PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Wannier Functions and the Phases of the Bloch Functions*

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(Received 4 August 1969; revised manuscript received 13 January 1970)

We discuss the problem of what phases should be attributed to the Bloch functions in order to obtain Wannier functions with minimal widths. An exact solution to this problem is found by means of the $\vec{k}\cdot\vec{p}$ perturbation formalism. We also consider localized crystal functions of a more general kind. These functions are found to obey a Schrödinger equation in reciprocal space, and may have some important assets when compared to the Wannier functions.

I. INTRODUCTION

Whenever we use Wannier functions

$$a_n(\vec{r}) = \int d^3k\, e^{-i\vec{k}\cdot\vec{R}}\, b_n(\vec{k},\vec{r}) \tag{1.1}$$

in the solution of quantum-mechanical problems in crystals, we are faced with the persistent problem of what phases should be attributed to the nth-band Bloch functions $b_n(\vec{k},\vec{r})$ associated with the wave vectors $\vec{k}$. The Wannier functions become an important complete set of basis functions when one deals with sharply localized potentials due to defects in crystals. For instance, they have been used in connection with the Koster-Slater[1] scheme to deal with highly localized potentials such as those encountered in the problem of magnetic impurities in metals,[2] vacancies in semiconductors,[3,4] and scattering of Bloch waves by crystal defects.[5] The phase of $b_n(\vec{k},\vec{r})$ in Eq. (1.1) should be chosen so that $a_n(\vec{r})$ is reasonably well localized. Indeed, if the perturbing potential is effective only in the neighborhood of a given crystal cell, we want to be certain that the influence of the perturbation on a Wannier function of a distant cell is vanishingly small. Thus, a minimal width for the Wannier function becomes a reasonable criterion for the choice of the phases of the Bloch functions.

By changing the phase of the Bloch functions, we can vary the width of the Wannier function over very large limits. As Kohn and Michaelson have shown,[6] it is always possible to choose the phases so that the Wannier function has a finite width.[7] On the other hand, if the phase is a nonanalytic function of $\vec{k}$, it can be rightly expected that the width of the Wannier function will become infinite. In this latter case, the tail would extend through the whole crystal and the Wannier functions would be utterly unsuitable in the handling of sharp perturbing potentials. It has been shown[4] that the finding of proper phases for the Bloch functions is a nontrivial one. Indeed, a wrong choice was shown to lead to very unsatisfying results in the case of vacancies in PbTe.[4]

In this paper we intend to show how to choose the phases of the Bloch functions so as to obtain Wannier functions with minimal widths, and to obtain an expression for the minimal width that can be attained. The Wannier functions are not the only localized functions of interest in crystals. For instance, Anderson[8] has recently shown how to obtain a particular type of localized function involving more than one band. We address ourselves to the problem of generalizing beyond the scope of the Wannier functions in another section of the present work.

II. POINT-BY-POINT BLOCH FUNCTIONS

A possible way to relate the phases of the Bloch functions throughout the reciprocal $\vec{k}$ space is by means of the $\vec{k}\cdot\vec{p}$ perturbation.[9] Consider a point $\vec{k}$ in the reciprocal space and assume that the energy bands $E_n(\vec{k})$ and the Bloch functions $b_n(\vec{k},\vec{r})$ are known. At a neighboring point $\vec{k}+\vec{s}$, the Bloch functions are

$$b_n(\vec{k}+\vec{s},\vec{r}) = e^{i\vec{s}\cdot\vec{r}} \sum_l C_{n,l}(\vec{k},\vec{s})\, b_l(\vec{k},\vec{r}), \tag{2.1}$$

where, if $\vec{s}$ is small,

$$C_{n,n}(\vec{k},\vec{s}) = 1 + O(\vec{s}^{\,2}),$$

and, for $l \neq n$,

$$C_{n,l}(\vec{k},\vec{s}) = \frac{\hbar}{m} \frac{\langle b_l(\vec{k},\vec{r}) \,|\, \vec{s}\cdot\vec{p} \,|\, b_n(\vec{k},\vec{r})\rangle}{E_n(\vec{k}) - E_l(\vec{k})}. \tag{2.2}$$

Therefore, starting at a certain point $\vec{k}_0$, from Eqs. (2.1) and (2.2), we obtain the Bloch functions at a neighboring point $\vec{k}_0+\vec{s}$. Repeating this procedure for the latter point, we find the Bloch functions at a point $\vec{k}_0+\vec{s}+\vec{s}'$. In this way, it is possible to define the Bloch functions with unequivocally determined phases throughout the whole reciprocal space.[10] For the Bloch functions so defined, we reserve the name of point-by-point (PP) Bloch functions, because we are using a $\vec{k}\cdot\vec{p}$ perturbation in a step-by-step procedure, thus relating the phases of neighboring Bloch functions through Eqs. (2.1) and (2.2). As will be shown in Sec. III, the PP Bloch functions have some features which make them important. It turns out that these are the Bloch functions which give a minimal width to the Wannier function. In an actual calculation, though, a PP $\vec{k}\cdot\vec{p}$ perturbation is not practical, and this problem is handled in Sec. V.

The PP Bloch functions are not necessarily periodic in the reciprocal space. Letting $\vec{g}$ be a reciprocal-lattice vector, we have

$$b_n(\vec{k}+\vec{g},\ \vec{r}) = e^{i\theta(\vec{g},\vec{k})}\, b_n(\vec{k},\vec{r}),$$

where $\theta(\vec{g},\vec{k})$ is a phase which is certainly dependent on $\vec{g}$. On the other hand, a simple argument proves that θ cannot depend on $\vec{k}$. Indeed, by a PP $\vec{k}\cdot\vec{p}$ perturbation we can move from $\vec{k}_1$ to $\vec{k}_2+\vec{g}$ either along the path $\vec{k}_1 \to \vec{k}_2 \to \vec{k}_2+\vec{g}$ or along the path $\vec{k}_1 \to \vec{k}_1+\vec{g} \to \vec{k}_2+\vec{g}$. From the first path, we obtain the relation

$$b_n(\vec{k}_2+\vec{g},\ \vec{r}) = e^{i\theta(\vec{g},\vec{k}_2)}\, b_n(\vec{k}_1,\vec{r})\ , \tag{2.3}$$

while, in the second path, at $\vec{k}_1+\vec{g}$, we obtain

$$b_n(\vec{k}_1+\vec{g},\ \vec{r}) = e^{i\theta(\vec{g},\vec{k}_1)}\, b_n(\vec{k}_1,\vec{r})\ .$$

When using Eqs. (2.1) and (2.2) from $\vec{k}_1+\vec{g}$ to $\vec{k}_2+\vec{g}$, we reproduce the motion from $\vec{k}_1$ to $\vec{k}_2$. Therefore,

$$b_n(\vec{k}_2+\vec{g},\ \vec{r}) = e^{i\theta(\vec{g},\vec{k}_1)}\, b_n(\vec{k}_2,\vec{r})\ . \tag{2.4}$$

A comparison between Eqs. (2.3) and (2.4) reveals that θ is independent of $\vec{k}$. Next, we compare the straight motion from $\vec{k}$ to $\vec{k}+\vec{g}_1+\vec{g}_2$ with the motion along the path $\vec{k} \to \vec{k}+\vec{g}_1 \to \vec{k}+\vec{g}_1+\vec{g}_2$. We reach the conclusion that

$$\theta(\vec{g}_1+\vec{g}_2) = \theta(\vec{g}_1) + \theta(\vec{g}_2)\ .$$

Then, we are led to

$$b_n(\vec{k}+\vec{g},\ \vec{r}) = e^{i\vec{g}\cdot\vec{R}_n}\, b_n(\vec{k},\ \vec{r})\ , \tag{2.5}$$

where $\vec{R}_n$ is a lattice vector and can be chosen within the Wigner-Seitz cell. If the crystal has a very low symmetry, it may happen that $\vec{R}_n$ depends on the band index n.

Observe, that the phases of the PP Bloch functions depend on the choice made for the origin of the coordinate system. If we translate the system of coordinates to the point $\vec{R}_0$, instead of $e^{i\vec{s}\cdot\vec{r}}$ in Eq. (2.1), we would have $e^{i\vec{s}\cdot(\vec{r}-\vec{R}_0)}$ and the PP Bloch functions would gain an extra phase: $e^{-i\vec{k}\cdot\vec{R}_0}$. In particular, if the origin $\vec{R}_0$ is placed at $\vec{R}_n$, the PP Bloch functions *become periodic in the reciprocal space.*

Next, suppose we have a group of rotations α around the origin which leaves the crystal invariant. Then, $b_n(\vec{k},\ \alpha\vec{r})$ and $b_n(\alpha^{-1}\vec{k},\vec{r})$ may differ at most by a phase factor. Thus,

$$\alpha^{-1} b_n(\alpha\vec{k},\vec{r}) \equiv b_n(\alpha\vec{k},\alpha\vec{r}) = e^{i\theta(\alpha,\vec{k})}\, b_n(\vec{k},\vec{r})\ .$$

But from Eq. (2.1), we see that

$$\alpha^{-1} b_n(\alpha\vec{k}+\alpha\vec{s},\vec{r}) = e^{i\theta(\alpha,\vec{k})}\, b_n(\vec{k}+\vec{s},\vec{r})\ .$$

So the phase θ does not depend on $\vec{k}$ and from

$$b_n(\alpha\beta\vec{k},\alpha\beta\vec{r}) = e^{i\theta(\alpha)+i\theta(\beta)}\, b_n(\vec{k},\vec{r})\ ,$$

we discover that $e^{i\theta(\alpha)}$ are a unidimensional representation of the rotation group. On the other hand, for free electrons we have $e^{i\theta(\alpha)}=1$. Therefore, if we think of the Bloch functions as being obtained from plane waves by turning on the potential perturbation, we conclude that

$$b_n(\alpha\vec{k},\alpha\vec{r}) = b_n(\vec{k},\vec{r})\ . \tag{2.6}$$

Finally, consider that

$$\begin{aligned}\alpha\, b_n(\vec{k}+\vec{g},\vec{r}) &= \alpha\{e^{i\vec{g}\cdot\vec{R}_n}\, b_n(\vec{k},\vec{r})\}\\ &= e^{i\vec{g}\cdot\vec{R}_n}\, b_n(\alpha\vec{k},\vec{r}) = b_n(\alpha\vec{k}+\alpha\vec{g},\ \vec{r})\\ &= e^{i\alpha\vec{g}\cdot\vec{R}_n}\, b_n(\alpha\vec{k},\vec{r})\ ,\end{aligned}$$

and, thus,

$$\alpha\vec{R}_n = \vec{R}_n + (\text{lattice vector}),$$

and if the crystal symmetry around the origin is higher than around any other point in the Wigner-Seitz cell and the space inversion is included in the point group, then $\vec{R}_n=0$, and the PP Bloch functions are periodic in the reciprocal space. This argument permits us to choose the origin of the coordinate system from symmetry considerations. In many cases the choice is unique. In a case such as that of the NaCl structure, though, the Na and Cl positions are completely equivalent. For some bands $\vec{R}_n$ will refer to the Na position while for others it will refer to a Cl position.

III. LOCALIZED CRYSTAL FUNCTIONS WITH MINIMAL WIDTH

In Sec. IV, we will find the Wannier functions

$$a_n(\vec{r}) = \Omega^{-1/2}\int_{\mathrm{Bz}} d^3k\, e^{i\lambda_n(\vec{k}) - i\vec{k}\cdot\vec{R}}\, b_n(\vec{k},\vec{r})\ , \tag{3.1}$$

which have minimal width. In Eq. (3.1) we let $\vec{R}$ be a lattice vector and $b_n(\vec{k},\vec{r})$ be the PP Bloch functions of the nth band. The origin of the coordinate system is chosen so the PP functions are periodic in the reciprocal space. Ω is the volume of the Brillouin zone and the integration in Eq. (3.1) is carried out within the zone. Our aim will be to find the periodic phase $\lambda_n(\vec{k})$ which leads to the most concentrated Wannier function.

In the present section, we make the problem more general by studying the functions

$$Z_n(\vec{r}) = \int_{\mathrm{Bz}} d^3k f_n(\vec{k})\, b_n(\vec{k}, \vec{r}) , \tag{3. 2}$$

where $f_n(\vec{k})$ is chosen periodic in the reciprocal space. In particular, we want $f_n(\vec{k})$ such that $Z_n(\vec{r})$ has minimal width. It is convenient to normalize $f_n(\vec{k})$ by

$$\int_{\mathrm{Bz}} d^3k f_n(\vec{k})^\dagger f_n(\vec{k}) = 1 , \tag{3. 3}$$

which assures that $Z_n(\vec{r})$ is itself normalized. Then, we define the width of $Z_n(\vec{r})$ around a given center $\vec{R}_0$ by

$$W = \int d^3r\, Z_n(\vec{r})^\dagger (\vec{r} - \vec{R}_0)^2 Z_n(\vec{r}) .$$

The width can also be obtained from the second derivative of

$$N(\vec{s}) = \int d^3r\, Z_n(\vec{r})^\dagger e^{i\vec{s}\cdot(\vec{r} - \vec{R}_0)} Z_n(\vec{r}) \tag{3. 4}$$

with respect to $\vec{s}$, in the limiting case $\vec{s} \to 0$. According to Eq. (3. 2),

$$N(\vec{s}) = \int d^3k\, d^3k'\, d^3r\, f_n(\vec{k}')^\dagger f_n(\vec{k}) e^{-i\vec{s}\cdot\vec{R}_0} \times b_n(\vec{k}', \vec{r})^\dagger e^{i\vec{s}\cdot\vec{r}} b_n(\vec{k}, \vec{r}) . \tag{3. 5}$$

Because of the periodicity of $f_n(\vec{k}')$ and $b_n(\vec{k}', \vec{r})$ in the reciprocal space, the integration in $\vec{k}'$ may be carried out inside a volume which is the Brillouin zone displaced by $\vec{s}$. Then, the integration in $\vec{r}$ requires that

$$\vec{k}' = \vec{k} + \vec{s} ,$$

and from Eqs. (2. 1) and (3. 5) we obtain

$$N(\vec{s}) = \int_{\mathrm{Bz}} d^3k\, C_{n,n}(\vec{k}, \vec{s}) f_n(\vec{k} + \vec{s})^\dagger \times f_n(\vec{k}) e^{-i\vec{s}\cdot\vec{R}_0} . \tag{3. 6}$$

Taking the Laplacian of Eq. (3. 6) with respect to the coordinates $\vec{s}$, we arrive at the following expression for the width:

$$W = \int_{\mathrm{Bz}} d^3k \left(-f_n^\dagger f_n \vec{\nabla}^2 C_{n,n} - f_n \vec{\nabla}^2 f_n^\dagger + \vec{R}_0^2 f_n^\dagger f_n + i\, 2 f_n \vec{R}_0 \cdot \vec{\nabla} f_n^\dagger \right) . \tag{3. 7}$$

The notation in Eq. (3. 7) has been shortened on purpose, but we remark that the differential operators $\vec{\nabla}$ and $\vec{\nabla}^2$ when applied to $C_{n,n}(\vec{k}, \vec{s})$ act on the coordinate $\vec{s}$ and, in a later step, the limit $\vec{s} \to 0$ is taken. When applied to $f_n(\vec{k} + \vec{s})$, these differential operators act on the coordinate $\vec{k}$ because

$$\lim_{\vec{s} \to 0} [\vec{\nabla}_{\vec{s}} f_n(\vec{k} + \vec{s})] = \vec{\nabla}_{\vec{k}} f_n(\vec{k}),$$

and this is also true for the operator $\vec{\nabla}^2$. When obtaining Eq. (3. 7) we made use of the fact that $\vec{\nabla} C_{n,n}$ is zero. Indeed, up to the second order in $\vec{s}$, $C_{n,n}(\vec{k}, \vec{s})$ may be obtained from Eq. (2. 2) and from the fact that the left-hand side of Eq. (2. 1) is normalized;

$$C_{n,n}(\vec{k}, \vec{s}) = \Big\{1 - {\sum_l}' \left| (\hbar/m)\vec{s} \cdot \vec{p}_{l,n}(\vec{k}) \right|^2 \times [E_n(\vec{k}) - E_l(\vec{k})]^{-2} \Big\}^{1/2} , \tag{3. 8}$$

where

$$\vec{p}_{l,n}(\vec{k}) = \langle b_l(\vec{k}, \vec{r}) | \vec{p} | b_n(\vec{k}, \vec{r}) \rangle . \tag{3. 9}$$

Thus, $\vec{\nabla} C_{n,n} = 0$.

Now, we perform a variation $\delta f_n^\dagger$ on W in order to make the width extremal. With the normalization given by Eq. (3. 3), we arrive at

$$-\vec{\nabla}^2 f_n(\vec{k}) - (\vec{\nabla}^2 C_{n,n}) f_n(\vec{k}) + \vec{R}_0^2 f_n(\vec{k}) - i\, 2\vec{R}_0 \cdot \vec{\nabla} f_n(\vec{k}) = \omega f_n(\vec{k}) , \tag{3. 10}$$

where ω is a Lagrange multiplier. To obtain Eq. (3. 10), some integrations by parts had to be performed, the surface terms vanishing because $f_n(\vec{k})$ is periodic in the $\vec{k}$ space. Finally, making

$$f_n(\vec{k}) = g_n(\vec{k})\, e^{-i\vec{k}\cdot\vec{R}_0} , \tag{3. 11}$$

we obtain

$$-\nabla^2 g_n(\vec{k}) + (-\vec{\nabla}^2 C_{n,n}) g_n(\vec{k}) = \omega g_n(\vec{k}) , \tag{3. 12}$$

where, from Eq. (3. 8),

$$-\vec{\nabla}^2 C_{n,n} = {\sum_l}' \left(\left| \frac{\hbar}{m} \vec{p}_{l,n}(\vec{k}) \right| \Big/ [E_n(\vec{k}) - E_l(\vec{k})] \right)^2 , \tag{3. 13}$$

which is positive in the whole reciprocal space.

Equation (3. 12) is a Schrödinger equation for a periodic positive potential $-\nabla^2 C_{n,n}$ in the $\vec{k}$ space. The primitive cell is the Brillouin zone, while the eigenvalue is the Lagrange multiplier ω. An eigenfunction of Eq. (3. 12) is associated with the quantum numbers R_x, R_y, and R_z, coordinates of a point $\vec{R}$ in the Wigner-Seitz cell, much in the same way as an eigenfunction of the crystal Schrödinger equation is associated with a wave vector $\vec{k}$ in the Brillouin zone. Since $f_n(\vec{k})$ must be periodic in $\vec{k}$ space, from Eq. (3. 11) we conclude that

$$\vec{R} = \vec{R}_0 .$$

Therefore, the vector $\vec{R}$ associated with a solution of Eq. (3. 12) is simply the center of the localized function $Z_n(\vec{r})$.

Now, if Eq. (3. 10) is used in Eq. (3. 7) we find that

$$W = \omega . \tag{3. 14}$$

Therefore, for each band, the set of localized functions $Z_n(\vec{r})$ constructed as in Eq. (3. 2), and with extremal width, form a discrete set of functions corresponding to the eigenvalues ω of the Schrödinger equation (3. 12) in the reciprocal space. The width of $Z_n(\vec{r})$ equals the eigenvalue of Eq. (3. 12), while its center is the wave vector $\vec{R}$ associated with the solution of Eq. (3. 12).

IV. WANNIER FUNCTIONS WITH MINIMAL WIDTHS

Equation (3.1) is a special case of Eq. (3.2), where

$$f_n(\vec{k}) = \Omega^{-1/2} \exp[i\,\lambda_n(\vec{k}) - i\,\vec{k}\cdot\vec{R}] \;.$$

Therefore, all the algebraic development of Sec. III that leads to Eq. (3.7) is still valid. The width of the Wannier function then becomes

$$\begin{aligned} W &= \frac{1}{\Omega}\int_{\mathrm{Bz}} d^3k\,[-\vec{\nabla}^2 C_{n,n} + (\vec{\nabla}\lambda_n)^2 \\ &\quad + (\vec{R}-\vec{R}_0)^2 + 2\vec{\nabla}\lambda_n\cdot(\vec{R}_0-\vec{R}) + i\,\vec{\nabla}^2\lambda_n] \\ &= \frac{1}{\Omega}\int d^3k[-\vec{\nabla}^2 C_{n,n} + (\vec{\nabla}\lambda_n)^2 + (\vec{R}-\vec{R}_0)^2] \;, \end{aligned} \tag{4.1}$$

because λ_n is periodic in $\vec{k}$. Equation (4.1) shows that the Wannier functions with minimal widths are such, that

$$\lambda_n(\vec{k}) = 0, \quad \vec{R}_0 = \vec{R},$$

and

$$W = \int d^3k(-\vec{\nabla}^2 C_{n,n})/\Omega \;, \tag{4.2}$$

i.e., it is constructed out of the PP Bloch functions and it is centered at a point which differs from the origin by a lattice translation.

At this point, we return to what we have said in the Introduction in connection with the problem of finding the energy levels due to sharply localized-defect potentials. In that problem it is certainly convenient to have a set of crystal functions with small widths. The set of Wannier functions with minimal width and localized at the different lattice points is certainly more convenient than the set of solutions to Eq. (3.12), in that the Wannier functions may be constructed without solving an extra Schrödinger equation. Because of Eq. (2.6), the symmetry of a localized function such as Eq. (3.2) is determined by the modulating function $f_n(\vec{k})$. In the case of a Wannier function centered at the origin,

$$f_n(\vec{k}) = 1/\Omega \;,$$

so that a Wannier function has the full symmetry of the point group, and therefore, an s-like behavior. On the other hand, it is always possible to find solutions to Eq. (3.12) with any symmetry compatible with the point group, and centered at any point in the Wigner-Seitz cell. Thus, when compared to the Wannier functions, the solutions of Eq. (3.12) have some assets which may turn out to be very convenient in some specific problems.

V. SINGLE-POINT BLOCH FUNCTIONS

The crystal functions with minimal width were defined in terms of the PP Bloch functions. We recall here that the PP Bloch functions are the ones whose phases are determined by a $\vec{k}\cdot\vec{p}$ perturbation expansion from point to point throughout the Brillouin zone. In an actual band calculation, however, one never makes a PP $\vec{k}\cdot\vec{p}$ perturbation, but expands all the Bloch functions in terms of those of a single point $\vec{k}_0$ (in general, the point of highest symmetry in the zone). This latter procedure is indeed one of the most promising methods of band calculation and has been shown remarkably successful both in Ge and Si [11] as in the case of PbTe.[4] This latter method leads to Bloch functions which will be named SP ($\vec{k}\cdot\vec{p}$ perturbation to a single point), and which differ from the PP functions by a phase $\mu_n(\vec{k})$. The purpose of this section will be to determine this phase. In doing so, we have put in practical terms the problem of determining the localized crystal functions with minimal widths.

Let $C_{n,l}(\vec{k})$ be the coefficients of the expansion of the PP Bloch functions $b_n(\vec{k},\vec{r})$ in terms of the Kohn-Luttinger functions $e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}\,b_l(\vec{k}_0,\vec{r})$ constructed from the Bloch functions at $\vec{k}_0$. That is,

$$b_n(\vec{k},\vec{r}) = e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}} \textstyle\sum_l C_{n,l}(\vec{k})\,b_l(\vec{k}_0,\vec{r}) \;. \tag{5.1}$$

An analogous expression for the PP Bloch functions at $\vec{k}+\vec{s}$ can be written. But, as the PP Bloch functions at $\vec{k}$ and $\vec{k}+\vec{s}$ are related by means of the $\vec{k}\cdot\vec{p}$ perturbation, we obtain

$$\begin{aligned} C_{n,l}(\vec{k}+\vec{s}) &= [1-\textstyle\sum_q' |\vec{s}\cdot\vec{r}_{q,n}(\vec{k})|^2]^{1/2} C_{n,l}(\vec{k}) \\ &\quad - i\textstyle\sum_q' (\vec{s}\cdot\vec{r}_{q,n}(\vec{k}))\,C_{q,l}(\vec{k}), \end{aligned} \tag{5.2}$$

where

$$\begin{aligned} \vec{r}_{q,n}(\vec{k}) &= \langle b_q(\vec{k},\vec{r})\,|\,\vec{r}\,|\,b_n(\vec{k},\vec{r})\rangle \\ &= \frac{i(\hbar/m)\vec{p}_{q,n}(\vec{k})}{[E_n(\vec{k})-E_q(\vec{k})]} \;, \end{aligned} \tag{5.3}$$

and where $\vec{p}_{q,n}(\vec{k})$ is defined by Eq. (3.9).

First, let $\dot{b}_n(\vec{k},\vec{r})$ and $\dot{C}_{n,l}(\vec{k})$ be the SP Bloch functions at $\vec{k}$ and the coefficients of their expansion in terms of the Kohn-Luttinger functions of $\vec{k}_0$, respectively. Since

$$b_n(\vec{k},\vec{r}) = e^{i\mu_n(\vec{k})}\,\dot{b}_n(\vec{k},\vec{r}) \;, \tag{5.4}$$

we obtain

$$C_{n,l}(\vec{k}) = e^{i\mu_n(\vec{k})}\,\dot{C}_{n,l}(\vec{k}) \;, \tag{5.5}$$

for all l. The phase of the coefficients $\dot{C}_{n,l}(\vec{k})$ may be fixed in the following way. Choose a reference state at $\vec{k}_0$, $b_N(\vec{k}_0,\vec{r})$, and require that

$$\dot{C}_{n,N}(\vec{k}) \text{ be real and continuous in } \vec{k}. \tag{5.6}$$

The choice of N is arbitrary, one possibility being $N=n$. Then, from Eq. (5.5), we obtain the following expression:

$$\dot{C}_{n,N}(\vec{k}+\vec{s})e^{i[\mu_n(\vec{k}+\vec{s})-\mu_n(\vec{k})]}$$

$$=\dot{C}_{n,N}(\vec{k})[1-{\sum_l}' \,|\vec{s}\cdot\dot{\vec{r}}_{l,n}(\vec{k})|^2]^{1/2}$$

$$-i{\sum_l}' \,[\vec{s}\cdot\dot{\vec{r}}_{l,n}(\vec{k})]\,\dot{C}_{l,N}(\vec{k}) \,, \qquad (5.7)$$

where $\dot{\vec{r}}_{l,n}(\vec{k})$ is analogous to $\vec{r}_{l,n}(\vec{k})$ only in that it is defined in terms of the SP Bloch functions. Dividing both sides of Eq. (5.7) by $\vec{s}$ and passing to the limit $\vec{s}\rightarrow 0$, we obtain, for the imaginary part of the resulting expression, the following relation:

$$\vec{\nabla}\mu_n(\vec{k})=-[\dot{C}_{n,N}(\vec{k})]^{-1}\,\mathrm{Re}[{\sum_l}' \,\dot{\vec{r}}_{l,n}(\vec{k})\,\dot{C}_{l,N}(\vec{k})] \,. \qquad (5.8)$$

Equation (5.8) can be integrated to yield the phases $\mu_n(\vec{k})$ to which one should multiply the SP Bloch functions in order to obtain the PP functions. It is remarkable that in the special case of a weak spin-orbit coupling in a crystal with inversion symmetry, the coefficients $\dot{C}_{n,l}(\vec{k})$ are all real because of time reversibility. Then, the matrix elements of $\vec{p}$ are also real, which makes the right-hand side of Eq. (5.8) null. *In this case, the* SP *and the* PP *Bloch functions coincide.*

VI. SUMMARY

In this paper we have solved the problem of finding Wannier functions with minimal widths. These Wannier functions were defined in terms of Bloch functions whose phases were determined by a PP $\vec{k}\cdot\vec{p}$ perturbation-expansion technique. The minimal Wannier functions are centered at the symmetry points and are associated with the invariant representation of the point group. The phases of the PP Bloch functions with respect to the Bloch functions coming from a $\vec{k}\cdot\vec{p}$ perturbation to a single point in the zone were also determined.

The problem of finding crystal functions with minimal widths was generalized beyond the strict scope of the Wannier functions. These generalized minimal functions turned out to satisfy a Schrödinger equation in the reciprocal space. Contrary to the Wannier functions, these generalized functions may belong to any irreducible representation of the point group and can be centered at any point in the Wigner-Seitz cell.

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*Work supported in part by the Conselho Nacional de Pesquisas, the Fundacao de Amparo a Pesquisa do Estado de Sao Paulo, Brazil, and by the Materials Theory Group, Massachusetts Institute of Technology.

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