

ON THE THEORY OF IMPURITY LEVELS

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A method for consistently and exactly taking interactions into account is proposed and is applicable to investigations of impurity levels in solids. The model case of a short-range potential, which yields an exact solution, is considered. The impurity-level problem is solved exactly in the one-dimensional Kronig-Penney model. An equation for the discrete energy values is derived and the explicit form of the impurity-state wave function is calculated.

1. FORMULATION OF PROBLEM

THE inapplicability of perturbation theory to the investigation of the spectrum is one of the main difficulties in the theory of impurity levels in solids. In the case of shallow levels in semiconductors, the problem becomes trivial because of the applicability of the effective-mass approximation. In the case of deeper levels, and also virtual levels lying within the limits of the allowed band, it is necessary, generally speaking, to take explicit account of the periodic potential of the ideal crystal. The latter becomes fundamental for impurity centers with short-range interaction potential, when the effective radius becomes of the same order of magnitude as the lattice constant (or smaller). To investigate such problems, one can start from the method of successive and exact allowance for interactions without the use of perturbation theory. In other words, it is necessary to formulate the problem in such a way as to be able to solve it with allowance for one interaction and then take the second interaction into account without thereby making any assumptions (see below).

Let us assume that the Hamiltonian of the problem of one electron contains two terms in the expression for the potential energy, $V_1(x)$ and $V_2(x)$. The equation for the Green's function $G_i(x, x')$, with allowance for the interaction of the electron with the potential $V_i(x)$, is ($i = 1, 2$):

$$[E - T_x - V_i(x)]G_i(x, x') = -\delta(x - x'). \tag{1}$$

The equation for the complete Green's function takes the form

$$[E - T_x - V_1(x) - V_2(x)]G(x, x') = -\delta(x - x'). \tag{2}$$

We seek for the complete Green's function an equation in a convenient form ($i \neq j$)

$$G(x, x') + \int dx'' G_i(x, x'') V_j(x'') G(x'', x') = G_i(x, x'). \tag{3}$$

We can verify directly that Eq. (3) with allowance for Eq. (1) actually reduces to Eq. (2).

Thus, on the basis of Eqs. (1) and (3) (or, in place of (1), on the basis of an integral equation of the type (3) with the unperturbed Green's function $G_0(x, x')$), we can take into account the two interactions in succession and exactly. It is immaterial which interaction is considered first. What is important is that the Green's

function for the i -th interaction is the kernel of the integral equation for the complete Green's function. If the i -th interaction leads to the occurrence of discrete levels (corresponding to poles of the Green's function), then it is impossible to use ordinary integration near these poles when solving Eq. (3), no matter how small the j -th interaction may be.

We investigate Eq. (3) in the model case of a short-range potential, which admits of an exact solution:

$$V_2(x) = V_2 \delta(x - x_0). \tag{4}$$

As the first interaction $V_1(x)$ we can choose any static interaction, which we shall not specify concretely for the time being.

In our case ($i = 1, j = 2$), the complete Green's function can be written in the form

$$G(x, x') = G_1(x, x') - \frac{V_2 G_1(x, x_0) G_1(x_0, x')}{1 + V_2 G_1(x_0, x_0)}. \tag{5}$$

Let us assume that the Green's function $G_1(x, x')$ is known; it can be represented in the form

$$G_1(x, x') = - \sum_l \frac{\bar{\psi}_l(x) \psi_l(x')}{E - E_l}, \tag{6}$$

where $\psi_l(x)$ are the exact wave functions of the solution of the Schrödinger equation with potential $V_1(x)$ and l numbers the states. The density of the energy states of the system is determined in terms of the complete Green's function from the well known formula

$$\rho(E) = \frac{2}{\pi} \int dx \text{Im } G(x, x). \tag{7}$$

Taking (5) and (6) into account, as well as that the functions $\psi_l(x)$ are orthonormal, we obtain for the density of states the exact formula

$$\rho(E) = \frac{2}{\pi} \text{Im} \left\{ - \sum_l \frac{1}{E - E_l} - \frac{\partial}{\partial E} \ln |1 + V_2 G_1(x_0, x_0)| \right\}. \tag{8}$$

For concreteness, let us consider the case of impurity levels in a solid with a short-range interaction potential, when it is reasonable to use the model potential (4). As the first interaction we take the periodic potential of an ideal lattice. We then have for the quantum number $l = \{n, k\}$, where n is the number of the band and k is a quasiwave vector; $E = E_n(k)$ is the dispersion law and $\psi_l(x) = e^{ikx} u_{n,k}(x)$ are Bloch func-

tions. The density of states assumes in this case the form

$$\rho(E) = \frac{2}{\pi} \text{Im} \left\{ - \sum_{n,k} \frac{1}{E - E_n(k)} - \frac{\partial}{\partial E} \ln \left| 1 - V_2 \sum_{n,k} \frac{|u_{n,k}(x_0)|^2}{E - E_n(k)} \right| \right\} \quad (9)$$

The obtained formula gives an exact criterion for the existence of a discrete level. Namely, a discrete level can arise only if the energy E lies within the limits of the forbidden band. On the other hand, if the energy is in the allowed band, then we have a virtual level, owing to the presence of an imaginary part in the denominator of (9). We see that the position of the level is influenced, generally speaking, by all the bands of the ideal lattice. It is important to emphasize that to determine the position of the level it is not sufficient merely to know the dispersion law of the ideal crystal (as is done in an analogous situation in the paper of I. M. Lifshitz^[1]); it is necessary also to know the Bloch functions.

2. EXACT SOLUTION OF THE IMPURITY-LEVEL PROBLEM IN THE KRONIG-PENNEY MODEL

The exact formulas obtained above are valid both in a real three-dimensional case and in a model one-dimensional case. It is of interest to consider the model problem, where an exact solution can be obtained.

Assume that we have a one-dimensional chain of periodically arranged atoms with δ -like potentials for the interaction with a light particle. Assume that the "crystal" deviates from ideal at one point x_0 . The deviation may be a vacancy, a foreign atom, or an atom in an interstice. In accordance with the formulation of the problem in Sec. 1, we can solve the problem first without taking into account, the deviation from ideality, and obtain the corresponding Green's function. Further, substituting this function in (5), we can obtain the exact Green's function for the system in the presence of the violation. We are interested in the spectrum of the system, which is determined from the equation

$$1 + V_2 G_1(x_0, x_0) = 0. \quad (10)$$

The determination of the Green's function of the ideal "crystal" entails no difficulty in our case. Its explicit form is known (see, for example,^[2]):

$$G_1(x, x') = G_0(x, x') + \frac{1}{2\pi a} \int dq dq' \frac{e^{iqx - iq'x'}}{(q'^2 - \alpha^2)(q^2 - \alpha^2)} \frac{\gamma_1}{1 - \gamma_2},$$

$$\gamma_1 = \sum_n V \delta(q - q' + b_n),$$

$$\gamma_2 = 1 - V \sum_n \frac{1}{(q' + b_n)^2 - \alpha^2}. \quad (11)$$

Here $G_0(x, x')$ is the Green's function of the free particle, a is the "lattice" constant, V is the amplitude of the δ -like potentials located at the "lattice" sites, $\alpha = \sqrt{E}$ ($\hbar = 2m = 1$), $b_n = 2\pi n/a$ ($n = 0, \pm 1, \pm 2, \dots$).

With allowance for the equation ($P = aV/2, 0 \leq x_0 \leq a$)

$$\sum_n \frac{V e^{ix_0 b_n}}{(q + b_n)^2 - \alpha^2} = \frac{P}{a(\cos qa - \cos aa)}$$

$$\times [e^{-iq(x_0 - a)} \sin \alpha x_0 + e^{-iqx_0} \sin \alpha(a - x_0)],$$

the expression for the Green's function takes the form

$$G_1(x, x') = \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \frac{e^{iq'(x-x')}}{q'^2 - \alpha^2} \left\{ 1 + \frac{(P/aa) [e^{-iq'(x-a)} \sin \alpha x + e^{-iq'x} \sin \alpha(a-x)]}{\cos q'a - \cos aa - (P/aa) \sin aa} \right\}$$

To calculate this integral it is convenient to use the following method. We break up the integral with respect to q' into integrals from b_n to b_{n+1} and sum over all n . Then, carrying out the corresponding summation under the integral sign, we obtain at $x = x' = x_0$

$$G_1(x_0, x_0) = \frac{\sin aa}{2\alpha} \left[1 + \frac{P}{aa} \frac{2 \sin \alpha x_0 \sin \alpha(a - x_0)}{\sin aa} \right] \frac{1}{2\pi} \int_0^{2\pi} \frac{dx}{\cos x - \cos aa - (P/aa) \sin aa}. \quad (12)$$

If we are interested in discrete levels lying within the limits of the forbidden bands, then the denominator of the integrand in (12) does not vanish and the integration yields

$$G_1(x_0, x_0) = \frac{\sin aa}{2\alpha} \left[1 + \frac{P}{aa} \frac{2 \sin \alpha x_0 \sin \alpha(a - x_0)}{\sin aa} \right] \times \left[\left(\cos aa + P \frac{\sin aa}{aa} \right)^2 - 1 \right]^{-1/2}.$$

The corresponding equation for the determination of the positions of the discrete levels is

$$\left[1 + \frac{P}{aa} \frac{2 \sin \alpha x_0 \sin \alpha(a - x_0)}{\sin aa} \right] P_2 \frac{\sin aa}{aa} = - \left[\left(\cos aa + P \frac{\sin aa}{aa} \right)^2 - 1 \right]^{1/2} \quad (13)$$

under the condition

$$\left| \cos aa + P \frac{\sin aa}{aa} \right| > 1.$$

As is evident from (13), the equation for the determination of the discrete levels depends on the location of the impurity atom x_0 . Consequently, the position of the discrete level can vary when the impurity atom is moved from a site to an interstice. It is also easily seen that the levels can be produced in all the forbidden bands both in the case $P_2 < 0$ and when $P_2 > 0$.

We now turn to the determination of the wave functions of the discrete impurity states. The wave function satisfies the integral equation (compare with (3))

$$\psi(x) + \int dx'' G_1(x, x'') V_2(x'') \psi(x'') = 0.$$

In our model case, obviously, we have

$$\psi(x) = -\psi(x_0) V_2 G_1(x, x_0), \quad (14)$$

where $\psi(x_0)$ is determined by the condition for the normalization of the wave functions. The explicit expression for the Green's function $G_1(x, x_0)$ of the ideal "lattice" is

$$\frac{1}{2\alpha} \frac{1}{\text{sh } \gamma} \left\{ \sin \alpha(r - x_0) e^{-\gamma|r-m+1|} + \left[\sin \alpha(a - r + x_0) + \frac{2P}{aa} \sin \alpha(a - r) \sin \alpha x_0 \right] e^{-\gamma|m|} \right\}$$

when $r \geq x_0$ and

$$\frac{1}{2\alpha} \frac{1}{\text{sh } \gamma} \left\{ \sin \alpha(x_0 - r) e^{-\gamma|m-1|} + \left[\sin \alpha(a + r - x_0) + \frac{2P}{aa} \sin \alpha(a - x_0) \sin \alpha r \right] e^{-\gamma|m|} \right\}$$

when $r \leq x_0$, where

$$\operatorname{ch} \gamma = \left| \cos \alpha a + P \frac{\sin \alpha a}{\alpha a} \right| > 1,$$

$$x = m a + r, \quad 0 \leq r \leq a, \quad 0 \leq x_0 \leq a$$

(m is a positive or negative integer).

We see that with increasing distance from the location of the impurity x_0 , the wave function decreases in the main like

$$\psi(x) \sim \exp\{-\gamma |x - x_0| / a\},$$

and therefore the quantity $r_i = a/\gamma_i$ serves as the radius of the local state.

The wave function of the discrete state depends on the position of the discrete level in the forbidden band. In the expression for the wave function (14), it is necessary to substitute those values of the energies (or α) which are obtained by solving Eq. (13). For the radius of the local state of the i -th level we have

$$r_i = a / \operatorname{Arch} \left[\cos \alpha a + P \frac{\sin \alpha a}{\alpha a} \right]_{\alpha = \alpha_i},$$

where α_i is the i -th solution of Eq. (13). It is easy to verify that the smallest localization radius is obtained when the discrete level is in the center of the forbidden band, and $r_i \sim a$ in order of magnitude. In the case of shallow levels, when the values of α_i are sufficiently close to the values of α corresponding to the edges of the forbidden bands, the radius of the local state can greatly exceed the "lattice" constant a .

In conclusion we note that the problem was considered in an analogous formulation by Koster and

Slater^[3], who confirmed themselves, however, to a one-band approximation, with the result that the solution obtained by them differs appreciably from the exact (13). In our case allowance is made for the contributions of all the bands, by determining the explicit form of the Green's function of the ideal "crystal." Thus we see that it is not always convenient to represent the Green's function in the form of a bilinear expansion in eigenfunctions. By forgoing the expansion here, we succeeded in solving the impurity-level problem exactly in the Kronig-Penney model. It is not particularly difficult to consider by the same method the problem of impurity levels in a one-dimensional diatomic chain with δ -like potentials (the analog of III-V crystals). Moreover, we can pose the problem of two, three, etc. impurity centers and obtain exact solutions. The indicated approach is equally valid in the three-dimensional case, but encounters computational difficulties.

¹I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys.-Usp. 7, 549 (1965)].

²S. V. Maleev, Fiz. Tverd. Tela 7, 2990 (1965) [Sov. Phys.-Solid State 7, 2423 (1966)].

³G. F. Koster and J. C. Slater, Phys. Rev., 95, 1167 (1954).