Electron Densities, Momentum Densities, and Density Matrices *

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Relationships among electron coordinate-space and momentum densities and the one-electron charge density matrix or Wigner function are examined. A knowledge of either or both densities places constraints on possible density matrices. Questions are approached in the context of a finite-basis-set model problem in which density matrices are elements in a Euclidean vector space of Hermitian operators or matrices, and densities are elements of other vector spaces. The maps (called "collapse") of the operator space to the density spaces define a decomposition of the operator space into orthogonal subspaces. The component of a density matrix in a given subspace is determined by one density, both densities, or neither. Linear dependencies among products of basis functions play a fundamental role. Algorithms are discussed for finding the subspaces and constructing an orthonormal set of functions spanning the same space as a linearly dependent set. Examples are presented and additional investigations suggested.

Key words: Electron density; Momentum density; Density matrix.

1. Introduction

This paper is concerned with the question of how much information about the one-electron charge (spinless) density matrix is provided by a knowledge of both the coordinate and momentum electronic densities for a system such as an atom, molecule, or periodic solid. Both densities are experimentally observable and the density matrix provides the starting point for many theoretical developments [1].

Many representations of the density matrix are possible: coordinate kernel $\gamma(r; r')$, momentum kernel $\tilde{\gamma}(p; p')$, discrete matrix with respect to some orbital basis set, or phase-space representations such as the Wigner function [2, 3], or the Husimi function [4, 5]. The Husimi function is *in principle* experimentally observable and can be directly interpreted as a probability density [6–8], but it will not be treated here. The analysis presented here is independent of the choice of representation for the density matrix. Coordinate and momentum densities are not entirely independent, and the relationships between them are also of significant interest [9–12].

These problems will be addressed here in the context of the model problem defined by the introduction of a finite basis set [13–15]. The relationship between the density matrix and the coordinate density is thus determined by linear dependency conditions among basis-set products [13–18]. The linear dependencies among products of momentum basis functions will in general be different from those involving the coordinate basis functions, so the momentum density provides information about the density matrix different from that provided by the coordinate density.

2. Subspaces of the Density-Matrix Space

We assume a Hilbert space $\mathscr{H}$ given as the span of some coordinate basis set $\{\chi_j(r), j = 1, \ldots, h\}$ and a space $\mathscr{E}$ containing linear operators from $\mathscr{H}$ to $\mathscr{H}$. Any operator $\hat{D}$ in $\mathscr{E}$ can be represented as an integral operator with a kernel of the form

$$D(r; r') = \sum_{j, k = 1}^{h} D_{jk}\, \chi_j(r)\, \chi_k^*(r'). \qquad (2.1)$$

We can equally well think of $\mathscr{E}$ as being the space whose elements are momentum kernels, $D(p; p')$, Wigner functions, $W_D(r, p)$, or $h \times h$ matrices, **D**. It is apparent that $\mathscr{E}$ is a linear space, and we use the trace scalar product

$$\langle \mathbf{A} | \mathbf{B} \rangle_{\mathscr{E}} = \mathrm{Tr}\, \mathbf{A}^\dagger \mathbf{B}, \quad \forall \mathbf{A}, \mathbf{B} \in \mathscr{E}. \qquad (2.2)$$

Unless otherwise specified, we will require the Hilbert-space basis to be orthonormal.

The set of all possible coordinate densities in the model problem is contained in a linear space $\mathscr{F}_r$ spanned by all basis-function products, one factor in each product being complex-conjugated if complex-valued functions are allowed. The appropriate scalar product for $\mathscr{F}_r$ is the usual integral

$$\langle f \mid g \rangle_{\mathscr{F}_r} = \int f^*(\boldsymbol{r})\, g(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}\,, \quad \forall f, g \in \mathscr{F}_r\,. \quad (2.3)$$

The coordinate collapse map $\hat{\delta}_r$ is defined as a linear map from $\mathscr{E}$ to $\mathscr{F}_r$ by

$$\hat{\delta}_r D(\boldsymbol{r}; \boldsymbol{r}') = D(\boldsymbol{r}; \boldsymbol{r}) = \sum_{j,\,k=1}^{d} D_{jk}\, \chi_j(\boldsymbol{r})\, \chi_k^*(\boldsymbol{r})\,, \quad (2.4)$$

or

$$\hat{\delta}_r W_D(\boldsymbol{r}, \boldsymbol{p}) = \int W_D(\boldsymbol{r}, \boldsymbol{p})\, \mathrm{d}\boldsymbol{p}\,. \quad (2.5)$$

This map defines a decomposition of $\mathscr{E}$ into orthogonal subspaces $\mathscr{E} = \mathscr{K}_r \oplus \mathscr{L}_r$, where $\mathscr{K}_r$ is the null space of $\hat{\delta}_r$ and $\mathscr{L}_r$, defined as the orthogonal complement of $\mathscr{K}_r$ in $\mathscr{E}$, has the property that its elements are in one-to-one correspondence with elements of $\mathscr{F}_r$.

The case where only the coordinate collapse map is considered has been treated previously [14] and the following properties established:

1. $\mathscr{E}$ and $\mathscr{F}_r$ are determined by $\mathscr{H}$. (They do not depend on the particular choice of basis for $\mathscr{H}$.)
2. The decomposition $\mathscr{E} = \mathscr{K}_r \oplus \mathscr{L}_r$ is independent of the particular choice of basis for $\mathscr{H}$.
3. The map $\hat{\delta}_r \colon \mathscr{L}_r \mapsto \mathscr{F}_r$ is one-to-one onto.
4. If $\mathscr{H}$ is complete (i.e. the span of a complete set of functions), then $\mathscr{F}_r$ is complete.
5. If $\mathscr{H}$ is complete, then each of the spaces $\mathscr{E}$, $\mathscr{K}_r$, and $\mathscr{L}_r$ is infinite-dimensional, and for each $g \in \mathscr{F}_r$ there is an infinite-dimensional subspace $\mathscr{E}_g \subset \mathscr{E}$ such that for any $\mathbf{D} \in \mathscr{E}_g$, $\hat{\delta}_r \mathbf{D} = g$.

We will seek here to find appropriate generalizations of these results.

We can equally well work in the momentum representation. The starting point is then a Hilbert space $\tilde{\mathscr{H}}$ spanned by the Fourier transforms, $\tilde{\chi}_j(\boldsymbol{p})$, of the coordinate basis functions. The operator space can be considered to include also kernels of integral operators in momentum space, and there is a momentum collapse map $\hat{\delta}_p$ from $\mathscr{E}$ ro $\mathscr{F}_p$, the space spanned by products of momentum functions. In this case we can think of the elements of $\mathscr{E}$ as operators with momentum-space kernels corresponding to those in Eq. (2.1) and $\hat{\delta}_p$ sets $\boldsymbol{p}'$ equal to $\boldsymbol{p}$. In the Wigner-function representation, it is integration over $\boldsymbol{r}$. It defines a decomposition $\mathscr{E} = \mathscr{K}_p \oplus \mathscr{L}_p$, where $\mathscr{K}_p$ is the null space of $\hat{\delta}_p$, and $\hat{\delta}_p$

provides a one-to-one map from $\mathscr{L}_p$ onto $\mathscr{F}_p$. The results established for the coordinate representation carry over immediately to the case in which only the momentum collapse map is considered.

The collapse of a one-electron reduced density matrix is a density. One significant aspect of the subspace decompositions defined above is thus that any density matrix can be resolved into two orthogonal components, one completely determined by the density and the other completely unrestricted by the density. We would like to make the decompositions corresponding to both coordinate and momentum densities at the same time and to examine the relationships between them. This process is complicated by the fact that in general, $\mathscr{K}_p$ (or $\mathscr{L}_p$) is neither contained in nor orthogonal to either $\mathscr{K}_r$ or $\mathscr{L}_r$. This will be discussed at greater length later, after some examples have been presented.

The appropriate decomposition of $\mathscr{E}$ when we consider both collapse maps is

$$\mathscr{E} = \mathscr{K} \oplus \mathscr{K}\mathscr{L} \oplus \mathscr{L}\mathscr{K} \oplus \mathscr{L} \oplus \mathscr{M} \quad (2.6)$$

with the subspaces defined as follows:

$$\mathscr{K} = \{\mathbf{D} \in \mathscr{E} \mid \hat{\delta}_r \mathbf{D} = 0 \text{ and } \hat{\delta}_p \mathbf{D} = 0\}\,,$$

$$\mathscr{L} = \{\mathbf{D} \in \mathscr{E} \mid \mathbf{D} \perp \mathscr{K}_r \text{ and } \mathbf{D} \perp \mathscr{K}_p\}\,,$$

$$\mathscr{K}\mathscr{L} = \{\mathbf{D} \in \mathscr{E} \mid \hat{\delta}_r \mathbf{D} = 0 \text{ and } \mathbf{D} \perp \mathscr{K}_p\}\,,$$

$$\mathscr{L}\mathscr{K} = \{\mathbf{D} \in \mathscr{E} \mid \mathbf{D} \perp \mathscr{K}_r \text{ and } \hat{\delta}_p \mathbf{D} = 0\}\,,$$

$$\mathscr{M} = \mathscr{E} \setminus (\mathscr{K} \oplus \mathscr{K}\mathscr{L} \oplus \mathscr{L}\mathscr{K} \oplus \mathscr{L})\,. \quad (2.7)$$

It is fundamental to this decomposition that *each of the subsets defined in* (2.7) *is a linear space and any two of them are orthogonal. Their direct sum is $\mathscr{E}$.* These properties are readily established.

Any density matrix γ will be an element of $\mathscr{E}$, and can be resolved into components in the various subspaces. The most restricted component of γ is that in $\mathscr{L}$. Not only is this component fixed by either the coordinate density ϱ or the momentum density π, but the one-to-one maps in each case imply relationships between the two densities. A trivial case that always occurs is the one-dimensional subspace $\mathscr{X} \subset \mathscr{E}$, which will always be contained in $\mathscr{L}$. The component in this subspace is fixed by normalization [19]. The component of γ in $\mathscr{L}\mathscr{K}$ is fixed by ϱ but completely independent of π, while the component of γ in $\mathscr{K}\mathscr{L}$ is fixed by π and independent of ϱ.

A new situation, different from that encountered when only one kind of density is considered, occurs for

$\mathcal{M}$. Any component of γ in $\mathcal{M}$ must have nonvanishing subcomponents in both $\mathcal{K}_r$ and $\mathcal{L}_r$, and similarly nonvanishing components in both $\mathcal{K}_p$ and $\mathcal{L}_p$. The component of γ in $\mathcal{M}$ is thus not determined by either of the densities alone. It *is* determined if *both* densities are specified.

Note finally that any component of γ in $\mathcal{K}$ remains completely unrestricted even if both densities are specified.

3. Some Simple Examples

Before going on with the formalism and discussing the significance of the results, we will find it useful to consider some simple examples. For convenience, we use harmonic oscillator functions in one dimension and a set of 1s Gaussians.

A) Harmonic Oscillator Functions

The one-dimensional harmonic oscillator eigenfunctions in the coordinate and momentum representations are

$$\chi_n(x) = c_n H_n(x) e^{-x^2/2},$$
$$\tilde{\chi}_n(p) = (-i)^n c_n H_n(p) e^{-p^2/2}, \qquad (3.1)$$

where H_n is the Hermite polynomial of degree n and $c_n = (2^n n! \sqrt{\pi})^{-1/2}$. The coordinate-density space $\mathcal{F}_r$ will include real functions of the form of linear combinations of

$$\chi_m(x)\chi_n(x) = c_m c_n H_m(x) H_n(x) e^{-x^2}, \qquad (3.2)$$

and similarly for $\mathcal{F}_p$. We will consider here only $n = 0, \ldots, 3$ and only real-symmetric kernels. The general case will be considered later.

For convenience, we introduce a compact notation for these kernels,

$$(j, k) = \begin{cases} \chi_j(s)\chi_j(s') & \text{if } j = k \\ \dfrac{1}{\sqrt{2}}[\chi_j(s)\chi_k(s') + \chi_k(s)\chi_j(s')] & \text{if } j < k, \end{cases} \qquad (3.3)$$

where $s = x$ or p. Which kernel is intended will be clear from context. The collapses of these kernels are of the form

$$\hat{\delta}_r(j, k) = \pi^{-1/2} \xi_{j,k}(x) e^{-x^2},$$
$$\hat{\delta}_p(j, k) = \pi^{-1/2} \eta_{j,k}(p) e^{-p^2}, \qquad (3.4)$$

where the common factors have been separated explicitly to simplify the forms of the polynomials ξ and η. They are given in Table 1.
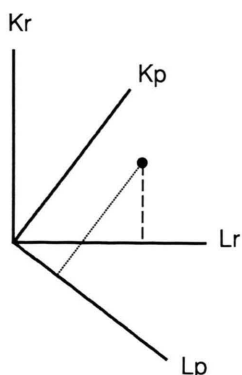
Table 1. Collapses of basis kernels for the harmonic-oscillator example.

(j, k)	$\xi_{jk}(x)$	$\eta_{jk}(p)$
$(0, 0)$	1	1
$(0, 1)$	$2x$	0
$(1, 1)$	$2x^2$	$2p^2$
$(0, 2)$	$2x^2 - 1$	$-2p^2 + 1$
$(1, 2)$	$\sqrt{2}(2x^3 - x)$	0
$(2, 2)$	$2x^4 - 2x^2 + \frac{1}{2}$	$2p^4 - 2p^2 + \frac{1}{2}$
$(0, 3)$	$\sqrt{6}(\frac{2}{3}x^3 - x)$	0
$(1, 3)$	$\dfrac{1}{\sqrt{3}}(4x^4 - 6x^2)$	$-\dfrac{1}{\sqrt{3}}(4p^4 - 6p^2)$
$(2, 3)$	$\dfrac{1}{\sqrt{3}}(4x^5 - 8x^3 + 3x)$	0
$(3, 3)$	$\frac{4}{3}x^6 - 4x^4 + 3x^2$	$\frac{4}{3}p^6 - 4p^4 + 3p^2$

Table 2. Subspace basis for a simple example.

$$Y_0 = \frac{1}{2}(0, 0) + \frac{1}{2}(1, 1) + \frac{1}{2}(2, 2) + \frac{1}{2}(3, 3)$$

$$Y_1 = \frac{1}{2\sqrt{3}}(0, 0) + \frac{1}{2\sqrt{3}}(1, 1) + \frac{1}{2\sqrt{3}}(2, 2) - \frac{\sqrt{3}}{2}(3, 3)$$

$$Y_2 = \frac{1}{\sqrt{3}}(0, 1) + \frac{\sqrt{2}}{\sqrt{3}}(1, 2)$$

$$Y_3 = \frac{1}{\sqrt{3}}(0, 1) - \frac{1}{\sqrt{6}}(1, 2) - \frac{1}{\sqrt{2}}(0, 3)$$

$$Y_4 = (2, 3)$$

$$Y_5 = \frac{\sqrt{2}}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}(0, 0) - \frac{1}{\sqrt{2}}(1, 1)\right] \pm \frac{1}{\sqrt{3}}(0, 2)$$

$$Y_6 = \mp \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}(0, 0) - \frac{1}{\sqrt{2}}(1, 1)\right] + \frac{\sqrt{2}}{\sqrt{3}}(0, 2)$$

$$Y_7 = \frac{\sqrt{2}}{\sqrt{3}}\left[\frac{1}{\sqrt{6}}(0, 0) + \frac{1}{\sqrt{6}}(1, 1) - \frac{2}{\sqrt{6}}(2, 2)\right] \pm \frac{1}{\sqrt{3}}(1, 3)$$

$$Y_8 = \mp \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{6}}(0, 0) + \frac{1}{\sqrt{6}}(1, 1) - \frac{2}{\sqrt{6}}(2, 2)\right] + \frac{\sqrt{2}}{\sqrt{3}}(1, 3)$$

$$Y_9 = \frac{1}{\sqrt{3}}(0, 1) - \frac{1}{\sqrt{6}}(1, 2) + \frac{1}{\sqrt{2}}(0, 3)$$

Linear-dependency conditions can be found by inspection, and orthogonalization is similarly accomplished. The results are summarized in Table 2, and the properties discussed below are readily verified.

Fig. 1. A two-dimensional subspace of $\mathcal{M}$.

Table 3. Exponential parameters for 1 s Gaussians.

$h = 4$		$h = 5$	
Coordinate	Momentum	Coordinate	Momentum
0.1233	2.0276	0.1013	2.4679
0.4539	0.5508	0.3119	0.8015
2.0018	0.1249	1.0671	0.2343
13.2626	0.0188	4.5750	0.0546
		29.8761	0.0084

Table 4. Subspace dimensions for two 1s Gaussian basis sets.

Space	h	
	4	5
$\mathcal{L}$	8	8
$\mathcal{L}\mathcal{K}$	0	1
$\mathcal{K}\mathcal{L}$	0	0
$\mathcal{M}$	2	6
$\mathcal{K}$	0	0
$\mathcal{E}$	10	15
$\mathcal{F}_r$	9	12
$\mathcal{F}_p$	9	11

The kernels Y_0 and Y_1 are orthogonal (with respect to the trace scalar product of $\mathcal{E}$) to any linear combination that collapses to zero under $\hat{\delta}_r$ or $\hat{\delta}_p$. They are thus in $\mathcal{L}$. Kernels Y_2, Y_3, and Y_4 have $\hat{\delta}_p Y_k = 0$, but are orthogonal to any Y_j for which $\hat{\delta}_r Y_j = 0$ so they are in $\mathcal{L}\mathcal{K}$. In this example the dimension of $\mathcal{K}\mathcal{L}$ is zero. The only kernel for which $\hat{\delta}_r Y = \hat{\delta}_p Y = 0$ is Y_9. It is in $\mathcal{K}$. The four kernels $Y_5, \ldots, Y_8$ have double signs in the table; either the upper sign or the lower sign should be used consistently. With either choice they provide a basis for $\mathcal{M}$.

With the upper signs, Y_5 and Y_7 are entirely in $\mathcal{K}_r$ while Y_6 and Y_8 are entirely in $\mathcal{L}_r$, but each of them has components in both $\mathcal{K}_p$ and $\mathcal{L}_p$. The lower signs reverse the priorities: Y_5 and Y_7 are in $\mathcal{K}_p$, Y_6 and Y_8 are in $\mathcal{L}_p$, and each has components in both $\mathcal{K}_r$ and $\mathcal{L}_r$.

An examination of the overlaps of one choice of Ys with the other shows that $\mathcal{M}$ can be decomposed as the direct sum of two orthogonal, two-dimensional subspaces, one spanned by Y_5 and Y_6, the other spanned by Y_7 and Y_8. The two choices of Ys lead to different coordinate systems in each of these subspaces. One of them is illustrated in Figure 1. Corresponding to the collapse maps are projectors in this subspace. Corresponding to $\hat{\delta}_r$ is a projection onto $Lr = Y_6$, which destroys any information about the component along $Kr = Y_5$. In this case the upper signs are used. Similarly, if lower signs are used, $\hat{\delta}$ corresponds to a projection onto $Lp = Y_6$, destroying information about the $Kp = Y_5$ component. However, the component of any $\mathbf{D}$ in this subspace is completely determined if its Lr component $\hat{\delta}_r \mathbf{D}$ and its Lp component $\hat{\delta}_p \mathbf{D}$ are both known.

B) Gaussian 1s Orbitals

As an example more closely related to practical basis sets we consider two sets of 1 s Gaussians that provide approximations to the H atom ground state. These functions are of the form $\chi_j = \exp(-\alpha_j r^2)$. The first set consists of four functions, and when linear expansion coefficients are optimized the H-atom variational energy is $-0.499277 E_h$. The second set has five functions and yields an energy $-0.499805 E_h$. The exponential parameters, α_j, are summarized in Table 3. Eigenvalues of the overlap matrices for product functions are comparable for r and p and range from about 8×10^0 to 2×10^{-10} for the first set and from 1.2×10^1 to 1.6×10^{-15} for the second set.

The subspace decomposition of $\mathcal{E}$ was obtained by an algorithm to be described in a later section, and the details will be omitted. Results obtained with the criterion that a matrix eigenvalue less than 1×10^{-10} is considered to be zero are summarized in Table 4. Two features are particularly relevant. In each case there are some (numerical) linear dependencies among both coordinate and momentum collapses so that the dimensions of $\mathcal{F}_r$ and $\mathcal{F}_p$ are less than that of $\mathcal{E}$. With these small basis sets, however, $\mathcal{L}$ accounts for most of $\mathcal{E}$ and the dimension of $\mathcal{K}$ is zero. It follows that the

two densities together would determine the density matrix in this model. The number of linear dependencies is more than proportionately greater for the five-function basis set, and we might reasonably expect that for still larger bases there may be a $\mathscr{K}$ subspace.

4. Basis Sets with Linearly Independent Products

It has been noted elsewhere that if a basis set has the property that all products of basis functions are linearly independent then $\mathscr{E} = \mathscr{L}_r$ and, in the model problem defined by this basis, density matrices are determined by their densities. Such bases have been called LIP bases [14]. LIP basis sets have been investigated in the coordinate representation [17, 18], and somewhat relaxed conditions under which a density matrix can be obtained from the density have also been reported [16]. It appears that only in the case of very-carefully-chosen bases for small problems can a good description of a system be given in terms of a LIP basis. The further decomposition of $\mathscr{E}$ discussed here suggests the question of under what conditions on a basis set will the one-matrix for a model problem defined by that basis set be completely determined if both coordinate and momentum density are specified.

This question can be restated as follows: Under what conditions on the orbital Hilbert space basis will the subspace $\mathscr{K}$ of $\mathscr{E}$ be of dimension 0? It is clearly sufficient for the coordinate basis to have linearly independent products (a CLIP basis) or for the corresponding, Fourier-transformed momentum basis to have linearly independent products (a MLIP basis). Another question which then arises is whether these conditions are equivalent: does CLIP imply MLIP and vice versa? It is also possible, however, to find bases that are neither CLIP nor MLIP but such that $\dim(\mathscr{K}) = 0$. The more important question is whether such a basis can be of practical utility.

For a harmonic oscillator basis, coordinate and momentum basis functions differ at most by a phase factor, so their products will also be essentially the same and any linear-dependency condition for one set of products implies a similar linear-dependency condition for the other. This is not always the case, however, as can be illustrated by another simple example.

Consider a basis set consisting of three normalized 1s Gaussians with exponential parameters $\alpha = 1, 2$ and 3. Their products will be such that $\chi_1 \chi_3 \propto \chi_2 \chi_2$, so this basis is not CLIP. The corresponding momen-

tum basis has exponential parameters 1/4, 1/8, and 1/12. The exponential parameters in the products are all different so there are no exact linear dependencies, and the basis is MLIP. We could equally well interchange the coordinate and momentum functions to obtain a basis that is CLIP but not MLIP.

The example of 1s Gaussians for the H atom presented above suggests that some reasonably good basis sets, while neither CLIP nor MLIP, can lead to a $\mathscr{K}$ subspace of dimension zero and thus define a model in which the density matrix is determined if both densities are known. A possible way of labeling such a basis set would be as "no K". Additional investigation is necessary before it will be possible to know if any common electronic structure basis sets are "no K" or if potentially useful "no K" bases can be constructed. As will become apparent in the next section, the results will depend on how small a matrix eigenvalue must be before it is considered to be zero.

5. An Algorithm for Finding Subspaces

In simple examples like those considered above, linear dependencies and orthonormality could be seen by inspection. This will not always be the case, and "by inspection" is difficult to code for a computer. We thus seek a generally applicable algorithmic approach.

A) Subspace Decomposition

The starting point for a decomposition of $\mathscr{E}$ into density-related subspaces is a characterization of the collapse maps $\hat{\delta}_s$, $s = r$ or p. If $\{b_\mu, \mu = 1, \ldots, d_\mathscr{E} = h^2\}$ is a basis for $\mathscr{E}$ and $\{\phi_\varkappa^s, \varkappa = 1, \ldots, d_{\mathscr{F}s}\}$ is a basis for $\mathscr{F}_s$, then $\hat{\delta}_s$ can be characterized by a matrix $\mathbf{\Delta}^s$ such that

$$\hat{\delta}_s b_\mu = \sum_{\varkappa = 1}^{d_{\mathscr{F}s}} \phi_\varkappa^s \Delta_{\varkappa, \mu}^s. \qquad (5.1)$$

Note that in general $d_{\mathscr{F}s} < d_\mathscr{E}$ so $\mathbf{\Delta}^s$ is rectangular.

It is readily shown that for a rectangular matrix $\mathbf{M}$, $\mathbf{M}\underline{u} = \underline{0}$ if and only if $\mathbf{M}^\dagger \mathbf{M}\underline{u} = \underline{0}$. It follows that $\mathscr{K}_s$ is spanned by those eigenvectors of $\mathbf{\Delta}^{s\dagger}\mathbf{\Delta}^s$ associated with eigenvalue 0, while $\mathscr{L}_s$ is spanned by the eigenvectors associated with nonzero eigenvalues.

A detailed discussion of the process by which the complete subspace decomposition of $\mathscr{E}$ is obtained is too long to present here. In outline, it is as follows. Let $\mathbf{U}^s$ be the matrix that diagonalizes $\mathbf{\Delta}^{s\dagger}\mathbf{\Delta}^s$, with $d_{\mathscr{K}s}$ zero eigenvalues and $d_{\mathscr{L}s}$ nonzero eigenvalues. From

U^r and Δ^p we can construct a $d_{\mathscr{F}_p} \times g_{\mathscr{K}_r}$ matrix $\mathbf{R}$, where $d_{\mathscr{F}_p}$ is the dimension of $\mathscr{F}_p$ or $\mathscr{L}_p$. The matrix $\mathbf{R}^\dagger \mathbf{R}$ is $d_{\mathscr{K}_r} \times d_{\mathscr{K}_r}$. It can be diagonalized by a matrix $\mathbf{V}$, and has $d_{\mathscr{K}_r}$ zero eigenvalues and dA nonzero eigenvalues. The eigenvectors associated with zero eigenvalue span $\mathscr{K}$, while the rest span an intermediate space $\mathscr{A}$ of dimension dA. From $\mathbf{V}$, U^r, and U^p we can construct a matrix $\mathbf{S}$ that is $d_{\mathscr{K}_p} \times d_{\mathscr{A}}$. The eigenvectors of $\mathbf{S}^\dagger \mathbf{S}$ associated with eigenvalue zero span $\mathscr{K}\mathscr{L}$ and the remainder span a space $\mathscr{M}_1$ that is part of $\mathscr{M}$.

A similar sequence of steps provides bases for $\mathscr{L}\mathscr{K}$, an intermediate space $\mathscr{B}$, and then $\mathscr{L}$ and $\mathscr{M}_2$, with $\mathscr{M} = \mathscr{M}_1 \oplus \mathscr{M}_2$. This decomposition of $\mathscr{M}$ is related to the different choices discussed in the example and depends on the particular algorithm used.

It should be noted that for a particular basis set, some of the subspaces may be nonexistent: none or all of a set of eigenvalues may be zero. In such a case the corresponding dimension will be zero and of course any subsubspaces of the nonexistent subspace are also nonexistent and their dimensions should be set to zero.

It might appear that the decomposition could be accomplished more readily by the use of projection operators, and that one could, for example, obtain $\mathscr{K}$ as the projection of $\mathscr{K}_r$ onto $\mathscr{K}_p$. The problem is that in general neither are $\mathscr{K}_p$ and $\mathscr{K}_r$ orthogonal nor is one of them contained within the other. The product of nonorthogonal projection operators is not a projection operator, and in this case projection of an element of $\mathscr{K}_r$ onto $\mathscr{K}_p$ will introduce components that are in $\mathscr{L}_r$.

B) Bases for $\mathscr{F}_s$

The density spaces $\mathscr{F}_s$ are defined by the spans of the collapses of basis elements of $\mathscr{E}$, but we need a linearly independent basis for each of them in order to define Δ^r and Δ^p. This can be done analytically for the harmonic-oscillator basis but we need a more generally applicable method. Such a method is provided by a generalization of the Löwdin symmetric orthogonalization procedure. Given a set of functions $\{f_j(s)\}$, define their overlap matrix $\mathbf{S}$ and find the unitary matrix $\mathbf{U}$ that diagonalizes it:

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \Sigma . \tag{5.2}$$

Not only is Σ diagonal, but some of its eigenvalues may be zero. If we assume them to be in nonincreasing

order, then

$$\Sigma_{\varkappa\varkappa} = \begin{cases} \sigma_\varkappa > 0 & 1 \le \varkappa \le M \\ 0 & M+1 \le \varkappa \le N \end{cases} . \tag{5.3}$$

Define

$$\phi_\varkappa = \sigma_\varkappa^{-1/2} \sum_k f_k U_{k\varkappa}, \quad 1 \le \varkappa \le M . \tag{5.4}$$

These functions are orthonormal and provide a basis for the space spanned by the f's. In terms of them,

$$f_k = \sum_{\varkappa=1}^{M} \phi_\varkappa A_{k\varkappa} . \tag{5.5}$$

with $A_{k\varkappa} = U_{k\varkappa}^* \sigma_\varkappa^{-1/2} = \sigma_\varkappa^{-1/2} U_{\varkappa k}^\dagger$.

6. General Treatment of Collapse Maps for Harmonic-Oscillator Functions

We start by generalizing the notation introduced previously. Let

$$(m, n)_\pm = \varepsilon_{mn}^\pm (|m\rangle \langle n| \pm |n\rangle \langle m|) \tag{6.1}$$

with

$$\varepsilon_{mn}^\pm = \begin{cases} 1/2 & \text{if } \pm = + \text{ and } m = n \\ 1/\sqrt{2} & \text{if } \pm = + \text{ and } m < n \\ i/\sqrt{2} & \text{if } \pm = - \text{ and } m < n \end{cases} . \tag{6.2}$$

An ordering must be defined. It is taken to be

$$(m', n')_{\pm'} \prec (m, n)_\pm \quad \text{if} \quad n' < n ,$$
$$(m', n)_{\pm'} \prec (m, n)_\pm \quad \text{if} \quad m' < m , \tag{6.3}$$
$$(m, n)_+ \prec (m, n)_- .$$

A) Method

The key to the general expression for the collapses is an expansion of products $H_m(x) H_n(x)$ in terms of $H_j(\sqrt{2}x)$. Because the Hermite polynomials are of definite parity, it is possible to write the expansion in the form

$$H_m(x) H_n(x) = \sum_{\varkappa=0}^{v} W_{mn\varkappa} H_{2\varkappa+\alpha}(\sqrt{2}x) , \tag{6.4}$$

where v and α ($\alpha = 0$ or 1) are defined by the condition $m + n = 2v + \alpha$. The coefficients $W_{mn\varkappa}$ can be shown to be

$$W_{mn\varkappa} = \left(\frac{1}{\sqrt{2}}\right)^\alpha \frac{m!\, n!}{(2\varkappa+\alpha)!} \frac{(-1)^{v-\varkappa}}{2^v} \tag{6.5}$$

$$\times \sum_{k=0}^{\min(m, n, v-\varkappa)} \frac{(-4)^k (2v+\alpha-2k)!}{k!\, (m-k)!\, (n-k)!\, (v-\varkappa-k)!} .$$

Table 5. Subspace dimensions for harmonic oscillator bases. The headings e, o, and t refer to the even or odd $m+n$ subspaces and the total, respectively.

	$N=1$			$N=2$			$N=3$			$N=4$			$N=5$			General
	e	o	t	e	o	t	e	o	t	e	o	t	e	o	t	N
$\mathscr{L}$	2	0	2	2	0	2	2	0	2	2	0	2	2	0	2	2
$\mathscr{L}\mathscr{K}$	0	1	1	0	2	2	0	3	3	0	4	4	0	5	5	N
$\mathscr{K}\mathscr{L}$	0	1	1	0	2	2	0	3	3	0	4	4	0	5	5	N
$\mathscr{M}$	0	0	0	2	0	2	4	0	4	6	0	6	8	0	8	$2(N-1)$
$\mathscr{K}$	0	0	0	1	0	1	2	2	4	5	4	9	8	8	16	$(N-1)^2$
$\mathscr{E}$	2	2	4	5	4	9	8	8	16	13	12	25	18	18	36	$(N+1)^2$

Odd and even cases (labeled by $\alpha=1$ or $\alpha=0$, respectively) can be considered separately.

Let μ be a single index corresponding to $b_\mu = (m,n)_\pm$. We choose as a basis for $\mathscr{F}_s$ the orthogonal but not normalized functions $H_{2\varkappa+\alpha}(\sqrt{2}\,s)\exp(-s^2)$ so that

$$\delta_s b_\mu = \delta_s(m,n)_\pm = \sum_{\varkappa=0}^{\nu} \Delta^{s\alpha}_{\varkappa\mu} H_{2\varkappa+\alpha}(\sqrt{2}\,s)\exp(-s^2) \quad (6.6)$$

with

$$\Delta^{s\alpha}_{\varkappa\mu} = \begin{cases} 0 & \begin{array}{l} \text{if } m+n \text{ is even and } \pm = +, \\ m+n \text{ is odd}, \pm = +, \text{ and } s=r, \text{ or} \\ m+n \text{ is odd}, \pm = -, \text{ and } s=p \end{array} \\ \sigma\, C_m C_n W(m,n,\varkappa) & \text{otherwise} \end{cases} \quad (6.7)$$

and

$$\sigma = \begin{cases} 1 & \text{if } m=n \\ \sqrt{2} & \text{if } m<n \text{ and } s=r \\ (-1)^{m+\nu}\sqrt{2} & \text{if } m<n \text{ and } s=p \end{cases} \quad (6.8)$$

With this starting point the remainder of the algorithm can be implemented.

B) Results

These formulae and the algorithm of the previous section have been implemented. Some results are given in Table 5 for bases $(m,n)_\pm$ with $m\le n\le N$ for various values of N. A regular pattern is apparent, and one is lead to conjecture the general results given in the last column. If correct, it is a very interesting result. The fact that the dimensions of $\mathscr{E}$ and $\mathscr{K}$ grow quadratically with N while the dimensions of the density spaces $\mathscr{F}_s$ and the subspaces of $\mathscr{E}$ corresponding to them grow linearly is to be expected. What is not expected is that the dimension of $\mathscr{L}$ remains constant at 2.

As noted above, one of the elements of $\mathscr{L}$ corresponds to the normalization condition, which must be dealt with in a consistent way for the density matrix and both densities. In the simple SHO example this was Y_0. An examination of the other component in these calculations shows that it is of a form similar to Y_1 in the simple SHO example,

$$a\sum_{n=0}^{N-1}(n,n)_+ - b(N,N)_+, \quad (6.9)$$

where a and b are determined by the conditions that this combination be normalized and orthogonal to the sum of all the $(n,n)_+$. In a sense, these two elements of $\mathscr{L}$ differ only in a contribution that "receeds to infinity" as $N\to\infty$.

Unfortunately, it has not yet been possible to prove these conjectures, and further calculations cast some doubt on their validity. The algorithm defined above depends critically on the distinction between zero and nonzero eigenvalues. Numerically, this distinction may not be clear. The dimensions of $\mathscr{E}$, $\mathscr{K}_r$, and $\mathscr{L}_r$ are known analytically for this model. They are

$$\dim \Delta^{r\dagger}\Delta^r = \dim \mathscr{E} = (N+1)^2 = N^2 + 2N + 1,$$

$$\dim \mathscr{L}_r = \dim \mathscr{F}_r = 2N+1, \quad (6.10)$$

$$\dim \mathscr{K}_r = \dim \mathscr{E} - \dim \mathscr{L}_r = N^2.$$

We have found in fact that for $N>5$ there is no clear break in the spectrum of $\Delta^{r\dagger}\Delta^r$ between eigenvalues N^2 and N^2+1, although one of them should be zero and the other nonzero. Further work and an improved algorithm are necessary.

7. Conclusions

The collapse map from the space containing density matrices or other operators to the space containing densities or other functions defines a decomposition of the matrix space into two orthogonal subspaces, one the null space of the collapse map, the other in one-to-one correspondence with the density space. For any complete basis there are an infinite number of density matrices corresponding to any density. There are finite basis sets such that, in the model problem defined by that basis, the density matrix is completely determined by the density. It has been found, however, that basis sets of practical utility are unlikely to be of this type.

If both collapse maps, from the matrix space to coordinate- *and* momentum-density spaces, are considered then the matrix space is divided into a total of five orthogonal subspaces. At one extreme is the subspace $\mathscr{L}$, which is in one-to-one correspondence with an appropriate subspace of each density space, and which thus implies a constraint on one density if the other is specified. At the other extreme is the subspace $\mathscr{K}$, which provides no information about either density and which contains density matrix components that cannot be evaluated from a knowledge of the densities. Between these extremes are three subspaces, $\mathscr{L}\mathscr{K}$, $\mathscr{K}\mathscr{L}$, and $\mathscr{M}$, containing components of a density matrix that are determined by the coordinate density, the momentum density, or both densities together, respectively.

Algorithms exist for the construction of bases for the density spaces and the subspaces of the matrix space but, although they are formally capable of providing the decomposition, initial numerical experience suggests that there may be problems associated with the unambiguous identification of "zero" eigenvalues. Better algorithms are thus necessary.

The formal, exact results available when only one collapse is considered are not yet available for the case when both maps are considered together. Some results for a harmonic oscillator basis suggest that in the limit of a complete basis the dimensions of all subspaces except $\mathscr{L}$ become infinite, with that of $\mathscr{K}$ increasing more rapidly than those of the others. The conjecture is thus that even if both densities are known there are an infinite number of density matrices consistent with this knowledge.

The dimension of $\mathscr{L}$ appears to be constant at 2 for the harmonic oscillator basis. One component is equivalent to the normalization condition, which must be consistent for the density matrix and both densities. An examination of the other basis element suggests that, although it is orthogonal to the normalization component, the difference between these two becomes increasingly small as the size of the basis increases.

The difficulty with these conjectures is that the conclusions have not been established formally and numerical problems cause difficulties with verification for large basis sets. They remain conjectures only.

An examination of 1s Gaussian bases for the H atom suggests that there may be reasonable "no K" bases, in which the dimension of $\mathscr{K}$ is zero and thus for which the density matrix is determined if both densities are known. More data for realistic, finite basis sets are clearly desirable.

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