

Wigner and Generalized Wigner Functions and their Connection to X-Ray Scattering

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É demonstrado que a função de Wigner, as densidades não diagonais de primeira ordem nos espaços da posição e do momento e a função A formam um conjunto completo com respeito a todas as transformadas de Fourier permitidas e possíveis. Todas as outras grandezas, geralmente consideradas como médias, podem ser obtidas destas quatro funções-chaves tomando-se o limite quando uma ou ambas variáveis vão a zero. São sugeridas generalizações da função de Wigner que relacionam o quadrado da função densidade de um elétron e a matriz densidade de segunda ordem com os espalhamentos elástico e total de raios X. Para o caso de funções de onda ou densidades que possuem um centro de simetria, também indicamos que a função A se torna uma função de Wigner, porém com os valores, tanto seu próprio como de suas duas variáveis independentes, todos reduzidos por um fator de dois.

The Wigner function, first order nondiagonal position and momentum space densities and the A function are shown to form a complete set with respect to all possible allowed Fourier transforms. All other quantities, usually considered as averages, can be obtained from these four key functions by taking the limit as one or both variables vanish. Generalizations of the Wigner function are suggested which relate the square of the one electron density and the diagonal second order density matrix to the elastic and total X-ray scattering. We also point out that in the case of wave functions or densities possessing a center of symmetry that the A function becomes a Wigner function with its value and the value of its two independent variables all reduced by a factor of two.

Key words: *Wigner functions, X-ray coherent scattering factor, X-ray incoherent scattering factor, Fourier transforms*

Introduction

Recent work on the Wigner function has shown that it provides a very sensitive means for analyzing molecular wave functions¹. This work complements earlier work on the wave function auto correlation function and its usefulness in analyzing wave functions². Recently Thakkar *et al* have published a comprehensive scheme for the connection of these functions and others by means of Fourier transformations and averages³. It is the purpose of this work to show that by use of a suitable set of Fourier transforms a set of functions may be defined that are closed with respect to all possible allowed Fourier transforms. In addition we explore generalizations of the Wig-

ner function which reduce as averages to functions that are directly measurable by means of X-ray scattering experiments.

Theory

We adopt the usual definition of the Wigner function⁴

$$W(\mathbf{P}, \mathbf{R}) = [1/(2\pi)^3] \int dx e^{i\mathbf{P}\cdot\mathbf{x}} \varrho(\mathbf{R}-\mathbf{x}/2, \mathbf{R}+\mathbf{x}/2) \quad (1)$$

where ϱ is a nondiagonal first order (single particle) density. We define the set of allowed Fourier transforms (superscript +) and their inverses (superscript -) as

$$\begin{aligned} \mathbf{T}^+(\mathbf{K}) &= [1/(2\pi)^3] \int d\mathbf{R} e^{i\mathbf{K}\cdot\mathbf{R}} \\ \mathbf{T}^-(\mathbf{R}) &= \int d\mathbf{K} e^{-i\mathbf{K}\cdot\mathbf{R}} \\ \mathbf{T}^+(\mathbf{P}) &= [1/(2\pi)^3] \int d\mathbf{S} e^{i\mathbf{P}\cdot\mathbf{S}} \\ \mathbf{T}^-(\mathbf{S}) &= \int d\mathbf{P} e^{-i\mathbf{P}\cdot\mathbf{S}} \end{aligned} \quad (2)$$

which are the proper ones for a density function with the property $\varrho(\mathbf{r}_1, \mathbf{r}_2)^* = \varrho(\mathbf{r}_2, \mathbf{r}_1)$ where the star denotes complex conjugation.

Application of the transforms defined in Eq. 2 to the definition of the Wigner function given in Eq. 1 generates the inner square of four functions shown in Fig. 1 where Π is the nondiagonal single particle momentum density and the function A is defined as

$$\mathbf{A}(\mathbf{K}, \mathbf{S}) = [1/(2\pi)^3] \int d\mathbf{u} e^{i\mathbf{K}\cdot\mathbf{u}} \varrho(\mathbf{u}-\mathbf{S}/2, \mathbf{u}+\mathbf{S}/2) \quad (3)$$

Inspection of Fig. 1 shows that the set of four functions (W, ϱ , Π , A) is closed with respect to all possible combinations of allowed Fourier transforms. Of course all operations where the function does not contain the variable of integration of the transform in question must be excluded from the allowed set. Further, by taking appropriate limits of the functions as one or both the variables are allowed to vanish produces all possible functions as displayed in the outer square in Fig. 1. Note that this is an alternative way to consider what most authors take as averages since the limit as the dummy variable in a Fourier transform approaches zero reduces to an average.

In Fig. 1 it should be noted that the outer square of functions contains the familiar wave function autocorrelation function, B(S), charge density, $\varrho(\mathbf{R})$, momentum density, $\Pi(\mathbf{p})$, and X-ray coherent scattering factor, F(K). A number of these limit functions are also related by Fourier transform as indicated by the solid lines in Fig. 1. Note that it is not possible to uniquely go from the outer square to the inner square in Fig. 1 by any mathematical operation. Nor is it possible to turn a corner in the outer square in either direction.

While in general the A function is not the same as a Wigner function, an interesting connection exists when the density exhibits inversion symmetry in the first variable. Suppose $\varrho(-\mathbf{r}_1, \mathbf{r}_2) = \varrho(\mathbf{r}_1, \mathbf{r}_2)$ then

$$\mathbf{A}(\mathbf{K}, \mathbf{S}) = (1/2) \mathbf{W}(\mathbf{K}/2, \mathbf{S}/2) \quad (4)$$

which is a Wigner function of reduced scale. In addition the limit functions associated with the Wigner function become the same as those associated with the A function, but with expanded scale as for example

$$\lim_{|\mathbf{R}| \rightarrow 0} \mathbf{W}(\mathbf{P}, \mathbf{R}) = [2/(2\pi)^3] \mathbf{F}(2\mathbf{P}) \quad (5)$$

Because none of the functions in Fig. 1 are directly measurable with the possible exception of F(K) it is of some interest to consider possible extensions of the definition of a Wigner function more directly connected to experimental measurement. One approach is to define what we chose to call a modified Wigner function of order one, $\omega_1(\mathbf{P}, \mathbf{R})$, as

$$\omega_1(\mathbf{P}, \mathbf{R}) = [1/(2\pi)^3] \int d\mathbf{x} e^{i\mathbf{P}\cdot\mathbf{x}} \varrho(\mathbf{R}-\mathbf{x}/2)^* \varrho(\mathbf{R}+\mathbf{x}/2) \quad (6)$$

where $\varrho(\mathbf{r})$ is the diagonal single particle density. The corresponding relations to those of Fig. 1 are shown in Fig. 2. Obviously $[\varrho(\mathbf{r}_1) \varrho(\mathbf{r}_2)]^* = \varrho(\mathbf{r}_2) \varrho(\mathbf{r}_1)$ since ϱ can always be taken as real. With this choice $\Pi(\mathbf{P}, \mathbf{P})$ becomes⁵ $|\mathbf{F}(\mathbf{P})|^2/(2\pi)^6$, which is proportional to the experimentally accessible elastic scattering from an oriented molecule or atom; B(S) becomes the well known Patterson function of X-ray crystallography⁶ which we call the classical electron pair correlation function, $\mathbf{P}(\mathbf{r}_{12})^{\text{cl}}$, and the normalization N is replaced by the average density⁷, $\langle \varrho \rangle$.

It is well known that the diagonal second order density, ϱ_2 , possesses the property that $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)^* = \varrho_2(\mathbf{r}_2, \mathbf{r}_1)$ which means that a second modified Wigner function of the form

$$\omega_2(\mathbf{P}, \mathbf{R}) = [1/2\pi)^3] \int d\mathbf{x} e^{i\mathbf{P}\cdot\mathbf{x}} \varrho_2(\mathbf{R}-\mathbf{x}/2, \mathbf{R}+\mathbf{x}/2) \quad (7)$$

can be defined. The form of Fig. 1 is reproduced in Fig. 3 for this choice where $\Pi_2(\mathbf{P}, \mathbf{P})$ is proportional to the total, elastic plus inelastic, X-ray scattering for a molecule or atom oriented in space⁵; and the B(S) function in Fig. 1 becomes the electron pair correlation function⁵ in Fig. 3 and is given as

$$\mathbf{P}(\mathbf{r}_{12}) = \int d\mathbf{R} \varrho_2(\mathbf{R}-\mathbf{r}_{12}/2, \mathbf{R}+\mathbf{r}_{12}/2) \quad (8)$$

Conclusion

The usefulness of the proposed functions (ω_1 , ω_2) and their corresponding A function analogs (α_1 , α_2)

$$\alpha_1(\mathbf{K}, \mathbf{S}) = [1/(2\pi)^3] \int d\mathbf{u} e^{i\mathbf{K}\cdot\mathbf{u}} \varrho(\mathbf{u}-\mathbf{S}/2) \varrho(\mathbf{u}+\mathbf{S}/2) \quad (9)$$

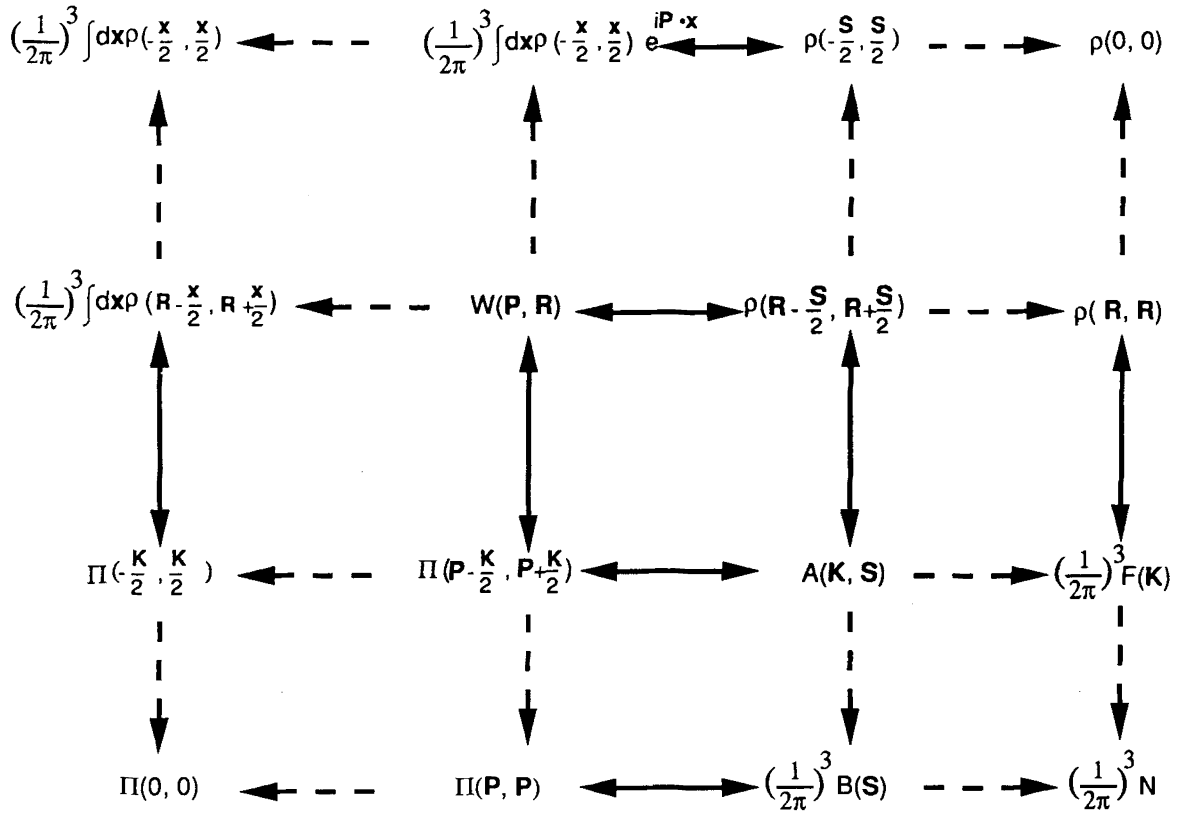
and

$$\alpha_2(\mathbf{K}, \mathbf{S}) = [1/(2\pi)^3] \int d\mathbf{u} e^{i\mathbf{K}\cdot\mathbf{u}} \varrho_2(\mathbf{u}-\mathbf{S}/2, \mathbf{u}+\mathbf{S}/2) \quad (10)$$

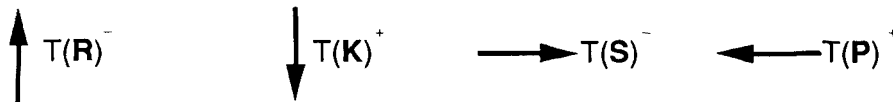
remains to be seen. The hope is that if they prove to be as sensitive to the details of molecular or atomic wave functions as the W and B functions have already been shown to be then they could play a useful role in experimental design since there is a direct unique path between these functions and the quantities actually observed in an experiment. For the case of atomic hydrogen where the one electron density and wave function have the same analytic form we can expect the sensitivity of ω_1 to be similar to that of W. This will not necessarily be true for more complex systems. The task of exploring the sensitivity of the new functions to the details of the actual wave functions is left as a task for the future.

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Fourier Transforms:



Limits as one of the variables vanishes:

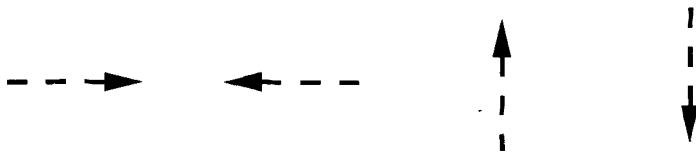
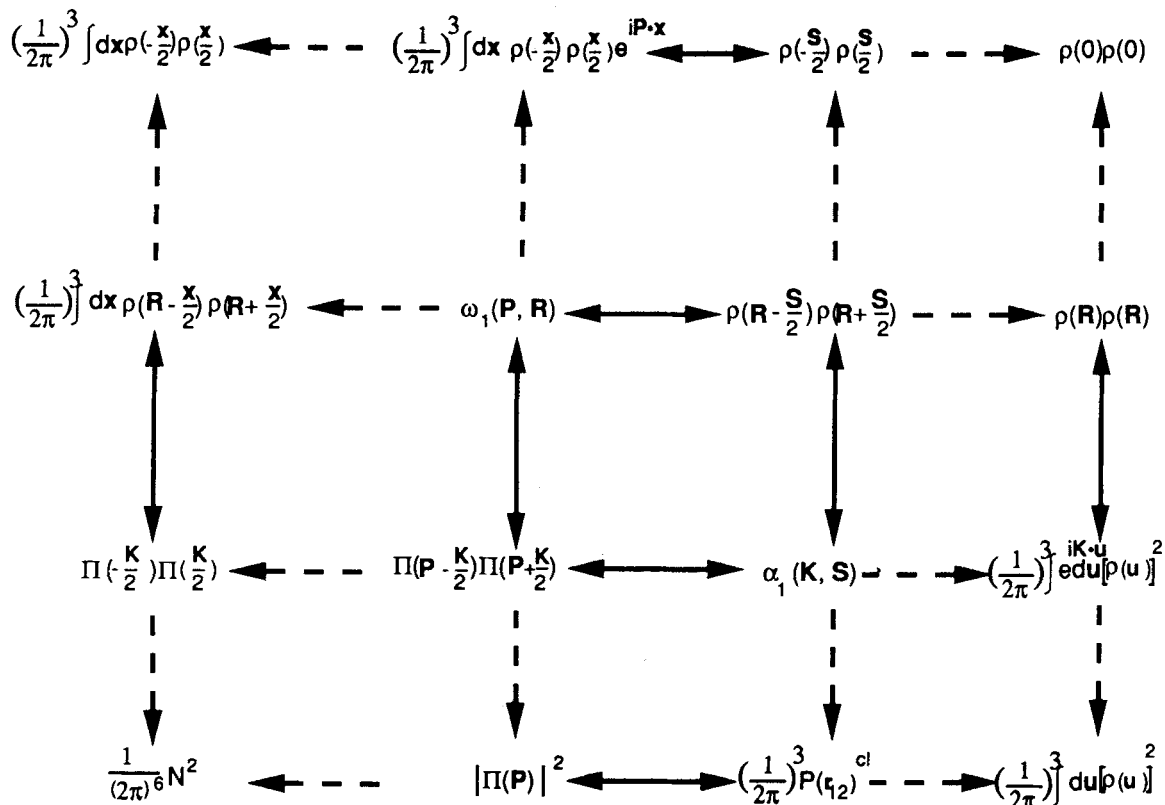


Figure 1. The relationship between Wigner functions, the A function and various density functions where

$B(S) = \int dx \rho(x-S, x)$, $F(K) = \int du e^{iK \cdot u} \rho(u, u)$, $\Pi(P, P')$ is the first order non diagonal momentum density and $\int du \rho(u, u) = N$, the number of electrons in the system. The solid lines indicate that Fourier transformations can be made in either direction. The dotted lines indicate a result obtained by taking the limit as one of the variables vanish.

The direction of the limit process is indicated by the arrows. The direction of the arrows at the ends of the solid lines indicates the transforms T as shown at the bottom of the figure. Note that all diagonal transforms are possible within the inner square. For example the transform $T(R) \rightarrow T(S)$ takes $\Pi(P-K/2, P+K/2)$ into $\rho(R-S/2, R+S/2)$. The functions on the inner square can be transformed into the nearest corner function on the outer square by taking the limit as both variables tend to zero. All dotted line limit paths represent irreversible transformations in the sense that a unique inverse does not exist.



Fourier Transforms:



Limits as one of the variables vanishes:

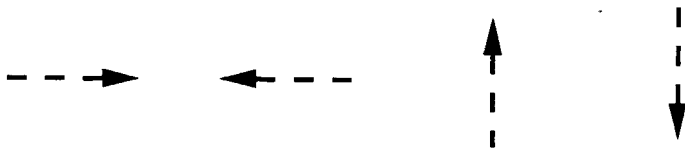
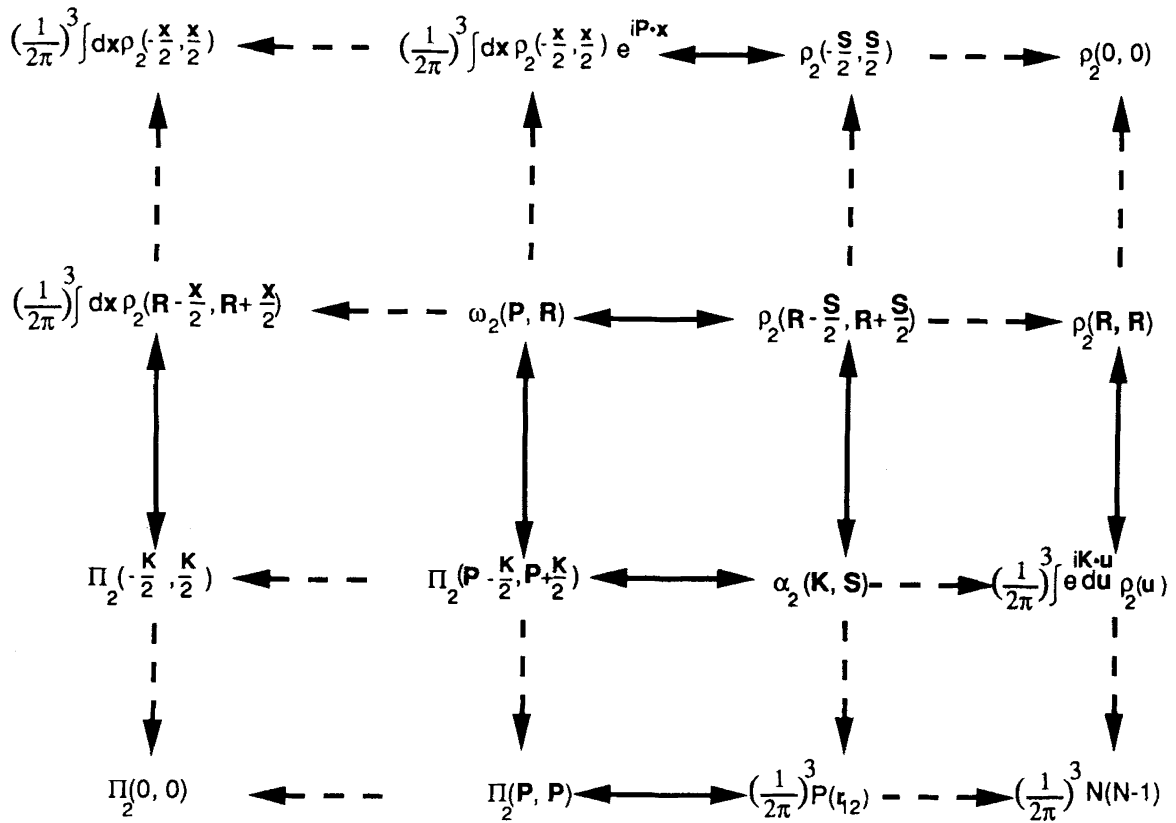
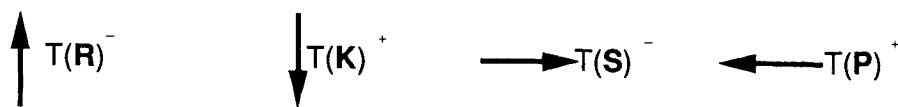


Figure 2. The relationship between the modified Wigner function $\omega_1(\mathbf{P}, \mathbf{R})$, the $\alpha_1(\mathbf{K}, \mathbf{S})$ function and various density functions where

$P(\tau_{12})^{cl} = [1/(2\pi)^3] \int du \varrho(\mathbf{u}-\mathbf{S}/2)^* \varrho(\mathbf{u}+\mathbf{S}/2)$, $F(\mathbf{P}) = \int du e^{i\mathbf{P}\cdot\mathbf{u}} \varrho(\mathbf{u})$ and $|\Pi(\mathbf{P})|^2 = (1/2\pi)^6 |F(\mathbf{P})|^2$ which is the elastically scattered X-ray intensity for a molecule in a rigid orientation in space. See the legend to Fig. 1 and the text for an explanation of the remaining symbols



Fourier Transforms:



Limits as one of the variables vanishes:

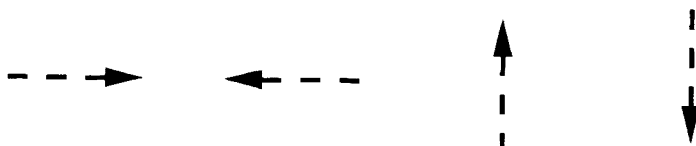


Figure 3. The relationship between the modified Wigner function $\omega_2(\mathbf{P}, \mathbf{R})$, the $\alpha_2(\mathbf{K}, \mathbf{S})$ function and various density functions where $P(r_{12}) = \int du \rho_2(u - S/2; u + S/2)$ and $\Pi_2(\mathbf{P}; \mathbf{P}) = [1/(2\pi)^6] \int dr_{12} e^{iP \cdot r_{12}} P(r_{12})$ which is proportional to the total (elastic plus inelastic) scattered X-ray intensity for a molecule in a rigid orientation in space. See the legend to Fig. 1 and the text for explanation of the remaining symbols.

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