PHYSICAL REVIEW VOLUME 179, NUMBER 3 15 MARCH 1969

Wannier Representation of Energy in Metals

L. A. GIRIFALCO
School of Metallurgy and Materials Science and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 5 September 1968)

A method is given for representing the energy of a metal as sums of one-, two-, three-, and four-body atomic interactions in the Hartree-Fock approximation by the use of Wannier functions. This method puts the energy in a form well suited for cohesive and structural studies. The differential equation that must be satisfied by the Wannier functions for the Hartree-Fock approximation is shown to be a generalization of that previously obtained by Koster, and explicit relations are obtained among localization of the Wannier functions, bandwidth, and effective mass. For full bands, it is shown that only pairwise forces exist, so that three- and four-body forces arise only from interactions involving partially full bands. An extension of Wannier-Bloch theory is outlined for elastically strained systems, showing that the quantum theory of perfect crystals can be adapted to strained crystals by a proper choice of coordinates.

I. INTRODUCTION

STUDIES of the cohesive and defect properties of metals have often been based on the assumption that the crystal consists of atoms interacting according to a pairwise force law in spite of the fact that the degree of validity of this assumption has not been rigorously determined.[1,2] The reason for this is that the usual quantum-mechanical calculations are difficult and have an indirect connection with structure, whereas calculations based on semiempirical atomic interactions are relatively simple and are directly related to structure through lattice sums.

Recent work based on pseudopotential theory[3–5] has improved the situation somewhat by allowing ion-ion pairwise potentials to be computed from model pseudopotentials. The degree of accuracy of these pair potentials is not definitely established. While there is approximate agreement between theoretical and experimental values of the elastic constants,[4,5] the ion-ion potential computed for sodium does not agree with that obtained from experimental phonon spectra.[4,6] Furthermore, the most recent pseudopotential calculations for sodium[4,5] give a pair potential with its first minimum beyond the second-nearest-neighbor distance. Calculations based on experimental scattering amplitudes, however, give a pair potential for sodium with a first minimum at a position less than the first-nearest-neighbor distance.[7]

The application of the pseudopotential method to the theory of cohesive properties of metals is usually based on second-order perturbation theory. In this form, the theory cannot give any information on three- or four-body forces. In order to estimate the contributions of three- and four-body forces from pseudopotential theory, it would be necessary to consider higher-order perturbation theory. This has been done by Bennemann,[8–10] who applied the T-matrix formalism to pseudopotential theory. The perturbation Hamiltonian was expressed as a sum of contributions over the atomic nuclei of the crystal, so that the multiple scattering represented by the T matrix gave rise to n-body contributions to the energy, where n is any integer. In this formalism, the existence of n-body interactions for all n is primarily a result of the formalism itself and does not depend on the existence of higher-order interactions among electrons in the Hamiltonian of the wave equation.

In view of this situation, it is of interest to investigate the validity of the statement that the energy of a metal can be represented as sums of atomic interactions by an alternative method. It is the purpose of this paper to point out that, at least within the limits of the Hartree-Fock (HF) approximation, such a representation can indeed be constructed in which the energy consists of one-, two-, three-, and four-body interactions.

The approach adopted in this paper is to express HF theory in terms of Wannier functions. These functions were introduced by Wannier in a study of excitation levels in insulating crystals,[11] and their properties have been investigated by a number of authors.[12–15] For our purposes, the important property of the Wannier functions is their localization on atomic sites. This has the effect of permitting the HF energy to be written as sums over atomic positions, thereby making it possible to define atomic interaction potentials. The effect of structure appears explicitly in this formulation in the form of generalized structure factors.

---

[1] L. A. Girifalco and V. G. Weizer, Phys. Rev. **114**, 687 (1959).

[2] See, for example, A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, Science Publishers, Inc., New York, 1963), Chap. I.

[3] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[4] Wei-Mei Shyu and G. D. Gaspari, Phys. Rev. **163**, 667 (1967).

[5] M. H. Cohen, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963), p. XI-1.

[6] Wei-Mei Shyu and G. D. Gaspari, Phys. Rev. **170**, 687 (1968).

[7] A. Meyer, W. H. Young, and J. M. Dickey, J. Phys. **C1**, 486 (1968).

[8] K. H. Bennemann, Phys. Rev. **133**, A1045 (1964).

[9] K. H. Bennemann, Phys. Rev. **137**, A1497 (1965).

[10] K. H. Bennemann, Phys. Rev. **139**, A482 (1965).

[11] Gregory H. Wannier, Phys. Rev. **52**, 191 (1937).

[12] G. F. Koster, Phys. Rev. **89**, 67 (1953).

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

[14] Gregory H. Wannier, Rev. Mod. Phys. **34**, 645 (1962).

[15] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), pp. 319–335.

The fact that n-body interactions for $n>4$ do not occur in the Wannier representation is a direct result of the fact that the HF Hamiltonian contains two-electron interactions. If higher-order electronic interactions existed in the Hamiltonian, higher n-body interactions would occur in the crystal energy—this is, in contrast to the T-matrix method, in which interactions of all orders always occur in the crystal energy.

Unfortunately, the correlation energy is not included in this method. The status of correlation theory is such that reasonable estimates of the correlation energy are available only for the uniform electron gas. No satisfactory method exists for determining the effect of structures on the correlation energy. We will therefore take the correlation energy into account by adding a term to the HF energy that depends only on volume, leaving open the question of how it varies with structure.

II. WANNIER REPRESENTATION OF HARTREE–FOCK THEORY

We consider a monatomic one-electron metal and write its energy as

$$E=E_{\mathrm{HF}}+\tfrac{1}{2}\sum_{i,j}{}' \frac{e^2}{|\mathbf{R}_i-\mathbf{R}_j|}+E_c(V)\,, \tag{1}$$

where E_{HF} is the HF energy of the conduction electrons, the double sum is the interaction energy of all the ion cores at positions $\mathbf{R}_i$, and $E_c(V)$ is the correlation energy which we assume depends only on the volume V. The HF energy is given by

$$E_{\mathrm{HF}}=2\sum_{\mathbf{k}}\langle\mathbf{k}|\hat{H}_0|\mathbf{k}\rangle+2\sum_{\mathbf{k},\mathbf{k}'}\langle\mathbf{k}\mathbf{k}'|Q|\mathbf{k}\mathbf{k}'\rangle - \sum_{\mathbf{k},\mathbf{k}'}\langle\mathbf{k}\mathbf{k}'|Q|\mathbf{k}'\mathbf{k}\rangle\,, \tag{2}$$

where

$$Q\equiv e^2/|\mathbf{r}_1-\mathbf{r}_2| \tag{3}$$

and

$$\hat{H}_0\equiv-(\hbar^2/2m)\nabla^2+V(\mathbf{r})\,. \tag{4}$$

$V(\mathbf{r})$ is the potential of an electron in the field of all ion cores, which can be written

$$V(\mathbf{r})=\sum_j V_j(\mathbf{r})\,, \tag{5}$$

$V_j(\mathbf{r})$ being the potential of an electron in the field of the jth ion core.

The second and third terms in (2) contain the Hartree and exchange matrix elements, respectively, and all sums are over occupied $\mathbf{k}$ states. The $|\mathbf{k}\rangle$ are the Bloch states that minimize E_{HF} and are determined by the HF equation

$$\hat{H}_0|\mathbf{k}\rangle+2\sum_{\mathbf{k}'}\langle\mathbf{k}'|Q|\mathbf{k}'\rangle|\mathbf{k}\rangle-\sum_{\mathbf{k}'}\langle\mathbf{k}'|Q|\mathbf{k}\rangle|\mathbf{k}'\rangle=\epsilon_{\mathbf{k}}|\mathbf{k}\rangle\,, \tag{6}$$

where $\epsilon_{\mathbf{k}}$ is the energy required to remove an electron in state $\mathbf{k}$ from the crystal.

Wannier functions can be identified in terms of the Bloch states by

$$|j\rangle\equiv\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}^{\mathrm{BZ}} e^{-i\mathbf{k}\cdot\mathbf{R}_j}|\mathbf{k}\rangle\,, \tag{7}$$

$$|\mathbf{k}\rangle=\frac{1}{\sqrt{N}}\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j}|j\rangle\,. \tag{8}$$

The Wannier function $|j\rangle$ is centered on the atom at $\mathbf{R}_j$ and falls off exponentially at large distances from this atom.[13] There is some lack of uniqueness in the definition of Wannier functions in that they may be multiplied by a phase factor periodic in $\mathbf{k}$. However, this does not affect our present problem, since the phase factors multiply to unity when (7) and (8) are substituted into (2). The result of this substitution is

$$E_{\mathrm{HF}}=\sum_{i,j}F(j-i)\langle i|\hat{H}_0|j\rangle+\tfrac{1}{4}\sum_{i,j,n,m}B_{nm}{}^{ij}\langle ij|Q|nm\rangle\,, \tag{9}$$

where

$$B_{nm}{}^{ij}\equiv 2F(n-i)F(m-j)-F(m-i)F(n-j)\,, \tag{10}$$

$$F(l)\equiv\frac{2}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_l}\,, \tag{11}$$

$$B_{jj}{}^{ij}=2F(i-j)-F(j-i)=F(i-j)\,,$$

the sum being over all occupied $\mathbf{k}$ states. Note that, from (11),

$$F(0)=1\,, \tag{12a}$$

$$F(l)=F(-l)\,, \tag{12b}$$

and that Eq. (10) gives the following symmetry relations:

$$B_{nm}{}^{ij}=B_{mn}{}^{ji}=B_{ij}{}^{nm}\,. \tag{13}$$

A trivial rearrangement of the terms in Eq. (9) shows how E_{HF} can explicitly be written as a sum of one-, two-, three-, and four-body atomic interactions. To do this, rewrite (9), using (4) and (5), as

$$E_{\mathrm{HF}}=-\frac{\hbar^2}{2m}\sum_{i,j}F(j-i)\langle i|\nabla^2|j\rangle+\sum_{i,j,n}F(j-i)\langle i|V_n|j\rangle +\tfrac{1}{4}\sum_{i,j,n,m}B_{nm}{}^{ij}\langle ij|Q|nm\rangle\,. \tag{14}$$

Now collect terms of the type for which $(i=j=n=m)$, $(i\neq j=n=m)$, $(i\neq j\neq n=m)$, and $(i\neq j\neq n\neq m)$, respectively, thereby converting (14) to the form

$$E_{\mathrm{HF}}=\sum_i U_i{}^{(1)}+\sum_{i,j}{}' U_{ij}{}^{(2)}+\sum_{i,j,n}{}' U_{ijn}{}^{(3)} +\sum_{i,j,n,m}{}' U_{ijnm}{}^{(4)}\,, \tag{15}$$

where

$$U_i^{(1)}=-\frac{\hbar^2}{2m}\langle i|\nabla^2|i\rangle+\langle i|V_i|i\rangle+\tfrac{1}{4}\langle ii|Q|ii\rangle, \tag{16}$$

$$\begin{aligned}U_{ij}^{(2)}=&-\frac{\hbar^2}{2m}F(j-i)\langle i|\nabla^2|j\rangle+F(j-i)(\langle i|V_i|j\rangle\\&+\langle i|V_j|j\rangle+\langle i|V_j|i\rangle)+\tfrac{1}{4}(B_{jj}{}^{ii}\langle ii|Q|jj\rangle\\&+B_{ij}{}^{ij}\langle ij|Q|ij\rangle+B_{ji}{}^{ij}\langle ij|Q|ji\rangle)\\&+B_{ij}{}^{ii}\langle ii|Q|ij\rangle,\end{aligned} \tag{17}$$

$$\begin{aligned}U_{ijn}^{(3)}=&F(j-i)\langle i|V_n|j\rangle+\tfrac{1}{4}(B_{jn}{}^{ii}\langle ii|Q|jn\rangle\\&+B_{in}{}^{ij}\langle ij|Q|in\rangle+B_{ni}{}^{ij}\langle ij|Q|ni\rangle\\&+B_{nn}{}^{ij}\langle ij|Q|nn\rangle+B_{jn}{}^{ij}\langle ij|Q|jn\rangle\\&+B_{nj}{}^{ij}\langle ij|Q|nj\rangle),\end{aligned} \tag{18}$$

$$U_{ijnm}^{(4)}=\tfrac{1}{4}B_{nm}{}^{ij}\langle ij|Q|nm\rangle. \tag{19}$$

The primes on the multiple sums in (15) indicate that $(i\neq j)$, $(i\neq j\neq n)$, and $(i\neq j\neq n\neq m)$, respectively.

These equations show explicitly that, in addition to volume-dependent and two-body forces, three-, and four-body forces exist in a metal. Also, at least within the HF approximation, there are no direct interactions involving five or more atoms.

III. HARTREE–FOCK BAND THEORY IN THE WANNIER REPRESENTATION

To convert the HF equation to Wannier form, first substitute (7) and (8) into (6). The result is

$$\begin{aligned}\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j}\hat{H}_0|j\rangle+\sum_{i,j,n}F(j-i)e^{i\mathbf{k}\cdot\mathbf{R}_n}\langle i|Q|j\rangle|n\rangle\\-\tfrac{1}{2}\sum_{i,j,n}F(n-i)e^{i\mathbf{k}\cdot\mathbf{R}_j}\langle i|Q|j\rangle|n\rangle\\=\epsilon_{\mathbf{k}}\sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i}|i\rangle.\end{aligned} \tag{20}$$

Now multiply (20) by $e^{-i\mathbf{k}\cdot\mathbf{R}_l}$ and sum on $\mathbf{k}$ over the Brillouin zone (BZ), using the orthogonality relation

$$\sum_{\mathbf{k}}^{\mathrm{BZ}} e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}=N\delta_{jl}. \tag{21}$$

The result is

$$\begin{aligned}\hat{H}_0|l\rangle+\sum_{i,j}F(j-i)(\langle i|Q|j\rangle|l\rangle-\tfrac{1}{2}\langle i|Q|l\rangle|j\rangle)\\=\sum_i \mathcal{E}_{il}|i\rangle,\end{aligned} \tag{22}$$

where

$$\mathcal{E}_{il}=\frac{1}{N}\sum_{\mathbf{k}}^{\mathrm{BZ}}\epsilon_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_l)}. \tag{23}$$

Equation (22) is just a generalization of Koster's equation[12] to the case of a HF Hamiltonian. This can be made more transparent by defining $\hat{H}^F$ as

$$\hat{H}^F\equiv\hat{H}_0+\sum_{i,j}F(j-i)\left(\langle i|Q|j\rangle-\tfrac{1}{2}\langle i|Q|l\rangle\frac{|j\rangle}{|l\rangle}\right) \tag{24}$$

and rewriting the sum on the right of (22) as

$$\sum_i \mathcal{E}_{il}|i\rangle=\sum_i \mathcal{E}_{i0}|l+i\rangle. \tag{25}$$

Thus, (22) becomes

$$\hat{H}^F|l\rangle=\sum_i \mathcal{E}_{i0}|l+i\rangle, \tag{26}$$

which has the same form as Koster's Eq. (16). The $\mathcal{E}_{i0}$ are given by

$$\mathcal{E}_{i0}=\frac{1}{N}\sum_{\mathbf{k}}^{\mathrm{BZ}}\epsilon_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_i}, \tag{27}$$

and are the coefficients of the Fourier expansion of the energy, i.e.,

$$\epsilon_{\mathbf{k}}=\sum_j \mathcal{E}_{j0}e^{-i\mathbf{k}\cdot\mathbf{R}_j}, \tag{28}$$

as is readily seen from (27) and the orthogonality relation

$$\sum_j e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_j}=N\delta_{\mathbf{k},\mathbf{k}'}. \tag{29}$$

An alternative expression of the HF equation in the Wannier representation is obtained by multiplying (20) by $e^{-i\mathbf{k}\cdot\mathbf{R}_l}$ and summing over all *occupied* $\mathbf{k}$ states. Using the definitions (10) and (11), this gives, after some rearrangement of subscripts,

$$\begin{aligned}\sum_j F(j-i)\hat{H}_0|j\rangle+\tfrac{1}{2}\sum_{j,n,m}B_{jm}{}^{in}\langle n|Q|m\rangle|j\rangle\\=\sum_j \lambda_{ij}|j\rangle,\end{aligned} \tag{30}$$

where

$$\lambda_{ij}\equiv\frac{2}{N}\sum_{\mathbf{k}}^{\mathrm{occ}}\epsilon_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_i)}. \tag{31}$$

Using the orthogonality relation (29), (31) gives

$$\epsilon_{\mathbf{k}}=\tfrac{1}{2}\sum_j \lambda_{0j}e^{-i\mathbf{k}\cdot\mathbf{R}_j}, \tag{32}$$

so that $\tfrac{1}{2}\lambda_{0j}$ are the coefficients of the Fourier expansion of the energy. The relation between the λ_{ij} and the $\mathcal{E}_{ij}$ can be found as follows: Multiply (22) by $F(l-n)$, sum on l, and rearrange subscripts, to get

$$\begin{aligned}\sum_j F(j-i)\hat{H}_0|j\rangle+\tfrac{1}{2}\sum_{j,n,m}B_{jm}{}^{in}\langle n|Q|m\rangle|j\rangle\\=\sum_{n,j}F(n-i)\mathcal{E}_{jn}|j\rangle.\end{aligned} \tag{33}$$

Comparison of (33) and (30) gives

$$\sum_j \lambda_{ij}|j\rangle=\sum_{n,j}F(n-i)\mathcal{E}_{jn}|j\rangle. \tag{34}$$

Since the $|j\rangle$ are an orthogonal set, this gives

$$\lambda_{ij}=\sum_n F(n-i)\mathcal{E}_{jn}. \qquad (35)$$

From (31), we see that λ_{00} is the average energy of the conduction electrons $\bar{\epsilon}$, so that setting $i=j=0$ in (35) gives an expansion of the average energy in terms of the $\mathcal{E}_{0n}$, i.e.,

$$\bar{\epsilon}=\sum_n F(n)\mathcal{E}_{0n}. \qquad (36)$$

From (36), the average energy can be written in terms of the matrix elements of $\hat{H}^F$, since multiplying (26) on the left by $\langle 0|$ gives

$$\mathcal{E}_{l0}=\mathcal{E}_{0l}=\langle 0|\hat{H}^F|l\rangle. \qquad (37)$$

Because of the localized nature of the Wannier functions, the matrix element with $l=0$ is expected to be considerably larger than those with $l\neq 0$, and $\mathcal{E}_{0l}$ decreases monotonically as l increases. It is instructive to write (36) as

$$\bar{\epsilon}=\langle 0|\hat{H}^F|0\rangle+\sum_{n(\neq 0)} F(n)\langle 0|\hat{H}^F|n\rangle, \qquad (38)$$

which displays the average energy as an integral centered on one unit cell, plus a series of two-body terms that decrease as the distance from the central atom increases.

Koster[12] has pointed out how the degree of localization of the Wannier functions controls the bandwidths. In our notation, this is evident from (28) and (37), which enable us to write

$$\epsilon_{\mathbf{k}}=\langle 0|\hat{H}^F|0\rangle+\sum_{n(\neq 0)} e^{-i\mathbf{k}\cdot\mathbf{R}_n}\langle 0|\hat{H}^F|n\rangle. \qquad (39)$$

In the case of extreme localization, when $\langle 0|\hat{H}^F|n\rangle$ for $n\neq 0$ are negligible, $\epsilon_{\mathbf{k}}=\bar{\epsilon}$ for all $\mathbf{k}$ and the band is infinitely narrow. In general, (39) gives, for the width of the occupied portion of the band,

$$\epsilon_{\mathbf{k}_F}-\epsilon_0=-\sum_{n(\neq 0)}(1-e^{-i\mathbf{k}_F\cdot\mathbf{R}_n})\langle 0|\hat{H}^F|n\rangle, \qquad (40)$$

where $\mathbf{k}_F$ is the wave-number vector at the Fermi surface.

The effective-mass approximation in the Wannier representation is obtained by expanding the exponential in (39) to the second order in $\mathbf{k}$. The result is

$$\epsilon_{\mathbf{k}}=\epsilon_0-\tfrac{1}{2}\sum_{n(\neq 0)}(\mathbf{k}\cdot\mathbf{R}_n)^2\langle 0|\hat{H}^F|n\rangle, \qquad (41)$$

where the ground-state energy of the conduction band is

$$\epsilon_0=\langle 0|\hat{H}^F|0\rangle+\sum_{n(\neq 0)}\langle 0|\hat{H}^F|n\rangle. \qquad (42)$$

From the definition of the effective-mass tensor,

$$\frac{1}{m_{\alpha\beta}^*}=\frac{1}{\hbar^2}\frac{\partial^2\epsilon_k}{\partial k_\alpha\partial k_\beta}, \qquad (43)$$

Eq. (41) gives

$$\frac{1}{m_{\alpha\beta}^*}=-\frac{1}{\hbar^2}\sum_{n(\neq 0)} R_n^\alpha R_n^\beta\langle 0|\hat{H}^F|n\rangle, \qquad (44)$$

where R_n^α ($\alpha=1, 2, 3$) are the components of $\mathbf{R}_n$. Equation (44) shows explicitly how the effective mass increases with increasing localization of the Wannier functions, and also relates the anisotropy of the effective mass to the crystal structure through the R_n^α.

IV. THEOREM FOR FULL BANDS

The theory thus far has been developed for a one-electron metal. An interesting result is obtained if a full band is considered. The HF energy in the Wannier representation is still given by an equation similar to (9), except that the structure factors are sums over the full Brillouin zone. This is,

$$\begin{aligned}E_{\mathrm{HF}}=&\sum_{i,j} S(j-i)\langle i|\hat{H}_0|j\rangle\\&+\tfrac{1}{4}\sum_{i,j,n,m} 2S(n-i)S(m-j)\langle ij|Q|nm\rangle\\&-\tfrac{1}{4}\sum_{i,j,n,m} S(m-i)S(n-j)\langle ij|Q|nm\rangle, \qquad (45)\end{aligned}$$

where the $S(l)$ are structure factors defined by

$$S(l)\equiv\frac{2}{N}\sum_{\mathbf{k}}^{\mathrm{BZ}} e^{i\mathbf{k}\cdot\mathbf{R}_l}. \qquad (46)$$

Now consider the sum f_n defined by

$$f_n\equiv\sum_m S(m-n)|m\rangle. \qquad (47)$$

Using (46), this becomes

$$f_n=\frac{2}{N}\sum_m\sum_{\mathbf{k}}^{\mathrm{BZ}} e^{i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)}|m\rangle. \qquad (48)$$

But, using the relation between Bloch and Wannier functions, this becomes

$$f_n=\frac{2}{\sqrt{N}}\sum_{\mathbf{k}}^{\mathrm{BZ}} e^{-i\mathbf{k}\cdot\mathbf{R}_n}|\mathbf{k}\rangle=2|n\rangle, \qquad (49)$$

so that we have

$$\sum_m S(m-n)|m\rangle=2|n\rangle. \qquad (50)$$

Putting this result in (45) gives

$$E_{\mathrm{HF}}=2\sum_i\langle i|\hat{H}_0|i\rangle+\sum_{i,j}(2\langle ij|Q|ij\rangle-\langle ij|Q|ji\rangle). \quad (51)$$

Thus, for full bands, three- and four-body forces do not exist, the energy being a sum of one- and two-body interactions, at least in the HF approximation.

V. ELECTRONIC STATES AND WANNIER DESCRIPTION OF STRAINED CRYSTALS

The theory developed thus far is applicable to crystals that are homogeneously deformed, since all that is necessary to define Bloch and Wannier functions is translational periodicity. However, the strain does not enter directly, and the theory is not valid for nonhomogeneous deformations.

In this section, we apply a method used by Gubanov[16] for liquid systems to the case of a strained system. We restrict ourselves to small strains so that linear elasticity theory is applicable.

Gubanov[16] points out that all that is necessary to apply the apparatus of Bloch theory is to find a coordinate system in which the potential of an electron is periodic. In fact, it is sufficient to find a coordinate system in which the electron-ion core potential is periodic, since then Bloch functions can be defined that produce a periodic self-consistent field potential in the HF equation. Gubanov states that a deformed coordinate system that conforms to the strain is such a system. This is rigorously true for any ion core potential if the strains are homogeneous. It is also true for nonhomogeneous strains if the potential of an electron is given by its interaction with the ion core in the unit cell containing the electron, i.e., if the interaction of the electron with ion cores in other unit cells is zero. If these interactions are not zero, then the periodicity in the deformed coordinate system is only approximate. However, the approximation to periodicity is much better in the deformed coordinate system than in an undeformed system. We will thus develop the theory in the deformed coordinates, taking the potential to be periodic in these coordinates, with the understanding that the results are approximate in the case of nonhomogeneous strains.

Consider a crystal in which the strain matrix is $e_{\alpha\beta}$. The deformed coordinates ξ_α are related to the initial Cartesian coordinates X^α by

$$d\xi_\alpha=dX_\alpha+e_{\alpha\beta}dX^\beta, \quad (52)$$

where we adopt the usual convention that repeated indices are summed.

In the deformed coordinates, we write the HF equation as[17]

$$-\frac{\hbar^2}{2m}\frac{1}{\sqrt{g}}\frac{\partial}{\partial\xi^\alpha}\left((g^{\alpha\beta}\sqrt{g})\frac{\partial\Psi_{\mathbf{q}}}{\partial\xi^\beta}\right)+\Phi_{\mathbf{q}}(\xi)\Psi_{\mathbf{q}}=\epsilon_{\mathbf{q}}\Psi_{\mathbf{q}}, \quad (53)$$

where $g^{\alpha\beta}$ is the contravariant metric tensor for the deformed coordinate system, related to the covariant metric tensor $g_{\alpha\beta}$ by

$$g^{\alpha\beta}g_{\gamma\beta}=\delta^\alpha{}_\gamma, \quad (54)$$

$$g^{\alpha\beta}=G^{\alpha\beta}/g. \quad (55)$$

In these equations $\delta^\alpha{}_\gamma$ is the Kronecker δ, g is the determinant

$$g=|g_{\alpha\beta}|, \quad (56)$$

and $G^{\alpha\beta}$ is the cofactor of the element $g_{\alpha\beta}$ in the determinant g. The metric tensor is given by the strain as

$$g_{\alpha\beta}=\delta_{\alpha\beta}+2e_{\alpha\beta}, \quad (57)$$

$\Psi_{\mathbf{q}}$ are the wave functions in the deformed coordinate system, and $\Phi_{\mathbf{q}}$ is the HF potential, taken as periodic with respect to lattice translations in the deformed system. The eigenfunctions are labeled by the vectors $\mathbf{q}$, which are wave-number vectors in the deformed wave-vector space which is reciprocal to the deformed coordinate system $\boldsymbol{\xi}$.

The lattice points in the undeformed crystal are given by

$$\mathbf{R}_n{}^0=n_i\mathbf{a}^0{}_{(i)}, \quad (n_i \text{ integers}) \quad (58)$$

where $\mathbf{a}^0{}_{(i)}$ are the undeformed basis vectors. In the deformed crystal, the lattice vectors are given by a form similar to (58), provided they are written in the deformed coordinate system:

$$\mathbf{R}_n=n_i\mathbf{a}_{(i)}. \quad (59)$$

The deformed basis vectors $\mathbf{a}_{(i)}$ are related to those in the initial undeformed coordinates by

$$a_{(i)\alpha}=a_{(i)}{}^0{}_\alpha+e_{\alpha\beta}a^0{}_{(i)}{}^\beta. \quad (60)$$

Since, in the deformed coordinate system, the lattice vectors are given by (59), a reciprocal lattice is readily defined by the basis vectors $\mathbf{b}^{(i)}$ given by

$$\mathbf{a}_{(j)}\cdot\mathbf{b}^{(i)}=2\pi\delta_j{}^i, \quad (61)$$

$$\mathbf{b}^{(i)}=(2\pi/v)\mathbf{a}_{(j)}\times\mathbf{a}_{(k)}, \quad (i,\ j,\ k \text{ in cyclic order}) \quad (62)$$

where v is the volume of the unit cell in the deformed crystal and the reciprocal-lattice vectors in the deformed system are

$$\mathbf{K}^l=l^i\mathbf{b}^{(i)}, \quad (l^i \text{ integers}). \quad (63)$$

---

[16] A. I. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Consultants Bureau Enterprises, Inc., New York, 1965), Chaps. IV and V.

[17] See, for example, I. S. Sokolnihoff, *Tensor Analysis* (John Wiley & Sons, Inc., New York, 1951), Chaps. 2 and 6.

The $\mathbf{q}$ vectors are obtained from the periodic boundary conditions applied to the deformed coordinate system:

$$\mathbf{q}=h^i\mathbf{b}^{(i)}, \quad (h^i \text{ rational fractions}). \tag{64}$$

It is clear that in the deformed coordinate system a method for the classification of wave functions and energy levels in terms of wave vectors can be constructed that is formally identical to the $\mathbf{k}$-vector scheme for undeformed crystals. Also, this method readily gives the effect of strain on the wave vector, as is readily seen by expressing the $\mathbf{b}^{(i)}$ and then $\mathbf{q}$ in the undeformed coordinate system. To do this, first substitute (60) into (62) to get, for the αth component,

$$b^{(i)\alpha}=(v_0/v)(1+e_{\beta\beta}+e_{\gamma\gamma})b_0{}^{(i)\alpha}-e_\beta{}^\alpha b_0{}^{(i)\beta} \\ -e_\gamma{}^\alpha b_0{}^{(i)\gamma}, \quad (\text{no sums}). \tag{65}$$

In arriving at this equation, terms quadratic in the strains were neglected, and use was made of the relation between the reciprocal-lattice basis vectors $\mathbf{b}_0{}^{(i)}$ and the real basis vectors $\mathbf{a}_i{}^0$. In (65) the indices α, β, and γ are in cyclic order, there are no sums on repeated indices, and v_0 is the unit-cell volume of the undeformed crystal. To first order in the strains,

$$v_0/v=1/(1+e)=1-e, \tag{66}$$

where e is the dilatation given by

$$e=e_{\alpha\alpha}.$$

Combining (66) and (65) gives the simple form

$$b^{(i)\alpha}=b_0{}^{(i)\alpha}-e_\beta{}^\alpha b_0{}^{(i)\beta}, \tag{67}$$

where the repeated indices now indicate summation. Equation (67) shows how the reciprocal lattice deforms. Substitution into (64) gives

$$q^\alpha=h^i(b_0{}^{(i)\alpha}-e_\beta{}^\alpha b_0{}^{(i)\beta}) \tag{68}$$

or

$$q^\alpha=k^\alpha-e_\beta{}^\alpha k^\beta, \tag{69}$$

where k^α are the components of the wave vector $\mathbf{k}$ in the undeformed crystal. Equation (69) provides a relation between the $\mathbf{q}$ and $\mathbf{k}$ energy descriptions. In the deformed coordinate system, the Brillouin zone is invariant throughout the crystal, and the $\mathbf{q}$ vectors, and therefore the energy, are independent of position. When referred to the initial undeformed coordinate system (the laboratory frame), however, the Brillouin-zone size and shape vary throughout the crystal according to the variation of the basis vectors given by (67). The wave vectors vary according to (69), and therefore the energy is a function of position.

In the deformed coordinate system, the density of states is

$$\frac{V}{8\pi^3}d\mathbf{q}$$

and the total band energy of the electrons is

$$E_T=\frac{V}{8\pi^3}\int\epsilon_{\mathbf{q}}d\mathbf{q}, \tag{70}$$

where $\epsilon_{\mathbf{q}}$, the energy of the $\mathbf{q}$th state referred to the deformed coordinates, is the solution of Eq. (53). Referred to the initial coordinates, the energy $\epsilon_{\mathbf{q}}$ becomes a function of $\mathbf{k}$ and position through Eq. (69), so that we get

$$\epsilon_{\mathbf{q}}(\mathbf{r})=\epsilon_{\mathbf{k}}(e_{\alpha\beta}). \tag{71}$$

To obtain a density of states for the deformed energies in the undeformed coordinate system, we recall that

$$V=\int(1+e)dV_0, \tag{72}$$

so that a local density of states can be defined by

$$\frac{1+e}{8\pi^3}d\mathbf{k}dV_0. \tag{73}$$

Thus, the total band energy can be written in the laboratory frame as

$$E_T=\frac{1}{8\pi^3}\int\int\epsilon_{\mathbf{k}}(e_{\alpha\beta})(1+e)d\mathbf{k}dV_0. \tag{74}$$

Since an electron sees an identical environment at corresponding points in the deformed lattice, the kinetic as well as the potential energy are invariant with respect to lattice translations in the deformed coordinate system. Thus, the entire apparatus of Bloch and Wannier theory can be adopted in the deformed coordinate system. In particular, Bloch and Wannier functions can be written as

$$\Psi_{\mathbf{q}}(\boldsymbol{\xi})\equiv|\mathbf{q}\rangle=e^{i\mathbf{q}\cdot\boldsymbol{\xi}}U_{\mathbf{q}}(\boldsymbol{\xi}), \tag{75}$$

$$a(\boldsymbol{\xi}-\mathbf{R}_n)\equiv|n\rangle_\xi=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}^{\mathrm{BZ}}e^{-i\mathbf{q}\cdot\mathbf{R}_n}|\mathbf{q}\rangle, \tag{76}$$

$$|\mathbf{q}\rangle=\frac{1}{\sqrt{N}}\sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j}|j\rangle_\xi. \tag{77}$$

The results of this section show that there is no difficulty in defining Bloch and Wannier functions in elastically deformed systems, provided that an appropriate coordinate system is chosen. Thus, just as for the perfect crystal, HF theory can be developed in the Wannier representation and one-, two-, three-, and four-body forces can be defined. This theory gives results formally analogous to those for the undeformed crystal, except that all matrix elements are integrals in the deformed space. However, these can readily be translated to the undeformed coordinate system using the Jacobian of the transformation defined by (52).

Thus, for matrix elements of one- and two-electron operators $\hat{O}_1$ and $\hat{O}_2$, respectively, we can write

$$\int a^*(\boldsymbol{\xi}_1-\mathbf{R}_i)\hat{O}_1 a(\boldsymbol{\xi}_1-\mathbf{R}_j)d\boldsymbol{\xi}_1$$

$$=\int a^*(\mathbf{r}_1-\mathbf{R}_i{}^0|e_{\alpha\beta})\hat{O}_1 a(\mathbf{r}_1-R_j{}^0|e_{\alpha\beta})J_1 d\mathbf{r}, \tag{78}$$

$$\int a^*(\boldsymbol{\xi}_1-\mathbf{R}_i)a^*(\boldsymbol{\xi}_2-\mathbf{R}_j)\hat{O}_2 a(\boldsymbol{\xi}_1-\mathbf{R}_n)a(\boldsymbol{\xi}_2-\mathbf{R}_m)d\boldsymbol{\xi}_1 d\boldsymbol{\xi}_2$$

$$=\int a^*(\mathbf{r}_1-\mathbf{R}_i{}^0|e_{\alpha\beta})a^*(\mathbf{r}_2-\mathbf{R}_j{}^0|e_{\alpha\beta})\hat{O}_2 a(\mathbf{r}_1-\mathbf{R}_n{}^0|e_{\alpha\beta})$$

$$\times a(\mathbf{r}_2-\mathbf{R}_m{}^0|e_{\alpha\beta})J_1J_2 d\mathbf{r}_1 d\mathbf{r}_2, \tag{79}$$

where the operators on the left-hand sides of these equations are expressed in the deformed coordinate system, whereas on the right-hand sides they are written in the undeformed coordinates. The Jacobians J_1 and J_2 are given by the determinant

$$|\partial\xi^\alpha/\partial X^\beta|=|\delta_\beta{}^\alpha+e^\alpha{}_\beta|. \tag{80}$$

Equations (78) and (79) show how the Wannier theory can be used to construct localized atomic interactions for strained crystals. Although the theory was developed for small strains, there is no essential difficulty in extending it to finite deformations. The resulting equations would, of course, be considerably more complicated than those given here.

VI. SUMMARY AND CONCLUSIONS

The Wannier functions provide a convenient and conceptually satisfying basis for the description of the cohesive properties of metals. By their use, an explicit reciprocal connection is readily established between the band and the bond approach to metallic cohesion. An ideal bond description would assign invariant pair potentials to atoms from which all cohesive properties could be computed. The Wannier formalism shows to what extent this can be done. The results show that pair potentials can indeed be constructed for metals, but that they do not comprise the entire energy. In addition to the expected volume-dependent term, there are terms that depend on the simultaneous interactions of three and four atoms. From the localized nature of the Wannier functions, it is clear that the three- and four-body terms must be smaller than the pairwise terms, so that to a first approximation the energy of a metal can be taken to be a sum of a volume-dependent term and two-body interactions. An estimate of the accuracy of this approximation will depend on the magnitude of the three- and four-body matrix elements relative to those for the pair interactions.

A valuable feature of the formalism is that it depends explicitly on structure. In Eqs. (14)–(19), this dependence is manifest in the structure factors F and B. In addition, of course, there is a more subtle structural dependence in that the Wannier functions are solutions of the structure-dependent equation (22). Clearly, the formalism is well suited to investigate the relations among wave functions, structure, and cohesive properties.

Several results first obtained by Koster[12] for a one-electron Hamiltonian that was independent of structure were generalized to the HF approximation. Koster's differential equation for the Wannier functions was shown to hold in the HF case, if an appropriate HF operator in the Wannier representation is defined. Also, Koster's results for the relation between localization and bandwidth was generalized to the HF case, and the dependence of effective mass on localization and structure was obtained explicitly.

A theorem was derived which shows that in the HF approximation, full bands give rise only to volume-dependent terms and pairwise interactions. Thus, for example, the HF approximation when applied to rare gases justifies the use of two-body potentials, since the volume-dependent and atom-atom correlation energies are small in these systems.

One of the important applications of empirical interatomic force laws in metals has been in the theory of crystal defects, so that it is of interest to investigate the applicability of the localized formalism to nonperiodic systems. This was done for the case of elastically deformed crystals using a procedure of Gubanov's[16] in which the wave equation is referred to a deformed coordinate system that conforms to the elastic strain. It was thereby shown that for this case, Bloch and Wannier functions can indeed be defined and the entire apparatus of Bloch and Wannier theory can be applied to strained crystals. Transforming the coordinates back to a laboratory frame of reference introduces the strains directly into the equations.

The major unsolved question involves, as usual, the correlation energy. The localized formalism presented here depends on the one-electron approximation, and the theory of the correlation energy is not sufficiently advanced to ascertain its relation to crystal structure. It was assumed in the present paper that the correlation energy depends only on volume. The validity of this assumption must await detailed calculations using wave functions for real metals and a comparison of the results with experiment.