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Interpolation Scheme for Energy Bands in Solids*

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The orthogonalized plane wave method is formulated as an interpolation scheme for use in conjunction with calculations made at symmetry points in the Brillouin zone. The Fourier coefficients of the crystal potential and the matrix components of the Hamiltonian between core functions are treated as parameters to be fitted to other calculations made at symmetry points by such methods as the cellular, orthogonalized plane wave, and augmented plane wave. The interpolation scheme then provides a method for making calculations at a general point in the Brillouin zone. The scheme is most useful for the case of valence and excited states where the wave function on one center overlaps many of its neighbors.

I. INTRODUCTION

BECAUSE of the computational difficulty in carrying out rigorous solutions most energy band calculations are made only at symmetry points in the Brillouin zone. It is therefore desirable to consider methods for interpolating between such symmetry points. In general, the requirement for a satisfactory interpolation scheme is the separation of spatial parts and **k** dependent parts in the relation determining E as a function of **k**. Further, the **k** dependence should have a relatively simple analytic form so that, e.g., enough general points in the Brillouin zone can be calculated to get an adequate density of states curve. The cellular method[1,2] or procedures which utilize solutions for an atomic interior joined to exterior plane wave solutions on some arbitrary surface,[3–6] do not seem suited to this type of separation.[7]

However, Slater and Koster,[8] starting with the LCAO (linear combination of atomic orbitals) or tight binding approximation, have succeeded in making such a separation and have used the integrals involving the Hamiltonian between two atomic functions as parameters to be fitted to calculations made at symmetry points. The number of parameters to adequately represent strongly overlapping atomic functions may become very large, however, and this method seems best suited to the more tightly bound states.

Another method for which an analytic **k** dependence can be separated from the spatial parts in the matrix components of the Hamiltonian is the orthogonalized plane wave method.[9] As with the orthogonalized plane wave method in general this scheme: (a) does not depend on an assumption of a spherical potential for atomic interiors, (b) is most easily applied when the wave functions for an atom in the crystal can readily be separated into a set of core or highly localized functions not overlapping neighboring atoms and a set of valence and excited functions which have very strong overlapping, (c) requires special consideration at certain **k** values where the plane waves are orthogonal by reasons of symmetry to all core states. The scheme seems particularly useful for bands with large overlapping and as such may be used to supplement the method of Slater and Koster.

II. PARAMETERIZATION OF THE ORTHOGONALIZED PLANE WAVE METHOD

The orthogonalized plane wave method was developed by Herring.[10] Our treatment differs from that of Herring primarily in use and interpretation and in that we set up the method in terms of less restrictive core functions than free atom functions. We consider N identical unit cells, each of which has volume Ω_0, and for simplicity we assume one atom per unit cell. The orthogonalized plane wave corresponding to the lattice vector $\mathbf{K}_n$ in **k** space is defined by

$$N^{\frac{1}{2}}\psi_n=\frac{e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}}}{\Omega_0}-\sum_i^{(\text{core})}\mu_{in}b_i, \tag{1}$$

where the Bloch sums are

$$b_i(\mathbf{k},\mathbf{r})=\sum_{R_j}e^{i\mathbf{k}\cdot\mathbf{R}_j}\varphi_i(\mathbf{r}-\mathbf{R}_j). \tag{2}$$

The μ_{in}'s are determined from the orthogonality

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[2] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[3] J. Korringa, Physica **13**, 392 (1947).

[4] J. C. Slater, Phys. Rev. **92**, 603 (1953); M. M. Saffren and J. C. Slater, Phys. Rev. **92**, 1126 (1953).

[5] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[6] P. M. Morse, "Multiple scattering of waves from a spatial array of spherical scatters" (unpublished).

[7] For a spherically symmetrical potential inside a radius r_i and constant between spheres, the methods given by Kohn and Rostoker (reference 5) and Morse (reference 6) may lead to a practical scheme for getting general points in the Brillouin zone. However, at present no estimate is available as to whether it will be practical to calculate a sufficient number of points for, e.g., a density of states curve.

[8] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954). A prior account of much of this work is given in J. C. Slater, Technical Report No. 4, Solid-State and Molecular Theory Group, MIT, July 15, 1953 (unpublished).

[9] This is also possible for the Fourier series or plane wave method, and a parameterization scheme could be set up using the Fourier coefficients of the potential as disposable parameters. However, the poor convergence of this method is well known and a rough estimate based on wave functions for sodium given by Slater [reference 2 and J. C. Slater, Revs. Modern Phys. **6**, 209 (1939)] show that for an adequate representation the resultant secular equation is well outside the range readily solvable by present high-speed digital computers.

[10] C. Herring, Phys. Rev. **57**, 1169 (1940).

condition

$$\int_\infty b_j^*\psi_n d\mathbf{r}=0. \tag{3}$$

We assume that the b_i's are orthogonal:

$$\frac{1}{N}\int_\infty b_i^* b_j d\mathbf{r}=\delta_{ij}. \tag{4}$$

This implies that the core functions φ_i form an *orthonormal* set with respect to functions on neighboring centers as well as on the same center. Both this assumption and the choice of core functions will be considered later. The μ_{in}'s resulting from (3) and (4) are then Fourier transforms of the core functions:

$$\mu_{in}=\int_\infty \frac{e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}\varphi_i^*(\mathbf{r})d\mathbf{r}. \tag{5}$$

Our one-electron energy band functions for a given $\mathbf{k}$ are now constructed from a linear combination of functions of the form (1):

$$\Psi(\mathbf{r},\mathbf{k})=\textstyle\sum_n A_n\psi_n. \tag{6}$$

Putting this in

$$H\Psi=E\Psi$$

yields the usual secular equation

$$\left|H_{mn}-E\int_\infty \psi_m^*\psi_n d\mathbf{r}\right|=0, \tag{7}$$

where

$$\begin{aligned}H_{mn}={}&\frac{1}{N}\int_\infty \frac{e^{-i(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}H\frac{e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}d\mathbf{r}\\&-\frac{1}{N}\int_\infty \frac{e^{-i(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}H\sum_j \mu_{jn}b_j d\mathbf{r}\\&-\frac{1}{N}\int_\infty \sum_i \mu_{im}^* b_i^* H\frac{e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}d\mathbf{r}\\&+\frac{1}{N}\int_\infty \sum_i \mu_{im}^* b_i^* H\sum_j \mu_{jn}b_j d\mathbf{r}.\end{aligned} \tag{8}$$

Let us consider the last term in (8). Defining

$$\int_\infty \varphi_i^*(\mathbf{r})H\varphi_j(\mathbf{r}-\mathbf{R}_q)d\mathbf{r}=\mathcal{H}_{ij}(\mathbf{R}_q), \tag{9}$$

the last term becomes

$$\sum_i\sum_j \mu_{im}^*\mu_{jn}\sum_{R_q} e^{i\mathbf{k}\cdot\mathbf{R}_q}\mathcal{H}_{ij}(\mathbf{R}_q). \tag{10}$$

Next, we treat the two middle or cross terms in (8). For these, we first consider the expansion of Hb_j since b_j is not necessarily an eigenfunction of the crystal Hamiltonian. The set of functions in which it is convenient to make this expansion are the Bloch sums made up from our initially chosen core functions,[11] φ_i. Thus, using (4),

$$Hb_j=\sum_i c_{ij}b_i=\frac{1}{N}\sum_i\left(\int_\infty b_i^* Hb_j d\mathbf{r}\right)b_i. \tag{11}$$

Putting (11) into the second term of (8) and using (5), (9) we have

$$\begin{aligned}&-\frac{1}{N}\int_\infty \frac{e^{-i(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{r}}}{\Omega_0^{\frac{1}{2}}}H\sum_j \mu_{jn}b_j d\mathbf{r}\\&=-\frac{1}{N}\sum_j \mu_{jn}\left(\sum_i\int_\infty e^{-i(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{r}}b_i d\mathbf{r}\right)\left(\frac{1}{N}\int_\infty b_i^* Hb_j d\mathbf{r}\right)\\&=-\sum_i\sum_j \mu_{im}^*\mu_{jn}\sum_{R_q} e^{i\mathbf{k}\cdot\mathbf{R}_q}\mathcal{H}_{ij}(\mathbf{R}_q).\end{aligned} \tag{12}$$

This is the negative of (10). Because of the Hermitian property of H the other cross term is equal to (12). To investigate the first term in (8) we write out the one-electron crystal Hamiltonian as

$$H=-\nabla^2+V(\mathbf{r}).$$

The first term then becomes

$$\begin{aligned}|\mathbf{k}+\mathbf{K}_n|^2\delta_{mn}&+\frac{1}{\Omega_0}\int_{\Omega_0} e^{i(\mathbf{K}_n-\mathbf{K}_m)\cdot\mathbf{r}}V(\mathbf{r})d\tau_c\\&\equiv|\mathbf{k}+\mathbf{K}_n|^2\delta_{mn}+V(\mathbf{n}-\mathbf{m}).\end{aligned}$$

Collecting the terms, Eq. (8) can thus be written

$$\begin{aligned}H_{mn}={}&|\mathbf{k}+\mathbf{K}_n|^2\delta_{mn}+V(\mathbf{n}-\mathbf{m})\\&-\sum_i\sum_j \mu_{im}^*\mu_{jn}\sum_{R_q} e^{i\mathbf{k}\cdot\mathbf{R}_q}\mathcal{H}_{ij}(\mathbf{R}_q).\end{aligned} \tag{8$'$}$$

Letting $H=1$ in (8), we also get

$$\int_\infty \psi_m^*\psi_n d\mathbf{r}=\delta_{mn}-\sum_i \mu_{im}^*\mu_{in}.$$

It is now the general method of our interpolation scheme to treat the integrals representing the Fourier coefficients of the potential $V(\mathbf{n}-\mathbf{m})$ and the matrix components $\mathcal{H}_{ij}(\mathbf{R}_q)$ as fitting parameters. The $V(\mathbf{n}-\mathbf{m})$ depend only on the differences of the sets of integers characterizing our initial choice of the vectors $\mathbf{K}_n$. The $\mathcal{H}_{ij}(\mathbf{R}_q)$ are the same parameters introduced by Slater and Koster[8] in their LCAO or tight binding approximation interpolation method. At symmetry points our secular Eq. (7) will factor, and we can determine the values of our integrals $V(\mathbf{n}-\mathbf{m})$

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[11] In this expansion the b_i's do not form a complete set, and in particular we are omitting any plane wave contribution to the part of b_j which differs from a crystal eigenfunction. It is hoped that in most cases Eq. (11) will be adequate, but there may be instances where an appreciable plane wave contribution enters. In such circumstances it will probably be best to assume that b_j is an eigenfunction and thus use only diagonal $\mathcal{H}$'s in Eq. (8$'$).

and $\mathcal{H}_{ij}(\mathbf{R}_q)$ by fitting to primary calculations made by other methods at these points. In the cases treated by Slater and Koster with the LCAO method, their secular equation factored to such an extent that they were able to fit integrals analytically and for approximately the same number of disposable constants we may also expect to accomplish our fitting analytically. However, for more complicated cases the fitting will probably be done most easily by a trial and error procedure.

III. DISCUSSION

A. Choice of Core Functions

In the formulation and use of the orthogonalized plane wave method, free atom wave functions have usually been assumed for the core functions φ_i.[10,12–15] Callaway[14] has found, however, that such an assumption may lead to considerable error. Since we are using a parameterization scheme and are thus not making extensive calculations with our core functions, we may use less restrictive functions.

If we assume the form

$$R(r)Y_l^m(\theta,\varphi), \tag{13}$$

where $R(r)$ may be a series of terms made up from polynomials in r times exponentials and the Y_l^m's are spherical harmonics, then the Fourier transforms which give the μ_{in}'s are spherical harmonics in $\mathbf{k}$ space times polynomials in $|\mathbf{k}+\mathbf{K}_n|$.[16,17] Further, we may use a technique suggested by Parmenter.[18] In his calculation for Li by the orthogonalized plane wave method, he assumed an exponential for the $1s$ core function and determined the coefficient in the exponent by a variation calculation using the crystal potential which he had constructed. It seems entirely feasible to introduce such variation parameters into $R(r)$ and, if desirable, to consider linear combination of terms of the form (13) determining such parameters and coefficients of the linear combinations by a variation calculation using the crystal potential constructed for the symmetry point solutions.

If a choice of core states is made which includes functions φ_i which overlap functions φ_j centered on neighboring sites, Eq. (4) is not satisfied and considerable additional effort is required to properly handle them. For this case it seems that the most satisfactory procedure for our interpolation scheme is to consider that set of functions on each center which overlap other centers and to construct from these a new orthogonal set. This can be carried out in a symmetrical manner by the method of Löwdin.[19] For example, in germanium, if we consider the core as those functions through $3d$, we could classify the functions through $3p$ as nonoverlapping and the $3d$ as overlapping nearest-neighbor $3s$, $3p$, and $3d$ functions. We would then orthogonalize the $3d$ to $3s$, $3p$, and $3d$ functions on nearest-neighbor sites.

B. Numerical Considerations

The basic problem is the solution of the secular equation, (7), at every value of $\mathbf{k}$ we wish to consider, and its order depends directly on the initial choice of the vectors $\mathbf{K}_n$. There is evidence that in using orthogonalized plane waves very few sets of neighboring $\mathbf{K}_n$ vectors in $\mathbf{k}$ space give a good representation of many of the valence and excited states.[12,14,18] If we consider the vectors $\mathbf{K}_n$ out through nearest neighbors in $\mathbf{k}$ space, the secular equations for the face-centered cubic structure are 9×9 and for the body-centered cubic are 13×13; through next to nearest neighbors these become 15×15 and 19×19, respectively. Solving such secular equations at a large number of points in the Brillouin zone is practicable on high-speed digital computers by a program like that developed by Dr. Alvin Meckler for Whirlwind I at M.I.T. This program has been successfully employed for 5×5 secular equations by Slater and Koster for the density of states curve computed using their LCAO interpolation method. It is worth noting that because of the large number of points involved, Slater and Koster also found it desirable to have the digital computer compute the matrix components even though these were expressed in a simple analytic form. It is expected that such a procedure would also be adopted for the present interpolation scheme.

The number of parameters $V(\mathbf{n}-\mathbf{m})$, of course, is governed by the choice of vectors $\mathbf{K}_n$; e.g., for the f.c.c. structure, going out to nearest neighbors yields four V's while if we go out to next to nearest neighbors we get a total of six V's (if it is convenient to take the average potential equal to zero we get one less in each case). The number of $\mathcal{H}_{ij}(\mathbf{R}_q)$ parameters arising from the matrix components of the Hamiltonian between core states depends on the particular solid and how many sets of neighboring atoms in real space are to be considered, and may be predicted directly from the tables given by Slater and Koster.[8] Since, in general, our core functions are chosen as those functions which do not overlap, we can use the much restricted set of $\mathcal{H}_{ij}(\mathbf{R}_q)$'s corresponding to $\mathbf{R}_q=0$. However, for those core functions which overlap to some extent (and have been made into an orthogonal set by the method given in the previous section), it is reasonable that only nearest neighbors will have to be considered.

C. Orthogonality by Virtue of Symmetry

It was originally pointed out by Herring[10] and also by others[12–14] that the plane wave parts of the wave func-

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[12] C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940).

[13] F. Herman, Phys. Rev. **93**, 1214 (1954).

[14] J. Callaway, Phys. Rev. **97**, 933 (1955). The author wishes to thank Dr. Callaway for being permitted to see his work before publication.

[15] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[16] B. Podolsky and L. Pauling, Phys. Rev. **34**, 109 (1929).

[17] R. McWeeny, Acta Cryst. **4**, 513 (1951).

[18] R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

[19] P. -O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

tions (6) at certain symmetry points (e.g., $\mathbf{k}=0$) form bases for irreducible representations of the crystal point group, some of which may be automatically orthogonal to core functions made from orbitals of the form (13). At such points we are left with the relatively poor convergence properties of the non-orthogonalized plane waves. For these circumstances Herring has suggested the addition of a Bloch sum of atomic-like functions of the expansion having the appropriate symmetry properties and the proper rapid variation near the nucleus. Callaway has constructed and successfully used such functions in his treatment of iron[14] (if we orthogonalize these functions to the core states as indicated in Part A they do not in principle have to be constructed so as to vanish at half the interatomic spacing as contemplated by Herring and used by Callaway). For our interpolation we first make an initial choice of the vectors $\mathbf{K}_n$ and then for a particular crystal investigate at which points the automatic orthogonality occurs. Then, in order to insure a good representation at and around these points, such atomic-like functions are to be included and treated in the same manner as the core functions.

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Response of Anthracene and Stilbene to Low-Energy Protons and X-Rays*

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The scintillation response of anthracene and stilbene to low-energy protons (170–570 kev) and x-rays (10–40 kev) has been investigated. In agreement with previous work at higher proton energies, the proton pulse height *vs* energy curves are quite nonlinear. The x-ray data are essentially linear down to 10 kev. This result is contrary to the reported response of these crystals to electron bombardment, but seems to be in agreement with the theory proposed by Birks. With the aid of this theory, proton response curves are obtained for stilbene and anthracene over an extended energy range.

INTRODUCTION

THE response of anthracene and stilbene to protons having energies greater than 500 kev has been extensively investigated.[1–3] Studies have been made of electron response below 500 kev,[4,5] but the response to protons in this energy range has not been reported. It is in this low-energy region that the nature of the scintillation response can be investigated in detail. The work of Hopkins[4] and Taylor *et al.*[3] shows that the response to electrons below 25 kev is nonlinear, and although the proton response is nonlinear above 500 kev, it becomes more pronounced at lower energies.

In the case of low-energy gamma rays or x-rays, the photoelectric process plays the major role. One might therefore expect gamma rays and electrons to have the same response. However, the nonlinearity observed for electrons[3,4] is not apparent in the curves presented here for x-rays which are linear within experimental error. An explanation of this discrepancy can be found in the relation developed by Birks,[6] between the luminescence S and the energy E of the ionizing particle:

$$dS/dr=\phi\frac{AdE/dr}{1+kBdE/dr}. \tag{1}$$

AdE/dr gives the number of "excitons" produced in the crystal by the incident particle. The term "exciton" refers to the quantity which links the energy of the incident particle to the fluorescence. Birks has given arguments which indicate that these "excitons" are photons of about 10-ev energy. The function ϕ is given by the expression

$$\phi=1-\tfrac{1}{2}[\exp(-r/a_0)-(r/a_0)E_i(r/a_0)],$$

where $E_i(r/a_0)$ is the exponential integral, a_0 is the mean free path of the "exciton" in the crystal, and r the range of the incident particle in the crystal. ϕ gives the probability of capture of an "exciton" before it escapes through a crystal surface. $kB\,dE/dr$ represents the quenching of these "excitons" by molecules damaged by the ionizing particle or by inactive impurity molecules.

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