N-Representability of Phase Space Functions for Electrons

JOHN E. HARRIMAN

Department of Chemistry, University of Wisconsin–Madison, Madison, Wisconsin 53706

Abstract

Conditions on one-electron Wigner and Husimi functions such that they correspond to *n*-representable charge density matrices are considered.

Introduction

The use of reduced density matrices to describe the behavior of electrons in an atom, molecule, or solid is well established. Conditions on a density matrix that it be a reduced density matrix for an *n*-electron system are known as *n*-representability conditions. For the case of the one-electron reduced density matrix, necessary and sufficient conditions are known [1]. These conditions are of interest not only in formal density matrix theory but also in density matrix functional theory [2–5] and in connection with the modeling of experimental x-ray diffraction data [6–12].

There is long-standing interest in the coordinate density, both in density functional theory and as a way of interpreting the results of calculations. There is also increasing interest in the momentum density for similar purposes. Both of these quantities are experimentally observable, but they are not independent: knowledge of one places some restrictions on the other. The treatment of coordinates and momenta simultaneously is restricted by the uncertainty principle, but there has been increasing interest in recent years in the use of phase space functions to characterize electronic behavior. The Wigner function [13–16] and the Husimi function [17–20] have both been employed for this purpose. As we examine these functions for particular systems, we would like to know what aspects of the results give specific information about the system of interest and which are simply manifestations of general properties of the functions. It may also be desirable while constructing models to work directly with a phase space function, where physical intuition may be a useful guide, rather than with a density matrix. In this article, *n*-representability conditions for these phase space functions will be considered.

In the next section, the *n*-representability of one-electron density matrices is reviewed and the conditions extended to the case of the charge (spinless) density matrix. In following sections, the translation of these conditions to conditions on one-particle Wigner and Husimi functions is considered. Some concluding remarks are contained in a final section.

Review of Density Matrix Conditions

Density Matrices

A density matrix can be represented as an operator, an integral operator kernel, or a discrete matrix. The conversions among these different representations is straightforward and will be assumed when required in this article. We will most often work with the integral kernel form. A kernel $D(\tau;\tau')$ is a density matrix if it is Hermitian, of unit trace, and positive:

$$D(\tau;\tau') = D^*(\tau';\tau), \qquad \int D(\tau;\tau)\, d\tau = 1$$

$$\int \phi^*(\tau)\, D(\tau;\tau')\phi(\tau')\, d\tau'\, d\tau \geq 0 \qquad \forall \phi. \tag{1}$$

Here τ represents any appropriate set of coordinates.

A pure state density matrix is a density matrix that is idempotent and is thus a projector onto a single state. In the theory of reduced density matrices it is also useful to consider density matrices that are idemproportional, that is

$$\int D(\tau;\tau')\, D(\tau';\tau'')\, d\tau' = CD(\tau;\tau''). \tag{2}$$

where τ represents the coordinates of an electron and C is a constant. Such density matrices play a special role in self-consistent field theory.

One Matrices

A one-electron reduced density matrix or one matrix $D^{(1)}(x,x')$, where $x = (\mathbf{r},\xi)$ represents the space and spin coordinates of an electron, is n representable if it can. be obtained by reduction from an n-electron density matrix:

$$D^{(1)}(x_1;x_1') \propto \int D^{(n)}(x_1,x_2, \ldots, x_n;x_1',x_2, \ldots, x_n)\, dx_2 \cdots dx_n \tag{3}$$

Various conventions as to normalization are employed, but results will be stated here in a way that is independent of the normalization chosen. If $D^{(1)}$ can be so-obtained from a pure-state $D^{(n)}$, it is said to be pure-state n representable. In this case $D^{(1)}$ comes from an n-electron wave function. It is well known [1] that a one-electron density matrix is n representable if and only if its eigenvalues are bounded between 0 and t/n, where

$$t = \text{trace } \mathbf{D}^{(1)} = \int D^{(1)}(x,x)\, dx. \tag{4}$$

Conditions for pure state n representability are not known in general, but an important special case is that $D^{(1)}$ is n representable by a single determinant wave function if and only if

$$\int D^{(1)}(x;x') \, D^{(1)}(x';x'') \, dx' = \frac{t}{n} \, D^{(1)}(x;x'') \tag{5}$$

or equivalently, $D^{(1)}$ has n eigenvalues equal to t/n and the remainder of its eigenvalues equal to zero [21–23].

These conditions are not only readily stated, they are also in "useful" form: A given matrix can readily be tested for n representability and parameterized families of n-representable one matrices can be constructed. Even the single-determinant pure state condition has been usefully imposed as a constraint in SCF calculations or fitting x-ray data.

Charge Density Matrices

A charge density matrix is obtained from a one matrix by integration over the spin coordinate:

$$D(\mathbf{r};\mathbf{r}') = \int D^{(1)}(\mathbf{r},\xi;\mathbf{r}',\xi) \, d\xi . \tag{6}$$

Note that $\operatorname{Tr} \mathbf{D} = \operatorname{Tr} \mathbf{D}^{(1)} = t$. It is the charge density matrix that is commonly converted into a phase space function, although this could also be done for the spin up and spin down components of the one matrix, or for the spin density matrix. The n-representability conditions for the charge density matrix have not, to the author's knowledge, been explicitly stated in the literature. It is thus appropriate to state explicitly

- A charge density matrix $D(\mathbf{r};\mathbf{r}')$ is n representable if and only if its eigenvalues are bounded between 0 and $2t/n$.

The proof is straightforward. Note that if $\mathbf{D}$ is to correspond to a spin eigenstate some additional conditions may be necessary. For a singlet state the spin density matrix is identically zero and a charge density matrix is n representable by a single determinant if and only if it is appropriately idemproportional.

Conditions on Wigner Functions

The Wigner Function Corresponding to a Charge Density Matrix

The Wigner function corresponding to a charge density matrix $D(\mathbf{r};\mathbf{r}')$ can be expressed in a number of ways, depending on how intermediate variables are defined. If we define $\mathbf{R} = (\mathbf{r} + \mathbf{r}')/2$ and $\Delta\mathbf{r} = \mathbf{r} - \mathbf{r}'$ then (in units with $\hbar = 1$)

$$W(\mathbf{R},\mathbf{P}) = C_D \int D\left(\mathbf{R} + \frac{1}{2}\Delta\mathbf{r};\mathbf{R} - \frac{1}{2}\Delta\mathbf{r}\right) e^{i\mathbf{P}\cdot\Delta\mathbf{r}} \, d(\Delta\mathbf{r}) . \tag{7}$$

The constant C_D is conventionally chosen [15] to be $(2\pi)^{-3}$ for the density matrix–Wigner function conversion, with the consequence that $\int\int W(\mathbf{R},\mathbf{P}) \, d\mathbf{R} \, d\mathbf{P} = t$. It is readily shown that the hermiticity of the density matrix requires $W(\mathbf{R},\mathbf{P})$ to be real, but it is not in general positive for all $\mathbf{R}$ and $\mathbf{P}$.

This transformation can be inverted to give

$$D(\mathbf{r};\mathbf{r}') = [(2\pi)^3 C_D]^{-1} \int W\left(\frac{\mathbf{r} + \mathbf{r}'}{2}, \mathbf{P}\right) e^{-i\mathbf{P}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{P} . \tag{8}$$

Some of what follows can be obtained by transforming back to the density matrix, dealing with it, and then reconstructing a Wigner function.

In practice, an electronic reduced density matrix is usually expressed in terms of a basis set. If

$$D(\mathbf{r};\mathbf{r}') = \sum_{l,m} D_{lm}\chi_l(\mathbf{r})\chi_m^*(\mathbf{r}') \tag{9}$$

then the Wigner function will be expressed in terms of basis functions

$$w_{lm}(\mathbf{R},\mathbf{P}) = \int \chi_l\left(\mathbf{R} + \frac{1}{2}\Delta\mathbf{r}\right)\chi_m^*\left(\mathbf{R} - \frac{1}{2}\Delta\mathbf{r}\right) e^{i\mathbf{P}\cdot\Delta\mathbf{r}} d(\Delta\mathbf{r}) \tag{10}$$

as

$$W(\mathbf{R},\mathbf{P}) = \sum_{l,m} D_{lm} w_{lm}(\mathbf{R},\mathbf{P}) , \tag{11}$$

with the same expansion coefficients. Note that the phase space functions w_{lm} correspond to *products* of coordinate–space basis functions rather than to individual functions in the coordinate Hilbert space. They thus correspond to basis elements in a matrix space [24].

When is a Phase Space Function a Wigner Function?

Necessary and sufficient conditions for a phase space function to be a Wigner function, i.e., that it can be obtained via Eq. (7) from a positive, Hermitian kernel D have been determined [25]. They can be related to an alternative way of expressing the conditions on the one matrix, and depend on the fact that any Hermitian kernal $A(\mathbf{r};\mathbf{r}')$ can be converted to a corresponding phase space function by an equation analogous to Eq. (7). When $\hat{A}$ is an observable, the conventional normalization [15] has $C_A = 1$. It is then readily shown that

$$\mathrm{Tr}\ \mathbf{AB} = \iint A(\mathbf{r};\mathbf{r}')B(\mathbf{r}';\mathbf{r})\ d\mathbf{r}'\ d\mathbf{r}$$

$$= [(2\pi)^3 C_A C_B]^{-1} \iint W_A(\mathbf{R},\mathbf{P})W_B(\mathbf{R},\mathbf{P})\ d\mathbf{R}\ d\mathbf{P} . \tag{12}$$

This equivalence allows a simple statement of the condition that a phase space function be a Wigner function.

The requirement that a density matrix be Hermitian corresponds in a straightforward way to the requirement that a Wigner function be real. The requirement that a density matrix be positive can be expressed as

$$\int \phi^*(\mathbf{r})\ \hat{D}\phi(\mathbf{r})\ d\mathbf{r} = \iint \phi^*(\mathbf{r})\ D(\mathbf{r};\mathbf{r}')\phi(\mathbf{r}')\ d\mathbf{r}'\ d\mathbf{r} \geq 0 \tag{13}$$

for any orbital ϕ. This can be expressed as Tr $\mathbf{PD} > 0$ where $\hat{P}$ is the projector onto ϕ. Any positive operator $\hat{\Omega}$ can be expressed (using the spectral expansion) as

$$\hat{\Omega} = \sum_k \omega_k \hat{P}_k \qquad (14)$$

where the ω_k's are all nonnegative and the $\hat{P}_k$'s are orthogonal projectors. Combining these results one sees that

$$\text{Tr } \mathbf{\Omega D} \geq 0 \qquad (15)$$

for any positive operator $\hat{\Omega}$. This is readily translated into a condition on the corresponding phase space functions, but further consideration will be postponed until n-representability conditions are included.

A different way of stating conditions on the Wigner function involves the symplectic Fourier transform, requiring it to be continuous, appropriately normalized, and of $\hbar$-positive type [25]. The latter condition can be related to the representation of a positive operator as the product of an operator with its adjoint, to be considered below. In no form that has been presented, however, are these conditions of the practical utility noted above for those on the density matrix.

N-representable Wigner Functions

It follows from the conditions on an n-representable charge density matrix that if $\hat{P}$ is a projector onto any one-electron, spinless pure state (i.e., an orbital), then $0 \leq \text{Tr } \mathbf{PD} \leq 2t/n$. Further, any positive, trace-class operator $\hat{D}_0$ normalized to trace 1 can be expressed as

$$\mathbf{D}_0 = \sum_k \lambda_k \mathbf{P}_k \qquad (16)$$

where each $\mathbf{P}_k$ is such a projector and $0 \leq \lambda_k \leq 1$, $\sum_k \lambda_k = 1$. This implies that

$$0 \leq \text{Tr } \mathbf{D}_0 \mathbf{D} \leq 2t/n \qquad (17)$$

for every possible $\mathbf{D}_0$, and this condition is equivalent to the n representability conditions on the eigenvalues of $\mathbf{D}$.

Using Eq. (12) and this form of the n representability condition, we find that

- A real-valued phase space function $W(\mathbf{R},\mathbf{P})$ is a Wigner function corresponding to an n-representable one-electron density matrix if and only if, for every function $W_\Omega(\mathbf{R},\mathbf{P})$ corresponding to a positive, Hermitian, trace one operator $\hat{\Omega}$ (i.e., a density matrix),

$$0 \leq [(2\pi)^3 C_\Omega C_D]^{-1} \iint W_\Omega(\mathbf{R},\mathbf{P}) W(\mathbf{R},\mathbf{P}) \, d\mathbf{R} \, d\mathbf{P} \leq 2t/n . \qquad (18)$$

This condition is not in a very useful form, however. Not only does it require the use of *all* W_Ω of the appropriate type, but there is no simple way of determining when a function W_Ω corresponds to a positive operator. Some help is possible, since for any operator $\hat{A}$, the operator $\hat{B} = \hat{A}^\dagger \hat{A}$ is positive, and any positive operator can be so expressed. It is possible to choose $\hat{A}$ to be Hermitian. To apply this to a

Wigner function we need an expression relating operator products to products in the phase space representation. This relationship has been extensively studied [26–28]. It is, unfortunately, not as simple as one might wish, although it can be made to look simple by the introduction of appropriate notation. The straightforward expression for the function W_C corresponding to $\hat{C} = \hat{A}\hat{B}$ is

$$W_C(\mathbf{R},\mathbf{P}) = (2\pi)^{-6} \frac{C_C}{C_A C_B} \iiiint d\mathbf{s} \, dt \, d\mathbf{U} \, d\mathbf{V}$$

$$\times W_A\left(\frac{1}{2}\mathbf{R} + \frac{1}{2}\mathbf{s}, \mathbf{U}\right) W_B\left(\frac{1}{2}\mathbf{R} - \frac{1}{2}t, \mathbf{U}\right)$$

$$\times \exp\{i[\mathbf{U}\cdot(\mathbf{R}+t) - \mathbf{V}\cdot(\mathbf{R}-\mathbf{s}) - \mathbf{P}\cdot(\mathbf{s}+t)]\} \,. \quad (19)$$

Combining this with the previous condition produces a somewhat more workable result. For any $A(\mathbf{R},\mathbf{P})$ corresponding to an operator $\hat{A}$ such that

$$\iint [A(\mathbf{R},\mathbf{P})]^2 \, d\mathbf{R} \, d\mathbf{P} = (2\pi)^3 C_A^2 \,, \quad (20)$$

and any $\tilde{W}(\mathbf{R},\mathbf{P})$ define

$$I[\tilde{W}, A] = (2\pi)^3 C_W \iint \tilde{W}(\mathbf{R},\mathbf{P}) W_{A^2}(\mathbf{R},\mathbf{P}) \, d\mathbf{R} \, d\mathbf{P} \quad (21)$$

where W_{A^2} corresponds to $\hat{A}^2$ according to Eq. (19). Then

- $\tilde{W}$ is an n-representable Wigner function if and only if $0 \le I[\tilde{W},A] \le 2t/n$ for all A satisfying Eq. (20).

Operators satisfying Eq. (20) are readily constructed, but since the condition must be satisfied for *all* such operators it is still not of practical utility. A useful way of directly constructing n-representable Wigner functions remains to be determined.

Single-determinant Wigner Functions

The product expression also leads to a phase–space form for the idempropor-tionality condition [Eq. (5)]. The phase space expression can be obtained in a straightforward way but it is lengthy and will not be reproduced here. A phase space function satisfying this condition is a Wigner function corresponding to an n-electron single determinant.

Conditions on Husimi Functions

The Husimi Function Corresponding to a Charge Density Matrix

The Husimi function is not useful for the calculation of expectation values but it has the advantage of being directly interpretable as a probability density. As we will see, n representability conditions for a Husimi function are also simpler in form than those for a Wigner function.

The key to defining a Husimi function is the introduction of a Gaussian wave-packet or coherent state [29]. Most of the literature relating to coherent states deals with abstract representations, and the specific coordinate-representation wave function is often not given. Functions that have been given are not always consistent with respect to the choice of a phase factor. This usually does not matter, but in some contexts it can. An important property of a coherent state in one dimension (sometimes taken as the definition) is

$$|z\rangle = e^{-1/2|z|^2} \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} |n\rangle \qquad (22)$$

where $|n\rangle$ is a harmonic oscillator eigenstate and z is a complex parameter whose real and imaginary parts give the phase space coordinates of the wavepacket center. If this equation is to hold in the coordinate representation with the standard phase convention for the oscillator functions, then the coherent state wave function is [30]

$$\phi(\sigma, q, k | x) = \left(\frac{\sigma^2}{\pi}\right)^{1/4} \exp\left[-\frac{\sigma^2}{2}(x - q)^2 + ikx - \frac{i}{2}kq\right], \qquad (23)$$

where $q = (\sqrt{2}/\sigma)\Re z$ and $k = \sqrt{2}\sigma\Im z$. The last term in the exponential is independent of x so it will cancel out of all expectation values or other expressions involving $\phi^*\phi$ or the equivalent. It is necessary for the following, however.

The Husimi function in one dimension can be defined by

$$\eta(\sigma | q, k) = \frac{1}{2\pi} \int\int \phi^*(\sigma, q, k | x) D(x; x')\phi(\sigma, q, k | x') \, dx' \, dx . \qquad (24)$$

The $1/2\pi$ factor is introduced so that $\int\int \eta dq \, dk = 2t$. A phase space representation of functions is also possible: if $\chi(x)$ is any quadratically-integrable function than [19,31]

$$f(q, k) = \int \phi^*(q, k | x)\chi(x) \, dx = b(z^*)e^{-1/2|z|^2} \qquad (25)$$

where $b(z)$ is an entire function (analytic throughout the finite complex plane) of $z^* = (\sigma q - ik/\sigma)/\sqrt{2}$. Bargmann has discussed the Hilbert space of such functions [31]. Let $\mathfrak{B}$ be the $\mathfrak{L}_2$ space of all entire functions $b(z)$ with respect to the norm

$$\|b\|^2 = \int |b(z)|^2 \, d\mu(z), \qquad d\mu(z) = \frac{1}{\pi} e^{-|z|^2} \, d^2z \qquad (26)$$

where $d^2z = d\Re z \, d\Im z \propto dq \, dk$. Then Eq. (25) defines a map from the Hilbert space $\mathfrak{H}$ of quadratically integrable functions $\chi(x)$ onto $\mathfrak{B}$. This map can be inverted by the use of Eq. (22) and the fact that the functions $z^n/\sqrt{n!}$ are orthonormal with respect to the measure $d\mu(z)$:

$$\chi(x) = \sum_n \int \frac{z^n}{\sqrt{n!}} b(z^*) \, d\mu(z)\langle x|n\rangle . \qquad (27)$$

These maps are unitary: the scalar product in one space is preserved by the transformation to the other space.

It can be shown that $\mathfrak{B}$ is a proper subspace of the Hilbert space $\mathfrak{H}_{qk}$ of all quadratically integrable functions of q and k. In addition, if $\{b_l(z)\}$ is an orthonormal set of functions in $\mathfrak{B}$ (linear independence would be sufficient, but orthonormality it convenient) then the set of all products $\{[b_l(z)]^*b_m(z)\}$ is linearly independent. Note that if $b_n(z)$ is an entire function of z then $[b_n(z)]^*$ is an entire function of z^*; if $b_n(z) = z^n/\sqrt{n!}$ or some other function involving only real coefficients, then $[b_n(z)]^* = b_n(z^*)$.

As a consequence of the linear independence of these products, the Husimi matrix [19] can be recovered from the Husimi function. This has been discussed in a formal sense by several authors [32,33]. A method involving a basis set will be presented below.

When is a Phase Space Function a Husimi Function?

We begin for convenience with the one-dimensional case. Extension to three dimensions is straightforward. Suppose that an orthonormal basis set $\{\chi_j\}$ has been introduced for $\mathfrak{H}$. Then Eq. (25) defines a corresponding orthonormal basis $\{b_j\}$ for $\mathfrak{B}$. If the density matrix is expressed as

$$D(x; x') = \sum_{l,m} D_{lm}\chi_l(x)\chi_m^*(x') \tag{28}$$

then the Husimi function corresponding to D is

$$\eta(\sigma|q,k) = \sum_{l,m} D_{lm}f_l(\sigma|q,k)f_m^*(\sigma|q,k)$$

$$= \sum_{l,m} D_{lm}b_l(z)[b_m(z)]^*e^{-|z|^2}. \tag{29}$$

Since Eq. (24) expresses the Husimi function at any phase space point q, k as the expectation value of the positive Hermitian operator $\hat{D}$, $\eta(\sigma|q,k)$ is necessarily real and positive everywhere.

Given a trial function $\tilde{\eta}(q,k)$ that is real and positive, we want to know if it can be obtained from a density matrix via Eq. (24). Note that $e^{-|z|^2} = e^{-\sigma^2q^2/2+k^2/2\sigma^2}$. Any $\tilde{\eta}$ that is in $\mathfrak{H}_{qk} = \mathfrak{H}_q \otimes \mathfrak{H}_k$ can be expressed as a linear combination of, for example, products of harmonic oscillator functions in q and k. This is equivalent via a nonsingular transformation to an expansion of the form given in Eq. (29). Since the products $b_l[b_m]^*$ are linearly independent, the expansion coefficients $\{D_{lm}\}$ can be recovered. It then follows that if these coefficients are treated as the elements of a matrix $\mathbf{D}$, $\tilde{\eta}$ will be an acceptable Husimi function if and only if $\mathbf{D}$ is positive. (A particular choice of normalization can be enforced by multiplying $\tilde{\eta}$ by a constant, if necessary.)

N-representable Husimi Functions

The generalization to n representable functions is in one sense trivial: We merely require that the expansion coefficients obtained via Eq. (29) define an n representable

D. An even simpler form is possible for a condition that is necessary and may be very nearly sufficient. Since the value of the Husimi function at any point is proportional to an expectation value of the charge density matrix,

- For a normalized function $\tilde{\eta}(\sigma|q,k)$ to be an n-representable Husimi function, it is necessary that $0 \leq \tilde{\eta}(\sigma|q,k) \leq 2t/n$ for all q and k.

The overcompleteness of the coherent states and their properties discussed above strongly suggest that this condition is also sufficient, apart possibly from a constraint on the asymptotic behavior [34].

Single Determinant Husimi Functions

For a trial Husimi function to correspond to an n-electron single determinant, it is necessary and sufficient that the expansion coefficients D_{lm} satisfy the idem-proportionality condition. While it is possible in principle to obtain an expression involving the proportionality of a Husimi function to an integral in which it appears twice, that expression would be extremely complicated and of doubtful utility.

Discussion

Quantum mechanical phase space functions provide a useful alternative representation of the information contained in a density matrix. In the case of the one-electron reduced density matrix or charge density matrix for the electrons in an atom or molecule, one does not expect behavior to be even approximately classical and much of what has been done with the Wigner and Husimi functions is not directly applicable. Nevertheless, these functions have proved to be useful in the investigation of electronic behavior. If one wishes to work with the charge density matrix directly, then n representability conditions must be imposed and the same is true if one wants to work directly with the Wigner or Husimi function.

The known conditions for a phase space function to be a Wigner function can be readily extended to include n representability constraints. Unfortunately, these conditions are of more formal than practical utility. There does not seem to be any way of recovering a matrix eigenvalue condition in the Wigner representation.

For the Husimi function, on the other hand, the special properties of coherent states and the representation they provide make it possible to recover the Husimi matrix from the Husimi function and thus to express conditions conveniently in terms of a matrix defined with respect to a phase space basis set. The existence of such basis sets has been established formally, but the choice of practical basis sets for molecular electronic structure investigations remains to be investigated.

Acknowledgment

Bibliography

[1] A. J. Coleman, Revs. Mod. Phys. **35**, 668 (1963).
[2] R. A. Donnelly and R. G. Parr, J. Chem. Phys. **69**, 4431 (1978).

[3] R. A. Donnelly, Int. J. Quantum Chem., Quantum Chem. Symp. **15**, 409 (1981).

[4] S. M. Valone, J. Chem. Phys. **73**, 1344 (1980).

[5] (a) A. Redondo, Phys. Rev. A **39**, 4366 (1989); (b) A. Redondo and J. C. Marshall, J. Chem. Phys. **91**, 5492 (1989); for appropriate references to earlier work, see (c) J. Cioslowski and M. Levy, Phys. Rev. A **40**, 6727 (1989) and (d) A. Redondo, Phys. Rev. A **40**, 6728 (1989).

[6] W. L. Clinton and L. J. Massa, Phys. Rev. Lett. **29**, 1363 (1972).

[7] C. Frishberg and L. J. Massa, (a) Phys. Rev. B **24**, 7018 (1981); (b) Int. J. Quant. Chem. **23**, 85 (1983).

[8] L. Cohen, C. Frishberg, C. Lee, and L. J. Massa, Int. J. Quantum Chem., Quantum Chem. Symp. **19**, 525 (1986).

[9] C. Frishberg, Int. J. Quant. Chem. **30**, 1 (1986).

[10] J. E. Harriman, Phys. Rev. A **27**, 632 (1983).

[11] J. E. Harriman, Phys. Rev. A **34**, 29 (1986).

[12] M. Levy and J. A. Goldstein, Phys. Rev. B **35**, 7887 (1987).

[13] E. Wigner, Phys. Rev. **40**, 749 (1932).

[14] J. P. Dahl, (a) Phys. Lett. **25**, 499 (1982); (b) C. R. Acad. Sc. Paris **114A**, 439 (1982).

[15] M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, Phys. Repts. **106**, 121 (1984).

[16] (a) J. P. Dahl and M. Springborg, Mol. Phys. **47**, 1001 (1982); (b) M. Springborg and J. P. Dahl, Phys. Rev. A **36**, 1050 (1987).

[17] K. Husimi, Proc. Phys.–Math. Soc. Japan **22**, 264 (1940).

[18] M. E. Casida, J. E. Harriman, and J. L. Anchell, Int. J. Quantum Chem., Quantum Chem. Symp. **21**, 435 (1987).

[19] J. E. Harriman, J. Chem. Phys. **88**, 6399 (1988).

[20] J. L. Anchell and J. E. Harriman (a) J. Chem. Phys. **89**, 6860 (1988); (b) J. Chem. Phys. **92**, 2943 (1990).

[21] P. A. M. Dirac, Proc. Camb. Phil. Soc. **27**, 240–243 (1931).

[22] R. McWeeny, (a) Proc. Roy. Soc. **A235**, 496 (1956); (b) Revs. Mod. Phys. **32**, 335 (1960).

[23] P. O. Lowdin, Phys. Rev. **97**, 1490 (1955).

[24] (a) J. E. Harriman, Phys. Rev. A **17**, 1249, 1257 (1978); (b) M. Casida and J. E. Harriman, Int. J. Quantum Chem. **30**, 161 (1986).

[25] F. J. Narcowich and R. F. O'Connell, Phys. Rev. A **34**, 1 (1986).

[26] D. Kastler, Commun. Math. Phys. **1**, 14 (1965).

[27] G. Loupias and S. Miracle–Sole, (a) Commun. Math. Phys. **2**, 31 (1966); (b) Ann. Inst. Henri Poincare **6**, 39 (1967).

[28] (a) J. C. Varilly and J. M. Gracia–Bondia, J. Math. Phys. **28**, 2390 (1987); (b) J. M. Gracia–Bondia and J. C. Varilly, J. Math. Phys. **29**, 869 (1988); (c) J. C. Varilly and J. M. Gracia–Bondia, J. Math. Phys. **29**, 880 (1988).

[29] R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

[30] V. Bargmann, P. Butera, L. Girardello, and J. R. Klauder, Repts. Math. Phys. **2**, 221 (1971).

[31] (a) V. Bargmann, Comm. Pure Appl. Math. **14**, 187 (1961); (b) Proc. NAS **48**, 199 (1962).

[32] S. Howard and S. K. Roy, Am. J. Phys. **55**, 1109 (1987).

[33] R. F. Bishop and A. Voudras, J. Phys. A: Math. & Gen. **20**, 3743 (1987).

[34] After this manuscript was accepted, Dr. M. E. Casida presented an argument showing this conjecture to be false.