

## A Trial Generator Function Common for Charge and Momentum Density Distributions in Valence Electron System in Solid

Teiji KOBAYASI

General Education, College of Medical Sciences, Tohoku University

### 固体価電子系の電荷密度および運動量密度分布関数 に対する共通母関数誘導の試み

小林 悌二

東北大学医療技術短期大学部 総合教育

Key words : Charge density distribution, Momentum density distribution, Generator function, Valence electron system

In a valence electron system of solid, the density distribution functions of electron charge and electron momentum are the functions described in terms of the electron wave functions in the real and the momentum spaces, respectively. The former density  $n(\mathbf{r})$  is a local function of the electron coordinate variable  $\mathbf{r}$  and the latter density  $\rho(\mathbf{q})$  is one of the local momentum variable  $\mathbf{q}$ . While the two kinds of wave functions are connected with each other through the Fourier transformation mathematically, there is no mathematical operation to transform the one of the distribution functions to the other directly.

In this note, by using the fact that the function  $\rho(\mathbf{q})$  can be Fourier-transformed into a form of autocorrelative function composed of nonlocal terms of the electron wave function with respect to the variable  $\mathbf{r}$ , a trial generating relation is proposed for connecting the two kinds of density distribution function. The generator function is a very simple and formal one, but gives a step in fair prospects for mathematical structure between the two different kinds of density distribution function in a unified framework.

In a valence electron system of crystalline solid, the electron charge density distribution function  $n(\mathbf{r})$  in the real  $\mathbf{r}$ -space is given, under abbreviation of the elementary charge  $e$ , by

$$n(\mathbf{r}) = 2 \sum_n \sum_{\mathbf{k}} |\Psi_{n\mathbf{k}}(\mathbf{r})|^2, \quad (1)$$

where  $\Psi_{n\mathbf{k}}(\mathbf{r})$  is a Bloch wave function of an electron with wave vector  $\mathbf{k}$  in the  $n$ th energy band and the summations on  $n$  and  $\mathbf{k}$  should be taken over all occupied electronic states. Here the solid is supposed to be nonmagnetic, so that the spin state summation gives only the factor 2 in eq. (1).

On the other hand, since the momentum density distribution function  $\rho(\mathbf{q})$  for the

---

Address: 2-1 Seiryō-machi, Aoba-ku, Sendai 980-8575, Japan  
e-mail: kobayasi@cms42.cms.tohoku.ac.jp

valence electron system is the electron density in the momentum  $\mathbf{q}$ -space described by the Fourier-transformed wave function

$$\Psi_{nk}(\mathbf{q}) = \int \Psi_{nk}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r / \sqrt{\Omega}, \quad (2)$$

it is given by

$$\rho(\mathbf{q}) = 2 \sum_n \sum_k |\Psi_{nk}(\mathbf{q})|^2 = 2 \sum_n \sum_k \left| \int \Psi_{nk}(\mathbf{r}) \times \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r / \sqrt{\Omega} \right|^2, \quad (3)$$

where  $\Omega$  is the crystal volume of the solid and the Planck constant  $\hbar$  is abbreviated.

The electrons distribute in the crystal according to the electronic potential field and distribute in the momentum space according to their energy dispersion structure. Under the framework of pseudopotential theory, these distributions are previously calculated in detail for some semiconductors with the diamond and the zincblende structure and visualized on contour maps in the (110) plane. Examples of the results for  $n(\mathbf{r})$  are given in ref. 1 for elemental semiconductors Si and Ge<sup>1)</sup>, and for  $\rho(\mathbf{q})$  in refs. 2~4 for Si, Ge and compound semiconductors GaAs and ZnSe<sup>2~4)</sup>. The two kinds of distribution are consistent with each other, but the relation is implicit in a very complicated way. The two kinds of distribution cannot be simply transformed to each other. There is no mathematical transforming operator between them.

In this note, a preliminary step will be introduced to relate  $n(\mathbf{r})$  to  $\rho(\mathbf{q})$  mathematically. The relation is given by an intermediary function and is not an operational one.

Fourier inverse transform of  $\rho(\mathbf{q})$  defines an  $\mathbf{r}$ -space function  $B(\mathbf{r})$  as

$$B(\mathbf{r}) = \sum_{\mathbf{q}} \rho(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) / \Omega. \quad (4)$$

The function  $\rho(\mathbf{q})$  is connected inversely with  $B(\mathbf{r})$  by

$$\rho(\mathbf{q}) = \int B(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r. \quad (5)$$

Substituting eq. (3) to eq. (4), one is led to the following autocorrelative expression, equivalently to the Wiener-Khinchin theorem<sup>5)</sup>;

$$B(\mathbf{r}) = 2 \sum_n \sum_k \int \Psi_{nk}^*(\mathbf{r}') \Psi_{nk}(\mathbf{r}' + \mathbf{r}) d^3r' / \Omega. \quad (6)$$

The function is often called as the Compton scattering  $B(\mathbf{r})$  function because of a direct relation to the Compton profile function<sup>6)</sup>. A key point in relating the two kinds of distribution is to generalize eq. (6) as an intermediary function. The  $B(\mathbf{r})$  at  $\mathbf{r}=0$  gives in fact the mean value of valence electron density:

$$\begin{aligned} B(0) &= 2 \sum_n \sum_k \int \Psi_{nk}^*(\mathbf{r}') \Psi_{nk}(\mathbf{r}') d^3r' / \Omega \\ &= \int n(\mathbf{r}') d^3r' / \Omega. \end{aligned} \quad (7)$$

Generalizing eq. (6), let us define a function  $G(\mathbf{r}, \mathbf{q})$  as follows;

$$\begin{aligned} G(\mathbf{r}, \mathbf{q}) &= 2 \sum_n \sum_k \int \Psi_{nk}^*(\mathbf{r}') \Psi_{nk}(\mathbf{r}' + \mathbf{r}) \\ &\quad \times \exp[-i\mathbf{q} \cdot (\mathbf{r}' + \mathbf{r})] d^3r' / \Omega. \end{aligned} \quad (8)$$

One obtains

$$\lim_{\mathbf{q} \rightarrow 0} G(\mathbf{r}, \mathbf{q}) = B(\mathbf{r}) \quad (9)$$

and

$$\lim_{\mathbf{r} \rightarrow 0} G(\mathbf{r}, \mathbf{q}) = n(\mathbf{q}) / \Omega. \quad (10)$$

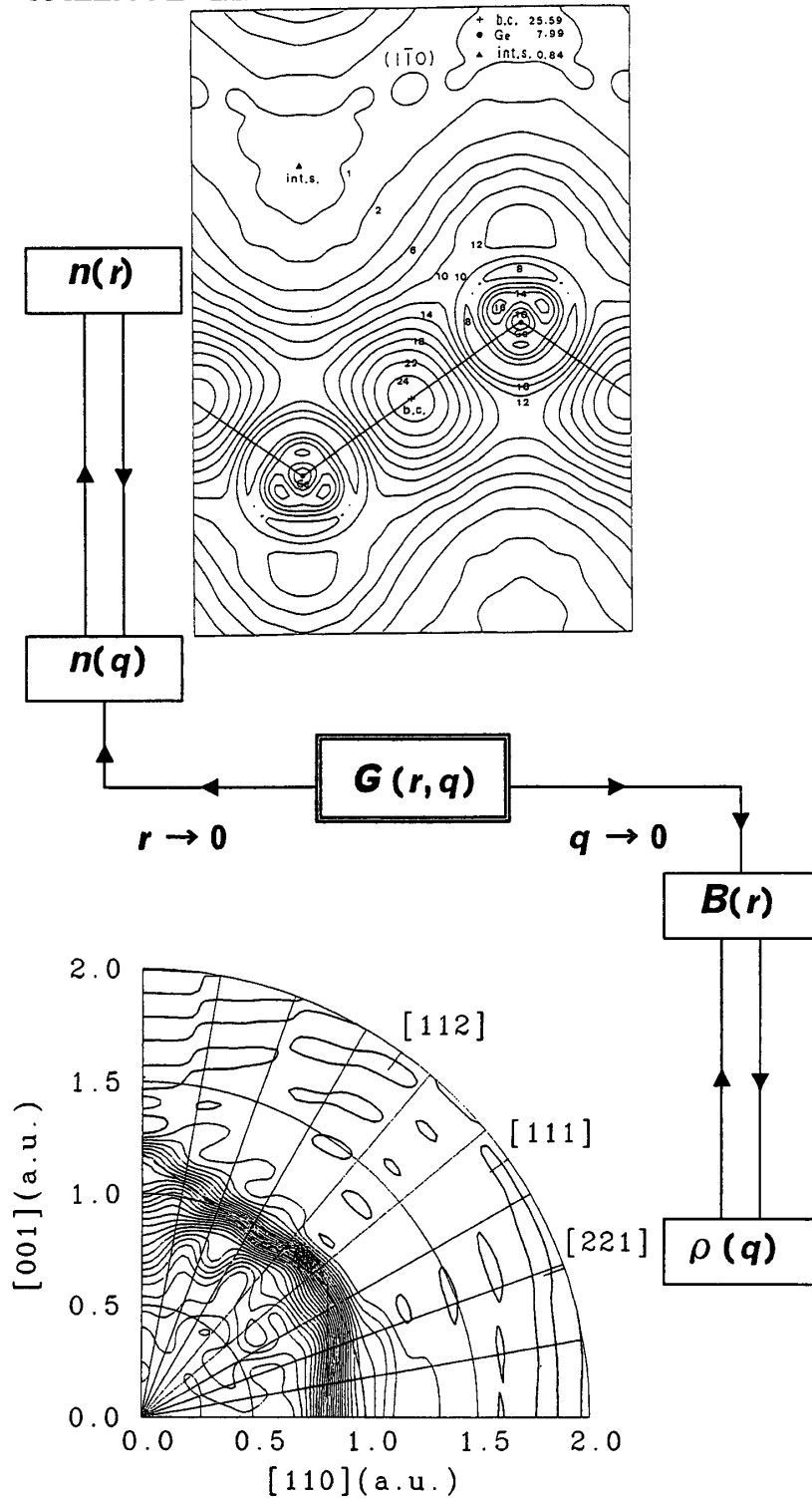
Here,  $n(\mathbf{q})$  is Fourier transform of  $n(\mathbf{r})$  defined by

$$n(\mathbf{q}) = \int n(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r, \quad (11)$$

as in the same form defining  $\rho(\mathbf{q})$  in eq. (5). As shown in eqs. (9) and (10), the generalization leading to  $G(\mathbf{r}, \mathbf{q})$  is the simplest one which can reproduce  $n(\mathbf{q})$  and  $B(\mathbf{r})$  under the same symmetrical operations  $\mathbf{r} \rightarrow 0$  and  $\mathbf{q} \rightarrow 0$ .

Equations (9) and (10) show that the

**VALENCE ELECTRON CHARGE DENSITY Ge**



**VALENCE ELECTRON MOMENTUM DENSITY Ge**

**Fig. 1.** Relations between  $G(r, q)$  and the charge density distribution function  $n(r)$  and between  $G(r, q)$  and the momentum density distribution function  $\rho(q)$ . Details of the contour maps are described in refs. 1 and 2.

$B(\mathbf{r})$  and the  $n(\mathbf{q})$  functions are indirectly connected with each other through the common function  $G(\mathbf{r}, \mathbf{q})$ . The  $\mathbf{q}$ -space density distribution  $\rho(\mathbf{q})$  is connected with  $B(\mathbf{r})$  through eq. (4) and the  $\mathbf{r}$ -space charge density distribution  $n(\mathbf{r})$  is connected with  $n(\mathbf{q})$  through

$$n(\mathbf{r}) = \sum_{\mathbf{q}} n(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) / \Omega. \quad (12)$$

This fact shows that the charge and momentum density distributions are connected with each other through the common intermediary function  $G(\mathbf{r}, \mathbf{q})$ . In this meaning, the function  $G(\mathbf{r}, \mathbf{q})$  can be regarded as a generator function formally for the two kinds of density distributions. Figure 1 shows these relations schematically with the charge and the momentum density distributions for Ge quoted from ref. 1 and ref. 2, respectively. Details of the calculation based on the pseudopotential theory and quantitative discussions for these contour-mapped distributions in the (110) plane are given in these references.

In a pseudopotential energy band approach, the function  $G(\mathbf{r}, \mathbf{q})$  is given by

$$G(\mathbf{r}, \mathbf{q}) = 2 \sum_n \sum_{\mathbf{k}} \sum_{\mathbf{G}} C_{n\mathbf{k}}^*(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G} + \mathbf{q}) \times \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] / \Omega \quad (13)$$

under the plane wave expansion of the wave function ;

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] / \sqrt{\Omega}, \quad (14)$$

where  $\mathbf{G}$ 's are the reciprocal lattice vectors corresponding to the crystal symmetry. In a crystal with pure periodic structure, the coefficients  $C_{n\mathbf{k}}(\mathbf{p})$  is generally nonzero only for  $\mathbf{p}$  being reciprocal lattice vector. Under the form of  $G(\mathbf{r}, \mathbf{q})$  in eq. (13), therefore, one express that only the terms of diagonal coupling  $C_{n\mathbf{k}}^*(\mathbf{G}) - C_{n\mathbf{k}}(\mathbf{G})$  contribute to the charge density distribution and the terms of off-diagonal

coupling  $C_{n\mathbf{k}}^*(\mathbf{G}) - C_{n\mathbf{k}}(\mathbf{G} + \mathbf{q})$  with reciprocal lattice vector  $\mathbf{q}$  yield  $B(\mathbf{r})$  and then contribute to the momentum density distribution.

As can be seen in eqs. (1) and (6), with respect to the real space variable  $\mathbf{r}$ , the function  $n(\mathbf{r})$  has the local or diagonal form of electron wave functions. On the other hand, the function  $B(\mathbf{r})$  is formed from the nonlocal or nondiagonal terms of the electron wave functions. This fact is one of reasons why the two functions cannot be transformed to each other by a simple mathematical operation. One will notice that, in Fig. 1, there exist no arrows with direction from  $n(\mathbf{q})$  to  $G(\mathbf{r}, \mathbf{q})$  and from  $B(\mathbf{r})$  to  $G(\mathbf{r}, \mathbf{q})$ . The interrelation between  $n(\mathbf{r})$  and  $\rho(\mathbf{q})$  given through the generator  $G(\mathbf{r}, \mathbf{q})$  is a very simple and formal one, but the generator will provides us with a step in fair prospects for mathematical structure between the two different kinds of density distribution function in a unified framework. If one can find a more fundamental function which leads to  $G(\mathbf{r}, \mathbf{q})$  itself or an equation satisfying by  $G(\mathbf{r}, \mathbf{q})$ , it will provide us with a new problem with a quantum mechanical interest.

## References

- 1) Kobayasi, T., Nara, H.: Core-Orthogonalization Effect in Pseudopotential Theory of the Charge Density Distribution of Valence Electrons in Semiconductors with Comments on the Effects in Momentum Space, *Z. Naturforsch.*, **48a**, 193-197, 1993
- 2) Kobayasi, T., Nara, H., Timms, T.D., Cooper, M.J.: Core-Orthogonalization Effects on the Momentum Density Distribution and the Compton Profile of Valence Electrons in Semiconductors, *Bull. Coll. Med. Sci. Tohoku Univ.*, **4(2)**, 93-104, 1995
- 3) Kobayasi, T.: Core-Orthogonalization Effect

A Common Generator for Charge and Momentum Density Distribution Functions

- on the Compton Profiles of Valence Electrons in Si, Bull. Coll. Med. Sci. Tohoku Univ., **5**(2), 149-164, 1996
- 4) Kobayasi, T. : Effect of Change in Character of Valence Electron Bond on Momentum Density Distribution in the Series of Ge-GaAs-ZnSe, Bull. Coll. Med. Sci. Tohoku Univ., **7**(1), 21-28, 1998
- 5) González-Velasco, E.A. : Chap. 7 Fourier Transforms § 7.4 Convolution *in* Fourier Analysis and Boundary Value Problems, Academic Press, New York, 1995, pp. 248-252
- 6) Kobayasi, T. : Coupling of Positron Annihilation and Compton Scattering: A Theoretical Possibility to Analyze Positron Distribution through Atom-like Local Patterns Appearing in Positron Annihilation  $A(\mathbf{r})$ - and Compton Scattering  $B(\mathbf{r})$ -Functions *in* Positron Annihilation ICPA-12 (edt. W. Triftshäuser, G. Kögel and P. Sperr, Trans Tech Publ., Switzerland): Materials Science Forum, Vols. **363-365**, 689-691, 2001