COMMENTS AND ADDENDA

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Comment on "*kq* Representation for the Impurity Problem in Semiconductors"

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Recently Zak has derived a novel form for the wave equation of an electron trapped near a defect in a semiconductor. We find that the *kq* representation only obfuscates Zak's analysis, and that Zak's equation is simply the many-band Wannier equation with the defect-potential matrix elements put into differential form. By reordering the operators in Zak's equation we also find that Zak's evaluation of corrections to the one-band Wannier equation involving successively higher derivatives of the defect potential is simply an approximate evaluation of a more general series of corrections derived earlier by Blount.

INTRODUCTION

Zak has recently considered corrections to the one-band Wannier equation for one-electron impurity states in semiconductors.[1] While his analysis is apparently based upon the *kq* representation originated by Zak, we will show that in fact his analysis is made in a Wannier function representation by virtue of a transformation employed at an early stage [Zak's Eq. (7)]. Consequently, Zak's form for the wave equation, his Eq. (12), should be identical with the wave equation in a Wannier representation. We will show that indeed this is the case and that Zak's use of the *kq* representation is irrelevant.

Since Zak's equation is the Wannier equation with the defect-potential terms expressed in differential rather than matrix form, it is reasonable to compare Zak's estimate of these defect-potential terms with previous estimates. We find that by reordering the operators in Zak's equation we can evaluate the defect-potential terms without resorting to Zak's power-series approximation to the wave-vector dependence of the Bloch functions. With this more general evaluation of the defect-potential terms we regain the same series of terms in derivatives of the defect potential previously obtained by Blount.[2]

PROOF THAT ZAK'S EQUATION IS IN WANNIER REPRESENTATION

Our demonstration that Zak has used the Wannier representation is based upon his transformation of the *kq* representation of the wave function $C(\vec{k}, \vec{q})$ to an unidentified representation in which the wave function is given by $F_n(\vec{R})$. This transformation is Zak's Eq. (7):

$$C(\vec{k}, \vec{q}) = \frac{1}{N^{1/2}} \sum_{n,\vec{R}} e^{-i\vec{k}\cdot\vec{R}} F_n(\vec{R})\, \psi_{n\vec{k}}(\vec{q}) , \tag{1}$$

where N is the number of unit cells and $\psi_{n\vec{k}}(\vec{q})$ is the Bloch function for band n and wave vector $\vec{k}$ normalized to the number of unit cells. We will show that $F_n(\vec{R})$ is the wave function in a Wannier representation. To do this we use the relation[3]

$$C(\vec{k}, \vec{q}) = (1/N^{1/2}) \textstyle\sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}}\, \psi(\vec{q}+\vec{R}), \tag{2}$$

which connects the *kq* representation of the wave function $C(\vec{k}, \vec{q})$ to the wave function in the coordinate representation $\psi(\vec{q}+\vec{R})$. Substituting Eq. (2) in (1) we obtain

$$\textstyle\sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} [\psi(\vec{q}+\vec{R}) - \sum_n F_n(\vec{R})\, \psi_{n\vec{k}}(\vec{q})] = 0 . \tag{3}$$

If we now multiply Eq. (3) by $\exp(i\vec{k}\cdot\vec{R}_0)/N^{1/2}$, sum over $\vec{k}$, and use the definition of the Wannier function $a_n(\vec{r}-\vec{R})$:

$$a_n(\vec{r}-\vec{R}) = (1/N)\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}}\,\psi_{n\vec{k}}(\vec{r}) \tag{4}$$

plus the identity

$$(1/N)\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}_0)} = \delta_{\vec{R},\vec{R}_0} \ , \tag{5}$$

we find that Eq. (3) becomes

$$\psi(\vec{r}) = \sum_{n,\vec{R}} F_n(\vec{R})\, a_n(\vec{r}-\vec{R}) \ , \tag{6}$$

with

$$\vec{r} = \vec{q} + \vec{R}_0 \ .$$

That is, Zak's $F_n(\vec{R})$ is simply the wave function in a Wannier representation.

kq REPRESENTATION IS IRRELEVANT

It will now be shown that Zak's analysis is both shortened and clarified by avoiding the kq representation. We begin by showing that the basic expansion of Zak's analysis, his Eq. (8), follows in two lines from the Wannier expansion, our Eq. (6).

To put Eq. (6) into the form used by Zak, substitute Eq. (4) in (6):

$$\psi(\vec{q}+\vec{R}_0) = \frac{1}{N}\sum_{n,\vec{k},\vec{R}} \psi_{n\vec{k}}(\vec{q}+\vec{R}_0)\, e^{-i\vec{k}\cdot\vec{R}}\, F_n(\vec{R})$$

$$= \sum_n \psi_{n,\,-i(\partial/\partial\vec{R}_0)}(\vec{q})\, F_n(\vec{R}_0) \ , \tag{7}$$

where we have introduced the operator (attributed to Roth[4]) obtained by replacing the $\vec{k}$ dependence of the Bloch function by a $-i(\partial/\partial\vec{R}_0)$ dependence. Comparison of our Eq. (7) with Zak's Eq. (8) indicates that Zak's "new wave function" $\psi(\vec{R},\vec{q})$ is given by

$$\psi(\vec{R},\vec{q}) = \psi(\vec{q}+\vec{R}) \ , \tag{8}$$

i.e., Zak's new wave function is the same as the usual wave function and its general dependence upon the two variables $(\vec{R},\vec{q})$ is only a dependence upon the usual coordinate $\vec{r}=\vec{q}+\vec{R}$. Thus Zak's use of the kq representation has so obscured the analysis as to lead him to a spurious generality.

The identification of Eq. (8) is also obtained from the Schrödinger equation in the usual *coordinate* representation. One simply shifts the origin by substituting $\vec{r}=\vec{q}+\vec{R}$ and the Schrödinger equation becomes

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial\vec{q}^2} + V(\vec{q}) + \upsilon(\vec{q}+\vec{R})\right)\psi(\vec{q}+\vec{R}) = \epsilon\psi(\vec{q}+\vec{R}) \ , \tag{9}$$

which is Zak's Eq. (6) for $\psi(\vec{R},\vec{q})$. Here $V(\vec{q})$ is the periodic crystal potential and $\upsilon(\vec{q}+\vec{R})$ is the defect potential. It is therefore untrue that "it would not be easy to arrive at (this form of) Schrödinger's equation without the kq representation."

We conclude that our Eqs. (7) and (9), which are the very equations Zak has claimed are difficult to derive except with the kq representation, are very immediate and clear consequences of the Wannier expansion and the Schrödinger equation, respectively. They are much less immediate and less clear when derived using the kq representation. It seems appropriate to term the kq representation *irrelevant* to the defect problem, at least when used as Zak has suggested.

DIFFERENTIAL FORM FOR IMPURITY-POTENTIAL TERMS

We have established that $F_n(\vec{R})$ is the wave function in the Wannier representation. Consequently, $F_n(\vec{R})$ satisfies the standard Wannier equation (e.g., see Blount[5])

$$[\epsilon_m(\vec{k}) - \epsilon]\, F_m(\vec{R}) + \sum_{n,\vec{R}_0} \upsilon_{mn}(\vec{R},\vec{R}_0)\, F_n(\vec{R}_0) = 0 \ , \tag{10}$$

where

$$\upsilon_{mn}(\vec{R},\vec{R}_0) = \int d^3r\, a_m^*(\vec{r}-\vec{R})\,\upsilon(\vec{r})\, a_n(\vec{r}-\vec{R}_0)$$

is the matrix element of the impurity potential $\upsilon(\vec{r})$ between Wannier functions and where $\epsilon_m(\vec{k})$ is the energy versus $\vec{k}$ relation for the mth band, and $\vec{k}$ is the operator given by

$$\vec{k} = -i\,\frac{\partial}{\partial\vec{R}} \ .$$

The impurity-potential-dependent term in Eq. (10) can be put into the same form as Zak's Eq. (12). This can be done as Zak suggests by substituting Eq. (7) into Eq. (9), or it can be done directly by using Dirac notation for matrix elements. Using either approach the defect-potential-dependent term becomes

$$\sum_{n,\vec{R}_0} \upsilon_{mn}(\vec{R},\vec{R}_0)\, F_n(\vec{R}_0)$$

$$= \sum_n \sum_{\vec{q}} \psi^*_{m,\,-i(\partial/\partial\vec{R})}(\vec{q})$$

$$\times [\upsilon(\vec{q}+\vec{R})\,\psi_{n,\,-i(\partial/\partial\vec{R})}(\vec{q})\cdot F_n(\vec{R})] \ .$$

Thus the Wannier equation [Eq. (10)] becomes

$$\left[\epsilon_m\left(-i\,\frac{\partial}{\partial\vec{R}}\right) - \epsilon\right] F_m(\vec{R})$$

$$+ \sum_n \upsilon_{mn}\left(\vec{R}, -i\,\frac{\partial}{\partial\vec{R}}\right) F_n(\vec{R}) = 0 \ , \tag{11}$$

where

$$\upsilon_{mn}\left(\vec{R}, -i\,\frac{\partial}{\partial\vec{R}}\right) = \sum_{\vec{q}} \psi^*_{m,\,-i(\partial/\partial\vec{R})}(\vec{q})\,\upsilon(\vec{q}+\vec{R})$$

$$\times \psi_{n,\,-i(\partial/\partial\vec{R})}(\vec{q}) \ . \tag{12}$$

Equations (11) and (12) are Zak's Eqs. (12) and (13),

respectively.

EVALUATION OF OPERATOR $v_{mn}[\vec{R}, -i(\partial/\partial\vec{R})]$

Zak has evaluated the operator $v_{mn}[\vec{R}, -i(\partial/\partial\vec{R})]$ by expanding the wave-vector dependence of the Bloch functions in a power series. We now will show that a more general result can be obtained if one uses a slightly different form of Eq. (12), viz.,

$$v_{mn}\left(\vec{R}, -i\frac{\partial}{\partial\vec{R}}\right) = \sum_{\vec{q}}\left[\psi^*_{m\vec{k}}(\vec{q})\, v\left(\vec{q}+\vec{R}+i\frac{\partial}{\partial\vec{k}}\right)\psi_{n\vec{k}}(\vec{q})\right]_{\vec{k}=-i(\partial/\partial\vec{R})}, \tag{13}$$

where in Eq. (13) it is to be understood that all the $\vec{R}$ dependence is to be placed to the right of all $\vec{k}$ dependence before the substitution $\vec{k}=-i(\partial/\partial\vec{R})$ is made. The equivalence of Eqs. (12) and (13) can be shown by expanding the Bloch function in Wannier functions:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{R}_0} e^{i\vec{k}\cdot\vec{R}_0}\, a_n(\vec{r}-\vec{R}_0)\,.$$

Then Eq. (13) becomes

$$v_{mn}\left(\vec{R}, -i\frac{\partial}{\partial\vec{R}}\right) = \sum_{\vec{q},\vec{R}_0}\left[\psi^*_{m,\vec{k}}(\vec{q})\, e^{i\vec{k}\cdot\vec{R}_0}\, v(\vec{q}+\vec{R}-\vec{R}_0) \times a_n(\vec{r}-\vec{R}_0)\right]_{\vec{k}=-i(\partial/\partial\vec{R})}.$$

Since now all the $\vec{R}$ dependence is to the right of all the $\vec{k}$ dependence we are free to replace $\vec{k}$ by $-i(\partial/\partial\vec{R})$ to obtain

$$\begin{aligned} v_{mn}\left(\vec{R}, -i\frac{\partial}{\partial\vec{R}}\right) &= \sum_{\vec{q},\vec{R}_0} \psi_{m,-i(\partial/\partial\vec{R})}(\vec{q})\, e^{\vec{R}_0\cdot(\partial/\partial\vec{R})} \times v(\vec{q}+\vec{R}-\vec{R}_0)\, a_n(\vec{r}-\vec{R}_0) \\ &= \sum_{\vec{q}} \psi^*_{m,-i(\partial/\partial\vec{R})}(\vec{q})\, v(\vec{q}+\vec{R})\, \psi_{n,-i(\partial/\partial\vec{R})}(\vec{q})\,, \end{aligned}$$

which is the result of Eq. (12).

The advantage of Eq. (13) over Eq. (12) is that we can now make a Taylor-series expansion of $v[\vec{q}+\vec{R}+i(\partial/\partial\vec{R})]$ about the lattice site $\vec{R}$ and thereby obtain correction terms to the one-band Wannier equation without any approximations to the wave functions. Thus

$$v\left(\vec{q}+\vec{R}+i\frac{\partial}{\partial\vec{k}}\right) = v(\vec{R}) + \left(\vec{q}+i\frac{\partial}{\partial\vec{k}}\right)\cdot\frac{\partial v}{\partial\vec{R}} + \text{etc.},$$

and Eq. (12) becomes

$$v_{mn}\left(\vec{R}, -i\frac{\partial}{\partial\vec{R}}\right) = v(\vec{R})\,\delta_{m,n} + \sum_{\vec{q}}\left[\psi^*_{m\vec{k}}(\vec{q})\left(\vec{q}+i\frac{\partial}{\partial\vec{k}}\right)\psi_{n\vec{k}}(\vec{q})\right]_{\vec{k}=-i(\partial/\partial\vec{R})}\cdot\frac{\partial v}{\partial\vec{R}} + \text{etc}\,. \tag{14}$$

The leading term in Eq. (14) leads to the one-band Wannier equation

$$\left[\epsilon_m\left(-i\frac{\partial}{\partial\vec{R}}\right) + v(\vec{R})\right]F_m(\vec{R}) = \epsilon F_m(\vec{R})\,. \tag{15}$$

The higher-order terms in Eq. (14) constitute corrections to the one-band Wannier equation dependent upon the rate of variation of the impurity potential $v(\vec{R})$. For example,

$$\begin{aligned} \sum_{\vec{q}}\left[\psi^*_{m\vec{k}}(\vec{q})\left(\vec{q}+i\frac{\partial}{\partial\vec{k}}\right)\psi_{n\vec{k}}(\vec{q})\right]_{\vec{k}=-i(\partial/\partial\vec{R})} &= \sum_{\vec{q}}\left(u^*_{m\vec{k}}(\vec{q})\, i\frac{\partial}{\partial\vec{k}}\, u_{n\vec{k}}(\vec{q})\right)_{\vec{k}=-i(\partial/\partial\vec{R})} \\ &\equiv \vec{X}_{mn}\left(-i\frac{\partial}{\partial\vec{R}}\right), \end{aligned} \tag{16}$$

where $u_{n\vec{k}}(\vec{q})$ is the periodic part of the Bloch function and the corresponding Wannier equation becomes the system of equations

$$\left[\epsilon_m\left(-i\frac{\partial}{\partial\vec{R}}\right) + v(\vec{R}) + \vec{X}_{mm}\left(-i\frac{\partial}{\partial\vec{R}}\right)\cdot\frac{\partial v(\vec{R})}{\partial\vec{R}}\right]F_m(\vec{R}) + \sum_{n\neq m}\left[\vec{X}_{mn}\left(-i\frac{\partial}{\partial\vec{R}}\right)\cdot\frac{\partial v(\vec{R})}{\partial\vec{R}}\right]F_n(\vec{R}) = \epsilon F_m(\vec{R})\,. \tag{17}$$

This result was obtained previously by Blount[2] as the first correction of a series of corrections to the one-band Wannier equation involving derivatives of the defect potential. The corrections involving higher derivatives of the defect potential are obtained by retaining more terms in the Taylor-series expansion of Eq. (14). If the important wave-vector dependence of the wave functions is restricted to the neighborhood of a band extremum, Blount's series of corrections reduces to that of Zak.

SUMMARY

In this paper it has been shown that (a) the wave equation obtained by Zak is in the Wannier representation; (b) Zak's use of the kq representation is irrelevant to the impurity problem, since the analysis can be both shortened and clarified by using the Wannier representation; and (c) one obtains the same corrections to the one-band Wannier equation previously derived by Blount[2] provided one avoids Zak's approximation to the wave-vector dependence of the wave functions.

ACKNOWLEDGMENT

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[1]J. Zak, Phys. Rev. B 2, 384 (1970).
[2]E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 318, Eq. (2.20).
[3]J. Zak, Phys. Rev. 168, 686 (1968), see especially Eqs. (39) and (30).
[4]L. M. Roth, J. Phys. Chem. Solids 23, 433 (1962).
[5]Reference 2, Sec. 4, p. 319.

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Comment on Electroreflectance Curve Fitting*

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We use one-electron theory to fit the direct-edge electroreflectance data of germanium taken by Handler, Jasperson, and Koeppen in 1969 and compare this fit to another done by Weinstein, Dow, and Lao using an excitonic theory. The results (Fig. 2) suggest that the data contain insufficient information to distinguish a single method of fitting.

The past few years have seen major experimental improvements occur in the field of electroreflectance.[1] Carefully controlled experimental conditions have allowed the experimenter to obtain spectra which can be confidently compared to theory. Since 1958, when Franz[2] and Keldysh[3] predicted the effect of a strong electric field on optical absorption, numerous improvements have been made on the one-electron theory of electroreflectance, culminating in the work of Aspnes,[4] who derived the exact form of the one-electron line shape for all types of three-dimensional critical points.

In addition, the effect of the Coulomb interaction has been taken into account numerically by several authors. Among these are Ralph,[5] Blossey,[6] and, most recently, Dow and Redfield.[7] Weinstein, Dow, and Lao[8] (WDL) fitted a portion of the electroreflectance data taken in our laboratory by Handler, Jasperson, and Koeppen[9] (HJK) in 1969. The data included structures attributed to transitions from the light- and heavy-hole valence bands and from the spin-orbit-split valence band to the lowest conduction band and spanned the energy range from 700 to 1200 meV.

The most important effect discussed by HJK was the "beating" or interference of the light- and heavy-hole line shapes. This phenomenon is as-

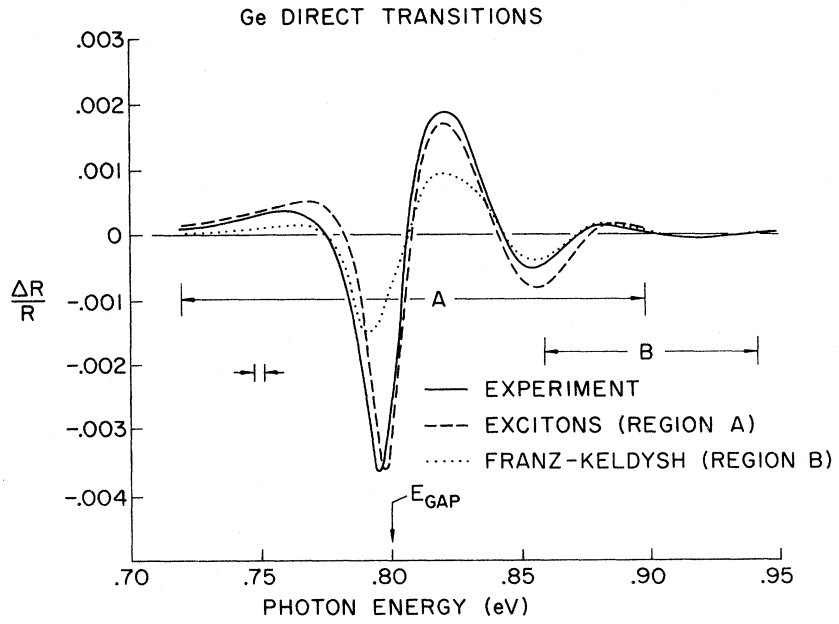

FIG. 1. $\Delta R/R$ electroreflectance data of HJK (Ref. 9) as fit by WDL (Ref. 8) using excitonic theory and by HJK using one-electron theory. Regions contributing to the least-squares sums used by the separate authors are shown. Though barely distinguishable from the abscissa in this linear plot, the data points in region B are well above the noise level and show up quite well on a logarithmic plot (see Ref. 8, Figs. 1 and 3).