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Perturbed crystals in the kq representation. I. The impurity problem*

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A method is developed for defining localized states and effective Hamiltonians in perturbed crystals. The method is based on the localization ideas in the kq representation for perfect lattices. An equation is derived defining localized states for perturbations caused by an impurity, a magnetic and electric fields. In this paper the impurity problem is considered in detail. A correction term is obtained to the one-band Koster-Slater effective Hamiltonian. It is shown to be significant for bound states and scattering cross sections of a localized impurity.

I. INTRODUCTION

The recent interest in the Koster-Slater impurity problem[1] was caused by a new idea put forward in a paper by Kohn and Onffroy.[2] The idea consists in defining one-band generalized Wannier functions (GWF) that are suitable for expanding the corresponding one-band eigenfunctions of a perturbed crystal. By doing so the multiband Koster-Slater equation reduces to a one-band problem. In addition, the local density of states and the charge density can directly be expressed in the GWF. This new idea was followed up in a whole series of papers.[3-8] Originally it was developed for a one-dimensional case[2-4] and then generalized to three dimensions.[7] References 6 and 8 present a one-dimensional model calculation.

The generalized Wannier functions are calculated in Ref. 2 by a variational procedure with an assumption that the impurity bound state is below the lowest band. This restriction was removed in Ref. 3 where a criterion was given for assigning the impurity state to a given band in a one-dimensional crystal. The inclusion of the impurity levels into one particular band is not entirely elementary in the case of a three-dimensional crystal and then the use of the one-band variational approach in defining the GWF needs further clarification.[7]

In this paper we postulate an equation for defining localized states and effective Hamiltonians in perturbed crystals. The equation is developed in the framework of localized states in perfect crystals in the kq representation. The localization problem on ideal lattices[9,10] was recently solved and the approach here will be an extension of Ref. 10 to perturbed crystals. A variety of perturbations will be considered, e.g., the impurity problem, the magnetic and electric fields. In this paper we shall construct localized states and effective Hamiltonians for the impurity problem. In a forthcoming publication perturbations caused by a magnetic and electric field are considered. A short review of this work is in press.[11]

II. EQUATION FOR LOCALIZED STATES IN PERTURBED CRYSTALS

Let us start with a number of remarks about the kq representation and the problem of localized states in perfect crystals.

The connections between a wave function $\psi(\vec{r})$ in configuration space and the corresponding wave function $C(\vec{k},\vec{q})$ in the kq representation are as follows:

$$\psi(\vec{r}) = \left(\frac{V_0}{(2\pi)^3}\right)^{1/2} \int d\vec{k}\, C(\vec{k},\vec{r}), \tag{1}$$

$$C(\vec{k},\vec{q}) = \left(\frac{V_0}{(2\pi)^3}\right)^{1/2} \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\psi(\vec{q}-\vec{R}), \tag{2}$$

where V_0 is the volume of a unit cell in the Bravais lattice, the integration in (1) is over the Brillouin zone, and the summation in (2) is over all the vectors $\vec{R}$ of the Bravais lattice. From (2) it follows that a Bloch function $C_{nk_B}(\vec{k},\vec{q})$ in the kq representation is

$$C_{nk_B}(\vec{k},\vec{q}) = \left(\frac{(2\pi)^3}{V_0}\right)^{1/2} \psi_{nk}(\vec{q}) \sum_{\vec{K}} \delta(\vec{k}-\vec{k}_B-\vec{K}), \tag{3}$$

where $\psi_{nk}(\vec{q})$ is the Bloch function in the coordinate representation (with $\vec{r}$ replaced by $\vec{q}$), $\vec{k}_B$ is the Bloch quasimomentum, and the summation is over all the vectors $\vec{K}$ of the reciprocal lattice. By definition, a Wannier function $a'_{nm}(\vec{k},\vec{q})$ in the kq representation belonging to the nth band and located on site $\vec{R}_m$ of the Bravais lattice is

$$\begin{aligned} a'_{nm}(\vec{k},\vec{q}) &= \left(\frac{V_0}{(2\pi)^3}\right)^{1/2} \int d\vec{k}_B \exp(-i\vec{k}_B\cdot\vec{R}_m) C_{nk_B}(\vec{k},\vec{q}) \\ &= \exp(-i\vec{k}\cdot\vec{R}_m)\psi_{nk}(\vec{q}). \end{aligned} \tag{4}$$

This is a very simple connection between a Wannier function in the kq representation and a Bloch function. The orthogonality of the Wannier functions (4) is seen immediately

$$\int d\vec{k}\,d\vec{q}\,a'^{*}_{nm}(\vec{k},\vec{q})a'_{n'm'}(\vec{k},\vec{q})$$

$$=\int \exp[i\vec{k}\cdot(\vec{R}_m-\vec{R}_{m'})]\psi^{*}_{nk}(\vec{q})\psi_{n'k}(\vec{q})d\vec{k}\,d\vec{q}$$

$$=\delta_{nn'}\delta_{mm'}. \qquad (5)$$

For arriving at (5), we used the following relation that Bloch functions satisfy:

$$\frac{(2\pi)^3}{V_0}\int \psi^{*}_{nk}(\vec{q})\psi_{n'k}(\vec{q})\,d\vec{q}=\delta_{nn'}. \qquad (6)$$

In what follows we shall prefer to work with the periodic part $U(\vec{k},\vec{q})$ of the wave function $C(\vec{k},\vec{q})$:

$$C(\vec{k},\vec{q})=\exp(i\vec{k}\cdot\vec{q})U(\vec{k},\vec{q}), \qquad (7)$$

where $U(\vec{k},\vec{q})$ is periodic in $\vec{q}$ with the period of a Bravais lattice vector $\vec{R}_n$ and Bloch periodic in $\vec{k}$,

$$U(\vec{k}+\vec{K}_m,q)=\exp(-i\vec{q}\cdot\vec{K})U(\vec{k},\vec{q}),$$

with $\vec{K}_m$ a reciprocal-lattice vector. In an unperturbed crystal we have

$$\left(\frac{[-i(\partial/\partial\vec{q})+\vec{k}]^2}{2m}+V(\vec{q})\right)U_{nk_B}(\vec{k},\vec{q})=\epsilon_n(\vec{k}_B)U_{nk_B}(\vec{k},\vec{q}), \qquad (8)$$

where $U_{nk_B}(\vec{k},\vec{q})$ is the periodic part of the Bloch function in the *kq* representation

$$U_{nk_B}(\vec{k},\vec{q})=\left(\frac{(2\pi)^3}{V_0}\right)^{1/2}u_{nk}(\vec{q})\sum_{K_m}\delta(\vec{k}-\vec{k}_B-\vec{K}_m) \qquad (9)$$

and $\epsilon_n(\vec{k}_B)$ are the energy bands ($\vec{k}_B$ being the conserved quasimomentum). The periodic part of the Wannier functions $a_{nm}(\vec{k},\vec{q})$ is therefore

$$a_{nm}(\vec{k},\vec{q})=\exp(-\vec{k}\cdot\vec{R}_m)u_{nk}(\vec{q}). \qquad (10)$$

In what follows $a_{nm}(\vec{k},\vec{q})$ [and not the $a'_{nm}(\vec{k},\vec{q})$ in (4)] will be called the Wannier functions. It is obvious that the Wannier functions (10) satisfy in the *kq* representation the Bloch equation

$$\left(\frac{[-i(\partial/\partial\vec{q})+\vec{k}]^2}{2m}+V(\vec{q})\right)a_{nm}(\vec{k},\vec{q})=\epsilon_n(\vec{k})a_{nm}(\vec{k},\vec{q}). \qquad (11)$$

It is of interest to compare Eq. (8) for Bloch functions with Eq. (11) for Wannier functions. In Eq. (8), $\epsilon_n(\vec{k}_B)$ is a constant independent of the *kq* coordinates while on the right-hand side of Eq. (11) we have $\epsilon_n(\vec{k})$, a function of $\vec{k}$. We see that the only difference between the equation defining Bloch functions [Eq. (8)] and the equation defining localized functions [Eq. (11)] is in the factor multiplying the function on the right-hand side. This fact will be used in postulating an equation for localized states in perturbed crystals.

The Schrödinger equation for a Bloch electron in a constant magnetic field $\vec{H}$ and perturbation $v(\vec{r})$ in the *kq* representation is[12]

$$\left[\frac{[-i\partial/\partial\vec{q}+\vec{k}+(e/2c)\vec{H}\times i\partial/\partial\vec{k}]^2}{2m}+V(\vec{q})+v\left(i\frac{\partial}{\partial\vec{k}}\right)\right]U(\vec{k},\vec{q})=\epsilon U(\vec{k},\vec{q}). \qquad (12)$$

Equation (12) is the eigenvalue equation (ϵ is a constant) for an electron in a perturbed crystal. The solutions $U(\vec{k},\vec{q})$ are eigenstates of the problem. In order to obtain an equation for localized states we shall use the analogy with equations (8) and (11). Equation (8) is an eigenstate equation [with a constant $\epsilon_n(\vec{k}_B)$ multiplying the function on the right-hand side], while Eq. (11) defines localized states $a_{nm}(\vec{k},\vec{q})$ [the energy $\epsilon_n(\vec{k})$ multiplies $a_{nm}(\vec{k},\vec{q})$ on the right-hand side]. Having this mind we shall postulate in correspondence with Eq. (12) the following equation for localized functions in a perturbed crystal:

$$\left[\frac{[-i\partial/\partial q+\vec{k}+(e/2c)\vec{H}\times i\partial/\partial\vec{k}]^2}{2m}+V(\vec{q})+v\left(i\frac{\partial}{\partial\vec{k}}\right)\right]A_{nm}(\vec{k},\vec{q})=E_n(\vec{k},\vec{R}_m)A_{nm}(\vec{k},\vec{q}), \qquad (13)$$

where $A_{nm}(\vec{k},\vec{q})$ are the perturbed localized functions and $E_n(\vec{k},\vec{R}_m)$ are the effective band energies. The explicit dependence on the site $\vec{R}_m$ appears in the equation if one follows the structure of localized functions (10) in the *kq*-representation

$$A_{mn}(\vec{k},\vec{q})-\exp(-i\vec{k}\cdot\vec{R}_m)U_{nm}(\vec{k},\vec{q}) \qquad (14)$$

with $U_{nm}(\vec{k},\vec{q})$ satisfying the equation

$$\left[\frac{[-i\partial/\partial\vec{q}+\vec{k}+(e/2c)\vec{H}\times(\vec{R}_m+i\partial/\partial\vec{k})]^2}{2m}+V(\vec{q})+v\left(i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)\right]U_{nm}(\vec{k},\vec{q})$$

$$=E_n(\vec{k},\vec{R}_m)U_{nm}(\vec{k},\vec{q}). \qquad (15)$$

In the absence of perturbations ($H=0$, $v=0$) Eq. (15) goes over into Eq. (11) for localized states of a perfect crystal. In the latter case the localized functions $U_{nm}(\vec{k},\vec{q})$ and the effective band energies $E_n(\vec{k},\vec{R}_m)$ are site $\vec{R}_m$ independent

$$U_{nm}(\vec{k},\vec{q})=u_{nk}(\vec{q}), \qquad (16)$$

$$E_n(\vec{k},\vec{R}_m)=\epsilon_n(\vec{k}). \qquad (17)$$

This is no longer so when a perturbation is present. As is seen from Eq. (15), both the localized functions $U_{nm}(\vec{k},\vec{q})$ and the effective band energies $E_n(\vec{k},\vec{R}_m)$ will, in general, be $\vec{R}_m$ dependent (an exception is the homogeneous electric field case). One should expect Eq. (15) to lead to localized states because the solution of the unperturbed equation [Eq. (11)] are localized and they should not be strongly affected by the perturbations. It is therefore possible, in principle, to solve Eq. (15) by a perturbation procedure starting with the unperturbed equation (11). This is the main advantage of the localized equation (15) over the eigenvalue equation (12). The eigenfunctions $U(\vec{k},\vec{q})$ of the latter are very different from the eigenfunctions $U_{nk_B}(\vec{k},\vec{q})$ of the unperturbed problem (8) and a perturbation procedure can, in general, not be applied to Eq. (12).

For comparison reasons let us write Eqs. (11) and (13) for localized states in the regular $\vec{r}$ representation. The left-hand sides of Eqs. (11) and (13) will just be the corresponding Hamiltonians applied to the function in the $\vec{r}$ representation. In order to obtain the right-hand side we expand the band energies $\epsilon_n(\vec{k})$ and $E_n(\vec{k},\vec{R}_m)$ in Fourier series and use formula (1). Equations (11) and (13) in the $\vec{r}$ representation will be

$$\left(\frac{p^2}{2m}+V(\vec{r})\right)a_n(\vec{r}-\vec{R}_m)=\sum_s h_n(\vec{R}_s)a_n(\vec{r}-\vec{R}_m+\vec{R}_s), \tag{18}$$

$$\left(\frac{[\vec{p}+(e/2c)\vec{H}\times\vec{r}]^2}{2m}+V(\vec{r})+v(\vec{r})\right)A_{nm}(\vec{r}-\vec{R}_m)=\sum_s H_n(\vec{R}_s,\vec{R}_m)A_{nm}(\vec{r}-\vec{R}_m+\vec{R}_s), \tag{19}$$

where

$$h_n(\vec{R}_s)=\frac{V_0}{(2\pi)^3}\int e^{-i\vec{k}\cdot\vec{R}_s}\epsilon_n(\vec{k})\,d\vec{k}, \tag{20}$$

$$H_n(\vec{R}_s,\vec{R}_m)=\frac{V_0}{(2\pi)^3}\int e^{-i\vec{k}\cdot\vec{R}_s}E_n(\vec{k},\vec{R}_m)\,d\vec{k}, \tag{21}$$

and $a_n(\vec{r}-\vec{R}_m)$, $A_{nm}(\vec{r}-\vec{R}_l)$ are the localized functions for the perfect and perturbed crystal, correspondingly. Equation (18) is well known and is the equation for Wannier functions $a_n(\vec{r})$ in a perfect crystal.[13] In this case the shape of the function $a_n(\vec{r}-\vec{R}_m)$ does not vary with the site and all the Wannier functions for a given band are derived from a single function $a_n(\vec{r})$. In the perturbed crystal the shape of the localized function $A_{nm}(\vec{r}-\vec{R}_l)$ depends also on the site

$$A_{nm}(\vec{r}-\vec{R}_l)=\left(\frac{V_0}{(2\pi)^3}\right)^{1/2}\int d\vec{k}\exp(-i\vec{k}\cdot\vec{R}_l)C_{nm}(\vec{k},\vec{r}), \tag{22}$$

where $C_{nm}(\vec{k},\vec{r})=\exp(i\vec{k}\cdot\vec{r})U_{nm}(\vec{k},\vec{r})$ [see Eq. (1)]. In the regular r representation, Eqs. (18) and (19) appear to be more complicated than Eqs. (11) and (13) and we find it more convenient to work in the *kq* representation.

III. IMPURITY PROBLEM: LOCALIZED FUNCTIONS

In the presence of an impurity perturbation v $(\vec{H}=0)$, Eq. (15) for localized states becomes

$$\left[\frac{(-i\partial/\partial\vec{q}+\vec{k})^2}{2m}+V(\vec{q})+v\left(i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)\right]U_{nm}(\vec{k},\vec{q})=E_n(\vec{k},\vec{R}_m)U_{nm}(\vec{k},\vec{q}). \tag{23}$$

We shall solve Eq. (23) by a perturbation procedure assuming that the unperturbed bands $\epsilon_n(\vec{k})$ are well separated. This will be needed for defining a parameter of smallness for the perturbation theory. Any function $U(\vec{k},\vec{q})$ can be expanded in the complete set of functions (10),

$$U(\vec{k},\vec{q})=\sum_{nm}B_{nm}\exp(-i\vec{k}\cdot\vec{R}_m)u_{nk}(\vec{q})=\sum_n B_n(\vec{k})u_{nk}(\vec{q}), \tag{24}$$

which is a well known expansion in the *kq* representation.[12] For the solutions $U_{nm}(\vec{k},\vec{q})$ of Eq. (23), expansion (24) will be

$$U_{nm}(\vec{k},\vec{q})=\sum_l B_{nl}(\vec{k},\vec{R}_m)u_{lk}(\vec{q}), \tag{25}$$

In this case the expansion coefficients are site $\vec{R}_m$ dependent. We substitute expansion (25) into Eq. (23), multiply it by $u^*_{sk}(\vec{q})$ from the left, and integrate over $\vec{q}$. We arrive at the following equation for the coefficients $B_{nl}(\vec{k},\vec{R}_m)$:

$$\epsilon_s(\vec{k})B_{ns}(\vec{k},\vec{R}_m)+\sum_l v_{sl}\left(\vec{k},i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)B_{nl}(\vec{k},\vec{R}_m)=E_n(\vec{k},\vec{R}_m)B_{ns}(\vec{k},\vec{R}_m), \tag{26}$$

where

$$v_{sl}\left(\vec{k},i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)=\frac{(2\pi)^3}{V_0}\int u^*_{sk}(\vec{q})v\left(i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)u_{lk}(\vec{q})\,d\vec{q}. \tag{27}$$

Expression (27) defines an operator which is to be applied to the coefficients $B_{nl}(\vec{k},\vec{R}_m)$, and the integrand from point of view of the quasimomentum $\vec{k}$ is a product of three operators. Equation (26) can be solved by perturbation theory.[14] Let us introduce the following notations:

$$B_{ns}(\vec{k},\vec{R}_m)=B^{(0)}_{ns}(\vec{k},\vec{R}_m)+B^{(1)}_{ns}(\vec{k},\vec{R}_m)+B^{(2)}_{ns}(\vec{k},\vec{R}_m)+\cdots, \tag{28}$$

$$E_n(\vec{k},\vec{R}_m)=\epsilon_n(\vec{k})+\epsilon^{(1)}_n(\vec{k},\vec{R}_m)+\epsilon^{(2)}_n(\vec{k},\vec{R}_m)+\cdots, \tag{29}$$

where the superscript denotes the order of perturbation. Up to second order in the perturbation we have (we apply perturbation theory to band n)

$$B_{ns}^{(0)}(\vec{k},\vec{R}_m)=\delta_{ns}, \tag{30}$$

$$B_{ns}^{(1)}(\vec{k},\vec{R}_m)=\frac{v_{sn}(\vec{k},\vec{R}_m)}{\epsilon_n(\vec{k})-\epsilon_s(\vec{k})},$$

$$s\neq n;\quad B_{nn}^{(1)}(\vec{k},\vec{R}_m)=0, \tag{31}$$

$$B_{ns}^{(2)}(\vec{k},\vec{R}_m)=\sum_{l\neq n}\frac{v_{sl}(\vec{k},i\partial/\partial\vec{k}+\vec{R}_m)B_{nl}^{(1)}(\vec{k},\vec{R}_m)}{\epsilon_n(\vec{k})-\epsilon_s(\vec{k})}$$

$$-\frac{v_{nn}(\vec{k},\vec{R}_m)v_{sn}(\vec{k},\vec{R}_m)}{[\epsilon_n(\vec{k})-\epsilon_s(\vec{k})]^2},\quad s\neq n, \tag{32}$$

$$B_{nn}^{(2)}(\vec{k},\vec{R}_m)=-\frac{1}{2}\sum_{l\neq n}\frac{|v_{ln}(\vec{k},\vec{R}_m)|^2}{[\epsilon_n(\vec{k})-\epsilon_l(\vec{k})]^2}, \tag{33}$$

$$\epsilon_n^{(1)}(\vec{k},\vec{R}_m)=v_{nn}(\vec{k},\vec{R}_m), \tag{34}$$

$$\epsilon_n^{(2)}(\vec{k},\vec{R}_m)=\sum_{l\neq n}v_{nl}\left(\vec{k},i\frac{\partial}{\partial\vec{k}}+\vec{R}_m\right)B_{nl}^{(1)}(\vec{k},\vec{R}_m). \tag{35}$$

In the above formulas in addition to the matrix operator (27) also the matrix $v_{ls}(\vec{k},\vec{R}_m)$ appears. The latter is a special case of the operator (27) when it no longer operates on a function of $\vec{k}$ [the operator $v(i\partial/\partial\vec{k}+\vec{R}_m)$ in the integrand of (27) operates in this case directly on the function $u_{lk}(\vec{q})$]

$$v_{sl}(\vec{k},\vec{R}_m)=\sum_R \exp(-i\vec{k}\cdot\vec{R})$$

$$\times\int d\vec{r}\,a_s^*(\vec{r}-\vec{R})v(\vec{r}+\vec{R}_m)a_l(\vec{r})$$

$$=\sum_R \exp(-i\vec{k}\cdot\vec{R})v_{sl}(\vec{R}_m+\vec{R},\vec{R}_m), \tag{36}$$

with

$$v_{sl}(\vec{R},\vec{R}')=\int a_s^*(\vec{r}-\vec{R})v(\vec{r})a_l(\vec{r}-\vec{R}')\,d\vec{r}. \tag{37}$$

For results (30)–(35) to have the meaning of perturbation corrections we have to assume that

$$\eta=v_{sn}(\vec{k},\vec{R}_m)/[\epsilon_n(\vec{k})-\epsilon_s(\vec{k})]\ll 1, \tag{38}$$

where η is in some sense the expansion parameter of the perturbation theory.

When (38) holds the localized functions $A_{nm}(\vec{k},\vec{q})$ for a crystal with an impurity up to second order in perturbation theory will be

$$A_{nm}(\vec{k},\vec{q})=\exp(-i\vec{k}\cdot\vec{R}_m)$$

$$\times\Big([1+B_{nn}^{(2)}(\vec{k},\vec{R}_m)]u_{nk}(\vec{q})$$

$$+\sum_{s\neq n}[B_{ns}^{(1)}(\vec{k},\vec{R}_m)+B_{ns}^{(2)}(\vec{k},\vec{R}_m)]u_{sk}(\vec{q})\Big), \tag{39}$$

where the coefficients $B_{ns}(\vec{k},\vec{R}_m)$ are given by (31)–(33).

The functions (39) by the construction of perturbation theory are normalized to second order in the perturbation

$$\int|A_{nm}(\vec{k},\vec{q})|^2d\vec{k}\,d\vec{q}\approx 1+B_{nn}^{(2)}(\vec{k},\vec{R}_m)+B_{nn}^{(2)*}(\vec{k},\vec{R}_m)$$

$$+\sum_{s\neq n}|B_{ns}^{(1)}(\vec{k},\vec{R}_m)|^2=1. \tag{40}$$

The last equality in (40) is a consequence of (31) and (33).

Let us now calculate the overlap integral for two localized functions belonging to different bands and different sites

$$\int A_{nm}^*(\vec{k},\vec{q})A_{lp}(\vec{k},\vec{q})d\vec{k}\,d\vec{q}$$

$$=\frac{V_0}{(2\pi)^3}\int d\vec{k}\exp[i\vec{k}\cdot(\vec{R}_m-\vec{R}_p)]\Big(\delta_{nl}+(1-\delta_{nl})[B_{nl}^{(1)*}(\vec{k},\vec{R}_m)+B_{nl}^{(2)*}(\vec{k},\vec{R}_m)+B_{ln}^{(2)}(\vec{k},\vec{R}_p)+B_{ln}^{(1)}(\vec{k},\vec{R}_p)]$$

$$+[B_{nn}^{(2)*}(\vec{k},\vec{R}_m)+B_{ll}^{(2)}(\vec{k},\vec{R}_p)]\delta_{nl}+\sum_{s\neq n,l}B_{ns}^{(1)*}(\vec{k},\vec{R}_m)B_{ls}^{(1)}(\vec{k},\vec{R}_p)\Big). \tag{41}$$

As is seen from (41) the localized functions $A_{nm}(\vec{k},\vec{q})$ for a crystal with an impurity are, in general, nonorthogonal. There is a nonvanishing overlap of the functions coming from both the first- and second-order perturbation coefficients. Let us calculate in more detail the overlap $S_{nm,lp}^{(1)}$ from the first-order coefficients for $n\neq l$ (when $n=l$ there is no overlap from the first-order perturbation),

$$S_{nm,lp}^{(1)}=\frac{V_0}{(2\pi)^3}\int d\vec{k}\exp[i\vec{k}\cdot(\vec{R}_m-\vec{R}_p)][B_{nl}^{(1)*}(\vec{k},\vec{R}_m)+B_{ln}^{(1)}(\vec{k},\vec{R}_p)]$$

$$=\frac{V_0}{(2\pi)^3}\int d\vec{k}\exp[i\vec{k}\cdot(\vec{R}_m-\vec{R}_p)]\,\frac{v_{ln}^*(\vec{k},\vec{R}_m)-v_{nl}(\vec{k},\vec{R}_p)}{\epsilon_n(\vec{k})-\epsilon_l(\vec{k})}. \tag{42}$$

By using formulas (36) and (37) the last expression can be given the form

$$S^{(1)}_{nm,lp}=\sum_{\vec{R}} g^{(1)}_{nl}(\vec{R}) \times[v_{nl}(\vec{R}_m, \vec{R}_p-\vec{R})-v_{nl}(\vec{R}_m+\vec{R}, \vec{R}_p)], \tag{43}$$

where $g^{(1)}_{nl}(\vec{R})$ is the Fourier transform of the energy denominator in (42),

$$g^{(1)}_{nl}(\vec{R})=\frac{V_0}{(2\pi)^3}\int\frac{d\vec{k}\exp(-i\vec{k}\cdot\vec{R})}{\epsilon_n(\vec{k})-\epsilon_l(\vec{k})}\,. \tag{44}$$

It follows from (42)–(44) that the overlap integral of the functions $A_{nm}(\vec{k}, \vec{q})$ depends on both the matrix elements of the perturbation potential and the band structure of the solid. It is seen from Eq. (43) that the Fourier component $g^{(1)}_{nl}(\vec{R})$ for $\vec{R}=0$ does not contribute to the overlap integral because the expression in the square brackets vanishes for $\vec{R}=0$. $g^{(1)}_{nl}(0)$ is of the order of $1/\epsilon_{nl}$, where ϵ_{nl} is of the order of the energy gap between the bands n and l. In the framework of the perturbation procedure developed above the Fourier coefficients $g^{(1)}_{nl}(\vec{R})$ for $\vec{R}\neq 0$ should be assumed to be smaller than $g^{(1)}_{nl}(0)$. This assumption is in accordance with (38) as can be seen by writing the energy difference $\epsilon_n(\vec{k})-\epsilon_l(\vec{k})$ in the following way:

$$\epsilon_n(\vec{k})-\epsilon_l(\vec{k})=\epsilon_{nl}+\Delta\epsilon_{nl}(\vec{k}), \tag{45}$$

where ϵ_{nl} is a constant of the order of the energy gap. For the assumption (38) to hold it is necessary that $\Delta\epsilon_{nl}(k)$ in (45) be smaller than ϵ_{nl},

$$\Delta\epsilon_{nl}(\vec{k})<\epsilon_{nl} \tag{46}$$

[otherwise the denominator in (38) could vanish]. On the other hand, when (46) holds, it is clear that $g^{(1)}_{nl}(\vec{R})<g^{(1)}_{nl}(0)$ for $\vec{R}\neq 0$. In what follows we shall assume that

$$\Delta\epsilon_{nl}(\vec{k})\ll\epsilon_{nl}\,. \tag{47}$$

Using (45) and (47) we find for $g^{(1)}_{nl}(\vec{R})$,

$$g^{(1)}_{nl}(\vec{R})=\frac{1}{\epsilon_{nl}}\left(\delta(\vec{R})+\frac{V_0}{(2\pi)^3}\int\frac{d\vec{k}e^{-i\vec{k}\cdot\vec{R}}\Delta\epsilon_{nl}(\vec{k})}{\epsilon_{nl}}+\cdots\right), \tag{48}$$

where higher-order terms in $\Delta\epsilon_{nl}(\vec{k})/\epsilon_{nl}$ were neglected. From (48) and (47) it follows that

$$g^{(1)}_{nl}(\vec{R})\ll g^{(1)}_{nl}(0) \quad\text{for } \vec{R}\neq 0. \tag{49}$$

Another assumption we are going to make is about the matrix elements $v_{sl}(\vec{R}, \vec{R}')$ in (37) of the perturbation potential. We shall assume that

$$v_{sl}(\vec{R}, \vec{R}')=v_{sl}(\vec{R})\delta(\vec{R}, \vec{R}'), \tag{50}$$

where

$$v_{sl}(\vec{R})=\int a_s^*(\vec{r})v(\vec{r}+\vec{R})a_l(\vec{r})\,d\vec{r}. \tag{51}$$

With the assumption (50) satisfied, the matrix elements of the perturbation potential (36) become

$$v_{sl}(\vec{k}, \vec{R}_m)=v_{sl}(\vec{R}_m). \tag{52}$$

There are many perturbation potentials for which assumption (50) is satisfied. In the original paper by Koster and Slater[1] the concept of a localized impurity on the origin was used[15]

$$v_{nl}(\vec{R}, \vec{R}')=v_{nl}\delta(\vec{R})\delta(\vec{R}'). \tag{53}$$

This can be seen to be a special case of assumption (50). Another region where assumption (50) holds is when the perturbation potential $v(r)$ varies slowly, e.g., it does not change much in the range of a unit cell of the Bravais lattice.[16] This can explicitly be proven from definition (37) when the Wannier functions are well localized on one unit cell. We then have

$$\begin{aligned}v_{sl}(\vec{R}, \vec{R}')&=\sum_{R_n}\int a_s^*(\vec{q}+\vec{R}_n-\vec{R})\;v(\vec{q}+\vec{R}_n)a_l(\vec{q}+\vec{R}_n-\vec{R}')\,d\vec{q}\\&\approx\sum_{R_n}v(\vec{R}_n)\int a_s^*(\vec{q}+\vec{R}_n-\vec{R})\\&\qquad\times a_l(\vec{q}+\vec{R}_n-\vec{R}')\,d\vec{q}\approx v_{sl}(\vec{R})\delta(\vec{R}-\vec{R}'),\end{aligned} \tag{54}$$

where the integration in (54) is on a unit cell and we have assumed that

$$\int a_s^*(\vec{q}+\vec{R}_n-\vec{R})a_l(\vec{q}+\vec{R}_n-\vec{R}')\,d\vec{q}\approx 0 \quad\text{for } \vec{R}'\neq\vec{R}. \tag{55}$$

In proving Eq. (54) we have assumed slow variation of $v(\vec{r})$ on one unit cell $[v(\vec{q}+\vec{R}_n)\approx v(\vec{R}_n)]$ and corresponding good localization of the Wannier functions [Eq. (55)]. In general, when the slow variation of $v(\vec{r})$ can be extended on a number of unit cells (say, p unit cells) then the requirement on the localization of the Wannier function can be relaxed and the integration in (55) extended on p unit cells.

With the assumption (50) fulfilled the overlap integral (43) becomes (for $n\neq l$)

$$S^{(1)}_{nm,lp}=g^{(1)}_{nl}(\vec{R}_p-\vec{R}_m)[v_{nl}(\vec{R}_m)-v_{nl}(\vec{R}_p)]. \tag{56}$$

It is of interest to compare in order of magnitude the overlap integral $S^{(1)}$ in (56) and the expansion parameter η in (38). The difference of the matrix elements in the square brackets of (56) is of the order of one matrix element, say v_{nl}, or less. This means that

$$S^{(1)} \lesssim g_{nl}^{(1)}(\vec{R}) v_{nl}, \quad R \neq 0 \tag{57}$$

(the sign "~" means "of the order"). On the other hand, $\eta \sim g_{nl}^{(1)}(0) v_{nl}$. Having in mind Eq. (49) we find that

$$S^{(1)} \ll \eta . \tag{58}$$

This relation will be used later in developing one-band effective Hamiltonians.

The first-order overlap $S^{(1)}$ has only interband matrix elements (there is no intraband first-order overlap). The second order-perturbation terms in (41) will contribute to the overlap integral both an intraband and interband part. Let us denote the second-order overlap by $S_{nm,lp}^{(2)}$. The interband part ($l \neq n$) will, in general, be smaller than the first-order overlap.

$$S_{nm,lp}^{(2)} < S_{nm,lp}^{(1)}, \quad l \neq n \tag{59}$$

and we shall neglect $S_{nm,lp}^{(2)}$ ($l \neq n$), keeping only the leading term $S_{nm,lp}^{(1)}$. However, since $S^{(1)}$ has no intraband elements, the leading intraband overlap will come from $S_{nm,lp}^{(2)}$. From (41) we have

$$S_{nm,np}^{(2)} = \frac{V_0}{(2\pi)^3} \int d\vec{k} \exp[i\vec{k} \cdot (\vec{R}_m - \vec{R}_p)] \times \Big(B_{nn}^{(2)*}(\vec{k}, \vec{R}_m) + B_{nn}^{(2)}(\vec{k}, \vec{R}_p) + \sum_{s \neq n} B_{ns}^{(1)*}(\vec{k}, \vec{R}_m) B_{ns}^{(1)}(\vec{k}, \vec{R}_p) \Big) . \tag{60}$$

Using the expressions (31) and (33) for $B^{(1)}$ and $B^{(2)}$ and assuming Eq. (50) for the perturbation potential, the intraband overlap becomes

$$S_{nm,np}^{(2)} = -\frac{1}{2} \sum_{s \neq n} g_{ns}^{(2)}(\vec{R}_p - \vec{R}_m) \times [\,|v_{sn}(\vec{R}_m)|^2 + |v_{sn}(\vec{R}_p)|^2 - 2v_{sn}^{*}(\vec{R}_m) v_{sn}(\vec{R}_p)], \tag{61}$$

where in analogy with Eq. (44),

$$g_{ns}^{(2)}(\vec{R}) = \frac{V_0}{(2\pi)^3} \int \frac{d\vec{k}\, e^{-i\vec{k} \cdot \vec{R}}}{[\epsilon_n(\vec{k}) - \epsilon_s(\vec{k})]^2} . \tag{62}$$

For $\vec{R}_p = \vec{R}_m$ the overlap $S_{nm,nm}^{(2)}$ is zero as it should be because the functions $A_{nm}(\vec{k}, \vec{q})$ are normalized [Eq. (40)]. Again, with assumption (41) satisfied we find that the intraband overlap $S_{nm,np}^{(2)}$ is much smaller than the square of the expansion parameter of [Eq. (38)]

$$S_{nm,np}^{(2)} \ll \eta^2 . \tag{63}$$

In developing one-band effective Hamiltonians for the impurity problem we shall keep terms only up to the order of η^2. The intraband second-order overlap $S_{nm,np}^{(2)}$ is much smaller than η^2 [Eq. (63)] and will therefore be neglected. In this approximation the overlap integral (41) will become

$$\int A_{nm}^{*}(\vec{k}, \vec{q}) A_{lp}(\vec{k}, \vec{q})\, d\vec{k}\, d\vec{q} = \delta_{nl} \delta(\vec{R}_m, \vec{R}_p) + S_{nm,lp}^{(1)}, \tag{64}$$

with $S_{nm,p}^{(1)}$ given in (56).

IV. IMPURITY PROBLEM: EFFECTIVE HAMILTONIANS

In this section a one-band effective Hamiltonian equation is derived for the impurity problem. The derivation will be based on the localized functions $A_{nm}(\vec{k}, \vec{q})$ [Eq. (39)] and the effective band energies (34) and (35). As was mentioned at the end of Sec. III we shall restrict ourselves with effective Hamiltonians up to second order η^2 in the perturbation expansion parameter η. Having this in mind and using assumptions (47) and (50), the localized functions $A_{nm}(\vec{k}, \vec{q})$ can be written (up to first order in perturbation theory)

$$A_{nm}(\vec{k}, \vec{q}) = \exp(-i\vec{k} \cdot \vec{R}_m) \times \Big(u_{nk}(\vec{q}) + \sum_{s \neq n} \frac{v_{ns}(\vec{R}_m)}{\epsilon_{ns}} u_{sk}(\vec{q}) \Big) . \tag{65}$$

The structure of the localized functions (65) is very simple and they can easily be written in the $\vec{r}$ representation

$$A_{nm}(\vec{r} - \vec{R}_m) = a_n(\vec{r} - \vec{R}_m) + \sum_{s \neq n} \frac{v_{ns}(\vec{R}_m)}{\epsilon_{ns}} a_s(\vec{r} - \vec{R}_m) . \tag{66}$$

Here, $A_{nm}(\vec{r} - \vec{R}_m)$ are the localized functions for a crystal with an impurity. It is seen that $A_{nm}(\vec{r} - \vec{R}_m)$ depends not only on the difference $\vec{r} - \vec{R}_m$ as in the unperturbed Wannier functions $a_n(\vec{r} - \vec{R}_m)$ but also explicitly on the site $\vec{R}_m$. As should be expected, the stronger the perturbation is on site $\vec{R}_m$, the more will the perturbed function $A_{nm}(\vec{r} - \vec{R}_m)$ differ from the unperturbed one $a_n(\vec{r} - \vec{R}_m)$ on this particular site $\vec{R}_m$.

Assumptions (47) and (50) simplify also considerably expressions (34) and (35) for the effective energies. To second order in perturbation theory we have

$$\epsilon_n^{(1)}(\vec{k}, \vec{R}_m) = v_{nn}(\vec{R}_m), \tag{67}$$

$$\epsilon_n^{(2)}(\vec{k}, \vec{R}_m) = \sum_{s \neq n} \frac{|v_{ns}(\vec{R}_m)|^2}{\epsilon_{ns}} . \tag{68}$$

Let us now construct a one-band effective Hamiltonian for the impurity problem. For this purpose we expand the solution $U(\vec{k}, \vec{q})$ of Eq. (12) (with $\vec{H} = 0$) in the localized functions $A_{lp}(\vec{k}, \vec{q})$,

$$U(\vec{k}, \vec{q}) = \sum_{lp} F_l(\vec{R}_p) A_{lp}(\vec{k}, \vec{q}), \tag{69}$$

where the expansion coefficients $F_l(\vec{R}_p)$ depend on the band index l and the site $\vec{R}_m$. Substituting (69) into (12) we have

$$\sum_{lp} E_l(\vec{k}, \vec{R}_p) F_l(\vec{R}_p) A_{lp}(\vec{k}, \vec{q}) = \epsilon \sum_{lp} F_l(\vec{R}_p) A_{lp}(\vec{k}, \vec{q}), \tag{70}$$

where

$$E_l(\vec{k}, \vec{R}_p) = \epsilon_l(\vec{k}) + v_{ll}(\vec{R}_p) + \sum_{s \neq l} \frac{|v_{ls}(\vec{R}_p)|^2}{\epsilon_{ls}}. \tag{71}$$

Let us now multiply Eq. (70) by $A^*_{nm}(\vec{k}, \vec{q})$ and integrate over $\vec{k}$ and $\vec{q}$. By using Eqs. (41) and (64) we arrive at the following equation:

$$\sum_p h_n(\vec{R}_p - \vec{R}_m) F_n(\vec{R}_p) + \left(v_{nn}(\vec{R}_m) + \sum_{s \neq n} \frac{|v_{ns}(\vec{R}_m)|^2}{\epsilon_{ns}} \right) F_n(\vec{R}_m)$$
$$+ \frac{V_0}{(2\pi)^3} \sum_{l \neq n, p} \int d\vec{k} \exp[i\vec{k} \cdot (\vec{R}_m - \vec{R}_p)] \, \epsilon_l(\vec{k}) \frac{v_{nl}(\vec{R}_p) - v_{nl}(\vec{R}_m)}{\epsilon_n(\vec{k}) - \epsilon_l(\vec{k})} F_l(\vec{R}_p)$$
$$+ \sum_{l \neq n, p} \left(v_{ll}(\vec{R}_p) + \sum_{s \neq l} \frac{|v_{ls}(\vec{R}_p)|^2}{\epsilon_{ls}} \right) S^{(1)}_{nm, lp} F_l(\vec{R}_p) = \epsilon F_n(\vec{R}_m) + \epsilon \sum_{l \neq n, p} S^{(1)}_{nm, lp} F_l(\vec{R}_p) \cdots, \tag{72}$$

where $h_n(\vec{R})$ is the Fourier transform of the energy band as given by Eq. (20). Equation (72) contains a number of interband terms: the second line (A), the third line (B), and the second term on the right-hand side (C). The terms B and C contain the small overlap $S^{(1)}$ which according to (58) is much smaller than η, the perturbation expansion parameter. Let us show that the term A is also on the order $S^{(1)}$. This can be seen by rewriting the term A [see Eq. (42)],

$$\frac{V_0}{(2\pi)^3} \sum_{l \neq n, p} \int d\vec{k} \exp[i\vec{k} \cdot (\vec{R}_m - \vec{R}_p)] \epsilon_l(\vec{k}) \frac{v_{nl}(\vec{R}_p) - v_{nl}(\vec{R}_m)}{\epsilon_n(\vec{k}) - \epsilon_l(\vec{k})} F_l(\vec{R}_p)$$
$$= \frac{V_0}{(2\pi)^3} \sum_{l \neq n, p} \int d\vec{k} \exp[i\vec{k} \cdot (\vec{R}_m - \vec{R}_p)] \epsilon_n(\vec{k}) \frac{v_{nl}(\vec{R}_p) - v_{nl}(\vec{R}_n)}{\epsilon_n(\vec{k}) - \epsilon_l(\vec{k})} F_l(\vec{R}_p) \sim \epsilon_n \sum_{l \neq n, p} S^{(1)}_{nm, lp}. \tag{73}$$

We have shown, therefore, that all the interband terms in Eq. (72) are of the order of $S^{(1)}$. If one attempts to diagonalize Eq. (72) by using well-known procedures[17,18] one finds that the interband terms of the order of $S^{(1)}$ will lead to intraband contributions of the order of $(S^{(1)})^2$. Since according to (58), $S^{(1)} \ll \eta$, this means that all the interband terms in Eq. (72) can be neglected if one is interested in a one-band equation containing terms only up to second order (η^2) in the perturbation theory. We find therefore that up to terms of the order of η^2 the one-band effective Hamiltonian equation for the impurity problem will be

$$\sum_p h_n(\vec{R}_p - \vec{R}_m) F_n(\vec{R}_p)$$
$$+ \left(v_{nn}(\vec{R}_m) + \sum_{s \neq n} \frac{|v_{ns}(\vec{R}_m)|^2}{\epsilon_{ns}} \right) F_n(\vec{R}_m) = \epsilon F_n(\vec{R}_m). \tag{74}$$

Equation (74) has a correction term

$$\sum_{s \neq n} \frac{|v_{ns}(\vec{R}_m)|^2}{\epsilon_{ns}}$$

to the well-known one-band classical equations for localized impurities of Koster and Slater[1] and for shallow impurities in the effective-mass approximation.[17] Equation (74) reproduces both mentioned equations when the correction term is neglected. However, the second-order perturbation term in Eq. (74) is of very simple structure and can lead to significant contributions in the one-band impurity potential. The significance of this term follows from the fact that while being a one-band band term it is influenced by the explicit band structure of the solid. This can in particular be easily seen in solving the Koster-Slater localized impurity problem.[19] Thus, by assuming that only two bands interact in Eq. (74) (band s influences band n) and that the impurity is localized at the origin, we find that the effective impurity potential at $\vec{R}_m = 0$ is

$$V_{nn}(0) + |v_{ns}(0)|^2 / \epsilon_{ns}. \tag{75}$$

This potential depends explicitly on the band gap ϵ_{ns} and the interband matrix elements $v_{ns}(0)$. The second-order correction term in (75) can be large and is restricted only by the applicability of perturbation theory. Both the binding energies of the impurity and scattering cross sections will be modified by the band structure.

Similar remarks can, in principle, be made about the significance of the correction term in Eq. (74) for the shallow impurity problem. In this case, however, one should, in general, expect that for gentle potentials $v(\vec{r})$ the second order term in (74) will be very small. This can be seen from definition (51). When $v(\vec{r})$ is slowly varying, it can be taken out from under the sign of the integral for a large region or $\vec{r}$ and the integral (51) will vanish for $s \neq l$. One could, however, imagine cases when (50) and (51) hold and still $v_{sl}(\vec{R})$ is not negligibly small. This is only a guess and it should be checked on real problems.

V. SUMMARY

This paper is the first in a series aimed to develop an approach for deriving localized states and effective Hamiltonians in perturbed crystals. The main idea is that localized states in a perturbed crystal when properly defined should not differ too much (because of their localized character) from the corresponding localized states in the perfect crystal. This is not true with respect to eigenstates which for a perturbed crystal are very different from those for a perfect one. The perturbed localized states can therefore be found by a perturbation procedure, while for finding the eigenstates of a perturbed crystal perturbative methods do not usually work. With the help of the perturbed localized states one-band effective Hamiltonians are developed containing interband effects.

The main tool for developing the approach of the perturbed localized functions is the *kq* representation. The usefulness of the representation in defining localized states on lattices is not surprising. As was shown in Ref. 9 operators defining the Bravais and reciprocal-lattice vectors are conjugate to the *kq* coordinates. One should therefore expect that functions localized on lattices would assume a simple form when expressed in the *kq* representation. Thus, Wannier functions on different sites [Eq. (10)] differ from one another by a simple exponential factor. This property appears also in the perturbed localized functions but is modified by the explicit site dependence [Eq. (39)].

Another important property of the *kq* representation used in this paper is the possibility of coordinate separation. The *k*-dependent perturbation theory in Sec. III was built by integrating out the *q* dependence of the wave functions. The split of the radius vector $\vec{r}$ into $\vec{k}$ and $\vec{q}$ in the *kq* representation is therefore a convenient framework for developing localized functions.

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