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kq Representation for the Impurity Problem in Semiconductors*

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It is shown that the *kq* representation leads to a separation of variables in the dynamics of electrons in perturbed crystals. The method is applied to the impurity problem in semiconductors, higher-order effects for the variation of the impurity potential being obtained. An explicit result is given for the second-order effect, which leads to a significant improvement of the theory.

The theory for the impurity problem in semiconductors started many years ago with the effective-mass approximation[1] (EMA). Since then, many improvements and corrections have been introduced into the theory in order to achieve a better agreement with experiment.[2] One of the main assumptions of all the theories based on the EMA is the slowness of variation of the impurity potential. Until now, no account has been taken of the higher-order effects connected with the slow variation of the impurity potential.

In this paper, a new approach is given to the EMA. It is well known that the solution of a given problem in physics can be significantly simplified by choosing suitable coordinates that best reflect the symmetry of the problem. In a solid, the most fundamental symmetry is its invariance under translations by a Bravais lattice vector $\vec{R}$. Because of this symmetry, the potential depends only on the location $\vec{q}$ of the electron inside a unit cell and does not depend on $\vec{R}$. This fact formed the basis for the application of the *kq* representation to the dynamics of electrons in solids.[3] Here the *kq* representation is applied to the impurity problem in semiconductors. Being based on the symmetry of the problem, the method developed is strikingly simple, leading for the first time to a qualitative explanation of the connection between the translational symmetry of a crystal and the simplicity of the fundamental results in the dynamics of electrons in perturbed solids. For the impurity problem, the method developed in this paper leads to an effective-mass equation to any order in the variation of the impurity potential. An explicit equation is derived, including the second-order effect, and it is shown that the correction can be very important in improving the agreement between theory and experiment.

We shall start with Schrödinger's equation in the coordinate representation for an electron in a periodic potential $V(\vec{r})$ and an impurity potential $\mathcal{V}(\vec{r})$,

$$[\vec{p}^{\,2}/2m + V(\vec{r}) + \mathcal{V}(\vec{r})]\,\psi(\vec{r}) = \epsilon\,\psi(\vec{r})\,. \tag{1}$$

In the *kq* representation, this equation becomes[3]

$$\left[-\frac{1}{2m}\frac{\partial^2}{\partial\vec{q}^{\,2}} + V(\vec{q}) + \mathcal{V}\left(i\frac{\partial}{\partial\vec{k}} + \vec{q}\right)\right]C(\vec{k}\vec{q}) = \epsilon\, C(\vec{k}\vec{q})\,. \tag{2}$$

In Eq. (2), $\vec{k}$ is the quasimomentum which gives the momentum of the electron up to a vector $\vec{K}$ of the reciprocal lattice $\vec{p}=\vec{K}+\vec{k}$, and $\vec{q}$ is the quasicoordinate which gives the radius vector of the electron up to a vector $\vec{R}$ of the Bravais lattice $\vec{r}=\vec{R}+\vec{q}$. Equation (2) is obtained from Eq. (1) by using the expressions for $\vec{p}$ and $\vec{r}$ in the *kq* representation[3] $\vec{p}=-i\,\partial/\partial\vec{q}$, $\vec{r}=i\,\partial/\partial\vec{k}+\vec{q}$. As was already mentioned before, the periodic potential V in Eq. (2) depends only on the quasicoordinate $\vec{q}$. The wave function[1] $C(\vec{k}\vec{q})$ in the *kq* representation is a Bloch-type function, and it satisfies the following conditions[3]:

$$C(\vec{k},\ \vec{q}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,C(\vec{k},\vec{q})\ , \tag{3}$$

$$C(\vec{k}+\vec{K},\ \vec{q}) = C(\vec{k},\vec{q})\ . \tag{4}$$

A straightforward treatment of the impurity problem is achieved by introducing the coordinates $\vec{R}$ and $\vec{q}$ (the Bravais lattice vector and the quasicoordinate correspondingly) into Schrödinger's equation. This can easily be carried out by using Eq. (2) and by defining a new wave function,

$$\psi(\vec{R},\vec{q}) = \int e^{i\vec{k}\cdot\vec{R}}\,C(\vec{k}\vec{q})\,d^3k\ , \tag{5}$$

where the integration in (5) is on the first Brillouin zone. Schrödinger's equation for the wave function $\psi(\vec{R},\vec{q})$ will be

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial\vec{q}^{\,2}} + V(\vec{q}) + \mathcal{V}(\vec{R}+\vec{q})\right)\psi(\vec{R},\vec{q}) = \epsilon\,\psi(\vec{R},\vec{q})\ . \tag{6}$$

In order to appreciate the simplicity achieved by the use of the coordinates $\vec{R}$ and $\vec{q}$, let us first analyze Eq. (6) qualitatively. In the absence of the impurity perturbation, the Hamiltonian does not depend on $\vec{R}$. This is a natural thing to expect and is a consequence of the translational symmetry of the crystal. According to the general rules of quantum mechanics if some coordinate does not appear in the Hamiltonian, the conjugate of this coordinate should be a constant of motion. For example, for a free electron, the radius vector $\vec{r}$ does not appear in the Hamiltonian and the momentum $\vec{p}$, the conjugate of the coordinate, is a constant of motion. For a Bloch electron [Eq. (6) with $\mathcal{V} = 0$], the Hamiltonian does not depend on $\vec{R}$ and the constant of motion is the quasimomentum $\vec{k}$ which by definition (5) is the conjugate of $\vec{R}$. That $\vec{R}$ and $\vec{k}$ are conjugate coordinates can also be seen from the expression of the radius vector $\vec{r}$ in the *kq* representation $\vec{r} = i\,\partial/\partial\vec{k} + \vec{q}$. Compare it with $\vec{r} = \vec{R} + \vec{q}$. It follows that $\vec{R} = i\,\partial/\partial\vec{k}$. From the last expression, one finds that the commutator of $\vec{R}$ and $\vec{k}$ equals i, i.e., that $\vec{R}$ and $\vec{k}$ are conjugate coordinates. The analogy between $\vec{r}$ and $\vec{p}$ for a free electron and $\vec{R}$ and $\vec{k}$ for a Bloch electron goes much further. To see it, we now develop an expansion for the wave function $\psi(\vec{R},\vec{q})$ in (5). This expansion will be of particular importance for the whole treatment of the impurity problem. The function $C(\vec{k}\vec{q})$ in (5) can be expanded in Bloch functions[3]

$$C(\vec{k}\vec{q}) = \sum_n B_n(\vec{k})\,\psi_{nk}(\vec{q}) = \sum_{n\vec{R}} e^{i\vec{k}\cdot\vec{R}}\,F_n(\vec{R})\,\psi_{nk}(\vec{q}) \,. \tag{7}$$

In Eq. (7), $F_n(\vec{R})$ is obtained from the expansion of the periodic function $B_n(\vec{k})$. By substituting (7) into (5), one gets

$$\psi(\vec{R},\ \vec{q}) = \sum_n \psi_{nk}(\vec{q})\,F_n(\vec{R}) \,, \tag{8}$$

where $\psi_{nk}(\vec{q})$ is an operator with $\vec{k}$ replaced by $-i\,\partial/\partial\vec{R}$ (here again $\vec{R}$ and $\vec{k}$ appear as conjugate coordinates) and was already used previously.[4] It should be noted that there are no assumptions and no approximations involved in expansion (8). In previous work,[4,5] the coordinate $\vec{R}$ was introduced without the quasicoordinate $\vec{q}$ and the separation of variables achieved by expansion (8) was not obtained before. It would not be easy to arrive at expansion (8) and Schrödinger's equation (6) without the *kq* representation.

Having expansion (8), let us continue the discussion of the Bloch electron ($\mathcal{V} = 0$). By substituting (8) into (6), multiplying from the left by the operator $\psi^{\dagger}_{mk}(\vec{q})$ [the operator $\psi^{\dagger}_{mk}(\vec{q})$ is obtained by replacing k by $-i\,\partial/\partial\vec{R}$ in the function $\psi^{\dagger}_{mk}(\vec{q})$, see Ref. 4], and integrating over $\vec{q}$ one finds the equation for $F_m(\vec{R})$,

$$\epsilon_m(\vec{k})\,F_m(\vec{R}) = \epsilon\,F_m(\vec{R}) \,. \tag{9}$$

This is a difference equation ($\vec{k} = -i\,\partial/\partial\vec{R}$) which for the energy $\epsilon = \epsilon_n(\vec{k})$ (here $\vec{k}$ is the quasimomentum) is satisfied by

$$F_m(\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\delta_{nm} \,. \tag{10}$$

The result in (10) is of great interest. It shows that in the $\vec{R}$ coordinate the Bloch electron moves like a free particle. In the latter case $\vec{p}$ and $\vec{r}$ come instead of $\vec{k}$ and $\vec{R}$. Result (10) also indicates that with respect to the $\vec{R}$ coordinate a crystal is a homogeneous medium. We see, therefore, that when described in the $\vec{R}$ coordinate an electron in a crystal behaves like a free particle with a Hamiltonian $\epsilon_m(\vec{k})$.

When the impurity potential is present in Eq. (6), the Hamiltonian clearly depends also on $\vec{R}$. There is, however, a very interesting feature of Eq. (6) that can be noted at once. If the perturbation potential does not change on a distance of a unit cell, then one can neglect the dependence of the perturbation in $\vec{q}$, and $\mathcal{V}$ will depend only on $\vec{R}$. The variables $\vec{R}$ and $\vec{q}$ separate in the Hamiltonian and one should therefore expect that in the $\vec{R}$ coordinate the electron will move as if there were no crystal. The Hamiltonian for the impurity problem will be

$$\epsilon_m(\vec{k}) + \mathcal{V}(\vec{R}) \,, \tag{11}$$

where $\epsilon_m(\vec{k})$ is the same operator as appeared for the unperturbed Bloch electron.

Let us now turn to the quantitative description of the problem. By substituting expansion (8) into Eq. (6), and by performing the same operations that led to Eq. (9), one finds the following equation for the function $F_m(\vec{R})$:

$$\epsilon_m(\vec{k})F_m(\vec{R}) + \sum_n \mathcal{V}_{mn}(\vec{R},\vec{k})F_n(\vec{R}) = \epsilon\,F_m(\vec{R}) \,, \tag{12}$$

where $\vec{k} = -i\,\partial/\partial\vec{R}$ and the operator $\mathcal{V}_{mn}$ is

$$\begin{aligned}\mathcal{V}_{mn}(\vec{R},\vec{k}) &= \int \psi^{\dagger}_{mk}(\vec{q})\,\mathcal{V}(\vec{R}+\vec{q})\,\psi_{nk}(\vec{q})\,d^3q \\ &= \int u^{\dagger}_{mk}(\vec{q})\,\mathcal{V}(\vec{r})\,u_{nk}(\vec{q})\,d^3q \,.\end{aligned} \tag{13}$$

In Eq. (13), $u_{nk}(\vec{q})$ is the periodic part of the Bloch function. Equation (12) is an exact multiband equation for the impurity problem for the wave function $F_m(\vec{R})$ in the *mR* representation (m is the band index and $\vec{R}$ is a Bravais lattice vector).

In the case when $\mathcal{V}(\vec{R})$ is a slowly varying function, it is convenient to interchange the order of two terms in (13):

$$\mathcal{V}(\vec{R})\,u_{nk}(\vec{q}) = u_{nk}(\vec{q})\,\mathcal{V}(\vec{R}) + [\,\mathcal{V}(\vec{R}),\ u_{nk}(\vec{q})] \,, \tag{14}$$

where the brackets in (14) stand for a commutator. Equation (13) will become

$$\mathcal{V}_{mn}(\vec{R},\vec{k}) = \mathcal{V}(\vec{R})\,\delta_{mn} + \int u^{\dagger}_{mk}(\vec{q})\,[\mathcal{V}(\vec{R}),\ u_{nk}(\vec{q})]\,d^3q \,. \tag{15}$$

The first term in (15) when substituted in Eq. (12) leads to the conventional effective-mass equation[1] with the Hamiltonian of Eq. (11)

$$[\epsilon_m(\vec{k}) + \mathcal{V}(\vec{R})]F_m(\vec{R}) = \epsilon F_m(\vec{R}) \ . \tag{16}$$

For a slowly varying $\mathcal{V}(\vec{R})$, it is now easy to obtain higher-order terms in the effective Hamiltonian from Eq. (15). To do this, let us write $u_{nk}(\vec{q})$ in powers of $\vec{k}$ about $\vec{k}_0$. Usually, $\vec{k}_0$ is chosen as an extremum of the energy function[1] $\epsilon_m(\vec{k})$. For simplicity, we assume $\vec{k}_0 = 0$ and no degeneracy. Then

$$u_{nk}(\vec{q}) = u_{n0}(\vec{q}) + \left(\frac{\partial u_{nk}}{\partial \vec{k}}\right)_0 \vec{k} + \frac{1}{2}\left(\frac{\partial^2 u_{nk}}{\partial \vec{k}\,\partial \vec{k}}\right)\vec{k}\ \vec{k} + \cdots . \tag{17}$$

This expansion can easily be generalized for any $\vec{k}_0$ and for a degenerate case.[6] The first term in (17) does not contain derivatives with respect to $\vec{R}$ and it gives a vanishing commutator in (15). The second term in (17) will lead to the following one-band first-order correction in (15):

$$\frac{\partial\, \mathcal{V}(\vec{R})}{\partial \vec{R}} \int u^*_{m0}(\vec{q}) \left(\frac{\partial u_{mk}(\vec{q})}{\partial \vec{k}}\right)_0 d^3q \ . \tag{18}$$

In general, this is a nonvanishing correction. However, most crystals of interest possess inversion symmetry and for them the integral in (18) vanishes.[1] We are left with the second-order one-band correction in (15)

$$-\frac{1}{2}\frac{\partial^2\, \mathcal{V}(\vec{R})}{\partial \vec{R}\,\partial \vec{R}} \int \left(\frac{\partial^2 u^*_{mk}(\vec{q})}{\partial \vec{k}\,\partial \vec{k}}\right)_0 u_{m0}(\vec{q})\, d^3q$$
$$+\frac{\partial\, \mathcal{V}(\vec{R})}{\partial \vec{R}}\ \frac{\partial}{\partial \vec{R}}\left[\int \left(\frac{\partial u^*_{mk}(\vec{q})}{\partial \vec{k}}\right)_0 \left(\frac{\partial u_{mk}(\vec{q})}{\partial \vec{k}}\right)_0 d^3q\right.$$
$$\left.+\int u^*_{m0}(\vec{q})\left(\frac{\partial^2 u_{mk}(\vec{q})}{\partial \vec{k}\,\partial \vec{k}}\right)_0 d^3q\right] . \tag{19}$$

For a known band structure [known $u_{mk}(\vec{q})$], the coefficients of $\partial^2 \mathcal{V}(\vec{R})/\partial\vec{R}\,\partial\vec{R}$ and $[\partial \mathcal{V}(\vec{R})/\partial\vec{R}]\,(\partial/\partial\vec{R})$ in (19) can be calculated. Here, let us give an estimate of the second-order correction. For this we write $u_{mk}(\vec{q})$ by means of Wannier functions[7] $a_m(\vec{q})$

$$u_{mk}(\vec{q}) = \sum_R \exp[i\vec{k}\cdot(\vec{R} - \vec{q})]\, a_m(\vec{q} - \vec{R}) . \tag{20}$$

Using formula (20), assuming very small overlap of the Wannier functions on different sites, and assuming also cubic symmetry for $a_m(\vec{q})$, the second-order correction becomes

$$\frac{1}{2}\frac{\partial^2 \mathcal{V}(\vec{R})}{\partial R^2}\ \bar{r}^2_m , \tag{21}$$

where $\bar{r}^2_m = \int d^3r\, r^2\, |a_m(\vec{r})|^2$ (22)

is the average of the square of the radius vector $\vec{r}$ in the Wannier state $a_m(\vec{r})$. In order to obtain result (21), we have also assumed that the impurity potential depends only on the absolute value of $\vec{R}$.

Let us now write down the corrected effective Hamiltonian equation. We assume that the impurity potential is $\mathcal{V} = - e^2/\chi r$ (χ is the dielectric constant). We have

$$[\epsilon_m(\vec{k}) - (\epsilon^2/\chi R) - \bar{r}^2_m\, e^2/\chi R^3]\ F_m(\vec{R}) = \epsilon\, F_m(\vec{R}) \ . \tag{23}$$

The third term on the right-hand side of (23) is of the order $(\bar{r}_m/R_i)^2$ with respect to the second term, where R_i is of the order of the impurity radius. That the correction term has to be of the order $(\bar{r}_m/R_i)^2$ was one of the main predictions[1] of the EMA. Here we have obtained the term explicitly. The important point is that the correction term depends on the band index and therefore one will, in general, have different corrections for different bands. In order to estimate the correction in the energy levels that is caused by this term let us notice that Eq. (23) can approximately be written without the correction term but with a modified dielectric constant

$$\chi_m = \frac{\chi}{1 + (\bar{r}_m/R_i)^2} \ . \tag{24}$$

The energy levels of the impurity atom for the conventional equation (11) are[1]

$$\epsilon_n = -(m^* e^4/2\hbar^2\chi^2)(1/n^2). \tag{25}$$

Here m^* is the effective mass for the band under consideration. For the corrected levels we have

$$\bar{\epsilon}_n \approx \epsilon_n[1 + 2(\bar{r}_m/R_i)^2] . \tag{26}$$

In order to compare the correction in (26) with experiment, one has to know the average radius $\bar{r}_m$ in the corresponding Wannier state. A reasonable number for $\bar{r}_m$ is the lattice constant, since it is reasonable to assume that a Wannier function is spread out over a unit cell of the Bravais lattice.[7] For a comparison with experiment, let us take as an example the ionization energy for acceptor levels in Ge where the EMA is known to work very well[8] (the following data are taken from this reference). The theoretical value according to formula (25) is 8.9 meV ($m^*_h/m \approx 0.3$, $\chi = 16$). The experimental ionization energy is almost the same for different acceptors and is about 10 meV. Since we have $R_i \approx 25$ Å for the ground state of an acceptor and we have $\bar{r}_m \approx a_{\text{latt}} = 5.6$ Å, the correction to the ionization energy according to formula (26) is about 10% (with the right sign). As we see, the agreement with experiment is excellent! One should note that, in general, the corrected formula (26) leads to larger ionization energies than does formula (25), and thus to better agreement with experiment.

In conclusion, we would like to make a number of remarks. First, the striking simplicity of the derivation of the EMA in the $\vec{R}$ and $\vec{q}$ coordinates should be stressed. These coordinates are most suitable for the description of the motion of an electron in a perturbed crystal because they lead to a separation of variables. It is because of the simplicity of the method developed in this paper that it becomes possible to calculate higher-order terms in the effective-mass Hamiltonian. Corrections that are connected with the slowness of variation of the impurity potential were never before introduced in the EMA. As was shown here, these corrections can be very significant and lead in general to a better agreement with experiments.

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Role of Oxygen in (Zn, O) Doped GaP

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A study of the temperature dependence of the decay time and luminescent intensity of the infrared emission in (Zn,O) doped GaP has unambiguously identified this emission at room temperature as a radiative transition resulting from the recombination of a bound electron at an oxygen donor with a free hole in the valence band. From the temperature dependence of the decay time and the variation of the decay times as a function of free-hole concentration at room temperature, it is concluded that the recombination of the bound electron at an oxygen donor with the free hole is primarily radiative.

I. INTRODUCTION

The ionization energy of the oxygen donor (E_D) in GaP at 1.6 °K is 0.895 eV.[1,2] GaP doped with oxygen and shallow acceptors has revealed the following radiative recombinations at low temperatures: (i) a bound exciton transition[3,4] at the nearest-neighbor O-Zn or O-Cd complex, responsible for the efficient luminescence in red diodes; (ii) overlapping with this bound exciton emission, a red pair emission[4] due to the recombination of an electron bound at the oxygen site of the complex with a hole at a remote Zn or Cd acceptor; (iii) an electron capture "internal" emission involving a transition from the excited state of the oxygen donor to its ground state[5]; (iv) conventional donor-acceptor (DA) pair recombination involving the oxygen donor and shallow acceptors such as C, Zn, and Cd. An example of (iv) involves an isolated oxygen donor and zinc acceptor ($E_A \sim 0.064$ eV) to yield a DA pair spectrum in the near infrared (peaked at ~1.35 eV) at low temperatures. At 300 °K and at higher temperatures most of the zinc acceptors are ionized,[6,7] which implies that DA spectra should be weak or absent at these temperatures. However, because of the increased availability of the free holes, the bound electrons at O^+ are likely to recombine with free holes. This paper reports on the association of the room-temperature infrared spectrum peaked at ~1.36 eV in (Zn, O) doped GaP with the luminescence caused by the radiative recombination of a bound electron at an oxygen site with a free hole (henceforth referred to as BF transition), as reflected in the decay time and the temperature dependence of the intensity of the infrared emission. In the past it