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Impurity states between two bands

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It is shown that an impurity state in a one-dimensional periodic potential can be associated uniquely with one of the bands between which its energy level lies. If the procedure of Kohn and Onffroy is then used to construct the generalized Wannier functions (GWF), equivalent to the scattering states and bound states associated with a given band, it is found that the GWF have the same exponential localization as the Wannier functions of the perfect crystal. This is true even though the impurity-state wave functions themselves may be longer ranged. In addition, the GWF approach the Wannier functions of the perfect crystal exponentially in the distance from the impurity site.

I. INTRODUCTION

The presence of an impurity in a crystal often leads to the existence of one or more localized bound states whose energy levels lie in the forbidden-energy regions. In the anaylsis of such impure crystals it is sometimes useful to deal with the generalized Wannier functions (GWF) of a given "band," which are appropriate *localized* superpositions of the energy eigenstates, including bound states, belonging to the band in question. A discussion of such GWF in one-dimensional crystals has been given by Kohn and Onffroy[1]; however, they restricted the impurity potential so that only a single impurity state was present below the lowest band. With a more general impurity potential, bound states may also lie in a forbidden gap between two bands, in which case the question arises: With which of these bands should a given impurity state be associated?

In this note we show that this question can be answered unambiguously, and that, with the proper choice, the conclusions of Kohn and Onffroy regarding the localization properties of the GWF remain valid for an arbitrarily strong, short-ranged impurity potential. We find that the impurity state is to be associated with the higher (lower) of the two bands n and $n+1$ if its energy is greater than (less than) the unique value E_n, which corresponds to the branch points of the energy surface $E(k)$ that connect the nth and the $(n+1)$th bands. A set of GWF may then be constructed[1] that span the same function space as the eigenstates of a given band, including any associated impurity states. We find that these GWF have the same degree of exponential localization as the Wannier functions of the perfect crystal, even though the impurity wave functions themselves may be less well localized. In addition, we find that the GWF approach the Wannier functions of the perfect crystal exponentially in the distance from the impurity location. Had we associated the impurity state with the other of the two bands, this would not have been the case.

II. IMPURITY BOUND STATES

We consider here a one-dimensional crystal of lattice constant a, to which a single impurity has been added. We make no restriction on the impurity potential strength, but we assume that this potential is symmetrical and short ranged. For simplicity in our discussion we assume that the impurity potential is confined to a single-crystal cell centered at the origin.

First let us summarize some properties of the perfect periodic lattice.[2] The crystal momentum k will be treated as a complex variable $k=g+ih$. If k is real, the corresponding eigenfunctions and eigenvalues are the Bloch waves $\varphi_{n,k}(x)$ with energies $E(n,k)$, n being the band index. They represent the branches of multivalued functions of k, $\varphi_k(x)$ and $E(k)$ which are analytic everywhere except at a set of branch points away from the real axis. If g is restricted to the fundamental interval $-\pi/a < g \leq \pi/a$, these branch points have the form $k_n = \alpha_n \pi/a \pm ih_n$, where $\alpha_n = 0$ or 1 for n odd or even, respectively. The corresponding energies at these points $E_n = E(k_n)$ are real. Starting from the real axis, the branch $E(n,k)$ of $E(k)$ may be continued analytically into the complex plane. If one starts on the real k axis from the branch $E(n,k)$, moves around the branch point k_n[or k_{n-1}], and returns to the real axis, one arrives at the branch $E(n+1,k)$ [or $E(n-1,k)$] (Fig. 1).

The real energy bands $E(n,k)$ and branch points k_n can be determined from the Kramers plot (Fig. 2) of $\cos ka$ versus real E. The branch point k_n corresponds to the $(n+1)$th extremum of this plot.

The eigenstates of the crystal *with* the impurity are, for real k, the scattering states $\varphi^{(\pm)}_{n,k}(x)$ and bound states $\varphi^B(x)$. Here (+) and (−) denote states with outgoing and incoming scattered waves, respectively. Outside the impurity cell the scattering states are appropriate linear combinations of Bloch waves[3]:

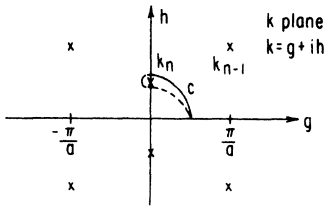

FIG. 1. Branch of the energy surface $E(k)$ corresponding to band n (assumed odd); $E(k)=E(n,k)$ on the real axis. On this branch $E(k)$ has branch points (×) at k_{n-1} and k_n. By moving along a contour C starting from the real axis in this branch (solid line), around the branch point k_n [or k_{n-1}], and back to the real axis (dashed line) on the next sheet, one arrives at the next band: $E(k)=E(n+1,k)$ [or $E(n-1,k)$].

$$\varphi^{(+)}_{n,k}(x)=[t_{22}(n,k)]^{-1/2}\begin{cases}\varphi_{n,k}(x)\,, & x>\frac{1}{2}a\\ t_{22}(n,k)\,\varphi_{n,k}(x) & \\ +t_{21}(n,k)\,\varphi_{n,-k}(x), & x<-\frac{1}{2}a,\end{cases}\tag{1}$$

$$\varphi^{(-)}_{n,k}(x)=\varphi^{(+)}_{n,-k}(-x).\tag{2}$$

The coefficients $t_{22}(n,k)$ and $t_{21}(n,k)$ are elements of the impurity transfer matrix.[4] These functions $\varphi^{(\pm)}_{n,k}(x)$ are branches of multivalued analytic functions of k, $\varphi^{(\pm)}_k(x)$. In the upper-half plane, including the real axis, the only singularities of $\varphi^{(\pm)}_k$ are branch points at the points k_n, previously defined, and at the points k_B corresponding to the bound states with energies $E_B=E(k_B)$.

Consider now the wave function $\varphi^B(x)$ of an impurity state between bands n and $n+1$. Since E_B is real, it follows from the Kramers plot (Fig. 2) that on both sides of the impurity cell, the impurity state $\varphi^B(x)$ is a decaying Bloch wave with complex wave number $k=\pm k_B$. Here k_B has the form $k_B=\alpha_n\pi/a+ih_B$, such that $0<h_B\leq|h_n|$, where $|h_n|$ is the distance from the real axis of the branch points k_n. At k_B, $t_{22}(k)$ vanishes on the appropriate branch.[5]

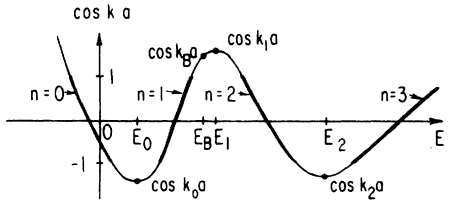

FIG. 2. Schematic version of a Kramers plot of coska vs real E. The energy bands $E(n,k)$ are determined by the regions for which $|\cos ka|\leq 1$. The branch points k_n correspond to the $(n+1)$th extremum of this plot at the energy E_n. The point $(E_B, \cos k_B a)$ indicates the position of an impurity bound state in the gap between bands 1 and 2.

An impurity level E_B is then naturally associated with band n or band $n+1$, depending on whether E_B is less than or greater than the unique value E_n, corresponding to the branch points k_n connecting these bands. The correctness of this assignment will be further substantiated in Sec. III.

As an illustration, let us examine a typical case[4] in which, as the impurity strength U is varied from 0 to ∞ through repulsive values, an impurity state splits off the top of band n, and eventually, as $U\to\infty$, asymptotically approaches band $n+1$ (Fig. 3). We observe that at a small value of U, a zero exists in the upper-half k plane of the function $t_{22}(k)$, corresponding to an impurity state at $k_B=\alpha_n\pi/a+ih_B$ with energy $E_B=E(k_B)$ just above band n. This state is to be associated with band n. As U is increased, the zero moves upward in the complex plane until, at a particular value U_n it just reaches a branch point k_n, at which $E_B=E_n$. As U is further increased, the zero moves down from the branch point on the next Riemann sheet. For these values, $U>U_n$, the impurity state is to be associated with band $n+1$. Eventually, as the strength $U\to\infty$, the zero asymptotically approaches the real axis, corresponding to an impurity state asymptotically close to the bottom of band $n+1$.

III. GENERALIZED WANNIER FUNCTIONS

The GWF for a given band, say band n, of the impure crystal are appropriate linear combinations of the scattering states and any bound states associated with that band, which are localized about the atomic sites. They form an orthonormal basis that is equivalent to this set of scattering eigenstates and bound states. The construction of the GWF in a one-dimensional crystal with a single impurity has been discussed by Kohn and Onffroy,[1] but with the restriction to the case of a single impurity state below the lowest band. In this section

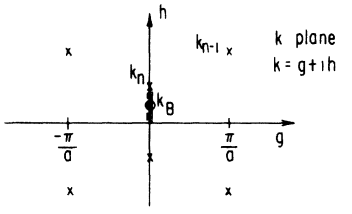

FIG. 3. Motion of the complex impurity-state wave number k_B as a function of the impurity strength U (see text). For small positive values of U the energy of the bound state is at $E(k_B)$ just above band n (assumed odd). As U is increased, the point k_B moves upward (solid line) until at the value U_n, $E(k_B)=E_n$. As U is further increased, the point k_B moves downward on the next branch (dashed line) and, in the limit $U\to\infty$, asymptotically approaches the bottom of band $n+1$.

we show that this is not a necessary restriction. Similar calculations may also be carried out for higher bands. Provided that the prescription of Sec. II for associating each impurity state with a particular band is adopted, it is shown that the GWF have the same localization properties as the Wannier functions for the perfect crystal.

In brief, the construction process for a given band is as follows[1]: One first constructs the *band projection operator* $P_n(x,x')$, which projects an arbitrary function onto the subspace spanned by all the functions associated with band n. The GWF are then constructed by applying P_n to all the Wannier functions of the perfect crystal and by subsequent orthonormalization. To establish the localization properties of the GWF it is essential to show (i) that $P_n(x,x')$ has the same localization properties as the band-projection operator $P_n^0(x,x')$ of the perfect crystal[6]:

$$\lim_{|x-x'|\to\infty} e^{h|x-x'|} P_n(x,x') = 0, \quad h < \bar{h}_n, \tag{3}$$

and (ii) that $P_n(x,x')$ approaches $P_n^0(x,x')$ exponentially in the distance from the impurity:

$$\lim_{|(x+x')/2|\to\infty} e^{2h|(x+x')/2|} \times \left|P_n(x,x') - P_n^0(x,x')\right| = 0, \quad h < \bar{h}_n. \tag{4}$$

Here $\bar{h}_n = \min(h_n, h_{n-1})$ is the imaginary part of the nearest of the branch points k_n, k_{n-1} to the real axis.

This we now show. In the upper-half k plane, including the real axis, the projection operator for a single scattering eigenstate of the impure crystal is given by[1]

$$P^{SC}_{n,k}(x,x') = \varphi^{(+)}_{n,k}(x)\,\varphi^{(-)}_{n,-k}(x'). \tag{5}$$

This function is regular in the upper-half k plane in a region between the real axis and the branch points k_n, k_{n-1} (simply k_0 in the case of the lowest band), except for possible pole singularities at the zeroes of $t_{22}(k)$ [see Eq. (1)], corresponding to the existence of impurity bound states. The complete

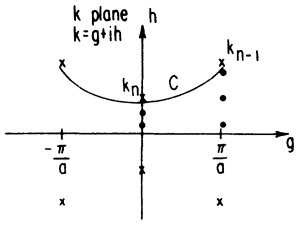

FIG. 4. Integration contour for the integral in Eq. (7). The dots indicate the positions of the wave numbers k_B of impurity states with energies between E_{n-1} and E_n.

band-projection operator $P_n(x,x')$ is thus given by an integral of $P^{SC}_{n,k}(x,x')$ over real k in the fundamental interval plus the contribution from the *associated* impurity states[7]:

$$P_n(x,x') = \int_{-\pi/a}^{\pi/a} dk\, P^{SC}_{n,k}(x,x') + \sum_i{}' P^B_i(x,x'). \tag{6}$$

Here $P^B_i(x,x') = \varphi^B_i(x)[\varphi^B_i(x')]^*$, and $\sum_i'$ extends over all impurity states with energy levels between E_{n-1} and E_n. By deforming the path of integration,[8] $P_n(x,x')$ can be expressed simply as an integral along a contour C between the bound-state poles and the branch points k_n, k_{n-1} (Fig. 4). This results because of the precise cancellation of the impurity-state contributions to Eq. (6) from the residues at the poles of $P^{SC}_{n,k}(x,x')$, as shown in Ref. 1:

$$P_n(x,x') = \int_C dk\, P^{SC}_{n,k}(x,x'). \tag{7}$$

Had we associated the impurity states incorrectly, this cancellation would not have been complete. Because of this cancellation, however, the localization properties (3) and (4) can now be concluded from Eqs. (5) and (7) using the bounds,

$$\left|\varphi^{(\pm)}_{n,k}(x)\right| < (\text{const})e^{\pm\bar{h}_n x}, \tag{8}$$

valid along the contour C, and the symmetry properties,[1]

$$P_n(x,x') = P_n(x',x) = P_n(-x,-x'). \tag{9}$$

The steps in this demonstration are similar to those followed in Ref. 1, as is the remaining proof of the localization of the GWF.

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[1] W. Kohn and J. R. Onffroy, Phys. Rev. B 8, 2485 (1973).

[2] W. Kohn, Phys. Rev. 115, 809 (1959).

[3] They are normalized as follows: $\lim_{L\to\infty} (2\pi/L) \times \int_{-L/2}^{L/2} \varphi^{(+)}_{n,k}(x)\,\varphi^{(-)}_{n,-k}(x)\,dx = 1$.

[4] D. S. Saxon and R. H. Hutner, Philips Res. Rep. 4, 81 (1949).

[5] This condition is equivalent to the existence of a pole in the impurity scattering matrix.

[6] J. des Cloizeaux, Phys. Rev. 129, 554 (1963); Phys. Rev. 135, A685 (1964); Phys. Rev. 135, A698 (1964).

[7] The normalization constant is chosen so that $\varphi^B(x) = \varphi_{n,k_B}(x)$, $x > \frac{1}{2}a$.

[8] The vertical portions cancel if the end points are shifted equally, because of the periodicity of the integrand.