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Densities, operators, and basis sets

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Relationships between density matrices and densities or between operators and local potentials are considered for model problems defined by the introduction of basis sets. Some properties depend only on the space spanned by the basis while others depend on a particular choice of basis functions. Linear-dependency conditions play a critical role. In a model problem defined by a basis with all products linearly independent, the effect of any operator can be reproduced by a local potential, but any complete basis must have linearly dependent products. A one-electron density matrix or single-determinant wave function can be determined from the density (or experimental measurements sensitive only to the density) in the model problem defined by a basis with linearly independent products, but not otherwise. A simple example illustrates some of the general results.

I. INTRODUCTION

This paper deals with the role of basis sets in density-matrix and density-functional theory, and how they affect the relationship between functions and operators. One of the most important questions to be addressed is that of how much information about an atomic, molecular or solid system is provided by a knowledge of the electronic density. We are not concerned here with the formal relationship implied by the Hohenberg-Kohn theorem,$^{1-3}$ but rather with functions, functionals, or algorithms that can be stated in explicit form.

Some previous work that is closely related to the present investigation is reviewed in Sec. II. This brief review will also serve to define notation and terminology. We are faced with the unfortunate fact that the word "kernel" is commonly used in two quite unrelated senses, both of which are relevant. One of these is the kernel of an integral operator, which will be called here the integral kernel. The other refers to the subset of the domain of an operator consisting of those elements which yield zero when acted upon by the (nonzero) operator. We will normally refer to this as the null space of the operator.

All of the results depend on properties of the basis set used, and a number of basis sets are considered in Sec. III. Some of these are of simple analytic form, while others are more complicated but have other desirable features. While the basis sets actually used in electronic-structure calculations do not fall completely within either of these types, an analysis of the simple cases provides the basis for an understanding of more realistic cases. A semirealistic set of well-tempered Gaussian orbitals is also discussed. Some rigorous, general results are presented in Sec. IV. Of particular interest are basis sets where all products are linearly independent. These linearly independent product (LIP) basis sets often occur in quantum-chemical calculations with limited-size basis sets, and in the model problem defined by such a basis the density plays a special role. This situation is considered in Sec. V.

Improvements in experimental and data-processing capabilities make the determination of electron densities in real physical systems ever more precise.^{4} There has been some interest in using this data to determine model wave functions or one-particle density matrices.^{5} In Sec. VI the foundations of this approach are examined. The results of the present paper and the conclusions that can be drawn from it are summarized in Sec. VII, and some examples which serve to illustrate the points made are presented in the Appendix.

II. BACKGROUND

The ideas presented in this paper are closely related to some of those which have been presented earlier in a series of papers "Geometry of Density Matrices. (N)," (GDM-I, . . . , -VI),$^{6-11}$ particularly GDM-IV.^{9} Insofar as possible, the notation and conventions established in those papers will be used here, but since the present approach is slightly different, some changes will be necessary. Some distinctions will be made between different, but isomorphic, spaces. These may seem unnecessarily pedantic, but have been found to be useful in avoiding potential confusion.

The starting point is a Hilbert space $\mathscr{H}$ of finite dimension, h. The set of all linear operators from $\mathscr{H}$ to $\mathscr{H}$ is also a linear space, and it will be denoted by $\hat{\mathscr{E}}$. Each operator $\hat{G}\in\hat{\mathscr{E}}$ can be uniquely represented by an integral operator with a kernel that is sesquilinear in the functions of a basis spanning $\mathscr{H}$ [see Eq. (3)]. Such an integral kernel will be denoted by $G(\tau;\tau')$, where τ represents the set of variables on which the functions in $\mathscr{H}$ depend. We will normally be interested in the case where $\tau=\mathbf{r}\in\mathbf{R}^3$, the coordinates of a single particle in three dimensions. It is also possible to define a space $\mathscr{E}_\tau$ with the integral kernels as elements, but the distinction between $\hat{\mathscr{E}}$ and $\mathscr{E}_\tau$ will not be of great significance. Since $\mathscr{H}$ is finite dimensional, $\hat{\mathscr{E}}$ will be also, and a finite set of linearly independent operators that spans $\hat{\mathscr{E}}$ can be found. A set of operators will be considered linearly dependent if there is a linear combination, with not all coefficients zero, of the corresponding integral kernels which vanishes for all τ and τ'.

An operation which will be called "collapse" defines a linear map from $\hat{\mathscr{E}}$ (or $\mathscr{E}_\tau$) to a space $\hat{\mathscr{F}}_\tau$ whose elements are functions of τ.^{9} It will be denoted by $\hat{\delta}$ and is defined by

$$\hat{\delta}\,\hat{G}=\hat{\delta}G(\tau;\tau')=G(\tau;\tau)\,, \tag{1}$$

where G is the integral kernel associated with the operator $\hat{G}$. The function $\hat{\delta}G$ is thus just the "diagonal part" of the integral kernel in the continuous τ representation. The space $\mathscr{F}_\tau$ is defined as the function space spanned by the collapses of a set of operators (integral kernels) that spans $\hat{\mathscr{E}}$ ($\mathscr{E}_\tau$).

It is frequently convenient to introduce a specific basis set $\{\phi_k(\tau), k=1,2,\ldots,s\}$ for $\mathscr{H}$, and unless otherwise stated this set will be assumed to be orthonormal with respect to the usual scalar product:

$$\int \phi_j^*(\tau)\phi_k(\tau)\,d\tau=\delta_{jk} \; . \tag{2}$$

The integral kernels can then be expanded as

$$G(\tau;\tau')=\sum_{j,k} G_{jk}\phi_j(\tau)\phi_k^*(\tau') \; , \tag{3}$$

and for an orthonormal basis (only) the expansion coefficients are the same as the matrix elements,

$$G_{jk}=\int \phi_j^*(\tau)\left[\int G(\tau;\tau')\phi_k(\tau')d\tau'\right]d\tau \; . \tag{4}$$

The matrices $\mathbf{G}$ are the elements of a linear space $\mathscr{E}$ that is isomorphic to $\hat{\mathscr{E}}$ and $\mathscr{E}_\tau$, but the relationship of an element of $\mathscr{E}$ to the corresponding element of $\hat{\mathscr{E}}$ or $\mathscr{E}_\tau$ is basis-set dependent. Previous work has concentrated on the matrix space.[6–17] It is convenient to introduce the trace scalar product

$$(\mathbf{F},\mathbf{G})=\mathrm{tr}(\mathbf{F}^\dagger G), \quad \mathbf{F},\mathbf{G}\in\mathscr{E} \tag{5}$$

so that $\mathscr{E}$ is a metric space. (Similar definitions apply in $\hat{\mathscr{E}}$ and $\mathscr{E}_\tau$.) A basis for $\mathscr{E}$ can be introduced. It will normally be assumed to be orthonormal with respect to the trace scalar product, and consists of a set of matrices. Such a basis will usually be denoted here by $\{\mathbf{Y}^K\}$.

The introduction of the basis functions $\{\phi_k(\tau)\}$ for $\mathscr{H}$ implies the use of a set of functions which span $\mathscr{F}_\tau$. This set consists of all basis-set products $\{\phi_j(\tau)\phi_k^*(\tau), 1\le j,k\le s\}$ [cf. Eqs. (1) and (3)]. It must be noted, however, that in general these products will be linearly dependent. It is always possible to choose an orthonormal basis $\{f_\kappa(\tau)\}$ for $\mathscr{F}_\tau$, and to express each of the products $\phi_j(\tau)\phi_k^*(\tau)$ as a linear combination of the $\{f_\kappa(\tau)\}$. A function $g(\tau)$ in the space $\mathscr{F}_\tau$ can be represented by a vector of coefficients $\mathbf{g}\in\mathscr{F}$, a linear space of vectors.

If no restrictions other than linearity are placed on the operators, then $\hat{\mathscr{E}}$ and $\mathscr{E}$ are spaces of dimension h^2 with complex coefficients or of dimension $2h^2$ with real coefficients. Note that individual matrices, including basis matrices, in $\mathscr{E}$ can have complex elements even when $\mathscr{E}$ is a vector space with real coefficients. The functions in $\mathscr{F}_\tau$ will in general be complex valued and the vectors in $\mathscr{F}$ will in general have complex components, so complex coefficients are allowed. If the operators are restricted to be Hermitian, then $\hat{\mathscr{E}}$ and $\mathscr{E}$ are spaces of dimension h^2 with real coefficients and the function in $\mathscr{F}_\tau$ and vectors in $\mathscr{F}$ are real, so real coefficients should be used there as well. The functions $\{\phi_k\}$ and the coefficients in $\mathscr{H}$ can be complex, but if only Hermitian operators are allowed then only the real functions $\phi_j\phi_k^*+\phi_k\phi_j^*$ will occur in their collapses. In what follows we will normally assume that matrices in $\mathscr{E}$ are Hermitian and that functions in $\mathscr{F}$ are real.

III. SOME SPECIFIC BASIS SETS

In order to investigate the nature and role of linear dependencies among basis-function products, we begin by examining a few common sets of functions that arise in connection with simple quantum-mechanical problems. We will then consider some basis sets in which the linear-dependency conditions among products are particularly simple. This section concludes with an examination of a more realistic basis set having products that are linearly independent in principle, but not in practice.

Harmonic oscillator functions. One of the simplest sets of functions to consider consists of the eigenfunctions of the simple harmonic oscillator Hamiltonian. These functions are of the form

$$\psi_n(x)=C_nH_n(x)e^{-x^2/2} \; , \tag{6}$$

where C_n is a normalization constant and $H_n(x)$ is a Hermite polynomial. Note that the Hermite polynomials $H_0,H_1,\ldots,H_n$ and the monomials $1,x,\ldots,x^n$ are linearly equivalent sets. Suppose that the orbital basis set consists of $\{\psi_n, n=0,1,\ldots,N\}$. The products are of the form

$$\psi_j(x)\psi_k(x)=C_jC_kH_j(x)H_k(x)e^{-x^2} \; . \tag{7}$$

The product $H_j(x)H_k(x)$ is a polynomial of degree $j+k$ in x, but it can also be expressed as a polynomial of degree $j+k$ in $\xi=\sqrt{2}x$ and thus as a linear combination of Hermite polynomials in ξ, with a corresponding result for the oscillator functions, so

$$\psi_j(x)\psi_k(x)=\sum_{m=0}^{2N} W_{jk,m}\psi_m(\sqrt{2}x) \; . \tag{8}$$

The maximum value of $j+k$ is $2N$, and the upper limit of the sum has been fixed at this constant value to make the transformation look more symmetric. All coefficients $W_{jk,m}$ with $m>j+k$ will be zero. These functions are all real, so there are $(N+1)(N+2)/2$ products $\psi_j\psi_k=\psi_k\psi_j$. According to Eq. (8), however, these products can all be expressed as linear combinations of only $2N+1$ independent functions, so there must be linear dependencies whenever $N\ge 2$.

Spherical harmonics. Products of spherical harmonics have been extensively studied in connection with angular momentum coupling.[18] The expansion relations involve the Clebsch-Gordan or Wigner coefficients

$$\begin{aligned} Y_{l_1m_1}(\theta,\phi)Y_{l_2m_2}^*(\theta,\phi)&=(-1)^{m_2}Y_{l_1m_1}(\theta,\phi)Y_{l_2m_2}(\theta,\phi)\\ &=\sum_{\lambda=0}^{2L}\sum_{\mu=-\lambda}^{\lambda}(-1)^{m_2}(l_1m_1l_2-m_2\,|\,l_1l_2\lambda\mu)Y_{\lambda\mu}(\theta,\phi) \; . \end{aligned} \tag{9}$$

Here L has been introduced as the maximum value of l for functions included in the original set and the limits on the sum have again been extended so as to be independent of the particular product being expanded. The coefficients will of course be zero unless $|l_1-l_2|\leq\lambda\leq l_1+l_2$ and $\mu=m_1-m_2$. In this case the number of products is h^2, where

$$h=\sum_{l=0}^{L}(2l+1)=(L+1)^2\ , \tag{10}$$

while the number of functions involved in the expansion is

$$\sum_{\lambda=0}^{2L}(2\lambda+1)=4L(L+1)\ , \tag{11}$$

which is less than h^2 for $L\geq 1$. Again there must be linear dependencies.

Plane waves. The functions e^{ikx} are not quadratically integrable, so they do not fit the general criteria for the basis sets considered here, but it will be instructive to consider them in the case when k is constrained to be an integer, as for periodic boundary conditions with an appropriately-scaled x. For the set $\{\phi_k, -\nu\leq k\leq\nu\}$ the number of distinct products $\phi_j\phi_k^*$ is $(\nu+1)(2\nu+1)$, and

$$\phi_j(x)\phi_k^*(x)=e^{i(j-k)x}=e^{imx}\ , \tag{12}$$

where $m=j-k$ has the range $-2\nu\leq m\leq 2\nu$, so there are only $4\nu+1$ independent functions in the product space $\mathcal{F}$. The "linear dependency" conditions in this case are particularly simple: all products $\phi_j\phi_k^*$ with the same value of $j-k$ are equal.

The real trigonometric (or particle-in-a-box) functions are closely related to the plane waves, but the analysis is complicated by the boundary conditions. This set is treated in the examples presented in the Appendix.

Gaussian wave packets. A set of functions which also has simple linear-dependency conditions but is potentially more useful for atomic and molecular problems consists of Gaussian wave packets (coherent states).[19,20] It is convenient to use the functions defined on the von Neumann lattice[20] which, with a scaled coordinate, can be written

$$\chi_{kl}(x)=\pi^{-1/4}\exp[-\tfrac{1}{2}(x-kq)^2+ilqx]\ , \tag{13}$$

where $q=(2\pi)^{1/2}$. Products of these functions will also be Gaussian wave packets

$$\chi_{kl}\chi_{k'l'}^*=\pi^{-1/2}\exp[-\tfrac{1}{2}(k-k')^2q^2]\times\exp[-(x-\tfrac{1}{2}K)^2+iLqx]\ , \tag{14}$$

with $K=k+k'$ and $L=l-l'$. These are no longer of von Neumann form, but it is apparent that all the products with the same values of K and L will be proportional to one another. (In the limit as an infinite number of functions are included, there will be additional linear dependencies, but we will not go into this here.)

Special equidensity orbitals. When the goal is to analyze the properties of density matrices or wave functions corresponding to some particular fixed and given density then there is a set of orbitals based on that density that have very useful properties. These are the special equidensity orbitals, or SEDOs.[3,21,22]

To define the SEDOs for a given density $\rho(\mathbf{r})$ one must find a set of functions $\{f_i(\mathbf{r}),\ i=1,2,3\}$ such that the Jacobian determinant is[22]

$$\frac{\partial(f_1,f_2,f_3)}{\partial(x,y,z)}=8\pi^3\rho(\mathbf{r})\ . \tag{15}$$

This condition does not uniquely specify a set of f's, but at least one solution is known.[22] The orbitals are then defined as

$$\phi_{\mathbf{k}}(\mathbf{r})=[\rho(\mathbf{r})]^{1/2}\exp[i\mathbf{k}\cdot\mathbf{f}(\mathbf{r})],\quad \mathbf{k}\in\mathbb{Z}^3\ . \tag{16}$$

(Half-integer values for the components of $\mathbf{k}$ are also possible[23] but offer no particular advantage in this context.) This set of functions is orthonormal and, in the limit as all integer indices are included, it is complete if $\rho>0$ almost everywhere. It is apparent that the square of the magnitude of any SEDO is the density, and more generally

$$\phi_{\mathbf{j}}(\mathbf{r})\phi_{\mathbf{k}}^*(\mathbf{r})=\rho(\mathbf{r})\exp[i\mathbf{m}\cdot\mathbf{f}(\mathbf{r})] \tag{17}$$

with $\mathbf{m}=\mathbf{j}-\mathbf{k}$. All products with the same value of $\mathbf{j}-\mathbf{k}$ are thus identical, as in the case of plane waves. Some of the properties of these functions have been explored elsewhere,[21-28] and will not be reviewed here. Two facts are of particular relevance, however. The first is that although the products $\rho\exp[i\mathbf{m}\cdot\mathbf{f}]$ are neither normalized nor orthogonal, they do form a complete set (when all $\mathbf{m}\in\mathbb{Z}^3$ are included). This can be shown by an argument similar to that used to show the completeness of the SEDOs themselves.[22] The second point is that for any given $\mathbf{m}$ there are an infinite number of ways in which $\mathbf{m}$ can be obtained as $\mathbf{j}-\mathbf{k}$, with $\mathbf{j},\mathbf{k}\in\mathbb{Z}^3$.

Well-tempered Gaussians. An examination of basis functions of the types actually used in quantum-chemical calculations is difficult to do in a systematic way. A more nearly realistic example than those treated above can be provided by well-tempered Gaussian orbitals.[29] Only the simplest case of s orbitals on a single center will be considered, and further simplifications (scaling) give a set of orbitals

$$\phi_k(r)=C_k\exp(-\beta^k r^2),\quad k=1,\ldots,n\ . \tag{18}$$

The constants C_k are chosen so that the functions are normalized, but they are not orthogonal. While the set will be linearly independent, in principle, for almost any $\beta\neq 1$ there will be near linear dependencies if n is large. Similarly, the products of these functions will not be exactly linearly dependent but will be nearly so for large n. (Exact linear dependency would require a β such that $\beta^j+\beta^k=\beta^l+\beta^m$ for integer j, k, l, and m in the range $1,\ldots,n$ being considered.) As a measure of near linear dependency we take the smallest eigenvalue of the overlap matrix. Some results are given in Table I for the lowest eigenvalues of the overlap matrices for the functions and the products, for various values of n, with $\beta=22/7$. It is apparent that near linear dependency will become a problem for the products before it does for the functions themselves. We can reasonably anticipate that this would continue to be the case for more general, multicenter sets of functions.

TABLE I. Smallest eigenvalues of overlap matrices for well-tempered Gaussians and for their products.

n[a]	S[b]	Δ[c]
2	0.208	6.01×10^{-3}
3	0.0786	6.11×10^{-6}
4	0.0430	1.10×10^{-9}
5	0.0293	2.93×10^{-14}
6	0.0227	10^{-16}[d]

[a] n is the number of Gaussian functions in the set. The functional form is defined in the text.

[b] S is the smallest eigenvalue of the overlap matrix for the normalized functions.

[c] Δ is the smallest eigenvalue for the overlap matrix for the normalized products of functions.

[d] These calculations were done using Turbo Pascal on an IBM PC/XT and round-off errors are becoming significant at this point.

IV. FORMAL THEORY

Some of the properties exhibited by the particular basis sets considered in the preceding section are in fact general. These properties and some others will be presented in this section as theorems with proofs.

One of the most fundamental questions is that of what happens to the spaces defined in Sec. II when the basis set for $\mathscr{H}$ is subjected to a nonsingular linear transformation. The answer is contained in the following.

Theorem 1. The spaces $\mathscr{E}_\tau$ (or $\hat{\mathscr{E}}$) and $\mathscr{F}_\tau$ are determined by the space $\mathscr{H}$; they do not depend on a particular choice of basis for $\mathscr{H}$.

Proof. The basis independence of $\hat{\mathscr{E}}$ and $\mathscr{E}_\tau$ follows immediately from the definitions: They are spaces of linear operators mapping $\mathscr{H}$ to $\mathscr{H}$. The basis independence of $\mathscr{F}_\tau$ is also a consequence of its definition as the span of the collapses of a set of operators spanning $\hat{\mathscr{E}}$. If $\hat{\mathscr{E}}$ is basis independent, then $\mathscr{F}_\tau$ must be also. Q.E.D.

The decomposition of the matrix space $\mathscr{E}$ into irreducible subspaces with respect to the group of unitary transformations of the basis for $\mathscr{H}$ has been extensively studied elsewhere,[6–17] and it has been shown that the known decomposition is complete.[11] In the case of the one-particle spaces being considered here, it is

$$\mathscr{E}=\mathscr{X}\oplus\mathscr{N}\ , \tag{19}$$

where $\mathscr{X}$ (also denoted by $\mathscr{E}_{1,0}$, etc.) is the space of matrices proportional to the unit matrix and $\mathscr{N}$ (also denoted by $\mathscr{E}_{1,1}$, etc.) is the space of trace-zero matrices. This decomposition is in terms of *matrix* properties, without involvement of the particular basis with respect to which the matrices are defined. In the present context, a further decomposition of the operator-kernel space $\mathscr{E}_\tau$ is possible. Let $\mathscr{K}_\tau$ be defined as the null space of $\hat{\delta}$ in $\mathscr{E}_\tau$,

$$\mathscr{K}_\tau=\{G(\tau;\tau')\in\mathscr{E}_\tau\,|\,G(\tau;\tau)=0\} \tag{20}$$

($\mathscr{K}$ stands for kernel in the null-space sense) and let $\mathscr{L}_\tau$ be the orthogonal complement of $\mathscr{K}_\tau$ in $\mathscr{E}_\tau$ ($\mathscr{L}$ refers to "local" for reasons that will become obvious). With these definitions we can state the following theorem.

Theorem 2. The orthogonal subspace decomposition $\mathscr{E}_\tau=\mathscr{K}_\tau\oplus\mathscr{L}_\tau$ is independent of the choice of basis for $\mathscr{H}$. (The corresponding decomposition for $\mathscr{E}$ cannot be defined without reference to a basis.)

Proof. The integral kernels $G(\tau;\tau')$ are simply given functions of τ and τ' which need not be expressed in terms of any basis set. Q.E.D.

Theorem 3. The collapse map $\hat{\delta}$ is one to one from $\mathscr{L}_\tau$ onto $\mathscr{F}_\tau$.

Proof. Since elements of $\mathscr{E}_\tau$ in $\mathscr{K}$ collapse to zero and $\mathscr{F}_\tau$ is defined as the span of collapses of elements of $\mathscr{E}_\tau$, the "onto" property is trivial. The definition of $\hat{\delta}$ does not allow a one-many map. If G_1 and G_2 in $\mathscr{E}_\tau$ are such that $\hat{\delta}G_1=\hat{\delta}G_2$, then $\hat{\delta}(G_1-G_2)=0$ and $G_1-G_2\in\mathscr{K}$, so G_1 and G_2 cannot both be in the linear subspace $\mathscr{L}_\tau$. This excludes the possibility that $\hat{\delta}$: $\mathscr{L}_\tau\rightarrow\mathscr{F}_\tau$ could be many-one. Q.E.D.

The proofs of the theorems above do not depend on the finiteness of the dimension of $\mathscr{H}$. We now proceed to some results specific to the infinite-dimensional case.

Theorem 4. If $\mathscr{H}$ is a complete, infinite-dimensional Hilbert space with a basis consisting of a complete set of functions $\{\phi_k\}$, then the set of products $\{\phi_j\phi_k^*\}$ is also complete, so $\mathscr{F}_\tau$ is also an infinite-dimensional space.

Proof.[30] Suppose that the set of products is not complete. Then there is a nonzero function ψ such that

$$\int\psi^*\phi_j\phi_k^*\,d\tau=0\quad\text{for all } j,k\ . \tag{21}$$

This can be rewritten as

$$\int(\psi\phi_k)^*\phi_j\,d\tau=0\quad\text{for all } j \tag{22}$$

and since the $\{\phi_j\}$ are complete (by assumption) it follows that $\psi\phi_k\equiv0$ for any k. This means, however, that

$$\int\psi\phi_k\,d\tau=0\quad\text{for all } k \tag{23}$$

and thus, by the completeness of the $\{\phi_k\}$, $\psi^*\equiv0$ so $\psi\equiv0$, which contradicts the original supposition. This requires that the set of products be complete, and since any complete set must be infinite, it also establishes the infinite dimensionality of $\mathscr{F}_\tau$. Q.E.D.

Since each function in a complete set can be expanded in terms of the functions in any other complete set, all complete sets are equivalent: they span the same space. This fact, together with the theorems above, allows us to establish the following theorem.

Theorem 5. If $\mathscr{H}$ is complete, then the dimensions of $\mathscr{E}_\tau$, $\mathscr{K}_\tau$, and $\mathscr{L}_\tau$ are all infinite, and for each function $g(\tau)\in\mathscr{F}_\tau$ there is an infinite-dimensional subspace of $\mathscr{E}_\tau$ such that every element of that subspace collapses to $g(\tau)$.

Proof. Since $\mathscr{F}_\tau$ is infinite dimensional (Theorem 4) and $\hat{\delta}$:$\mathscr{L}_\tau\rightarrow\mathscr{F}_\tau$ is one-to-one onto (Theorem 3), the dimension of $\mathscr{L}_\tau$ must also be infinite. In the case of a SEDO basis, it was shown above that there are an infinite number of products all having the same collapse, and thus there are an infinite number of elements of the form $[\phi_{\mathbf{j+m}}(\tau)\psi_{\mathbf{j}}^*(\tau') - \phi_{\mathbf{k+m}}(\tau)\phi_{\mathbf{k}}^*(\tau')]$. These are nonzero when $\mathbf{j} \neq \mathbf{k}$, and linearly independent (as elements of $\mathscr{E}_\tau$). It follows that dim $\mathscr{K}$ is infinite with this basis, so it will be with any basis (Theorem 2). Finally, note that for any $g \in \mathscr{F}_\tau$ there is a unique $\hat{\delta}^{-1} g \in \mathscr{L}_\tau$, and for any $K \in \mathscr{K}_\tau$, $\hat{\delta}(\hat{\delta}^{-1} g + K) = g$. Since $\mathscr{K}_\tau$ is infinite dimensional, the set $\{\hat{\delta}^{-1} g + K \mid K \in \mathscr{K}_\tau\}$ is also infinite dimensional. Q.E.D.

V. LIP BASES AND THEIR CONSEQUENCES

It is apparent from the theorems above that for any complete basis there must be linear dependencies among basis set products, and the well-tempered Gaussian example presented in Sec. III suggests that near linear dependencies may become a problem even with limited basis sets where there are no exact linear dependencies. Nevertheless, there are many instances of practical calculations in which the basis-set products remain effectively independent. The acronym LIP was introduced in Sec. I to characterize such a basis. The model problem defined by a LIP basis has some very interesting properties, which will be explored in this section.

The collapse map $\hat{\delta}$ is most fundamentally defined from the integral-kernel space $\mathscr{E}_\tau$ to the function space $\mathscr{F}_\tau$, although the isomorphism of $\hat{\mathscr{E}}$ and $\mathscr{E}_\tau$ permits us to think of it as $\hat{\delta}: \hat{\mathscr{E}} \to \mathscr{F}_\tau$ as well. The relationships between these spaces and the matrix spaces $\mathscr{E}$ and $\mathscr{F}$ depend on a choice of basis, but for fixed bases we can define a matrix representation for $\hat{\delta}$.

We take a set of matrices $\{\mathbf{Y}^K\}$ which provides a basis for $\mathscr{E}$. Then any $\mathbf{G} \in \mathscr{E}$ can be expressed as

$$\mathbf{G} = \sum_K G_K \mathbf{Y}^K . \tag{24}$$

Suppose that this matrix corresponds to an integral kernel $G(\tau;\tau') \in \mathscr{E}_\tau$ and that $\hat{\delta} G(\tau;\tau') = g(\tau) \in \mathscr{F}_\tau$. We introduce a basis $\{f_\kappa\}$ for $\mathscr{F}_\tau$ so that

$$g(\tau) = \sum_\kappa g_\kappa f_\kappa(\tau) , \tag{25}$$

and the expansion coefficients $\{G_K\}$ and $\{f_\kappa\}$ are the elements of vectors in $\mathscr{E}$ and $\mathscr{F}$, respectively, and the map from $\mathscr{E}$ to $\mathscr{F}$ can be characterized by a matrix $\mathbf{M}$ such that

$$\mathbf{g} = \mathbf{M}\mathbf{G} . \tag{26}$$

The matrix elements $M_{\kappa K}$ will be determined by the choice of the basis sets $\{\mathbf{Y}^K\}$ and $\{f_\kappa\}$. We assume these bases to be orthonormal with respect to the appropriate scalar products [Eqs. (5) and (2), respectively]. Note that although the space $\mathscr{E}_\tau$ determines the space $\mathscr{F}_\tau$, the choice of a basis for $\mathscr{E}$ does not define a basis for $\mathscr{F}$.

Introduce $Y^K(\tau;\tau')$ as the integral kernel in $\mathscr{E}_\tau$ corresponding to the basis matrix $\mathbf{Y}^K \in \mathscr{E}$. Then

$$g(\tau) = \sum_K G_K \hat{\delta} Y^K(\tau;\tau') = \sum_K G_K Y^K(\tau;\tau) , \tag{27}$$

and

$$g_\kappa = \sum_K \left[\int f_\kappa^*(\tau) \hat{\delta} Y^K(\tau;\tau') d\tau \right] G_K , \tag{28}$$

so that $\mathbf{M}$ is the matrix corresponding to $\hat{\delta}$ in the usual quantum-mechanical sense. For convenience in what follows, we will assume that the matrices in $\mathscr{E}$ are Hermitian and that the functions in $\mathscr{F}$ are real.

In general $\mathscr{E}$ and $\mathscr{F}$ have different dimensions and $\mathbf{M}$ is rectangular. If the orbital basis is LIP, however, $\mathbf{M}$ is square and has an inverse. The relationship between the two spaces can be expressed in two ways that are not obviously equivalent:

1. Given $g(\tau) \in \mathscr{F}_\tau$, what is $\mathbf{G} \in \mathscr{E}$ such that $\mathbf{M}\mathbf{G} = \mathbf{g}$, corresponding to $g(\tau)$?
2. Given $\mathbf{G} \in \mathscr{E}$, what is $\mathbf{v} \in \mathscr{F}$ such that $\mathbf{G}$ is the matrix of the corresponding $v(\tau)$, considered as a (local) potential?

Question 1 is directly related to the previous discussion. From Eq. (26) we have

$$G_K = \sum_\kappa (\mathbf{M}^{-1})_{K\kappa} g_\kappa . \tag{29}$$

In order to address question 2, we need to be a little more explicit about the basis sets. Let the orbital basis be $\{\phi_k, k = 1, \ldots, s\}$. A possible basis for $\mathscr{E}$ consists of the matrix equivalent of the s^2 ket-bra combinations $|j\rangle\langle k|$.[31] Alternatively (with particular utility for the consideration of Hermitian and real symmetric matrices), we can use symmetrized combinations.[6] These alternatives can be combined in such a way that the form of the equations will be the same with either choice (although the values of coefficients will be different). The definitions are given in Table II.

The basis $\{\mathbf{Z}^{jk}\}$ defined in this way is orthonormal (trace scalar product) and is one possible choice for $\{\mathbf{Y}^K\}$. Other choices of $\{\mathbf{Y}^K\}$ offer advantages for particular purposes, however, so we do not assume that $\mathbf{Y}^K = \mathbf{Z}^{jk}$ in all cases. The two sets are certainly related by a unitary transformation

$$\mathbf{Y}^K = \sum_{j,k} U_{K,jk} \mathbf{Z}^{jk} . \tag{30}$$

The products $\{\phi_j^* \phi_k\}$ are linearly independent (by assumption) and form a basis for $\mathscr{F}_\tau$ (by definition), but will not in general be normalized or orthogonal. Clearly there is a nonsingular matrix $\mathbf{W}$ such that

$$\phi_j \phi_k^* = \sum_\kappa \mathbf{W}_{jk,\kappa} f_\kappa , \tag{31}$$

$$f_\kappa = \sum_{j,k} (\mathbf{W}^{-1})_{\kappa,jk} \phi_j \phi_k^* . \tag{32}$$

TABLE II. Simple bases for $\mathscr{E}$.

	Z^{jk}	
Case	Unsymmetrized	Symmetrized
$j = k$	$\|k\rangle\langle k\|$	$\|k\rangle\langle k\| \leftrightarrow \mathbf{A}^k$
$j < k$	$\|j\rangle\langle k\|$	$(1/\sqrt{2})[\,\|j\rangle\langle k\| + \|k\rangle\langle j\|\,] \leftrightarrow \mathbf{B}^{jk}$
$j > k$	$\|k\rangle\langle j\|$	$(i/\sqrt{2})[\,\|j\rangle\langle k\| - \|k\rangle\langle j\|\,] \leftrightarrow \mathbf{C}^{jk}$

Note next that the matrix $\mathbf{G}$ corresponding to a local potential $v(\tau)$ has matrix elements

$$\begin{aligned} G_{jk} &= \int \phi_j^*(\tau) v(\tau) \phi_k(\tau) d\tau \\ &= \int [\phi_j^* \phi_k] v(\tau) d\tau \\ &= \sum_\kappa \mathbf{W}_{kj,\kappa} \sum_\lambda v_\lambda \int f_\lambda f_\kappa d\tau \\ &= \sum_\kappa \mathbf{W}_{kj,\kappa} v_\kappa , \end{aligned} \tag{33}$$

where $v = \sum v_\lambda f_\lambda$. It follows that if a matrix $\mathbf{G}$ is given, the $v(\tau)$ that will reproduce it has expansion coefficients

$$v_\kappa = \sum_{j,k} (\mathbf{W}^{-1})_{\kappa,kj} G_{jk} . \tag{34}$$

Some illustrative examples are included in the Appendix. The relationship between $\mathbf{M}$ and $\mathbf{W}$ will be explored in a future paper.

The invertibility of the collapse map when a LIP basis is used might seem innocuous, but it has far-reaching consequences. It is common, particularly in density-functional theory, to distinguish between local and nonlocal operators. A local operator is typically an external potential, or the Coulomb operator in self-consistent field (SCF) theory. The expectation value of such an operator can be evaluated if the density for the system is known. For a nonlocal (one-electron) operator such as the kinetic energy or the SCF exchange operator, on the other hand, the one-electron density matrix is required for the evaluation of expectation values. In the model problem defined by a LIP basis, the density determines the density matrix and the matrix of any operator can be reproduced as the matrix of a local potential. There can thus be no meaningful distinction between local and nonlocal operators in such a model problem. Local functions which reproduce the matrices of the kinetic energy and exchange operators for a simple LIP model are presented in the Appendix.

VI. DENSITIES AND FITS TO EXPERIMENTAL DATA

A number of experimental techniques, preeminently x-ray diffraction, can in principle be used to determine electron densities. In practice the finite amount of data collected and the finite signal-to-noise ratio limit the precision that is possible in such a determination. We will not be concerned here with these limitations, but will continue to assume a finite-basis expansion chosen so that the number of free parameters is less than the number of experimental data.

It will be convenient to define some subspaces of the function space $\mathscr{F}_\tau$ defined in Sec. II. The space of acceptable densities is[32]

$$\mathscr{F}_+ = \{ f(\tau) \in \mathscr{F}_\tau \,|\, f(\tau) \geq 0 \text{ for all } \tau \} , \tag{35}$$

with a restriction fixing a particular normalization often added as well. In the basis-free or complete basis case, every $\rho(\tau) \in \mathscr{F}_\tau$ such that $\int \rho \, d\tau = c < \infty$ is n representable.[3,21,22,33] For finite-basis models, however, this is not always the case.[9] For some reasonable basis sets there are some normalized functions in $\mathscr{F}_\tau$ that cannot be obtained as the collapse of any n-representable 1-matrix and are thus unacceptable. We therefore define

$$\mathscr{F}^{(n)} = \{ f(\tau) \in \mathscr{F}_+ \,|\, f = c\hat{\delta}\mathbf{D} \text{ for some } \mathbf{D} \in \mathscr{P}_1^{(n)} \} , \tag{36}$$

where c is a positive normalization constant included for flexibility in normalization and $\mathscr{P}_1^{(n)}$ is the set of n-representable 1-matrices[34]

$$\mathscr{P}_1^{(n)} = \left\{ \mathbf{D} \in \mathscr{E} \,|\, \mathbf{D}^\dagger = \mathbf{D}, \mathrm{tr}\mathbf{D} = 1, 0 \leq \mathbf{D} \leq \frac{1}{n} \mathbf{1} \right\} . \tag{37}$$

It is possible to further restrict the (renormalized) density matrix to be idempotent, $(n\mathbf{D})^2 = n\mathbf{D}$, which will assure that it corresponds to an SCF-type single-determinant wave function. We therefore define a final set

$$\mathscr{F}_{\det}^{(n)} = \{ f \in \mathscr{F}^{(n)} \,|\, f = c\hat{\delta}\mathbf{D}, \mathbf{D} \in \mathscr{P}_1^{(n)}, \mathbf{D}^2 = \mathbf{D} \} . \tag{38}$$

It is apparent from these definitions that

$$\mathscr{F}_{\det}^{(n)} \subset \mathscr{F}^{(n)} \subset \mathscr{F}_+ \subset \mathscr{F}_\tau . \tag{39}$$

The appropriateness of strict inclusion, implying a proper subset, is readily verified in each case as well.

In fitting x-ray or other data to determine an "experimental" density, it is clearly desirable to allow as much flexibility as possible in order to avoid biasing the result. This goal must be balanced against the need to obtain a unique result with a limited set of experimental data, and the choice of an appropriate basis set may prove to be quite helpful. Once the basis set is chosen and the space $\mathscr{F}$ thus determined, the most flexible method would be to restrict the trial density ρ only to be positive and normalized, i.e., $\rho \in \mathscr{F}_+$. Unfortunately, however, a usable characterization of this set is not known. (It is readily shown to be convex.[9])

One obvious way of assuring that the density be positive is to write it as $\rho = |\psi|^2$, where $\psi \in \mathscr{H}$. If the basis set $\{\phi_k\}$ defining $\mathscr{H}$ is sufficiently flexible, most ρ's could be well approximated in this way. With a LIP basis, however, such a ρ is uniquely associable with a one-electron density matrix γ having a single nonzero eigenvalue. In the model defined by the basis, such a density matrix is never n representable for $n > 1$. A more general density can be obtained as

$$\rho = \hat{\delta}\mathbf{A}^\dagger\mathbf{A} , \tag{40}$$

where $\mathbf{A}$ is any matrix in $\mathscr{E}$. The product $\mathbf{A}^\dagger\mathbf{A}$ is necessarily positive, and the collapse of a positive matrix is a positive function. This matrix will not in general be n representable, however, and ρ's of this form do not span $\mathscr{F}_+$ because there are (at least for some bases) densities which can be obtained only from nonpositive matrices.[9] If only the density is of interest, then n representability within the given basis is not required and either of these approaches provides a usable, though not completely general, parametrization of positive densities which will be n representable in some (possibly different) basis. If one seeks a density matrix or wave function as well as a density within the given basis, however, then n representability in that basis is necessary.

A consistent method can be developed by considering densities in the subset $\mathscr{F}^{(n)}$. To require $\rho\in\mathscr{F}^{(n)}_{\mathrm{det}}$ is unnecessarily restrictive but leads to conditions which are easier to work with than the more general restriction $\rho\in\mathscr{F}^{(n)}$. The recent work of Massa *et al.*[5] is based upon earlier work[35] and ultimately on the methods of Clinton and co-workers published in 1969.[36] The fact that any density is *n* representable was not known at that time, and the use of more general *n*-representable 1-matrices had not been extensively developed, so idempotent density matrices were introduced as a means of assuring *n* representability. In that series of papers the many-to-one relationship between density matrices and densities does not seem to have been discussed. The sample calculations were done with basis sets that are small enough that they are probably LIP, so problems did not arise.

In their most recently reported investigation, Massa *et al.*[5] obtain an approximate wave function for a fragment consisting of a single Be atom in Be metal. The fragment is considered to be a four-electron closed-shell system and the wave function is approximated as a single determinant with a frozen core consisting of a doubly occupied Huzinaga Be 1*s* orbital.[37] This can be taken to be the first basis function ϕ_1. The valence orbital is a linear combination of two other basis functions. The Huzinaga 2*s* orbital can be taken as ϕ_2, and ϕ_3 is a symmetry-adapted combination of orbitals generated by symmetry from a single floating 1*s*-type Gaussian and orthogonalized to the Be orbitals. The variational parameters affecting the wave function thus consist of the location and exponent of the unique floating Gaussian and the mixing coefficient for ϕ_2 and ϕ_3 in the valence orbital. With this model an excellent fit to the x-ray data is obtained, as indicated by a very low *R* factor.

The overlap matrix for products in this basis has not been evaluated, but because of the small basis size and the rather different characters of the orbitals involved, it seems probable that the products are linearly independent. There is thus no inconsistency between the apparently unique result obtained and the general theory developed here. Attention must be called, however, to a difference between the results presented in this paper and one of the claims of Massa *et al.* They make a strong point of the fact that "The only property expectation values that can be obtained from the density alone are those represented by operators which are purely multiplicative such as various powers of the distance *r*. . . . But . . . the important point demonstrated numerically is that even such nonmultiplicative properties as the kinetic energy are available from our method since we obtain a density matrix in an orbital representation." It has been shown here that (1) in a LIP basis the density matrix and thus all one-electron properties are uniquely determined by the density, even without the unnecessarily stringent restriction to idempotency, and (2) if a non-LIP basis (including any basis approaching completeness) is used, then the density matrix cannot be determined from data such as x-ray scattering factors, which are sensitive only to the density.

Another problem which would arise in most cases, although it has been avoided in the particular case of Be, is the indeterminateness of individual orbitals in the single determinant case. It is well known that only the determinant itself, or the density matrix, is uniquely defined. Because of the degeneracy of the eigenvalues of the density matrix, the orbitals themselves are defined only to the extent of a division of $\mathscr{H}$ into occupied and unoccupied subspaces. In the usual SCF variational procedure the canonical orbitals have approximate physical interpretations based on Koopman's theorem, etc. There is nothing in the fitting of x-ray data to uniquely define a particular choice of the orbitals. In the calculation reported for Be (Ref. 5) this problem is avoided by the use of the closed-shell frozen-core approximation which results in only one orbital being considered explicitly. The space of occupied orbitals is two dimensional and is required to contain the 1*s* core orbital, so the only occupied orbital orthogonal to the core is unique to within a phase.

VII. CONCLUSIONS

This paper has dealt with the relationship between a density matrix and a density or between an operator and a local potential, in the model problem defined by an orbital basis set. A critical role is played by linear-dependency relationships among basis-function products, and we are led to consider special LIP bases in which all such products are linearly independent. A complete set can never be LIP, and the large but finite basis sets used in high-quality electronic structure calculations are likely to involve effective linear dependencies among products (in a numerical sense) even when exact linear dependencies are absent. The rather small basis sets of lesser-quality calculations may well be LIP, however.

A LIP basis defines a model problem with some very interesting features. Only the finite matrices corresponding to operators, not the operators themselves, are significant for any finite-basis model. For a LIP-basis model any matrix, and thus the effect of any operator, can be exactly reproduced as the matrix of some function which can be regarded as a local potential. This is illustrated in the Appendix for a simple model. In such a model problem, then, no meaningful distinction can be made between local and nonlocal operators.

In the model defined by a LIP basis, a local density functional theory can be exact at the SCF level. In particular, the kinetic and exchange energies are given exactly by

$$\begin{aligned} E_{KE} &= \int t(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\ , \\ E_x &= \int v_x(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\ , \end{aligned} \tag{41}$$

where $t(\mathbf{r})$ is independent of ρ and $v_x(\mathbf{r})$ is given by

$$v_x(\mathbf{r}) = \int X(\mathbf{r};\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'\ . \tag{42}$$

The functions $t(\mathbf{r})$ and $X(\mathbf{r};\mathbf{r}')$ (or, more precisely, their expansion coefficients in terms of the $\mathscr{F}$ basis $\{f_\kappa\}$) depend on the orbital basis set defining the model but do not depend on the particular system under consideration or its state. The fact that E_{KE} is linear and E_x bilinear in the density is in sharp contrast to usual density-functional theory expressions.

The apparent simplifications of a LIP-basis model are a consequence of the fact that in such a model the spaces $\mathscr{E}$ and $\mathscr{F}$ are of the same size. A basis-set density-functional approach at the SCF level thus seems to offer no advantage over conventional Roothaan SCF. In addition, the limitation to a LIP basis is quite restrictive. Once a basis has been chosen, nonsingular linear transformations do not affect the essential structure of the spaces considered here. A novel challenge will be to find basis sets with energy optimizing or other desirable features which nevertheless remain LIP. In extending this work it will clearly be appropriate to examine the basis sets used in practical electronic structure calculations. In cases where they are LIP, the functions t and X can be evaluated and may suggest physically interesting features. It will also be of interest to attempt to extend this approach to include correlation effects.

The distinctions developed here clarify the relationship between density matrices or wave functions and experiments sensitive only to the density. If the density can be well represented in the function space $\mathscr{F}$ defined by a LIP basis then a unique, n-representable or idempotent one-electron density matrix can be determined as that which best approximates the density. The fact that expectation values of nonlocal operators can then be evaluated is just a consequence of the general properties discussed above. For a non-LIP basis, the best density matrix is not uniquely determined by the density.

TABLE III. Basis sets for $\mathscr{H}$. The functions are defined for $-\pi/2 \le x \le \pi/2$ and $C=(2/\pi)^{1/2}$.

k	ϕ_k Set 1	ϕ_k Set 2
	Even functions	
1	$C\cos x$	$C\cos x$
2	$C\cos(3x)$	$C\cos(5x)$
	Odd functions	
3	$C\sin(2x)$	$C\sin(2x)$
4	$C\sin(4x)$	$C\sin(6x)$

Of course, even if an essentially exact density can be expressed in terms of a given basis set, which might happen to be LIP, the density matrices and wave function need not be restricted to being expressed in terms of that basis. Those uniquely determined within the LIP model are but representatives from among infinite sets of possible density matrices and wave functions. The extent to which they represent a good choice depends on the judiciousness with which the basis set has been chosen. If the primary purpose is to fit experimental data to determine a density, then the use of a well-chosen basis set is likely to help, but derivability of the density from an idempotent, or even just n-representable, density matrix in the same basis may be too restrictive. The question of the best parametrization of the set of acceptable densities within a given finite basis remains as an important but unsolved problem.

TABLE IV. Bases for $\mathscr{F}_x$. $f_\kappa = C_\kappa \sum_n a_{\kappa n} \mathrm{circ}\, nx$, where circ = cos for even functions and circ = sin for odd functions. Any $a_{\kappa n}$ not listed are zero.

Even functions, set 1

κ	C_κ	$a_{\kappa 0}$	$a_{\kappa 2}$	$a_{\kappa 4}$	$a_{\kappa 6}$	$a_{\kappa 8}$
0	$[3(2\pi)^{1/2}]^{-1}$	4	1	−1	1	−1
1	$(3\pi)^{-1/2}$	0	2	1	−1	0
2	$\pi^{-1/2}$	0	0	1	1	0
3	$(6\pi)^{-1/2}$	0	1	−1	1	3

Odd functions, set 1

κ	C_κ	$a_{\kappa 1}$	$a_{\kappa 3}$	$a_{\kappa 5}$	$a_{\kappa 7}$
4	$(3\pi)^{-1/2}$	2	1	−1	0
5	$\pi^{-1/2}$	0	1	1	0
6	$(6\pi)^{-1/2}$	1	−1	1	3

Even functions, set 2

κ	C_κ	$a_{\kappa 0}$	$a_{\kappa 2}$	$a_{\kappa 4}$	$a_{\kappa 6}$	$a_{\kappa 8}$	$a_{\kappa 10}$	$a_{\kappa 12}$
0	$[3(2\pi)^{1/2}]^{-1}$	4	1	−1	0	0	1	−1
1	$(3\pi)^{-1/2}$	0	1	2	0	0	1	0
2	$\pi^{-1/2}$	0	1	0	0	0	−1	0
3	$(6\pi)^{-1/2}$	0	1	−1	0	0	1	3
4	$\pi^{-1/2}$	0	0	0	1	1	0	0
5	$[3(13\pi)^{1/2}]^{-1}$	2	−4	4	9	−9	−4	4

Odd functions, set 2

κ	C_κ	$a_{\kappa 1}$	$a_{\kappa 3}$	$a_{\kappa 5}$	$a_{\kappa 7}$	$a_{\kappa 11}$
6	$\pi^{-1/2}$	1	1	0	0	0
7	$(2\pi)^{-1/2}$	1	−1	−1	1	0
8	$\pi^{-1/2}$	0	0	1	1	0
9	$(10\pi)^{-1/2}$	1	−1	1	−1	4

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APPENDIX: SOME EXAMPLES

In order to illustrate some of the points made in this paper we consider here a series of simple examples for a system of particles in a one-dimensional box of length π, symmetrically placed about the origin. Two different basis sets for $\mathscr{H}$ are introduced, with four functions in each, as shown in Table III. Note that since the functions are ordered so as to place the odd functions together and the even functions together, the functions corresponding to the lowest kinetic energy are ϕ_1 and ϕ_3 in each case. Basis set 1 is the most natural choice for this problem, and it has linear dependencies among its products. Basis set 2 has been chosen so that all products are linearly independent.

In each case a space $\mathscr{F}_x$ (now writing x in place of τ) is defined and an orthonormal basis for it can be defined. These functions are given in Table IV. They have also been chosen as even or odd functions of x and functions of like parity are grouped together. Note that the individual trigonometric functions appearing in the expansions of the $\{f_\kappa\}$ do not vanish at $\pm\pi/2$, but that the linear combinations appearing all do.

Basis matrices $\mathbf{Y}^K$ for the two $\mathscr{C}$ spaces are given in Table V. They also fall naturally into two subsets for each space. Those in the first subset are block diagonal and correspond to operators that preserve the parity of x; the second subset contains block-off-diagonal matrices. In each case $\mathbf{Y}^0$ is in fact proportional to the unit matrix, and thus provides a basis for the subspace $\mathscr{E}$. In the case of orbital basis set 1, $\mathscr{C}=\mathscr{K}\oplus\mathscr{L}$. Each of these subspaces has both block-diagonal and block-off-diagonal parts. The basis matrices $\mathbf{Y}^K$ with $K=0,1,2,3,6,7,8$ span $\mathscr{L}$ while those with $K=4,5,9$ span $\mathscr{K}$. For orbital basis set 2 there is no $\mathscr{K}$ subspace—$\mathscr{L}$ is all of $\mathscr{C}$. The collapse maps that exhibit this structure are given in Table VI.

Matrices corresponding to any one-electron operator can be constructed for either basis set. We will consider only parity-conserving operators and can thus limit attention to the block-diagonal subspace of $\mathscr{C}$. Expansions of the matrices corresponding to the local operator x^2 and the nonlocal kinetic energy operator $-\frac{1}{2}(d^2/dx^2)$ are given in Table VII in terms of their expansion coefficients in the $\{\mathbf{Y}^K\}$ basis. It is apparent that the nonlocal operator includes a component in $\mathscr{K}$, as indicated by nonzero $K=4$ and 5 coefficients for basis 1. For the local operator these coefficients vanish. (The fact that the coeffi-

TABLE V. Basis for $\mathscr{C}$. For each K, $\mathbf{Y}^K$ is C_K times the sum of the $\mathbf{Z}=\mathbf{A}$ or $\mathbf{B}$ each multiplied by the coefficient given under it.

			Set 1				
K	C_K	$\mathbf{A}^1$	$\mathbf{A}^2$	$\mathbf{A}^3$	$\mathbf{A}^4$	$\mathbf{B}^{12}$	$\mathbf{B}^{34}$
0	2^{-1}	1	1	1	1	0	0
1	$42^{-1/2}$	2	-1	-1	0	$3\times 2^{1/2}$	$3\times 2^{1/2}$
2	$6^{-1/2}$	0	1	-1	0	$2^{1/2}$	$-2^{1/2}$
3	$(2\times 3^{1/2})^{-1}$	1	1	1	-3	0	0
4	$14^{-1/2}$	$2\times 2^{1/2}$	$-2^{1/2}$	$-2^{1/2}$	0	-1	-1
5	$6^{-1/2}$	0	$2^{1/2}$	$2^{1/2}$	0	-1	1

K	C_K	$\mathbf{B}^{13}$	$\mathbf{B}^{14}$	$\mathbf{B}^{23}$	$\mathbf{B}^{24}$
6	$2^{-1/2}$	1	0	-1	0
7	$6^{-1/2}$	1	2	1	0
8	1	0	0	0	1
9	$3^{-1/2}$	1	-1	1	0

			Set 2				
K	C_K	$\mathbf{A}^1$	$\mathbf{A}^2$	$\mathbf{A}^3$	$\mathbf{A}^4$	$\mathbf{B}^{12}$	$\mathbf{B}^{34}$
0	2^{-1}	1	1	1	1	0	0
1	$6^{-1/2}$	1	1	-2	0	0	0
2	$2^{-1/2}$	1	-1	0	0	0	0
3	$(2\times 3^{1/2})^{-1}$	1	1	1	-3	0	0
4	$2^{-1/2}$	0	0	0	0	1	-1
5	$2^{-1/2}$	0	0	0	0	1	1

K	C_K	$\mathbf{B}^{13}$	B^{14}	B^{23}	$\mathbf{B}^{24}$
6	1	1	0	0	0
7	1	0	0	1	0
8	1	0	1	0	0
9	1	0	0	0	1

TABLE VI. Collapses of basis matrices. The sets $\{\mathbf{Y}^K\}$ and $\{f_\kappa\}$ are different for the two basis sets, but results are presented together for convenience. The collapse of the $\mathbf{Y}^K$ of the appropriate set is given in terms of the f_κ's for that set.

	Basis set 1	Basis set 2
$\hat{\delta}\mathbf{Y}^0$	$3/(2\pi)^{1/2}f_0$	$3(2/\pi)^{1/2}f_0$
$\hat{\delta}\mathbf{Y}^1$	$(7/2\pi)^{1/2}f_1$	$(2/\pi)^{1/2}f_1$
$\hat{\delta}\mathbf{Y}^2$	$(3/2\pi)^{1/2}f_2$	$(3/\pi)^{1/2}/2f_2$
$\hat{\delta}\mathbf{Y}^3$	$(2\pi)^{-1/2}f_3$	$(2/\pi)^{1/2}f_3$
$\hat{\delta}\mathbf{Y}^4$	0	$\pi^{-1/2}f_4$
$\hat{\delta}\mathbf{Y}^5$	0	$-3^{-1}(2\pi)^{-1/2}f_0-(6\pi)^{-1/2}f_1+2(3\pi)^{-1/2}f_2+(13/\pi)^{1/2}/3f_5$
$\hat{\delta}\mathbf{Y}^6$	$(3/\pi)^{1/2}f_4$	$(2/\pi)^{1/2}f_6$
$\hat{\delta}\mathbf{Y}^7$	$(3/\pi)^{1/2}f_5$	$-(2\pi)^{-1/2}f_6+\pi^{-1/2}f_7+(2\pi)^{-1/2}f_8$
$\hat{\delta}\mathbf{Y}^8$	$(2/3\pi)^{1/2}f_5+2/(3\pi)^{1/2}f_6$	$(2/\pi)^{1/2}f_8$
$\hat{\delta}\mathbf{Y}^9$	0	$(2\pi)^{-1/2}f_6+\pi^{-1/2}/2f_7+(5/\pi)^{1/2}/2f_9$

TABLE VII. Expansion coefficients for various matrices in terms of the $\{\mathbf{Y}^K\}$ bases.

	K	KE	x^2	Coulomb	Exchange
Basis 1	0	7.500	1.289	−4.543	2.267
	1	−0.849	−0.885	1.770	−0.816
	2	1.021	0.085	−0.170	0.152
	3	−4.907	−0.169	0.339	−0.169
	4	−2.079	0.000	0.000	−0.028
	5	1.443	0.000	0.000	−0.048
Basis 2	0	10.500	1.315	−4.670	2.335
	1	3.674	−0.110	0.220	−0.110
	2	−8.485	−0.339	0.679	−0.339
	3	−0.866	−0.174	0.348	−0.174
	4	0.000	−0.024	0.049	−0.026
	5	0.000	0.163	−0.326	0.160

TABLE VIII. Matrix elements and expansion coefficients for some operators in basis 2.

i,j[a]	KE	x^2	Coulomb	Exchange
1,1	0.500	0.332	−1.664	0.832
2,2	12.500	0.802	−2.624	1.312
3,3	2.000	0.697	−2.414	1.207
4,4	18.000	0.809	−2.637	1.318
1,2	0.000	0.069	−0.139	0.066
3,4	0.000	0.094	−0.187	0.093
Coefficients[b]				
C_0	13.7886	1.099	−3.902	1.951
C_1	9.209	−0.276	0.533	−0.276
C_2	−21.269	−0.851	1.701	−0.276
C_3	−28.220	−0.437	0.873	−0.437
C_4	0.000	−0.043	0.086	−0.048
C_5	−15.731	0.573	−1.481	0.735

[a] The number opposite i,j for each operator is the i,j matrix element with respect to the $\{\phi_i\}$ basis set 2.

[b] For each operator the potential function $\sum_\kappa C_\kappa f_\kappa(x)$ will have the same matrix elements as the operator.

cients of $\mathbf{Y}^4$ and $\mathbf{Y}^5$ are zero for the kinetic energy in basis 2 is coincidental. The kinetic energy matrix is diagonal in this basis and $\mathbf{Y}^4,\mathbf{Y}^5$ contribute only to off-diagonal matrix elements.)

In order to further illustrate this distinction, an SCF calculation has been done in each basis. It is assumed that there are four particles of spin $\frac{1}{2}$ in the system, and a restricted model is assumed with each of the two lowest-energy SCF orbitals doubly occupied. A model particle-particle interaction potential is taken to be of repulsive Hook's-law form. (If the system were not confined to a box, this interaction would be divergent, but for the confined system it presents no problems.) The magnitude of the interaction, in the units defined by the effective choice $\hbar=m=1$ implied by the form of the kinetic energy and a box length of π, is taken to be such that interactions are significant but not dominant. The SCF energy differs from the energy of the noninteracting system by about 20%. The (local) Coulomb and (nonlocal) exchange matrices are also given in Table VII.

Table VIII gives matrix elements of some operators for basis set 2, the LIP basis. Also tabulated there are expansion coefficients, in terms of the $\{f_\kappa\}$ basis, for functions which will reproduce these matrices when used as local potentials. Even the nonlocal kinetic energy and exchange operators can have their matrices reproduced by local potentials in a LIP basis.

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