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Geometry of density matrices. IV. The relationship between density matrices and densities

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The relationship between densities and density matrices is explored in the case of a finite-basis-set expansion. The space of one-electron density matrices can be divided into two orthogonal subspaces with elements in one of them in one-to-one correspondence with densities. A component in the other does not contribute to the density. The set of densities is convex but there may be densities which cannot be obtained from a density matrix. The matrix of a local potential has a component only in the first subspace, and any such matrix can be obtained from a local potential. It is possible for Hamiltonian matrices differing by the matrix of a local potential to have a common ground-state eigenvector, so a Hohenberg-Kohn theorem cannot always be established. When it can, the explicit local potential with a given ground-state density can be formally obtained when appropriate conditions are satisfied. The details of the decomposition of the space of matrices and of subsequent developments depend on linear-dependency relationships among basis-set products, and are thus basis-set dependent.

I. INTRODUCTION

In previous papers in this series[1–3] (referred to as GDM I–III) density matrices defined with respect to a finite basis set have been treated as elements in Euclidean vector spaces.[1] The mapping relationship corresponding to reduction of a density matrix has been considered, and the advantages of a special choice of basis demonstrated.[2] Irreducible tensorial spin components have been defined for density matrices for any number of electrons, and relationships among them have been explored. In the finite-basis case, each spatial density-matrix component can again be considered as an element in an appropriate vector space.[3] In the present paper, the relationship between density matrices and densities will be considered in terms of finite-basis-set expansions.

The one-electron spinless (or charge) density is of considerable contemporary interest. In contrast to a wave function, the density is in principle observable. Many molecular properties can be expressed in terms of the density,[4] and it is the fundamental quantity in density functional theory.[5] It is clear that the density contains less information than the density matrix. If primed and unprimed variables are regarded as continuous matrix indices, then the density (in which the primed variables are equal to the corresponding unprimed variables) is the "diagonal" part of the density matrix. In a discrete basis-set representation it is not at once apparent what this means. Indeed, an exploration of this concept is a major purpose of this paper.

It will be shown that in general a density matrix can be divided into components in two orthogonal subspaces. The component in one subspace is completely determined by the density, with which it is in a one-to-one relationship. The component in the other subspace does not contribute to the density and is in no way determined by it. This is similar to the decomposition of a density-matrix space into subspaces with elements in one-to-one correspondence with fewer-electron reduced density matrices as developed in GDM II. An important difference is that the present decomposition depends critically on certain features of the basis set. The previous results depended only on the number of basis functions, so long as they were orthonormal. Much of the formal development herein presented is independent of which density-matrix component is involved or even the number of electrons. We could be dealing with charge density matrices, spin density matrices, two-electron charge density matrices, etc. When appropriate, discussion will be specialized to a particular case.

This paper continues in Sec. II with a brief review of the relevant features of the GDM treatment and other background development. The results for the density are developed in general and illustrated by an example in following sections. It is shown in Secs. V and VI that in the finite basis case the

Hohenberg-Kohn theorem does not always apply and not all densities are n representable. The v-representability problem is considered in Sec. VII, and the paper concludes with a review and discussion in Sec. VIII.

II. MATHEMATICAL PRELIMINARIES

We begin by reviewing the starting point of the GDM treatment. It is assumed that we have a set of R orthonormal functions $\{\Phi_j(\tau)\}$, where τ has been introduced to represent the variables of which the Φ's are functions. Normally it is assumed that there is a set of r orthonormal spin orbitals and that the many-electron basis functions are built up as determinants so that for n electrons, $R=\binom{r}{n}$. All operators are restricted to the space spanned by the $\{\Phi_j\}$, so that they can be replaced by $R\times R$ matrices.

The R^2-dimensional, Euclidean vector space $\mathscr{E}$ consists of $R\times R$ Hermitian matrices $\{\vec{U},\vec{V},\dots\}$ with scalar product

$$(\vec{U},\vec{V})=\mathrm{tr}\vec{U}\vec{V}=\sum_{j,k} U_{jk}V_{kj}\ . \tag{1}$$

It can be divided into a one-dimensional subspace $\mathscr{X}$ of elements proportional to

$$\vec{X}=R^{-1}\vec{1} \tag{2}$$

and an (R^2-1)-dimensional subspace $\mathscr{N}$ orthogonal to $\vec{X}$. It is readily shown that $\mathrm{tr}\vec{X}=1$ and that any element of $\mathscr{N}$ has trace zero. Additional partitioning is possible and will be referred to in Sec. V.

In order to establish a relationship with densities, we use the integral-operator kernels associated with the matrices in $\mathscr{E}$

$$U(\tau;\tau')=\sum_{k,l} U_{kl}\Phi_k(\tau)\Phi_l^*(\tau')\ . \tag{3}$$

A simple basis then consists of

$$\left.\begin{aligned} &A_k(\tau;\tau')=\Phi_k(\tau)\Phi_k^*(\tau')\ ,\quad 1\le k\le R\\ &B_{kl}(\tau;\tau')=\frac{1}{\sqrt{2}}[\Phi_k(\tau)\Phi_l^*(\tau')+\Phi_l(\tau)\Phi_k^*(\tau')]\ ,\\ &C_{kl}(\tau;\tau')=\frac{i}{\sqrt{2}}[\Phi_k(\tau)\Phi_l(\tau')-\Phi_l(\tau)\Phi_k^*(\tau')]\ ,\end{aligned}\right\}\ 1\le k<l\le R\ . \tag{4}$$

The kernel corresponding to $\vec{X}$ is

$$X(\tau;\tau')=R^{-1}\sum_{k=1}^{R} A_k(\tau;\tau') \tag{5}$$

and the basis elements of $\mathscr{N}$ can be chosen to correspond to the B's, C's, and $R-1$ linear combinations of the A's orthogonal to X, denoted by $\bar{A}_k$, $k=1,\dots,R-1$. ($\bar{A}_0=\sqrt{R}X$ is the normalized basis element corresponding to X.) A linear mapping of $\mathscr{E}$ into a space $\mathscr{F}$ of real functions is now introduced. It will be called "collapse" and denoted by the symbol $\hat{\delta}$. It consists of setting $\tau'=\tau$ in each of the integral kernels. Thus

$$\begin{aligned}&\hat{\delta}A_k(\tau;\tau')=|\Phi_k(\tau)|^2\ ,\\ &\hat{\delta}B_{kl}(\tau;\tau')=\sqrt{2}\,\mathrm{Re}\Phi_k(\tau)\Phi_l^*(\tau)\ ,\\ &\hat{\delta}C_{kl}(\tau;\tau')=-\sqrt{2}\,\mathrm{Im}\Phi_k(\tau)\Phi_l^*(\tau)\ .\end{aligned} \tag{6}$$

These functions will not in general be normalized, orthogonal (with respect to the usual integral scalar product), nor even linearly independent.

The space $\mathscr{F}$ has a maximum dimension R^2. If there are l independent linear-dependency conditions among the functions defined in Eq. (6), $\mathscr{F}$ has dimension R^2-l. [If the original functions and matrices are real, the C's drop out as do the $\hat{\delta}C$'s. The dimension of $\mathscr{F}$ is then $R(R+1)/2-l$, where l is the number of linear-dependence conditions among the $\hat{\delta}A$'s and $\hat{\delta}B$'s.] We retain $\vec{Y}_0=\bar{A}_0=R^{1/2}\vec{X}=R^{1/2}\vec{1}$ as the basis element for $\mathscr{X}$. It is possible to make a unitary transformation of the basis of $\mathscr{N}$ to a set $\{\vec{Y}_\kappa,\kappa=0,\dots,R^2-1\}$, with

$$\hat{\delta}\vec{Y}_\kappa\equiv 0,\quad \kappa=R^2-l,\dots,R^2-1\ . \tag{7}$$

The l equations giving these $\vec{Y}_\kappa$ can be taken as the linear-dependency equations. Orthogonalization of the remaining basis elements of $\mathscr{N}$ will give the

$$Y_\kappa,\kappa=1,\dots,R^2-l-1$$

having all their $\hat{\delta}Y_\kappa$ as linearly independent. (It is not in general possible to make them normalized or orthogonal by a transformation which preserves the orthonormality of the Y_κ, since the same transformation would have to be unitary in the latter context and nonunitary in the former.) By the transformation to the Y_κ's, we have divided $\mathscr{N}$ into two orthogonal subspaces: $\mathscr{M}$ spanned by the

$$Y_\kappa, \kappa=1, \ldots, R^2-l-1$$

and $\mathscr{K}$ spanned by the

$$Y_\kappa, \kappa=R^2-l, \ldots, R^2-1 \ .$$

An orthonormal basis for $\mathscr{F}$ can be introduced, and will be denoted by $\{f_k(\tau)\}$. It is convenient to take one of the basis functions to be

$$f_0(\tau)=c_0\hat{\delta}X(\tau;\tau')=\frac{c_0}{R}\sum_{k=1}^{R}|\Phi_k(\tau)|^2 \ , \tag{8}$$

where c_0 is a normalization constant. It follows from the normalization of the $\{\Phi_k\}$ that

$$c_0^{-1}\int f_0(\tau)d\tau=1 \ . \tag{9}$$

This function is proportional to the sum of the squares of all the basis functions of $\mathscr{E}$ and is thus appropriately referred to as the average density. The remaining basis functions are collapses of elements of $\mathscr{M}$, and thus of $\mathscr{N}$, so they will have the property

$$\int f_\kappa(\tau)d\tau=0, \ \ \kappa\geq 1 \ . \tag{10}$$

If we denote by $\overline{\mathscr{F}}$ the subspace of $\mathscr{F}$ orthogonal to f_0 (and thus spanned by the $f_\kappa, \kappa\geq 1$), then we note that the collapse mapping $\hat{\delta}$ is a one-to-one mapping from $\mathscr{M}$ onto $\overline{\mathscr{F}}$ or from $\mathscr{E}-\mathscr{K}=\mathscr{M}\oplus\mathscr{X}$ onto $\mathscr{F}$. As a mapping from $\mathscr{N}$ to $\overline{\mathscr{F}}$, $\hat{\delta}$ is many-to-one.

It must be noted, of couse, that in computational practice "linear independence" is not as clearly defined as it is in formal mathematics. In practice, functions which are very nearly equal to linear combinations of others must be treated as exactly so. The remainder will span the space $\mathscr{F}$ "well enough."

III. THE RELATIONSHIP BETWEEN DENSITY MATRICES AND DENSITIES

Let us now specialize to the case of one-electron spatial functions or orbitals $\{\Phi_i(\underline{r})\}$ and one-electron, spin-independent operators. The space $\mathscr{E}$ $(=\mathscr{E}_{1,r})$ then includes the charge-density matrices $\gamma^0(\underline{r};\underline{r}')$, and densities $\rho(\underline{r})$ are elements of $\mathscr{F}$ $(=\mathscr{F}_{1,r})$. Normalization conditions $\mathrm{tr}\gamma^0=C_\gamma$ and $\int\rho(\underline{r})d\underline{r}=C_\rho$ fix the Y_0 component of γ^0 and the f_0 component of ρ. Let $\bar{\gamma}\in\mathscr{N}$ and $\bar{\rho}\in\overline{\mathscr{F}}$ be the remaining components of these quantities. A fundamental result can now be stated.

If $\gamma^0(\underline{r};\underline{r}')$ is any charge density matrix consistent with density $\rho(\underline{r})$, so that $\hat{\delta}\gamma=\rho$, then the component of $\bar{\gamma}$ in $\mathscr{M}$ is completely determined by $\bar{\rho}$ and the component of $\bar{\gamma}$ in $\mathscr{K}$ has no effect on ρ.

The charge-density matrix γ^0 can be combined with a spin-density matrix γ^z or, alternatively, replaced by the α-spin density matrix γ^+ and the β-spin density matrix γ^- (with densities ρ^+ and ρ^-, respectively) to give the full density matrix $\gamma(x;x')$ corresponding to a spin-dependent density $\rho(x)$.

The decomposition of a density matrix into components in $\mathscr{X}$, $\mathscr{M}$, and $\mathscr{K}$ can be combined with the results of GDM II to divide any p matrix with $p\leq n$ (n is the number of electron in the system) into a component completely determined by ρ and a component of which ρ is independent.

Of course all elements of $\mathscr{F}$ are not densities, nor all elements of $\mathscr{E}$ density matrices. If we ignore normalization constraints, which are easily dealt with, then the essential characteristic of a density matrix is positivity in a matrix sense. Let $\mathscr{P}$ be the set of all positive, Hermitian, $r\times r$ matrices. It is well known that $\mathscr{P}$ is a convex subset of $\mathscr{E}$ but is not a linear space. Correspondingly, the defining characteristic of a density is that it must be positive as a function, i.e.,

$$\rho(\underline{r})\geq 0, \ \ \text{all } \underline{r} \ . \tag{11}$$

We will denote by $\mathscr{F}_+$ the set of all functions in $\mathscr{F}$ which are nowhere negative. This is a convex set as well, and

$$\hat{\delta}\mathscr{P}\subset\mathscr{F}_+ \ . \tag{12}$$

The convexity of $\mathscr{F}_+$ is trivially established. If $\rho_1(\underline{r})$ and $\rho_2(\underline{r})$ are both non-negative for all $\underline{r}$, then

$$\rho(\underline{r})=\alpha\rho_1(\underline{r})+\beta\rho_2(\underline{r})\geq 0, \ \ \rho\in\mathscr{F}_+ \ ,$$

$$\alpha,\beta\geq 0, \ \ \alpha+\beta=1 \ , \tag{13}$$

and this is just the definition of convexity. Equation (12) means that for any $\vec{\mathrm{D}}\in\mathscr{P}$, $\hat{\delta}\vec{\mathrm{D}}\in\mathscr{F}_+$. This follows from the fact that for any $\vec{\mathrm{D}}\in\mathscr{P}$ there is a natural expansion

$$D(\underline{r};\underline{r}')=\sum_{k=1}^{r}\lambda_k\phi_k(\underline{r})\phi_k^*(r') \tag{14}$$

with $\lambda_k \geq 0$, all k. Then it is obvious that

$$\hat{\delta} D = \sum_k \lambda_k \, | \phi_k(\underline{r}) |^2$$

cannot be negative anywhere.

Only the inclusion relation of Eq. (12) has been established. If it could be shown that for each $\rho \in \mathscr{F}_+$ there is at least one $\vec{\mathrm{D}} \in \mathscr{P}$, such that $\hat{\delta}\vec{\mathrm{D}} = \rho$, then it could be said that $\hat{\delta}\mathscr{P} = \mathscr{F}_+$. This is closely related to the n-representability problem for densities, and has been established when the densities and density matrices are not restricted to finite-basis-set expansions. In Sec. VI, it will be shown by a counterexample not to be true in general for the finite-basis case.

Corresponding to the density-matrix reduction mapping $\hat{L}_n^p$ considered in GDM II, it was convenient to define an inverse mapping $\hat{\Gamma}_p^n$. In a similar way we can define an inverse mapping for $\hat{\delta}$, denoting it by $\hat{\delta}^{-1}$. For any function $g \in \mathscr{F}$,

$$\hat{\delta}^{-1} g = \{ G \in \mathscr{E} \mid \hat{\delta} G = g \} \ . \tag{15}$$

Although density matrices are confined to $\mathscr{P}$ and densities to $\mathscr{F}_+$, the mappings $\hat{\delta}$ and $\hat{\delta}^{-1}$ are defined for all $\mathscr{E}$ and $\mathscr{F}$, respectively. If, for some $g \in \mathscr{F}$,

$$\vec{\mathrm{G}} \in \hat{\delta}^{-1} g \ , \tag{16}$$

then in general $\vec{\mathrm{G}}$ can have components in $\mathscr{X}$, $\mathscr{M}$, and $\mathscr{K}$. A one-to-one mapping, $\hat{\delta}_m^{-1}$, from $\mathscr{F}$ into $\mathscr{E}$ can be recovered by eliminating the $\mathscr{K}$ component. It can be expressed in several ways, such as

$$\begin{aligned} \hat{\delta}_m^{-1} g &= \cdots \\ &= \hat{\delta}^{-1} g \cap (\mathscr{X} \oplus \mathscr{M}) \ , \end{aligned} \tag{17}$$

where the ellipsis represents the element of $\hat{\delta}^{-1} g$ of minimum norm. It does not follow, however, that $\hat{\delta}_m^{-1} \hat{\delta} \vec{\mathrm{G}} = \vec{\mathrm{G}}$.

To obtain explicit results in a particular case, one can use the following procedure. The given function g is expanded in terms of the linearly independent basis $\{ \hat{\delta} Y_k \}$,

$$g = \sum_{\kappa=0}^{r^2-l-1} C_\kappa \hat{\delta} Y_\kappa \ , \tag{18}$$

uniquely determining the expansion coefficients C_κ. Then

$$\hat{\delta}_m^{-1} g = \sum_{\kappa=0}^{r^2-l-1} C_\kappa Y_\kappa \ , \tag{19}$$

and any element of $\hat{\delta}^{-1} g$ can be expressed as

$$\vec{\mathrm{G}} = \sum_{\kappa=0}^{r^2-1} C_\kappa Y_\kappa \ , \tag{20}$$

where the coefficients C_κ with $\kappa \geq r^2 - l$ are arbitrary. A transformation from the $\{ Y_\kappa \}$ to any other basis for $\mathscr{E}$ can always be carried out.

IV. AN EXAMPLE

As a simple example to illustrate the relationships discussed above, we consider the spaces generated by five real, orthonormal functions on the line segment $-\pi \leq x \leq \pi$:

$$\begin{aligned} \{ \phi_i \} = \{ & (2\pi)^{-1/2}, \pi^{-1/2}\sin x, \pi^{-1/2}\cos x \ , \\ & \pi^{-1/2}\sin 2x, \pi^{-1/2}\cos 2x \} \ . \end{aligned} \tag{21}$$

The basis kernels for $\mathscr{E}$ are given in Table I, as are the results of collapse. Simple trigonometric relationships can be used to simplify the results. For example,

$$\begin{aligned} X &= \frac{1}{\sqrt{5}} \bar{A}_0 \\ &= \tfrac{1}{5} [\phi_1(x)\phi_1(x') + \cdots + \phi_5(x)\phi_5(x')] \\ &= \frac{1}{5\pi} (\tfrac{1}{2} + \sin x \, \sin x' + \cos x \, \cos x' \\ &\qquad + \sin 2x \, \sin 2x' + \cos 2x \, \cos 2x') \\ &= \frac{1}{5\pi} [\tfrac{1}{2} + \cos(x - x') + \cos 2(x - x')] \ . \end{aligned} \tag{22}$$

In this case the average density is simply a constant

$$f_0 \propto \hat{\delta} \mathscr{X} = \frac{1}{2\pi} \ . \tag{23}$$

The choice of the $\bar{A}_k$ is of course somewhat arbitrary. As they have been chosen here, two of them collapse to zero and are thus appropriate basis function for $\mathscr{K}$. In addition, the following linear-dependency conditions can be written (by inspection):

$$\begin{aligned} & \sqrt{2} \hat{\delta} \bar{A}_3 + \hat{\delta} B_{15} = 0 \ , \\ & \sqrt{2} \hat{\delta} B_{12} + \hat{\delta} B_{25} - \hat{\delta} B_{34} = 0 \ , \\ & \sqrt{2} \hat{\delta} B_{13} - \hat{\delta} B_{24} - \hat{\delta} B_{35} = 0 \ , \\ & \hat{\delta} B_{14} - \sqrt{2} \hat{\delta} B_{23} = 0 \ , \end{aligned} \tag{24}$$

so that in this example, $l = 6$. An orthonormal basis for $\mathscr{F}$ can be taken as

TABLE I. Basis elements of $\mathscr{E}$ and their collapses.

$\bar{A}_0 = \frac{1}{\sqrt{5}}\frac{1}{\pi}(\frac{1}{2} + \sin x \sin x' + \cos x \cos x' + \sin 2x \sin 2x' + \cos 2x \cos 2x')$	$\hat{\delta}\bar{A}_0 = \frac{\sqrt{5}}{2\pi}$
$\bar{A}_1 = \frac{1}{2\sqrt{5}}\frac{1}{\pi}(2 - \sin x \sin x' - \cos x \cos x' - \sin 2x \sin 2x' - \cos 2x \cos 2x')$	$\hat{\delta}\bar{A}_1 = 0$
$\bar{A}_2 = \frac{1}{2}\frac{1}{\pi}(\sin x \sin x' + \cos x \cos x' - \sin 2x \sin 2x' - \cos 2x \cos 2x')$	$\hat{\delta}\bar{A}_2 = 0$
$\bar{A}_3 = \frac{1}{\sqrt{2}}\frac{1}{\pi}(-\sin x \sin x' a + \cos x \cos x')$	$\hat{\delta}\bar{A}_3 = \frac{1}{\sqrt{2}}\frac{1}{\pi}\cos 2x$
$\bar{A}_4 = \frac{1}{\sqrt{2}}\frac{1}{\pi}(-\sin 2x \sin 2x' + \cos 2x \cos 2x')$	$\hat{\delta}\bar{A}_4 = \frac{1}{\sqrt{2}}\frac{1}{\pi}\cos 4x$
$B_{12} = \frac{1}{2\pi}(\sin x + \sin x')$	$\hat{\delta}B_{12} = \frac{1}{\pi}\sin x$
$B_{13} = \frac{1}{2\pi}(\cos x + \cos x')$	$\hat{\delta}B_{13} = \frac{1}{\pi}\cos x$
$B_{14} = \frac{1}{2\pi}(\sin 2x + \sin 2x')$	$\hat{\delta}B_{14} = \frac{1}{\pi}\sin 2x$
$B_{15} = \frac{1}{2\pi}(\cos 2x + \cos 2x')$	$\hat{\delta}B_{15} = \frac{1}{\pi}\cos 2x$
$B_{23} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\sin x \cos x' + \cos x \sin x')$	$\hat{\delta}B_{23} = \frac{1}{\sqrt{2}}\frac{1}{\pi}\sin 2x$
$B_{24} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\sin x \sin 2x' + \sin 2x \sin x')$	$\hat{\delta}B_{24} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\cos x - \cos 3x)$
$B_{25} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\sin x \cos 2x' + \cos 2x \sin x')$	$\hat{\delta}B_{25} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(-\sin x + \sin 3x)$
$B_{34} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\cos x \sin 2x' + \sin 2x \cos x')$	$\hat{\delta}B_{34} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\sin x + \sin 3x)$
$B_{35} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\cos x \cos 2x' + \cos 2x \cos x')$	$\hat{\delta}B_{35} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\cos x + \cos 3x)$
$B_{45} = \frac{1}{\sqrt{2}}\frac{1}{\pi}(\sin 2x \cos 2x' + \cos 2x \sin 2x')$	$\hat{\delta}B_{45} = \frac{1}{\sqrt{2}}\frac{1}{\pi}\sin 4x$

$$\{f_\lambda, \lambda = 0, 1, \ldots, 8\} = \left\{ \frac{1}{\sqrt{2\pi}}, \frac{1}{\sqrt{\pi}}\sin x, \frac{1}{\sqrt{\pi}}\cos x, \frac{1}{\sqrt{\pi}}\sin 2x, \frac{1}{\sqrt{\pi}}\cos 2x, \frac{1}{\sqrt{\pi}}\sin 3x, \frac{1}{\sqrt{\pi}}\cos 3x, \frac{1}{\sqrt{\pi}}\sin 4x, \frac{1}{\sqrt{\pi}}\cos 4x \right\}. \tag{25}$$

The corresponding basis elements for $\mathscr{M}$ and $\mathscr{L}$ are included in Table II, along with those for $\mathscr{K}$.

It is readily verified that the elements in Table II represent an orthogonal transformation of the original basis elements for $\mathscr{E}$, so that they are again orthonormal. The basis for $\mathscr{M} \oplus \mathscr{L}$ happens, in this case, to collapse to an orthogonal basis for $\mathscr{F}$. In general, only linear independence can be attained.

TABLE II. Basis elements for $\mathscr{L}$, $\mathscr{M}$, and $\mathscr{K}$, and their collapses.

$\mathscr{L}$	
$Y_0=\bar{A}_0$	$\hat{\delta}Y_0=\left[\dfrac{5}{2\pi}\right]^{1/2}f_0$
$\mathscr{M}$	
$Y_1=\dfrac{1}{\sqrt{2}}B_{12}-\frac{1}{2}B_{25}+\frac{1}{2}B_{34}$	$\hat{\delta}Y_1=\left[\dfrac{4}{2\pi}\right]^{1/2}f_1$
$Y_2=\dfrac{1}{\sqrt{2}}B_{13}+\frac{1}{2}B_{24}+\frac{1}{2}B_{35}$	$\hat{\delta}Y_2=\left[\dfrac{4}{2\pi}\right]^{1/2}f_2$
$Y_3=(\frac{2}{3})^{1/2}B_{14}+\dfrac{1}{\sqrt{3}}B_{23}$	$\hat{\delta}Y_3=\left[\dfrac{3}{2\pi}\right]^{1/2}f_3$
$Y_4=\dfrac{1}{\sqrt{3}}\bar{A}_3+(\frac{2}{3})^{1/2}B_{15}$	$\hat{\delta}Y_4=\left[\dfrac{3}{2\pi}\right]^{1/2}f_4$
$Y_5=\dfrac{1}{\sqrt{2}}B_5+\dfrac{1}{\sqrt{2}}B_{34}$	$\hat{\delta}Y_5=\left[\dfrac{2}{2\pi}\right]^{1/2}f_5$
$Y_6=-\dfrac{1}{\sqrt{2}}B_{24}+\dfrac{1}{\sqrt{2}}B_{35}$	$\hat{\delta}Y_6=\left[\dfrac{2}{2\pi}\right]^{1/2}f_6$
$Y_7=B_{45}$	$\hat{\delta}Y_7=\left[\dfrac{1}{2\pi}\right]^{1/2}f_7$
$Y_8=-\bar{A}_4$	$\hat{\delta}Y_8=\left[\dfrac{1}{2\pi}\right]^{1/2}f_8$
$\mathscr{K}$[a]	
$Y_9=\bar{A}_1$	
$Y_{10}=\bar{A}_2$	
$Y_{11}=\dfrac{1}{\sqrt{2}}B_{12}+\frac{1}{2}B_{25}-\frac{1}{2}B_{34}$	
$Y_{12}=\dfrac{1}{\sqrt{2}}B_{13}-\frac{1}{2}B_{24}-\frac{1}{2}B_{35}$	
$Y_{13}=\dfrac{1}{\sqrt{3}}B_{14}-(\frac{2}{3})^{1/2}B_{23}$	
$Y_{14}=(\frac{2}{3})^{1/2}\bar{A}_3-\dfrac{1}{\sqrt{3}}B_{15}$	

[a] All elements of $\mathscr{K}$ collapse to zero.

A particular matrix is presented in Table III, with its expansion in the various bases and its collapse. The matrix of minimum norm within the set generated by $\hat{\delta}^{-1}$, which is the result of $\hat{\delta}_m^{-1}$ acting on the density corresponding to the original matrix, and an element of $\mathscr{K}$ are also given in Table III.

The original matrix $\vec{D}$ is positive, symmetric, and of trace 1, so it is a density matrix. The matrix $\vec{D}_0=\hat{\delta}_m^{-1}\hat{\delta}\vec{D}$ is not positive, however, so although it collapses to the same density as does $\vec{D}$, it is not a density matrix. All matrices of the form $\vec{D}_0+\vec{D}'(\alpha,\beta,\gamma)$ will also have the same density as $\vec{D}$, for any values of the real parameters α, β, and γ, but they will not in general be positive.

V. LOCAL POTENTIALS AND THE HOHENBERG-KOHN THEOREM

Density functional theory is based on the Hohenberg-Kohn theorem,[6] which says that for Hamiltonians of the form (in atomic units)

$$\mathscr{H}=-\frac{1}{2}\sum_i \nabla_i^2+\sum_i v(\underline{r}_i)+\sum_{i<j}\frac{1}{r_{ij}}\ , \tag{26}$$

differing only in having different "local potentials" $v(\underline{r})$, there is a one-to-one correspondence between the ground-state density $\rho_0(\underline{r})$ and the potential $v(\underline{r})$. Hohenberg and Kohn[6] then go on to establish the existence of a functional $F[\rho]$, which is "universal" in the sense that it does not depend on v, such that

$$E_v[\rho]=\int v(\underline{r})\rho(\underline{r})d\underline{r}+F[\rho]\ \geq E_0=E_v[\rho_0]\ . \tag{27}$$

Various approximate forms for the functional $F[\rho]$ have been used in variational calculations to determine ρ_0 and E_0. It is implicitly assumed in doing such calculations that densities in the neighborhood of ρ_0 are "v representable"; that is, that any such density is the ground-state density for some Hamiltonian with a local potential.

In ordinary quantum mechanics (in the coordinate representation of the Schrödinger picture) it is clear what a local potential is. There is an electrostatic potential in real, three-dimensional space which we denote by $v(\underline{r})$. This defines a function in the n-electron configuration space

$$V(\underline{r}_1,\underline{r}_2,\ldots,\underline{r}_n)=\sum_{j=1}^{n} v(\underline{r}_j)\ . \tag{28}$$

One term in the Hamiltonian is then an operator $\hat{V}$ which acts on an n-electron function simply by multiplying it by the function $V(\underline{r}_1,\ldots,\underline{r}_n)$. We can also write

$$\hat{V}=\sum_{j=1}^{n}\hat{v}_j\ , \tag{29}$$

where $\hat{v}_j$ is a one-electron operator involving the coordinates of electron j. It can be characterized as the operation of multiplying by the function $v(\underline{r}_j)$ or expressed as an integral operator

TABLE III. Some related matrices in various representations.

$$\vec{\mathrm{D}} = \begin{pmatrix} \frac{10}{21} & 0 & \frac{2}{7} & 0 & \frac{2}{21} \\ 0 & \frac{4}{15} & 0 & \frac{2}{15} & 0 \\ \frac{2}{7} & 0 & \frac{6}{35} & 0 & \frac{2}{35} \\ 0 & \frac{2}{15} & 0 & \frac{1}{15} & 0 \\ \frac{2}{21} & 0 & \frac{2}{35} & 0 & \frac{2}{105} \end{pmatrix}$$

$$=\frac{10}{21}\vec{\mathrm{A}}_1+\frac{4}{15}\vec{\mathrm{A}}_2+\frac{6}{35}\vec{\mathrm{A}}_3+\frac{1}{15}\vec{\mathrm{A}}_4+\frac{2}{105}\vec{\mathrm{A}}_5+\frac{2\sqrt{2}}{7}\vec{\mathrm{B}}_{13}+\frac{2\sqrt{2}}{21}\vec{\mathrm{B}}_{15}+\frac{2\sqrt{2}}{15}\vec{\mathrm{B}}_{24}+\frac{2\sqrt{2}}{35}\vec{\mathrm{A}}_{35}$$

$$=\frac{1}{\sqrt{5}}\overset{\rightrightarrows}{\mathrm{A}}_0+\frac{29}{42\sqrt{5}}\overset{\rightrightarrows}{\mathrm{A}}_1+\frac{37}{310}\overset{\rightrightarrows}{\mathrm{A}}_2+\frac{\sqrt{2}}{21}\overset{\rightrightarrows}{\mathrm{A}}_3+\frac{1}{21\sqrt{2}}\overset{\rightrightarrows}{\mathrm{A}}_4+\frac{2\sqrt{2}}{7}\vec{\mathrm{B}}_{13}+\frac{2\sqrt{2}}{21}\vec{\mathrm{B}}_{15}+\frac{2\sqrt{2}}{15}\vec{\mathrm{B}}_{34}+\frac{2\sqrt{2}}{35}\vec{\mathrm{B}}_{35}$$

$$=\left[\frac{1}{\sqrt{5}}\vec{\mathrm{Y}}_0\right]+\left[\frac{6+2\sqrt{2}}{21}\vec{\mathrm{Y}}_2+\frac{4-\sqrt{2}}{21\sqrt{3}}\vec{\mathrm{Y}}_4-\frac{8}{105}\vec{\mathrm{Y}}_6-\frac{1}{21\sqrt{2}}Y_8\right]$$

$$+\left[\frac{29}{42\sqrt{5}}\vec{\mathrm{Y}}_9+\frac{37}{210}\vec{\mathrm{Y}}_{10}+\frac{6-2\sqrt{2}}{21}\vec{\mathrm{Y}}_{12}+\frac{2+2\sqrt{2}}{21\sqrt{3}}\vec{\mathrm{Y}}_{14}\right]$$

$$=\vec{\mathrm{D}}(\mathscr{X})+\vec{\mathrm{D}}(\mathscr{M})+\vec{\mathrm{D}}(\mathscr{K})$$

$$\vec{\mathrm{D}}_0=\vec{\mathrm{D}}(\mathscr{X})+\vec{\mathrm{D}}(\mathscr{M})$$

$$=\begin{pmatrix} \frac{1}{\sqrt{5}} & 0 & \frac{1}{2} & 0 & \frac{1}{\sqrt{3}} \\ 0 & \frac{1}{\sqrt{5}}+\frac{1}{2\sqrt{3}} & 0 & \frac{1}{2\sqrt{2}}-\frac{1}{2} & 0 \\ \frac{1}{2} & 0 & \frac{1}{\sqrt{5}}+\frac{1}{2\sqrt{3}} & 0 & \frac{1}{2\sqrt{2}}+\frac{1}{2} \\ 0 & \frac{1}{2\sqrt{2}}-\frac{1}{2} & 0 & \frac{1}{\sqrt{5}}-\frac{1}{2\sqrt{3}}-\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{3}} & 0 & \frac{1}{2\sqrt{2}}+\frac{1}{2} & 0 & \frac{1}{\sqrt{5}}-\frac{1}{2\sqrt{3}}+\frac{1}{\sqrt{2}} \end{pmatrix}$$

$$\hat{v}\phi(x_j)=\int v(x_j,x_j')\phi(x_j')dx_j' \; . \qquad (30)$$

As usual, $x=\underline{r}$, ξ represents the position and spin coordinates of one electron, and the kernel is

$$v(x,x')=v(\underline{r})\delta(\underline{r}-\underline{r}')\delta(\xi-\xi') \; . \qquad (31)$$

In any formulation, the operator $\hat{V}$ is determined by the function $v(\underline{r})$.

When a finite basis set is introduced and one deals with matrices, this clarity is blurred. It is necessary to have criteria for determining if a given matrix $\vec{\mathrm{V}}$ is the matrix of an operator of the form given in Eqs. (28)–(31). Two caveats must be observed as a consequence of restriction to a finite basis. Operators which differ in the full Hilbert space may be the same when restricted to a finite-dimensional subspace. In particular, a nonlocal operator may, when restricted, be completely equivalent to the operator determined by a local potential. Secondly, operators which commute in the full Hilbert space may have restrictions which do not commute. Any two local potentials $v_1(\underline{r})$ and $v_2(\underline{r})$ obviously have operators $\hat{V}_1$ and $\hat{V}_2$, defined by Eqs. (28)–(31), which commute, but their matrices $\vec{\mathrm{V}}_1$ and $\vec{\mathrm{V}}_2$ in the finite-dimensional space may not commute.

Epstein and Rosenthal,[7] and Katriel *et al.*,[8,9] have considered finite-dimensional matrix problems in connection with the Hohenberg-Kohn theorem and related matters. They take diagonal matrices to be analogous to local potentials. This is appropriate in their context, since a diagonal matrix can be regarded as a discrete approximation to a local potential, and since all diagonal matrices commute. If

TABLE III. (*Continued.*)

another element of $\mathscr{K}$:

$$\vec{\mathrm{D}}'=\alpha\vec{\mathrm{Y}}_{11}+\beta\vec{\mathrm{Y}}_{13}+\gamma\vec{\mathrm{Y}}_{14}=\begin{bmatrix} 0 & \frac{\alpha}{2} & 0 & \frac{\beta}{\sqrt{6}} & \frac{\gamma}{\sqrt{3}} \\ \frac{\alpha}{2} & \frac{\gamma}{\sqrt{3}} & -\frac{\beta}{\sqrt{3}} & 0 & \frac{\alpha}{2\sqrt{2}} \\ 0 & -\frac{\beta}{\sqrt{3}} & -\frac{\gamma}{\sqrt{3}} & -\frac{\alpha}{2\sqrt{2}} & 0 \\ \frac{\beta}{\sqrt{6}} & 0 & -\frac{\alpha}{2\sqrt{2}} & 0 & 0 \\ \frac{\gamma}{\sqrt{3}} & \frac{\alpha}{2\sqrt{2}} & 0 & 0 & 0 \end{bmatrix},$$

$$\begin{aligned}\hat{\delta}\vec{\mathrm{D}}=\hat{\delta}\vec{\mathrm{D}}_0=\hat{\delta}(\vec{\mathrm{D}}_0+\vec{\mathrm{D}}')&=\frac{1}{\sqrt{2}\pi}\left[f_0+\frac{12+4\sqrt{2}}{21}f_2+\frac{4-\sqrt{2}}{21}f_4-\frac{8\sqrt{2}}{105}f_6-\frac{1}{21\sqrt{2}}f_8\right]\\ &=\frac{1}{105\pi}(5+3\sqrt{2}\cos x+\sqrt{2}\cos 2x)^2+\frac{1}{15\pi}(2\sin x+\sin 2x)^2 .\end{aligned}$$

one wishes to establish a connection with specific physical operators restricted to a finite basis, however, there are difficulties with this analogy. On one hand, an appropriate choice of basis will make any (Hermitian) matrix diagonal, and, on the other, finite matrices corresponding to different local potentials will not necessarily commute. A different criterion for local character will therefore be sought.

We have already noted that the $\hat{V}$ of Eq. (29) is a "one-electron" operator—i.e., although it acts on n-electron functions, it is a sum of operators each depending only on the coordinates of a single electron. This means that the matrix element of $\hat{V}$ between two n-electron basis functions can be expressed in terms of the one-electron reduced transition-density matrix between those basis functions. The Hermitian matrix $\vec{\mathrm{V}}$ is an element of the space $\mathscr{E}_n$ of such matrices. In GDM II it is shown that $\mathscr{E}_n$ can be decomposed into a series of orthogonal subspaces

$$\mathscr{E}_n=\sum_{\pi=0}^{n}\oplus\,\mathscr{E}_{n,\pi}\ , \tag{32}$$

where $\mathscr{E}_{n,\pi}$ consists of those elements $\vec{\mathrm{A}}^{(n,\pi)}$ of $\mathscr{E}_n$ such that

$$\begin{aligned}&\hat{L}_n^{\pi-1}\vec{\mathrm{A}}^{(n,\pi)}\equiv 0\ ,\\ &\hat{L}_n^{\pi}\vec{\mathrm{A}}^{(n,\pi)}\neq 0\ ,\end{aligned} \tag{33}$$

where $\hat{L}_n^p$ is the reduction mapping from $\mathscr{E}_n$ to $\mathscr{E}_p$. It follows that the matrix of a one-electron operator such as $\vec{\mathrm{V}}$ has components in $\mathscr{E}_{n,1}$ (and in general in $\mathscr{E}_{n,0}$) but not in the $\mathscr{E}_{n,\pi}$ with $\pi>1$. In addition (as a consequence), all the matrix elements of $\vec{\mathrm{V}}$ can be expressed in terms of $\vec{\mathrm{v}}$, a matrix in $\mathscr{E}_1$ with elements

$$\begin{aligned}v_{jk}&=\int\int\phi_j^*(x)v(x,x')\phi_k(x')dx'dx\\ &=\int\phi_j^*(x)v(\underline{r})\phi_k(x)dx\ ,\end{aligned} \tag{34}$$

where $\{\phi_i\}$ is the one-electron basis. The spin dependence could be separated, by the techniques of GDM III, but we will not be concerned with these details here. We will simply ignore spin and replace x by $\underline{r}$.

We now have a criterion for identifying the matrix of a one-electron operator, but not yet of a local potential. This criterion can be established in terms of $\vec{\mathrm{v}}$. From the results of Sec. III, the space $\mathscr{E}=\mathscr{E}_1$, of which $\vec{\mathrm{v}}$ is an element, can be deomposed into three orthogonal subspaces, $\mathscr{E}=\mathscr{X}\oplus\mathscr{M}\oplus\mathscr{K}$, where $\mathscr{X}$ is a one-dimensional space with basis Y_0 [in the notation of Eq. (32), $\mathscr{X}$ is $\mathscr{E}_{1,0}$] and $\mathscr{M}\oplus\mathscr{K}=\mathscr{N}$. The space $\mathscr{M}$, of dimension r^2-l-1 (r is the number of one-electron basis functions), is in one-to-one correspondence with the space $\overline{\mathscr{F}}$ of densities integrating to zero, and any element of $\mathscr{K}$ gives zero on collapse. The criterion that will be used to define a local potential is that the matrix $\vec{v}$ have no component in $\mathscr{K}$. The appropriateness of this criterion is readily established.

Equation (34) gives expressions for the elements of the matrix $\vec{v}$. When we think of $\vec{v}$ as a vector in $\mathscr{E}_1$, it is more convenient to think of the components

$$v_j^a = v_{jj} \quad (\text{if } k = j) \;,$$

or

$$v_{jk}^b = (v_{jk} + v_{kj})/\sqrt{2}$$

and

$$v_{jk}^c = -i(v_{jk} - v_{kj})/\sqrt{2} \quad (\text{if } k \neq j) \;.$$

These components are, for example,

$$\begin{aligned} v_{jj}^a &= \int \int v(\underline{r},\underline{r}')A^k(\underline{r},\underline{r}')d\underline{r}\,d\underline{r}' \\ &= \int v(\underline{r})\hat{\delta}A^k(\underline{r})d\underline{r} \end{aligned} \tag{35}$$

with similar expressions for v_{jk}^b and v_{jk}^c. If we use for $\mathscr{E}_1$ not the A,B,C basis but the $\{Y_\kappa\}$ basis, it is apparent that

$$v_\kappa = \int v(\underline{r})\hat{\delta}Y_\kappa(\underline{r})d\underline{r} \tag{36}$$

and thus that $v_\kappa = 0$ for $\kappa > r^2 - l - 1$, so $\vec{v}$ has no component in $\mathscr{K}$. If $v(\underline{r})$ is modified by the addition of a constant, only the $\kappa = 0$ component of $\vec{v}$ (the component in $\mathscr{H}$) will be changed.

The function $v(\underline{r})$ can be written as

$$v(\underline{r}) = \sum_{\kappa=0}^{r^2-l-1} \beta_\kappa f_\kappa(\underline{r}) + v_\perp(\underline{r}) \;, \tag{37}$$

where $v_\perp(\underline{r})$ is orthogonal to the space $\mathscr{F}$ spanned by the $\{f_\kappa\}$ or the $\{\hat{\delta}Y_\kappa\}$. Any such component, if present, will not affect $\vec{v}$ at all. Suppose now that $\vec{v}$ is a given matrix with no component in $\mathscr{K}$, so that it can be written as

$$\vec{v} = \sum_{\kappa=0}^{r^2-l-1} \alpha_\kappa \vec{Y}_\kappa \;, \tag{38}$$

i.e., $v_\kappa = \alpha_\kappa$ for

$$0 \le \kappa \le r^2 - l - 1$$

and $v_\kappa = 0$ for $\kappa \ge r^2 - l$. A potential function $v(\underline{r})$ can be defined by Eq. (37) with $v_\perp \equiv 0$, and the $\{\beta_\kappa\}$ given in terms of the $\{\alpha_\kappa\}$ and the transformation linking the bases $\{\hat{\delta}Y_\kappa\}$ and $\{f_\kappa\}$ for $\mathscr{F}$, such that Eq. (36) will reproduce the expansion coefficients $v_\kappa = \alpha_\kappa$. The given matrix is thus the same as the matrix for a local potential, even though this may not have been its origin.

In terms of the mappings defined in Sec. III, we can say that $\vec{v}$ is the matrix of a local potential if and only if

$$\hat{\delta}_m^{-1}(\hat{\delta}\vec{v}) = \vec{v} \;. \tag{39}$$

In the example of Sec. IV, if we think of the density as corresponding to the local-potential function, $\vec{D}_0$ is the matrix of a local potential but $\vec{D}$ is not.

Equipped with a suitable definition of a local potential, we are now prepared to investigate the Hohenberg-Kohn theorem in the finite basis case. Hohenberg and Kohn[6] began the proof of their theorem by introducing Ψ and Ψ' as the ground-state wave functions of $\mathscr{H}$ and $\mathscr{H}'$, respectively, where the two Hamiltonians differ by having different local potentials $v(\underline{r})$ and $v'(\underline{r})$. They then state, "Now clearly [unless $v'(\underline{r}) - v(\underline{r}) = \text{const}$] Ψ' cannot be equal to Ψ since they satisfy different Schrödinger equations" and proceed with the now-well-known proof. A corresponding statement is not true in the matrix case. It is easy to construct many matrices having the same ground-state eigenvector. Of course we might not expect this to happen for matrices of operators which differ only by a local potential, but it can. In consequence, there is in general no Hohenberg-Kohn theorem for finite-basis-set models.

We consider a simple example to illustrate the breakdown. Take a "particle-in-a-box" problem wth $v(x) = 0$ for $-\pi < x < \pi$ and $v(x) = \infty$ for $|x| > \pi$. In the inner region

$$\hat{\mathscr{H}} = \hat{\mathscr{T}} = -\tfrac{1}{2}(d^2/dx^2)$$

in appropriate units. As a basis set we introduce the first three odd eigenfunctions

$$\{\phi_n(x) = (1/\sqrt{\pi})\sin nx, \quad n = 1,2,3\} \;.$$

Then

$$\vec{H} = \vec{T} = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{4}{2} & 0 \\ 0 & 0 & \frac{9}{2} \end{bmatrix} \tag{40}$$

has eigenvectors (1,0,0), (0,1,0), and (0,0,1).

Now introduce a potential

$$v'(x) = \cos x + \cos 3x$$

for $-\pi < x < \pi$ [with again

$$v'(x) = v(x) = \infty$$

for $|x| > \pi$]. The only nonzero matrix elements of this potential for our basis set are $V'_{2,3} = V'_{3,2} = \frac{1}{2}$, and

$$\vec{\mathrm{H}}'=\vec{\mathrm{T}}+\vec{\mathrm{V}}'=\begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{4}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{9}{2} \end{bmatrix} . \tag{41}$$

This matrix also has (1,0,0) as its ground-state eigenvector. [This vector is associated with the eigenvalue $\frac{1}{2}$ for both $\vec{\mathrm{H}}$ and $\vec{\mathrm{H}}'$. The other eigenvalues of $\vec{\mathrm{H}}'$ are $(13\pm\sqrt{29})/4=4.596\ldots$, $1.908\ldots$.]

It may be worthwhile to establish the validity of the Hohenberg-Kohn assertion for the true problem, i.e., the Schrödinger equation. We will use a notation slightly different from theirs and let

$$\hat{\mathscr{H}}_i=\hat{\mathscr{T}}+\hat{\mathscr{U}}+\hat{\mathscr{V}}_i,\quad i=1,2 \tag{42}$$

where (in atomic units)

$$\begin{aligned} \hat{\mathscr{T}}&=-\tfrac{1}{2}\sum_j \nabla_j^2 , \\ \hat{\mathscr{U}}&=\sum_{j<k} 1/r_{jk} , \\ \hat{\mathscr{V}}_i&=\sum_j v_i(\underline{r}_j) . \end{aligned} \tag{43}$$

Assume that Ψ_i is an eigenfunction of $\hat{\mathscr{H}}_i$ (not necessarily the ground state):

$$\hat{\mathscr{H}}_i\Psi_i=E_i\Psi_i . \tag{44}$$

Now suppose that $\Psi_1=\Psi_2=\Psi$. Then

$$(\hat{\mathscr{H}}_1-\hat{\mathscr{H}}_2)\Psi=(E_1-E_2)\Psi$$

but

$$\hat{\mathscr{H}}_1-\hat{\mathscr{H}}_2=\hat{\mathscr{V}}_1-\hat{\mathscr{V}}_2 ,$$

so, with $E_2-E_1=\Delta E$,

$$(\hat{\mathscr{V}}_1-\hat{\mathscr{V}}_2+\Delta E)\Psi=0 . \tag{45}$$

In the case of a single electron ($\hat{\mathscr{U}}$ is then omitted) $\hat{\mathscr{V}}_i=v_i(\underline{r})$ and Eq. (45) requires as a consequence of the assumption $\Psi_1=\Psi_2$ that $v_1(\underline{r})=v_2(\underline{r})+\Delta E$ except possibly where $\Psi(\underline{r})=0$. We expect Ψ to be nodeless for the ground state, and in any state Ψ will be different from zero and thus permit v_2 to differ from v_1 + const only on a set of measure zero. In the many-electron case, let

$$\Psi=\sum_\kappa \Phi_\kappa(\underline{r}_1,\ldots,\underline{r}_n)\sigma_\kappa , \tag{46}$$

where the $\{\sigma_\kappa\}$ are an orthonormal set of spin functions. Since the $\hat{\mathscr{H}}_i$ are (by assumption) spin independent, Eq. (45) leads to

$$(\hat{\mathscr{V}}_1-\hat{\mathscr{V}}_2+\Delta E)\Phi_\kappa=0,\quad \text{all } \kappa . \tag{47}$$

If we define $\Delta e=\Delta E/n$, these equations can be written

$$\sum_{j=1}^{n}[v_1(\underline{r}_j)-v_2(\underline{r}_j)+\Delta e]\Phi_\kappa(\underline{r}_1,\ldots,\underline{r}_n)=0 . \tag{48}$$

Fix the values of $\underline{r}_2,\ldots,\underline{r}_n$ at some set of constant vectors. Then

$$\begin{aligned} &\sum_{j=2}^{n}[v_1(\underline{r}_j)-v_2(\underline{r}_j)+\Delta e]=c , \\ &\Phi_\kappa(\underline{r}_1,\underline{r}_2,\ldots,\underline{r}_n)=\phi_\kappa(\underline{r}_1) , \end{aligned} \tag{49}$$

and for all values of $\underline{r}_1$ for which $\phi_\kappa(\underline{r}_1)\neq 0$ for any κ,

$$v_2(\underline{r}_1)=v_1(\underline{r}_1)+c . \tag{50}$$

If the constant values of $\underline{r}_2,\ldots,\underline{r}_n$ were unwisely chosen it would be possible that $\phi_\kappa(\underline{r}_1)\equiv 0$ for some and possibly all κ. They certainly can be chosen so that this is not the case, and such will be assumed. We then expect that all the $\phi_\kappa(\underline{r}_1)$ will not vanish over some range of $\underline{r}_1$ values, but at most on a set of measure zero. It has been shown that, if two Hamiltonians of the form given in Eqs. (42) and (43) have any eigenfunctions in common, then the local potentials v_1 and v_2 differ only by a constant, except possibly on a set of measure zero. If the potentials are required to be continuous, even the latter possibility ceases to exist, and the potentials are essentially the same.

Now we return to the finite-basis-set case, but consider a more realistic many-electron situation. We will determine the circumstances under which a vector can be an eigenvector (possibly the ground state) of two Hamiltonians differing only by the matrix of a local potential. We can parallel the preceding treatment, replacing operators by matrices defined with respect to the n-electron basis. If $\underline{C}$ is an eigenvector of two Hamiltonian matrices $\vec{\mathrm{H}}$ and $\vec{\mathrm{H}}'$, then

$$\Delta\vec{\mathrm{V}}\underline{C}=0 , \tag{51}$$

where

$$\Delta\vec{\mathrm{V}}=\vec{\mathrm{V}}-\vec{\mathrm{V}}'+(E'-E)\vec{1}$$

is the matrix of a local potential:

$$\Delta v(\underline{r})=v(\underline{r})-v'(\underline{r})+(E'-E)/n . \tag{52}$$

Let $R^2-l-1=s$ [or $(\frac{1}{2})R(R-1)-l-1=s$ in the real case] so that the dimension of $\mathscr{F}$ is $s+1$ and there are s orthonormal functions $\{f_\kappa\}$ providing a basis for $\overline{\mathscr{F}}$. Then

$$\Delta v(\underline{r})=\sum_{\kappa=0}^{s}\Delta v_\lambda f_\lambda(\underline{r})+\Delta v_\perp(\underline{r})\ , \tag{53}$$

where $\Delta v_\perp(\underline{r})$ is the component (if any) of $\Delta v(\underline{r})$ orthogonal to $\mathscr{F}$. It will not contribute to $\Delta\vec{V}$ and will thus have no effect on the matrix problem. The effective information about $\Delta v(\underline{r})$ is contained in the coefficients

$$\Delta\underline{v}=(\Delta v_0,\Delta v_1,\ldots,\Delta v_s)\ .$$

We have seen above how $\Delta v(\underline{r})$ determines the n-electron matrix $\Delta\vec{V}$. If the components of $\Delta\vec{V}$ with respect to an appropriate basis for $\mathscr{E}_n$ (to be specified later) are labeled by an index (J), we can write

$$\Delta\vec{V}_{(J)}=\sum_{\kappa=0}^{s}T_{(J),\kappa}\Delta v_\kappa\ . \tag{54}$$

The transformation described by $\{T_{(J),\kappa}\}$ includes the invertible but not unitary transformation between the $\{\hat{\delta}Y_\kappa\}$ and $\{f_\kappa\}$ as well as possible unitary transformations of the basis for the matrix space.

Equation (51) can be written in terms of components of $\Delta\vec{V}$ and $\underline{C}$ defined with respect to the n-electron function basis (referred to as the configuration space) as

$$\sum_{K}\Delta V_{JK}C_K=0\ . \tag{55}$$

Let $\underline{A}$ be an arbitrary vector in this n-electron configuration space. From Eq. (55) and the fact that ΔV is Hermitian, we have

$$\sum_{J,K}\Delta V_{JK}P_{JK}(\underline{A})=0\ , \tag{56}$$

where

$$P_{JK}(\underline{A})=A_J^*C_K+A_KC_J^* \tag{57}$$

is, apart possibly from a constant, a "transition density matrix" between the pure states $\underline{A}$ and $\underline{C}$, which has been symmetrized so it is in $\mathscr{E}_n$. Equation (56) follows from Eq. (55) for any $\underline{A}$. If Eq. (56) is satisfied for each $\underline{A}^k$ in a basis for the configuration space, then Eq. (55) must also hold.

Equation (56) is in the form of a scalar product of $\mathscr{E}_n$, so it can be written as well in any other orthonormal basis:

$$\sum_{(J)}\Delta V_{(J)}P_{(J)}=0\ . \tag{58}$$

We now specify that the basis labeled by (J) be the reducing basis defined in GDM II, and further that the elements with $\pi=1$ be grouped to separate $\mathscr{N}$ $(=\mathscr{N}_1)$ into $\mathscr{M}$ and $\mathscr{K}$ as discussed in Sec. II. The only nonzero components of ΔV will be the $\pi=0$ component and the $\pi=1$ components reducing to components in $\mathscr{M}$. Only those same components of $P(\underline{A})$ need be considered, and these are just the components which contribute to a density corresponding to $P(\underline{A}),\underline{d}(\underline{A})$ with

$$d_\kappa(\underline{A})=\sum_{(J)}(T^{-1})_{\kappa,(J)}P_{(J)}(\underline{A})\ . \tag{59}$$

The "inverse" relationship implied by the use of T^{-1} is symbolic, but appropriate. In particular, $P(\underline{A})$ can be replaced in Eq. (58) by $\underline{\bar{P}}(\underline{A})$ with

$$\bar{P}_{(J)}(\underline{A})=\sum_{\kappa}T_{(J),\kappa}d_\kappa(\underline{A})\ , \tag{60}$$

and thus Eq. (58) becomes

$$\begin{aligned}0&=\sum_{(J)}\sum_{\kappa,\lambda}T_{(J),\kappa}T_{(J),\kappa}\Delta v_\kappa d_\lambda(\underline{A})\\&=\sum_{\kappa,\lambda}\Delta v_\kappa S_{\kappa\lambda}d_\lambda(\underline{A})\\&=\sum_{\kappa}\Delta v_\kappa\bar{d}_\kappa(\underline{A})\ ,\end{aligned} \tag{61}$$

where

$$S_{\kappa\lambda}=\sum_{(J)}T_{(J),\kappa}T_{(J),\lambda} \tag{62}$$

is dependent on the nonorthogonality of the one-electron basis-function products, and

$$\begin{aligned}\bar{d}_\kappa(\underline{A})&=\sum_{\lambda}S_{\kappa\lambda}d_\lambda\\&=\sum_{\lambda}\sum_{(J)}S_{\kappa\lambda}(T^{-1})_{\lambda,(J)}P_{(J)}(\underline{A})\ .\end{aligned} \tag{63}$$

Equation (61) is of the form of a scalar product in $\mathscr{F}$. Given some n-electron eigenvector C, we can construct a set of vectors $\underline{\bar{d}}(\underline{A}^K)$ where $\underline{A}^K$ ranges over a complete set of n-electron basis vectors. The vectors $\underline{\bar{d}}(\underline{A}^K)$ will surely be linearly dependent, and they may or may not provide a basis for $\mathscr{F}$. If they do, then any $\Delta\underline{v}$ orthogonal to all of them must vanish so $\underline{C}$ cannot be an eigenvector of two Hamiltonians with different potentials. However, if the $\{\underline{\bar{d}}(\underline{A}^K)\}$ do not span $\mathscr{F}$, then a nonzero $\Delta\underline{v}$ orthogonal to all of them can be found, and $\underline{C}$ can be an eigenvector of of $\vec{H}$ and $\vec{H}'$ differing by a local $\Delta\vec{V}$.

VI. n REPRESENTABILITY

By analogy with the terminology used in density-matrix theory,[10] a density is said to be n representable if it can be obtained from an n-electron (antisymmetric) wave function. This could be referred to as pure-state n representability, with an ensemble n-representable denstiy being one which can be obtained from an ensemble (but not a pure-state) n-electron density matrix. When a basis-set expansion is not involved, any density, i.e., any element of $\mathscr{F}_+$, is pure-state n representable and the functions from which it can be obtained include single determinants.[11,12] This is not the case with a finite-basis-set expansion.

Suppose that a particular basis has been chosen and a density is given in terms of basis-set products or some equivalent basis for $\mathscr{F}$. We ask whether there is always a density matrix from which this density can be obtained. The negative answer is readily provided by a simple example.

Take as a real basis set

$$\phi_1=\pi^{-1/2}\sin x,\ \phi_2=\pi^{-1/2}\cos x\ ,$$

and

$$\phi_3=\pi^{-1/2}\sin 2x\ ,$$

and consider the density

$$\begin{aligned}\rho(x)&=\frac{1}{2\pi}(1+b-2b\sin^2 2x)\\&=\frac{1}{2\pi}(1+b\cos 4x)\end{aligned}\tag{64}$$

on the interval $-\pi\leq x\leq\pi$. This function will be positive, and thus an acceptable density, so long as $|b|<1$. It is readily shown, however, that the only real symmetric matrix in this basis for which $D(x,x)=\rho(x)$ is

$$\vec{\mathrm{D}}=\begin{bmatrix}\frac{1+b}{2} & 0 & 0\\ 0 & \frac{1+b}{2} & 0\\ 0 & 0 & -b\end{bmatrix}\ .\tag{65}$$

This is not a density matrix because it has a negative eigenvalue for $b>0$. We conclude that this ρ is not even ensemble n representable within the given basis.

VII. v REPRESENTABILITY

As noted above, in the variational implementation of density functional theory,[13] is it assumed that any density, at least in a neighborhood containing the true ground-state density and an initial guess, is the ground-state density for some local potential. The question of whether this is in fact the case has been referred to as the v-representability problem.[14] It remains open.

We have seen in the preceding sections that in the context of a finite-basis-set expansion the Hohenberg-Kohn theorem does not always apply and that there can become densities which are not n representable. Suppose, however, that for an appropriately chosen basis set we can find a subset $\mathscr{F}_{\mathrm{HK}}\subset\mathscr{F}$ such that every appropriately normalized density in $\mathscr{F}_{\mathrm{HK}}$ is n representable and that within this subset the Hohenberg-Kohn theorem can be established. In this case we can state an explicit, although formal, relationship between ρ and v.

For functions $\rho(\underline{r})$ and $v(\underline{r})$ expressible in terms of the basis for $\mathscr{F}$,

$$\begin{aligned}\rho(\underline{r})&=c_\rho f_0(\underline{r})+\sum_{\kappa=1}^{s}\rho_\kappa f_\kappa(\underline{r})\ ,\\ v(\underline{r})&=c_v f_0(\underline{r})+\sum_{\kappa=1}^{s}v_\kappa f_\kappa(\underline{r})\ .\end{aligned}\tag{66}$$

The f_0 components are fixed by the normalization condition on ρ and the choice of the zero of energy for v. The remaining coefficients are restricted only by the requirement that ρ remain in $\mathscr{F}_{\mathrm{HK}}$. They define vectors $\underline{\rho}$ and $\underline{v}$ in $\mathscr{F}$, and the energy functional of Eq. (27) simply becomes a function of the expansion coefficients:

$$E(\underline{v},\underline{\rho})=c_v c_\rho+\sum_{\kappa=1}^{s}v_\kappa\rho_\kappa+F(\underline{\rho})\ .\tag{67}$$

For a given $\underline{v}$, if $\underline{\rho}$ is chosen to minimize E, certain conditions must be satisfied. It is convenient to define a gradient vector $\underline{F}'$ and a Hessian matrix $\vec{\mathrm{F}}''$ with components

$$F'_\kappa=\frac{\partial F}{\partial\rho_\kappa},\quad F''_{\kappa\lambda}=\frac{\partial^2 F}{\partial\rho_\kappa\partial\rho_\lambda}\ ,\tag{68}$$

so that

$$\frac{\partial E}{\partial\rho_\kappa}=v_\kappa+F'_\kappa,\quad \frac{\partial^2 E}{\partial\rho_\kappa\partial\rho_\lambda}=F''_{\kappa\lambda}\ .\tag{69}$$

At a minimum of E the first derivative must be zero,[15] implying that $\underline{F}'=-\underline{v}$, and the Hessian matrix $\vec{\mathrm{F}}''$ must be positive. There is nothing in what has been presented thus far to prevent these equations from being satisfied for more than one $\underline{\rho}$: E may have local minima, but one of them is presumably a global minimum unless there are degeneracies.

Now let us ask what properties a Hohenberg-Kohn function F and a domain set $\mathscr{F}_{\mathrm{HK}}$ must have it the densities in the set are to be v representable. If every ρ in $\mathscr{F}_{\mathrm{HK}}$ is to be the ground-state density for some potential, then $\vec{\mathrm{F}}''(\underline{\bar{\rho}})>0$ for all $\underline{\rho}$ in $\mathscr{F}_{\mathrm{HK}}$. The potential will be given by

$$\underline{\bar{v}}=-\underline{F}'(\underline{\rho}) \ . \tag{70}$$

Suppose that two densities $\underline{\rho}$ and $\underline{\rho}'$ give the same $\underline{\bar{v}}$, i.e., $\underline{F}'(\underline{\bar{\rho}})=\underline{F}'(\underline{\bar{\rho}}')$. Then either

$$E(\underline{\bar{v}},\underline{\bar{\rho}})=E(\underline{\bar{v}},\underline{\bar{\rho}}')$$

and there is a degeneracy or one of the densities (e.g., $\underline{\rho}'$) is not the ground-state density for $\underline{v}$. But since $\underline{F}'(\underline{\bar{\rho}}')=-\underline{\bar{v}}$, there can be no other potential for which Eqs. (69) will be satisfied at $\underline{\rho}'$, and thus $\underline{\rho}'$ cannot be the ground-state density for any potential. We conclude that another requirement for v representability is that, in the absence of degeneracies, $\underline{F}'(\underline{\bar{\rho}})$ must be distinct for all $\underline{\rho}$ in $\mathscr{F}_{\mathrm{HK}}$.

VIII. DISCUSSION

When a finite basis set is introduced, Hermitian matrices replace operators. These matrices can be considered as elements in a vector space. Densities, obtained by "collapse" of a density martrix, can be considered as elements of a related vector space. The relationship between these two spaces depends on the linear-dependency conditions among products of basis functions.

It has been shown that a density matrix can be separated into components in two orthogonal subspaces. The component in one subspace is in one-to-one correspondence with the density while the component in the other space does not contribute to the density and is not restricted when a density is specified. A many-to-one mapping of the space of matrices to the space of densities is thus defined. An inverse mapping generates for any density a set of matrices leading to that density. The matrices in this set are not necessarily density matrices, however, since they need not be positive. The reduced density matrices leading to a given density lie in the intersection of the inverse mapping of that density with the space of n-representable reduced density matrices.

A similar decomposition of the space of matrices can be used to define a local potential. It has been shown that any local potential has a component in only the subspace of nonvanishing densities, and that any such matrix can be reproduced as the matrix of a local potential. These relationships are basis-set dependent, however. In the extreme case where all basis function products are linearly independent, any operator is equivalent to (i.e., has the same matrix as) as local potential. In this case it also follows that the density completely determines the density matrix.

It has been shown that two or more Hamiltonian matrices, differing by matrices of a local potential, can have the same ground-state eigenvector. This means that a Hohenberg-Kohn theorem cannot be established in general. A criterion has been developed which can be applied to vectors in the n-electron space to determine which of them could be eigenvectors of more than one Hamiltonian. A more convenient characterization of such vectors and of the densities corresponding to them would be desirable, however. It was also shown that there are densities which are not n representable within the given basis-set model. A convenient way of identifying such densities is desirable but has not been developed.

Of course the Hohenberg-Kohn theorem is true and any density is n representable if basis-set restrictions are not introduced. We thus expect that, as a basis set becomes "almost complete" in a practical sense, these problems will disappear. It would be of interest to be able to show how this happens.

When a basis-set expansion is involved, the Hohenberg-Kohn functional becomes a function of the expansion coefficients of the density. If such a function and a domain set in which the Hohenberg-Kohn theorem is valid can be established, then v representability would further require that the matrix of second derivatives be everywhere positive and the gradient be distinct at each density, except when there are degeneracies.

The results of this paper have established connections between some aspects of density functional theory and the results of density-matrix theory expressed in geometric terms.

[1] J. E. Harriman, Phys. Rev. A 17, 1249 (1978).

[2] J. E. Harriman, Phys. Rev. A 17, 1257 (1978).

[3] J. E. Harriman, Int. J. Quantum Chem. 15, 611 (1979).

[4] The electron density is fundamental in the spatial partitioning of molecules developed by Bader: (a) R. F. W. Bader and P. M. Beddall, Chem. Phys. Lett. 8, 29 (1971); (b) R. F. W. Bader and P. M. Beddall, J. Chem. Phys. 56, 3320 (1972); (c) R. F. W. Bader, Acc. Chem. Res. 8, 34 (1975); (d) S. Srebrenik and R. F. W. Bader, J. Chem. Phys. 63, 3945 (1975); (e) S. Srebrenik, R. F. W. Bader, and T. T. Nguyen-Dang, J. Chem. Phys. 68, 3667 (1978); (f) R. F. W. Bader, S. Srebrenik, and T. T. Nguyen-Dang, J. Chem. Phys. 68, 3680 (1978); (g) R. F. W. Bader, T. T. Nguyen-Dang, and Y. Tal, J. Chem. Phys. 70, 4316 (1979); (h) R. F. W. Bader, S. G. Anderson, and A. J. Duke, J. Am. Chem. Soc. 101, 1389 (1979); (i) R. F. W. Bader, Y. Tal, S. G. Anderson, and T. T. Nguyen-Dang, Israel J. Chem. 19, 8 (1980); (j) Y. Tal, R. F. W. Bader, T. T. Nguyen-Dang, M. Ojha, and S. G. Anderson, J. Chem. Phys. 74, 5162 (1981).

[5] Density functional theory is the subject of two recent reviews: (a) A. K. Rajagopal, Adv. Chem. Phys. 41, 59 (1980); (b) A. S. Bamzai and M. B. Deb, Rev. Mod. Phys. 53, 95 (1981).

[6] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[7] S. T. Epstein and C. M. Rosenthal, J. Chem. Phys. 64, 247 (1976).

[8] E. Meron and J. Katriel, Phys. Lett. 61A, 19 (1977).

[9] J. Katriel, C. J. Appellof, and E. R. Davidson, Int. J. Quantum Chem. 19, 293 (1981).

[10] A. J. Coleman, Rev. Mod. Phys. 35, 668 (1963).

[11] T. L. Gilbert, Phys. Rev. B 12, 2111 (1975).

[12] J. E. Harriman, Phys. Rev. A 24, 680 (1981).

[13] See, e.g., W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[14] The term was coined by E. G. Larsen in informal discussion at the 1975 Boulder Summer Research Conference on Theoretical Chemistry.

[15] See also, R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, J. Chem. Phys. 68, 3801 (1978), Sec. V.