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Green's-Function Method in the Energy-Band Problem*

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The formulation of the Green's-function method, recently suggested by Ziman, for solving the energy-band problem in a so-called "muffin-tin" potential (zero outside spheres representing the various atoms, and spherically symmetrical within each sphere) is transformed to a form very much like that of the Augmented-plane-wave (APW) method, but cannot be transformed exactly into the APW formulation. The wave function set up by the Green's-function method is a superposition of plane waves satisfying the wave equation inside as well as outside the spheres representing the atoms, having a discontinuity of slope at the surfaces of the atomic spheres, enough to produce the correct solution of the Schrödinger problem outside the spheres. To get correct wave functions inside the atoms, one would have to construct augmented plane waves from these plane waves.

TWO different methods are available in the literature for solving the problem of the motion of electrons in the so-called "muffin-tin" potential, which forms an approximation to the potential in a crystal, equal to zero outside spheres representing the various atoms, and spherically symmetrical within each sphere. These are the (APW) augmented-plane-wave method,[1] and one or another variation of the Green's-function method, as described originally by Korringa, Kohn, and Rostocker, and Morse, and recently discussed by Ziman.[2] By intercomparison of results computed by both methods on the same potential,[3] it has been established that the two methods lead to identical results for the copper crystal, but it has not been shown formally that the two methods are equivalent. Ziman, in the paper just quoted, has gone a long way toward demonstrating the equivalence. In the present article, we transform Ziman's formulation to a form suggesting the APW method even more closely, and show that in this form it has a very simple interpretation.

Ziman's Eq. (52) can be written in the language used in the APW method, in which we are finding matrix elements of the Hamiltonian between augmented plane waves with wave vectors $\mathbf{k}_i=\mathbf{k}+\mathbf{K}_i$, $\mathbf{k}_j=\mathbf{k}+\mathbf{K}_j$, where $\mathbf{k}$ is the reduced wave vector, $\mathbf{K}_i$ and $\mathbf{K}_j$ vectors of the reciprocal lattice. In either method we can write the matrix elements of H-E, where H is the Hamiltonian and E the energy, in the form

$$(H-E)_{ij}=(\mathbf{k}_i\cdot\mathbf{k}_j-E)\delta_{ij}+(1/\Omega)\sum(n)\times\exp i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_nF_{nij},\quad(1)$$

where Ω is the volume of the unit cell, the summation over n is over the atoms in the unit cell, $\mathbf{r}_n$ is the vector from the origin to the nth atom in the cell. In the APW method the quantity F_{nij} is given by

$$(F_{nij})_{\rm APW}=4\pi R_n^2[-(\mathbf{k}_i\cdot\mathbf{k}_j-E)\times j_1(|\mathbf{k}_j-\mathbf{k}_i|R_n)/|\mathbf{k}_j-\mathbf{k}_i|+\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta_{ij})\times j_l(|\mathbf{k}_i|R_n)j_l(|\mathbf{k}_j|R_n)u_{nl}'(R_n)/u_{nl}(R_n)].\quad(2)$$

In this expression, R_n is the radius of the sphere representing the nth atom, the j_l's are spherical Bessel functions, $P_l(\cos\theta_{ij})$ is the Legendre function of the cosine of the angle between $\mathbf{k}_i$ and $\mathbf{k}_j$. The function $u_{nl}(r)$ is the radial wave function inside the sphere representing the nth atom, u_{nl}' is its radial derivative, both to be computed in Eq. (2) at R_n, for an energy equal to the eigenvalue of the secular equation.

In Ziman's equation (52), the equivalent formula for F_{nij} is

$$(F_{nij})_{\rm Ziman}=-\frac{4\pi}{\kappa}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta_{ij})\times j_l(|\mathbf{k}_i|R_n)j_l(|\mathbf{k}_j|R_n)\tan\eta_{nl}'/[j_l(\kappa R_n)]^2.\quad(3)$$

Here $\kappa^2=E$, the eigenvalue of the secular equation. The phase η_{nl}' is defined by the equation

$$\cot\eta_{nl}'=\cot\eta_{nl}-n_l(\kappa R_n)/j_l(\kappa R_n),\quad(4)$$

where n_l is the spherical Neumann function, and η_{nl} is given by

$$\tan\eta_{nl}=\frac{j_l'(\kappa R_n)-j_l(\kappa R_n)u_{nl}'(R_n)/u_{nl}(R_n)}{n_l'(\kappa R_n)-n_l(\kappa R_n)u_{nl}'(R_n)/u_{nl}(R_n)}.\quad(5)$$

We can use Eqs. (4) and (5) to write $\tan\eta_{nl}'$ directly. We then use the Wronskian relation

$$n_l'(\kappa R_n)j_l(\kappa R_n)-j_l'(\kappa R_n)n_l(\kappa R_n)=1/\kappa R_n^2\quad(6)$$

which can be easily proved from the properties of the

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[1] J. C. Slater, Phys. Rev. **51**, 846 (1937). For a more complete discussion, see J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1965), Vol. 2, Chap. 9 and Appendix 6.

[2] J. Korringa, Physica **13**, 392 (1947); W. Kohn and N. Rostocker, Phys. Rev. **94**, 1111 (1954); P. M. Morse, Proc. Natl. Acad. Sci. U. S. **42**, 276 (1956); J. M. Ziman, Proc. Phys. Soc. (London) **86**, 337 (1965). Further references are given in Ziman's paper.

[3] B. Segall, Phys. Rev. **125**, 109 (1962); G. A. Burdick, *ibid.* **129**, 138 (1963).

Bessel and Neumann functions. When this is done, Ziman's expression of Eq. (3) takes the alternative form

$$(F_{nij})_{\text{Ziman}}=4\pi R_n^2\sum_{l=0}^{\infty}(2l+1)\times P_l(\cos\theta_{ij})j_l(|\mathbf{k}_i|R_n)j_l(|\mathbf{k}_j|R_n)\times\left[\frac{u_{nl}'(R_n)}{u_{nl}(R_n)}-\frac{j_l'(\kappa R_n)}{j_l(\kappa R_n)}\right]. \tag{7}$$

The terms in $u_{nl}'(R_n)/u_{nl}(R_n)$ are exactly as in Eq. (2), but the remaining terms are different, and it can be shown that they cannot be transformed into the remaining terms of Eq. (2). This can be shown, for example, by considering the case $\mathbf{k}_j=0$, in which case the summations reduce to the single term $l=0$, and it can be shown by inspection that the two expressions cannot be equal in general.

The expression (7), together with Eq. (1), can be given a simple interpretation. We set up on the surface of the sphere of radius R_n a singularity of potential, depending both on energy and on l, such that V_{nl}, the potential to be used for waves of azimuthal quantum number l, for the nth atom, is zero except on the surface of the sphere, infinite there, in such a way that

$$\int_{R_n-\epsilon}^{R_n+\epsilon}V_{nl}\,dr=\frac{u_{nl}'(R_n)}{u_{nl}(R_n)}-\frac{j_l'(\kappa R_n)}{j_l(\kappa R_n)}, \tag{8}$$

where ϵ is infinitesimal. We interpret this potential as follows. We first write the solution as a sum of terms, each being a spherical harmonic of angle, times a radial function. The radial wave equation in the usual way is

$$\frac{d^2P(r)}{dr^2}+\left[E-V_{nl}-\frac{l(l+1)}{r^2}\right]P(r)=0, \tag{9}$$

where P is r times the radial wave function, and V_{nl} is the potential discussed above, zero except on the surface of the nth sphere. The energy E is κ^2, as before. The solution of Eq. (9), regular at the origin, is

$$P(r)=rj_l(\kappa r) \tag{10}$$

for r less than R_n. The potential V_{nl}, however, will produce a discontinuity in slope as we go through the surface of the sphere.

We can get at this discontinuity by integrating Eq. (9) from $R_n-\epsilon$ to $R_n+\epsilon$. We have

$$\int_{R_n-\epsilon}^{R_n+\epsilon}\frac{d^2P}{dr^2}dr=\frac{dP}{dr}\bigg|_{R_n-\epsilon}^{R_n+\epsilon}=\int_{R_n-\epsilon}^{R_n+\epsilon}V_{nl}P(r)\,dr, \tag{11}$$

where the terms arising from E and $l(l+1)/r^2$ go to zero as ϵ is reduced to zero. Hence we see that the discontinuity in $(dP/dr)/P$, as we go through the surface of the sphere, is given by Eq. (8). It is easy to show, if the wave function itself is continuous at the surface, that this will also be the discontinuity in the logarithmic derivative of the wave function itself, or its derivative divided by the function. Thus the singular potential set up in Eq. (8) is just correct to take the Bessel function solution inside the sphere, and change the slope outside the sphere to that which would be found for the function $u_{nl}(r)$ which is the wave function for the actual spherical potential within the sphere, for the same energy value.

It follows, then, that the solution of the wave equation set up in this way, with no potential except for the singular potentials V_{nl} at the surface of the sphere, will have a solution outside the spheres which is a true solution of Schrödinger's equation, since the potential is zero there, and the wave equation and Schrödinger's equation are identical. Inside the spheres, however, the solution of the wave equation, set up by using Ziman's secular equation, is not at all equal to the solution of Schrödinger's equation there, for the wave equation omits the potential in the regions inside the spheres, which profoundly affects the solutions. However, the functions u_{nl}, which are the radial parts of the solutions of Schrödinger's equation inside the spheres, have a logarithmic derivative at the sphere radius R_n which equals the logarithmic derivative of the solution of the wave equation just outside this sphere. Hence the solution of Schrödinger's equation within the spheres will join with continuous logarithmic derivatives to the solution of Schrödinger's equation outside, and this composite solution forms the desired solution of Schrödinger's equation throughout all space.

We now carry out the solution of this problem by expanding the wave function in plane waves, $\exp i\mathbf{k}_i\cdot\mathbf{r}$. We shall need the matrix elements of the Hamiltonian between two such plane waves. As far as the terms $-\nabla^2-E$, in the Hamiltonian and the energy, are concerned, we arrive at once at the equivalent forms

$$(\mathbf{k}_i^2-E)\delta_{ij}=(\mathbf{k}_i\cdot\mathbf{k}_j-E)\delta_{ij}=(\mathbf{k}_j^2-E)\delta_{ij}, \tag{12}$$

so that we obtain the first term in Eq. (1); it is assumed in setting up that equation that we are integrating over unit volume. For the effect of the potential of Eq. (8), we expand the plane wave in the familiar form

$$\exp i\mathbf{k}_i\cdot\mathbf{r}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(2l+1)i^l\frac{(l-|m|)!}{(l+|m|)!}\times j_l(|\mathbf{k}_i|r)P_l^{|m|}(\cos\theta)\times P_l^{|m|}(\cos\theta_i)\exp[im(\phi-\phi_i)], \tag{13}$$

where θ_i, ϕ_i determine the direction of the wave vector $\mathbf{k}_i$. We multiply two series like (13) together, one representing $\exp-\mathbf{k}_i\cdot\mathbf{r}$, the other $\exp i\mathbf{k}_j\cdot\mathbf{r}$, and multiply under the summation over l by the appropriate potential $V_{nl}(r)$. Since this is a function of r only, we may first integrate over angles, in finding the matrix element of the potential between the two plane waves. We use the well-known fact that all terms in the integration over angles will vanish except for the case where the l and m of the two summations are identical. Furthermore,we use values of the various integrals concerned as given in Appendix 6 of the text quoted in Ref. 1. When we have carried out these steps, and used Eq. (8) for the radial integration, the result is precisely as in the expression $(F_{nij})_{\mathrm{Ziman}}$ of Eq. (7).

We have verified, then, our statement that Ziman's matrix elements are for the solution in plane-wave expansion of a problem whose potential is everywhere zero except for the singularity on the surfaces of the spheres. This solution will be the true solution of the Schrödinger problem in the regions between the spheres, but not inside the spheres. If we wish the solutions in the spheres, we can join each plane wave onto a solution of the spherical problem, composed of the u_{nl}'s, making an augmented plane wave out of it. This final solution will give a wave function identical with that found by the APW method, as well as having identical energy values. This does not necessarily mean, however, that each plane wave will have the same amplitude as in the APW solution, or that there is necessarily a one-to-one correspondence between matrix elements of the secular equations for the two problems. We discuss this situation in the next paragraph.

It is hard to believe that an expansion of the wave function in the region between the spheres, in plane waves, is not unique, and yet it is not. A little reflection will convince the reader of this fact. Any function, with a reasonable amount of continuity, can be expanded in Fourier series, or in three dimensions, in plane waves. Thus the true wave function between the spheres could be combined with any arbitrary function inside the spheres, and a plane-wave expansion could be carried out. Since these different solutions would converge to different functions inside the spheres, they obviously would not be identical, and yet they would all represent the same function in the region between the spheres. For example, we could take the true solution of the Schrödinger equation everywhere, including the interior of the spheres, as found for instance from the APW method, and carry out a plane-wave expansion of this solution. This would be notoriously slowly convergent, since the plane waves would have to describe all the fine details of the wave function within the spheres, including many nodes, if we are dealing with heavy atoms. On the other hand, the solution of the secular problem which we have been discussing in the present article has a much smoother behavior within the spheres, and would be expected to be much more rapidly convergent. A similar situation holds for the APW method, in which the plane waves are called on only to express the function outside the spheres. But it is not at all obvious that the expansions in these two latter cases would be identical.

Before we leave our problem, we should make some comments on Ziman's equation as expressing a Green's-function solution of Schrödinger's equation. A Green's function of course is a spherical wave spreading out from a point source, satisfying the wave equation everywhere except at the singularity at the origin of the wave. The standard application of the Green's-function method to such a problem as the present one distributes point sources throughout the volume where the potential energy is different from zero; that is, in this case, throughout the volume of the spheres. The solution would be a true solution of Schrödinger's equation everywhere. However, transformations can be made in which the Green's functions are distributed only over surfaces. It appears that such a transformation must have been made in Ziman's derivation of his matrix elements. A distribution of suitable spherical waves originating on the surfaces of the spheres would produce an exact solution of Schrödinger's equation, which is identical with the wave equation, outside the spheres, but it would produce a solution of the wave equation also within the spheres, where the wave equation is not identical with Schrödinger's equation. This is clearly the situation with Ziman's solution. But it is significant that, as we can see from the discussion of the preceding paragraph, it is just this fact that we are satisfying the wave equation rather than Schrödinger's equation within the spheres which makes the function well-enough behaved in that region so that the plane-wave expansion can be fairly rapidly convergent.

We should also make some comments on the relation of this solution to pseudopotential methods of discussing the energy-band problem. Ziman, in the paper quoted in Ref. 2, has laid a good deal of stress on this relation, so that we can be brief about it. It is clear that the F_{nij}'s play the part of matrix elements of a pseudopotential between plane waves, and that if they are all small, we shall have an almost plane-wave type of solution. Our quantities V_{nl} give a more graphic picture of one way of defining this pseudopotential, however, than has usually been possible in the literature.

In this connection, we may point out a discussion which the present author has given of the corresponding situation with the APW method, in the text quoted in Ref. 1, Sec. 9–4 and Appendix 6.[4] It is there shown that an alternative expression to that of Eq. (2) is

$$(F_{nij})_{\mathrm{APW}}=4\pi R_n^2\{-(\mathbf{k}_j^2-E)j_1(|\mathbf{k}_j-\mathbf{k}_i|R_n)/|\mathbf{k}_j-\mathbf{k}_i|$$

$$+\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta_{ij})j_l(|\mathbf{k}_i|R_n)j_l(|\mathbf{k}_j|R_n)$$

$$\times[u_{nl}'(R_n)/u_{nl}(R_n)-j_l'(|\mathbf{k}_j|R_n)/j_l(|\mathbf{k}_j|R_n)]\}. \tag{14}$$

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[4] Since giving this discussion in the textbook mentioned in Ref. 1, the author has noticed that a formula essentially equivalent to Eq. (14) is given by H. C. Schlosser and P. M. Marcus, Phys. Rev. **131**, 2529 (1963). For the record, the author might mention that he was aware of this formula at the time of writing the 1937 paper quoted in Ref. 1, and realized at that time that it led easily to the almost-free-electron case.

A discussion is given in the reference cited showing that in the almost-free-electron case, the APW method leads to energies, and wave functions outside the spheres, almost exactly characteristic of free electrons. Graphs are also given showing that for an alkali metal like sodium, the quantities like F_{nij} of Eq. (7), or the summation over l in Eq. (14), can be very small over considerable ranges of energies, leading to the free-electron behavior of the energy bands in such a case, whereas for such an element as copper, this situation does not hold at all. Of course, the wave functions inside the spheres are entirely different from plane waves. In the reference cited, the similarity of this problem to the Ramsauer effect in the scattering of electrons by atoms is stressed, in which in certain cases a single plane wave outside an atomic sphere matches almost perfectly to the solution inside, without the requirement of scattered waves. This is the same case in which a single plane wave outside the spheres, or a single augmented plane wave, forms very nearly an exact solution of the energy-band problem.

I am much obliged to Professor Ziman for correspondence and conversation relating to this problem, and to my colleague Dr. Keith Johnson for valuable discussions. Dr. Johnson is investigating further the relation between the APW and Green's-function methods.[5]

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[5] *Note added in proof.* Since sending in this paper, Professor Ziman has pointed out to the author the very recent paper by P. Lloyd, Proc. Phys. Soc. (London) **86**, 825 (1965), who arrives at conclusions similar to those of the present paper.

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Phonon-Broadened Optical Spectra: Urbach's Rule

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Starting from Frölich's Hamiltonian for conduction-electron–optical-phonon interactions, an approximate Green's function $G(p,t)$ is derived. The spectral density derived from this Green's function is shown to possess an exponential tail at low energies, $E/\omega_0 \ll 0$. This demonstrates that Urbach's rule can be derived from Frölich's Hamiltonian. The approximate Green's function $G(p,t)$ is shown to be related to the intermediate-coupling models for polarons.

I. INTRODUCTION

THE low-energy tail of the direct absorption edge of polar materials decreases exponentially in energy. This phenomenon, known as Urbach's[1] rule, has been observed in many materials.[2]

The major result of this calculation is showing that Urbach's rule can be theoretically derived from Fröhlich's Hamiltonian[3]

$$H=\epsilon_p+\omega_0\sum\nolimits_{\mathbf{q}} a_{\mathbf{q}}{}^{\dagger}a_{\mathbf{q}}+\sum\nolimits_{\mathbf{q}} iQ(\mathbf{q})(a_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}}-a_{\mathbf{q}}{}^{\dagger}e^{-i\mathbf{q}\cdot\mathbf{r}}),$$
$$Q(\mathbf{q})^2=4\pi\alpha\omega_0{}^{3/2}/q^2(2m)^{1/2},$$
$$\epsilon_p=p^2/2m,$$

for electrons in a parabolic conduction band having a linear interaction with optical phonons in a polar crystal. Starting from this Hamiltonian, the spectral function[4] $A(p,E)$ is evaluated using a modification of second-order perturbation theory. This spectral density has an exponential tail for $E/\hbar\omega_0<0$. The exponential tail in the spectral density leads to an Urbach's rule in optical absorption. This represents the first derivation of an exponential tail caused by a linear interaction between conduction-band electrons and optical phonons.

Previous theoretical discussions[2,5–12] of Urbach's rule were either based upon impurity effects or conventional perturbation theory. Toyozawa's[5] model of quadratic coupling between localized exciton and optical phonons, which is similar to an impurity model in form, has received much attention.[2,10] The semiclassical derivation of quadratic exciton-phonon interactions, which neglects the exciton recoil, predicts an exponential tail. However, Keil[13] has recently shown that a quantum-mechanical derivation of quadratic coupling does not generally predict an Urbach's rule, and the usefulness of Toyozawa's model is now in doubt. Some other impurity models[11,12] are based on the low-energy band

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