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Localized Functions in Molecules and Crystals*

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The Wannier function in crystals is defined in terms of a differential equation and a variation procedure. This variation procedure is also used to define localized functions in molecules which can be used to build solutions of Schrödinger's equation. Illustrations of the procedure of building solutions of Schrödinger's equation from localized functions is given for examples taken from crystalline and molecular problems. Contact is made with Slater's work on the two-dimensional Mathieu problem. A numerical method of carrying out the variation procedure is discussed.

I. INTRODUCTION

IN the study of energy bands in solids, it is sometimes convenient to express the solutions of Schrödinger's equation in terms of Wannier functions.[1] These are functions constructed from the solutions of the periodic potential problem which are localized about a given atom in a crystal and are orthogonal to the same function about any other center. The purpose of this paper is first: define the Wannier function in terms of a differential equation, and second: find a variation procedure for finding the Wannier function. It will be seen that these two goals are most easily reached using the terminology of group theory[2] and that when phrased in this terminology the results can be generalized to define localized functions in molecules which have many of the desirable properties of Wannier functions in crystals.

Imagine a crystal which is periodic with respect to translations $\mathbf{R}_n$, where the $\mathbf{R}_n$ are expressible in the form

$$\mathbf{R}_n=n_1\mathbf{R}_1+n_2\mathbf{R}_2+n_3\mathbf{R}_3, \tag{1}$$

where $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$ form the edges of the unit cell in the crystal and the n's are integers. In the one-electron approximation, Schrödinger's equation (in atomic units)[3] takes the form

$$[-\nabla^2+V(\mathbf{r})]\psi_l(\mathbf{k},\mathbf{r})=E_l(\mathbf{k})\psi_l(\mathbf{k},\mathbf{r}). \tag{2}$$

Here $V(\mathbf{r})$ has the property that

$$V(\mathbf{r}-\mathbf{R}_n)=V(\mathbf{r}). \tag{3}$$

We specify the states $\psi_l(\mathbf{k},\mathbf{r})$ in terms of a pseudomomentum $\mathbf{k}$ and the band to which the wave function belongs. The subscript l in Eq. (2) denotes the l^{th} band. The vector $\mathbf{k}$ specifies the translational properties of the wave function, and as Bloch has shown,[4] allows us to write the wave function in the form:

$$\psi_l(\mathbf{k},\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}\mu_l(\mathbf{k},\mathbf{r}), \tag{4}$$

where $\mu_l(\mathbf{k},\mathbf{r})$ is periodic with respect to the translations $\mathbf{R}_n$.

In this notation, Wannier functions are defined as

$$a_l(\mathbf{r}-\mathbf{R}_n)=(1/N^{\frac{1}{2}})\sum(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_n}\psi_l(\mathbf{k},\mathbf{r}), \tag{5}$$

where N is the number of unit cells in the macrocrystal over which ψ is normalized. The factor $(1/N^{\frac{1}{2}})$ normalizes $a_l(\mathbf{r})$. The summation extends over all $\mathbf{k}$ in the first Brillouin zone. Using the fact that

$$\sum(\mathbf{R}_n)e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n}=N\delta_{\mathbf{k},\mathbf{k}'}, \tag{6}$$

we can find by multiplying both sides of Eq. (5) by $e^{i\mathbf{k}'\cdot\mathbf{R}_n}$ and summing over $\mathbf{R}_n$ that

$$\psi_l(\mathbf{k}',\mathbf{r})=(1/N^{\frac{1}{2}})\sum(\mathbf{R}_n)e^{i\mathbf{k}'\cdot\mathbf{R}_n}a_l(\mathbf{r}-\mathbf{R}_n). \tag{7}$$

From the orthogonality of the solutions of Schrödinger's equation and the fact that

$$\sum(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)}=\delta_{m,n}, \tag{8}$$

it can be shown that

$$\int a_l(\mathbf{r}-\mathbf{R}_n)a_j(\mathbf{r}-\mathbf{R}_m)d\tau=\delta_{lj}\delta_{mn}. \tag{9}$$

It might be pointed out here that in the summation over $\mathbf{k}$ in Eq. (5), we could equally well have added up the wave functions from one band over part of the first Brillouin zone and wave functions from another band over the rest of the first zone without destroying the orthogonality properties of the Wannier function.

II. A DIFFERENTIAL EQUATION FOR THE WANNIER FUNCTION

Using the results of the preceding paragraphs, we can find a differential equation for the Wannier function. Let us apply the Hamiltonian operator $H=-\nabla^2+V$ to both sides of Eq. (5):

$$Ha_l(\mathbf{r}-\mathbf{R}_n)=(1/N^{\frac{1}{2}})\sum(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_n}H\psi_l(\mathbf{k},\mathbf{r}). \tag{10}$$

Using Eq. (2) we find that

$$Ha_l(\mathbf{r}-\mathbf{R}_n)=(1/N^{\frac{1}{2}})\sum(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_n}E_l(\mathbf{k})\psi_l(\mathbf{k},\mathbf{r}). \tag{11}$$

A well-known property of energy bands is that the

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

[2] For treatments of group theory see Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1947), p. 172–189; E. Wigner, *Gruppentheorie* (Friedr. Vieweg und Sohn, Braunschweig, 1931); A. Speiser *Die Theorie der Gruppen* (Julius Springer, Berlin, 1927).

[3] The unit of length is the Bohr radius. The unit of energy is the Rydberg.

[4] F. Bloch, Z. Physik 52, 555 (1928).

energy has the periodicity of the reciprocal lattices. By this we mean that

$$E_l(\mathbf{k}+\mathbf{K}_j)=E_l(\mathbf{k}), \tag{12}$$

where $\mathbf{K}_j$ are the primitive translations of the reciprocal space and are defined by the equations

$$\mathbf{R}_n\cdot\mathbf{K}_j=2\pi\times(\text{integer}). \tag{13}$$

We can, therefore, express $E_l(\mathbf{k})$ as a Fourier series:

$$E_l(\mathbf{k})=\sum(\mathbf{R}_j)e^{-i\mathbf{k}\cdot\mathbf{R}_j}\mathcal{E}_l(\mathbf{R}_j). \tag{14}$$

Substituting Eq. (14) in Eq. (11) and expressing $\psi_l(\mathbf{k},\mathbf{r})$ in terms of Wannier functions, we find that

$$\begin{aligned}Ha_l(\mathbf{r}-\mathbf{R}_n)&=(1/N^{\frac{1}{2}})\sum(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_n}\\&\times\sum(\mathbf{R}_j)e^{-i\mathbf{k}\cdot\mathbf{R}_j}\mathcal{E}_l(\mathbf{R}_j)\sum(\mathbf{R}_m)e^{i\mathbf{k}\cdot\mathbf{R}_m}a_l(\mathbf{r}-\mathbf{R}_m).\end{aligned} \tag{15}$$

By making use of Eq. (8) this reduces to

$$Ha_l(\mathbf{r}-\mathbf{R}_n)=\sum(\mathbf{R}_j)\mathcal{E}_l(\mathbf{R}_j)a_l(\mathbf{r}-\mathbf{R}_n-\mathbf{R}_j). \tag{16}$$

The set of Eqs. (16) for all values of $\mathbf{R}_n$ are the desired set of differential equations for the Wannier function. If we multiply (16) by $a_k(\mathbf{r})$ and integrate over all space, we find by use of (9) that

$$\int a_k(\mathbf{r})Ha_l(\mathbf{r}-\mathbf{R}_n)d\tau=\delta_{kl}\mathcal{E}_l(\mathbf{R}_n). \tag{17}$$

From Eqs. (16) and (17) we can see qualitatively how the width of the bands depends on the degree of localization of the Wannier function and how the Wannier functions approach the solutions of the Schrödinger one-electron equation for the isolated atoms which make up the crystal. Consider a crystal with an atomic like potential situated at each lattice point. We notice from Eq. (17) as the distance between lattice points increases that, because of the localization of $a_l(\mathbf{r})$, $\mathcal{E}_l(\mathbf{R}_n)$ approaches zero for $\mathbf{R}_n>0$. This means that $E_l(\mathbf{k})$ approaches $\mathcal{E}_l(0)$ for all values of $\mathbf{k}$. The bands become flat. As $\mathcal{E}_l(\mathbf{R}_n)$ approaches zero, Eq. (16) becomes

$$Ha_l(\mathbf{r}-\mathbf{R}_n)=\mathcal{E}_l(0)a_l(\mathbf{r}-\mathbf{R}_n). \tag{18}$$

As the distance between lattice points increases, the Hamiltonian approaches the isolated atom Hamiltonian over the region in which $a_l(\mathbf{r})$ has an appreciable value. The Wannier function approaches an atomic function about $\mathbf{R}_n$, and $\mathcal{E}_l(0)$ becomes the atomic level.

III. A VARIATION PROCEDURE FOR LOCALIZED FUNCTIONS

We shall now derive a variation procedure for localized functions in molecules and crystals.

Consider any Hamiltonian H which is invariant under some group of unitary operations G of order g. Let R represent any operation in this group and consider the following variation procedure for a function $a(\mathbf{r})$. Let us make

$$\int a(\mathbf{r})Ha(\mathbf{r})d\tau \tag{19}$$

have an extremum subject to the constraints

$$\int a(\mathbf{r})Ra(\mathbf{r})d\tau=d(R) \tag{20}$$

for all R in G, or for all R in any invariant subgroup[5] $\mathcal{H}$ of G of order h. These constants $d(R)$ should be chosen to give the desired kind of localization to $a(\mathbf{r})$. In order to have these constraints be consistent, we must have

$$d(R)=d(R^{-1}), \tag{21}$$

since

$$\int a(\mathbf{r})Ra(\mathbf{r})d\tau=\int a(\mathbf{r})R^{-1}a(\mathbf{r})d\tau \tag{22}$$

because of the unitary nature of R. By using the method of Lagrangian multipliers, this problem is equivalent to taking the variation of[6]

$$\int a(\mathbf{r})[H-\textstyle\sum'(R)\mathcal{E}(R)R]a(\mathbf{r})d\tau$$

and setting it equal to zero. Here $\mathcal{E}(R)$ are the Lagrangian multipliers for the constraints (20). This leads to the equation

$$Ha(\mathbf{r})-\sum{}'(R)\frac{\mathcal{E}(R)+\mathcal{E}(R^{-1})}{2}Ra(\mathbf{r})=0. \tag{23}$$

Since the constraint for R is exactly the same as that for R^{-1} we have that $\mathcal{E}(R)=\mathcal{E}(R^{-1})$; therefore

$$Ha(\mathbf{r})-\sum{}'(R)\mathcal{E}(R)Ra(\mathbf{r})=0. \tag{24}$$

If we take any other member R' of the subgroup $\mathcal{H}$, and operate on Eq. (24) with it we get a differential equation involving $R'a(\mathbf{r})$:

$$HR'a(\mathbf{r})-\sum{}'(R)\mathcal{E}(R)R'Ra(\mathbf{r})=0. \tag{25}$$

Rewriting the summation as

$$\sum{}'(R)\mathcal{E}(R)R'RR'^{-1}R'a(\mathbf{r}), \tag{26}$$

and letting $R''=R'RR'^{-1}$ we have that

$$H[R'a(\mathbf{r})]-\sum{}'(R'')\mathcal{E}(R'^{-1}R''R')R''[R'a(\mathbf{r})]=0. \tag{27}$$

We can see how this yields Eq. (16) for a crystal. In this case, the subgroup is the group of translations in the crystal. All the elements of the translation group commute with one another, therefore, $R'^{-1}R''R'=R''$. If we consider R as being a translation through $\mathbf{R}_n$, then Eq.

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[5] An invariant subgroup has the property that $R''=RR'R^{-1}$ is in $\mathcal{H}$ for any R in G and R' in $\mathcal{H}$.

[6] In this equation and the following $\Sigma'(R)$ means summation over $\mathcal{H}$. $\Sigma(R)$ means summation over G.

(27) becomes

$$Ha(\mathbf{r}-\mathbf{R}_n)=\sum(\mathbf{R}_j)\mathcal{E}_l(\mathbf{R}_j)a_l(\mathbf{r}-\mathbf{R}_n-\mathbf{R}_j). \quad (16)$$

In this case, the constraints would be taken such that $d(R)=0$ except for the identity operation E, for which the constraint would be $d(E)=1$ in order to assure the normalization of $a(\mathbf{r})$. We see that for the case of crystals this variation procedure yields functions satisfying the same differential equation as the Wannier functions satisfy.

In the case of the crystal, we were able to express the coefficients $\mathcal{E}(\mathbf{R}_n)$ in terms of integrals involving Wannier functions and the Hamiltonian [Eq. (17)]. In the case of the general problem, we can do a similar thing: multiply Eq. (25) by $a(\mathbf{r})$ and integrate over all space. This yields

$$\int a(\mathbf{r})HR'a(\mathbf{r})d\tau=\sum(R)\mathcal{E}(R)d(R'R). \quad (28)$$

Since $R'R$ is also a member of the invariant subgroup $\mathcal{H}$ we have a set of h simultaneous equations for $\mathcal{E}(R)$ which will express these quantities in terms of the constraints $d(R)$ and integrals of the form $\int a(\mathbf{r})HRa(\mathbf{r})d\tau$. The case of the crystal corresponds to the case $d(R'R)=0$ unless $R'R=E$, i.e., $R'=R^{-1}$. Therefore, Eqs. (28) reduce to

$$\int a(\mathbf{r})HR'a(\mathbf{r})d\tau=\mathcal{E}(R'^{-1})=\mathcal{E}(R'). \quad (29)$$

We know how to combine Wannier functions to give us a solution of Schrödinger's equation. Let us now see how we may combine the functions defined by Eq. (25) to give us solutions of Schrödinger's equation.

We know that the solutions of Schrödinger's equation of a given energy for a Hamiltonian which is invariant under a group G must form a basis for one of the irreducible representations of the group G. Let $\Gamma_l(R')_{mp}$ be the m, pth matrix element in the matrix $\Gamma_l(R')$ which is equivalent to the operation R' in the lth irreducible representation. Let g_l be the dimension of this representation. Let us multiply each of the Eqs. (25) by $\Gamma_l(R')_{mp}$ and sum over all R' in G.

$$\begin{aligned}H\sum(R')\Gamma_l(R')_{mp}R'a(\mathbf{r})\\ =\sum{}'(R)\mathcal{E}(R)\sum(R')\Gamma_l(R')_{mp}R'Ra(\mathbf{r}). \quad (30)\end{aligned}$$

Let us now expand $a(\mathbf{r})$ in terms of functions which transform according to the irreducible representations given by $\Gamma_i(R')$.

$$a(\mathbf{r})=\sum(ijk)c_{ijk}\varphi_j{}^{ik}. \quad (31)$$

Here $\varphi_j{}^{ik}$ transforms according to the jth row of the ith irreducible representation. The superscript k specifies which of the functions which transforms according to the jth row of the ith irreducible representations is specified in the summation. The $\varphi_j{}^{ik}$, therefore, have the property that

$$R\varphi_j{}^{ik}=\sum(j')\Gamma_i(R)_{j'j}\varphi_{j'}{}^{ik}. \quad (32)$$

Using this fact in Eq. (30) we find that

$$\begin{aligned}\sum(R')\Gamma_l(R')_{mp}R'Ra(\mathbf{r})=\sum(ijk)c_{ijk}\sum(j')\Gamma_i(R)_{j'j}\\ \times\sum(j'')\sum(R')\Gamma_l(R')_{mp}\Gamma_i(R')_{j''j'}\varphi_{j''}{}^{ik}. \quad (33)\end{aligned}$$

We also know that

$$\sum(R')\Gamma_l(R')_{mp}\Gamma_i(R')_{j''j'}=\frac{g}{\sqrt{g_i}\sqrt{g_l}}\delta_{il}\delta_{j'p}\delta_{j''m}, \quad (34)$$

where g_i is the order of the ith irreducible representation. Using (34) in (33) we find that

$$\begin{aligned}\sum(R')\Gamma_l(R')_{mp}R'Ra(\mathbf{r})\\ =(g/g_l)\sum(j)\Gamma_l(R)_{pj}\sum(k)c_{ljk}\varphi_m{}^{lk}. \quad (35)\end{aligned}$$

For $R=E$, $\Gamma_l(E)_{pj}$ is the unit matrix, and we find that

$$\sum(R')\Gamma_l(R')_{mp}R'a(\mathbf{r})=(g/g_l)\sum(k)c_{lpk}\varphi_m{}^{lk}. \quad (36)$$

If we define

$$f_{mp}{}^l=\sum(k)c_{lpk}\varphi_m{}^{lk}, \quad (37)$$

substituting (37), (36), and (35) in Eq. (30) will yield

$$Hf_{mp}{}^l=\sum{}'(R)\mathcal{E}(R)\sum_1^{g_l}(j)\Gamma_l(R)_{pj}f_{mj}{}^l. \quad (38)$$

$f_{mp}{}^l$ transforms according to the mth row of the lth irreducible representations because of (32). The partners of this function in the same basis can easily be shown to be the functions $f_{j'p}{}^l$ $j'=1\cdots g_l$. Therefore, the functions $f_{11}{}^l$, $\cdots f_{g_l{}'}{}^l$, form a basis for the lth irreducible representation as do the other sets:

$$\begin{matrix} f_{12}{}^l, & f_{22}{}^l & \cdots & f_{g_l2}{}^l \\ & & \vdots & \\ f_{1g_l}{}^l & \cdots & \cdots & f_{g_lg_l}{}^l. \end{matrix}$$

Equation (38) therefore expresses the function $f_{mp}{}^l$ as a linear combination of the other functions $f_{mj}{}^l$, $j=1\cdots g_l$, which transform according to the same row of the same irreducible representation but are in different bases.

Equations (38) can be expressed most easily in matrix form. Regard $f_{mj}{}^l$ for $j=1\cdots g_l$ as a column vector. Then Eqs. (38) become

$$H\begin{bmatrix} f_{m1}{}^l \\ \cdot \\ \cdot \\ \cdot \\ f_{mg_l}{}^l \end{bmatrix}=[\sum{}'(R)\mathcal{E}(R)\Gamma_l(R)]\begin{bmatrix} f_{m1}{}^l \\ \cdot \\ \cdot \\ \cdot \\ f_{mg_l}{}^l \end{bmatrix}. \quad (39)$$

To find the solutions of Schrödinger's equation, let us multiply both sides of this equation by a numerical matrix O

$$HO\begin{bmatrix} f_{m1}{}^l \\ \cdot \\ \cdot \\ \cdot \\ f_{mg_l}{}^l \end{bmatrix}=O[\sum{}'(R)\mathcal{E}(R)\Gamma_l(R)]O^{-1}O\begin{bmatrix} f_{m1}{}^l \\ \cdot \\ \cdot \\ \cdot \\ f_{mg_l}{}^l \end{bmatrix}. \quad (40)$$

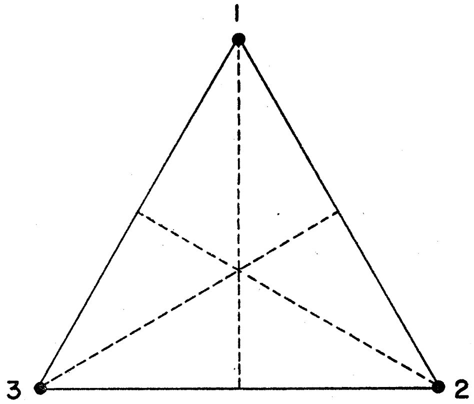

FIG. 1. A molecule whose symmetry is C_{3v}. Heavy dots represent the nuclei.

Clearly all we need to do to find the solutions of Schrödinger's equation is to find the matrix O which diagonalizes the matrix $\sum'(R)\mathcal{E}(R)\Gamma_l(R)$. The Eq. (40) will become

$$HO\begin{bmatrix} f_{m1}^{l} \\ \cdot \\ \cdot \\ f_{mg_l}^{l} \end{bmatrix} = \begin{bmatrix} E_1 & & & 0 \\ & \cdot & & \\ & & \cdot & \\ 0 & & & E_{g_l} \end{bmatrix} O \begin{bmatrix} f_{m1}^{l} \\ \cdot \\ \cdot \\ f_{mg_l}^{l} \end{bmatrix}. \qquad (41)$$

The g_l functions given by

$$O\begin{bmatrix} f_{m1}^{l} \\ \cdot \\ \cdot \\ f_{mg_l}^{l} \end{bmatrix}$$

are the solutions to Schrödinger's equation and the eigenvalues E_j of $\sum'(R)\mathcal{E}(R)\Gamma_l(R)$ are the corresponding energies. Clearly once we have solved for the matrix O we have solved the problem for all values of m in Eq. (39). In other words, we have found g_l sets of g_l functions which are solutions of Schrödinger's equation. The g_l functions $\sum(j)O_{nj}f_{mj}^{l}$, $m=1\cdots g_l$, all have the same energy E_n and form a basis for the irreducible representation l. The above procedure is essentially quite simple, but its simplicity may be obscured by the details necessary for the mathematical justification of the procedure. It is, therefore, profitable to state in words just how to go about finding solutions of Schrödinger's equation from the solution $a(\mathbf{r})$ of our variational procedure. If we seek functions which belong to the l^{th} irreducible representation and which solve the wave equations, we form the matrix $\sum'(R)\mathcal{E}(R)\Gamma_l(R)$. This matrix is of order g_l. Diagonalize this matrix by a unitary transformation O. The diagonal elements in this transformed matrix are the energies E_n of the g_l levels all of which have a degeneracy g_l, and each of these energies has functions associated with it which form a basis for the l^{th} irreducible representation. To find the g_l functions which have the energy E_n, form the g_l^2 functions $\sum(R)\Gamma_l(R)_{mp}a(\mathbf{r})=f_{mp}^{l}$. Then form the vectors

$$O\begin{bmatrix} f_{m1}^{l} \\ \cdot \\ \cdot \\ f_{mg_l}^{l} \end{bmatrix}, \quad m=1\cdots g_l,$$

for all m. The n^{th} element in these vectors are the g_l functions belonging to the energy E_n.

There are a great many special cases in which we need not diagonalize $\sum'(R)\mathcal{E}(R)\Gamma_l(R)$. For all nondegenerate levels the matrices $\Gamma_l(R)$ are already diagonal since the matrices are all one-dimensional matrices. Another important case is the case in which we specify constraints for an abelian invariant subgroup of the total group. (An invariant subgroup in which all the elements commute.) In this case, all the matrices $\Gamma_l(R)$ for R belonging to the subgroup can all be chosen to be diagonal. $\sum'(R)\mathcal{E}(R)\Gamma_l(R)$ where the summation extends over the subgroup will be, therefore, diagonal. This is just the case we are confronted with in crystals and will be discussed in more detail later.

IV. EXAMPLES FROM MOLECULAR GROUPS

Consider the hydrogen molecule. The molecule is invariant with respect to a reflection in the plane passing midway between the nuclei and perpendicular to the line joining them. Let us call this operation σ. Let us look for a function $a(\mathbf{r})$ for which[7]

$$\int a(\mathbf{r})Ha(\mathbf{r})d\tau=\min, \qquad (42)$$

with constraints

$$\int a(\mathbf{r})\sigma a(\mathbf{r})d\tau=0,$$
$$\int a(\mathbf{r})a(\mathbf{r})d\tau=1. \qquad (43)$$

We are, therefore, led to the equation

$$Ha(\mathbf{r})-\mathcal{E}(E)a(\mathbf{r})-\mathcal{E}(\sigma)\sigma a(\mathbf{r})=0. \qquad (44)$$

There are two irreducible representations of this group; the symmetric representation with matrices $\Gamma_1(E)=(1)$, $\Gamma_1(\sigma)=(1)$; and the antisymmetric representation with matrices $\Gamma_2(E)=(1)$, $\Gamma_2(\sigma)=(-1)$. We can, therefore, form two molecular orbitals from our function $a(\mathbf{r})$. The symmetric molecular orbital is $\sum(R)\Gamma_1(R)Ra(\mathbf{r})=a(\mathbf{r})+\sigma a(\mathbf{r})$ with energy $\sum(R)\Gamma_1(R)\mathcal{E}(R)=\mathcal{E}(E)+\mathcal{E}(\sigma)$. The antisymmetric representation produces the molecular orbital $\sum(R)\Gamma_2(R)Ra(\mathbf{r})=a(\mathbf{r})-\sigma a(\mathbf{r})$ with energy $\mathcal{E}(E)-\mathcal{E}(\sigma)$. $a(\mathbf{r})$ will be a function localized about one nucleus and $\sigma a(\mathbf{r})$ will be a function localized about the other nucleus. $\mathcal{E}(E)$ is the average energy of the two states. One lies an energy $\mathcal{E}(\sigma)$ above this average, and the other an energy $\mathcal{E}(\sigma)$ below this average. Our Lagrangian multipliers $\mathcal{E}(E)$ and $\mathcal{E}(\sigma)$ can be expressed

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[7] H in this integral is a one-electron Hamiltonian.

in terms of integrals by use of Eqs. (43) and (44)

$$\int a(\mathbf{r})Ha(\mathbf{r})d\tau=\mathcal{E}(E);\quad \int a(\mathbf{r})H\sigma a(\mathbf{r})=\mathcal{E}(\sigma). \tag{45}$$

The next special case we will consider is that of a system with a symmetry C_{3v}. Imagine a molecule consisting of three identical nuclei at the corners of an equilateral triangle (see Fig. 1). The symmetry operations of this group are σ_1, σ_2, σ_3 (reflections through planes perpendicular to the plane of the molecule and to the sides of the triangle passing through the points 1, 2, and 3, respectively) E, the identity operation and C_3 and C_3^2 (rotations clockwise through 120° and 240°, respectively). There are three irreducible representations to this group, two of them are one-dimensional and one of them is two-dimensional. Their matrices are given in Table I.[8] For arbitrary constraints the wave function for the representation Γ_1 will be [Eq. (38)]:

$$\begin{aligned}\psi_1=f_{11}{}^1=a(\mathbf{r})+\sigma_1a(\mathbf{r})+\sigma_2a(\mathbf{r})&\\ +\sigma_3a(\mathbf{r})+C_3a(\mathbf{r})+C_3{}^2a(\mathbf{r}),&\end{aligned} \tag{45}$$

with energy

$$E_1=\mathcal{E}(E)+\mathcal{E}(\sigma_1)+\mathcal{E}(\sigma_2)+\mathcal{E}(\sigma_3)+\mathcal{E}(C_3)+\mathcal{E}(C_3{}^2). \tag{46}$$

Similarly, for the representation Γ_2,

$$\begin{aligned}\psi_2=f_{11}{}^2=a(\mathbf{r})-\sigma_1a(\mathbf{r})-\sigma_2a(\mathbf{r})&\\ -\sigma_3a(\mathbf{r})+C_3a(\mathbf{r})+C_3{}^2a(\mathbf{r}),&\quad (47)\\ E_2=\mathcal{E}(E)-\mathcal{E}(\sigma_1)-\mathcal{E}(\sigma_2)-\mathcal{E}(\sigma_3)+\mathcal{E}(C_3)+\mathcal{E}(C_3{}^2).&\end{aligned}$$

For the degenerate representation Γ_3 the energies will be obtained by diagonalizing the matrix

$$\sum(R)\Gamma_3(R)\mathcal{E}(R)=(c_{ij}). \tag{48}$$

This matrix has elements

$$\begin{aligned}c_{11}=\mathcal{E}(E)-\mathcal{E}(\sigma_1)+\tfrac{1}{2}\mathcal{E}(\sigma_2)&\\ +\tfrac{1}{2}\mathcal{E}(\sigma_3)-\tfrac{1}{2}\mathcal{E}(C_3)-\tfrac{1}{2}\mathcal{E}(C_3{}^2),&\\ c_{12}=(\surd\tfrac{3}{2})[-\mathcal{E}(\sigma_2)+\mathcal{E}(\sigma_3)+\mathcal{E}(C_3)-\mathcal{E}(C_3{}^2)],&\\ c_{21}=(\surd\tfrac{3}{2})[-\mathcal{E}(\sigma_2)+\mathcal{E}(\sigma_3)-\mathcal{E}(C_3)+\mathcal{E}(C_3{}^2)],&\\ c_{22}=\mathcal{E}(E)+\mathcal{E}(\sigma_1)+\tfrac{1}{2}[-\mathcal{E}(\sigma_2)&\\ -\mathcal{E}(\sigma_3)-\mathcal{E}(C_3)-\mathcal{E}(C_3{}^2)].&\end{aligned} \tag{49}$$

If we denote by $O=(o_{ij})$ the matrix which diagonalizes (c_{ij}), then the eigenfunctions corresponding to the two eigenvalues of (48) will be [see Eq. (41)] $o_{11}f_{11}{}^3+o_{12}f_{12}{}^3$ and $o_{11}f_{21}{}^3+o_{12}f_{22}{}^3$ corresponding to the first eigenvalue, and $o_{21}f_{11}{}^3+o_{22}f_{12}{}^3$ and $o_{21}f_{21}{}^3+o_{22}f_{22}{}^3$ corresponding to the second eigenvalue. Here

$$\begin{aligned}f_{11}{}^3=a(\mathbf{r})-\sigma_1a(\mathbf{r})+\tfrac{1}{2}[\sigma_2a(\mathbf{r})+\sigma_3a(\mathbf{r})&\\ -C_3a(\mathbf{r})-C_3{}^2a(\mathbf{r}),&\\ f_{12}{}^3=(\surd\tfrac{3}{2})[-\sigma_2a(\mathbf{r})+\sigma_3a(\mathbf{r})+C_3a(\mathbf{r})-C_3{}^2a(\mathbf{r})],&\\ f_{21}{}^3=(\surd\tfrac{3}{2})[-\sigma_2a(\mathbf{r})+\sigma_3a(\mathbf{r})-C_3a(\mathbf{r})+C_3{}^2a(\mathbf{r})],&\\ f_{22}{}^3=a(\mathbf{r})+\sigma_1a(\mathbf{r})+\tfrac{1}{2}[-\sigma_2a(\mathbf{r})-\sigma_3a(\mathbf{r})&\\ -C_3a(\mathbf{r})-C_3{}^2a(\mathbf{r})].&\end{aligned} \tag{50}$$

Thus, we see that from the one function $a(\mathbf{r})$ which is a solution to our variation problem we are able to construct two nondegenerate states and two sets of doubly degenerate states. We cannot always construct so many states from one function $a(\mathbf{r})$. Suppose we had chosen our constraints $d(E)=d(\sigma_1)=1$; $d(\sigma_2)=d(\sigma_3)=d(C_3)=d(C_3{}^2)=0$. In other words, so that $a(\mathbf{r})$ has the property that $\sigma_1a(\mathbf{r})=a(\mathbf{r})$, i.e., $a(\mathbf{r})$ is a symmetric function, which is localized about the point 1, with respect to the reflection σ_1. Under these conditions

$$\mathcal{E}(E)=\mathcal{E}(\sigma_1)\quad\text{and}\quad\mathcal{E}(\sigma_2)=\mathcal{E}(\sigma_3)=\mathcal{E}(C_3)=\mathcal{E}(C_3{}^2),$$

the last equality resulting from the fact that $\sigma_2a(\mathbf{r})=C_3a(\mathbf{r})=\sigma_3a(\mathbf{r})=C_3{}^2a(\mathbf{r})$ which is a consequence of $\sigma_1a(\mathbf{r})=a(\mathbf{r})$. Under these conditions, using Eqs. (45), (46), and (47):

$$\begin{aligned}&\psi_1=a(\mathbf{r})+C_3a(\mathbf{r})+C_3{}^2a(\mathbf{r});\quad &&E_1=2\mathcal{E}(E)+\mathcal{E}(C_3);\\ &\psi_2=0; &&E_2=0.\end{aligned} \tag{51}$$

For the degenerate representation, we note that the matrix (c_{ij}) is already diagonal ($c_{11}=c_{12}=c_{21}=0$; $c_{22}=2\mathcal{E}(E)-2\mathcal{E}(C_3)$). Therefore, we only have one doubly degenerate state with energy $2\mathcal{E}(E)-2\mathcal{E}(C_3)$ and wave functions

$$\begin{aligned}f_{21}{}^3&=\surd 3[-C_3a(\mathbf{r})+C_3{}^2a(\mathbf{r})],\\ f_{22}{}^3&=2a(\mathbf{r})-C_3a(\mathbf{r})-C_3{}^2a(\mathbf{r}).\end{aligned} \tag{52}$$

For the other doubly degenerate state, $f_{11}{}^3=f_{12}{}^3=0$. We could equally well have adjusted the constraints so that $\sigma_1a(\mathbf{r})=-a(\mathbf{r})$. That is, so that $a(\mathbf{r})$ is antisymmetric with respect to σ_1. In this case, one doubly degenerate level would appear and the nondegenerate wave function forming a basis for Γ_2 would appear.

V. CRYSTALLINE GROUPS

Crystalline groups contain translations as well as the rotations, reflections, and inversions which appear in the study of molecules. It is convenient to introduce the notation used by Seitz,[9] in his series of papers on space groups, for the combined translations and rotations that appear in these groups. Let us denote the operation which consists of a rotation[10] α followed by a translation through $\mathbf{t}$ by

$$\{\alpha|\mathbf{t}\}. \tag{53}$$

TABLE I. Irreducible representations of the group C_{3v}.

Γ \ R	E	σ_1	σ_2	σ_3	C_3	$C_3{}^2$
$\Gamma_1(R)$	1	1	1	1	1	1
$\Gamma_2(R)$	1	−1	−1	−1	1	1
$\Gamma_3(R)$	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}-1&0\\0&1\end{matrix}$	$\begin{matrix}\frac{1}{2}&-\surd\frac{3}{2}\\-\surd\frac{3}{2}&-\frac{1}{2}\end{matrix}$	$\begin{matrix}\frac{1}{2}&\surd\frac{3}{2}\\\surd\frac{3}{2}&-\frac{1}{2}\end{matrix}$	$\begin{matrix}-\frac{1}{2}&\surd\frac{3}{2}\\-\surd\frac{3}{2}&-\frac{1}{2}\end{matrix}$	$\begin{matrix}-\frac{1}{2}&-\surd\frac{3}{2}\\\surd\frac{3}{2}&-\frac{1}{2}\end{matrix}$

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[8] These matrices are given in *Quantum Chemistry*, p. 179 (reference 2).

[9] F. Seitz, Z. Krist. **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936).

[10] Here the word rotation includes inversions and reflections.

By this we mean, the transformation from one rectangular coordinate system x_1, x_2, x_3 to another x_1', x_2', x_3' given by the equations

$$\begin{aligned} x_1' &= \alpha_{11}x_1+\alpha_{12}x_2+\alpha_{13}x_3+t_1, \\ x_2' &= \alpha_{21}x_1+\alpha_{22}x_2+\alpha_{23}x_3+t_2, \\ x_3' &= \alpha_{31}x_1+\alpha_{32}x_2+\alpha_{33}x_3+t_3. \end{aligned} \tag{54}$$

Here the matrix (α_{ij}) represents the rotational part of the operator (53) and t_1, t_2, t_3 are the components of the translation in the operator. $\{\epsilon|0\}$ denotes the identity operator, $\{\alpha|0\}$ a rotation about the origin, and $\{0|\mathbf{t}\}$ a pure translation. The symbols (53) have the property [using Eq. (54)]

$$\{\alpha|\mathbf{t}\}\{\beta|\mathbf{t}'\}=\{\alpha\beta|\alpha\mathbf{t}'+\mathbf{t}\}. \tag{55}$$

$\alpha\mathbf{t}'$ is the vector arising from operating on $\mathbf{t}'$ with the matrix α. From Eq. (55) we see that the inverse of $\{\alpha|\mathbf{t}\}$ is $\{\alpha^{-1}|-\alpha^{-1}\mathbf{t}\}$. We know from the results of Seitz that any operator R of the space group can be written in the form $\{\epsilon|\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}$. In the case of no glide planes or screw axis, all the $\mathbf{t}_\alpha$ are zero and the set of operators $\{\alpha|\mathbf{t}_\alpha\}$ form a group called the point group of the crystal.

We set up our variation procedure as follows: We seek a function $a(\mathbf{r})$ for which

$$\int a(\mathbf{r})Ha(\mathbf{r})d\tau=\min, \tag{56}$$

subject to the constraints

$$\int a(\mathbf{r})\{\epsilon|\mathbf{R}_n\}a(\mathbf{r})d\tau=\delta_{\mathbf{R}_n,0}. \tag{57}$$

If we call $\mathcal{E}(\mathbf{R}_n)$ the Lagrangian multipliers corresponding to the constraints (57), Eq. (38) becomes in this case

$$\begin{aligned} H\sum(R)\Gamma(R)_{mp}a(r) &= \sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n) \\ &\quad\times\sum(j)\Gamma(\{\epsilon|\mathbf{R}_n\})_{pj}\sum(R)\Gamma(R)_{mj}Ra(r). \end{aligned} \tag{58}$$

Here $\sum(R)$ denotes summation over all operations in the space group, $\sum(\mathbf{R}_n)$ denotes summation over just the pure translations in the space group, and $\sum(j)$ denotes summation over a row of the irreducible representation. The results of Seitz[11] on the reduction of space groups tells us how to find the matrices $\Gamma(R)_{mp}$ for a space group. In particular the matrices $\Gamma(\{\epsilon|\mathbf{R}_n\})$ are diagonal matrices. Equation (58) reduces to

$$\begin{aligned} &H\sum(R)\Gamma(R)_{mp}Ra(r) \\ &=[\sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n)\Gamma(\{\epsilon|\mathbf{R}_n\})_{pp}]\sum(R)\Gamma(R)_{mp}Ra(r). \end{aligned} \tag{59}$$

Therefore, $\sum(R)\Gamma(R)_{mp}Ra(r)$ for all m are eigenfunctions with eigenvalue $\sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n)\Gamma(\{\epsilon|\mathbf{R}_n\})_{pp}$. Since $\Gamma(\{\epsilon|\mathbf{R}_n\})_{pp}$ has the form $e^{i\mathbf{k}_p\cdot\mathbf{R}_n}$, the energy has the form $\sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n)e^{i\mathbf{k}_p\cdot\mathbf{R}_n}$. The eigenvectors can also be simplified.

$$\begin{aligned} \sum(R)\Gamma(R)_{mp}Ra(\mathbf{r}) &= \sum(\mathbf{R}_n)\sum(\alpha) \\ &\quad\times[\Gamma(\{\epsilon|\mathbf{R}_n\})\Gamma(\{\alpha|\mathbf{t}_\alpha\})]_{mp}\{\epsilon|\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r}). \end{aligned} \tag{60}$$

Using the diagonal property of $\Gamma(\{\epsilon|\mathbf{R}_n\})$, we see that

$$[\Gamma(\{\epsilon|\mathbf{R}_n\})\Gamma(\{\alpha|\mathbf{t}_\alpha\})]_{mp}=e^{i\mathbf{k}_m\cdot\mathbf{R}_n}\Gamma(\{\alpha|\mathbf{t}_\alpha\})_{mp}.$$

The wave functions corresponding to the eigenvalue $\sum(\mathbf{R}_n)e^{i\mathbf{k}_p\cdot\mathbf{R}_n}\mathcal{E}(\mathbf{R}_n)$ are

$$\sum(\mathbf{R}_n)e^{i\mathbf{k}_m\cdot\mathbf{R}_n}\{\epsilon|\mathbf{R}_n\}\sum(\alpha)\Gamma(\{\alpha|\mathbf{t}_\alpha\})_{mp}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r}), \qquad m=1\cdots g_l, \tag{61}$$

where g_l is the order of the irreducible representation. Associated with the lattice point at the origin is the function $\sum(\alpha)\Gamma(\{\alpha|\mathbf{t}_\alpha\})_{mp}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})$. This function when translated through $\mathbf{R}_n$, multiplied by $e^{i\mathbf{k}_m\cdot\mathbf{R}_n}$ and summed over $\mathbf{R}_n$ gives the m^{th} wave function associated with the energy

$$\sum(\mathbf{R}_n)e^{i\mathbf{k}_p\cdot\mathbf{R}_n}\mathcal{E}(\mathbf{R}_n).$$

Before we go on to consider a special case of the application of the variation procedure to a crystal lattice, it will be necessary to review the results of Seitz[11,12] on the reduction of space groups. We observe, first of all, the effect of a general operator $R=\{\alpha|\mathbf{t}_\alpha+\mathbf{R}_n\}$ on a wave function whose $\mathbf{k}$ value is $\mathbf{k}_1$

$$\psi(\mathbf{k}_1,\mathbf{r})=\sum(\mathbf{R}_n)e^{i\mathbf{k}_1\cdot\mathbf{R}_n}\{\epsilon|\mathbf{R}_n\}a(\mathbf{r}).$$

Applying R to this wave function yields

$$\begin{aligned} R\psi &= \{\epsilon|\mathbf{R}_m\}\{\alpha|\mathbf{t}_\alpha\}\psi \\ &= \{\epsilon|\mathbf{R}_m\}\sum(\mathbf{R}_n)e^{i\mathbf{k}_1\cdot\mathbf{R}_n}\{\alpha|\mathbf{t}_\alpha\}\{\epsilon|\mathbf{R}_n\}a(\mathbf{r}) \\ &= \{\epsilon|\mathbf{R}_m\}\sum(\mathbf{R}_n)e^{i\mathbf{k}_1\cdot\mathbf{R}_n}\{\epsilon|\alpha\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r}). \end{aligned} \tag{62}$$

Since $\alpha\mathbf{R}_n$ is also an allowed translation, we can change the index of summation in (62) to $\alpha\mathbf{R}_n=\mathbf{R}_n'$:

$$\begin{aligned} R\psi &= \{\epsilon|\mathbf{R}_m\}\sum(\mathbf{R}_n') \\ &\qquad\times\exp(i\mathbf{k}_1\cdot\alpha^{-1}\mathbf{R}_n')\{\epsilon|\mathbf{R}_n'\}[\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})] \\ &= \{\epsilon|\mathbf{R}_m\}\sum(\mathbf{R}_n') \\ &\qquad\times\exp(i\alpha\mathbf{k}_1\cdot\mathbf{R}_n')\{\epsilon|\mathbf{R}_n'\}[\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})] \\ &= \exp(i\alpha\mathbf{k}_1\cdot\mathbf{R}_m)\sum(\mathbf{R}_n') \\ &\qquad\times\exp(i\alpha\mathbf{k}_1\cdot\mathbf{R}_n')\{\epsilon|\mathbf{R}_n'\}[\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})]. \end{aligned} \tag{63}$$

We see that the effect of any space group operation whose rotational part is α is to transform $\psi(\mathbf{k}_1,\mathbf{r})$ to a wave function with wave vector $\alpha\mathbf{k}_1$. If $\alpha\mathbf{k}_1-\mathbf{k}_1\neq\mathbf{K}_j$, we see that we have generated a function which is orthogonal to $\psi(\mathbf{k}_1,\mathbf{r})$ and which has the same energy as $\psi(\mathbf{k}_1,\mathbf{r})$. (The same energy because the effect of any operator, which commutes with the Hamiltonian on a

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[11] F. Seitz, Ann. Math. **37**, 17 (1936).

[12] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

wave function, is to produce another function with the same energy.) The results of Seitz state that if for a wave function with wave vector $\mathbf{k}_1$, $\alpha\mathbf{k}_1-\mathbf{k}_1\neq\mathbf{K}_j$ for all α in the space group and any $\mathbf{K}_j$ then the functions

$$\psi_0(\mathbf{k}_1, r);\ \psi_1=\{\alpha_1|\mathbf{t}_{\alpha 1}\}\psi_0;\ \cdots\ \psi_n=\{\alpha_n|\mathbf{t}_{\alpha n}\}\psi_0, \tag{64}$$

form a basis for an irreducible representation of the space group. If certain operators leave the wave vector unchanged, then we shall manufacture by this process different wave functions with the same value of $\mathbf{k}$ as $\mathbf{k}_1$. Seitz's results go on to state that the wave functions with a given value of $\mathbf{k}$ must form the basis for an irreducible representation of that subgroup to the total space group which leaves that value of $\mathbf{k}$ unchanged.

The other point that might also be mentioned here concerns the symmetry properties of a given band in reciprocal space. As can be seen from the previous paragraph, if there is an energy associated with some value of $\mathbf{k}$ in reciprocal space there must be an equal energy associated with all points generated from $\mathbf{k}$ by the operators α. Thus it is that the collection of all energies from all bands plotted in reciprocal space has all the symmetry properties of the reciprocal lattice. This would allow us to define bands which have all the symmetry properties of reciprocal space. Here, however, we shall define a band as that collection of energies arising from $E(\mathbf{k})=\sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n)e^{i\mathbf{k}\cdot\mathbf{R}_n}\mathcal{E}(\mathbf{R}_n)$ where $\mathcal{E}(\mathbf{R}_n)$ is given by our variational procedure. Let us see under what conditions a band defined in this manner has all the symmetry of $\mathbf{k}$ space. We notice from Eq. (63) if $\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})=ca(\mathbf{r})$ for all α where $|c|=1$ then $E(\mathbf{k})=E(\alpha\mathbf{k})$ for all α. In the case of no glide planes or screw axis ($\mathbf{t}_\alpha=0$), $a(\mathbf{r})$ forms a basis of one dimension for an irreducible representation of the point group. If we desire to find a Wannier function which describes a band which is completely symmetric in $\mathbf{k}$ space, this Wannier function must have the property that any operation of the point group has the effect of multiplying it by a constant whose absolute value is one.

There is no reason to believe that our variation procedure will not admit solutions which have other symmetry properties than this simple one. In this case $\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})$, is also a distinct solution to our variation problem. If we multiply Eq. (16) by $\{\alpha|\mathbf{t}_\alpha\}$, we get

$$\begin{aligned}H[\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})]&\\ &=\sum(\mathbf{R}_n)\mathcal{E}(\mathbf{R}_n)\{\epsilon|\alpha\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})\\ &=\sum(\mathbf{R}_n)\mathcal{E}(\alpha^{-1}\mathbf{R}_n)\{\epsilon|\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r}).\end{aligned}\tag{65}$$

The constraints are also satisfied since

$$\begin{aligned}\int\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})\{\epsilon|\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})d\tau&\\ &=\int a(\mathbf{r})\{\alpha^{-1}|-\alpha^{-1}\mathbf{t}_\alpha\}\{\epsilon|\mathbf{R}_n\}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})d\tau\\ &=\int a(\mathbf{r})\{\epsilon|\alpha^{-1}\mathbf{R}_n\}a(\mathbf{r})d\tau=\delta_{\mathbf{R}_n,\,0}.\end{aligned}\tag{66}$$

But if we have assumed $\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})$ is not just a multiple of $a(\mathbf{r})$, then from (65) the energies associated with this Wannier function are $\sum(\mathbf{R}_n)\mathcal{E}(\alpha^{-1}\mathbf{R}_n)e^{i\mathbf{k}\cdot\mathbf{R}_n}$, where

$$\begin{aligned}\mathcal{E}(\alpha^{-1}\mathbf{R}_n)&=\int a(\mathbf{r})\{\epsilon|\alpha^{-1}\mathbf{R}_n\}Ha(\mathbf{r})d\tau\\ &=\int\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})\{\epsilon|\mathbf{R}_n\}H\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})d\tau\\ &\neq\int a(\mathbf{r})\{\epsilon|\mathbf{R}_n\}a(\mathbf{r})d\tau.\end{aligned}$$

Thus, the band of energies this Wannier function generates are distinct, at any point in reciprocal space, from those of $a(r)$ and, therefore,

$$\int a(\mathbf{r})\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})d\tau=0, \tag{67}$$

by Eq. (9). We can, however, easily get the energy band associated with $\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})$ from that of $a(\mathbf{r})$ by performing the operation α on $E(\mathbf{k})$, since

$$\begin{aligned}\sum(\mathbf{R}_n)\mathcal{E}(\alpha^{-1}\mathbf{R}_n)\exp(i\mathbf{k}\cdot\mathbf{R}_n)&\\ &=\sum(\mathbf{R}_n')\mathcal{E}(\mathbf{R}_n')\exp(i\mathbf{k}\cdot\alpha\mathbf{R}_n')\\ &=\sum(\mathbf{R}_n')\mathcal{E}(\mathbf{R}_n')\exp(i\alpha^{-1}\mathbf{k}\cdot\mathbf{R}_n')\\ &=\alpha E(\mathbf{k}).\end{aligned}\tag{68}$$

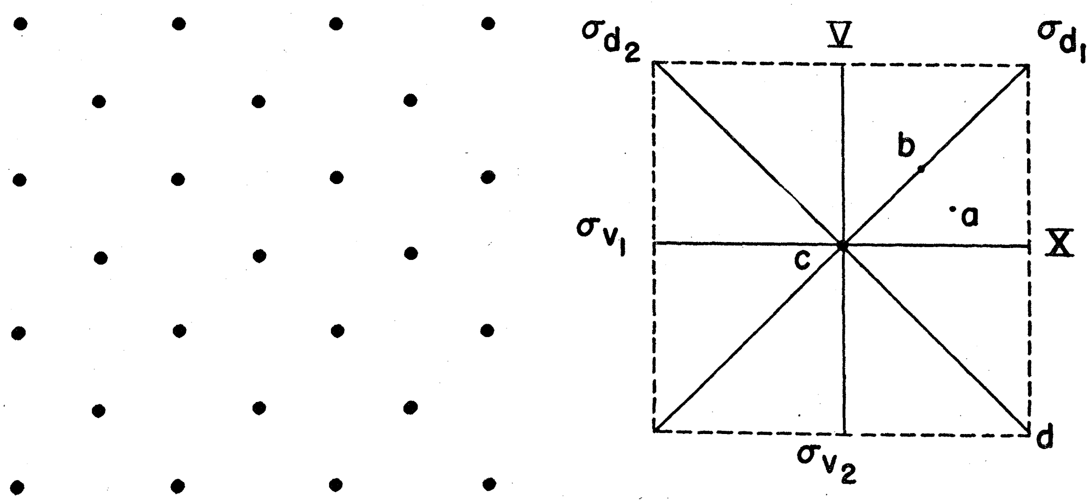
Thus we see that the symmetry properties of the band defined in terms of a Wannier function may be summed up by saying that if for any operation of the point group $\{\alpha|0\}a(\mathbf{r})=ca(\mathbf{r})$; $|c|=1$ then $\alpha E(\mathbf{k})=E(\mathbf{k})$. We shall now illustrate these general remarks with a special case.

Consider a two-dimensional cubic lattice [see Fig. 2(a)]. This space group has no glide planes or screw axes. The point group is the group C_{4v}. In Fig. 2(b) we have drawn reciprocal space. The dotted lines represent the edges of the first Brillouin zone. The operations of the point group are shown as well as points of special interest in reciprocal space. σ_{v1} and σ_{v2} are reflections through the X and Y axes, respectively. σ_{d1} and σ_{d2} are reflections through the 45-degree lines. The other operations of the point group are E, C_4, C_2, $C_4{}^3$, the identity and clockwise rotations through 90°, 180°, and 270°, respectively. Let us consider a wave function whose $\mathbf{k}$ vector reaches from the origin to the point a in Fig. 2(b). Let us find $\alpha\mathbf{k}_1$ for all α in the point group. Figure 3 shows the $\mathbf{k}$ values generated by this process. We notice that no two operators generate the same value of $\mathbf{k}$. Therefore, the functions

$$\psi_1;\quad \psi_2=\{\sigma_{d1}|0\}\psi_1;\quad \cdots;\quad \psi_8=\{C_4{}^3|0\}\psi_1$$

form a basis for an irreducible representation of the space group. Clearly the translations have for matrices

$$\Gamma(\{\epsilon|\mathbf{R}_n\})_{ij}=\delta_{ij}e^{i\mathbf{k}_i\cdot\mathbf{R}_n};\quad i, j=1\cdots 8. \tag{69}$$



(a) (b)

FIG. 2. (a) A two-dimensional lattice with square symmetry; (b) The first Brillouin zone for the two-dimensional square lattice, showing the operations of the point group and points of special interest in reciprocal space.

The matrix representing C_2 is an eight-by-eight matrix.

$$\Gamma(\{C_2|0\})=\begin{bmatrix} 0&0&0&0&1&0&0&0\\ 0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&1\\ 1&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0\\ 0&0&0&1&0&0&0&0 \end{bmatrix}. \qquad (70)$$

This is merely a permutation matrix which is obtained by rotating Fig. 3 through 180° and writing in matrix form the permutation this induces on the numbers one through eight. We can similarly find matrices for all the operators of the point group. Using the matrices found in this way, let us construct our Bloch functions from Wannier functions by the use of Eq. (61). Let us assume that we have found a solution to our variation principle, $a_x(\mathbf{r})$, which has the same symmetry properties as a p_x-like atomic orbital under the point group, i.e., a function whose symmetry properties are like $xf(|\mathbf{r}|)$. Thus

$$\begin{aligned} &\sigma_{v1}a_x(\mathbf{r})=a_x(\mathbf{r}), && \sigma_{v2}a_x(\mathbf{r})=-a_x(\mathbf{r}),\\ &\sigma_{d1}a_x(\mathbf{r})=a_y(\mathbf{r}), && \sigma_{d2}a_x(\mathbf{r})=-a_y(\mathbf{r}),\\ &C_4a_x(\mathbf{r})=-a_y(\mathbf{r}), && C_2a_x(\mathbf{r})=-a_x(\mathbf{r}).\\ &C_4{}^3a_x(\mathbf{r})=-a_y(\mathbf{r}), && \end{aligned} \qquad (71)$$

Let us use the notation

$$\begin{aligned} E_x{}^{(j)}&=\sum(\mathbf{R}_n)e^{i\mathbf{k}_j\cdot\mathbf{R}_n}\mathcal{E}_x(\mathbf{R}_n),\\ \mathcal{E}_x(\mathbf{R}_n)&=\int a_x(\mathbf{r})Ha_x(r-\mathbf{R}_n)d\tau. \end{aligned} \qquad (72)$$

We see at once, from our discussion of the symmetry properties of energy bands, that

$$\begin{aligned} E_x{}^{(1)}=E_x{}^{(8)}=E_x{}^{(4)}=E_x{}^{(5)},\\ E_x{}^{(2)}=E_x{}^{(3)}=E_x{}^{(6)}=E_x{}^{(7)}. \end{aligned} \qquad (73)$$

Using Eqs. (61), (69), (70), and (71), we are able to construct Table II. The entries in the table denote the quantity $\sum(\alpha)\Gamma(\{\alpha|\mathbf{t}_\alpha\})_{mp}\{\alpha|\mathbf{t}_\alpha\}a(\mathbf{r})$, i.e., the function associated with each lattice point which when added up give the Bloch function [Eq. (61)]. The columns give all the Bloch functions which have the same energy, and the rows give all the Bloch functions with the same $\mathbf{k}$ value. Thus, if we wished to construct from this table a band which was completely symmetric and which had the energies of $a_x(\mathbf{r})$ in region I of Fig. 4, we would need to take $a_x(\mathbf{r})$ in regions I and VIII, $a_y(\mathbf{r})$ in regions II and III, $-a_x(\mathbf{r})$ in regions IV and V, and $-a_y(\mathbf{r})$ in regions VI and VII. If we wished to describe a band

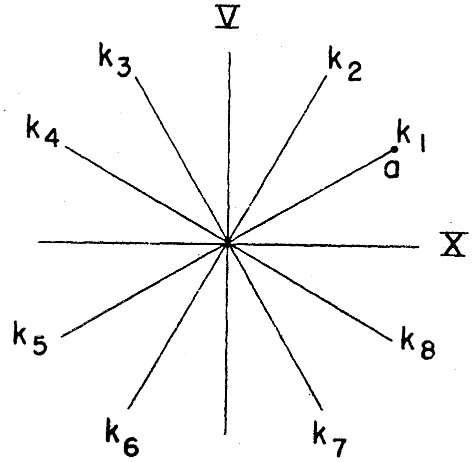


FIG. 3. $\mathbf{k}_1$ and all of the $\mathbf{k}$ vectors generated from it by the elements of the point group for the two-dimensional square lattice.

which was completely symmetric and had the energies of $a_y(\mathbf{r})$ in region I, we would need to take $a_y(\mathbf{r})$ in region I, $a_x(\mathbf{r})$ in region II, $-a_x(\mathbf{r})$ in region III, $a_y(\mathbf{r})$ in region IV, $-a_y(\mathbf{r})$ in region V, $-a_x(\mathbf{r})$ in region VI, $a_x(\mathbf{r})$ in region VII, and $-a_y(\mathbf{r})$ in region VIII.

We notice at once the similarity of these results to those of Slater[13] for the perturbed two-dimensional Mathieu problem. In his case he started out with Wannier functions, which were an exact solution to the two-dimensional Mathieu problem and had p_x-like and p_y-like symmetry. In order to construct bands that had the symmetry properties of reciprocal space, he was forced to make bands whose Wannier functions were p_x-like over part of momentum space and p_y-like over the rest of momentum space. A single Wannier function can describe the symmetric band in our case, just as a single Wannier function could describe the symmetric band in Slater's case. Thus, using column 1 of Table II, we see that our symmetric band, whose energies are those of $a_x(\mathbf{r})$ in region I, could be described in terms of the wave function

$$\psi(\mathbf{k},\mathbf{r})=\sum(\mathbf{R}_n)e^{i\mathbf{k}\cdot\mathbf{R}_n}[a(\mathbf{k})a_x(\mathbf{r}-\mathbf{R}_n)+b(\mathbf{k})a_y(\mathbf{r}-\mathbf{R}_n)], \quad (73)$$

where $a(\mathbf{k})$ is a function which is $+1$ in regions I and VIII, 0 in regions II, III, VI, and VII, and -1 in regions IV and V, and $b(\mathbf{k})$ is the same function rotated through 90°. Expanding $a(\mathbf{k})$ and $b(\mathbf{k})$ in Fourier series,

$$\begin{aligned} a(\mathbf{k})&=\sum(\mathbf{R}_n)e^{-i\mathbf{k}\cdot\mathbf{R}_n}c(\mathbf{R}_n),\\ b(\mathbf{k})&=\sum(\mathbf{R}_n)e^{-i\mathbf{k}\cdot\mathbf{R}_n}d(\mathbf{R}_n),\end{aligned} \quad (74)$$

we find that we can write $\psi(\mathbf{k},\mathbf{r})$ as

$$\begin{aligned}\psi(\mathbf{k},\mathbf{r})&=\sum(n,m)e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}[c(\mathbf{R}_m)a_x(\mathbf{r}-\mathbf{R}_n)+d(\mathbf{R}_m)a_y(\mathbf{r}-\mathbf{R}_n)]\\ &=\sum(q)e^{i\mathbf{k}\cdot\mathbf{R}_q}\sum(m)[c(\mathbf{R}_m)a_x(\mathbf{r}-\mathbf{R}_m-\mathbf{R}_q)+d(\mathbf{R}_m)a_y(\mathbf{r}-\mathbf{R}_m-\mathbf{R}_q). \quad (75)\end{aligned}$$

TABLE II. Wannier functions associated with the points of reciprocal space indicated in Fig. 3.

$\mathbf{k}\diagdown E_x^{(i)}$	$E_x^{(1)}$	$E_x^{(2)}$	$E_x^{(3)}$	$E_x^{(4)}$	$E_x^{(5)}$	$E_x^{(6)}$	$E_x^{(7)}$	$E_x^{(8)}$
$\mathbf{k}_1$	a_x	a_y	$-a_y$	$-a_x$	$-a_x$	$-a_y$	a_y	a_x
$\mathbf{k}_2$	a_y	a_x	$-a_x$	$-a_y$	$-a_y$	$-a_x$	a_x	a_y
$\mathbf{k}_3$	a_y	$-a_x$	a_x	$-a_y$	$-a_y$	a_x	$-a_x$	a_y
$\mathbf{k}_4$	$-a_x$	a_y	$-a_y$	a_x	a_x	$-a_y$	a_y	$-a_x$
$\mathbf{k}_5$	$-a_x$	$-a_y$	a_y	a_x	a_x	a_y	$-a_y$	$-a_x$
$\mathbf{k}_6$	$-a_y$	$-a_x$	a_x	a_y	a_y	a_x	$-a_x$	$-a_y$
$\mathbf{k}_7$	$-a_y$	a_x	$-a_x$	a_y	a_y	$-a_x$	a_x	$-a_y$
$\mathbf{k}_8$	a_x	$-a_y$	a_y	$-a_x$	$-a_x$	a_y	$-a_y$	a_x

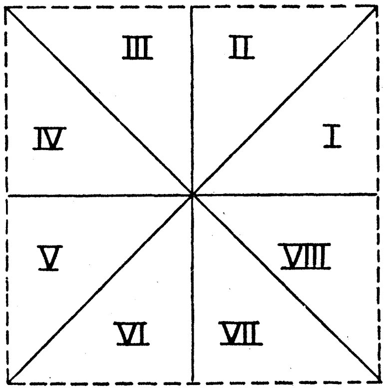


FIG. 4. Reciprocal space with various regions numbered.

The Wannier function describing the symmetric band (upper band in Slater's case) is thus

$$a'(\mathbf{r}-\mathbf{R}_q)=\sum(m)[c(\mathbf{R}_m)a_x(\mathbf{r}-\mathbf{R}_m-\mathbf{R}_q)+d(\mathbf{R}_m)a_y(\mathbf{r}-\mathbf{R}_m-\mathbf{R}_q)]. \quad (76)$$

The $c(\mathbf{R}_m)$ and $d(\mathbf{R}_m)$ we have here are exactly analogous to the c_{nm} which appear in Eqs. (52) and (53) of Slater's paper. The Wannier function forming the symmetric band whose energies are those of $a_y(\mathbf{r})$ in region I (Slater's lower band) can be described in a similar manner.

We can gain some insight into what energies will be associated with the $a_x(\mathbf{r})$ Wannier function in our case by using the results of Slater's paper. In that paper we see that after perturbations of a general cubic nature are applied to the unperturbed two-dimensional Mathieu problem there are two symmetric bands, an upper one and a lower one, which touch only at the center and corners of the unit cell. In regions I and VIII, our p_x-like Wannier function has energies that are those of the upper band. In regions II and III they become those of the lower band with a discontinuous change along the 45° diagonal. In regions IV and V they are those of the upper band and in region VI and VII they are those of the lower band. Thus we see that our Wannier function $a_x(\mathbf{r})$ does indeed generate an energy surface which does not have all the symmetry of reciprocal space. We can also see that we may expect a general $a_x(\mathbf{r})$ to produce energy surfaces with discontinuities along the 45° diagonals.

Since the 45° diagonals in momentum space seem to be lines of special interest, as a final example of the application of our variation procedure let us find the Bloch functions constructed from $a_x(\mathbf{r})$ for a wave function with $\mathbf{k}$ vector at the point b of Fig. 2(b). In Fig. 5 we show all the wave vectors which arise from $\mathbf{k}_1$ by the operations of the point group. We notice that the operations E and σ_{d1}, leave the vector $\mathbf{k}_1$ invariant. The wave functions with wave vector $\mathbf{k}_1$, must form a basis for an irreducible representation of the group consisting of E and σ_{d1}. This group has a symmetric b_1 and an antisymmetric representation b_2. If we seek a representation of the space group whose wave function with $\mathbf{k}$

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[13] J. C. Slater, Phys. Rev. **87**, 807 (1952).

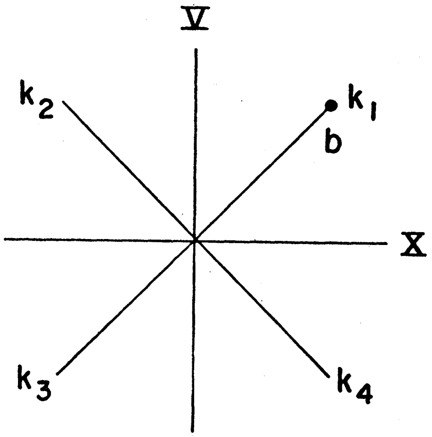

FIG. 5. $\mathbf{k}_1$ and all of the $\mathbf{k}$ vectors generated from it for the point b in reciprocal space.

value $\mathbf{k}_1$ forms a basis b_1, the matrices of the operations of the space group are

$$\Gamma(\{\epsilon|\mathbf{R}_n\})=\delta_{ij}e^{i\mathbf{k}_i\cdot\mathbf{R}_n},$$

$$\{C_2|0\}=\begin{bmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{bmatrix},\quad \{C_4|0\}=\begin{bmatrix}0&1&0&0\\0&0&1&0\\0&0&0&1\\1&0&0&0\end{bmatrix},\text{ etc.}\tag{77}$$

If we carry out the procedure of Eq. (61) we can, in analogy to Table II, construct Table III. Notice all the wave functions corresponding to a given $\mathbf{k}$ value are the same, since $E_x^{(1)}=E_x^{(2)}=E_x^{(3)}=E_x^{(4)}$. If we carry out the procedure for the Bloch functions which are to form a basis for b_2, we must multiply the matrices of all the reflections of (77) by -1 and once again carry out the procedure of Eq. (61). This yields Table IV. Therefore, we see that at the boundary of regions I and II in momentum space the wave functions become the sum and difference of Bloch functions constructed from x and y like Wannier functions, which reflect the anomalous behavior of the energy at these points. Similar calculations to the above can easily be carried out for the other special points. The points c and d are of some interest because if we carry out our procedure for them we find that we can construct two wave functions with the same wave vector and energy, hence these are points at which bands "stick together."

From the discussion of the two-dimensional square net we see we can get a band of energies associated with a Wannier function $a_x(\mathbf{r})$ and another band associated with the Wannier function $a_y(\mathbf{r})$ whose energies are the same as for the band rotated through 90°. These two bands can be cut along the 45° diagonals and combined to form two symmetric bands with Wannier functions like (76) associated with them. Thus, there are two alternative ways of describing these two bands. If we describe them in terms of x-like and y-like Wannier functions as the atoms get further apart, these functions have symmetry properties which allow them to become solutions of Schrödinger's equation for one isolated atom. If we describe them in terms of functions like (76), since the value of $c(\mathbf{R}_n)$ or $d(\mathbf{R}_n)$ at any lattice point is independent of the nuclear separation, being given by symmetry properties, the Wannier functions will not reduce to a wave function about a single atom. This method of description, however, has the advantage of giving symmetric bands without any discontinuities along the 45° diagonals. For large internuclear distances, Wannier functions with x-like symmetry are clearly advantageous since they reduce to atomic wave functions. It may be, however, that at smaller internuclear distances the Wannier functions (76) will be an equally convenient way to describe energy bands since the atomic correspondence may be completely lost anyway. These alternative ways of describing energy bands will exist for all lattices in three dimensions as well, since none of the remarks we have made here made special use of a two-dimensional lattice.

VI. A NUMERICAL METHOD

The variation procedure outlined in this paper can, of course, be carried out numerically. We shall do it here for the calculation of Wannier functions in crystals.

Suppose we were to approximate our Wannier function for the crystal by a linear combination of functions which form a complete orthogonal set (for instance atomic orbitals),

$$a(\mathbf{r})=\sum(n)c_nu_n(\mathbf{r}).\tag{78}$$

Under these conditions

$$\begin{gathered}\int a(\mathbf{r})Ha(\mathbf{r})d\tau=\sum(n,m)c_nc_mH_{nm},\\ H_{nm}=\int u_n(\mathbf{r})Hu_m(\mathbf{r})d\tau,\end{gathered}\tag{79}$$

and our constraints can be written

$$\begin{gathered}\int a(\mathbf{r})a(\mathbf{r}-\mathbf{R}_p)=\sum c_nc_mO_{nm}{}^p=\delta_{\mathbf{R}_p,\,0};\\ O_{nm}{}^p=\int u_n(\mathbf{r})u_m(\mathbf{r}-\mathbf{R}_p)d\tau.\end{gathered}\tag{80}$$

Using the method of Lagrangian multipliers and varying

TABLE III. Wannier functions associated with the points of reciprocal space indicated in Fig. 5 (for a symmetric representation).

$\mathbf{k}$ \ $E_x^{(i)}$	$E_x^{(1)}$	$E_x^{(2)}$	$E_x^{(3)}$	$E_x^{(4)}$
$\mathbf{k}_1$	a_x+a_y	$-a_x-a_y$	$-a_x-a_y$	a_x+a_y
$\mathbf{k}_2$	$-a_x+a_y$	a_x-a_y	a_x-a_y	$-a_x+a_y$
$\mathbf{k}_3$	$-a_x-a_y$	a_x+a_y	a_x+a_y	$-a_x-a_y$
$\mathbf{k}_4$	a_x-a_y	$-a_x+a_y$	$-a_x+a_y$	a_x-a_y

the c's to make $\int a(\mathbf{r})Ha(\mathbf{r})d\tau$ a minimum, and using the orthogonality of the u's, we get the simultaneous equations

$$\sum(m)c_m[H_{mn}-\mathcal{E}(0)\delta_{mn}-\sum_{p>0}(p)O_{mn}{}^{p}\mathcal{E}(\mathbf{R}_p)]=0,\quad n=1,\cdots. \tag{81}$$

In order to find the solutions of these equations, we must set the determinant of the coefficients equal to zero.

$$|H_{mn}-\delta_{mn}\mathcal{E}(0)-\sum_{p>0}(p)\mathcal{E}(\mathbf{R}_p)O_{mn}{}^{p}|=0. \tag{82}$$

This equation merely determines a relation between the unknown quantities $\mathcal{E}(\mathbf{R}_n)$. Equation (82), coupled with the simultaneous Eqs. (81) and the constraints, however, is sufficient to determine the $\mathcal{E}(\mathbf{R}_n)$ and the c's. We can notice, however, that if we make our initial functions orthogonal, in the sense

$$O_{mn}{}^{p}=\delta_{mn}\delta_{po}, \tag{83}$$

our secular equation would reduce to

$$|H_{mn}-\delta_{mn}\mathcal{E}(0)|=0. \tag{84}$$

The orthogonality (83) means that we must combine the function $u_n(\mathbf{r})$ at the origin with other atomic functions about the other lattice points to produce a function $u_n'(\mathbf{r})$ with the necessary orthogonality. This could for example be carried out by the method of Löwdin.[14] The secular Eq. (84) could be solved directly for the average energy of the band. We could then proceed to compute the shape of the band by calculating the Fourier coefficients of the energy

$$\mathcal{E}(\mathbf{R}_n)=\int a(\mathbf{r}-\mathbf{R}_n)Ha(\mathbf{r})d\tau;\quad a(\mathbf{r})=\sum c_n u_n'(\mathbf{r}). \tag{85}$$

Löwdin carries out a discussion of the case where only one atomic orbital is used in this process.

TABLE IV. Wannier functions associated with the points of reciprocal space indicated in Fig. 5 (for an antisymmetric representation).

$\mathbf{k}\diagdown E_x{}^{(i)}$	$E_x{}^{(1)}$	$E_x{}^{(2)}$	$E_x{}^{(3)}$	$E_x{}^{(4)}$
$\mathbf{k}_1$	a_x-a_y	a_x-a_y	$-a_x+a_y$	$-a_x+a_y$
$\mathbf{k}_2$	a_x+a_y	a_x+a_y	$-a_x-a_y$	$-a_x-a_y$
$\mathbf{k}_3$	$-a_x+a_y$	$-a_x+a_y$	a_x-a_y	a_x-a_y
$\mathbf{k}_4$	$-a_x-a_y$	$-a_x-a_y$	a_x+a_y	a_x+a_y

VII. CONCLUSION

In this paper we have been able to define the Wannier function in a crystal in terms of a differential equation and a variation procedure. These two methods of defining the Wannier function are methods that make no recourse to defining the Wannier function in terms of Bloch functions. We are thus able to find the Wannier function for a crystal without ever solving Schrödinger's equation. It is also seen that the methods used in this paper may also be used to advantage to actually compute energy bands in a solid.

Through the medium of group theory we have also been able to define localized functions in molecules which have many of the properties of Wannier functions in a solid. They have orthogonality properties. They also have the advantage that one of these localized functions can be operated on and combined with itself in many ways to give many solutions to Schrödinger's equation. In this sense, these functions relate the wave functions and energies of a great many states of the molecule or crystal. The localized functions are similar in many ways to the "equivalent orbitals" of Lennard-Jones.[15]

The author wishes to express his appreciation for the privilege of being a guest at the Brookhaven National Laboratory where this work was carried out. He also wishes to thank Professor J. C. Slater for many valuable discussions throughout the course of this work.

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[14] P. O. Löwdin, Phys. Rev. **18**, 365 (1950).

[15] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 14 (1949).