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Energy Band Structure of Lithium by a Modified Plane Wave Method

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The one-electron Schrödinger equation is discussed for a periodic lattice. A variational procedure is applied to a set of trial functions consisting mainly of plane waves of low wave number. Rapid convergence is obtained by use of one or more auxiliary functions whose Fourier coefficients for high wave numbers approximate those of the correct eigenfunctions. The orthogonalized plane wave (OPW) method is a special case of this general method and the equivalence is shown. When applied to lithium the method gives a band structure in substantial agreement with that of cellular methods.

1. INTRODUCTION

A STANDARD treatment of electron energy levels in pure crystals depends on the solution of a one-electron Schrödinger equation in which the potential has the periodicity of the crystal lattice. A large number of methods have been applied to this problem. Broadly speaking, they fall into two major categories.[1] In the first are the cellular methods, in which the Schrödinger equation is applied within a unit cell of the crystal. The condition on the wave function that it be of the Bloch form (a product of a plane wave and a cell periodic function) takes the form of a boundary condition.[2] In the second category are those methods which apply a variational principle to an expansion in terms of functions which are already in the Bloch form. The procedure leads to a discrete matrix eigenvalue equation which may be solved by setting the secular determinant equal to zero. These methods differ essentially in the choice of basis functions. For calculational simplicity one obviously would like to choose these in such a way as to get rapid convergence to the states of interest. At the same time it is desirable to deal with functions which are analytically simple such as plane waves. These, unfortunately, are unsatisfactory from the standpoint of convergence. The poor convergence is well known to be due to the need for many waves of high wave number in order to give an adequate representation to the rapidly varying part of the true wave function near the nuclei.[3] On the other hand, cellular functions probably give the best fit in this region and are weakest near the cell boundaries. As this discussion suggests, one should benefit by supplementing a plane wave expansion with terms made up of cellular orbitals. This suggestion has already been made for the purpose of speeding up the slow convergence to certain states in connection with the method of orthogonalized plane waves (OPW).[4–6] These suggestions, however, do not make full use of the inherent possibilities in the use of such auxiliary functions. In Sec. 2 we describe a way in which such functions may be utilized conveniently. The procedure makes use of a set of orthogonal functions, thereby resulting in a matrix equation in which the energy eigenvalues appear only on the main diagonal. This feature makes numerical computations simple and may enable one to handle more terms in the expansion than would otherwise be the case. It proves instructive to compare our method with that of OPW since there are many features in common; by choosing our auxiliary functions as lower band states of similar symmetry to the eigenfunction of interest, the methods are mathematically equivalent. The comparison of methods is made in Sec. 3. In Sec. 5 our method is applied to some conduction band states for metallic lithium.

2. DISCUSSION OF METHOD

General Remarks

For purpose of discussion we envision a solid as made up of individual atoms placed on a lattice structure of variable lattice constant. When the atoms are far apart, the one-electron wave functions of the valence states may be represented by Bloch sums of atomic orbitals. As the lattice shrinks, the orbitals begin to overlap and the wave functions as well as the energy eigenvalue are altered. If we think of the wave function in any unit cell as made up of an expansion of products of radial functions and spherical harmonics, we can see that the wave functions will be altered least in the atomic cores near the nuclei. This follows because (1) in the region of large potential energy the form of the radial function is insensitive to the energy eigenvalue, and (2) the introduction of higher spherical harmonics by the perturbation of the lattice potential has the least effect here because of the centrifugal repulsive term $l(l+1)/r^2$ which appears in the radial Schrödinger equation.

The insensitivity of the rapidly varying core part of

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[1] For a survey of one-electron methods in periodic lattices, see the article by J. R. Reitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.

[2] A variational method which is particularly appropriate to this problem has been developed by W. Kohn, Phys. Rev. **87**, 472 (1952).

[3] See reference 1, Sec. 26.

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

[5] F. Herman, Ph.D. thesis, Columbia University, 1953 (unpublished).

[6] J. Callaway, Phys. Rev. **97**, 933 (1955).

the function to lattice parameter will be reflected in a similar insensitivity of the Fourier coefficients of high wave number.[7] From this follows the basic premise of our method: only the lower Fourier coefficients need be subject to free variation. The relative amplitude of the remaining coefficients is frozen so that one depends on getting a good fit to these from the transform of a function made up of linear combinations of approximate atomic or cellular orbitals.

Details of Method

The one-electron eigenfunctions in a periodic lattice have the Bloch form,

$$\psi_{\mathbf{k}}(\mathbf{r})=u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.1}$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice and may be expanded in a Fourier series

$$u_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{K}} A_{\mathbf{k},\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{2.2}$$

where we sum over all principal vectors of the reciprocal lattice.[8] It is thus possible to expand $\psi_{\mathbf{k}}(\mathbf{r})$ in a discrete series of plane waves with the general form

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{K}} A_{\mathbf{k},\mathbf{K}}e^{i(\mathbf{K}+\mathbf{k})\cdot\mathbf{r}}. \tag{2.3}$$

We suppose now that we have at our disposal a specific approximate eigenfunction $\phi_{\mathbf{k}}(\mathbf{r})$ which is in the Bloch form and has the expansion

$$\phi_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{K}} B_{\mathbf{k},\mathbf{K}}e^{i(\mathbf{K}+\mathbf{k})\cdot\mathbf{r}}. \tag{2.4}$$

Such a function might be obtained from a simplified cellular calculation.

Following our premise of dividing Fourier coefficients into two types, consider a spherical region about the origin in reciprocal space of arbitrary radius. We denote the reciprocal lattice vectors inside this sphere by $\mathbf{K}_i$ and those of the outer region by $\mathbf{K}_o$. We can then write

$$\phi_{\mathbf{k}}(\mathbf{r})=\phi_{\mathbf{k}}{}^{i}(\mathbf{r})+\phi_{\mathbf{k}}{}^{o}(\mathbf{r}), \tag{2.5}$$

$$\phi_{\mathbf{k}}{}^{i}(\mathbf{r})=\sum_{\mathbf{K}_i} B_{\mathbf{k},\mathbf{K}_i}e^{i(\mathbf{K}_i+\mathbf{k})\cdot\mathbf{r}}, \tag{2.6}$$

$$\phi_{\mathbf{k}}{}^{o}(\mathbf{r})=\sum_{\mathbf{K}_o} B_{\mathbf{k},\mathbf{K}_o}e^{i(\mathbf{K}_o+\mathbf{k})\cdot\mathbf{r}}. \tag{2.7}$$

Let the number of vectors $\mathbf{K}_i$ be N and to each one of these associate a plane wave $e^{i(\mathbf{K}_i+\mathbf{k})\cdot\mathbf{r}}$. Then the $N+1$ functions consisting of the N plane waves and $\phi_{\mathbf{k}}{}^{o}(\mathbf{r})$ obviously constitute an orthogonal set. If $\phi_{\mathbf{k}}{}^{o}(\mathbf{r})$ is normalized to average value unity, the set of functions can be conveniently used as a basis for a computational procedure.

We have investigated both iterative and variational methods, but in the present discussion we shall employ Kohn's[2] variational principle since it yields a particularly well-defined recipe for using the basis functions. This variational principle states that the solutions of the Schrödinger equation satisfying the periodic boundary condition make the functional $J=\mathrm{Re}(I+G)$ an extremum, where

$$I=\int_{\Omega}\psi^{*}(-\nabla^{2}+V-E)\psi d\tau, \tag{2.8}$$

$$G=\int_{S}\psi^{*}(\mathbf{r}')\frac{\partial\psi(\mathbf{r})}{\partial n}\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_{r})d\sigma. \tag{2.9}$$

The integrals are over the cell volume and cell boundary respectively, $\mathbf{r}$ and $\mathbf{r}'$ being points on the cell boundary separated by the primitive translation $\boldsymbol{\tau}_r$, i.e., $\mathbf{r}'=\mathbf{r}+\boldsymbol{\tau}_r$.

We now expand ψ in terms of the N plane waves and the (single) auxiliary function $\phi_{\mathbf{k}}{}^{o}(\mathbf{r})$ with the expansion coefficients C_1, C_2, $\cdots C_N$ and C_{N+1}, respectively. The calculations are shown in Appendix I. The result is an eigenvalue problem in the coefficients.

$$\sum_{m=1}^{N+1} H_{l,m}C_m=EC_l,\quad l=1,2,\cdots N+1, \tag{2.10}$$

where

$$H_{l,m}=\int_{\Omega}\psi_l{}^{*}H\psi_m d\tau\quad l,m\neq N+1,$$

$$H_{N+1,l}=H_{l,N+1}{}^{*}=\int_{\Omega}\psi_{N+1}{}^{*}V\psi_l d\tau,\quad l\neq N+1, \tag{2.11}$$

$$H_{N+1,N+1}=\int\psi_{N+1}{}^{*}H\psi_{N+1}d\tau+\int\psi_{N+1}{}^{*}\nabla\psi_{N+1}\cdot\mathbf{n}d\sigma.$$

The evaluation of the matrix elements reduces (Appendix I) to the calculation of a number of Fourier coefficients and several finite sums. In particular, it is not necessary to have an explicit expression for the $\mathbf{k}$-space asymptotic function $\phi_{\mathbf{k}}{}^{o}(\mathbf{r})$, since relevant integrals can be obtained from $\phi_{\mathbf{k}}(\mathbf{r})$ and its lower-order Fourier coefficients $B_{\mathbf{K}_i}$. Moreover, we have found that a further good approximation is to consider $\phi_{\mathbf{k}}{}^{o}e^{-i\mathbf{k}\cdot\mathbf{r}}$, the periodic part of $\phi_{\mathbf{k}}{}^{o}$, to be independent of $\mathbf{k}$. In this case the matrix elements for arbitrary $\mathbf{k}$ can be evaluated by computing the integrals once and for all at $\mathbf{k}=0$. The energy eigenvalues of (2.10) may be found by solving the secular equation

$$\det\{H_{l,m}-E\delta_{l,m}\}=0. \tag{2.12}$$

The energy of interest usually corresponds to a valence or conduction state and is usually not the lowest eigenvalue of (2.10) as it is in OPW. The selection of the proper eigenvalue presents no special difficulties and is discussed in the next section.

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[7] Actually the insensitivity referred to is in the asymptotic behavior of the Fourier-integral-transform of the function whose domain is a unit cell. The Fourier coefficients may be obtained by sampling this transform at the reciprocal lattice points.

[8] We have chosen reciprocal lattice vectors which are a factor of 2π larger than those defined in the usual way.

3. COMPARISON WITH OPW METHOD

The method as outlined in the preceding section bears a strong resemblance to that of OPW. It is interesting to display the similarities and differences of the two methods with a one-dimensional illustration. A single plane wave may be specified by its amplitude (which we assume, for convenience, to be real) and its wave number. Thus, if we choose a space with wave number as abscissa and amplitude as ordinate, a plane wave is represented by a point. (We use a vertical bar in the diagrams for the sake of clarity.) A Bloch function will then be represented by a set of points whose abscissas are separated by reciprocal lattice vectors. Figure 1(a) shows the function $\phi_{\mathbf{k}}(\mathbf{r})$ represented on such a reciprocal-space plot. The function $\phi_{\mathbf{k}}^{o}(\mathbf{r})$ is shown in Fig. 1(b); it lacks plane waves of low wave number. The effect of the variational treatment is to reintroduce into the central region a modified-amplitude set which makes the functional J stationary.

The OPW procedure requires a slightly more complex description. We assume, for simplicity, that there is one band of lower energy than the band of interest. We assume also that an eigenfunction from this band has been obtained rather accurately, say, by a tight-binding approximation. In Fig. 2(a) we represent in k space (for a one-dimensional case) such a function. In Fig. 2(b) is shown a single plane wave and in Fig. 2(c) is shown a linear combination of the two which is orthogonal to that of Fig. 2(a). The function illustrated in Fig. 2(c) is then an orthogonalized plane wave corresponding to the plane wave of Fig. 2(b). The OPW procedure is then to form a finite set of such functions, each corresponding to a particular plane wave, and use them to extremize the Hamiltonian. Since each of these orthogonalized plane waves has the same asymptotic form as that of Fig. 2(a), any linear combination of them will have the identical form. The variational procedure is similar to the previous one in that the free variation of the wave function takes place in the central domain of k space while the outer form is fixed.[9]

It is now clear that while a variety of choices of $\phi_{\mathbf{k}}(\mathbf{r})$ are possible, the specific choice of a lower-band state function makes the present method identical to the OPW method. Any linear combination of N orthogonalized plane waves can be expressed as a linear combination of the $N+1$ basis functions. In other words, the N orthogonalized plane waves form a subspace of our $(N+1)$-dimensional function space. The extra degree of freedom in the larger space is due to the fact that the $N+1$ functions can also represent the function to which the plane waves of OPW have been orthogonalized. Moreover, since this function is *presumably an exact solution of the Schrödinger equation* it will satisfy (2.10). Thus, the lowest eigenvalue of (2.10) will correspond to a core state. By a well-known property of Hermitian matrices, the remaining eigenfunctions will be orthogonal to this state and thus span the same subspace as do the orthogonalized plane waves. These remaining eigenfunctions will then be exactly those which are obtained in OPW since they satisfy the same variational problem.

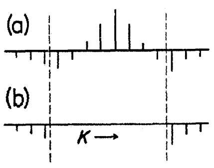

FIG. 1. Schematic representation of auxiliary function by an expansion in plane waves. The diagram depicts the function before (a) and after (b) orthogonalization to the plane waves whose wave vectors lie between the dotted lines.

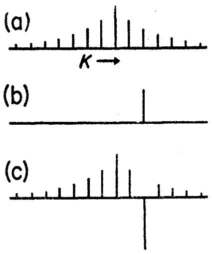

FIG. 2. Representation of a single basis function used in OPW. (a) represents a Bloch sum of core orbitals, (b) is a single plane wave, and (c) is a linear combination of these which is orthogonal to (a).

The merit of our method is its greater flexibility as compared to OPW. In the first place, even an approximate function $\phi_{\mathbf{k}}(\mathbf{r})$ obtained from a cellular calculation can be expected to be as good or better a starting function for the valence state as the somewhat artificially constructed orthogonal plane wave. Moreover, two particular situations which cause trouble in the OPW method are not critical here: first, if the required symmetry type does not appear in the core functions,[6] OPW convergence is slow—the present method takes care of this easily; second, if core functions are not accurate, the OPW valence energy can be quite inaccurate—the corresponding question here is whether the major part of an approximate (cellular) function is a better representation of the valence state than a minor part of an approximate core function. This latter question can be critically tested only with specific calculation, but in many cases it seems to us that the choice of a cellular approximation would lead to less labor. A less serious drawback of OPW is the lack of orthogonality of the basis functions, leading to a secular determinant nondiagonal in energy. Finally, mention was made of the identification of eigenvalues. In actual modern computation it is quite practical to calculate all the eigenvalues for reasonable numbers of plane waves. One of these is very close in energy to the approximate energy corresponding to $\phi_{\mathbf{k}}(\mathbf{r})$. In the test calculation discussed in Sec. 5, the identification was perfectly straightforward.

4. EXTENSION OF METHOD

The previous discussion has been based on the use of a single auxiliary function. The method is easily

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[9] This statement must be modified if there are several lower energy states. The outer form is then a linear combination of those of the lower states.

extended to incorporate any number. The basic program is to subtract from each of these functions the first N terms of its Fourier expansion, resulting in functions which are orthogonal to each of the corresponding plane waves. In order to have a completely orthogonal set these functions must be orthogonalized to one another by means of the Schmidt process. The necessary mathematical steps are shown in Appendix II. The resulting functions are then used as a basis for a variational procedure. If the method is applied to points of high symmetry in the Brillouin zone, group theory may be applied to reduce the order of the matrix equations in the same manner as is used in OPW.

5. APPLICATION TO LITHIUM

As the one-electron Schrödinger equation which is our starting point is the result of extensive approximations, it proves difficult to test the accuracy of a solution by a comparison with experiment. We have therefore chosen a crystal potential for which calculations have already been made with which to compare our method. Lithium was chosen for convenience. The potential was that originally used by Seitz[10] and modified by Kohn and Rostoker.[11]

The auxiliary function was obtained by numerical integration of the Schrödinger equation for the $2s$ function corresponding to an energy of -0.6832 ry which is the energy calculated from the spherical approximation. Fifty-five plane waves were used. However, because of symmetry the size of the matrix equation was effectively reduced to 6 by 6 at $\mathbf{k}=0$, 16 by 16 along the [111] direction and 15 by 15 along [100]. These were solved by an iteration procedure developed by one of us to handle large matrices of this type.[12]

The procedure was used to obtain energy eigenvalues and eigenfunctions at several points in the [100] and [111] directions of the Brillouin zone. The results are shown in Tables I and II. The eigenvalues of the cellular methods with which comparison is made are obtained from a series expansion in which the original data were presented.[11] This expansion is not expected to hold all the way out to the zone boundary so that the energy at $\mathbf{k}=(0.5; 0.5; 0.5)$ is not to be taken seriously for the cellular methods. Also, the iteration procedure used to solve the matrix equation at this value of $\mathbf{k}$ converged too slowly for us to obtain an accurate eigenvalue. The comparison at other points is rather good.

TABLE I. Comparison of energy eigenvalues at several points in the Brillouin zone.

Wave vector units of $2\pi/a$	Kohn and Rostoker	Eigenvalues ry spherical approx.[b]	Present
0, 0, 0	−0.6832	−0.6832	−0.6827
0.2, 0, 0	−0.6542	−0.6542	−0.6525
0.5, 0, 0	−0.4979	−0.5033	−0.4948
0.2, 0.2, 0.2	−0.5962	−0.5964	−0.5896
0.4, 0.4, 0.4	−0.3322	−0.3409	−0.3358
0.5, 0.5, 0.5[a]	−0.1314	−0.1543	−0.1754

[a] The accuracy of the present method at the zone corner is questionable because of the need for a different auxiliary function.
[b] R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950).

TABLE II. Fourier coefficients of wave functions.

	Along [111] direction[a]		
$\mathbf{K}_i$[b]	$\mathbf{k}=0$	$\mathbf{k}=0.2, 0.2, 0.2$	$\mathbf{k}=0.4, 0.4, 0.4$
0, 0, 0	0.9455	0.9432	0.9071
1, 1, 0	−0.0624	−0.0266	−0.0113
1, −1, 0	−0.0624	−0.0511	−0.0055
−1, −1, 0	−0.0624	−0.1166	−0.2246
2, 0, 0	−0.0435	−0.0279	−0.0047
−2, 0, 0	−0.0435	−0.0481	−0.0347
2, 1, 1	−0.0301	−0.0180	−0.0039
2, 1, −1	−0.0301	−0.0217	−0.0065
2, −1, −1	−0.0301	−0.0265	−0.0113
−2, 1, 1	−0.0301	−0.0265	−0.0113
−2, −1, 1	−0.0301	−0.0338	−0.0245
−2, −1, −1	−0.0301	−0.0445	−0.0581
2, 2, 0	−0.0214	−0.0142	−0.0040
2, −2, 0	−0.0214	−0.0190	−0.0087
−2, −2, 0	−0.0214	−0.0276	−0.0271
C_{N+1}	−0.1438	−0.1292	−0.0641

	Along [100]		
$\mathbf{K}_i$[c]	$\mathbf{k}=0$	$\mathbf{k}=0.2, 0, 0$	$\mathbf{k}=0.5, 0, 0$
0, 0, 0	0.9455	0.9442	0.9419
1, 1, 0	−0.0624	−0.0431	−0.0137
0, 1, 1	−0.0624	−0.0596	−0.0379
−1, 0, 1	−0.0624	−0.0851	−0.1197
2, 0, 0	−0.0435	−0.0311	−0.0146
0, 2, 0	−0.0435	−0.0420	−0.0316
−2, 0, 0	−0.0435	−0.0596	−0.0956
2, 1, 1	−0.0301	−0.0237	−0.0135
1, 2, 1	−0.0301	−0.0262	−0.0171
−1, 2, 1	−0.0301	−0.0325	−0.0311
−2, 1, 1	−0.0301	−0.0365	−0.0448
2, 2, 0	−0.0214	−0.0178	−0.0110
0, 2, 2	−0.0214	−0.0207	−0.0162
−2, 2, 0	−0.0214	−0.0245	−0.0267
C_{N+1}	−0.1438	−0.1390	−0.1114

[a] All but the last term are the coefficients of the wave of wave vector $\mathbf{K}_i+\mathbf{k}$. The last term is the coefficient of the orthonormalized auxiliary function.
[b] Reciprocal lattice points which differ by a permutation of the arguments are equivalent along [111].
[c] Points which differ by permutations and/or changes of algebraic sign of the latter two arguments are equivalent along [100].

The amount of labor involved in making these calculations on a computer of moderate capacity is relatively small. The lithium problem was done quickly on an IBM card-programmed calculator. It is true that the lithium example is probably the simplest system one can choose; nonetheless, the excellent agreement with Kohn and Rostoker (Table I) is satisfying.

It is a pleasure to acknowledge the assistance of the Watson Scientific Laboratory, and the personal help of Richard Pappert, Cornell University, in the numerical calculations.

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[10] F. Seitz, Phys. Rev. **47**, 400 (1935).
[11] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).
[12] E. Brown, Ph.D. thesis, Cornell University, 1954 (unpublished).

APPENDIX I. DERIVATION OF MATRIX EQUATION FROM KOHN'S VARIATIONAL PRINCIPLE

We wish to make stationary $J=\mathrm{Re}(I+G)$, where

$$I=\int_\Omega \psi^*(H-E)\psi d\tau, \tag{A1.1}$$

$$G=\int_S \psi^*(\mathbf{r}')\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_\mathrm{r})(\nabla\psi\cdot\mathbf{n})d\sigma, \tag{A1.2}$$

for the particular ψ given by

$$\psi=\sum_{l=1}^{N+1} C_l\psi_l(\mathbf{r}), \tag{A1.3}$$

where

$$\psi_l=e^{i(\mathbf{K}_l+\mathbf{k})\cdot\mathbf{r}},\quad i\neq N+1, \tag{A1.4}$$
$$\psi_{N+1}=\phi_\mathbf{k}{}^o(\mathbf{r}).$$

When (A1.3) is substituted in (A1.1) we get terms of the following types:

$$\begin{aligned}
I_1&=C_l{}^*C_m\Omega\biggl\{[(\mathbf{K}_l+\mathbf{k})^2-E]\delta_{l,m}\\
&\qquad+\frac{1}{\Omega}\int_\Omega e^{-i(\mathbf{K}_l-\mathbf{K}_m)\cdot\mathbf{r}}Vd\tau\biggr\},\\
I_2&=C_{N+1}{}^*C_l\int_\Omega e^{-i\mathbf{k}\cdot\mathbf{r}}\phi_\mathbf{k}{}^oVe^{i\mathbf{K}_l\cdot\mathbf{r}}d\tau,\\
I_3&=C_l{}^*C_{N+1}\biggl\{\int_\Omega e^{-i\mathbf{K}_l\cdot\mathbf{r}}V\phi_\mathbf{k}{}^oe^{-i\mathbf{k}\cdot\mathbf{r}}d\tau\\
&\qquad-\int_S e^{-i(\mathbf{K}_l+\mathbf{k})\cdot\mathbf{r}}\nabla\phi_\mathbf{k}{}^o\cdot\mathbf{n}d\sigma\biggr\},\\
I_4&=C_{N+1}{}^*C_{N+1}\int_\Omega \phi_\mathbf{k}{}^{o*}H\phi_\mathbf{k}{}^od\tau,
\end{aligned} \tag{A1.5}$$

where in evaluating I_3 we have made use of Green's theorem and the fact that $\phi_\mathbf{k}{}^o$ is continuous at the cell boundary (but not necessarily its derivatives). Substituting (A1.3) in (A1.2), we get the following terms:

$$\begin{aligned}
G_1&=G_2=0,\\
G_3&=C_l{}^*C_{N+1}\int_S e^{-i(\mathbf{K}_l+\mathbf{k})\cdot\mathbf{r}}\nabla\phi_\mathbf{k}{}^o\cdot\mathbf{n}d\sigma,\\
G_4&=C_{N+1}{}^*C_{N+1}\int_S \phi_\mathbf{k}{}^{o*}\nabla\phi_\mathbf{k}{}^o\cdot\mathbf{n}d\sigma.
\end{aligned} \tag{A1.6}$$

When we combine terms to form J, we see that the surface integral in I_3 is canceled by that of G_3.

Combining I_4 and G_4, we get

$$J_4=C_{N+1}{}^*C_{N+1}\biggl\{\int_\Omega \phi_\mathbf{k}{}^{o*}(V-E)\phi_\mathbf{k}{}^od\tau+\int_\Omega \nabla\phi_\mathbf{k}{}^{o*}\cdot\nabla\phi_\mathbf{k}{}^od\tau\biggr\}, \tag{A1.7}$$

where we have used Green's theorem in combining the surface integral with the volume integral. Making the function J an extremum by equating its derivatives with respect to the real and imaginary parts of the coefficients to zero, we obtain the matrix equation

$$\textstyle\sum_m H_{l,m}C_m=EC_l, \tag{A1.8}$$

where

$$\begin{aligned}
H_{l,m}&=\delta_{l,m}(\mathbf{K}_l+\mathbf{k})^2+\Omega^{-1}\int_\Omega e^{-i(\mathbf{K}_l-\mathbf{K}_m)\cdot\mathbf{r}}Vd\tau,\\
H_{l,N+1}&=H_{N+1,l}{}^*=\Omega^{-1}\int_\Omega e^{-i\mathbf{K}_l\cdot\mathbf{r}}V\phi_\mathbf{k}{}^oe^{-i\mathbf{k}\cdot\mathbf{r}}d\tau,\\
H_{N+1,N+1}&=\Omega^{-1}\int\{|\phi_\mathbf{k}{}^oe^{-i\mathbf{k}\cdot\mathbf{r}}|^2V+|\nabla\phi_\mathbf{k}{}^o|^2\}d\tau.
\end{aligned} \tag{A1.9}$$

For practical reasons it is desirable to simplify the above expressions. In particular, since the method is a Fourier method by nature, it is useful to use Fourier coefficients as effectively as possible.

For the plane waves l, $m\neq N+1$ the result is straightforward and we have

$$H_{l,m}=\delta_{l,m}(\mathbf{k}+\mathbf{K}_l)^2+V(\mathbf{K}_l-\mathbf{K}_m),$$

where $V(\mathbf{K})$ is a Fourier coefficient of the expansion of the crystal potential.

Of particular interest is the fact that integrals involving $\phi_\mathbf{k}{}^o$ can be expressed in terms of the Fourier coefficients of $\phi_\mathbf{k}$ for $\mathbf{K}_i$ only. From (2.5) and (2.6), we have

$$\phi_\mathbf{k}{}^o=\phi_\mathbf{k}-\sum_{\mathbf{K}_i} B_{\mathbf{k},\mathbf{K}_i}e^{i(\mathbf{K}_i+\mathbf{k})\cdot\mathbf{r}}.$$

Defining $g_\mathbf{k}(\mathbf{r})=V\phi_\mathbf{k}e^{-i\mathbf{k}\cdot\mathbf{r}}$ and denoting its Fourier coefficients by $G_\mathbf{k}(\mathbf{K})$, we can find that

$$H_{l,N+1}=G_\mathbf{k}(\mathbf{K}_l)-\sum_{\mathbf{K}_i} B_{\mathbf{K}_i}V(\mathbf{K}_l-\mathbf{K}_i). \tag{A1.10}$$

In similar fashion, using Green's theorem and periodicity properties of the functions, we find

$$\begin{aligned}
H_{N+1,N+1}&=\Omega^{-1}\int_\Omega\{V|\phi_\mathbf{k}|^2+|\nabla\phi_\mathbf{k}|^2\}d\tau\\
&\qquad+\sum_{\mathbf{K}_i,\mathbf{K}_j} B_{\mathbf{K}_i}{}^*B_{\mathbf{K}_j}V(\mathbf{K}_i-\mathbf{K}_j)\\
&\qquad-2\,\mathrm{Re}\sum_{\mathbf{K}_i} B_{\mathbf{K}_i}{}^*G_{\mathbf{K}_i}-\sum_{\mathbf{K}_i}(\mathbf{K}_i+\mathbf{k})^2|B_{\mathbf{K}_i}|^2.
\end{aligned} \tag{A1.11}$$

In deriving this expression we used the approximation (usually quite good for our purposes) that the cell periodic function $\phi_\mathbf{k}{}^oe^{-i\mathbf{k}\cdot\mathbf{r}}$ is independent of $\mathbf{k}$; if necessary, the specific $\mathbf{k}$ dependence can be introduced easily.

APPENDIX II. EXTENSION TO SEVERAL AUXILIARY FUNCTIONS

If we have a set of auxiliary Bloch functions f_1, $f_2\cdots f_m$, we first orthogonalize these to the set of plane waves in the usual way:

$$f_n^o = f_n - \sum_{\mathbf{K}_i} \tilde{f}_n(\mathbf{K}_i) e^{i(\mathbf{K}_i+\mathbf{k})\cdot\mathbf{r}}. \tag{A2.1}$$

We normalize each f_n^o to average value unity. This is equivalent to adjusting f_n so that

$$\Omega^{-1} \int_\Omega |f_n|^2 d\tau - \sum_{\mathbf{K}_i} |\tilde{f}_n(\mathbf{K}_i)|^2 = 1. \tag{A2.2}$$

Calling the first normalized function ϕ_1^o, we proceed to orthogonalize f_2^o to this. We obtain, after several obvious steps,

$$\phi_2^o = (f_2^o - C\phi_1^o)(1-C^2)^{-\frac{1}{2}}, \tag{A2.3}$$

where

$$C = \Omega^{-1} \int_\Omega f_2^* f_1 d\tau - \sum_{\mathbf{K}_i} \tilde{f}_2^*(\mathbf{K}_i) \tilde{f}_1(\mathbf{K}_i), \tag{A2.4}$$

and f_1, f_2 have been adjusted in accord with (A2.2).

We can carry through the remaining orthonormalization by repeated application of the procedure used in (A2.3). For example, f_3^o may be orthogonalized to ϕ_1^o by replacing f_2^o by f_3^o. If the resulting function is then resubstituted for f_2^o and if ϕ_2^o is substituted for ϕ_1^o, the function ϕ_3^o results. The coefficient C must be calculated for each case.

The matrix elements can be computed in the same manner as before.

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K-Emission Spectrum of Metallic Lithium*

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The emission spectrum of an evaporated lithium target has been investigated in the spectral region extending from 60 to 600 A. The intensity distribution of the characteristic K emission band has been determined photometrically. Some features of the distribution $I(E)/\nu^2$ are as follows: the band has a maximum at 54.02 ev (229.50 A); the distribution drops to one-half of its maximum value on the high-energy side at 54.58 ev; and the decay in intensity from the peak to the high-energy limit of the band occurs in an energy interval of 1.18 ev. In agreement with the results of earlier investigators, the band does not show a sharp high-energy cutoff. A second band, similar in shape and having a maximum at 82.83 ev, has been observed and is presently identified as a K satellite.

INTRODUCTION

THE present investigation was undertaken with a view to re-examine the intensity distribution of the lithium K emission band which lies in the soft x-ray region. The spectrum is observed when the metal is bombarded by electrons possessing energies of a few hundred electron volts. The K emission spectrum is a result of electronic transitions from valence levels (2*s* band) into vacancies created in the K shell. The radiation was first detected photoelectrically by Skinner,[1] the band was observed previously by O'Bryan and Skinner,[2] and its shape was examined by Skinner.[3] These observations first pointed to a somewhat surprising lack of sharpness prevailing over the high-energy region of the band.

Unlike the case of the band spectra emitted by metals such as magnesium or aluminum which possess a more complex electronic structure, the K emission band of the lightest alkali metal is expected to be more susceptible of theoretical interpretation. It was therefore considered worthwhile to determine the spectral characteristics of the lithium K band with attentive concern for operational details in conducting the experiment and with adoption of a more critical attitude in the reduction of the experimental record.

In the radiative process referred to above, the core level is sharp, energy-wise, and has well-defined symmetry properties. Hence the spectral distribution of the observed radiation emitted in these transitions should provide some information of the nature of the level structure of the valence band for those transitions which are allowed.

If one writes the usual radiation formulas in a form appropriate for transitions from a group of closely spaced levels to a sharp inner level, the power radiated by the source in the frequency range $d\nu$ is found[4] to be

$$I(\nu)d\nu = \frac{8}{3} \frac{ne^2\hbar^3\Omega}{m^2c^3} \nu^2 \int_S \frac{\sum_i \left| \left(0 \left| \frac{\partial}{\partial x_i} \right| k \right) \right|^2}{|\mathrm{grad}_k E|} dS d\nu, \tag{1}$$

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