Study of Valence Electronic Bond Character through Kinematical Structure Parameters in Compton Scattering $\beta$-Function of Semiconductors

KOBAYASHI Teiji

Bulletin of College of Medical Sciences, Tohoku University

Volume 11, Number 1, Page 37-44, 2002-02-28

URL: http://hdl.handle.net/10097/33779
Study of Valence Electronic Bond Character through Kinematical Structure Parameters in Compton Scattering $B(r)$-Function of Semiconductors

Teiji KOBAYASI

General Education, College of Medical Sciences, Tohoku University

コンプトン散乱 $B(r)$ 関数中の運動学的構造
パラメタによる半導体価電子結合性の研究

小林 悟二
東北大学医療技術短期大学部 総合教育

Key words: Kinematical structure, Compton scattering $B(r)$ function, Electronic bond character, Semiconductor

A real space $B(r)$ function of valence electron system in semiconductor is a function defined by the Fourier inversion transform of the valence electron momentum density distribution $\rho(q)$, which is a quantity having direct connection with the Compton profile $J(q_z)$. The $B(r)$ function can be described in terms of an autocorrelation function among the valence electron wave functions.

By applying the Taylor-Maclaurin expansion method to the autocorrelation expression of the $B(r)$ function, it has been shown that the fundamental kinematical structure parameters of the electron system such as electron density, total momentum, total kinetic energy, etc. can be related systematically to the expansion coefficients. Using this fact, a possibility to discuss valence electronic bond character through a particularly sensitive relation between the kinetic energy density parameter in $B(r)$ function and degree of locality in electron distribution has been studied under an example of semiconductor series of Ge, GaAs and ZnSe.

§ 1 Introduction

Compton scattering process provides us with a very useful physical information of electronic states in solids. For example, Compton profile $J(q_z)$ is a primarily fundamental source for electron distribution in momentum space:

$$J(q_z) = (1/2\pi)^2 \int_{-\infty}^{\infty} dq_x \int_{-\infty}^{\infty} dq_y \rho(q_x, q_y, q_z),$$

(1)

where $q_z$ is the component of the electron momentum $q$ along the observational direction $z$. The momentum density distribution function $\rho(q)$ can be reconstructed by using a set of $J(q_z)$'s obtained in various directions. It will
be compared with a theoretical \( \rho(\mathbf{q}) \). For the valence electron system in single crystalline semiconductor, an energy band theory gives \( \rho(\mathbf{q}) \) as

\[
\rho(\mathbf{q}) = 2 \sum_{n} \sum_{k} \left| \Psi_{nk}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) \right| d^3r / \sqrt{\Omega},
\]

(2)

where \( \Psi_{nk}(\mathbf{r}) \) is the wave function of an electron with wave vector \( \mathbf{k} \) in the \( n \)th energy band and the summations on \( n \) and \( k \) should be taken over all occupied valence electronic states and \( \Omega \) is the crystal volume. In eq.(2) the electron spin states are supposed to be degenerate.

A real space function \( B(\mathbf{r}) \) is defined by the Fourier inversion transform of \( \rho(\mathbf{q}) \);

\[
B(\mathbf{r}) = \sum_{q} \rho(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) / \Omega.
\]

(3)

There is an excellent convenience that an explicit appearance of the momentum-conserving delta function can be avoided in \( B(\mathbf{r}) \) itself and then in \( f(\mathbf{q}) \) or \( \rho(\mathbf{q}) \) expressions derived using the \( B(\mathbf{r}) \) function. With no requiring a very fine mesh points of wave vector in the Brillouin zone, one can attain a high resolution calculation of these functions.

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

\[
B(\mathbf{r}) = 2/\Omega \sum_{n} \sum_{k} C_{nk}(\mathbf{G})^2 \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}],
\]

(4)

under the plane wave expansion of the electron wave function;

\[
\Psi_{nk}(\mathbf{r}) = \sum_{G} C_{nk}(\mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] / \sqrt{\Omega}.
\]

(5)

On the other hand, as pointed out previously\(^1\), the \( B(\mathbf{r}) \) function is an interesting physical quantity reflecting electronic bond character of the system on itself. For the semiconductor series of Ge, GaAs and ZnSe belonging to the common fourth row group in the periodic table, a systematic linear change of various structural parameters in \( B(\mathbf{r}) \) function are observed reflecting the change in valence electronic bond character which is purely covalent in Ge and increases ionic component toward ZnSe. The other interesting property is that\(^2\) an atom-like local pattern appears in anisotropic part of the \( B(\mathbf{r}) \) contour map. The pattern can be analysed to be an image of intra-unit-cell atom arising from the orthogonality between valence and core electron states. The origin of this "Compton microscope effect" was understood using an autocorrelative form of the \( B(\mathbf{r}) \) function\(^3--^5\):

\[
B(\mathbf{r}) = 2 \sum_{n} \sum_{k} \int \Psi_{nk}(\mathbf{r}') \Psi_{nk}(\mathbf{r} + \mathbf{r}') d^3r' / \Omega,
\]

(6)

which is mathematically equivalent to eq.(3).

The purpose of this paper is to make a complementary discussion on sensitivity of the \( B(\mathbf{r}) \) structure to kinematical property of the electron system and to point out a possibility of higher order differential structure of the \( B(\mathbf{r}) \) function to probe for electronic bond character through a kinematical parameter closely related to degree of locality in electron distribution. It will be shown that the second order differential structure of the \( B(\mathbf{r}) \) function being connected with kinetic energy density is particularly sensitive probe for discussing the covalent-ionic character of typical series of semiconductors.

Method of systematic extraction of kinematical parameters from the \( B(\mathbf{r}) \) function is described in § 2. Reflection of electronic bond character on the kinematical parameters is discussed in § 3.

§ 2 Physical Meaning of Terms in Taylor-Maclaurin-expanded \( B(\mathbf{r}) \) Function

By applying the method of Taylor-Maclaurin expansion to eq.(6) around \( r = 0 \), one
obtains
\[
B(r) = 2 \sum_{n, k} \int \Psi_{nk}^*(r') \Psi_{nk}(r') d^3r' / |\Omega|
+ 2 \sum_{n, k} \int \Psi_{nk}^*(r') \cdot \nabla_r \Psi_{nk}(r') d^3r' / |\Omega|
+ 2 \sum_{n, k} \int \Psi_{nk}^*(r') \cdot \frac{1}{2} \left[ (r' \cdot \nabla r')^2 - r' \cdot \nabla r' \right] \Psi_{nk}(r') d^3r' / |\Omega|
+ \cdots.
\]
(7)

An equivalent form with no explicit inclusion of wave functions is simply given from eq.(3) as
\[
B(r) = \int \rho(q) d^3q / |\Omega| + \int r' \cdot q \rho(q) d^3q / |\Omega|
+ \frac{1}{2} \left[ r' \cdot q \right]^2 \rho(q) d^3q / |\Omega| + \cdots.
\]
(8)
The first term in the right hand side of eq.(7) or eq.(8) is the uniform density of valence electrons, \( \bar{n} \), namely,
\[
\text{leading term of } B(r) = B(0) = \bar{n}.
\]
(9)

For Ge crystal with diamond structure and for GaAs and ZnSe crystals with zincblende structure, \( \bar{n} = \Omega_n / \Omega \), where \( \Omega_n \) is the crystal volume per constituting atom. From eq.(7) one obtains the leading term of the first order derivative of \( B(r) \) as
\[
\text{leading term of } \nabla_r B(r) = \int \Psi_{nk}^*(r') \nabla_r \Psi_{nk}(r') d^3r' / |\Omega|.
\]
(10)

Equation (10) means that the first derivative of \( B(r) \) at \( r = 0 \) corresponds to an averaged spatial density of momentum distribution in the electron system;
\[
\lim_{r \to 0} \nabla_r B(r) = \frac{i}{\hbar} \cdot \sum_{n, k} \int \Psi_{nk}^*(r') \mathbf{p} \Psi_{nk}(r') d^3r' / |\Omega|
= \frac{i}{\hbar} \cdot (\mathbf{P} / |\Omega|),
\]
(11)

where \( \mathbf{p} = -i\hbar \nabla \) is an electron linear momentum operator and \( \mathbf{P} \) is a total momentum of the electron system. However, the total momentum \( \mathbf{P} \) should be zero, because, for an arbitrary momentum \( \mathbf{p} \), the momentum \( -\mathbf{p} \) exists with the same probability in the system. Therefore, the \( B(r) \) function starts at \( r = 0 \) from its maximum value of \( \bar{n} \) with the derivative of zero toward all directions of \( r \).

Similarly, the leading term of the second derivative of \( B(r) \) derived from eq.(10) can be related directly to an averaged spatial density of kinetic energy distribution of the electron system as
\[
\text{leading term of } \nabla_r^2 B(r) = \frac{-2m}{\hbar^2} \cdot 2 \sum_{n, k} \int \Psi_{nk}^*(r') \mathbf{i} \Psi_{nk}(r') d^3r' / |\Omega|
= \frac{-2m}{\hbar^2} \cdot (T / |\Omega|),
\]
(12)
where \( \mathbf{i} = -\hbar^2 \nabla^2 / 2m \) is an electron kinetic energy operator and \( T \) is a total kinetic energy of the electron system. This means that the first derivative function of \( B(r) \) starts at \( r = 0 \) from the finite value proportional to the averaged density of kinetic energy.

A general view of sensitivity of the \( B(r) \) function to the electron distribution parameters can be taken in the case of a free electron system. Let us consider a free electron system with Fermi wave number \( k_F \) and Fermi energy \( E_F \). The \( B(r) \) function is easily obtained as follows;
\[
B(r) = \frac{k_F^2}{\pi^2} \cdot j_1(z) = \frac{k_F^2}{\pi^2} \cdot f_0(z),
\]
(13)
where \( z = k_Fr \) and \( j_1(z) \) is the first order spherical Bessel function of \( z \). Therefore, the first and the second derivative functions of the free electron \( B(r) \) is given by the following eq.(14) and eq.(15), respectively.
\[
\nabla_r B(r) = \frac{k_F^2}{\pi^2} \cdot \left( \frac{j_1(z)}{z} \right) = \frac{k_F^2}{\pi^2} \cdot f_1(z)
\]
(14)
and
\[ \nabla^2 B(r) = \frac{k^2}{r^3} \cdot \frac{1}{5z} (2j_2(z) - 3j_1(z)) = \frac{k^2}{r^2} f_2(z), \]
or, equivalently,
\[ = -\frac{k^2}{r^2} \cdot \frac{1}{z} (3j_2(z) - zj_1(z)). \quad (15) \]

Therefore, one obtains a direct relation to the averaged spatial density of kinetic energy as
\[ \lim_{r \to \infty} \nabla^2 B(r) = -\frac{k^2}{5 \pi^2} = -\frac{2m}{\hbar^2} \cdot \frac{3}{5} E_v, \quad (16) \]
where \( \bar{n} = \frac{k^2}{3 \pi^2} \) is the uniform density of electrons and \( \frac{3}{5} E_v \) is the kinetic energy per electron. Here, notice that, in the three dimensional polar coordinate system, the function \( f_2(z) \) is derived from \( f_1(z) \) by \( z^{-2} \partial (z^2 f_1) / \partial z \), not by a simple \( \partial f_1 / \partial z \). Figure 1(a), (b) and (c) are plots of the free electron universal functions \( f_0(z) \), \( f_1(z) \) and \( f_2(z) \), respectively. Let us denote the three first zeros of \( f_0(z) \), \( f_1(z) \) and \( f_2(z) \), respectively, as \( z_0 \), \( z_1 \) and \( z_2 \), and denote the first point of inflection of \( f_0(z) \) as \( z_v \), at which \( f_1(z) \) makes the deepest valley corresponding to the point of the steepest slope of \( f_0(z) \). These values are
\[ z_0 = 4.4934 \cdots, \]
\[ z_1 = 5.7634 \cdots, \]
\[ z_2 = 3.8702 \cdots, \]
\[ z_v = 2.5011 \cdots. \quad (17) \]

In the \( r \)-space, these points shift along the radial direction proportionally to \( 1/k_r \), namely, to \( 1/\bar{n}^{1/3} \). (The point of inflection of \( f_0(z) \) does not coincide with the zero point of \( f_2(z) \). This is due to the nature of \( f_2(z) \) mentioned above.) On the other hand, at \( z = 0 \), the values of \( f_0 \), \( f_2 \) and \( f_1 \) are \( 1/3 \), \( 0 \) and \(-1/5 \), respectively, and at the bottom of the deepest valley of \( f_1(z) \), \( f_v = -0.10402 \cdots \). In the \( r \)-space, the corresponding values \( B(0), \nabla B(r) \) and \( \nabla^2 B(0) \) are proportional to \( \bar{n} \), \( \langle q \rangle \bar{n} \) and \( \langle E \rangle \bar{n} \), respectively, where \( \langle q \rangle = (3/4) k_v \) and \( \langle E \rangle = (3/5) E_v \) are a
mean momentum and kinetic energy per electron (the value $\nabla B(0)$ is identically zero). As can be expected naturally, the sensitivity to a change in the electronic state parameter $k_F$ or $E_F$ becomes higher, the more the differential order for $B(r)$ increases.

§ 3 Discussion on Valence Electronic Bond Character using Kinematical Structure Parameters in $B(r)$ Function

In practical valence electron system of semiconductors, the electronic state is not free-electron-like. The valence electrons strongly localize among atoms making the covalent bond and shift their distribution toward the atom of higher electronegativity depending on the ionic character. Instead of the simple parameter $k_F$ or $E_F$, a parameter of degree of the ionic character to the covalent one, the so-called ionicity parameter, becomes a significant parameter. However, the above discussed general feature that the higher order differential structures of $B(r)$ are more sensitive to the electronic state parameter will be kept also in the practical valence electron system. For the $B(r)$ function calculated on the basis of the pseudopotential energy band theory for semiconductors Ge with diamond structure, GaAs and ZnSe with zincblende structure (Fig. 2), which belong to the same fourth row group in the periodic table, let us compare the ionicity parameter dependence of $\nabla^2 B(r)$ at $r=0$ with the radial part of $\nabla B(r)$ at $r=r_v$ (the steepest derivative) in the [111] covalent bond direction. Calculation was performed by applying Fourier-Hankel transform method to the $B(r)$ function of eq.(4). Outline of the calculation is given in ref.1. Figure 3 shows results of

![Diagram](image)

**Fig. 2.** Diamond structure corresponds to the case that atom A=atom B, and zincblende structure corresponds to the case that atom A≠atom B.
the [111] directional behaviour of the $B(r)$ function for Ge, GaAs and ZnSe. Let us adopt the values of Phillips' ionicity parameter $f$. Results are given in Table I and Fig. 4. The symbol $D_t$ refers to the radial component of $\nabla B(r)$ at $r=r_0$ and $D_b$ refers to $\nabla^2 B(r)$ at $r=0$. The values of $r_0$ are given in units of the lattice constant $a$. For these materials with the same atomic configuration (diamond structure and zincblende structure), the lattice constants are 10.67715 a.u., 10.68338 a.u. and 10.70908 a.u., respectively, for Ge, GaAs and ZnSe.

In Fig. 4, one finds a clear difference between the sensitivities of the two differential structure parameters on the ionicity parameter. As was predicted above, the second order differential parameter $D_b$ is more sensitive to the ionicity parameter than the first order differential parameter $D_t$. Since the valence electron number is commonly 4 in the atomic volume of $\Omega_o$ ($=a^3/4$)) and the lattice constants are nearly equal to each other, the differences in the values of $D_t$ and of $D_b$ come mainly from the differences in the mean momentum density and in the mean kinetic energy density among these materials, respectively. Kinetic energy of the system increases with the localization of electron distribution. This is due to a lowering of potential energy and to an increase of higher momentum in the electronic state. In these materials, the electrons strongly localize between neighbouring atoms, making the valence electronic bond. This fact just corresponds to the large absolute values of $D_b$. Additionally, the electron localization increases with difference of electronegativity between the constituting atoms. Valence electrons shift toward the atom with larger electronegativity. As a result, a component of ionic character increases in the electronic bond. This is an
origin of the ionicity parameter. According to the Phillips modification\textsuperscript{7}, the electronegativities of Zn, Ga, Ge, As and Se are 0.91, 1.13, 1.35, 1.57 and 1.79, respectively. The differences between the constituting atoms are 0 for Ge–Ge (purely covalent), 0.44 for Ga–As and 0.88 for Zn–Se. The phillips’ ionicity parameters are 0 for Ge, 0.310 for GaAs and 0.630 for ZnSe\textsuperscript{7}. Ionic character in GaAs is rather weak, but, in ZnSe is far stronger. This fact is reflected on the increase of kinetic energy density of the electron system and explains consistently well the increasing tendency of the structural parameter $D_2$ shown in Fig. 4. It is also well understood that the increasing tendency of momentum density parameter $D_t$ of lower differential order is weaker than that of kinetic energy parameter.
Table I. Values of the two differential structure parameters of $B(r)$ and the ionicity parameter for Ge, GaAs and ZnSe. Parameters $D_1$ and $D_2$ are in units of $(a\Omega_e)^{-1}$ and $(a^2\Omega_e)^{-1}$, respectively, and $r$ is in units of the lattice constant $a$.

<table>
<thead>
<tr>
<th></th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$f_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(at $r=0.21$)</td>
<td>(at $r=0.19$)</td>
<td>(at $r=0.16$)</td>
</tr>
<tr>
<td>1</td>
<td>$-13.143$</td>
<td>$-13.488$</td>
<td>$-14.794$</td>
</tr>
<tr>
<td>2</td>
<td>$-50.889$</td>
<td>$-58.950$</td>
<td>$-77.664$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.310</td>
<td>0.630</td>
</tr>
</tbody>
</table>

$D_2$ of higher differential order. In ref.1, ionicity dependence of the other various structural parameters of the $B(r)$ function are discussed.

It is shown in this paper that, if one notice relations between the structure of $B(r)$ function and the kinematical structure of the electron system, the $B(r)$ function plays a role of more sensitive probe for investigating the electronic bond character in solids.

References