline{D}^{(4)}$ becomes a $\binom{r}{4}^2$-element column vector.

Before considering the matrix form of Eq. (2) further, we note that an extension is possible.[6] Instead of the matrix form of the Schrödinger equation, we could consider the commutator or anticommutator of $\underline{H}^{(n)}$ with the n-electron (transition) density matrix

$$\underline{\rho}^{(n)}_{IJ} = c_I c_J , \tag{4}$$

$$\underline{H}^{(n)}\underline{\rho}^{(n)}_{IJ} \pm \underline{\rho}^{(n)}_{IJ}\underline{H}^{(n)} = (E_I \pm E_J)\underline{\rho}^{(n)}_{IJ} . \tag{5}$$

We are primarily interested in the case $I=J$, for which Eqs. (5) reduce to

$$\hat{K}_+ \underline{D}^{(4)} = 2E_J \hat{L}\underline{D}^{(4)} , \tag{6a}$$

$$\hat{K}\underline{D}^{(4)} = 0 . \tag{6b}$$

The operators $\hat{K}_\pm$ are simply related to $\hat{K}$, and Eqs. (6a) and (2) are of the same form while (6b) is the special case of Eq. (2) corresponding to $E=0$.

The rectangular matrices corresponding to $\hat{K}$ (or $\hat{K}_\pm$) and $\hat{L}$ can be partitioned as

$$\hat{K} \leftrightarrow \underline{K} = (\underline{K}', \underline{K}''), \quad \hat{L} \leftrightarrow \underline{L} = (\underline{L}', \underline{L}''); \tag{7}$$

where $\underline{K}'$ and $\underline{L}'$ are the square matrices of dimension $\binom{r}{2}^2$ and $\underline{K}''$, $\underline{L}''$ are rectangular $\binom{r}{2}^2 \times [\binom{r}{4}^2 - \binom{r}{2}^2]$ matrices. Similarly

$$\underline{D}^{(4)} = \begin{pmatrix} d' \\ d'' \end{pmatrix}, \tag{8}$$

where d' is the column vector of the first $\binom{r}{2}^2$ elements of $\underline{D}^{(4)}$ and d'' is the column vector of the remaining elements. Equation (2) can then be rewritten

$$(\underline{K}' - E\underline{L}')d' + (\underline{K}'' - E\underline{L}'')d'' = 0 \tag{9}$$

and for *any* E such that

$$|\underline{K}' - E\underline{L}'| \neq 0 \tag{10}$$

d'' can be chosen *arbitrarily* with

$$d' = -(\underline{K}' - E\underline{L}')^{-1}(\underline{K}'' - E\underline{L}'')d'' \tag{11}$$

completing a solution. The degeneracy for each E is the number of linearly independent d'', which is $\binom{r}{4}^2 - \binom{r}{2}^2$. If the reducing bases[8] are used for $\mathcal{S}_2$ and $\mathcal{S}_4$, $\underline{L}''=0$ and $\underline{L}'$ is diagonal with positive diagonal elements, so

$$(\underline{K}' - E\underline{L}')c' = 0 \tag{12}$$

is a conventional generalized eigenvalue problem,[9] and we expect at most $\binom{r}{2}^2$ discrete values of E for which Eq. (10) will not be satisfied.[10]

The same argument can be extended to show that a large family of $\underline{D}^{(4)}$ will satisfy Eq. (6a) for almost any E, even if the same $\underline{D}^{(4)}$ is required to satisfy Eq. (6b), although the degeneracy will then be reduced to $\binom{r}{4}^2 - 2\binom{r}{2}^2$.

The density equation [Eq. (2)] is linear and homogeneous, so the solution vectors $\underline{D}^{(4)}$ associated with a particular value of E form a linear subspace of $\mathcal{S}_4$. A trace constraint

$$\mathrm{tr}\underline{D}^{(4)} = 1 \tag{13}$$

must also be imposed. This is readily done if the reducing basis is used: The component in the $\underline{X}_{0,1}(4)$ direction, which we could take to d'_1, is fixed at $\binom{r}{4}^{-1/2}$.[8] Solutions of Eq. (2) satisfying Eq. (13) form a convex set $\mathcal{C}(E)$ for each value of E. The dimensionality is reduced by one of the trace condition.[11]

The set $\mathcal{P}^{(4)}_n$ of four-electron N-representable RDMs is also convex. In addition, most of the necessary N-representability conditions known define convex sets. Let ξ denote a set of N-representability constraints and $\mathcal{P}^{(4)}_n(\xi)$ denote the convex set of elements of $\mathcal{S}_4$ satisfying these conditions.

Nakatsuji suggests that the density equation on the N-representable space is equivalent to the Schrödinger equation. If this is to be the case, the intersection $\mathcal{C}(E) \cap \mathcal{P}^{(4)}_n$ must be empty if E is not an eigenvalue of $\underline{H}^{(n)}$ and must consist of a single point if $E=E_I$ is a nondegenerate eigenvalue of $\underline{H}^{(n)}$. If E_I is a degenerate eigenvalue of $\underline{H}^{(n)}$, then $\mathcal{C}(E_I) \cap \mathcal{P}^{(4)}_n$ must be a convex set with dimension[11] equal to one less than the degeneracy. Consider now the imposition of a set of constraints ξ which are necessary but not sufficient to assure N representability. Then $\mathcal{P}^{(4)}_n(\xi) \supset \mathcal{P}^{(4)}_n$. We note also that the definition of $\mathcal{C}(E)$ suggests that its boundary moves in $\mathcal{S}_4$ continuously with changes in E.

For simplicity we now consider a nondegenerate eigenvalue of $\underline{H}^{(n)}$, E_I. Then

$$\mathcal{C}(E_I) \cap \mathcal{P}^{(4)}_n = \{\underline{D}^{(4)}_I\} . \tag{14}$$

Unless the boundary of $\mathcal{P}^{(4)}_n(\xi)$ actually coincides with that of $\mathcal{P}^{(4)}_n$ in some neighborhood of $\underline{D}^{(4)}_I$, we expect that $\mathcal{C}(E) \cap \mathcal{P}^{(4)}_n(\xi)$ will be nonempty for a range of E about E_I, and that, except possibly for the endpoints of the interval in E, the intersection will be a convex set of finite extent with dimension the same as that of $\mathcal{C}(E)$. We thus have, at least locally, the same problem we faced in the absence of N-representability constraints.

III. CONCLUSIONS

In the absence of N-representability constraints the density equation contains no information about energies. Even if the correct energy were known, the high degree of degeneracy would make it very difficult to locate the correct (N representable) $\underline{D}^{(4)}$. If approximate N-representability constraints are imposed, it seems likely that the same situa-

tion will arise in the vicinity of each desired solution. In particular, since it is not possible for two convex sets in a continuous space to intersect in a set of distinct, discrete points, there is no chance that a solution of the density equation with approximate constraints would yield a set of discrete solutions which could be individually checked for N representability.

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[9]J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965), *p.* 337.
[10]Other methods can be used to arrive at these conclusions. See, e.g., F. R. Gantmacher, *The Theory of Matrices* (Chelsea, New York, 1959), Vol. 2, p. 24.
[11]The term "dimension" as applied to a convex set is used here to mean the dimension of the linear space of minimum dimension in which it can be contained. Equivalently, it is the maximum number of linearly independent vectors from an origin in the set to other points also within the set. Other definitions which are equivalent to those above in this case are also possible. See, e.g., R. T. Rockafellar, *Convex Analysis* (Princeton University, Princeton, N. J., 1970), p. 12.