PHYSICAL REVIEW VOLUME 186, NUMBER 3 15 OCTOBER 1969

Band Structure and Impurity States

F. Bassani
Istituto di Fisica, Università di Pisa, Italy, Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Recerche, Sezione di Pisa, Italy

G. Iadonisi and B. Preziosi
Istituto di Fisica Teorica, Università di Napoli, Italy, Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Recerche, Sezione di Napoli, Italy

(Received 14 April 1969)

A general formulation of the theory of electron impurity states in a lattice in the extended zone scheme is presented. The dependence of the impurity states on the band structure is discussed, and it is shown that the existence of secondary extrema in the band structure may produce additional bound and resonant states. A prescription is given for computing such states and for estimating the probabilities of transitions to them from the ground state; some properties of these transition probabilities are discussed. Solutions of one-dimensional models are presented explicitly.

I. INTRODUCTION

The problem of the electron eigenstates of an impurity in a periodic lattice is a classical one in the physics of semiconductors and insulators.[1] Koster and Slater[2] have developed an approach based on the expansion of the exact eigenfunctions in Wannier functions[3] and have shown how to compute the bound states for the case of strongly localized potentials. Adams[4] and Kohn and Luttinger[5] have developed an approach based on the expansion of the exact eigenfunctions in Bloch functions and have shown that for slowly varying impurity potentials this leads to the effective-mass formalism. This formalism has been applied with great success to computing the bound states of impurities in semiconductors and insulators.[1,6]

More recently, attention has been focused on the existence of resonant states which are degenerate with the continuum and originate from subsidiary minima in the band structure.[7] Peterson[8] has investigated the nature of such resonant states in the framework of the effective-mass approximation and has given an estimate of their lifetimes. Liu and Brust[9] have developed a formalism appropriate to resonant states introduced by impurities in a zero-gap semiconductor.

Experimental evidence which points to the existence of resonant states in semiconductors has been given by Kosicki and Paul[10] for donor states, and for the case of acceptor states by Zwerdling, Button, Lax, and Roth[11] and more recently by Onton, Fisher, and Ramdas.[12] In alkali-halide crystals, F-center transitions of energies well above ionization have been known for some time as the L bands,[13] and recent modulated absorption experiments have demonstrated that they all originate from the same ground state.[14] Sharp excitonic transitions above the exciton ionization energy have also been observed by optical experiments.[15]

The present paper is an attempt to develop a general formulation of the problem of impurity states in a periodic potential and to draw some conclusions on the nature of the bound and resonant states. To simplify the formalism, we use the extended zone scheme as in a previous paper[16]; but all the results could be rewritten in the reduced zone scheme using the appropriate band indices. The presence of secondary minima at energies higher than the absolute minimum of the conduction band is shown to influence the bound states produced by an attractive potential. It displaces their energies with respect to the values obtained using the effective-mass approximation, and it may produce new bound and resonant states. For the case of slowly varying potentials, a detailed prescription is given to evaluate such states taking into account intervalley coupling in first order. The transition probabilities between impurity states are examined, and the contribution of the secondary minima is shown to be of importance. The

---

[1] J. Callaway, in *Energy Band Theory* (Academic Press Inc., New York, 1964), Chap. 4; W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257; W. Beall Fowler, *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968).

[2] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); **96**, 1208 (1954).

[3] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

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

[5] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[6] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[7] H. Kaplan, J. Phys. Chem. Solids **24**, 1593 (1963).

[8] G. A. Peterson, in *Proceeding of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 771.

[9] L. Liu and D. Brust, Phys. Rev. **157**, 627 (1967).

[10] B. B. Kosicki and W. Paul, Phys. Rev. Letters **17**, 246 (1966); See also W. Paul, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors* (Nauka Publishing House, Leningrad, 1968) Vol. I, p. 16.

[11] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters **4**, 173 (1960).

[12] A. Onton, P. Fisher, and A. K. Ramdas, Phys. Rev. **163**, 868 (1967).

[13] W. D. Compton and J. H. Shulman, *Color Centers in Solids* (Pergamon Publishing Corp., New York, 1962), Sec. 3.7, p. 101.

[14] G. Chiarotti and U. Grassano, Phys. Rev. Letters **16**, 124 (1966); G. Chiarotti and U. Grassano, Nuovo Cimento **46B**, 78 (1966).

[15] J. E. Ebey, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959); H. R. Phillip and H. E. Ehrenreich, Phys. Rev. **131**, 2016 (1963); G. Baldini and B. Bosacchi, *ibid.* **166**, 863 (1968).

[16] G. Iadonisi and B. Preziosi, Istituto di Fisica Teorica, University of Naples, Naples, 1968 (unpublished).

above results are instructively displayed with the aid of appropriate one-dimensional models.

In Sec. II, we present a formal discussion of the eigenvalues and eigenfunctions appropriate to any type of impurity potential and give a general method to compute them. In Sec. III, we investigate in detail the influence of the band structure on the impurity states for the case of a slowly varying potential. In Sec. IV, we discuss the transition probabilities including the contribution of different minima in the band structure to the localized wave functions. In Sec. V, we present soluble one-dimensional examples to show the behavior of bound and resonant states. In Sec. VI, we summarize the results and discuss the connection with some experimental data.

II. DISCUSSION OF BOUND AND SCATTERING STATES

The general equation in the extended zone scheme for the states of the Bloch electron in an impurity potential is[2–5,16]

$$[E(\mathbf{k})-E]\varphi(\mathbf{k})+\int d\mathbf{k}'U(\mathbf{k},\mathbf{k}')\varphi(\mathbf{k}')=0\,, \qquad (1a)$$

where $E(\mathbf{k})$ describes the energy-band structure, $\varphi(\mathbf{k})$ indicates the coefficients of the electron wave function when expanded in Bloch functions

$$\Phi(\mathbf{r})=\int d\mathbf{k}\;\varphi(\mathbf{k})\psi(\mathbf{k},\mathbf{r})\,, \qquad (1b)$$

and $U(\mathbf{k},\mathbf{k}')$ is the Bloch matrix element of the impurity potential $U(\mathbf{r})$:

$$U(\mathbf{k},\mathbf{k}')=\frac{1}{(2\pi)^3}\int d\mathbf{r}\,\psi^*(\mathbf{k},\mathbf{r})U(\mathbf{r})\psi(\mathbf{k}',\mathbf{r})\,. \qquad (1c)$$

In the preceding formulas and in the following, the integrals on $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{r}$ refer to the whole space, unless otherwise specified. The solutions of Eq. (1a) give all the states of the electron in the presence of the periodic potential and of the impurity potential.

We can obtain formal solutions of Eq. (1a) by reducing the kernel (1c) of the integral equation to a sum of products of functions of $\mathbf{k}$ alone by functions of $\mathbf{k}'$ alone, according to a general procedure which is well known in the theory of integral equations[17] and has found applications in scattering theory.[18] We introduce a complete set of states $g_n(\mathbf{r})$ and insert in (1c),

$$\int \delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'=\sum_n\int d\mathbf{r}'g_n^*(\mathbf{r})g_n(\mathbf{r}')$$

to obtain

$$U(\mathbf{k},\mathbf{k}')=\frac{1}{(2\pi)^3}\sum_n\int d\mathbf{r}\int d\mathbf{r}'\psi^*(\mathbf{k},\mathbf{r})\times U(\mathbf{r})g_n^*(\mathbf{r})g_n(\mathbf{r}')\psi(\mathbf{k}',\mathbf{r}')\,. \qquad (2a)$$

It can be noticed that $U(\mathbf{k},\mathbf{k}')$ is a sum of separable potentials. To simplify the discussion, we consider explicitly only the case in which the potential $U(\mathbf{r})$ is attractive and write

$$U(\mathbf{k},\mathbf{k}')=-\sum_n f_n^*(\mathbf{k})f_n(\mathbf{k}')\,, \qquad (2b)$$

where

$$f_n(\mathbf{k})=\frac{1}{(2\pi)^{3/2}}\int d\mathbf{r}\,\psi(\mathbf{k},\mathbf{r})[-U(\mathbf{r})]^{1/2}g_n(\mathbf{r})\,. \qquad (2c)$$

In the case of a finite range potential, we can always choose a discrete set $g_n(\mathbf{r})$ such that the overlap of $g_n(\mathbf{r})$ with $U(\mathbf{r})$ becomes negligible for n larger than a finite $\bar{n}$. The integral equation (1a) becomes

$$[E(\mathbf{k})-E]\varphi(\mathbf{k})-\sum_n f_n^*(\mathbf{k})\int d\mathbf{k}'f_n(\mathbf{k}')\varphi(\mathbf{k}')=0\,. \qquad (3)$$

A general solution of Eq. (3) will be of the form

$$\varphi(\mathbf{k})=P\sum_n f_n^*(\mathbf{k})\int d\mathbf{k}'\,f_n(\mathbf{k}')\varphi(\mathbf{k}')/[E(\mathbf{k})-E]+\alpha(\mathbf{k},E)\delta(E(\mathbf{k})-E)\,, \qquad (4)$$

where $\alpha(\mathbf{k},E)$ is a function to be determined from the boundary conditions, and P indicates that the principal part has to be taken in any integral. Introducing a_n, the set of constants given by

$$a_n=\int d\mathbf{k}'f_n(\mathbf{k}')\varphi(\mathbf{k}')\,, \qquad (5a)$$

we obtain the infinite number of consistency conditions

$$a_n=\sum_{n'}a_{n'}P\int d\mathbf{k}'\frac{f_n(\mathbf{k}')f_{n'}^*(\mathbf{k}')}{E(\mathbf{k}')-E}+\int d\mathbf{k}'f_n(\mathbf{k}')\alpha(\mathbf{k}',E)\delta(E(\mathbf{k}')-E)\,. \qquad (5b)$$

The general wave function (1′) of the impurity problem can be written in terms of the coefficients a_n and of the function $\alpha(\mathbf{k},E)$ as

$$\Phi_E(\mathbf{r})=\sum_n a_nP\int d\mathbf{k}\frac{f_n^*(\mathbf{k})\psi(\mathbf{k},\mathbf{r})}{E(\mathbf{k})-E}+\int d\mathbf{k}\alpha(\mathbf{k},E)\psi(\mathbf{k},\mathbf{r})\delta(E(\mathbf{k})-E)\,. \qquad (6)$$

---

[17] F. G. Tricomi, *Integral Equations* (Wiley-Interscience, Inc., New York, 1957), p. 55–64, 98.

[18] R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill Book Co., New York, 1966).

Equations (5b) and (6) allow an analysis of all the properties of the eigenstates as functions of the band structure $E(\mathbf{k})$ and of the impurity potential contained in $f_n(\mathbf{k})$.

First, let us consider energies such that $E\neq E(\mathbf{k})$ for any value of $\mathbf{k}$; they correspond to the negative-energy states of the usual scattering theory, but in the present case, with the periodic potential, they may occur whenever there is an energy gap in $E(\mathbf{k})$. The second terms on the right-hand sides of Eqs. (5b) and (6) vanish. The eigenvalues are obtained from the condition that the homogeneous system of Eq. (5b) admits nonvanishing solutions for a_n. This happens in correspondence to the zeros of the Fredholm determinant

$$\mathrm{Det}\left|\delta_{nn'}-\int d\mathbf{k}'\frac{f_n(\mathbf{k}')f_{n'}^*(\mathbf{k}')}{E(\mathbf{k}')-E}\right|=0. \tag{7}$$

The values of E which satisfy Eq. (7) give the bound states of the system, and it can be easily shown that the corresponding wave functions (6) are localized.

Let us now consider the scattering states such that a surface in $\mathbf{k}$ space exists where $E=E(\mathbf{k})$. The function $\alpha(\mathbf{k},E)$ is specified on that surface by requiring that the function $\Phi(\mathbf{r})$ of Eq. (6) contain an incoming wave only in a given direction defined by the initial velocity, as indicated by Lifshitz and Kaganoff.[19] Consequently, the value of $\alpha(\mathbf{k},E)$ is arbitrary only in that specific direction $\mathbf{k}_0$, while in the other directions all incoming waves cancel. This corresponds to replacing the second term on the right-hand side of Eq. (4) by $\alpha\delta(\mathbf{k}-\mathbf{k}_0)$, with $E(\mathbf{k}_0)=E$, and to extending the energies of the first term into the complex plane by substituting $E+i\epsilon$ for E. The result obtained is that $\Phi(\mathbf{r})$ is composed of an incoming Bloch wave and of outgoing waves. If we subtract from $\Phi(\mathbf{r})$ its asymptotic part, we are left with a localized function. Under specific conditions and for some values of the energy, the localized function contained in $\Phi(\mathbf{r})$ may be abnormally large, and this corresponds to the resonances well known in scattering theory. Next we show that in our formulation the energies at which resonances occur can be found as the real parts of the complex solutions of Eq. (7) extended into the domain of E complex. In fact, let us normalize the incoming wave so that $\alpha=1$, and let us suppose that the analytic continuation of Eq. (7) onto the nonphysical sheet admits a complex solution with real part E_0 and with imaginary part Γ such that $\Gamma\ll E_0$, the zero of energy being referred to the minimum of the band in which the resonant state is contained. The condition $\Gamma\ll E_0$ corresponds to a solution near the real axis and far from the origin of the cuts in the complex E plane.

The system of linear equations (5b) for that energy becomes

$$\sum_{n'}\left(\delta_{nn'}-\int d\mathbf{k}'\frac{f_n(\mathbf{k}')f_{n'}^*(\mathbf{k}')}{E(k')-E-i\epsilon}\right)a_{n'}=f_n(\mathbf{k}_0), \tag{5'}$$

and admits an exceptionally small determinant for E near to E_0. Consequently, the coefficients a_n are exceptionally large when E is near E_0. For the case of a finite range potential, since with an appropriate choice of the set $g_n(\mathbf{r})$, the functions $f_n(\mathbf{k})$ become first-order small for all values of k for $n>\bar{n}$, we have only a finite number $\bar{n}$ of exceptionally large coefficients a_n. That this is the condition for the existence of a resonant state can be seen by writing the wave function (6) for the present case as

$$\Phi(\mathbf{r})=\sum_n a_n\int d\mathbf{r}'\,G(\mathbf{r},\mathbf{r}')g_n(\mathbf{r}')[-U(\mathbf{r}')]^{1/2} +\psi(\mathbf{k}^0,\mathbf{r}), \tag{6'}$$

where

$$G(\mathbf{r},\mathbf{r}')=\frac{1}{(2\pi)^3}\int d\mathbf{k}\frac{\psi^*(\mathbf{k},\mathbf{r})\psi(\mathbf{k},\mathbf{r}')}{E(\mathbf{k})-E-i\epsilon}. \tag{6''}$$

Since the contributions to the first term on the right-hand side of Eq. (6′) are given essentially by the terms with $n<\bar{n}$, the overlap of $g_n(\mathbf{r})$ with $U(\mathbf{r})$ is negligible for $n>\bar{n}$, and the values of a_n for $n<\bar{n}$ are very large when E is near E_0, the first term is abnormally large for E near E_0. This is the condition for the existence of a resonant state, because the first term consists of outgoing waves in all directions and a localized part for values of $\mathbf{r}$ near the origin of the potential. When this is abnormally large, we have a resonant state, which in the usual formulation is seen as an abnormally large scattering amplitude or a pole of the S matrix.[17] If we expand the determinant (7) for E complex, we see that to first order it is proportional to $(E-E_0)+i\Gamma$ so that the coefficients a_n are proportional to the quantity $[(E-E_0)+i\Gamma]^{-1}$, which gives a measure of the strength of the resonance.

As is generally the case with the solutions of quantum-mechanical problems,[20] symmetry considerations greatly simplify the preceding analysis. The symmetry properties of the impurity potential $U(\mathbf{r})$ in the lattice can be taken into account by choosing the functions of the set $g_n(\mathbf{r})$ as the basis for the irreducible representations of the symmetry of $U(\mathbf{r})$. It follows from (2c) that if $g_n(\mathbf{r})$ belongs to a given row of an irreducible representation α, $f_n(\mathbf{k})$ also belongs to the same row of the same irreducible representation. As a consequence, the matrix elements of Eqs. (7) and (5′) vanish when n and n' label functions of different representations or of different rows of the same representation. This allows the reduction of the matrices (7) and (5′) to block form, each block associated with a particular row of an

---

[19] I. M. Lifshitz and M. I. Kaganov, Usp. Fiz. Nauk **69**, 419 (1959) [English transl.: Soviet Phys.—Usp. **2**, 831 (1959)].

[20] See for instance M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill Book Co., New York, 1964); F. Seitz, Ann. Math. **37**, 17 (1936).

irreducible representation. As a consequence, the bound states are classified according to the irreducible representations of the symmetry group of the impurity in the lattice, and the same property holds for the resonant part of the scattering state (6′), because the coefficients a_n which are abnormally large correspond to a row of a given irreducible representation.

We can conclude from the above analysis that the known results of scattering theory can be extended to the case of a periodic potential. The existence of bound and resonant states will depend not only on the impurity potential but also on the band structure through the functions $f_n(\mathbf{k})$ and $E(\mathbf{k})$, which determine the properties of the solutions of Eq. (7) and, consequently, of (6) or (6′). The present formulation is connected with the Green's-function method[1,16] and with the method of Slater and Koster,[2] but we feel it has advantages over them. Some advantages will appear clearly in connection with soluble one-dimensional models which will be discussed in Sec. V. The prescription we have given can also be used for practical purposes and seems to be particularly well suited for strongly localized potentials, where one can hope to be able to consider a determinant (7) of small size by a judicious choice of the expansion set $g_n(\mathbf{r})$.

The above procedure can also be used to clarify the correlation between bound and resonant states and critical points of the Brillouin zone where $\nabla_k E(\mathbf{k})=0$. A detailed calculation could explain how saddle points in the band structure produce resonant states, whose existence is still controversial but seems to have now received decisive experimental support.[21] In the particular hypothetical case in which the potential factorizes in the form

$$U(\mathbf{k},\mathbf{k}')=\rho^*(\mathbf{k})\rho(\mathbf{k}')\,, \qquad (2')$$

Eq. (5′) becomes

$$\left[1-P\int d\mathbf{k}\frac{|\rho(\mathbf{k})|^2}{E(\mathbf{k})-E} \pm i\pi\int d\mathbf{k}\,|\rho(\mathbf{k})|^2\delta(E(\mathbf{k})-E)\right]a=f(\mathbf{k}_0)\,, \qquad (5'')$$

and the conditions for the existence of a resonance at E_0 are that

$$1-P\int d\mathbf{k}'\frac{|\rho(\mathbf{k})|^2}{E(\mathbf{k})-E_0}=0$$

and that the second integral in (5″) be small. Such conditions could also be satisfied when $E(\mathbf{k})$ is near a saddle point, and this suggests that resonances may exist, in general, also at saddle-point singularities. For the case of extrema in the band structure, a more detailed study is made in Sec. III.

III. CONNECTION BETWEEN BAND STRUCTURE AND IMPURITY STATES

From the analysis in Sec. II, we have seen how bound and resonant states can result from an impurity in a periodic potential. We wish to illustrate further the difference between the case considered and the case of bound and resonant states of scattering theory. In the present case, various critical points in $E(\mathbf{k})$ may contribute to give the bound states and are essential in producing resonances characterized by long life-times which would not exist in ordinary scattering theory. A Coulomb potential, for instance, does not have any resonant states in the usual scattering of free particles, while we are going to show that it can have resonant states if the $E(\mathbf{k})$ function has a relative minimum at $\mathbf{k}=\mathbf{k}_0$ besides the absolute minimum at $\mathbf{k}=0$.

To express quantitatively the above considerations is not easy in the framework of Sec. II, because for a slowly varying impurity potential, the order of the Fredholm determinant (7) may be extremely large. We prefer to use an equivalent formulation based on the integral transform of Eq. (1a) which is particularly suited for slowly varying potentials. The solutions of Eq. (1a) can be written as

$$\varphi(\mathbf{k})=\delta(\mathbf{k}-\mathbf{k}_E)-\int d\mathbf{k}'\frac{U(\mathbf{k},\mathbf{k}')\varphi(\mathbf{k}')}{E(\mathbf{k})-E-i\epsilon}, \qquad (8)$$

where the boundary conditions discussed in Sec. II are automatically satisfied. We now separate the domain of definition of the function $\varphi(\mathbf{k})$ into a number of subzones Ω_i such that every one contains a minimum in the curve $E(\mathbf{k})$ at the point $\mathbf{k}_{0i}$. If such a minimum occurs

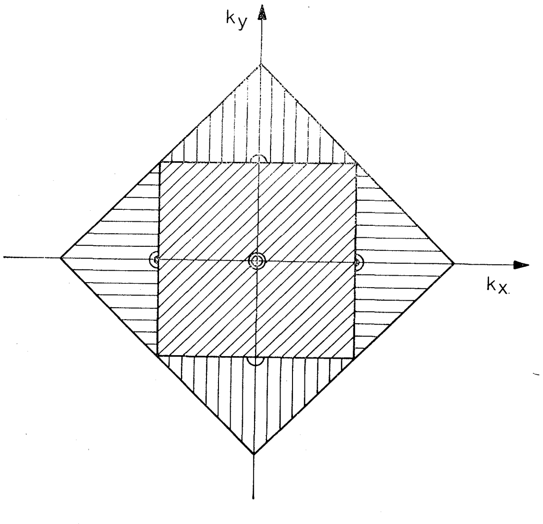

FIG. 1. Schematic representation of some possible subzones in a two-dimensional quadratic lattice. The three values of $\mathbf{k}_{0i}$, where the minima in the energy bands occur, are indicated by circles; they are at the center of the first Brillouin zone and at the boundary between the first and the second Brillouin zone. The subzone associated with every minimum is indicated by the shading of the surface.

---

[21] J. E. Rowe, F. H. Pollak, and M. Cardona, Phys. Rev. Letters **22**, 933 (1969) and quoted references.

on the boundary between the first and the second Brillouin zone, a translation of the reciprocal lattice brings this point into an equivalent point which contributes equally to define the subzone of $\mathbf{k}$ space about $\mathbf{k}_{0i}$. Every region about $\mathbf{k}_{0i}$ will be brought into another subzone by a symmetry operation of the lattice R since the point $\mathbf{k}_{0i}$ will be brought into another point of the star $R\mathbf{k}_{0i}$, so that all the reciprocal space will be covered. If there is only one minimum at $\mathbf{k}=0$, the subzone becomes the entire reciprocal space. If there is only one minimum at $\mathbf{k}=0$ in the first Brillouin zone, but subsidiary minima at the smallest values of $\mathbf{k}$ in the second Brillouin zone, one subzone coincides with the first Brillouin zone, and other subzones are defined in the second Brillouin zone. An example to illustrate the above schema is given in Fig. 1 for a two-dimensional case with quadratic symmetry. In general, the positions in $\mathbf{k}$ space, where the condition $\nabla_k E(\mathbf{k})=0$ must be satisfied, are indicated by symmetry considerations, and semiquantitative studies of the band structure allow a choice of those where the band has a minimum.[22] Needless to say, we would consider the maxima as favored critical points, if the potential were repulsive. We will write the envelope function as

$$\begin{aligned}\varphi(\mathbf{k}) &= \varphi_1(\mathbf{k}) \quad \text{in} \quad \Omega_1 \\ &= \varphi_i(\mathbf{k}) \quad \text{in} \quad \Omega_i \\ &= \varphi_n(\mathbf{k}) \quad \text{in} \quad \Omega_n,\end{aligned} \tag{9}$$

where φ_i is zero outside of Ω_i. The integral equation (8) can be split into n coupled integral equations for the components of φ by substituting (9) into (8). We will discuss separately the case of bound states, where $E\neq E(\mathbf{k})$ for all values of $\mathbf{k}$ and the case of scattering states.

For bound states, the system of coupled integral equations becomes

$$\begin{aligned}[E(\mathbf{k})-E]\varphi_i(\mathbf{k}) = &-\int_{\Omega_1} U_{i,1}(\mathbf{k},\mathbf{k}')\varphi_1(\mathbf{k}')d\mathbf{k}' - \cdots \\ &-\int_{\Omega_i} U_{i,i}(\mathbf{k},\mathbf{k}')\varphi_i(\mathbf{k}')d\mathbf{k}' - \cdots \\ &-\int_{\Omega_n} U_{i,n}(\mathbf{k},\mathbf{k}')\varphi_n(\mathbf{k}')d\mathbf{k}',\end{aligned} \tag{10}$$

where the matrix element $U_{r,s}(\mathbf{k},\mathbf{k}')$ is defined for $\mathbf{k}$ in the subzone Ω_r, $\mathbf{k}'$ in the subzone Ω_s, and zero outside. Equations (10) can be solved approximately, if we suppose that all matrix elements $U_{rs}(\mathbf{k},\mathbf{k}')$ for $r\neq s$ are first-order small compared with the matrix elements for $r=s$. This condition is certainly satisfied when the impurity potential is slowly varying on the elementary cell, and the two minima at $\mathbf{k}_{0r}$ and $\mathbf{k}_{0s}$ do not differ by a reciprocal-lattice vector. We can then solve Eqs. (10) by iteration. Neglecting first-order contributions, we have a set of independent homogeneous equations

$$[E(\mathbf{k})-E]\varphi_{in}{}^0(\mathbf{k}) = -\int_{\Omega_i} d\mathbf{k}'\, U_{i,i}(\mathbf{k},\mathbf{k}')\varphi_{in}{}^0(\mathbf{k}'), \tag{11}$$

each giving a set of eigenvalues $E_{in}{}^0$. Each equation of (11) can be reduced to the corresponding differential equation and solved in the effective-mass approximation, as shown by Kohn and Luttinger.[6] In the appendix, we discuss explicitly the case when the minimum occurs at the boundary between two Brillouin zones, because we intend to make use of some properties of the envelope function in Sec. IV. For a Coulombic potential, the effective-mass equation is particularly simple and reduces to an hydrogenlike equation, if the effective-mass tensor is isotropic. The matrix elements $U_{r,s}(\mathbf{k},\mathbf{k}')$ with $r\neq s$ connect states of different subzones through the impurity potential. Their effect can be taken into account in first order by expanding the envelope function (9) in the set of functions $\varphi_{in}{}^0(\mathbf{k})$ relative to all eigenstates n of all subzones i. We put

$$\varphi(\mathbf{k}) = \sum_{i'n'} c_{i'n'}\varphi_{i'n'}{}^0(\mathbf{k}). \tag{12}$$

The general equation (1) becomes

$$\begin{aligned}[E(\mathbf{k})-E]&\sum_{n'i'} c_{i'n'}\varphi_{i'n'}{}^0(\mathbf{k}) \\ &+\sum_{n'i'} c_{i'n'}\int d\mathbf{k}'\, U(\mathbf{k},\mathbf{k}')\varphi_{i'n'}{}^0(\mathbf{k}')=0.\end{aligned} \tag{13}$$

Multiplying by any of the states $\varphi_{in}{}^{0*}(\mathbf{k})$, integrating over $\mathbf{k}$, and taking into account the results at zero order and the orthonormality of the functions in $\mathbf{k}$ space, we obtain the following system of secular equations for the coefficients c_{in}:

$$(E_{in}{}^0-E)c_{in}+\sum_{i'\neq in'} c_{i'n'}\mathcal{U}_{in,i'n'}=0, \tag{14a}$$

where

$$\mathcal{U}_{in,i'n'}=\int d\mathbf{k}\, d\mathbf{k}'\, \varphi_{in}{}^{0*}(\mathbf{k})U_{i,i'}(\mathbf{k},\mathbf{k}')\varphi_{i'n'}{}^0(\mathbf{k}'), \tag{14b}$$

the domain of $\mathbf{k}$ being Ω_i, and the domain of k' being $\Omega_{i'}$. The eigenvalues are obtained as solutions of the secular determinant

$$\mathrm{Det}|(E_{in}{}^0-E)\delta_{in,i'n'}+\mathcal{U}_{in,i'n'}(1-\delta_{ii'})|=0, \tag{15}$$

and the eigenvectors give to first order the contributions of the different subzones to the envelope function $\varphi(\mathbf{k})$ for any eigenvalue. We wish to remark that the indices n and n' can be extended to the states of the continuum of every subzone. This procedure, of course, is of practical use for bound states, when the size of determinant (15) can be limited so that only a small number of states n, n' need be considered. This will be the case

---

[22] See for instance F. Bassani, in *Proceedings of the International School Enrico Fermi* (Academic Press Inc., New York, 1966), Vol. XXXIV, p. 33; J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 55.

for states well separated from the absolute minimum. We wish to emphasize that the above procedure gives the valley-orbit splitting, when the absolute minimum is at $\mathbf{k}_0 \neq 0$ and tells when additional bound states are produced by the secondary minima.

We now wish to consider the case of scattering states which have energies above the absolute minimum and below the other minima. Performing the same subdivision (9) for $\varphi(\mathbf{k})$, we can write a set of coupled integral equations similar to (10) except for the presence of a scattering term in the first subzone:

$$\varphi_i(\mathbf{k}) = \delta(\mathbf{k}-\mathbf{k}_E)\delta_{1i} - \sum_j \int_{\Omega_j} \frac{d\mathbf{k}'\, U_{i,j}(\mathbf{k},\mathbf{k}')\varphi_j(\mathbf{k}')}{E(\mathbf{k})-E-i\epsilon\delta_{ij}}. \tag{16}$$

In the following we will first show that this system of coupled equations admits solutions of the type discussed in Sec. II with a localized part and a running wave part, and that we have resonant states for some values of the energy which, in lowest order, coincide with the eigenvalues inside the continuum, which one would obtain by considering the higher minima alone. We will show this explicitly for the case of two minima only; one at $\mathbf{k}=0$, and a higher minimum at a point $\mathbf{k}_0$. The minima at the other points of the star of $\mathbf{k}_0$ are included automatically in zero order and could be treated to first order, as indicated above, for the case of localized states. The result can be extended to the case where there are more subsidiary minima. Let us write Eq. (16) for the present case in the symbolic form

$$\begin{aligned} \varphi_1 &= \delta + \mathcal{V}_{11}\varphi_1 + \mathcal{V}_{12}\varphi_2, \\ \varphi_2 &= \mathcal{V}_{21}\varphi_1 + \mathcal{V}_{22}\varphi_2. \end{aligned} \tag{17}$$

The equation $\varphi_2{}^0 = \mathcal{V}_{22}{}^*\varphi_2{}^0$ coincides with Eq. (11) for $i=2$, since it can be reduced to Hermitian form; we suppose that it gives localized eigenfunctions and corresponding eigenvalues above the minimum at $\mathbf{k}=0$. Let us consider one of such eigenvalues $E_2{}^0$ and a corresponding eigenfunction $\varphi_2{}^0$. The alternative theorem[17] requires that the solutions of the system (17) must satisfy the condition

$$(\varphi_2{}^0, \mathcal{V}_{21}\varphi_1) = 0, \tag{18}$$

and that φ_2 must take the form

$$\varphi_2 = f_2 + \lambda\varphi_2{}^0, \tag{19}$$

where f_2 depends on φ_1 and is orthogonal to $\varphi_2{}^0$. As before, we can consider $\mathcal{V}_{12}$ and $\mathcal{V}_{21}$ first-order small compared to $\mathcal{V}_{11}$ and $\mathcal{V}_{22}$, and we neglect the term $\mathcal{V}_{12}f_2$ when we substitute (19) into the first of Eqs. (17), because f_2 is first order in $\mathcal{V}_{21}$. We then obtain for φ_1 the equation

$$\varphi_1 = \delta + \lambda\mathcal{V}_{12}\varphi_2{}^0 + \mathcal{V}_{11}\varphi_1. \tag{20a}$$

The solution of Eq. (20a) is

$$\varphi_1 = (1-\mathcal{V}_{11})^{-1}(\delta + \lambda\mathcal{V}_{12}\varphi_2{}^0), \tag{20b}$$

the operator $(1-\mathcal{V}_{11})^{-1} = 1 + \mathcal{V}_{11} + \mathcal{V}_{11}{}^2 + \cdots$ being the resolvent kernel of Eq. (20a). To determine λ, we impose condition (18) and obtain

$$\lambda = -\frac{(\varphi_2{}^0, \mathcal{V}_{21}(1-\mathcal{V}_{11})^{-1}\delta)}{(\varphi_2{}^0, \mathcal{V}_{21}(1-\mathcal{V}_{11})^{-1}\mathcal{V}_{12}\varphi_2{}^0)}. \tag{21}$$

The fact that a value $\lambda \neq 0$ exists indicates that in correspondence to $E_2{}^0$ we have a state with a localized part of the wave function $\lambda\varphi_2{}^0$. Furthermore, when the potential is slowly varying, λ becomes large because the denominator of Eq. (21) is one order smaller than the numerator, since $\mathcal{V}_{12}$ represents a coupling between different subzones. To go beyond zero order in finding the position of the resonant states and their lifetimes, the coupling between the continuous band in the first Brillouin zone and the states originating from the secondary minima have to be taken into account. We can carry out the same type of analysis given in Sec. II to define the resonant states and their lifetimes by including a scattering state in Eqs. (14) and by extending Eq. (15) onto the complex plane. If this continuation of Eq. (15) admits complex solutions $E_0 - i\Gamma$ and $\Gamma \ll E_0$, then the localized part is abnormally large for E near E_0, and we have a resonant state at that energy. To exemplify this result, we consider only a state $E_2{}^0$ originating from the secondary minimum and will show how it is affected by the interaction with the states of the band in the first Brillouin zone which correspond to the continuum above the absolute minimum. Equations (12), in this case, can be written as

$$\varphi(\mathbf{k}) = c_0\varphi_2{}^0(\mathbf{k}) + \int_{\Omega_1} d\mathbf{k}'\, C(\mathbf{k}')\varphi_{\mathbf{k}'}(\mathbf{k})d\mathbf{k}', \tag{22}$$

where $\mathbf{k}'$ belongs to the first Brillouin zone.

The system of linear equations (14a) becomes

$$\begin{aligned} (E_2{}^0 - E)c_0 + \int_{\Omega_1} d\mathbf{k}'\, C(\mathbf{k}')\mathcal{U}_{12}(\mathbf{k}') &= 0, \\ c_0\mathcal{U}_{21}(\mathbf{k}) + [E(\mathbf{k}) - E]C(\mathbf{k}) &= 0, \end{aligned} \tag{23}$$

where (14b) becomes

$$\mathcal{U}_{21}(\mathbf{k}') = \int d\mathbf{k}\, d\mathbf{k}''\, \varphi_2{}^{0*}(\mathbf{k})U_{21}(\mathbf{k},\mathbf{k}'')\varphi_{\mathbf{k}'}{}^0(\mathbf{k}'').$$

From the second of Eq. (23), we obtain

$$C(\mathbf{k}) = \delta(\mathbf{k}-\bar{\mathbf{k}}) - c_0\{\mathcal{U}_{21}(\mathbf{k})/[E(\mathbf{k})-E-i\epsilon]\}, \tag{23$'$}$$

where $\bar{\mathbf{k}}$ gives the direction of the incoming wave. Substituting into the first equation, we obtain

$$\left[(E_2{}^0 - E) - \int_{\Omega_1} d\mathbf{k} \frac{|\mathcal{U}_{21}(\mathbf{k})|^2}{E(\mathbf{k})-E-i\epsilon}\right]c_0 = -\mathcal{U}_{12}(\bar{\mathbf{k}}), \tag{23$''$}$$

and, consequently, the resonance may occur in correspondence to the value of the real part of E for which the coefficient of c_0 vanishes, if the imaginary part is small. We can observe that this condition amounts to solving Eq. (15) for complex values of E on the nonphysical sheet. In fact, considering only coupling of a state from the secondary minimum to the continuum of the lowest band, Eq. (15) becomes

$$E_2^0-E=\int_{\Omega_1} d\mathbf{k}\frac{|\mathcal{U}_{21}(\mathbf{k})|^2}{E(\mathbf{k})-E}. \tag{24}$$

This equation, in the effective-mass approximation, reduces to Peterson's equation for the resonant states.[8] Considerations on the lifetime of the state can be made from the above equations in the same way as done by Peterson.[8] In general, we may conclude that the real solutions of Eq. (15) give the bound states; and the complex solutions, with a small imaginary part obtained going through the cuts of the positive axis into the lower half of the complex plane, give the resonant states, the whole analysis being appropriate to the case of slowly varying potentials.

IV. TRANSITION PROBABILITIES

The general analysis given in the preceding sections can be used to make semiquantitative remarks on the optical transition probability between impurity states. In the dipole approximation, the transition probability between the ground state i and the final state f will be proportional to

$$|W_{if}|^2=\left|\int \Phi_i^*(\mathbf{r})\mathbf{A}_0\cdot\hat{\mathbf{p}}\Phi_f(\mathbf{r})d\mathbf{r}\right|^2, \tag{25}$$

where $\mathbf{A}_0$ indicates the direction of polarization of the electric field. Substituting the expansion (1b) for the impurity state, we obtain

$$W_{if}=\int d\mathbf{k}\,d\mathbf{k}'\,d\mathbf{r}\;\varphi_i^*(\mathbf{k})\varphi_f(\mathbf{k}')\psi^*(\mathbf{k},\mathbf{r})\mathbf{A}_0\cdot\hat{\mathbf{p}}\psi(\mathbf{k}',\mathbf{r}). \tag{26a}$$

Because of translational symmetry, the integral in α is different from zero only when $\mathbf{k}'=\mathbf{k}+\mathbf{h}$, where $\mathbf{h}$ is a reciprocal-lattice vector and can be written in the form

$$\int d\mathbf{r}\,\psi^*(\mathbf{k},\mathbf{r})\mathbf{A}_0\cdot\hat{\mathbf{p}}\psi(\mathbf{k}',\mathbf{r}) =C(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')+\sum_h{}' C(\mathbf{k},\mathbf{h})\delta(\mathbf{k}-\mathbf{k}'-\mathbf{h}). \tag{26b}$$

In the more common language of the reduced zone scheme, the term with $\mathbf{h}=0$ indicated as $C(\mathbf{k})$ in (26b) gives contributions originating from the same band, while the terms with $\mathbf{h}\neq 0$ indicated as $C(\mathbf{k},\mathbf{h})$ in (26b) give contributions originating from different bands. The intraband contributions $C(\mathbf{k})$ are not present in the case of electronic transitions in the perfect lattice because of energy conservation for the Bloch states,[22] while in the present case, energy is conserved between impurity states and, in general, the integral (26b) is different from zero for $\mathbf{k}=\mathbf{k}'$. The amplitude of the transition probability is proportional to

$$W_{if}=\int d\mathbf{k}\;\varphi_i^*(\mathbf{k})\varphi_f(\mathbf{k})C(\mathbf{k}) +\sum_k{}'\int d\mathbf{k}\;\varphi_i^*(\mathbf{k})\varphi_f(\mathbf{k}+\mathbf{h})C(\mathbf{k},\mathbf{h}). \tag{26c}$$

When the band structure is such that two or more relevant extrema occur at values of $\mathbf{k}$ differing by a reciprocal-lattice vector, both intraband and interband terms to the right-hand side of Eq. (4) must be considered. This corresponds to nearly degenerate cases in the reduced zone scheme, such as those of acceptors in cubic semiconductors. In the other cases, when the relevant extrema correspond to different values of $\mathbf{k}$ in the reduced zone, only the intraband terms need to be considered in Eq. (26c). In this case, it may be of interest to analyze the dependence of W_{if} on the energy position of the excited states. Let us consider the case of a crystal with inversion symmetry and let the initial ground state be even. Then the envelope function $\varphi_i^*(\mathbf{k})$ is even in $\mathbf{k}$ and, since $C(\mathbf{k})$ is odd in $\mathbf{k}$, the term $\varphi_i^*(\mathbf{k})C(\mathbf{k})$ is also odd. To obtain a transition probability different from zero, the envelop function of the final state $\varphi_f(\mathbf{k})$ must have the same symmetry as $C(\mathbf{k})\varphi_i^*(\mathbf{k})$.

With the above considerations in mind, let us consider the case where the impurity states originate from two minima, an absolute one at $\mathbf{k}=0$ and a relative one at $\mathbf{k}=\mathbf{k}_0$. We can show that the transition probability to the excited states below the minimum at $\mathbf{k}=0$ decreases with increasing energy, while it may well increase with increasing energy for the excited states below the secondary minimum. In fact, the antisymmetric function $\varphi_i^*(\mathbf{k})C(\mathbf{k})$ decreases to zero for $\mathbf{k}\rightarrow\infty$ and has only one node at $\mathbf{k}=0$. Its behavior along a particular direction of $\mathbf{k}$ which contains $\mathbf{k}_0$ is exemplified in Fig. 2(a) (the polarization direction $\mathbf{A}_0$ for simplicity is chosen to coincide with this direction). The envelope functions of the excited states below the minimum at $\mathbf{k}=0$ are more localized in $\mathbf{k}$ space as their energy increases as indicated schematically in two typical functions $\varphi_{f_1}(\mathbf{k})$ and $\varphi_{f_2}(\mathbf{k})$ of Fig. 2(b). It follows that the overlap of $\varphi_i^*(\mathbf{k})\mathrm{C}(\mathbf{k})$ with $\varphi_{f_1}(\mathbf{k})$ is larger than with $\varphi_{f_2}(\mathbf{k})$, and, consequently, the transition probability decreases with increasing energy. The opposite situation may well occur for the resonant excited states, whose localized part has an envelope function about $\mathbf{k}=\mathbf{k}_0$ of the type described in the appendix. The behavior of two envelope functions $\varphi_{f1}(\mathbf{k})$ and $\varphi_{f_2}(\mathbf{k})$ for resonant states of increasing energy is exemplified in Fig. 2(c). Since the state $\varphi_{f_1}(\mathbf{k})$ is less

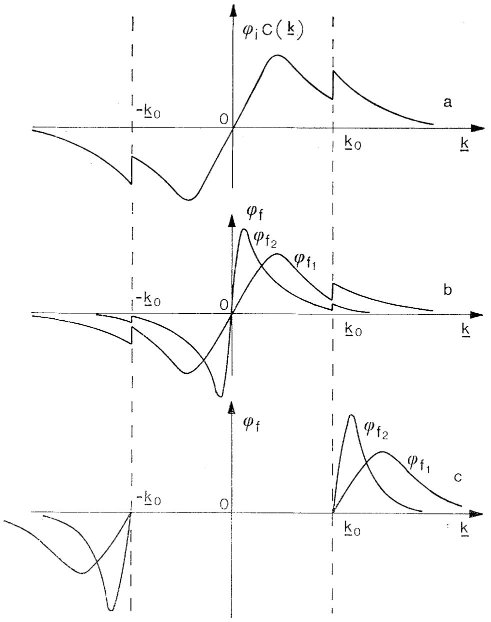

FIG. 2. Schematic representation of the terms which contribute to the transition probability amplitude. (a) Ground-state envelope function $\varphi_i(\mathbf{k})$ times the transition matrix element between Bloch functions $C(\mathbf{k})$ in the specific direction $\mathbf{k}_0$. (b) Final-states envelope functions $\varphi_{f_1}(\mathbf{k})$ and $\varphi_{f_2}(\mathbf{k})$ in the direction $\mathbf{k}_0$. These functions originate from the principal minimum and are in order of increasing energies. (c) Final-states envelope functions $\varphi_{f_1}(\mathbf{k})$ and $\varphi_{f_2}(\mathbf{k})$ in the direction $\mathbf{k}_0$. These functions originate from the subsidiary minima and are in order of increasing energy. It can be seen that the overlaps of the functions of case (a) with those of case (b) behave differently with increasing energy from the overlaps with those of case (c).

localized about $\mathbf{k}_0$ than $\varphi_{f_2}(\mathbf{k})$, its overlap with $\varphi_i^*(\mathbf{k})C(\mathbf{k})$ will be smaller, as can be seen by inspection of Fig. 2. Consequently, in the case of resonant states originating from secondary minima, we expect the transition probability from the ground state to increase with increasing energy of the resonant states.

V. ONE-DIMENSIONAL EXAMPLES

In order to make explicit some results of the previous sections and to bring out some features to be found in physical problems, we consider soluble one-dimensional models.

Let us first consider the case of an extremely localized impurity potential of the type

$$U=V_0\delta(x). \tag{27a}$$

This case is similar but not identical to the case considered by Koster and Slater,[2] whose procedure amounted to solving the one-dimensional impurity problem taking into account only matrix elements of the potential which are constant within each zone and negligible between different zones. The matrix elements (1c) of our potential become

$$U(k,k')=(V_0/2\pi)\psi^*(k,0)\psi(k',0), \tag{27b}$$

which are already of a separable type. The eigenvalue determinant (7) in this case reduces to the single equation

$$\frac{2\pi}{V_0}+\int dk\frac{|\psi(k,0)|^2}{E(k)-E}=0, \tag{28}$$

and the envelope function takes the form

$$\varphi(k)=-(V_0/2\pi)a[\psi^*(k,0)/(E(k)-E)], \tag{29a}$$

with

$$a=\int dk'\,\psi(k',0)\varphi(k'). \tag{29b}$$

A bound state exists for $E<E(k)$, and other bound states exist in the energy gaps of the band structure as solutions of Eqs. (28) and (29a). We wish to study the solutions in an energy gap between two bands, a lower one with a maximum at E_1 and a higher one with a minimum at E_2. We can split the integral contained in Eq. (28) in two parts $C_1(E)$ and $C_2(E)$, the first one corresponding to values of k for which $E(k)\leqslant E_1$ (lower bands), and the other extended to all values of k for which $E(k)\geqslant E_2$ (higher bands). We have

$$C_1(E)=\int_{E(k)\leqslant E_1} dk\frac{|\psi(k,0)|^2}{E(k)-E} \tag{28'}$$

and

$$C_2(E)=\int_{E(k)\geqslant E_2} dk\frac{|\psi(k,0)|^2}{E(k)-E}. \tag{28''}$$

It can be seen by inspection that, for $E_1\leqslant E\leqslant E_2$, both functions $C_1(E)$ and $C_2(E)$ are monotonically increasing functions, the former being negative and the latter positive. The values of $C_1(E)$ and $C_2(E)$ at E_1 and E_2 allow a qualitative study of the solutions of Eq. (28). Those values depend on the functions $\psi(k,r)$ which have opposite parity at E_1 and E_2 in the case of a one-dimensional lattice with inversion symmetry. Let us suppose, for instance, that the state at E_2 is even and the state at E_1 is odd. Then $C_1(E_1)=-\alpha$, $C_1(E_2)=-\beta$, and $C_2(E_1)=\gamma$, $C_2(E_2)=\infty$ with $\alpha>\beta$. The quantities α, β, and γ indicate positive values and depend on the periodic potential through $E(k)$ and $\psi(k,0)$ in (28′) and (28″). We show in Fig. 3 a plot of the integrals appearing in Eq. (28) as the sum of $C_1(E)$ and $C_2(E)$. We present in Figs. 3(a) and 3(b) the cases where $\alpha>\gamma$ and $\alpha<\gamma$, respectively. The former case always occurs for a sufficiently large energy gap. It can be seen by inspection of Fig. 3(a) ($\alpha>\gamma$) that if the impurity potential is repulsive ($-2\pi/V_0$ negative), Eq. (28) admits a solution only when V_0 is sufficiently large, while if the impurity potential is attractive ($-2\pi/V_0$ positive), we always obtain a solution of Eq. (28) however small V_0. In the latter case, the bound state splits from the higher band however small V_0 and decreases to a limiting value in the gap with increasing $|V_0|$. In the case $\alpha<\gamma$ [Fig. 3(b)], we have no bound state if the potential is repulsive, while if the potential is attractive, the state splits from the higher band and its energy decreases with increasing strength of the potential until it reaches the value E_1; for a larger potential, the bound state disappears and becomes a resonance in the lower band. A similar analysis can be made when the parity of the states E_1 and E_2 is reversed; in this case, an attractive potential gives a bound state only if its strength is larger than a critical value, while a repulsive potential gives a bound state however small the potential. To conclude this example, we can remark that Eq. (29a), in correspondence to a solution of Eq. (28), gives for (1b) a square integrable function, whose asymptotic behavior is that of an exponentially decreasing function sufficiently far from the impurity where Floquet's theorem can be applied. We could approximate the Bloch functions $\psi(k,x)$ with plane waves and perform the integral (28) to obtain analytic expressions for the bound states, similarly to what was done by Koster and Slater[2] for a single band. In this approximation, we would lose the symmetry effect and, consequently, the possible resonant states. By solving Eqs. (28) and (29a) with a band model $E(k)$, we could show explicitly the effect of including more bands on the eigenvalues and eigenfunctions and extend somewhat the results of Koster and Slater.[2] With an attractive potential, we obtain a bound state for $E<0$ and another bound state in every energy gap independently of the potential strength. We can also compute the effect of including more bands. We will not report the details of such easy calculations, rather we turn to a model where the potential has a finite range so as to obtain some insight into the resonant states as well.

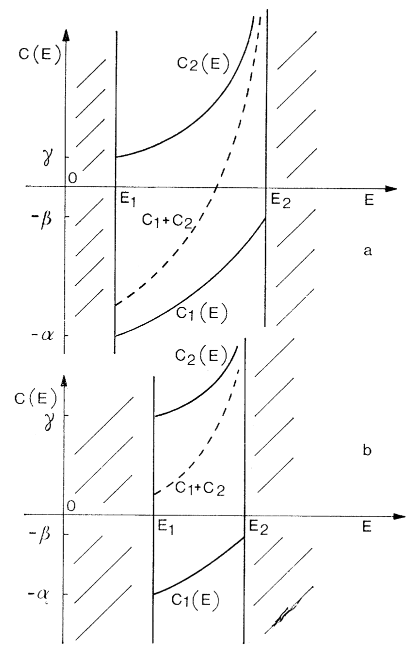

FIG. 3. Schematic plots of the functions $C_1(E)$ and $C_2(E)$ as functions of the energy in the gap for the case where E_2 is an even state and E_1 an odd state. The eigenvalue is given by the intersection of C_1+C_2 with $-2\pi/V_0$. (a) Case of a band structure such that $\alpha>\gamma$. For an attractive potential a solution always exists, for a repulsive one the potential must be sufficiently strong. (b) Case of a band structure such that $\alpha<\gamma$. A solution can exist only for an attractive potential when such potential is not too strong.

Let the impurity potential have the range of the lattice spacing a and be schematically represented by two extremely localized potentials centered at $\pm\frac{1}{2}a$,

$$U(x)=V_0[\delta(x-\tfrac{1}{2}a)+\delta(x+\tfrac{1}{2}a)]. \tag{30}$$

The determinant equation (7) reduces in this case to

$$\begin{vmatrix} 1+\dfrac{V_0}{2\pi}\displaystyle\int\frac{|\psi(k',\frac{1}{2}a)|^2}{E(k')-E}dk' & -\dfrac{V_0}{2\pi}\displaystyle\int\frac{\psi(k',\frac{1}{2}a)\psi^*(k',\,-\frac{1}{2}a)}{E(k')-E}dk' \\ -\dfrac{V_0}{2\pi}\displaystyle\int\frac{\psi(k',\,-\frac{1}{2}a)\psi^*(k',\frac{1}{2}a)}{E(k')-E}dk' & 1+\dfrac{V_0}{2\pi}\displaystyle\int\frac{|\psi(k',\,-\frac{1}{2}a)|^2}{E(k')-E}dk' \end{vmatrix}=0. \tag{31}$$

In order to give explicit examples of the qualitative features of the impurity states derived in the preceding sections, we wish to solve Eq. (31) in the approximation in which the Bloch functions are replaced by plane waves. We choose a model band structure with two bands, the higher one having a secondary minimum at the boundary between the first and the second Brillouin zone,

$$\begin{aligned} E(k)&=(1/2m^*)(k+\pi/a)^2+2E_0+\Delta, && k<-\pi/a \\ &=E_0(1-\cos ka), && |k|<\pi/a \\ &=(1/2m^*)(k-\pi/a)^2+2E_0+\Delta, && k>\pi/a, \end{aligned} \tag{32}$$

with $2E_0+\Delta>0$. Of course, in a one-dimensional lattice, Δ cannot be negative, but for the purpose of exemplification, we can let Δ be either positive or negative. The effective mass is $(E_0a^2)^{-1}$ at the absolute minimum as at the top of the first band, and m^* at the subsidiary minimum. By substituting (32) into (31) with $|\psi(k,0|^2=1$ and performing the integrals, we obtain the following system of equations:

$$\begin{gathered} \frac{1}{V_0}-\frac{1}{E_0a}+\frac{1}{E_0a}\left(\frac{2E_0-E}{-E}\right)^{1/2}+\frac{1}{2}\frac{(2m^*)^{1/2}}{(2E_0+\Delta-E)^{1/2}} \\ \times[1-e^{-a(2m^*)^{1/2}(2E_0+\Delta-E)^{1/2}}]=0, \\ \frac{1}{V_0}-\frac{1}{E_0a}+\frac{1}{E_0a}\left(\frac{-E}{2E_0-E}\right)^{1/2}+\frac{1}{2}\frac{(2m^*)^{1/2}}{(2E_0+\Delta-E)^{1/2}} \\ \times[1-e^{-a(2m^*)^{1/2}(2E_0+\Delta-E)^{1/2}}]=0. \end{gathered} \tag{33a}$$

From a study of the above equations, we can make the following observations:

(a) For $E<0$ and $V_0<0$, we have a bound state however small V_0 from the first of Eqs. (33a). A second bound state appears when $|V_0|$ is larger than the value which satisfies the equation

$$(V_0a)^{-1}+(E_0a^2)^{-1}+(2a)^{-1}\frac{(2m^*)^{1/2}}{(2E_0+\Delta)^{1/2}} \times[1+e^{-a(2m^*)^{1/2}(2E_0+\Delta)^{1/2}}]=0. \quad (33b)$$

The above condition indicates that the second bound state appears for a potential of smaller strength the larger the effective masses of the two minima $1/E_0a^2=m'$ and m^*, and the smaller the separation $2E_0+\Delta$ between the two minima.

(b) For $\Delta>0$, we always obtain from the second of Eqs. (33a) a bound state in the energy gap $2E_0<E<2E_0+\Delta$; its energy is close to $2E_0$ for a small repulsive potential and close to $2E_0+\Delta$ for a small attractive potential. For $V_0<0$, this bound state, which splits off from the secondary minimum, remains in the gap however strong the potential, its minimum value being given by the second of Eqs. (33a) with $|V_0|\to\infty$. A second bound state appears in the gap as $|V_0|$ increases; it splits from the secondary minimum as a solution of the first of Eqs. (33a) when

$$\frac{1}{V_0}=am^*\left\{\frac{m'}{m^*}\left[1-\left(\frac{\Delta}{2E_0+\Delta}\right)^{1/2}\right]-1\right\}. \quad (33c)$$

Since V_0 is negative, this new state appears more easily the larger m^* compared to m'. From the first of Eqs. (33a), we also obtain that this second state reaches the top of the valence band $2E_0$ when

$$\frac{1}{V_0}=am^*\left[\frac{m'}{m^*}-\frac{1}{a(2m^*\Delta)^{1/2}}(1-e^{-a(2m^*\Delta)^{1/2}})\right]=0. \quad (33d)$$

This happens more easily if Δ is small and m^* large compared to m'. If Δ is very large, one cannot satisfy Eq. (33c), and the second state remains in the gap however strong the potential.

(c) For $\Delta<0$ and an attractive potential $V_0<0$, both of Eqs. (33a) can have complex solutions of the type $E-i\Gamma$ with $\Gamma>0$ inside the lowest band $0<E<2E_0$. The resonant state originating from the first equation appears only for $|V_0|$ large and does not have a long lifetime. The resonant state originating from the second of Eqs. (33a) exists for any value of the potential, and the value of Γ is proportional to $a(E)^{1/2}$ and to $a(2E_0+\Delta-E)^{1/2}$, so that its lifetime becomes infinitely large at both minima. The energy of the resonant state, in the hypothesis $\Gamma\ll E$, is given by

$$(V_0)^{-1}+(aE_0)^{-1}+\frac{1}{2}\frac{(2m^*)^{1/2}}{(2E_0+\Delta-E)^{1/2}} \times(1+e^{-a(2m^*)^{1/2}(2E_0+\Delta-E)^{1/2}})=0. \quad (33e)$$

This equation, apart from the term $(aE_0)^{-1}$, would coincide with the bound-state equation one would obtain neglecting the band in the first Brillouin zone $(|k|<\pi/a)$. We can conclude that the approximation of taking into account only the band states above the subsidiary minimum in computing the energy of the resonant state (our zero-order approximation of Sec. III) is justified when

$$-(1/V_0a)\gg(1/a^2E_0)=m'. \quad (33f)$$

This means that the accuracy of the zero-order approximation increases the smaller are the potential and the effective mass m' of the absolute minimum. Equation (33e) coincides with (33b), when $|V_0|$ becomes so large that Eq. (33e) can be satisfied by $E=0$. At this critical value of V_0, the resonant state becomes the second bound state which splits off below the bottom of the band for larger values of $|V_0|$, as explained in *a*.

The above one-dimensional models illustrate explicitly the conclusions derived in Secs. II and III. In particular, the second model shows that the qualitative results obtained in Sec. III as to the effects of band structure on bound and resonant states are not confined to slowly varying impurity potentials, but can be expected to hold for any extended potential.

VI. CONCLUSIONS AND DISCUSSION

The main results of the preceding sections can be summarized as follows:

(a) The eigenstates of an impurity potential are formed, in general, from Bloch functions of many Brillouin zones, and their respective contributions depend on the band structure and on the strength and the nature of the impurity potential. In the language of band theory, this corresponds to having to consider a number of bands when computing impurity states.

(b) The existence of more extrema with large effective masses may increase the number of bound states with respect to the number the potential would have without the lattice. For slowly varying potentials, most of the contributions to the bound states comes from Bloch functions near the extrema of the unperturbed energy bands, and a prescription has been given in Sec. III for computing the states in this case.

(c) The energy-band structure may produce resonant states in the continuum which are more localized and have longer lifetimes than the usual resonant states considered in scattering theory. Subsidiary minima above the absolute minimum in the band structure give resonant states in the presence of an attractive potential. Saddle points in the band structure could also give resonant states as discussed at the end of Sec. II, but we think that to prove this point a detailed three-dimensional calculation is required.

(d) Transitions from the ground state to states which originate from secondary minima may have transition probabilities which increase with increasing energy, while this cannot happen if all the states originate from the principal minimum.

Though we hope to have given a more convincing and general analysis than before, we wish to point out that most of the above concepts are already present in the literature[7–9] and have been used in connection with a number of experimental results in semiconductors. The existence of a multiplicity of bound states associated with degenerate minima at $\mathbf{k}\neq 0$ has been shown by Ramdas and collaborators[23] in their spectroscopic investigation of donor states in a number of III-V compounds. The existence of resonant states in the continuum in connection with secondary minima of the conduction band has been shown experimentally by Kosiki and Paul[10] on Se-doped GaSb and more recently by Ahlburn and Ramdas[23] on Se-doped AlSb. Acceptor states associated with the spin-orbit-split secondary maximum of the valence band in cubic semiconductors have also been observed.[11,12]

In the above scheme, one can also explain the origin of the L bands of the F center, which lie above ionization energy.[13] Chiarotti and Grassano[14] have shown that those bands are due to transitions from the ground state to some states above the continuum. A number of hypotheses have been made on the nature of such states,[24] but the present results, and particularly conclusion (c), give strong theoretical support to the conviction that they are resonant states with long lifetimes which originate from subsidiary minima with large effective masses at $\mathbf{k}=(2\pi/a)$ (1,0,0) and equivalent points, the existence of such minima in the band structure being strongly suggested by recent theoretical calculations.[25] Since the coupling between equivalent minima is expected to be fairly large for an F-center potential in alkali halides, it is not surprising to find three or more such states separated in energy by about 1 eV. Furthermore, our conclusion (d) agrees with the fact that the oscillator strength of the L bands increases with increasing energy. We also wish to point out that to have transitions from the ground state to the resonant states it is necessary that both contain Bloch functions of the same $\mathbf{k}$ value, which for resonant states originating from the subsidiary minima implies that the ground state also contain Bloch functions from the same minima. This is in agreement with the analysis of the paramagnetic resonance of the F center given by Peckar,[26] which requires a predominant contribution from the Bloch function at the point X of the Brillouin zone.

More detailed numerical calculations for real problems can be carried out with the approaches of Sec. II and III, and we hope that existing results for bound states can be improved and quantitative results for resonant states can be obtained.

Similar techniques could be also applied to exciton transitions, where the excitonic interaction substitutes the impurity potential.

ACKNOWLEDGMENTS

The authors are greatly indebted to Professor R. Stroffolini for many useful suggestions. They also wish to thank Dr. M. Marinaro and Professor T. O. Woodruff for helpful discussions.

APPENDIX

Let us consider the case when the minima of energy E^0 occur in the conduction band at a point at the border between the first and the second Brillouin zone, for example, in a fcc lattice at the points

$$\mathbf{k}_{01}=(2\pi/a)(1,0,0),\quad \mathbf{k}_{02}=(2\pi/a)(0,1,0),\quad \mathbf{k}_{03}=(2\pi/a)(0,0,1)$$

and

$$-\mathbf{k}_{01}=(2\pi/a)(\bar{1},0,0),\quad -\mathbf{k}_{02}=(2\pi/a)(0,\bar{1},0),\quad -\mathbf{k}_{03}=(2\pi/a)(0,0,\bar{1}).$$

For any couple of points which differ by a reciprocal-lattice vector, we can write, for values of $\mathbf{k}$ in the second Brillouin zone in the vicinity of the secondary minima, Eq. (11) in the form

$$\left[\frac{\hbar^2(k_x-k_{0x})^2}{2m_{\shortparallel}^*}+\frac{\hbar^2(k_y^2+k_z^2)}{2m_\perp^*}+E^0-E\right]\varphi(\mathbf{k})+\int_{|k_x'|>2\pi/a}U(\mathbf{k},\mathbf{k}')\varphi(\mathbf{k}')d\mathbf{k}'=0$$

for $k_x>2\pi/a$ and

$$\left[\frac{\hbar^2(k_x+k_{0x})^2}{2m_{\shortparallel}^*}+\frac{\hbar^2(k_x^2+k_z^2)}{2m_\perp^*}+E^0-E\right]\varphi(\mathbf{k})+\int_{|k'|>2\pi/a}U(\mathbf{k},\mathbf{k}')\varphi(\mathbf{k}')d\mathbf{k}'=0 \quad \text{(A1)}$$

for $k_x<-2\pi/a$,

---

[23] See, for instance, B. T. Ahburn and A. K. Ramdas, Phys. Rev. **167**, 717 (1968) and related references.

[24] F. Bassani, *Atti del Convegno Nazionale dei cristalli ionici* (G. Spinolo and R. Fieschi, Milano, 1966), p. 172.

[25] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Japan **22**, 833 (1967); S. Oyama and T. Miyakawa, *ibid* **21**, 868, (1966); P. D. Cicco, Phys. Rev. **153**, 931 (1967); A. Barry Kunz, *ibid.* **175**, 1147 (1968).

[26] S. I. Peckar, Nuovo Cimento **60B**, 291 (1969).

where we have neglected interaction between non-equivalent valleys. Choosing as the origin of $\mathbf{k}$ the critical points $\mathbf{k}_{01}$, $-\mathbf{k}_{01}$, and performing appropriate transformations under the integrals, Eq. (A1) becomes

$$\left[\frac{\hbar^2 k_x^2}{2m_{\shortparallel}^*}+\frac{\hbar^2(k_y^2+k_z^2)}{2m_\perp^*}+E^0-E\right]\varphi(k_x+k_{0x},\,k_y,\,k_z)$$
$$+\int_{k_x'>0} d\mathbf{k}'\;U(k_x+k_{0x},\,k_y,\,k_z;\,k_x'+k_{0x},\,k_y',\,k_z')\,\varphi(k_x'+k_{0x},\,k_y',\,k_z')$$
$$+\int_{k_x'<0} d\mathbf{k}'\;U(k_x+k_{0x},\,k_y,\,k_z;\,k_x'-k_{0x},\,k_y',\,k_z')\,\varphi(k_x'-k_{0x},\,k_y',\,k_z')=0\,,$$

for $k_x>0$, and, with more compact notations,

$$\left[\frac{\hbar^2 k_x^2}{2m_{\shortparallel}^*}+\frac{\hbar^2(k_y^2+k_z^2)}{2m_\perp^*}+E^0-E\right]\varphi(\mathbf{k}-\mathbf{k}_{01})$$
$$+\int_{k_x'<0} d\mathbf{k}'\;U(\mathbf{k}-\mathbf{k}_{01},\,\mathbf{k}'-\mathbf{k}_{01})\,\varphi(\mathbf{k}'-\mathbf{k}_{01})+\int_{k_x'>0} d\mathbf{k}'\;U(\mathbf{k}-\mathbf{k}_{01},\,\mathbf{k}'+\mathbf{k}_{01})\,\varphi(\mathbf{k}'+\mathbf{k}_{01})=0\,,\quad\text{(A2)}$$

for $k_x<0$.

Equations (A2) can be written in the condensed form

$$\left[\frac{\hbar^2 k_x^2}{2m_{\shortparallel}^*}+\frac{\hbar^2(k_y^2+k_z^2)}{2m_\perp^*}+E^0-E\right]f(\mathbf{k})+\int d\mathbf{k}'\;U_1(\mathbf{k},\mathbf{k}')f(\mathbf{k}')=0\,,\quad\text{(A3a)}$$

with

$$\begin{aligned} f(\mathbf{k}) &= \varphi(k_x+k_{0x},\,k_y,\,k_z) && \text{for } k_x>0\,,\\ &= \varphi(k_x-k_{0x},\,k_y,\,k_z) && \text{for } k_x<0\,, \end{aligned}\quad\text{(A3b)}$$

and

$$\begin{aligned} U_1(\mathbf{k},\mathbf{k}') &= U(\mathbf{k}+\mathbf{k}_{01},\,\mathbf{k}'+\mathbf{k}_{01})\,, && k_x>0\;\;k_x'>0\\ &= U(\mathbf{k}+\mathbf{k}_{01},\,\mathbf{k}'-\mathbf{k}_{01})\,, && k_x>0\;\;k_x'<0\\ &= U(\mathbf{k}-\mathbf{k}_{01},\,\mathbf{k}'+\mathbf{k}_{01})\,, && k_x<0\;\;k_x'>0\\ &= U(\mathbf{k}-\mathbf{k}_{01},\,\mathbf{k}'-\mathbf{k}_{01})\,, && k_x<0\;\;k_x'<0. \end{aligned}\quad\text{(A3c)}$$

The above expressions for U_1 can be simplified in the vicinity of the minimum by taking $\psi(\mathbf{k},r)=e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{k}_0,\mathbf{r})$ and making use of the property that $\psi(\mathbf{k}_0,\mathbf{r})=\psi(-\mathbf{k}_0,-\mathbf{r})$. We obtain then

$$U_1(\mathbf{k},\mathbf{k}')=\int d\mathbf{r}\;e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}U(\mathbf{r})\,|u(\mathbf{k}_0,\mathbf{r})|^2.\quad\text{(A4)}$$

With this substitution, we can write Eq. (A3a) as

$$\left[-\frac{\hbar^2}{2m_{\shortparallel}^*}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m_\perp^*}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+E^0-E\right]f(\mathbf{r})+U(\mathbf{r})\,|u(\mathbf{k}_0,\mathbf{r})|^2 f(\mathbf{r})=0\,,\quad\text{(A5)}$$

where $f(\mathbf{r})$ is the Fourier transform of $f(\mathbf{k})$. The modulating term $|u(\mathbf{k}_0,\mathbf{r})|^2$, in general, must be taken into account, and it gives an effect related to the symmetry at the point $\mathbf{k}_0$. If the Bloch state at $\mathbf{k}_0$ is odd, for instance, the potential goes to zero at the origin. When the potential $U(\mathbf{r})$ is slowly varying, the term $|u(\mathbf{k}_0,\mathbf{r})|^2$ can be taken equal to 1, and we have the usual effective-mass equation at $\mathbf{k}_{01}$.[5] Similar equations can be obtained about the minima at $\mathbf{k}_{02}$ and $\mathbf{k}_{03}$, and they give in this approximation degenerate eigenvalues. Because of the definition (A3b), any solution $\varphi(\mathbf{k})$ of Eq. (A1) is obtained from (A5) or (A3a) displacing symmetrically any function $f(\mathbf{k})$ on the second Brillouin zone.