Band Center—A Conserved Quantity in Solids

J. Zak[(a)]
Department of Physics, The University of British Columbia, Vancouver, British Columbia V6R 2T4, Canada

(Received 2 December 1981)

The average positions of different bands in a solid are shown to be equal to the symmetry centers of the space group of the solid. These positions turn out to be eigenvalues of a band-center operator which is a conserved quantity for translationally invariant systems.

PACS numbers: 71.25.-s, 61.50.Em

One of the important consequences of translational symmetry in solids is the conservation of quasimomentum $\vec{k}$ (also known as Bloch momentum and crystal momentum). This conservation law has to do with the symmetry only and does not depend on the particular form of the periodic potential.[1] Another widely used conserved quantity in solids is the one-band $\vec{V}_{nn}(\vec{k})$ velocity operator.[2-4] Unlike $\vec{k}$, which is universally conserved, the conservation of the velocity for the band n depends explicitly on the existence of such a band in the solid. What this means is that the velocity conservation depends not only on the translational invariance of the solid but also on its band structure. When well-separated bands exist their symmetry specification is closely related to the symmetry centers of the space group of the solid.[5-7] One should expect that in a solid with well-defined bands the symmetry centers of its space group should be expressible in terms of a band-position operator. Such an operator should be a conserved quantity because the symmetry centers of each space group have fixed values for each solid.

In this Letter I define a positionlike conserved operator for a solid with well-defined bands. I call it the band-center (BC) operator. Its eigenvalues turn out to give the average positions of an electron in different bands and they coincide with the symmetry centers of the space group of the solid.

Recently, a lattice operator $\vec{R}_n$ was defined and it was shown to be connected to the one-band $\vec{r}_{nn}(\vec{k})$ coordinate operator.[8] For each band n with a Bloch function $\psi_{nk}(\vec{r})$ and a Wannier function $a_n(\vec{r})$ the spectrum of $\vec{R}_n$ is a lattice relative to the expectation value of the radius vector $\vec{r}$:

$$\langle \vec{X}_{nn}(\vec{k})\rangle = \int a_n^*(\vec{r})\vec{r}a_n(\vec{r})\,d^3r. \tag{1}$$

The lattice operator $\vec{R}_n$ and the quantity (1) will be used in this Letter in defining the BC operator.

Let us start with a one-dimensional crystal and define the following band-center operator $Q_{mn}(2\pi/a)$:

$$Q_{mn}(2\pi/a) = \exp[iq_n(k)2\pi/a]\delta_{mn}. \tag{2}$$

Here $2\pi/a$ is the reciprocal lattice constant and $q_n(k)$ is the one-band $x_{nn}(k)$ position operator[8]:

$$q_n(k) = x_{nn}(k) = i\partial/\partial k + X_{nn}(k), \tag{3}$$

where

$$X_{nn}(k) = \frac{2\pi}{a}\int \psi_{nk}^*(x)\left(i\frac{\partial}{\partial k} + x\right)\psi_{nk}(x)\,dx \tag{4}$$

and the integration is over the unit cell of the Bravais lattice. The operator $Q_{mn}(2\pi/a)$ is by definition diagonal in the band index. We want to show that $Q_{mn}(2\pi/a)$ is a conserved quantity. For this we have to show that it commutes with the Hamiltonian of the Bloch electron. It was shown in Ref. 8 that the Wannier functions $a_n(x-\nu a)$ for the minimal uncertainty of the coordinate are the eigenfunctions of the operator (3) with the eigenvalues $a\nu + \langle X_{nn}(k)\rangle$, where $\langle X_{nn}(k)\rangle$ is given by Eq. (1) and $\nu = 0, \pm 1, \ldots$. Correspondingly, $a_n(x-\nu a)$ are also eigenfunctions of $Q_{mn}(2\pi/a)$ but with the single eigenvalue $\langle X_{nn}(k)\rangle$. This means that any linear combination of the $a_n(x-\nu a)$ is an eigenfunction of $Q_{mn}(2\pi/a)$. In particular, the Bloch function $\psi_{nk}(x)$ corresponding to the coordinate-minimal-uncertainty Wannier function is also an eigenfunction of $Q_{mn}(2\pi/a)$. We see therefore that $Q_{mn}(2\pi/a)$ and the Hamiltonian have a common complete set of eigenfunctions (the Bloch functions), meaning that these two operators commute. In its diagonal form the band-center operator $Q_{mn}(2\pi/a)$ becomes

$$Q_{mn}(2\pi/a) = \exp(iq_n 2\pi/a) \quad \text{with} \quad q_n = \langle X_{nn}(k)\rangle. \tag{5}$$

In what follows q_n will be called the band quasicoordinate for the BC operator. It should be pointed out that $\langle X_{nn}(k)\rangle$ by itself is phase dependent[4,8] and it is defined only modulo a (the constant of the crystal). However, since in Eq. (5) $q_n = \langle X_{nn}(k)\rangle$ appears in the exponential, the operator $Q_{mn}(k)$ is phase independent. Equation

(5) [or more generally, Eq. (2)] defines therefore a conserved quantity for an electron in a one-dimensional crystal. The eigenvalues of this operator are given by the band quasicoordinate q_n. They are the expectation values $\langle X_{nn}(k)\rangle$ (modulo a) of the position operator x in different bands of the solid. One can also check directly that the quantities $\langle X_{nn}(k)\rangle$ do not change with time. For this let us assume that at $t=0$, $\langle X_{nn}(k)\rangle$ was given by Eq. (1) for the one-dimensional crystal. For $t>0$, $a_n(x,t)$ will be

$$a_n(x,t)=\int \exp[-(i/\hbar)\epsilon_n(k)t]\psi_{nk}(x)\,dk, \tag{6}$$

where $\epsilon_n(k)$ is the energy of the band. This means that at any later time the Wannier function $a_n(x,t)$ is defined by a Bloch function which differs from the original one by the phase $\exp[-(i/\hbar)\epsilon_n(k)t]$. However, since a phase change of the Bloch function does not change $\langle X_{nn}(k)\rangle$ (modulo a), we conclude that the eigenvalues of the BC operator are conserved quantities.

The band-center operator (2) has an exponential form and is of the same nature as the operators defining the quasimomentum $\vec{k}$ {which is defined by the exponential operator $\exp[(i/\hbar)pa]$} and the quasicoordinate q {the latter is defined by $\exp[ix(2\pi/a)]$}. It is for this reason that q_n defined by the BC operator (2) [or (5)] is called the band quasicoordinate.

When the crystal possesses inversion symmetry one can easily check that the band quasicoordinate q_n in (5) assumes only two values, $q_n=0$ or $\frac{1}{2}a$. This follows from the following argument. When the crystal has the inversion symmetry, the phase of the Bloch function can always be chosen in such a way as to make the Wannier function even or odd around either of the centers[9]: (1) $x=0$ or (2) $x=\pm\frac{1}{2}a$. By using Eq. (1) for a one-dimensional crystal, it follows that for the center $x=0$ $[Ia_n(x)=\pm a_n(x)]$, $\langle X_{nn}(k)\rangle=0$ while for $x=\pm\frac{1}{2}a$ $[Ia_n(x\pm\frac{1}{2}a)=\pm a_n(x\pm\frac{1}{2}a)]$, $\langle X_{nn}(k)\rangle=\pm\frac{1}{2}a$. Since this holds for any band n and since the eigenvalues of $Q_{nn}(2\pi/a)$ are phase independent it follows that for one-dimensional crystals with a center of inversion and with no other restriction on the periodic potential the band quasicoordinate $q_n=0$ or $\frac{1}{2}a$. On the other hand it is known that a one-dimensional crystal with inversion symmetry has two inequivalent inversion centers,[5-7] one at $x=0$ and one at $x=\frac{1}{2}a$. The existence of two inequivalent inversion centers in a crystal is a consequence of the translational symmetry alone (if there is one there are always two!) and it does not depend on the particular form of the periodic potential. We arrive here at a very interesting result that the eigenvalues q_n of the BC operator coincide with the symmetry centers (for the inversion) of the crystal. The band center can therefore be given the physical meaning of an operator describing the symmetry centers of the solid. This also holds in the case when the crystal has no symmetry center. In the latter case q_n will, in general, assume different values for different bands and it will cover all the range from 0 to a in the unit cell of its variation. This is in full agreement with the fact that for crystals with no symmetry (apart from translations) all the points in the Wigner-Seitz cell have the unit element symmetry only (no symmetry). The band center can therefore be interpreted in any one-dimensional crystal as describing its symmetry centers. With this interpretation the conservation of the BC operator should come as no surprise because the symmetry centers have a well-defined physical meaning in the space of the crystal. Thus, if by measuring q_n we find only two possible values (0 or $\frac{1}{2}a$) this should be an indication that the crystal has the inversion symmetry. However, when q_n also has other values, the crystal has no inversion symmetry.

The definition of a band-center operator can also be extended to three-dimensional crystals. For a simple band the extension is straightforward. Before doing it the following remark should, however, be made. Unlike one-dimensional crystals which have, as a rule, a well-defined band structure, three-dimensional crystals may have only a few well-separated bands in their energy spectrum.[5,9] Only such bands will be considered in this Letter. For each simple band its very existence is sufficient in order for one to be able to define a band-center operator. For composite bands, we shall use the symmetry of the solid in the definition of the BC operator.

A simple band in a solid has a well-defined one-band position operator $\vec{r}_{nn}(\vec{k})$. In general, the components of this vector do not commute and we shall use its laminar part[8] $\vec{r}_{nn}{}^{(L)}(\vec{k})$ in the definition of the BC operator $Q_{nn}(\vec{K})$:

$$Q_{nn}(\vec{K})=\exp[i\vec{q}_n(\vec{k})\cdot\vec{K}], \tag{7}$$

where $\vec{K}$ is a reciprocal lattice vector and

$$\vec{q}_n(\vec{k})=\vec{r}_{nn}{}^{(L)}(\vec{k})=i\,\partial/\partial\vec{k}+\vec{X}_{nn}{}^{(L)}(\vec{k}), \tag{8}$$

with $\vec{X}_{nn}{}^{(L)}(\vec{k})$ being the laminar part $[\mathrm{rot}\vec{X}_{nn}{}^{(L)}(\vec{k})=0]$ of the quantity $\vec{X}_{nn}(\vec{k})$ [see Eq. (4) for its definition]. As in the one-dimensional case one can show that the operator (7) is a conserved quantity. This follows immediately from the fact that the radius-vector–minimal-uncertainty Wannier functions $a_n(\vec{r}-\vec{R}_\nu)$ are the eigenfunctions of the operator $\vec{q}_n(\vec{k})$ with the spectrum $\vec{R}_\nu + \langle \vec{X}_{nn}(\vec{k})\rangle$, where $\vec{R}_\nu$ is a Bravais lattice vector and $\langle \vec{X}_{nn}(\vec{k})\rangle$ is given in Eq. (1). Correspondingly, the eigenvalues of the BC operator (7) are the same for all the Wannier functions $a_n(\vec{r}-\vec{R}_\nu)$. This means that also the Bloch function $\psi_{nk}(\vec{r})$ with the special choice of phase (leading to the coordinate-minimal-uncertainty Wannier function) is an eigenfunction of $Q_{nn}(\vec{K})$. The BC operator (7) commutes therefore with the Hamiltonian and is a conserved quantity. Its diagonal form is

$$Q_{nn}(\vec{K}) = \exp(i\vec{q}_n \cdot \vec{K}) \quad \text{with } \vec{q}_n = \langle \vec{X}_{nn}(\vec{k})\rangle \tag{9}$$

and is a straightforward generalization of the one-dimensional formula (5). When the crystal possesses no point symmetry there is no restriction on $\langle \vec{X}_{nn}(\vec{k})\rangle$ and the value of the band quasicoordinate $\vec{q}_n$ will depend on the particular form of the potential $V(\vec{r})$. However, when there is point symmetry in addition to translations, the $\vec{q}_n$ value of the band will coincide with one of the symmetry centers of the space group. Thus, one can check by using formula (1) for $\vec{q}_n$ that for crystals of the $C_i^{\,1}$ symmetry the band quasicoordinate can assume eight different values: 0, $\frac{1}{2}\vec{a}$, $\frac{1}{2}\vec{b}$, $\frac{1}{2}\vec{c}$, $\frac{1}{2}(\vec{a}+\vec{b})$, $\frac{1}{2}(\vec{a}+\vec{c})$, $\frac{1}{2}(\vec{b}+\vec{c})$, $\frac{1}{2}(\vec{a}+\vec{b}+\vec{c})$, where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the unit vectors of the Bravais lattice. This is in full agreement with the eight inequivalent inversion centers for this group.[6,7] We have here a very interesting result showing that from the knowledge of the inversion symmetry centers of the space group $C_i^{\,1}$ we can find the possible values of $\vec{q}_n$ and vice versa (if the $\vec{q}_n$'s are known we have information on the symmetry centers of the space group). This connection between the symmetry centers of the space group and the possible eigenvalues of the BC operator also holds for crystals with any space-group symmetry. It should be stressed that in the definition (7), only the existence of a simple band was used and no assumption was made about the symmetry of the crystal. Despite that, the latter information is contained in the simple band and the eigenvalue $\vec{q}_n$ of the BC operator coincides with one of the symmetry centers of the crystal. As in one-dimensional crystals, the BC operator for a simple band has the physical meaning of an operator for the symmetry centers of the crystal.

In a composite band there are f Bloch functions $(f>1)$ $\psi_{sk}(\vec{r})$, $s=1,2,\ldots,f$ for each vector $\vec{k}$ in the Brillouin zone. Such a composite band is usually said to have f branches. An f-branch band has, in general, a complicated structure[5] and there does not seem to be a simple way to define for it a BC operator. However, in what follows I show that if the branching of the band is caused by symmetry or, in other words, if the composite band belongs to an irreducible band representation of the space group,[6] then the definition of a band-center operator becomes quite straightforward. Consider, for example, the valence band of Ge with the diamond symmetry group $O_h^{\,7}$. This is a four-branch band which, as can be shown belongs to the $(c,1)$-band representation.[5,10] What this means is that this band is built on the following four orbitals:

$$\begin{aligned} a_1(\vec{r}) &= a^{(c,1)}(\vec{r}), & a_2(\vec{r}) &= C_2^{\,x} a_1(\vec{r}), \\ a_3(\vec{r}) &= C_2^{\,y} a_1(\vec{r}), & a_4(\vec{r}) &= C_2^{\,z} a_1(\vec{r}). \end{aligned} \tag{10}$$

Here $a^{(c,1)}(\vec{r})$ is a fully symmetric function (the superscript "1" denotes this) of the group D_{3d} with respect to the symmetry center[7] $\vec{q}_c = (\frac{1}{8}a, \frac{1}{8}a, \frac{1}{8}a)$ and $C_2^{\,x}$, $C_2^{\,y}$, and $C_2^{\,z}$ are rotations by π around the axes x, y, and z correspondingly (with respect to the origin of the crystal). By assuming that the orbitals $a_s(\vec{r})$, $s=1,2,3,4$ in Eq. (10) are the Wannier functions for the valence band of Ge we can construct the quantities [see Eq. (1)]

$$\vec{q}_s = \langle \vec{X}_{ss}(\vec{k})\rangle = \int a_s^*(\vec{r})\vec{r}a_s(\vec{r})\,d^3r, \qquad s=1,\ldots,4. \tag{11}$$

The results of Ref. 8 and the formulas (7)–(9) can now be used for each branch of the composite band. Correspondingly, for the valence band of Ge the eigenvalues of the band-center operator will be

$$Q_{ss}(\vec{K}) = \exp(i\vec{q}_s \cdot \vec{K}), \quad s=1,\ldots,4. \tag{12}$$

This procedure of defining a BC operator can be applied to any composite band as long as it belongs to a given band representation. A detailed description of such a procedure for a general composite band will be given elsewhere. For the particular band under discussion (the valence band of Ge) it is easy to find the band quasicoordinates $\vec{q}_s$ in (11) from symmetry arguments. First, it is clear that $\vec{q}_1 = \vec{q}_c$. This follows from the fact that $a_1(\vec{r})$ is fully symmetric under the elements of D_{3d} with respect to the symmetry center $\vec{q}_c$. In particular, $(I|\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)a_1(\vec{r}) = a_1(\vec{r})$. By applying this relation to the integral (11) which defines $\vec{q}_1$ we have

$$\vec{q}_1 = \int a_1^*(\vec{r})\vec{r}a_1(\vec{r})\,d^3r = -\vec{q}_1 + (\tfrac{1}{4}a, \tfrac{1}{4}a, \tfrac{1}{4}a). \tag{13}$$

From here, $\vec{q}_1 = \vec{q}_c = (\frac{1}{8}a, \frac{1}{8}a, \frac{1}{8}a)$. Similarly, from the relations (10) and (11) we find $\vec{q}_2 = C_2{}^x \vec{q}_c = (\frac{1}{8}a, -\frac{1}{8}a, -\frac{1}{8}a)$, $\vec{q}_3 = C_2{}^y \vec{q}_c = (-\frac{1}{8}a, \frac{1}{8}a, -\frac{1}{8}a)$, and $\vec{q}_4 = C_2{}^z \vec{q}_c = (-\frac{1}{8}a, -\frac{1}{8}a, \frac{1}{8}a)$. This result shows that the values of the band quasicoordinates $\vec{q}_n$ for the valence band of Ge coincide with the vectors of the star for the symmetry center $\vec{q}_c$ of the space group $O_h{}^7$. In proving this result no use was made of the explicit form of the periodic potential. What this means is that the band quasicoordinates $\vec{q}_n$ for any composite band of the $(c, 1)$ symmetry will reproduce the star of $\vec{q}_c$ for $O_h{}^7$. It can be checked that the values of $\vec{q}_s$ in Eq. (11) will reproduce the star of the symmetry center for any of the irreducible band representations of the space group $O_h{}^7$. This result can be generalized to any composite band with given symmetry of a solid belonging to any space group: The eigenvalues of the BC operator will give the symmetry centers of the space group of the solid and vice versa (if the latter are given we also know the possible eigenvalues of the BC operator).

In summary, it has been shown that for each band in a solid one can define a band-center operator which is a conserved quantity. Its eigenvalues are the average position of the electron in different bands, and they also coincide with the symmetry centers of the space group for the particular solid.

The author enjoyed discussions on the subject with Professor R. Barrie and Professor W. Opechowski. It is a pleasure to thank the Physics Department of the University of British Columbia for its kind hospitality.

---

[a] On leave from the Physics Department, Technion–Israel Institute of Technology, Haifa, Israel.

[1] F. Bloch, Z. Phys. 52, 555 (1928).

[2] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).

[3] E. N. Adams, J. Chem. Phys. 21, 2013 (1953).

[4] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13.

[5] J. Des Cloizeaux, Phys. Rev. 129, 554 (1963), and 135, A685, A689 (1964).

[6] J. Zak, Phys. Rev. Lett. 45, 1025 (1980), and Phys. Rev. B 23, 2824 (1981).

[7] *International Tables of X-ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch, Birmingham, 1952), Vol. 1.

[8] J. Zak, Phys. Rev. B 20, 2228 (1979); J.-P. Rouyet and J. Zak, Phys. Rev. B 23, 561 (1981); J. Zak, Phys. Lett. 83A, 287 (1981).

[9] W. Kohn, Phys. Rev. 115, 809 (1959).

[10] J. Zak, Phys. Rev. Lett. 47, 450 (1981).

Fermi-Surface Sum Rule and its Consequences for Periodic Kondo and Mixed-Valence Systems

Richard M. Martin
Xerox Palo Alto Research Centers, Palo Alto, California 94304, and Laboratoire de Physique des Solides,
Université de Paris-Sud, F-91405 Orsay, France, and Departement de Recherches Physiques,
Université Pierre et Marie Curie, F-75230 Paris Cédex 05, France

(Received 24 July 1981)

The Friedel sum rule for impurities is related to the Luttinger requirement that the volume of the Fermi surface of a crystal is independent of interactions. As a consequence important results derived by use of the Friedel sum rule, e.g., the $T \to 0$ properties of the Kondo problem, can be extended to periodic cases. Considered explicitly are the remarkable consequences for Fermi surfaces and Fermi-liquid properties of periodic Kondo and mixed-valence systems.

PACS numbers: 71.45.Gm, 72.15.Qm, 75.20.Hr

There are two well-known sum rules which relate properties of states at the Fermi energy μ to the number of fermions, the Friedel sum rule[1] on phase shifts at μ caused by an impurity and the Luttinger sum rule[2] on the volume enclosed by the Fermi surface in a perfect crystal. The derivation by Luttinger showed that the sum rule[2] is a rigorous result of the analytic properties of Fermi liquids,[2,3] including interactions between fermions to all orders. The same techniques were used by Langer and Ambegaokar[4] to provide a general proof of the Friedel sum rule. In subsequent years Fermi-liquid theory including the Friedel sum rule has been one of the