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Effect of Gradients of the Perturbation in Effective-Mass Theory

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Ionization energies of donors and acceptors in semiconductors generally differ from computed values by 10–30%. We discuss a suggestion that the discrepancy may be due to the neglect in the theory of the gradients of the impurity potential in the region of the orbit of the trapped electron or hole. This effect is shown here to be too small to account for the discrepancy. Hence, it must be due to the originally suggested cause—the character of the impurity potential in the immediate vicinity of the impurity.

When theoretical and experimental results for the ionization energies of donors and acceptors are compared, the agreement is only fair. The observed values are generally 10–30% larger than the computed values.[1,2]

Kohn and Luttinger[3] have suggested that the discrepancy is due to the deviation from Coulomb form of the impurity potential in the immediate vicinity of the impurity ion (i.e., in the "central cell"). A second possibility mentioned by them is the assumption in effective-mass theory about the nature of the impurity potential $v(\vec{r})$ acting on the trapped electron or hole. The theory assumes $v(\vec{r})$ to vary slowly, compared to the lattice interaction in a unit cell of the crystal. This assumption may be invalid in the central cell.

A third suggestion has been given by Zak.[4] He has succeeded in obtaining exact corrections to the effective-mass differential equation. The result is expressed by adding a series to the usual effective-mass differential equation. The jth term in the series gives the effect of the jth-order spatial derivatives of $v(\vec{r})$; the usual equation contains only the zeroth-order term.

The result is then applied to the problem of the ground state of holes in Ge. It is found that the first-order term vanishes, but the second-order term gives a substantial correction to the ionization energy, increasing its magnitude by about 10%.

Unlike the two possibilities suggested by Kohn and Luttinger, the correction found by Zak is not a "central-cell" effect. The correction is obtained without alteration in the functional form of the acceptor potential $v(r)$ from its asymptotic (large r) form $v(r) = e^2/\chi r$. (Here χ is the static dielectric constant, while r is the distance to the impurity.)

Schechter,[5] in an earlier work, had estimated the effect considered by Zak by using a variational calculation. He found its size to be too small to be observed.

In this paper, we attempted to find the reason for the differing conclusions of Ref. 4 and 5 and were motivated by the fact that the work of Ref. 4 implies that theoretical efforts must consider corrections other than central-cell effects.

For this purpose, we begin by considering the exact differential equation for the impurity envelope function $F_m(\vec{R})$ derived by Zak [Eq. (12) of

Ref. 4]:

$$\epsilon_m(\vec{k}) \, F_m(\vec{R}) + \sum_n v_{mn}(\vec{R},\vec{k}) \, F_n(\vec{R}) = \epsilon \, F_m(\vec{R}). \quad (1)$$

In Eq. (1), ϵ is the energy of the impurity state, the vector $\vec{k}$ denotes the operation $-i\hbar\vec{\nabla}$, and $\epsilon_m(\vec{k})$ is the Bloch energy for band m and wave vector $\vec{k}$. The index m denotes the band from which the impurity state originates, when we take the limit in which the impurity potential $v(\vec{R})$ vanishes.

The differential operator $v_{mn}(\vec{R},\vec{k})$ is defined by the relation

$$v_{mn}(\vec{R},\vec{k}) = v(\vec{R}) \, \delta_{mn} + \int u_m^\dagger(\vec{q},\vec{k}) \, [v(\vec{R}), \, u_n(\vec{q},\vec{k})] \, d^3q.$$

$$(2)$$

Here

$$u_n(\vec{q},\vec{k}) = e^{-i\vec{k}\cdot\vec{q}} \, \psi_n(\vec{q},\vec{k}),$$

where $\psi_n(\vec{q},\vec{k})$ is the Bloch state of wave vector $\vec{k}$ for band n. The sum on n in Eq. (1) is over all bands n, including the band m.

If Eq. (2) is inserted into Eq. (1), then the first term of Eq. (2) reproduces the conventional effective-mass equation. Corrections to the equation are then obtained in systematic fashion by expanding the operators $u_m^\dagger(\vec{q},\vec{k})$ and $u_n(\vec{q},\vec{k})$ of Eq. (2) in a power series about the value or set of values of $\vec{k}$ for which $\epsilon_m(\vec{k})$ is an extremum. The second-order terms in $\vec{k}$ were found in Ref. 4 to be responsible for about a 10% increase in the magnitude of the energy ϵ. Following Zak, we consider the case where the extremum lies at $\vec{k}=0$ and the band is nondegenerate. Then the expansion is

$$u_n(\vec{q},\vec{k}) = u_n(\vec{q},0) + \sum_\alpha \left(\frac{\partial}{\partial k_\alpha} u_n(\vec{q},\vec{k})\right)_0 k_\alpha$$

$$+ \frac{1}{2} \sum_\alpha \sum_\beta \left(\frac{\partial^2 u_n(\vec{q},\vec{k})}{\partial k_\alpha \, \partial k_\beta}\right)_0 k_\alpha k_\beta + \cdots. \quad (3)$$

The sums on α and β are over the three Cartesian components of $\vec{k}$, denoted k_1, k_2, k_3. The zero subscript in Eq. (3) indicates that the derivatives are to be evaluated at $\vec{k}=0$.

Substituting Eq. (3) in Eq. (2), we note that there are no zeroth-order terms in $\vec{k}$, due to the fact that the commutator contains no derivatives with respect to $\vec{R}$.

The $n \neq m$ terms of Eq. (1) are "band-mixing" effects. They have been examined by Luttinger and Kohn[6] and shown to be negligible, constituting only a 0.2% correction. We shall then only consider the $n=m$ term of Eq. (1).

The first-order term in $\vec{k}$ of the right-hand side of Eq. (1) is given by the expression

$$i \sum_\alpha \frac{\partial v(\vec{R})}{\partial R_\alpha} \int u_m^\dagger(\vec{q},0) \left(\frac{\partial u_m(\vec{q},\vec{k})}{\partial k_\alpha}\right)_0 d^3q. \quad (4)$$

Now we can evaluate $\partial u_m(\vec{q},\vec{k})/\partial k_\alpha$ by $\vec{k}\cdot\vec{p}$ perturbation theory.[7] Only first-order terms need be kept, since the derivative is to be evaluated at $\vec{k}=0$. But the first-order wave function has no component of the unperturbed state, when expanded in eigenstates of the unperturbed Hamiltonian. Thus, the expansion of $[\partial u_m(\vec{q},\vec{k})/\partial k_\alpha]_0$ in the set of Bloch states at the center of the zone will have no $u_m(\vec{q},0)$ component. It follows that the integral of Eq. (4) is exactly zero by the orthogonality of the states $u_n(\vec{q},0)$.

Now consider the second-order terms in $\vec{k}$ of Eq. (2). From the expansion Eq. (3), $v_{mm}(\vec{R})$ is given by

$$v_{mm}(\vec{R}) = v(\vec{R}) + \frac{1}{2} \sum_\alpha \sum_\beta I_{\alpha\beta} \left(\frac{\partial^2 v}{\partial R_\alpha \partial R_\beta} + \frac{\partial v}{\partial R_\alpha}\frac{\partial}{\partial R_\beta} + \frac{\partial v}{\partial R_\beta}\frac{\partial}{\partial R_\alpha}\right) + \sum_\alpha \sum_\beta J_{\alpha\beta} \left(\frac{\partial^2 v}{\partial R_\alpha \partial R_\beta} + \frac{\partial v}{\partial R_\beta}\frac{\partial}{\partial R_\alpha}\right), \quad (5)$$

up to second order in $\vec{k}$. $I_{\alpha\beta}$ and $J_{\alpha\beta}$ are defined by

$$I_{\alpha\beta} = \int u_m^*(\vec{q},0) \left(\frac{\partial^2 u_m(\vec{q},\vec{k})}{\partial k_\alpha \, \partial k_\beta}\right)_0 d^3q, \quad (6)$$

$$J_{\alpha\beta} = \int \left(\frac{\partial u_m^*(\vec{q},\vec{k})}{\partial k_\alpha}\right)_0 \left(\frac{\partial u_m(\vec{q},\vec{k})}{\partial k_\beta}\right)_0 d^3q. \quad (7)$$

The integrals $I_{\alpha\beta}$ and $J_{\alpha\beta}$ are real, a fact that follows from the symmetry relation $U_m^*(\vec{q},\vec{k})$ $= U_m(\vec{q},-\vec{k})$. Further, $J_{\alpha\beta} = -I_{\alpha\beta}$ follows from the fact that the normalization integral

$$\int u_m^*(\vec{q},\vec{k}) \, u_m(\vec{q},\vec{k}) \, d^3q$$

is independent of $\vec{k}$ and thus gives zero when differentiated first with respect to k_α and then with respect to k_β. Eq. (5) can thus be simplified to

$$v_{mm}(\vec{R}) = v(\vec{R}) - \tfrac{1}{2} \nabla^2 v(\vec{R})$$

$$- \left(I_{12} \frac{\partial^2 v}{\partial R_1 \partial R_2} + I_{23} \frac{\partial^2 v}{\partial R_2 \partial R_3} + I_{31} \frac{\partial^2 v}{\partial R_3 \partial R_1}\right). \quad (8)$$

In obtaining Eq. (8), we have made use of the fact that $I_{\alpha\alpha}$ is independent of α, assuming cubic symmetry, and have defined $I = I_{\alpha\alpha}$.

For an impurity potential, the form $v(R) = e^2/\chi R$ is valid for distances R much larger than the dimensions of the unit cell. Then the second term

of Eq. (8) is zero, since $\nabla^2 R^{-1} = 0$ for $R \neq 0$. In Ref. 4, a calculational error yielded an incorrect result [Eq. (21) of Ref. 4] for the second term of Eq. (8). This term was then estimated to increase the ionization energy by 10%.

Choosing $v(r) = e^2/\chi R$ as the acceptor potential, Eq. (8) can be written

$$v_{mm}(\vec{R}) = e^2/\chi R - (3e^2/\chi R^5) \; (I_{12} R_1 R_2 + I_{23} R_2 R_3 + I_{31} R_3 R_1).$$

$$(9)$$

To apply this to the ground state of holes in Ge, we adopt the simplified model of acceptor states used by Zak. The Bloch energy $\epsilon_m(k)$ for the valence band is assumed to be independent of the direction of $\vec{k}$ and given by the parabolic form $\epsilon_m(k) = (\hbar^2/2m^*)k^2$. m^* is an appropriately chosen effective mass.[8]

This model should certainly give results for physical properties correct to within a factor of two, and is probably much better. Since the correction term in the differential equation has been obtained explicitly in Eq. (9), this accuracy should also hold for the correction. Equation (1) is then

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2 + \frac{e^2}{\chi R} + H'\right) F_m(\vec{R}) = \epsilon F_m(\vec{R}), \qquad (10)$$

where the energy is measured from the top of the valence band. H' is the last term of Eq. (9):

$$H' = -(3e^2/\chi R^5) \; (I_{12} R_1 R_2 + I_{23} R_2 R_3 + I_{31} R_3 R_1).$$

$$(11)$$

H' will be nonzero only if the integrals I_{12}, I_{23}, and I_{31} do not vanish. In a tight-binding approximation, such as is used in Ref. 4, these integrals are zero.[9]

However, the $I_{\alpha\beta}$ is not zero, in general, unless assumptions are made concerning the symmetry properties of the Bloch states. If the effect of H' on ϵ is desired for the case where $I_{\alpha\beta} \neq 0$, it would be necessary to apply perturbation theory to H'. The first-order contribution would be zero, since H' changes sign when R_1, R_2, or R_3 changes sign, while the unperturbed ground state is unchanged. Hence, second-order perturbation theory would be necessary; the resulting correction would be smaller than the effect of the interband terms $n \neq m$ of Eq. (1). These interband terms give, as previously noted, a correction which is well under 1%.

Thus, the effect considered in Ref. 4 (gradients of the impurity potential in the vicinity of the impurity orbit) is too weak to affect the ionization energy. The R^{-1} potential varies too slowly to produce appreciable corrections.

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[8] Strictly speaking, when applied to the valence band of Si and Ge, the expansion Eq. (3) cannot be made unless the coefficients of k_α and $k_\alpha k_\beta$ are given an angular dependence on $\vec{k}$. This is due to the fact that the Bloch energy $\epsilon_m(k)$ has no Taylor-series expansion at $\vec{k} = 0$, due to the anisotropy of $\epsilon_m(k)$. However, if the anisotropy parameter C in the expansions for $\epsilon_m(k)$ is set to zero, then $\epsilon_m(k)$ and $u_m(\vec{q}, \vec{k})$ do possess the desired expansions. [See Eqs. (63) and (64) of the paper of G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955) for a definition of C.] We estimate that setting C to zero produces an error of at most 30% in the ionization energy and in the magnitude of the correction. Hence, setting C to zero does not affect the main conclusion of this note.

[9] To verify this one can insert the tight-binding form [Eq. (20) of Ref. 4] into the definition of the integrals $I_{\alpha\beta}$ [Eq. (6)] for $\beta \neq \alpha$. Assuming negligible overlap between the localized states, $I_{\alpha\beta}$ is proportional to an integral whose integrand is the product of the square of the localized wave function and the two perpendicular cartesian coordinates corresponding to α and β. Taking the square of the localized orbital to be an even function, $I_{\alpha\beta}$ is zero.