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A COMBINED REPRESENTATION METHOD FOR USE IN BAND STRUCTURE CALCULATIONS: I. METHOD*

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Abstract

A representation is described whose basis levels combine the important physical aspects of a finite set of plane waves with those of a set of Bloch tight-binding levels. The chosen combination has a particularly simple dependence on the wave vector $\underset{\sim}{k}$ within the Brillouin Zone, and its use in reducing the standard one-electron band structure problem to the usual secular equation has the advantage that the lattice sums involved in the calculation of the matrix elements are actually independent of $\underset{\sim}{k}$. For systems with complicated crystal structures, for which the Korringa-Kohn-Rostoker (KKR), Augmented-Plane Wave (APW) and Orthogonalized-Plane Wave (OPW) methods are difficult to apply, the present method leads to results with satisfactory accuracy and convergence.

1. Introduction

The method described below evolved from an attempt to obtain the band structure of a system such as molecular hydrogen in a relatively complex crystal structure, and in a variety of density regimes. For certain regions of the density it is expected on general grounds that neither the low density tight-binding approach (with a representation of linear combinations of atomic orbitals (LCAO) Bloch functions), nor the methods using a representation with a basis of simple plane waves (PW), are physically adequate.

For reasons principally connected with the structure, the other standard methods are also not entirely adequate.[1,2] The Korringa-Kohn-Rostoker (KKR) and Augmented-Plane Wave (APW) methods not only require an extraordinary amount of computational effort, but are based on a muffin-tin approximation to the actual one-electron potential.[3,4,5] This means a "sphericalization" (taking the average over angles) of the potential arising from the contents of a unit cell, a procedure which is difficult to justify when the molecules in the crystal have no obvious spherical symmetry. Although such models yield useful physical information especially at lower densities, it is difficult to estimate their accuracy, particularly at higher densities, where steric effects and the requirements of proper crystal symmetry may become important. The effects of the latter on the resulting band structure may well be important.

Furthermore, there is often no clear cut separation between core levels (actually non-existent for hydrogen) for which tight-binding is adequate, and the rest of band levels (valence and conduction), which would make an orthogonalized plane wave (OPW) method appropriate. Even if one makes an arbitrary separation between valence and conduction levels, and treats the first with tight-binding and the second with OPW functions, orthogonalized to the valence levels,[6] one still has the possibility of significant overlap of these "core" levels in situations where large variations in density are of physical interest.

For these reasons it is natural to investigate alternative representations whose basis levels combine in some way the advantages of both the LCAO functions (with their physically correct atomic behaviour near the nuclei) and the PW which are more satisfactory in the region between atoms. One such basis set was recently used by Ramaker *et al*[7] in exact-exchange crystal Hartree-Fock-calculations of molecular and metallic hydrogen. Another, based on a more general and flexible approach is described below. It is a modification of an idea used successfully by Brown and Krumhansl,[8] which was shown to be mathematically equivalent to but in fact more general than the orthogonalized-plane wave method.

In the next Section the representation will be developed and its basic properties described. Section III is devoted to a discussion of the application of the representation to the solution of the one electron problem in crystals. ~~In Section IV we discuss briefly the possible~~ applications of the method, which although originating from the study of a specific material is of more general interest and can be used to study the electronic structure of a wide class of materials. The specific results for the band structure of molecular hydrogen will be given in a following paper.[9]

II. Representation

The representation we introduce is formally incomplete but only in the sense that it has a finite set of basis wave functions. This set is made up of a finite number of PW and a set of specially constructed Bloch levels. It is constructed in such a way that the whole set is orthonormal, and although the set *is* finite, linear combinations of them are expected to give variationally good approximations to the eigenfunctions and corresponding eigenvalues. This expectation is based on the physical way the set is constructed, which will be explained in what follows.

Consider first a monatomic (for example, a simple cubic) lattice with lattice constant $\underset{\sim}{a}$ and LCAO-Bloch level $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ defined with atomic orbital $\Phi(\underset{\sim}{r})$ as follows:

$$h_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \, \Phi(\mathbf{r}-\mathbf{R}), \tag{1}$$

where N is the number of cells in a volume Ω, $\mathbf{R}$ designates their position vectors, and $\mathbf{k}$ is the Bloch wave vector. Expressing this Bloch level in its well known form

$$h_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} \; e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}, \tag{2}$$

where $\mathbf{K}$ is the set of reciprocal lattice vectors corresponding to $\mathbf{R}$, it is easy to see that

$$c_{\mathbf{q}} = \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \Phi_{\mathbf{q}} \tag{3}$$

where $\Phi_{\mathbf{q}}$ is the Fourier transform of $\Phi(\mathbf{r})$.

For the purposes of defining a trial function, $\Phi(\mathbf{r})$ may be <u>any</u> localized orbital, and not necessarily an atomic one. This observation will be used to construct a particularly convenient type of Bloch level. But instead of defining it directly (i.e. in $\mathbf{r}$-space) it is inferred from conditions imposed on $c_{\mathbf{q}}$. In this way it is easier to enforce(through them) the properties that one would like the Bloch levels to have. First, some general observations:

One expects the eigenfunctions not to change too much very near (and particularly inside, if there is a core) the atoms or molecules forming the solid from the values they assume in corresponding free atoms or molecules. This remains true even at fairly high densities. Thus one wants to include in the basis set, Bloch levels built with atomic or molecular orbitals to obtain a good representation in this region. But it is clear that for this purpose only those components $c_{\mathbf{k}-\mathbf{K}}$ with sufficiently large $\mathbf{K}$ are relevant (here $\mathbf{k}$ is assumed to be restricted to the first Brillouin zone $\underline{B_o}$). On the other hand, if the itinerant or free electron character becomes important (as it will at high densities) plane waves with wave vectors (about the origin) not too large in terms of $2\pi/\underline{a}$ are obviously indicated. We now construct basis functions incorporating these features. The Bloch level is first modified by truncating its Fourier components of low wave vectors, say $\mathbf{G}$ in some finite subset $\underline{G}$ of the reciprocal lattice $\underline{K}$. In this way the plane waves with wave vectors $\underset{\sim}{k}-\underset{\sim}{G}$ have been set free to be included in the basis set as independent members orthogonal to the Bloch levels. (For simplicity in some of the algebraic manipulations the subset $\underline{G}$ may be chosen symmetrically to include both $\underset{\sim}{G}$ and $-\underset{\sim}{G}$, although this is not required in general by the method.) For the simple cubic lattice case, for example, we may choose $\underset{\sim}{G}$ to be the set of all reciprocal lattice vectors within or on the surface of a cube centered at the origin, and with faces perpendicular to the axes. Further, let $\underline{T}$ be the complement of $\underline{G}$, that is $\underline{G}\cap\underline{T}$ is empty and $\underline{G}\cup\underline{T} = \underline{K}$. Next, the Bloch levels of the basis are to be chosen to have <u>as simple</u> a form as possible, a requirement for both analytical and computational purposes. In particular, the most simple functional dependence on $\underset{\sim}{k}$ is essential.

In the case of a Bravais lattice, a set of Bloch levels satisfying these criteria can be taken to have components

$$\phi_{\underset{\sim}{q}} = \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \sum_{\underset{\sim}{K}} \chi_{\underline{B_o}}(\underset{\sim}{q}-\underset{\sim}{K})\ \chi_{\underline{T}}(\underset{\sim}{K})\ \Phi_{\underset{\sim}{K}}, \qquad (4)$$

where the characteristic function $\chi_{\underline{A}}(\underset{\sim}{x})$ is given by

$$\chi_{\underline{A}}(\underset{\sim}{x}) = \begin{cases} 1\ , \ \text{if } \underset{\sim}{x} \in \underline{A}\ , \\ 0\ , \ \text{otherwise.} \end{cases}$$

Here $\Phi(\underset{\sim}{r})$ is a localized orbital. Figure 1 shows a schematic one-dimensional example of the procedure just outlined; there the dotted curve represents the Fourier transforms Φ_q of a localized orbital and the discontinuous curve the components $(\Omega/N)^{\frac{1}{2}}c_q$ given by Eq. (4); note also that the set $\underline{G}$ contains by choice only the reciprocal lattice vectors 0 and ± $2\pi/a$.

The levels defined by Eq. (4) all have the properties of Bloch levels, and can of course be written as

$$h_{\underset{\sim}{q}}(\underset{\sim}{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\underset{\sim}{K}} c_{\underset{\sim}{q}-\underset{\sim}{K}}\ e^{i(\underset{\sim}{q}-\underset{\sim}{K})\cdot\underset{\sim}{r}} \qquad (5)$$

This reduces, for $\mathbf{q} = \mathbf{k} \in \underline{B_o}$, to the standard form:

$$h_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left[\frac{\sqrt{N}}{\Omega} \sum_{\mathbf{K}\in\underline{T}} \Phi_{\mathbf{K}} \; e^{i\mathbf{K}\cdot\mathbf{r}} \right] , \qquad (6a)$$

and is equivalent also to:

$$h_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{r}} \left[\sum_{\mathbf{R}} \Phi(\mathbf{r}-\mathbf{R}) - \frac{N}{\Omega} \sum_{\underline{G}\in\underline{G}} \Phi_{\mathbf{G}} \; e^{i\mathbf{G}\cdot\mathbf{r}} \right] , \qquad (6b)$$

where the quantity in [ ] clearly has the periodicity of the lattice. The prefactor in the expression for $c_{\mathbf{q}}$ is not important except to keep track formally, and in a consistent way, of the various constants and factors involved. (It cancels when normalizing the functions.)

The norm of $h_{\mathbf{k}}(r)$, $\|h\|$, is independent of $\mathbf{k}$ and is given by

$$\|h\|^2 = \frac{N}{\Omega} \sum_{\mathbf{K}\in\underline{T}} |\Phi_{\mathbf{K}}|^2 , \qquad (7)$$

or equivalently by

$$\|h\|^2 = \sum_{\mathbf{R}} \langle \Phi(\mathbf{r}) | \Phi(\mathbf{r}-\mathbf{R}) \rangle - \frac{N}{\Omega} \sum_{\mathbf{G}\in\underline{G}} |\Phi_{\mathbf{G}}|^2 . \qquad (8)$$

With the normalized levels $(h_{\mathbf{k}}(\mathbf{r})/\|h\|)$ the corresponding Wannier function $w(\mathbf{r})$ can be obtained, and is given by

$$w(\mathbf{r}) = \frac{1}{\|h\|\sqrt{N\Omega}} \sum_{\mathbf{q}(\text{all})} c_{\mathbf{q}} \; e^{i\mathbf{q}\cdot\mathbf{r}} , \qquad (9)$$

which in this form is automatically normalized. It is, of course, orthogonal to $w(\mathbf{r}-\mathbf{R})$ for $\mathbf{R}\neq 0$. Substituting in Eq. (10) for $c_{\mathbf{q}}$, one gets the more explicit form:

$$w(\mathbf{r}) = \frac{1}{\|h\|} \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \left[\sum_{\mathbf{K}\in\underline{T}} \Phi_{\mathbf{K}} \; e^{i\mathbf{K}\cdot\mathbf{r}} \right] w_o(\mathbf{r}) , \qquad (10a)$$

or

$$w(\underset{\sim}{r}) = \frac{1}{\|h\|}\left(\frac{\Omega}{N}\right)^{\frac{1}{2}} \left[\sum_{\underset{\sim}{R}} \Phi(\underset{\sim}{r}-\underset{\sim}{R}) - \frac{N}{\Omega} \sum \Phi_{\underset{\sim}{G}} \; e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}\right] w_o(\underset{\sim}{r}), \qquad (10b)$$

where for the case of a simple cubic Bravais lattice

$$w_o(\underset{\sim}{r}) = \frac{1}{\sqrt{N\Omega}} \sum_{\underset{\sim}{k}\in B_{\underline{o}}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}$$

$$= \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \frac{\sin(\pi x/\underline{a})}{(\pi x/\underline{a})} \; \frac{\sin(\pi y/\underline{a})}{(\pi y/\underline{a})} \; \frac{\sin(\pi z/\underline{a})}{(\pi z/\underline{a})} \qquad (11)$$

is the empty lattice lowest band Wannier function.

It is clear from the form of $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ and $w(\underset{\sim}{r})$ that these functions have the right behaviour near and at the lattice sites $\underset{\sim}{R}$, particularly if the finite set $\underline{G}$ does not contain large wave vectors. And for all $\underset{\sim}{G} \in \underline{G}$, $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ is automatically orthogonal to the plane waves with wave vector $\underset{\sim}{k}-\underset{\sim}{G}$.

In this way we have an incomplete but orthonormal basis set which would clearly be sufficient for a monatomic lattice if it were not necessary to use more than one localized $\Phi(\underset{\sim}{r})$.

Except for small $\underset{\sim}{k}$, the Bloch level $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ just defined will in general not be a good approximation to the solution $\Psi_{\underset{\sim}{k}}(\underset{\sim}{r})$ of the one-electron problem of the crystal, if $\underline{G}$ is empty (i.e. if no PW are included in the basis). The functions $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ and $\Psi_{\underset{\sim}{k}}(\underset{\sim}{r})$ can differ substantially for larger $\underset{\sim}{k}$, particularly near the boundaries of the Brillouin zone, simply because the Fourier components of $\exp(-i\underset{\sim}{k}.\underset{\sim}{r})\ \psi_{\underset{\sim}{K}}(\underset{\sim}{r})$ are functions of $\underset{\sim}{k}$, while those of $\exp(-i\underset{\sim}{k}.\underset{\sim}{r})\ h_{\underset{\sim}{k}}(\underset{\sim}{r})$ are not. Nevertheless, considering their expansions in reciprocal space, as $\underset{\sim}{K}$ increases the differences in their components decrease, since by construction both functions have the same form inside the atoms. Therefore, by truncating the components of low $\underset{\sim}{K}$, and including the corresponding PW with wave-vector $\underset{\sim}{k}-\underset{\sim}{K}$ in the basis, we will increasingly improve the approximation as the number of PW increases.

Certainly it would be a better approximation to start by truncating the usual tight-binding Bloch level $h^{TB}_{\underset{\sim}{k}}(\underset{\sim}{r})$ (defined with $\Phi(\underset{\sim}{r})$) and choosing components

$$c_{\underset{\sim}{g}} = \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \Phi_{\underset{\sim}{g}} \quad , \tag{12}$$

so that

$$h^{TB}_{\underset{\sim}{k}}(\underset{\sim}{r}) = \frac{\sqrt{N}}{\Omega} \sum_{\underset{\sim}{K}\in\underline{T}} \Phi_{\underset{\sim}{k}-\underset{\sim}{K}}\, e^{i(\underset{\sim}{k}-\underset{\sim}{K})\cdot\underset{\sim}{r}} \quad . \tag{13}$$

But this would not have the immense computational advantages of form (6), which permits all the terms there to be expressed in lattice sums independent of $\underset{\sim}{k}$. Nevertheless, for some cases higher accuracy requirements together with the necessity to keep the number of PW within reasonable limits might make it mandatory to use better Bloch levels than those defined by Eqs. (6). [One way of defining these that would still give lattice sums independent of $\underset{\sim}{k}$, is to take

$$c_{\underset{\sim}{k}-\underset{\sim}{K}} = \left(\frac{N}{\Omega}\right)^{\frac{1}{2}} \left[\Phi_{-\underset{\sim}{K}} + \underset{\sim}{k}\cdot\left(\nabla_{\underset{\sim}{k}}\, \Phi_{\underset{\sim}{k}-\underset{\sim}{K}}\right)_{\underset{\sim}{k}=0} + \cdots\right] \quad , \tag{14}$$

up to some order, but of course the higher the order chosen the more cumbersome and time consuming become the computations.]

For the case where a set of more than one linearly independent localized orbital must be used, a special Bloch level $h_{\underset{\sim}{k}}(\underset{\sim}{r})$ must be included for each. If the cell contains several atoms, say M atoms, with position vectors $\underset{\sim}{B}_i$ (i=1,2,...,M), a set $h_{\underset{\sim}{k}}(\underset{\sim}{r}-\underset{\sim}{B}_i)$ (i=1,2,...,M) of linearly independent Bloch levels, or M independent linear combinations of them, must be included in the basis set. All the special Bloch levels are assumed constructed with a truncated set of plane waves of wave vectors $\underset{\sim}{k}-\underset{\sim}{G}$ with reciprocal lattice vectors $\underset{\sim}{G}$ belonging to one and the same subset $\underline{G}$. The basis will then contain for the same $\underset{\sim}{k}$ (other than the truncated set of plane waves) a set of linearly independent Bloch levels orthogonal to them but not in general to each other. An orthogonalization procedure must then be used to get an orthonormal basis set. The use of this orthonormal basis ultimately results in a secular equation with the energy eigenvalues residing only on the main diagonal, and has distinct analytical and computational advantages. The selection of one particular linearly independent set of Bloch levels (over other possible equivalent sets) depends on a judicious evaluation (as far as this is possible) of how well they represent the true eigenfunctions of the crystal, and how their form may help the orthogonalization procedure in efficiently producing a physically convenient orthogonal set.

Let the initial set of Bloch levels, before the orthogonalization procedure, be a set of linearly independent combinations defined by

$$f_{n\underset{\sim}{k}}(\underset{\sim}{r}) = \sum_{j=1}^{M} a_{nj} \; h_{j\underset{\sim}{k}}(\underset{\sim}{r}) \; , \qquad n=1,2,\ldots,M, \tag{15}$$

where the constants a_{nj} are determined in a moment. Here the $h_{i\underset{\sim}{k}}(\underset{\sim}{r})$ are the Bloch levels defined for simplicity (but without loss of generality) with only one localized orbital in one of the monatomic sublattiices of the basis. Hence:

$$h_{j\underset{\sim}{k}}(\underset{\sim}{r}) = h_{\underset{\sim}{k}}(\underset{\sim}{r}-\underset{\sim}{B}_j) \; . \tag{16}$$

Now we use the Gram-Schmidt orthogonalization procedure to get from $\{f_{n\underset{\sim}{k}}\}$ an orthonogonal set $\{g_{n\underset{\sim}{k}}\}$. The $g_{n\underset{\sim}{k}}$ have the following recursion relations

$$|g_{1\underset{\sim}{k}}\rangle = |f_{1\underset{\sim}{k}}\rangle \quad , \tag{17}$$

$$|g_{n\underset{\sim}{k}}\rangle = \frac{|f_{n\underset{\sim}{k}}\rangle}{\|f_{n\underset{\sim}{k}}\|} - \sum_{m=0}^{n-1} \frac{|g_{m\underset{\sim}{k}}\rangle}{\|g_{m\underset{\sim}{k}}\|} \cdot \frac{\langle g_{m\underset{\sim}{k}}|f_{n\underset{\sim}{k}}\rangle}{\|g_{m\underset{\sim}{k}}\| \, \|f_{n\underset{\sim}{k}}\|} \; , \quad \text{for } n=2,3\ldots,M,$$

and the norms $\|g_{n\underset{\sim}{k}}\|$ are given by

$$\|g_{n\underset{\sim}{k}}\|^2 = 1 - \sum_{m=0}^{n-1} \frac{|\langle g_{m\underset{\sim}{k}}|f_{n\underset{\sim}{k}}\rangle|^2}{\|g_{m\underset{\sim}{k}}\|^2 \, \|f_{n\underset{\sim}{k}}\|^2} \; . \tag{18}$$

These may be used in slightly modified form which subsequently reduce the numerical work. Let $g_{n\underset{\sim}{k}}(\underset{\sim}{r})$ be expressed first as linear combinations of $h_{j\underset{\sim}{k}}(\underset{\sim}{r})$:

$$|g_{n\underset{\sim}{k}}\rangle = \sum_{j} b_{nj\underset{\sim}{k}}\,|h_{j\underset{\sim}{k}}\rangle , \quad \text{for } n=2,3,\ldots,M. \qquad (19)$$

Then

$$\langle g_{m\underset{\sim}{k}}|f_{n\underset{\sim}{k}}\rangle = \sum_{i}\sum_{j} b^{*}_{mi\underset{\sim}{k}}\; a_{nj}\; \langle h_{i\underset{\sim}{k}}|h_{j\underset{\sim}{k}}\rangle \quad , \qquad (20)$$

and

$$b_{nj\underset{\sim}{k}} = \frac{a_{nj}}{\|f_{n\underset{\sim}{k}}\|} - \sum_{m=0}^{n-1} b_{mj\underset{\sim}{k}}\; \frac{\langle g_{m\underset{\sim}{k}}|f_{n\underset{\sim}{k}}\rangle}{\|g_{m\underset{\sim}{k}}\|^{2}\;\|f_{n\underset{\sim}{k}}\|} \quad , \text{ for } n=2,3,\ldots,M. \qquad (21)$$

(Note that in general these are functions of $\underset{\sim}{k}$.)

Further

$$\|f_{n\underset{\sim}{k}}\|^{2} = \sum_{i}\sum_{j} a^{*}_{ni}\; a_{nj}\; \langle h_{i\underset{\sim}{k}}|h_{j\underset{\sim}{k}}\rangle . \qquad (22)$$

Next let an orthonormal (incomplete) basis set $\left\{\overset{(o)}{\Psi}_{\alpha\underset{\sim}{k}}(\underset{\sim}{r}),\ \alpha \in \underline{A},\ \underset{\sim}{k} \in \underline{B_o}\right\}$ be defined by

$$\overset{(o)}{\Psi}_{\alpha\underset{\sim}{k}}(\underset{\sim}{r}) = \begin{cases} \overset{(o)}{\Psi}_{\underset{\sim}{G}\underset{\sim}{k}}(\underset{\sim}{r}) = \dfrac{1}{\sqrt{\Omega}}\, e^{i(\underset{\sim}{k}-\underset{\sim}{G})\cdot\underset{\sim}{r}} & \text{for } \alpha = \underset{\sim}{G} \in \underline{G}\ , \\[2ex] \overset{(o)}{\Psi}_{n\underset{\sim}{k}}(\underset{\sim}{r}) = g_{n\underset{\sim}{k}}(\underset{\sim}{r})/\|g_{n\underset{\sim}{k}}\| & \text{for } \alpha = n, 1 \leq n \leq M. \end{cases} \qquad (23)$$

Then $\underline{A} = \underline{G} \cup \{n, 1 \leq n \leq M\}$. The superscript zero indicates this is a basis in which to expand the unknown variational approximations to the eigenfunctions $\Psi_{\underset{\sim}{k}}(r)$, i.e.

$$\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}) = \sum_{\alpha\in\underline{A}} x_{\alpha\underset{\sim}{k}}\; \overset{(o)}{\Psi}_{\alpha\underset{\sim}{k}}(\underset{\sim}{r}) \ . \qquad (24)$$

Equation (24), as an expansion of the one-electron function, will be used in the next section as a trial function for the one-electron problem in crystals. Note that, although incomplete, the finite basis set (23) is orthonormal and contains by construction localized orbitals appropriate for the cores of the molecules forming the crystal and plane waves adequate for the intermolecular region. Therefore, we can expect linear combinations of them to be good approximations for the eigenfunctions of the lower bands, the accuracy improving as the number of PW in $\underline{G}$ increases, particularly for $\underset{\sim}{k}$ near the boundaries of the Brillouin Zone.

III. Application to the solution of the one-electron problem in crystals

Substituting Eq. (24) into the one-particle Schrödinger equation for the crystal, the band structure problem reduces to

$$\sum_{\beta\epsilon\underline{A}} H_{\alpha\beta\underset{\sim}{k}}\, x_{\beta\underset{\sim}{k}} = E_{\underset{\sim}{k}}\, x_{\alpha\underset{\sim}{k}} \quad \text{for all } \alpha \in \underline{A} \quad , \tag{25}$$

with

$$H_{\alpha\beta\underset{\sim}{k}} = \langle \Psi^{(o)}_{\alpha\underset{\sim}{k}} |\, \hat{H}\, | \Psi^{(o)}_{\beta\underset{\sim}{k}} \rangle \quad . \tag{26}$$

Here $\hat{H}$ is the single particle crystal Hamiltonian. The reason why only one $\underset{\sim}{k}$ is involved everywhere is that $\hat{H}$ is a linear operator invariant under the translation group of the crystal, for which:

$$\langle \Psi^{(o)}_{\alpha\underset{\sim}{k}} |\, \hat{H}\, | \Psi^{(o)}_{\beta\underset{\sim}{k}'} \rangle = \delta_{\underset{\sim}{k}\underset{\sim}{k}'} \quad \langle \Psi^{(o)}_{\alpha\underset{\sim}{k}} |\, \hat{H}\, | \Psi^{(o)}_{\beta\underset{\sim}{k}} \rangle . \tag{27}$$

The matrix elements $H_{\alpha\beta\underset{\sim}{k}}$ are given by:

$$H_{\underset{\sim}{G}'\underset{\sim}{G}\underset{\sim}{k}} = \frac{\hbar^2}{2m} (k-G)^2 \quad \delta_{\underset{\sim}{G}'\underset{\sim}{G}} + U_{\underset{\sim}{G}'-\underset{\sim}{G}} \quad , \tag{28}$$

$$H_{\underset{\sim}{G}n\underset{\sim}{k}} = \sum_j b_{nj\underset{\sim}{k}} \langle \Psi^{(o)}_{\underset{\sim}{G}\underset{\sim}{k}} |\, \hat{H}\, | h_{j\underset{\sim}{k}} \rangle \, \| g_{n\underset{\sim}{k}} \|^{-1} \tag{29}$$

$$H_{n'n\underset{\sim}{k}} = \sum_i \sum_j b^*_{n'j\underset{\sim}{k}} \, b_{ni\underset{\sim}{k}} \langle h_{j\underset{\sim}{k}} | \hat{H} | h_{i\underset{\sim}{k}} \rangle \, \| g_{n'\underset{\sim}{k}} \|^{-1} \, \| g_{n\underset{\sim}{k}} \|^{-1} \, , \tag{30}$$

where, as usual, the plane wave matrix element of the local one-electron crystal potential is given by

$$U_{\underset{\sim}{K}} = \frac{N}{\Omega} V_{\underset{\sim}{K}} \, , \tag{31}$$

with

$$V_{\underset{\sim}{K}} = \int d\underset{\sim}{r} \;\; e^{-i\underset{\sim}{K}.\underset{\sim}{r}} \, V(\underset{\sim}{r}) \, , \tag{32}$$

and

$$U(\underset{\sim}{r}) = \sum_{\underset{\sim}{R}} V(\underset{\sim}{r}-\underset{\sim}{R}) \quad . \tag{33}$$

Because of the special form (6) of $h_{i\underset{\sim}{k}}(\underset{\sim}{r})$ the products $\langle h_{i\underset{\sim}{k}} | h_{j\underset{\sim}{k}} \rangle$ and the matrix elements $\langle \Psi^{(o)}_{G\underset{\sim}{k}} | \hat{H} | h_{j\underset{\sim}{k}} \rangle$ and $\langle h_{i\underset{\sim}{k}} | \hat{H} | h_{j\underset{\sim}{k}} \rangle$, can be expressed in terms of reciprocal (or reciprocal and direct) lattice sums which are independent of the point in the Brillouin zone (all the $\underset{\sim}{k}$-dependence being factored out). For the case of only one localized orbital but with a basis of several atoms, we have

$$\langle h_{i\underset{\sim}{k}} | h_{j\underset{\sim}{k}} \rangle = \frac{N}{\Omega} \; e^{i\underset{\sim}{k}\cdot(\underset{\sim}{B}_i - \underset{\sim}{B}_j)} \; S_{ij} \quad , \tag{34}$$

$$\langle \Psi^{(o)}_{G\underset{\sim}{k}} | \hat{H} | h_{j\underset{\sim}{k}} \rangle = \sqrt{\frac{N}{\Omega}} \; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{B}j} \; S_{\underset{\sim}{G}j} \quad , \tag{35}$$

and

$$\langle h_{i\underset{\sim}{k}} | \hat{H} | h_{j\underset{\sim}{k}} \rangle = \frac{N}{\Omega} \; e^{i\underset{\sim}{k}\cdot(\underset{\sim}{B}_i - \underset{\sim}{B}_j)} \left[\frac{h^2}{2m} \left(S''_{ij} - 2i\underset{\sim}{k}\cdot\underset{\sim}{S}'_{ij} + k^2 S_{ij} \right) + S^D_{ij} \right] \, , \tag{36}$$

where

$$S_{ij} = \sum_{\underset{\sim}{K}\in \underline{T}} |\Phi_{\underset{\sim}{K}}|^2 \; e^{i\underset{\sim}{K}\cdot(\underset{\sim}{B}_i - \underset{\sim}{B}_j)} \quad , \tag{37}$$

$$\underset{\sim}{S}'_{ij} = \overline{\sum_{\underset{\sim}{K}\in\underline{T}}} i\underset{\sim}{K} \, |\Phi_{\underset{\sim}{K}}|^2 \, e^{i\underset{\sim}{K}\cdot(\underset{\sim}{B}_i-\underset{\sim}{B}_j)} , \tag{38}$$

$$S''_{ij} = \overline{\sum_{\underset{\sim}{K}\in\underline{T}}} K^2 \, |\Phi_{\underset{\sim}{K}}|^2 \, e^{i\underset{\sim}{K}\cdot(\underset{\sim}{B}_i-\underset{\sim}{B}_j)} , \tag{39}$$

$$S_{\underset{\sim}{G}j} = \overline{\sum_{\underset{\sim}{K}\in\underline{T}}} \Phi_{-\underset{\sim}{K}} \, U_{\underset{\sim}{G}-\underset{\sim}{K}} \, e^{i\underset{\sim}{K}\cdot\underset{\sim}{B}_j} , \tag{40}$$

and

$$S^D_{ij} = \sum_{\underset{\sim}{K}\in\underline{T}} \sum_{K'\in\underline{T}} \Phi^*_{\underset{\sim}{K}'} \, \Phi_{\underset{\sim}{K}} \, U_{\underset{\sim}{K}'-\underset{\sim}{K}} \, e^{i(\underset{\sim}{K}'\cdot\underset{\sim}{B}_i-\underset{\sim}{K}\cdot\underset{\sim}{B}_j)} . \tag{41}$$

These lattice sums can be expressed in part as direct lattice sums, using the convolution theorem or by application of Eq. (6b). For example:

$$S_{ij} = \sum_{\underset{\sim}{R}} \langle \Phi(\underset{\sim}{r}) | \Phi(\underset{\sim}{r}+\underset{\sim}{B}_i-\underset{\sim}{B}_j-\underset{\sim}{R}) \rangle - \frac{N}{\Omega} \sum_{\underset{\sim}{G}\in\underline{G}} |\Phi_G|^2 \, e^{i\underset{\sim}{G}\cdot(\underset{\sim}{B}_i-\underset{\sim}{B}_j)} . \tag{42}$$

From this, $\underset{\sim}{S}_{ij}$ and S''_{ij} can be obtained respectively by taking the gradient and the negative of the Laplacian with respect to the spatial variable. A similar result can be obtained with $S_{\underset{\sim}{G}j}$ and S^D_{ij}, but here it would be of no advantage if only the Fourier transform of the potential is available.

The number of different lattice sums that must be actually computed is greatly reduced by exploiting crystal symmetries. First of all, the sums are invariant under a transposition of indices, except for $\underset{\sim}{S}'_{ij}$ (which only changes sign) and $S_{\underset{\sim}{G}j}$. In general a simultaneous change of $\underset{\sim}{B}_i$, $\underset{\sim}{B}_j$ and $\underset{\sim}{G}$ (in the case of $S_{\underset{\sim}{G}j}$) under the same cubic or other symmetry will also leave S_{ij}, S''_{ij}, $S_{\underset{\sim}{G}j}$ and S^D_{ij} unaltered, and will take $\underset{\sim}{S}'_{ij}$ into the corresponding symmetric vector. In this way, for example, the sixty four S^D_{ij} sums of the Pa3 (or α-N_2) crystal structure(10) are reduced to only four, and the $S_{\underset{\sim}{G}j}$ sums to only two for each $\underset{\sim}{G}$, and in both classes of sums this leads to an enormous reduction in computational time.

Once the lattice sums are evaluated, we can proceed to solve the secular eigenvalue problem (25) for a particular $\underset{\sim}{k}$ by first obtaining the corresponding basis set (23) with the help of Eqs. (19)-(22), then the matrix elements $H_{\alpha\beta\underset{\sim}{k}}$ with Eqs. (28)-(30), and finally diagonalizing Eq. (25). In this way we obtain the valence and lowest conduction bands and the coefficients $x_{\alpha\underset{\sim}{k}}$ in the expansion of the corresponding eigenfunctions in terms of the basis set (23).

IV. Summary and Conclusions

We have shown that subspace spanned by the orthonormal finite basis set of functions (23), can be expected to be a satisfactory approximation to the actual eigenfunctions. The set is of manageable size and at the same time leads to good convergence because by construction it contains orbitals which represent well both the core and intermolecular features. This is accomplished in a rather simple way, with a few plane waves and orbitals depending on $\underset{\sim}{k}$ *only* through a factor exp $(i\underset{\sim}{k}.\underset{\sim}{r})$. It leads to lattice sums independent of $\underset{\sim}{k}$ when calculating the matrix elements of the secular eigenvalue problem (25), to which the band structure calculation has been reduced. It is then necessary to evaluate these lattice sums *only once* for a given lattice parameter and crystal structure. Finally, it is straightforward to obtain the necessary matrix element for any $\underset{\sim}{k}$ even for complicated crystal structures.

The method is potentially more flexible than the KKR and APW methods, since it does not require the muffin-tin approximation for the crystal potential, and is readily adaptable to molecular and complex crystal structures. The level of analytic complexity and computation difficulty does not exceed that of the standard methods. When, compared specifically with the OPW method its main advantage is the simpler and more flexible formulation, which makes no particular reference to core levels.

There is another sense in which we can also expect good convergence, namely the evaluation of the lattice sums (37)-(41). Notice that with the present method the choice between the purely reciprocal space lattice sums or sums divided between reciprocal and direct space will depend on the convergence properties of the particular case at hand. For example, in the case of solid molecular hydrogen, $\Phi(r)$ can be taken as a 1s-orbital, namely:

$$\Phi(\underset{\sim}{r}) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r} , \tag{43}$$

with Fourier transform:

$$\Phi_{\underset{\sim}{q}} = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} \frac{8\pi\alpha}{(q^2+\alpha^2)^2} . \tag{44}$$

For the direct lattice sum in Eq. (42), we then find:[11]

$$\left\langle \Phi(\underset{\sim}{r}-\underset{\sim}{r}') \middle| \Phi(\underset{\sim}{r}') \right\rangle = e^{-\alpha r} \left(1 + \alpha r + \frac{1}{3}\alpha^2 r^2\right) , \tag{45}$$

which leads to rapid convergence in direct space for the S_{ij}, $\underset{\sim}{S}_{ij}$ and S''_{ij}. Since $S_{\underset{\sim}{G}i}$ and S^D_{ij} involve $\Phi(\underset{\sim}{r})$ (which falls exponentially with $\underset{\sim}{r}$) and $V(\underset{\sim}{r})$ (which goes more or less as r^{-1}) a similar conclusion can be drawn about their convergence in direct space. But note that in reciprocal space, the lattice sums of Eqs. (37)-(41) also converge fairly well, since $\Phi_{\underset{\sim}{K}}$ goes as K^{-4}, and $U_{\underset{\sim}{K}}$ approximately as K^{-2}.

The method has been applied to solid molecular hydrogen in the α-N_2 structure for densities varying from the zero pressure value up to more than ten times that value. The details and results will be published in a later paper.[9] It is sufficient here to say that we obtain results with satisfactory accuracy and convergence. They corroborate well with the results of other methods. However, as mentioned earlier the method described above is of more general interest in the context of band theory.

References and Footnotes

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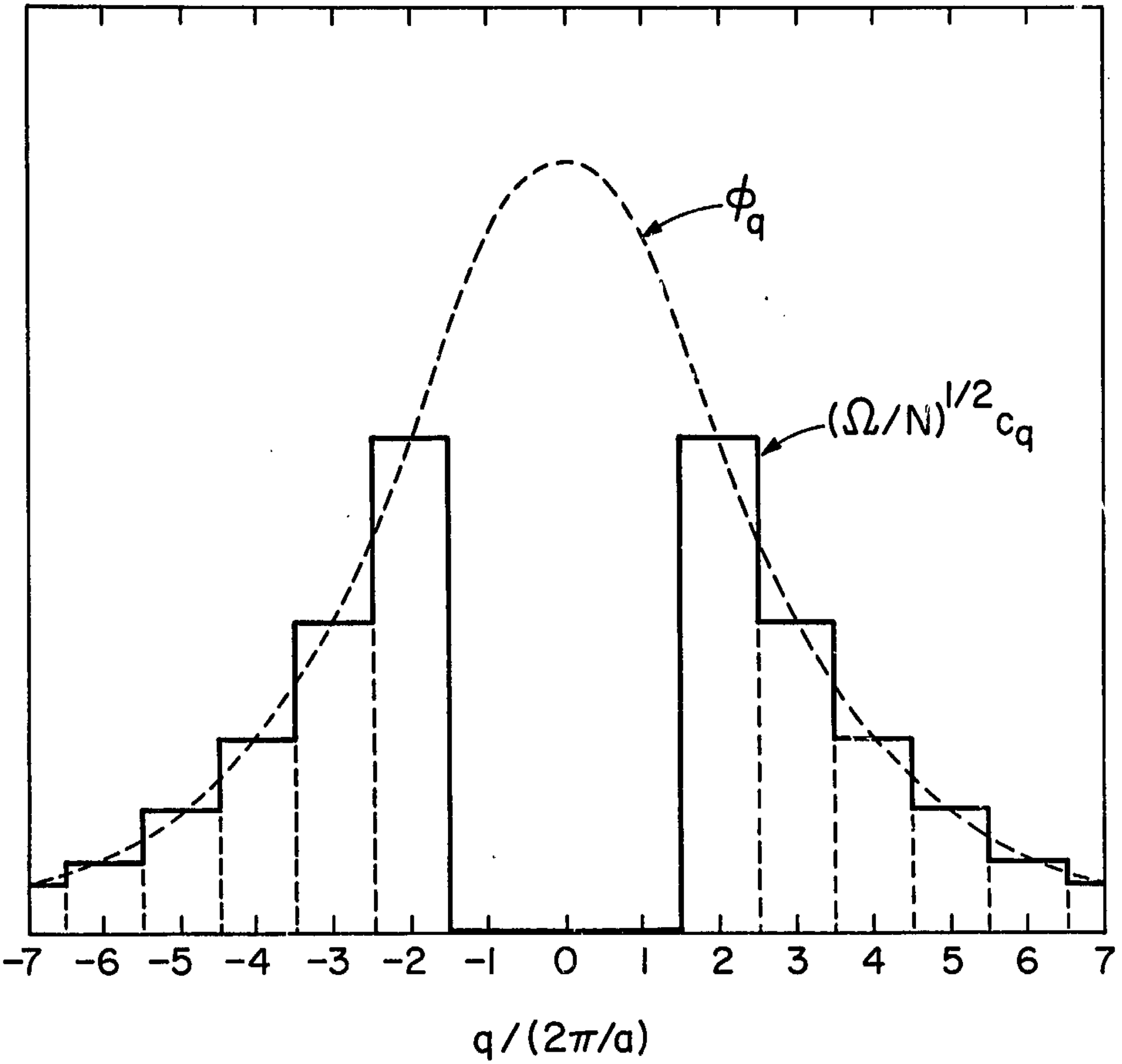
Figure Captions

Figure 1. Schematic one-dimensional example of components $(\Omega/N)^{\frac{1}{2}}c_q$ of a member of the new representation given by Eq. (4) (discontinuous curve) in terms of the Fourier transform Φ_q of a localized orbital (dotted curve). The reciprocal lattice vectors correspond here to $q/(2\pi/\underline{a})$ = integer. Note that c_q is identically zero in the central zones (corresponding to a choice here of a set of reciprocal lattice vectors $\underline{G} = \{ -2\pi/\underline{a},\ 0\ ,\ 2\pi/\underline{a} \}$) and constant within each zone corresponding to the reciprocal lattice vectors falling outside $\underline{G}$ (set $\underline{T}$).


ϕ_q
$(\Omega/N)^{1/2}c_q$
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
7
$q/(2\pi/a)$