than the shape parameters (E_d and Γ) on which the above comparisons are based. The amplitude-shape connection $\Gamma = \pi D(E_d)V^2$ is not well obeyed by the above parameters. Using the low-concentration value of V^2 and an estimated value of $D(E_d) = 0.23$ eV^{-1}, the relation predicts $\Gamma = 0.45$ eV, almost a factor of 2 too large. We expect that including $l=0$ and $l=1$ phase-shift contributions in Eq. (1) probably will reduce V^2, improving the agreement.

Further work is currently under way on magnetic alloys.[11]

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Construction of Wannier Functions and Applications to Energy Bands*

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This paper is a contribution to the theory of Wannier functions. The main emphasis is on practical methods for the *ab initio* construction of Wannier functions for simple and composite bands from appropriate variational principles. The cases of a simple *s* band, a hybridized *s-d* band, and the valence and conduction bands of the diamond structure are treated in detail. The calculations of Bloch waves, energy bands, and densities of states from Wannier functions is described. Questions of uniqueness and nonuniqueness and problems due to attachment to other bands are also discussed.

I. INTRODUCTION

Since their first introduction in 1937,[1] the notion of Wannier functions has played a very extensive and important role in the conceptual development of the electron theory of solids. However, while the existence of this convenient set of localized and orthonormal functions has often been invoked in theoretical discussions[2] and while their general properties have been exhibited in considerable detail,[3–10] they have, to the author's knowledge, found no significant use in quantitative calculations. While Wannier functions have lain quantitatively neglected, there has been, in the last fifteen years, a tremendous surge of calculations of their transforms, the Bloch waves, and the associated energy bands.[11] No doubt an important reason for this state of affairs has been the preoccupation, during this period, of solid-state physicists with the physical properties of relatively wide-band, pure solids such as nontransition metals and group-IV elements. These could be best analyzed in terms of extended Bloch waves which are similar, in general character, to free-electron states.

In recent years we have felt in our own work on superconductivity of narrow-band superconductors, on properties of disordered systems and on properties of solid surfaces, a strong need for a framework which highlights the atomic character of the electrons. In a series of papers of which this is the first, it is our aim to develop practical methods for the calculation of Wannier functions for simple and composite bands in perfectly periodic crystals, and of their generalizations for nonperiodic systems such as crystals with point defects, crystal surfaces, and disordered systems. The present paper deals with periodic crystals, and is divided into two parts: Sections II–V pertain to simple bands. Sections VI–X pertain to composite bands.

The starting point for the present work is the variational principle satisfied by Wannier functions, which was first described by Koster[4] and Parzen.[5] As preliminary trial functions one may take highly localized, nonorthogonal functions f, following Anderson's[12] notion of ultralocalized functions. They do not need to approximate the complicated oscillatory tails of the actual Wannier functions a. The tails are automatically generated in the next step, which orthogonalizes the f's by methods developed by Des Cloizeaux[9] and Löwdin.[13] The orthogonalization also avoids the need for imposing subsidiary conditions, as was already pointed out by Koster.[4]

We illustrate the entire procedure by three characteristic and physically important examples: (1) an isolated, simple (noncomposite) band; (2) a hybridized s-d band; (3) the valence and conduction bands of crystals of the diamond structure.

Once the Wannier function or functions are found, Bloch waves, energy eigenvalues[14] and moments of the density of states are easily obtained. Thus, a small number of Wannier functions—one in cases (1) and (3) and three in case (2)—which are solutions of a simple one-electron variational problem, incorporate conveniently the relevant information about a simple or composite band. It seems to us that, in some cases, starting with the Wannier functions and then, if needed, deriving Bloch functions and energies, may be a practical alternative computational approach to the electronic structure of solids. We plan to conduct some numerical computations in the near future.

PART I: SIMPLE BANDS

II. BASIC RELATIONS

We consider a Bravais lattice with atoms located at the lattice points

$$\vec{n} = n_1\vec{\tau}_1 + n_2\vec{\tau}_2 + n_3\vec{\tau}_3 , \tag{2.1}$$

which are also centers of inversion.

The one-electron Hamiltonian is

$$H = -\nabla^2 + V(\vec{r}) , \tag{2.2}$$

where

$$V(\vec{r} + \vec{n}) = V(\vec{r}) . \tag{2.3}$$

The eigenfunctions of H are the Bloch waves $\varphi_{m,\vec{k}}(\vec{r})$. We consider those belonging to a particular isolated simple band which we denote simply by $\varphi_{\vec{k}}(\vec{r})$. These functions have the periodicity property

$$\varphi_{\vec{k}}(\vec{r} + \vec{n}) = e^{i\vec{k}\cdot\vec{n}}\varphi_{\vec{k}}(\vec{r}) , \tag{2.4}$$

satisfy the Schrödinger equation

$$H\varphi_{\vec{k}} = E_{\vec{k}}\varphi_{\vec{k}} , \tag{2.5}$$

where $E_{\vec{k}}$ are the band energies, and obey the following orthonormality relations over the volume Ω of the crystal:

$$(\varphi_{\vec{k}},\ \varphi_{\vec{k}'}) \equiv \int_\Omega \varphi^*_{\vec{k}}(\vec{r})\varphi_{\vec{k}'}(\vec{r})\,d\vec{r} = \delta_{\vec{k}\vec{k}'} . \tag{2.6}$$

For the moment we shall leave undetermined the phases of the functions $\varphi_{\vec{k}}$.

A set of Wannier functions for the band in question is now defined by the equations

$$a(\vec{r} - \vec{n}) = N^{-1/2}\sum_{\mathrm{BZ}} \varphi_{\vec{k}}(\vec{r} - \vec{n}) = N^{-1/2}\sum_{\mathrm{BZ}} \varphi_{\vec{k}}(r)e^{-i\vec{k}\cdot\vec{n}} , \tag{2.7}$$

where N is the number of unit cells and BZ denotes summation of $\vec{k}$ in the fundamental Brillouin zone. The periodicity (2.4) and orthonormality (2.6) of the Bloch waves lead immediately to the following orthonormality of the Wannier function:

$$(a(\vec{r} - \vec{n}),\ a(\vec{r} - \vec{n}\,')) = \delta_{nn'} . \tag{2.8}$$

The equations (2.7) may be inverted to yield

$$\varphi_{\vec{k}}(\vec{r}) = N^{-1/2}\sum_n a(\vec{r} - \vec{n})e^{i\vec{k}\cdot\vec{n}} . \tag{2.9}$$

As already remarked, the Bloch waves $\varphi_{\vec{k}}(\vec{r})$ are so far determined only to within a multiplicative phase factor of the form $e^{i\theta(\vec{k})}$. This indeterminacy introduces a large ambiguity into the functional form of the Wannier function $a(\vec{r})$. We do not wish to burden this presentation with a discussion of this problem in all generality. We therefore assume that $\varphi_{\vec{k}}(0) \neq 0$ for all $\vec{k}$ and then choose $\theta(\vec{k})$ such that

$$\varphi_{\vec{k}}(0) = \text{real and positive} . \tag{2.10}$$

This makes $\varphi_{\vec{k}}(\vec{r})$ a periodic and analytic function of $\vec{k}$ and results in an exponential decay of the Wannier function $a(\vec{r})$.[6,8,9] In addition, $a(0)$ clearly has the maximum possible value and so $a(\vec{r})$ is well localized. Since, with the choice (2.10),

$$\varphi_{-\vec{k}}(\vec{r}) = [\varphi_{\vec{k}}(\vec{r})]^* = \varphi_{\vec{k}}(-\vec{r}) , \tag{2.11}$$

it follows that $a(\vec{r})$ is real and symmetric under inversion,

$$a(\vec{r}) = a^*(\vec{r}) = a(-\vec{r}) . \tag{2.12}$$

Furthermore, it is shown in the Appendix that the Wannier function thus constructed is (to within a factor ±1) the *only* Wannier function for this band which has the properties (2.12) and decays exponentially.

III. VARIATIONAL PRINCIPLE

We consider here, as in the preceding section, a simple band in a Bravais lattice with a center of inversion at the origin. Although the problem of constructing the Wannier function is, of course, a one-electron problem, we find it convenient to consider the state Ψ_0 of N spinless fermions occupying the N Bloch states of the band in question. This state is given by the following equivalent Slater determinants:

$$\Psi_0=(N\,!)^{-1/2}\det|\varphi_{\vec{k}}(\vec{r}_i)|=(N\,!)^{-1/2}\det|a(\vec{r}_i-\vec{n})|, \tag{3.1}$$

since the function $\varphi_{\vec{k}}(\vec{r})$ and $a(\vec{r}-\vec{n})$ are related by a unitary transformation, Eqs. (2.7) and (2.9). The corresponding energy per atom,

$$\mathcal{E}_0=N^{-1}\left(\Psi_0,\ \sum_{i=1}^{N} H_i\Psi_0\right)=N^{-1}\sum_{\mathrm{BZ}} E_{\vec{k}}=(a(\vec{r}),\ Ha(\vec{r})), \tag{3.2}$$

is a stationary value of the expression

$$\mathcal{E}(\Psi)\equiv N^{-1}\left(\Psi,\ \sum_{i=1}^{N} H_i\Psi\right)\Big/(\Psi,\ \Psi), \tag{3.3}$$

where Ψ is an arbitrary antisymmetric function. If the band in question is the lowest and not overlapped by other bands, then $\mathcal{E}_0$ is the minimum value of $\mathcal{E}(\Psi)$, and the minimizing function Ψ is a multiple of Ψ_0. However, physical applications deal almost never with the lowest band of a solid.

To construct an approximation to $a(\vec{r})$ we begin with an initial trial function $f(\vec{r})$ which has the same reality and point-group-symmetry properties as $a(\vec{r})$ and decreases at least exponentially for large $\vec{r}$. In general, however, the functions $f(\vec{r}-\vec{n})$ are not orthogonal to each other. In the customary manner of variational calculations, $f(\vec{r})$ is made dependent on an adequate number of parameters,

$$f(\vec{r})=f(\vec{r};\ \gamma_1,\ \gamma_2,\ \ldots), \tag{3.4}$$

and must be chosen so that for some values of the parameters, say $\gamma_1^{(0)}$, $f(\vec{r})$ is a much closer approximation to $a(\vec{r})$ than to the Wannier function of any other band. In principle, we could now immediately evaluate $\mathcal{E}(\Psi)$, Eq. (3.3), using

$$\Psi=\det|f(\vec{r}_i-\vec{n})| \tag{3.5}$$

as the trial function, and determine the γ_i (near $\gamma_i^{(0)}$) from the variational principle. However, because the functions $f(\vec{r}-\vec{n})$ are, in general, not orthogonal, this would lead to well-known divergence problems.[15]

Orthonormalization

To circumvent these problems we construct trial functions which, like the Wannier functions themselves, are orthonormal. The usual Schmidt successive orthogonalization procedure is not suitable since it destroys the identity of the functional forms of $f(\vec{r}-\vec{n})$. Instead, we use the following simple orthonormalization method which is suitable for a periodic system.[9]

First, we form the orthonormal trial Bloch waves

$$\varphi_{\vec{k}}^{t}(\vec{r})\equiv N^{-1/2}[G(\vec{k})]^{-1/2}\sum_{\vec{n}} f(\vec{r}-\vec{n})\,e^{i\vec{k}\cdot\vec{n}}, \tag{3.6}$$

where

$$\begin{aligned} G(\vec{k})&=\sum_{\vec{n}}\ (f(\vec{r}),\ f(\vec{r}-\vec{n}))\,e^{i\vec{k}\cdot\vec{n}}\\ &=\sum_{\vec{n}}\ (f(\vec{r}),\ f(\vec{r}-\vec{n}))\cos\vec{k}\cdot\vec{n}\,. \end{aligned} \tag{3.7}$$

Clearly, $G(\vec{k})$ is an analytic function of $\vec{k}$. Further, if $f(\vec{r})$ is reasonably close to the Wannier function $a(\vec{r})$, then $G(\vec{k})\approx 1$ for all $\vec{k}$ and hence, unequal to zero. Therefore, $[G(\vec{k})]^{-1/2}$ and $\varphi_{\vec{k}}^{t}$ are also analytic functions of $\vec{k}$.

Next, we reconstitute a set of localized functions following the prescription (2.7),

$$a^{t}(\vec{r}-\vec{n})\equiv N^{-1/2}\sum_{\mathrm{BZ}}\ \varphi_{\vec{k}}^{t}(\vec{r}-\vec{n})\,. \tag{3.8}$$

It can be immediately checked that these functions, like the $a(\vec{r}-\vec{n})$, are real; have the proper point symmetry; are orthonormal; and—because of the analyticity of $\varphi_{\vec{k}}^{t}$ as function of $\vec{k}$[6,8,9]—decrease exponentially with $|\vec{r}|$. They constitute our trial Wannier functions.

Substitution of (3.6) into (3.8) gives the following expression for $a^t(\vec{r})$ in terms of the initial functions $f(\vec{r})$:

$$a^{t}(\vec{r})=\sum c(\vec{n})f(\vec{r}-\vec{n}), \tag{3.9}$$

where

$$\begin{aligned} c(\vec{n})&=N^{-1}\sum_{\mathrm{BZ}}\ \frac{e^{i\vec{k}\cdot\vec{n}}}{G^{1/2}(\vec{k})}\\ &=N^{-1}\sum_{\mathrm{BZ}}\ \frac{\cos\vec{k}\cdot\vec{n}}{[\sum_{n'}(f(\vec{r}),\ f(\vec{r}-\vec{n}'))\cos\vec{k}\cdot\vec{n}']^{1/2}}\,. \end{aligned} \tag{3.10}$$

When the corresponding N-electron trial function

$$\Psi^{t}\equiv(N\,!)^{-1/2}\det|a^{t}(\vec{r}-\vec{n};\ \gamma_1,\ \gamma_2,\ \ldots)| \tag{3.11}$$

[which is a multiple of the Ψ of Eq. (3.5)] is substituted into the energy expression (3.3), one obtains simply

$$\mathcal{E}=(a^{t}(\vec{r}),\ Ha^{t}(\vec{r})) \tag{3.12}$$

as the stationary quantity; or, going back to the initial trial function $f(\vec{r})$,

$$\mathcal{E}=\sum_{\vec{n}}\ (f(\vec{r}),\ Hf(\vec{r}-\vec{n}))\sum_{\vec{n}'} c^{*}(\vec{n}')c(\vec{n}+\vec{n}'), \tag{3.13}$$

where $c(\vec{n})$ is given in terms of f by Eq. (3.10). The series in (3.13) converges exponentially. The parameters γ_1 in $f(\vec{r})$ are now varied near $\gamma_1^{(0)}$ until $\mathcal{E}$ attains its extremum. The corresponding function a^t represents an approximation to the unique a, from which various properties of the energy band can be simply obtained (see Sec. IV).

In the Appendix we show that the stationary expression (3.12) has many extrema, most of them *not* the Wannier functions of the system. However, the only extremum near the exact $a(\vec{r})$ in question that is accessible via exponentially localized trial functions $a^t(\vec{r})$ is $a(\vec{r})$ itself.

Although the Wannier function $a(\vec{r})$ of our band is uniquely defined (see the Appendix), the function $f(\vec{r})$ giving rise to it via Eqs. (3.9) and (3.10) is not unique. The resulting flexibility can be put to computational advantage. This is discussed further in Sec. V.

IV. ENERGY-BAND PROPERTIES

In this section we describe how approximations to the properties of the energy band are obtained from an approximate $a^t(\vec{r})$. First, we invert Eq. (3.9), giving

$$\varphi_{\vec{k}}^t = N^{-1/2}\sum_{\vec{n}} a^t(\vec{r}-\vec{n})\,e^{i\vec{k}\cdot\vec{n}}\,. \tag{4.1}$$

Clearly, the error of $\varphi_{\vec{k}}^t$ is of the same order as the error of a^t,

$$\delta a^t(\vec{r}) \equiv a^t(\vec{r}) - a(\vec{r})\,. \tag{4.2}$$

Next, we calculate the band energies using the stationary expression

$$E_{\vec{k}} = (\varphi_{\vec{k}},\ H\varphi_{\vec{k}})/(\varphi_{\vec{k}},\ \varphi_{\vec{k}})\,. \tag{4.3}$$

Substitution of (4.1) gives[13]

$$E_{\vec{k}}^t = \sum_{\vec{n}} E_{\vec{n}}^t e^{i\vec{k}\cdot\vec{n}}\,, \tag{4.4}$$

where

$$E_{\vec{n}}^t = (a^t(\vec{r}),\ Ha^t(\vec{r}-\vec{n}))\,. \tag{4.5}$$

Because of the stationary property of (4.3),

$$\delta E_{\vec{k}}^t \sim (\delta a^t)^2\,, \tag{4.6}$$

so that, as usual, the accuracy of $E_{\vec{k}}^t$ is much greater than that of a^t. Further, we note that because of the exponential decay of a^t, the coefficients $E_{\vec{n}}^t$ in the series (4.4) decrease exponentially with $\vec{n}$.

Finally, consider the density of states per atom of the band in question, $n(E)$. The moments,

$$M_s \equiv \int E^s n(E)\,dE\,, \tag{4.7}$$

provide a useful characterization of $n(E)$. If a sufficient number is known, $n(E)$ may be reconstructed from the M_s. Now M_s may be expressed as follows in terms of $a(\vec{r})$:

$$\begin{aligned} M_s &= N^{-1}\sum_{\mathrm{BZ}}(E_{\vec{k}})^s = N^{-1}\sum_{\mathrm{BZ}}(\varphi_{\vec{k}},\ H^s\varphi_{\vec{k}}) = N^{-1}\,\mathrm{Tr}H^s \\ &= N^{-1}\sum_{\vec{n}}(a(\vec{r}-\vec{n}),\ H^s a(\vec{r}-\vec{n})) = (a(\vec{r}),\ H^s a(\vec{r}))\,, \end{aligned} \tag{4.8}$$

where Tr means trace over the space spanned by the $\varphi_{\vec{k}}$. Alternatively, denoting the Fourier coefficient of $E(\vec{k})$ by

$$E_{\vec{n}} \equiv (a(\vec{r}),\ Ha(\vec{r}-\vec{n}))\,, \tag{4.9}$$

we can substitute the corresponding expression (4.4) for $E_{\vec{k}}$ in (4.8). This gives

$$M_s = \sum_{\vec{n}_1+\vec{n}_2+\cdots+\vec{n}_s=0} E_{\vec{n}_1}E_{\vec{n}_2}\cdots E_{\vec{n}_s}\,. \tag{4.10}$$

Clearly, if one calculates M_s^t with an approximate a^t, its error will be of order $(\delta a^t)^2$.

V. ADDITIONAL REMARKS

One may wonder whether it may not be very complicated to find an adequate primary trial function $f(\vec{r})$, since $a(\vec{r})$ has a rather complex oscillatory form. Here, the observation of Anderson[12] is relevant, namely, that there exist "ultralocalized" nonorthogonal functions $f(\vec{r})$, in terms of which the exact Bloch waves $\varphi_{\vec{k}}(\vec{r})$ may be expanded in the form (3.6) and (3.7). In our procedure these $f(\vec{r})$ will give the exact Wannier functions, including the correct oscillations, by Eqs. (3.9) and (3.10). Thus, for our initial functions $f(\vec{r})$, simple short-range functions of the proper symmetry should be sufficient.

There is, however, one complication compared, for example, to the problem of finding the ground state of a particle in an isolated potential well $V_0(\vec{r})$. For this latter problem a very convenient method is the Rayleigh–Ritz method. There one expands the trial function $\psi^t(\vec{r})$ as a linear combination of suitably chosen functions:

$$\psi^t(\vec{r}) = \sum_{1}^{M}\gamma_i\psi_i(\vec{r})\,. \tag{5.1}$$

Then both $(\psi^t,\ H\psi^t)$ and $(\psi^t,\ \psi^t)$ are quadratic forms of the γ_i, and requiring the expectation value of the energy to be stationary, leads to linear equations for the γ_i; these, in turn, yield a convenient secular equation for the energy. In the present case, if $f(\vec{r})$ is similarly expanded, the stationary quantity,

$$\mathcal{E} = N^{-1}\frac{(\Psi,\ \sum H_i\Psi)}{(\Psi,\ \Psi)}\,, \tag{5.2}$$

is given by Eq. (3.13) and, in view of Eq. (3.10), is not a ratio of two quadratic forms. Thus, the extremization must be done numerically by simultaneous variation of the parameters γ_i. This is a well-known problem in numerical analysis and, provided one has a reasonably good starting function for $f(\vec{r})$ (such as an atomic function), presents no serious difficulty.

If, when dealing with a higher band, one prefers to work with a minimum principle rather than the merely stationary quantity (5.2), one has two choices. Suppose the band in question is the second, $m=2$, and the Wannier functions for the first, $a_1(\vec{r}-\vec{n})$, are already known. (They may, for all practical purposes, be atomic functions.) Then one may first orthogonalize the preliminary trial function $f_2(\vec{r})$ for the second band to all $a_1(\vec{r}-\vec{n})$ in the manner of the orthogonalized-plane-wave (OPW) method,[16]

$$f_2'(\vec{r})=f_2(\vec{r})-\sum d(\vec{n})a_1(\vec{r}-\vec{n}), \qquad (5.3)$$

where

$$d(\vec{n})=(a_1(\vec{r}-\vec{n}),\ f_2(\vec{r})). \qquad (5.4)$$

Now the stationary expression (5.2) becomes a minimum. Alternatively, if a_1 is not known, one may treat the two lowest bands together as a composite band, as discussed in the following sections. The total energy for both bands is then a minimum.

PART 2: COMPOSITE BANDS

VI. GENERAL CONSIDERATIONS

In Secs. II–V we have discussed the Wannier functions corresponding to an isolated simple band, e.g., $E(\vec{k})$. We now consider a *set* of crystal eigenfunctions, $\varphi_{m\vec{k}}(\vec{r})$, satisfying the Schrödinger equation

$$H\varphi_{m\vec{k}}(\vec{r})=E\varphi_{m\vec{k}}(\vec{r}),\quad m=1,2,\ldots,\bar{m} \qquad (6.1)$$

whose eigenvalues $E_{m\vec{k}}$ are disconnected from all other bands. The $E_{m\vec{k}}$ may all be connected to each other, or they may be partly or wholly disconnected from each other. We wish to construct a useful set of localized Wannier functions,

$$a_m(\vec{r}-\vec{n}),\quad m=1,2,\ldots,\bar{m} \qquad (6.2)$$

related to the $\varphi_{m,\vec{k}}(\vec{r})$ by a unitary transformation.

This problem arises in two kinds of circumstances. Either the levels are so interconnected that no single branch $E_{m\vec{k}}$ is both an analytic and periodic function of $\vec{k}$. In that case *no* Wannier function of the form

$$a_m(\vec{r}-\vec{n})\equiv N^{-1/2}\sum_{\vec{k}}\varphi_{m\vec{k}}(\vec{r})e^{i\theta(\vec{k})} \qquad (6.3)$$

constructed from one branch *alone* will be exponentially localized. This case is examplified by fully hybridized s-d bands in transition metals. Or, even though the levels $E_{m,\vec{k}}$ may be wholly disconnected from each other as well as from other bands, more desirable Wannier functions, with better localization or higher symmetry, can sometimes be constructed by treating all branches $E_{m,\vec{k}}$ together. This case is exemplified by systems in which slight lattice distortions have produced small energy gaps but where much better localized Wannier functions can be constructed by lumping the split bands together. This latter case has been treated by Onffroy (unpublished). Related questions are also discussed in Sec. VIII.

The construction of the Wannier functions $a_m(\vec{r}-\vec{n})$ for composite bands in terms of the Bloch waves has been described in detail by Des Cloizeaux.[7–9] Here we wish to show how to calculate them directly, i.e., without using the Bloch waves, by means of a variational method.

The most general case requires elaborate group-theoretic consideration, for which we refer the reader to Des Cloizeaux's papers. Here we shall illustrate the procedure by two characteristic examples, namely, hybridized s-d bands in a cubic material discussed in Sec. VII and the valence and conduction bands in diamond-type structures, discussed in Sec. VIII.

VII. HYBRIDIZED *s-d* BANDS IN A bcc LATTICE

In this section we consider hybridized s-d bands in a bcc lattice, assumed to be disconnected from all other bands. Such a band is characterized by six Wannier functions $a_m(\vec{r}-\vec{n})$ centered on each atomic site $\vec{n}$, with the symmetry and degeneracy properties[7] shown in Table I.

In addition to their symmetry characteristics these functions have the following properties: They are real, exponentially localized, and orthonormal,

$$(a_m(\vec{r}-\vec{n}),\ a_{m'}(\vec{r}-\vec{n}\,'))\delta_{mm'}\delta_{\vec{n}\vec{n}'}; \qquad (7.1)$$

and the Bloch waves can be obtained from them by means of a unitary transformation of the form[14]

$$\varphi_{m\vec{k}}(\vec{r})=\sum_{m'}\left(N^{-1/2}\sum_{\vec{n}}a_{m'}(\vec{r}-\vec{n})e^{i\vec{k}\cdot\vec{n}}\right)U_{m'm}(\vec{k}), \qquad (7.2)$$

where

$$\sum_{m''}U^*_{mm''}(\vec{k})U_{m''m'}(\vec{k})=\delta_{mm'}. \qquad (7.3)$$

Now we consider the eigenstate of a system of $\bar{m}N$ spinless electrons occupying the $\bar{m}N$ levels $E_{m\vec{k}}$ of the s-d band. In view of the fact that the $\varphi_{m\vec{k}}$ and $a_m(\vec{r}-\vec{n})$ are connected by a unitary transformation, the wave function for this state can be written in either of the following two forms:

$$\begin{aligned}\Psi&=[(\bar{m}N)!]^{-1/2}\det|\varphi_{m\vec{k}}(\vec{r}_i)|\\&=[(\bar{m}N!)]^{-1/2}\det|a_m(\vec{r}_i-\vec{n})|,\end{aligned} \qquad (7.4)$$

where each site $\vec{n}$ is occupied by electrons in each of the six Wannier states. The corresponding total energy per atom,

$$\mathcal{E}(\Psi)=N^{-1}\left(\Psi,\ \sum_{i=1}^{\bar{m}N}H_i\Psi\right)\Big/(\Psi,\Psi), \qquad (7.5)$$

is stationary with respect to arbitrary variations

TABLE I. The six Wannier functions of a hybridized s-d band.

Irreducible representation	Corresponding atomic state	Symmetry type	Degeneracy
Γ_1	s	1	1
Γ_{12}	d	$x^2-y^2,\ z^2-\frac{1}{2}(x^2+y^2)$	2
Γ_{25}'	d	xy, yz, zx	3

of the functions $a_m(\vec{r})$. If the trial functions $a_m^t(\vec{r})$ satisfy the orthonormality conditions (7.1), then (7.5) can be written as

$$\mathcal{E}(\Psi)=\sum_{m=1}^{\bar{m}}(a_m^t(\vec{r}),\ Ha_m^t(\vec{r}))\,. \tag{7.6}$$

We now turn to the construction of localized, orthonormal trial functions of the correct symmetry types. We begin with a set of normalized, localized but nonorthogonal functions, depending on variational parameters γ_i,

$$f_m(\vec{r})=f_m(\vec{r};\ \gamma_1,\gamma_2,\ldots),\quad m=1,\ldots,6 \tag{7.7}$$

which belong, respectively, to the irreducible representations Γ_1, Γ_{12}, and Γ_{25}' (see Table I). There are thus only three independent functional forms. For example, functions behaving under rotation like atomic s and d functions can be used. For greater precision, higher cubic harmonics must be added. It is convenient and easy to orthogonalize each $f_m(\vec{r})$ to all localized core states $\psi_j(\vec{r}-\vec{n})$; this will convert the expression (7.5) from an extremum to a minimum.

It remains to mutually orthonormalize the functions $f_m(\vec{r})$ while maintaining their symmetry properties. This can be done in a manner adapted from the work of Des Cloiseaux.[9] We begin by constructing a first intermediate set of quasi-Bloch functions, having the translational symmetry of the lattice,

$$\chi_{m,\vec{k}}(\vec{r})\equiv N^{-1/2}\sum_{\vec{n}}f_m(\vec{r}-\vec{n})\,e^{i\vec{k}\cdot\vec{n}}\,. \tag{7.8}$$

These are not yet orthonormal. For each $\vec{k}$ we introduce the Hermitian inner-product matrix,

$$\begin{aligned}G(\vec{k})_{m'm}&\equiv(\chi_{m'\vec{k}}(\vec{r}),\ \chi_{m\vec{k}}(\vec{r}))\\&=\sum_{\vec{n}}(f_{m'}(\vec{r}),\ f_m(\vec{r}-\vec{n}))\,e^{i\vec{k}\cdot\vec{n}}\,,\end{aligned} \tag{7.9}$$

and the derived matrix $G^{-1/2}(\vec{k})_{m'm}$, defined by

$$G^{-1/2}(\vec{k})_{m'm'''}G(\vec{k})_{m'''m''}G^{-1/2}(\vec{k})_{m''m}=\delta_{m'm}\,. \tag{7.10}$$

($G^{-1/2}$ can be easily constructed by first bringing G to diagonal form.) Then the following second set of intermediate quasi-Bloch functions,

$$\begin{aligned}\psi_{m,\vec{k}}(\vec{r})&\equiv\sum_{m'}\chi_{m'\vec{k}}(\vec{r})G^{-1/2}(\vec{k})_{m'm}\\&=N^{-1/2}\sum_{m',\vec{n}}e^{i\vec{k}\cdot\vec{n}}\left(\sum_{m'}f_{m'}(\vec{r}-\vec{n})G^{-1/2}(\vec{k})_{m'm}\right),\end{aligned} \tag{7.11}$$

is orthonormal, as may be verified by direct substitution. As in Sec. III, since $G(\vec{k})$ and $G^{-1/2}(\vec{k})$ are analytic functions of $\vec{k}$, so is $\psi_{m\vec{k}}$. For our trial Wannier functions we now take

$$a_m^t(\vec{r})=N^{-1/2}\sum_{\vec{k}}\psi_{m\vec{k}}(\vec{r})\,. \tag{7.12}$$

These are clearly exponentially localized and orthonormal. Since the process of orthogonalization has in no way violated the cubic symmetry of the crystal, the a_m^t transform under operations of the cubic point group just like the $f_m(\vec{r})$. This may also be directly verified. Resubstituting in (7.12) from (7.11),

$$a_m^t(\vec{r})=\sum_{m',\vec{n}}f_{m'}(\vec{r}-\vec{n})\,c_{m'm}(\vec{n})\,, \tag{7.13}$$

where

$$c_{m'm}(\vec{n})=N^{-1}\sum_{\vec{k}}e^{i\vec{k}\cdot\vec{n}}\,G^{-1/2}(\vec{k})_{m'm}\,. \tag{7.14}$$

The stationary energy expression (7.6) becomes

$$\mathcal{E}=\sum_{m'm''\vec{n}}(f_{m'}(\vec{r}),\ Hf_{m''}(\vec{r}-\vec{n}))\,C_{m'm''}(\vec{n})\,, \tag{7.15}$$

where

$$C_{m'm''}(\vec{n})\equiv\sum_{m,\vec{n}'}c^*_{m''m}(\vec{n}\,')c_{m''m}(\vec{n}+\vec{n}\,')\,. \tag{7.16}$$

Often the original functions $f_m(\vec{r}-\vec{n})$ are not far from orthogonal. In that case the orthogonalization can be accomplished by an alternative method, using a rapidly convergent infinite series.[13] We write

$$\alpha\equiv(m,\vec{n}),\quad f_\alpha(\vec{r})\equiv f_m(\vec{r}-\vec{n})\,, \tag{7.17}$$

$$G_{\alpha'\alpha}\equiv(f_{\alpha'},f_\alpha)=\delta_{\alpha'\alpha}+S_{\alpha'\alpha}\,, \tag{7.18}$$

where the overlap integral $S_{\alpha'\alpha}$ is

$$S_{\alpha'\alpha}=(f_{\alpha'},f_\alpha)(1-\delta_{\alpha'\alpha})\,. \tag{7.19}$$

Then

$$G^{-1/2}_{\alpha'\alpha}=\delta_{\alpha'\alpha}-\tfrac{1}{2}S_{\alpha'\alpha}+\tfrac{3}{8}S_{\alpha'\alpha''}S_{\alpha''\alpha}+\cdots \tag{7.20}$$

and

$$\begin{aligned}a_\alpha^t&=\sum_{\alpha'}f_{\alpha'}G^{-1/2}_{\alpha'\alpha}\\&=f_\alpha-\frac{1}{2}\sum_{\alpha'\neq\alpha}f_{\alpha'}(f_{\alpha'},f_\alpha)\\&\quad+\frac{3}{8}\sum_{\alpha'}f_{\alpha'}\sum_{\alpha''\neq\alpha,\alpha'}(f_{\alpha'},f_{\alpha''})(f_{\alpha''},f_\alpha)+\cdots\,.\end{aligned} \tag{7.21}$$

With this the energy expression (7.6) can be directly evaluated in terms of the quantities

$$(f_{\alpha'},\ Hf_\alpha)\ \text{and}\ (f_{\alpha'},f_\alpha) \tag{7.22}$$

and minimized with respect to the parameters γ_i occurring in f.

Energy-Band Properties

Since the Bloch waves are unitary transforms of the Wannier functions and are eigenfunctions of the translation operator, they must have the form (7.2),

$$\varphi_{m\vec{k}}(\vec{r})=\sum_{m'}\left(N^{-1/2}\sum_{\vec{n}}a_{m'}(\vec{r}-\vec{n})\,e^{i\vec{k}\cdot\vec{n}}\right)U(\vec{k})_{m'm}\,, \tag{7.23}$$

where the $U(\vec{k})_{m'm}$ are unitary 6×6 matrices. Substituting this form into the Schrödinger equation (6.1) and using the orthonormality of the $a_m(\vec{r}-\vec{n})$ gives

$$\sum_{m''} \mathcal{E}(\vec{k})_{m'm''} U(\vec{k})_{m''m} = EU(\vec{k})_{m'm}\,, \tag{7.24}$$

where

$$\mathcal{E}(\vec{k})_{m'm''} \equiv \sum_{\vec{n}} (a_{m'}(\vec{r}),\ Ha_{m''}(\vec{r}-\vec{n}))e^{i\vec{k}\cdot\vec{n}}. \tag{7.25}$$

Equation (7.24) determines the eigenvalues $E = E_{m\vec{k}}$ as solutions of the 6×6 eigenvalue problem[14]

$$\det|\mathcal{E}(\vec{k})_{m'm''} - E\delta_{m'm''}| = 0\,. \tag{7.26}$$

The corresponding coefficients $U(\vec{k})_{m'm}$ are then obtained by means of (7.24) and yield the Bloch waves $\varphi_{m\vec{k}}(\vec{r})$ via (7.23).

Because of the linear connection (7.13) between the a_m and the nonorthogonal functions f_m, Eq. (7.23) may be replaced by

$$\varphi_{m\vec{k}}(\vec{r}) = N^{-1/2} \sum_{m'\vec{n}} f_{m'}(\vec{r}-\vec{n})e^{i\vec{k}\cdot\vec{n}}\beta_{m'm}(\vec{k})\,, \tag{7.27}$$

leading to the alternative form of the secular equation

$$\det|\mathcal{E}'(\vec{k})_{m'm''} - \mathfrak{N}'(\vec{k})_{m'm''}| = 0\,, \tag{7.28}$$

where

$$\mathcal{E}'(\vec{k})_{m'm''} \equiv \sum_{\vec{n}} (f_{m'}(\vec{r}),\ Hf_{m''}(\vec{r}-\vec{n}))e^{i\vec{k}\cdot\vec{n}} \tag{7.29}$$

and

$$\mathfrak{N}'(\vec{k})_{m'm''} = \sum_{\vec{n}} (f_{m'}(\vec{r}),\ f_{m''}(\vec{r}-\vec{n}))e^{i\vec{k}\cdot\vec{n}}. \tag{7.30}$$

Since generally the f_m will be shorter ranged than the a_m,[12] the sums over $\vec{n}$ in (7.29) and (7.30) should converge more rapidly than in (7.25).

The moments of the density of states per atom can be discussed as in Sec. IV, leading to the following result:

$$\begin{aligned} M_s &\equiv \int E^s n(E)dE = N^{-1}\,\mathrm{Tr}H^s \\ &= N^{-1}\sum_{m\vec{n}} (a_m(\vec{r}-\vec{n}),\ H^s a_m(\vec{r}-\vec{n})) \\ &= \sum_m (a_m(\vec{r}),\ H^s a_m(\vec{r}))\,. \end{aligned} \tag{7.31}$$

Or noting that

$$\begin{aligned} (a_m(\vec{r}),\ H^2 a_m(\vec{r})) = \sum_{m_1 n_1} (a_m(\vec{r}),\ Ha_{m_1}(\vec{r}-\vec{n}_1)) \\ \times (a_{m_1}(\vec{r}-\vec{n}_1),\ Ha_m(\vec{r}))\,, \end{aligned} \tag{7.32}$$

etc., we find, as a generalization of (4.10),

$$M_s = \sum_{\vec{n}_1+\vec{n}_2+\cdots+\vec{n}_s=0} \sum E(\vec{n}_1)_{mm_1}E(\vec{n}_2)_{m_1m_2}\cdots E(\vec{n}_s)_{m_{s-1}m}\,, \tag{7.33}$$

where

$$E(\vec{n})_{m'm''} \equiv (a_{m'}(\vec{r}),\ Ha_{m''}(\vec{r}-\vec{n}))\,; \tag{7.34}$$

these are just the Fourier-expansion coefficients of the matrix elements $\mathcal{E}(\vec{k})_{m'm''}$, Eq. (7.25), appearing in the secular equation (7.26) for the energy eigenvalues $E_{m\vec{k}}$.

VIII. HYBRIDIZED *s-p* BANDS IN THE DIAMOND STRUCTURE

We consider here the bands in a diamond structure of cube edge a arising out of s and p atomic orbitals. Corresponding Wannier functions have been previously discussed by Hall[3] and Des Cloizeaux[7] and used by Slater and Koster[14] as a basis for their interpolation scheme. Here we discuss briefly the method of constructing the Wannier function with the aid of the variational principle.

Solids with the diamond structure have two atoms (I and II, Fig. 1) and eight s and p electrons per unit cell. The translation subgroup is fcc. Corresponding to the eight atomic s and p spatial orbitals per unit cell, there are eight branches of a band or bands which, allowing for spin, can accommodate 16 electrons per unit cell. Hence, only half of these states will be occupied in the ground state. In C (diamond), Si, and Ge the eight branches split into two disconnected bands, the lower, valence, or bounding band and the upper, conduction or antibonding band. Only the lower is occupied.[17] In grey Sn, the valence and conduction bands are connected.[18] We shall, from here on, discuss the situation pertaining to C, Si, and Ge.

In constructing the Wannier functions we have the following choices: We can either construct a set of eight atom-centered Wannier functions in each unit cell in terms of which the Bloch waves of all eight branches can be expressed; or we can construct two sets of four bond-centered Wannier functions, one set giving rise to the Bloch waves of the valence band while the other generates the Bloch waves of the conduction band.

A. Atom-Centered Wannier Functions

Take the nucleus of the first atom in the unit cell as the origin of coordinates, and let the second

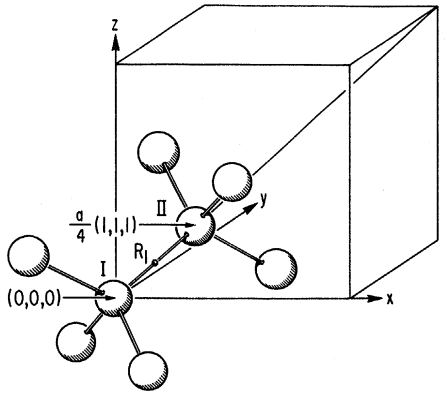

FIG. 1. Atoms in the diamond structure. The translation lattice is fcc and there are two atoms, I and II, per unit cell. The point R_1 at $\frac{1}{8}a\,(1,1,1)$ is the center of the bond joining atoms I and II.

atom, of the unit cell have coordinates $(\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)$. (See Fig. 1.)

The four Wannier functions centered on the first atom have the symmetry properties shown in Table II, which refers to the tetrahedral group T_d. The remaining four functions centered on atom II are obtained by inversion in the midpoint R_1 between I and II,

$$a_{\mathrm{II}s}(x, y, z) = a_{\mathrm{I}s}(\tfrac{1}{4}a - x, \tfrac{1}{4}a - y, \tfrac{1}{4}a - z), \qquad (8.1)$$

etc.

To obtain these functions variationally we proceed in analogy with Sec. VII. We start with normalized trial functions,

$$f_{\mu m}(\vec{r}), \quad \mu = \mathrm{I}, \mathrm{II}, \quad m = s, x, y, z \qquad (8.2)$$

with the correct point-group symmetries, but—in general—not obeying the orthogonality conditions imposed on the Wannier functions. Next we form the first intermediate set of quasi-Bloch functions,

$$\chi_{\mu m \vec{k}}(\vec{r}) = N^{-1/2} \sum_{\vec{n}} f_{\mu m}(\vec{r} - \vec{n})\, e^{i\vec{k}\cdot\vec{n}}, \qquad (8.3)$$

where $\vec{n}$ runs over the fcc lattice vectors and N is the number of unit cells. We then form the inner-product matrix,

$$G(\vec{k})_{\mu' m', \mu m} = (\chi_{\mu' m' \vec{k}}, \chi_{\mu m \vec{k}}), \qquad (8.4)$$

and then the second set of intermediate quasi-Bloch functions

$$\psi_{\mu m}(\vec{k}) = N^{-1/2} \sum \chi_{\mu' m'}(\vec{k})\, G^{-1/2}(\vec{k})_{\mu' m', \mu m}, \qquad (8.5)$$

which is orthonormal. The corresponding trial Wannier functions, having all the required properties, are

$$a^t_{\mu m}(\vec{r}) = N^{-1/2} \sum_{\mathrm{BZ}} \psi_{\mu m \vec{k}}(\vec{r}). \qquad (8.6)$$

Alternatively, particularly when the $f_{\mu m}(\vec{r} - \vec{n})$ are nearly orthogonal to one another, one can follow a procedure analogous to that described in Sec. VII, Eqs. (7.17)–(7.21), in order to obtain orthonormal trial Wannier functions $a^t_{\mu m}$.

The stationary expression for the energy per unit cell of $8N$ spinless electrons filling all eight branches of the s-p band structure is

$$\begin{aligned} \mathcal{E}(\Psi) &= \sum_{\mu, m} (a^t_{\mu m}(\vec{r}), H a^t_{\mu m}(\vec{r})) \\ &= 2 \sum_{m=1}^{4} (a^t_{\mathrm{I}m}(\vec{r}), H a^t_{\mathrm{I}m}(\vec{r})), \end{aligned} \qquad (8.7)$$

and the parameters which occur in the $f_{\mu m}$ and hence also in $a^t_{\mathrm{I}m}$ can now be determined from the stationary property of $\mathcal{E}$.

TABLE II. The atom-centered Wannier functions of a hybridized s-p band.

Irreducible representation	Corresponding atomic state	Symmetry type	Degeneracy
Γ_1	s	1	1
Γ_{15}	p	x, y, z	3

We remark that the energy can also be expressed in terms of a single hybridized tetrahedral orbital. As is well known,[19] the four tetrahedral functions

$$a'_1 = \tfrac{1}{2}(a_s + a_x + a_y + a_z), \qquad a'_2 = \tfrac{1}{2}(a_s + a_x - a_y - a_z),$$

$$a'_3 = \tfrac{1}{2}(a_s - a_x + a_y - a_z), \qquad a'_4 = \tfrac{1}{4}(a_s - a_x - a_y + a_z) \qquad (8.8)$$

(where the common subscript I has been suppressed), the orthogonal combinations of the four s- and p-like functions a_s, a_x, a_y, a_z. Since they are also equivalent to each other, we may write

$$\mathcal{E}(\Psi) = 8(a'_1(\vec{r}), H a'_1(\vec{r})). \qquad (8.9)$$

Energy-Band Properties

All eigenfunctions and eigenvalues of the eight-branch s, p-band structure can be derived from the two functions $a_s(\vec{r})$, $a_x(\vec{r})$ or even from the single tetrahedral function $a'_1(\vec{r})$ from which evidently $a_s(\vec{r})$ and $a_x(\vec{r})$ can be separately obtained. The procedure is quite analogous to that of Sec. VII. Here we only give the 8×8 secular equation for the energy eigenvalues:

$$\det \left| \mathcal{E}(\vec{k})_{\mu' m', \mu m} - E \delta_{\mu' m', \mu m} \right| = 0, \qquad (8.10)$$

where

$$\mathcal{E}(\vec{k})_{\mu' m'; \mu m} = \sum_{\vec{n}} (a_{\mu' m'}(\vec{r}), H a_{\mu m}(\vec{r} - \vec{n}))\, e^{i\vec{k}\cdot\vec{n}}. \qquad (8.11)$$

Moments of the density of states for the entire eight-branch structure can also be obtained as in Sec. VII.

B. Bond-Centered Wannier Functions

As we have already remarked, in diamond, Si, and Ge, the eight-branch s-p band structure splits into a four-branch valence band and a four-branch conduction band. Instead of representing the entire eight-branch structure by eight atom-centered Wannier functions per unit cell, one can also represent the valence and conduction bands separately by four bond-centered Wannier functions, $a^{(v)}_m(\vec{r})$ and $a^{(c)}_m(\vec{r})$ $(m = 1, \ldots, 4)$, respectively. Let us denote the midpoints between the atom I at the origin and its four nearest neighbors by $\vec{R}_m$ $(m = 1, \ldots, 4)$. Thus, for example,

$$\vec{R}_1 = \frac{a}{8}(1, 1, 1). \qquad (8.12)$$

(See Fig. 1.) Then the function $a^{(v)}_m(\vec{r})$ belongs to the identity representation of the point group C_{3i} (or S_6) associated with the "bond center" R_m; similarly, $a^{(c)}_m(\vec{r})$ belongs to the one-dimensional antisymmetric representation of the same group. Of course the four functions $a_m^{(v)}(\vec{r})$ differ only in orientation and can be transformed into one another by appropriate C_3 rotations; the same is true of the four functions $a_m^{(c)}(\vec{r})$.

We shall now deal with the symmetric valence-band Wannier functions $a_m^{(v)}$; the discussion for the antisymmetric conduction-band functions $a_m^{(c)}$ is completely analogous.

The Bloch waves of the valence band $\varphi_{m\vec{k}}^{(v)}$, $m=1, \ldots, 4$, are spanned by the Wannier functions

$$a_m^{(v)}(\vec{r}-\vec{n}), \quad m=1, \ldots, 4 \tag{8.13}$$

where the $\vec{n}$ are the lattice vectors of the fcc translation lattice. The construction of orthogonal trial Wannier functions from nonorthogonal starting functions $f_m^{(v)}(\vec{r})$ follows the same procedure as before. The stationary expression for the energy per unit cell of $4N$ spinless electrons filling the valence-band states is

$$\mathcal{E}(\Psi)=4(a_1^{(v)}(\vec{r}),\ Ha_1^{(v)}(\vec{r})). \tag{8.14}$$

The energy eigenvalues are given by the 4×4 secular equation

$$\det\left|\mathcal{E}(\vec{k})_{m'm}-E\delta_{m'm}\right|=0, \tag{8.15}$$

where

$$\mathcal{E}(\vec{k})_{m'm}=\sum_{\vec{n}}(a_{m'}^{(v)}(\vec{r}-\vec{n}),\ Ha_m^{(v)}(\vec{r}-\vec{n}))e^{i\vec{k}\cdot\vec{n}}. \tag{8.16}$$

We wish to make some concluding remarks about the relationship of the eight atom-centered Wannier functions per unit cell, $a_{\mu m}(\vec{r})$ or $a'_{\mu m}(\vec{r})$ ($\mu=\mathrm{I}, \mathrm{II}$; $m=1, \ldots, 4$) and the eight bond-centered Wannier functions $a_m^{(v)}$ and $a_m^{(c)}$. From qualitative chemical reasoning one might expect that the bonding function $a_m^{(v)}$ can be written as the symmetrized combination of two atom-centered tetrahedral functions $a'_{\mu m}$ which "point" along the same bond line. (See Fig. 1.) Call this normalized symmetric combination $a_m^{(s)}$. Similarly, one might expect the antibonding functions to be given by the antisymmetrized linear combination $a_m^{(a)}$ of the same "tetrahedral" functions $a'_{\mu m}$. In fact, the totality of functions,

$$a_m^{(s)}(\vec{r}-\vec{n}), \quad a_m^{(a)}(\vec{r}-\vec{n}), \tag{8.17}$$

does form a perfectly satisfactory alternative set of Wannier functions for the entire eight-branch structure. However, whereas clearly

$$(a_m^{(v)}(\vec{r}-\vec{n}),\ Ha_m^{(c)}(\vec{r}-\vec{n}'))=0 \tag{8.18}$$

and thus the $a_m^{(v)}$ and $a_m^{(c)}$ are completely decoupled, in general

$$(a_m^{(s)}(\vec{r}-\vec{n}),\ Ha_m^{(a)}(\vec{r}-\vec{n}'))\neq 0. \tag{8.19}$$

This observation is related to a practical matter. Suppose the valence and conduction bands are separated by a very small direct-energy gap Δ_1, while the nearest-lying other bands are well separated from both bands by a substantial gap Δ_2. In this case we expect the separate valence- and conduction-band wave functions, $a^{(v)}$ and $a^{(c)}$, to be necessarily rather spread out, having an exponential decay constant of the order of[6,8,9]

$$r^{(v)}\approx r^{(c)}\approx \Delta_1^{-1/2}. \tag{8.20}$$

On the other hand, the atom-centered Wannier functions $a_{\mu m}$ describing the entire eight-branch structure can be well localized, with an exponential decay constant of the order of

$$r\approx \Delta_2^{-1/2}. \tag{8.21}$$

Thus, in such a situation the atom-centered functions may be much easier to approximate by simple trial functions and hence be preferable for a variational calculation.

To complete the discussion of the relationship between the atom-centered tetrahedral functions $a'_{\mu m}$ and the bond-centered functions $a_m^{(v)}$ and $a_m^{(c)}$ we observe that, starting from the latter, one can very simply form acceptable atom-centered tetrahedral functions, namely,

$$a''_{\mu m}=(1/\sqrt{2})(a_m^{(v)}\pm a_m^{(c)}). \tag{8.22}$$

But these are, in general, not the same as the $a'_{\mu m}$ which are directly constructed for the entire eight-branch structure. The nonuniqueness of Wannier functions of composite bands, which is implied by the last statement, is further discussed in the next section.[20]

IX. NONUNIQUENESS OF WANNIER FUNCTIONS OF COMPOSITE BANDS

Whereas we saw in the Appendix that for a simple band in a lattice with inversion center there existed a unique, real, and exponentially decaying Wannier function with the symmetry of the lattice, this is, in general, no longer true for composite bands. Let $a_m(\vec{r}-\vec{n})$ be a set of Wannier functions. Any other set must arise from these by a unitary transformation

$$\bar{a}_m(\vec{r}-\vec{n})=\sum a_{m'}(\vec{r}-\vec{n}')(m'\vec{n}'|U|m\vec{n}). \tag{9.1}$$

Since the $\bar{a}_m$'s, like the a's, must be real, the matrix U has the form

$$U=e^{iS}, \tag{9.2}$$

where S is a Hermitian and purely imaginary, hence antisymmetric, matrix,

$$(m'\vec{n}'|S|m\vec{n})=-(m\vec{n}|S|m'\vec{n}'). \tag{9.3}$$

In addition, U must preserve the symmetry properties and short-range character of the a's. For a simple band with inversion center we have seen that only $U=\pm 1$ satisfies all these conditions. For the present case we shall presently give an explicit illustration of nonuniqueness which we believe to be typical. Of course, if desired, this nonuniqueness can be removed by additional requirements such as[10]

$$\sum_{m=1}^{\bar{m}} \langle a_m^2(\vec{r})\, r^2 \rangle = \text{minimum}\,, \tag{9.4}$$

or the maximization of the sum of orbital self-repulsion energies.[21] But such conditions are difficult to impose in practice and we believe that the nonuniqueness will, for most purposes, lead to no significant problems.

Now for the illustration. We consider a hybridized s-p band in a simple cubic lattice of cube edge a. Let one set of Wannier functions for this band be a_s and a_x, a_y, a_z with symmetries Γ_1 and Γ_{15}, respectively. Then, if ϵ is an infinitesimal, to first order in ϵ the following functions constitute an alternative set with all the required properties:

$$\begin{aligned} \bar{a}_s(\vec{r}) = a_s(\vec{r}) + \epsilon[&a_x(x-a,\ y,\ z) - a_x(x+a,\ y,\ z) \\ &+ a_y(x,\ y-a,\ z) - a_y(z,\ y+a,\ z) \\ &+ a_z(x,\ y,\ z-a) - a_z(x,\ y,\ z+a)]\,, \\ \bar{a}_x(\vec{r}) = a_x(\vec{r}) + \epsilon[&a_s(x-a,\ y,\ z) - a_s(x+a,\ y,\ z)]\,, \end{aligned} \tag{9.5}$$

with $\bar{a}_y$ and $\bar{a}_z$ analogous.

A general analysis of the nonuniqueness of composite Wannier functions has not yet been carried out.

X. NONIDEAL WANNIER FUNCTIONS

In many, if not most, real band problems the conditions which we have stipulated do not hold. For example, in all of the alkali metals the conduction s band is attached at points or lines of symmetry to higher bands,[22] and calculations for the transition metals[23] show the hybridized s-d bands of transition metals also to be attached to higher bands. Such attachment may be viewed as a remnant of free-electron-like behavior,[24] and Wannier functions—which emphasize the relationship of Bloch waves to atomic functions—are, of course, not ideally suited to such cases. Trying to incorporate the next higher band in an enlarged composite band generally does not eliminate the difficulty, since that band is usually itself connected higher up, etc.

Nevertheless, in such cases one can still construct "nonideal" Wannier functions in the general manner indicated in the preceding sections. However, because the Bloch waves, when taken to be periodic functions of $\vec{k}$, are nonanalytic functions of $\vec{k}$ either at points on the Brillouin-zone boundary or at points of contact in the interior or both, the exact, nonideal Wannier functions are not exponentially localized.

A well-known example is free electrons in a simple cubic lattice, of lattice constant a, for which the exact, nonideal Wannier function corresponding to the lowest band is

$$a(r) = \frac{a^{3/2}}{\pi^3}\, \frac{\sin(\pi x/a)}{x}\, \frac{\sin(\pi y/a)}{y}\, \frac{\sin(\pi z/a)}{z}\,. \tag{10.1}$$

If one makes a variational calculation, using exponentially localized f's and hence exponentially localized trial Wannier functions a_m^t, the Bloch waves (= plane waves) and energy eigenvalues near the zone boundary will not be properly reproduced. However, one can easily verify in this example that if $a(\vec{r})$ is cut off at a large distance $r \approx r_0$, only Bloch waves and eigenvalues within $\Delta k \sim \pi/r_0$ of the zone boundary are significantly affected.

Clearly, this result is typical of nonideal Wannier functions in general. We conclude that in the case of nondetached bands, use of sufficiently extended trial Wannier functions, even if they decay exponentially for very large r, can give arbitrarily accurate results for general points in the interior of the zone boundary, but may give incorrect results at points on and near the zone boundary and at or near any interior point where there is an attachment to another band. In any given case this last statement can be made more precise.

Another difficulty, connected with nonexponential falloff, is that the spurious solutions of the variational principle, which are composed of Bloch waves from several bands, cannot now be generally ruled out. However, if by means discussed in Sec. V, the stationary principle has been turned into a minimal principle, only correct Wannier functions will be constructed.

APPENDIX: UNIQUENESS OF WANNIER FUNCTION $a(\vec{r})$ FOR A SIMPLE BAND

We consider a simple band in a Bravais lattice with center of inversion at $r = 0$ and assume that $\varphi_{\vec{k}}(0) \neq 0$ for all $\vec{k}$. In this case we shall first show that (to within a factor of ± 1) there exists only one Wannier function for this band, as defined by Eq. (2.7), which is real and symmetric under inversion and which decays exponentially.

Let $\varphi_{\vec{k}}(\vec{r})$ be the normalized Bloch waves with phases chosen so that $\varphi_{\vec{k}}(0)$ is real and positive. As explained in Sec. II, the corresponding Wannier function,

$$a(\vec{r}) = N^{-1/2} \sum_{\text{BZ}} \varphi_{\vec{k}}(\vec{r})\,, \tag{A1}$$

has the required properties. Every other Wannier function corresponding to a different choice of phase has the form

$$\bar{a}(\vec{r}) = N^{-1/2} \sum_{\text{BZ}} \varphi_{\vec{k}}(\vec{r})\, e^{i\theta(\vec{k})}\,. \tag{A2}$$

Reality and inversion symmetry of $\bar{a}$, combined with Eqs. (2.11), require, respectively,

$$e^{-i\theta(\vec{k})} = e^{i\theta(-\vec{k})}\,, \quad e^{i\theta(\vec{k})} = e^{i\theta(-\vec{k})}\,, \tag{A3}$$

so that

$$e^{i\theta(\vec{k})} = \pm 1 . \tag{A4}$$

Now if $e^{i\theta(\vec{k})}$ has the same value for *all* $\vec{k}$, then

$$\bar{a}(\vec{r}) = \pm a(\vec{r}) . \tag{A5}$$

If, however, $e^{i\theta(\vec{k})}$ changes from +1 to −1 (necessarily discontinuously), then since

$$\bar{a}(\vec{n}) = N^{-1/2} \sum_{\mathrm{BZ}} [\varphi_{\vec{k}}(0) e^{i\theta(\vec{k})}] e^{i\vec{k}\cdot\vec{n}} \tag{A6}$$

is the Fourier transform of a discontinuous function, $\bar{a}(\vec{n})$ does not decay exponentially as required.

Next, we determine the totality of extrema of the stationary expression (3.12). First, we expand $a^t(\vec{r})$ in the series

$$a^t(\vec{r}) = N^{-1/2} \sum_{\mathrm{BZ}} g^t_{\vec{k}}(\vec{r}) , \tag{A7}$$

where

$$g^t_{\vec{k}}(\vec{r}+\vec{n}) = e^{i\vec{k}\cdot\vec{n}} g^t_{\vec{k}}(\vec{r}) . \tag{A8}$$

Because of the orthonormality condition (2.8), satisfied by $a^t(\vec{r}-\vec{n})$, we must have

$$\delta_{n0} = \frac{1}{N} \sum_{\mathrm{BZ}} (g^t_{\vec{k}}(\vec{r}), g^t_{\vec{k}}(\vec{r})) e^{-i\vec{k}\cdot\vec{n}} , \tag{A9}$$

so that the $g^t_{\vec{k}}(\vec{r})$ are normalized to unity:

$$(g^t_{\vec{k}'}, g^t_{\vec{k}}) = \delta_{\vec{k}',\vec{k}} . \tag{A10}$$

The stationary expression (3.12) can now be written as

$$\mathcal{E} = \sum_{\mathrm{BZ}} (g^t_{\vec{k}}, H g^t_{\vec{k}}) . \tag{A11}$$

This will be an extremum if, and only if, all $g^t_{\vec{k}}$ are eigenfunctions of H, i.e.,

$$g^t_{\vec{k}} = \varphi_{m(\vec{k})\vec{k}} , \tag{A12}$$

where the band index m may be chosen *arbitrarily* for each $\vec{k}$. Thus, the most general function, subject only to the orthonormality condition (2.8), which makes (3.12) stationary is

$$a^t(\vec{r}) = N^{-1/2} \sum_{\mathrm{BZ}} \varphi_{m(\vec{k})\vec{k}}(\vec{r}) . \tag{A13}$$

Of course, unless all $m(\vec{k})$ are equal, this is not a Wannier function.

However, since we work only with exponentially localized trial functions $a^t(\vec{r})$, all $m(\vec{k})$ must, in fact, be equal. For (A7) can also be written as

$$g^t_{\vec{k}}(\vec{r}) = (1/N^{-1/2}) \sum a^t(\vec{r}-\vec{n}) e^{i\vec{k}\cdot\vec{n}} , \tag{A14}$$

which shows that because of the exponential convergence of $a^t(\vec{r})$, $g^t_{\vec{k}}$ is an analytic function of $\vec{k}$. Hence, $m(\vec{k})$ in (A12) cannot be a discontinuous function of $\vec{k}$.

Thus, we conclude that the correct and unique Wannier function $a(\vec{r})$ is the only extremum of the stationary quantity (3.12) in the "vicinity" of $a(\vec{r})$, provided the trial functions $a^t(\vec{r}-\vec{n})$ are restricted by the conditions of reality, point-group symmetry, orthonormality, and exponential localization.

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