(f) The Curie temperatures are found to depend upon the number of nonmagnetic ions substituted independent of the type and to follow nearly a linear decrease with increasing concentration of Al^{3+} or Ga^{3+}.

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An Augmented Plane-Wave Method for the Periodic Potential Problem. II*

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It is shown that the augmented plane-wave method recently proposed can be given an alternative interpretation which leads to a much simpler analytical formulation. We join a plane wave of energy E_0 outside the spherical atoms continuously, but with a derivative which is discontinuous, to spherical solutions of Schrödinger's equation inside the spherical atoms, corresponding to an energy E, to be determined. We compute the expectation value of the energy for this combined wave function, consisting of contributions from the plane-wave region, the spherical atoms, and also a surface contribution from the surface of the sphere, since the discontinuous derivative is equivalent to an infinite Laplacian which integrates to a finite contribution over the sphere. We now regard E as a parameter, and vary it to make the expectation value of energy stationary. The resulting wave function is proved to be identical with that set up in Part (I). Furthermore, the energy E inside the spheres proves to be identical with the expectation value of the energy, so that our functions are exact solutions of Schrödinger's equation inside the sphere, but not outside the sphere, since the energy of the plane wave E_0 is different from E. However this discrepancy is just canceled in the expectation value of energy by the surface integral. The resulting formulas for energy and wave function are much more convenient to use then those in Part (I).

THIS note forms an extension to the paper by one of the authors,[1] outlining a method for fitting approximate solutions of a spherical Schrödinger equation within the atoms of a crystal onto a plane wave in the region between the atoms. The reader is assumed to be familiar with this paper, which we shall describe as (I). In Eq. (9) of (I) we have set up the expansion coefficients of the assumed function within the spherical atoms, corresponding to energy values given by Eq. (8) of (I). Both these equations contain infinite sums which would be hard to evaluate in practice. By noting the resemblance of these sums to the expansions of Green's functions in terms of eigenfunctions of Schrödinger's equation, it occurred to one of us (MMS) that these sums in Eqs. (8) and (9) could be rewritten in a closed form. In this note we state the resulting equations, and the simple physical interpretation which can be given them.

Outside the atoms, in a region whose potential energy is taken to be zero, we have a plane wave of propagation vector k, energy E_0. Let us now set up a solution of Schrödinger's equation inside the ith spherical atom, with energy E [so far undetermined, though later to be identified with the E of (I)]. We build up this solution from solutions of the Schrödinger equation for each l value, for the assumed E; let such a solution, regular at the origin of the ith atom, be $u_{il}(E;r)$. We can superpose such functions, with appropriate coefficients, to set up a function which is continuous with the plane wave at the surface of the sphere; in general, however, the derivative will be discontinuous at the surface. We can now compute the expectation value of the energy for the wave function consisting of the plane wave of energy E_0 outside the sphere, and the spherical solution of energy E inside the sphere. There will be contributions to the integral of the Hamiltonian function consisting of E_0 times the integral of the square of the amplitude of the plane wave outside the sphere, and E times the integral of the square of the spherical solution inside the sphere. These are not the only contributions, however: on account of the discontinuity of derivative on the surface of the sphere, the Laplacian, or kinetic energy, is infinite there, and integrates to a finite contribution over the surface of the sphere.

We can now show that the augmented plane-wave function as set up in (I) is just such a function as we have described, in which further the expectation value of the energy is identical with the value E for which we

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[1] J. C. Slater, Phys. Rev. 92, 603 (1953).

have a solution of Schrödinger's equation inside the sphere. In other words, our functions within the sphere are exact solutions of Schrödinger's equation, for an energy equal to the expectation value of the energy, and the discrepancy in expectation value of energy arising because the energy E_0 of the plane wave differs from E is exactly compensated by a contribution arising from the surface discontinuity. We can further show that if the value of E is varied, the expectation value of the energy is an extremum for just those values of E which we have just described, so that we can derive our functions from a variation principle, using E as the quantity to be varied.

It will be recognized that the method as described in this language has a close resemblance to that proposed in 1937 by one of the authors.[2] The difference is that in that earlier paper, the energy E of the solutions inside the spheres was carried as a parameter all through the calculation, including the secular equation involved in making a linear combination of augmented plane waves, and was finally constrained at the end of the calculation to equal the expectation value of energy for the linear combination of waves. This process proved in practice to be extremely difficult to carry out, and prevented the practical use of that method. The present method avoids this difficulty, and as will be apparent from the mathematical formulation to be presented, it is now very easy to get the energy values of the separate plane waves.

The statements which we have made about the present method can be easily verified, and lead to greatly simplified formulas to replace Eqs. (8) and (9) of (I). We proceed by expanding the functions $u_{il}(E;r)$ as series of the functions $u_{inl}(r)$ of (I). Those functions were solutions of the Schrödinger equation for such energies E_{inl} that the functions u_{inl} had the same logarithmic derivatives at the surface of the atomic sphere, $r=r_i$, as the corresponding spherical Bessel functions $j_l(kr)$ appearing in the expansion of the plane wave. The expansion coefficients c_{inl} in the expansion $u_{il}(E;r)=\sum(n)c_{inl}u_{inl}$ can be easily shown to be

$$c_{inl}=(2l+1)^{-1}4\pi r_i^2 u_{inl}(r_i)u_{il}(E;r_i)(E_{inl}-E)^{-1} \times[d\ln u_{il}(E;r)/dr-d\ln j_l(kr)/dr]_{r=r_i}. \quad (1)$$

We can multiply these coefficients by $u_{inl}(r)$, and sum over n, obtaining a formula for $u_{il}(E;r)$. If we build up a sum of these functions inside the sphere, continuous with the plane wave outside, we have

$$a_0\exp(i\mathbf{k}\cdot\mathbf{R}_i)\sum(l)(2l+1)i^l P_l(\cos\theta)j_l(kr_i) \times u_{il}(E;r)[u_{il}(E;r_i)]^{-1}, \quad (2)$$

in the notation of (I). If we expand the functions $u_{il}(E;r)$ and $u_{il}(E;r_i)$ in terms of the u_{inl}'s, as described in Eq. (1), we can then immediately show that the expression (2) becomes identical with the wave function inside the sphere as derived in (I), which we find by multiplying the coefficients a_{inl} of Eq. (9) in (I) by the functions $u_{inl}(r)$, and summing over all values of n and l.

Next we consider the energy. It is immediately obvious how to compute the contributions of the plane wave, and of the spherical solutions, to the integral of the Hamiltonian operator over the wave function. As for the surface contribution, we note that the integral of the Laplacian kinetic energy operator over a thin spherical shell over which there is a discontinuity of normal derivative is $\int u[(du/dr)_1-(du/dr)_2]da$, where $(du/dr)_1$, $(du/dr)_2$, respectively, are the normal derivatives inside and outside the shell, and $\int da$ indicates integration over the surface of the sphere. Using this result, we find that the surface contribution to the integral of the energy can be written in the alternative forms:

$$a_0^*a_0 4\pi r_i^2\sum(l)(2l+1)j_l^2(kr_i) \times[d\ln u_{il}(E;r)/dr-d\ln j_l(kr)/dr]_{r=r_i} \quad (3)$$

or

$$a_0^*a_0\sum(l)(2l+1)^2 j_l^2(kr_i) \times[\sum(n)u_{inl}^2(r_i)/(E_{inl}-E)]^{-1}. \quad (4)$$

The second term in the square bracket in (3) can be eliminated if we wish by using the relation $\sum(l)(2l+1)\times j_l(z)dj_l(z)/dz=0$, which can be proved from the properties of spherical Bessel functions.

When we add the three contributions to the energy integral, and use Eq. (10), (I), giving the normalization, we find that if we express everything in terms of the u_{inl}'s, our condition for the energy becomes identical with Eq. (8), (I). However, if we express the same thing in terms of the $u_{il}(E;r)$'s, we have the much simpler but equivalent formula

$$\Omega(E-E_0)=\sum(i,l)4\pi r_i^2(2l+1)j_l^2(kr_i) \times[d\ln u_{il}(E;r)/dr)]_{r=r_i}. \quad (5)$$

We can now use Eq. (5) to determine the energy E. This is a very simple formula to use, since we can plot the right side as a function of E, requiring only the logarithmic derivative of the function $u_{il}(E;r)$ on the surface of the sphere. This function has a resemblance to a cotangent curve, with an infinite number of branches. The intersections of this curve with the straight line $\Omega(E-E_0)$ give the required values of E. When these are determined the wave functions can be set up in terms of (2), and it is then a simple matter to calculate the matrix components of energy between different wave functions, required in setting up the secular equation for interaction of different augmented plane waves. Further properties of the method will be described later in connection with its application to specific cases.

It is interesting to see how the wave functions within the sphere, which were originally intended to join onto the plane wave continuously and with continuous derivative, have acquired a discontinuity of derivative

[2] J. C. Slater, Phys. Rev. 51, 846 (1937).

at the surface of the sphere. Such a discontinuity is not present if we break off the series in n at a finite point, for each of the functions u_{inl} joins the plane wave with continuous slope. Superposition of the infinite number of functions introduces a discontinuity of slope, however, just as we know that a Fourier series can introduce such a discontinuity. The infinite series representation of the function inside the sphere cannot be differentiated at the surface of the sphere; its discontinuity of slope at the surface is related to the fact that it can be identified with a Green's function for Schrödinger's equation.

In the Appendix (the work of MMS), we shall show three things: that the slope of the function represented by the right side of Eq. (5) is always negative, verifying its resemblance to a cotangent curve, since it has asymptotes wherever one of the $u_{il}(E;r_i)$'s is zero, and goes monotonically from an infinite value at one asymptote to a negatively infinite value at the next; that our statement regarding the energy being an extremum as we vary E is true; and that the sums over n encountered in (I) are expressible in terms of Green's functions, the fact which led to the motivation of the present treatment, and which explains the discontinuity of slope.

APPENDIX

Let us define the quantity

$$\sum(i,l)4\pi r_i^2(2l+1)j_l^2(kr_i)[d\ln u_{il}(E;r)/dr]_{r=r_i}$$

as $f(E)$. It is this function which appears on the right side of Eq. (5). Comparison with Eq. (8), (I), shows that it can also be written in the form

$$f(E)=\sum(i,l)(2l+1)^2j_l^2(kr_i)\times[\sum(n)u_{inl}^2(r_i)/(E_{inl}-E)]^{-1}.$$

Let us differentiate this expression with respect to E. Then we have

$$df/dE=-\sum(i,l)(2l+1)^2j_l^2(kr_i)\times[\sum(n)u_{inl}^2(r_i)/(E_{inl}-E)^2]\times[\sum(n)u_{inl}^2(r_i)/(E_{inl}-E)]^{-2}. \quad (6)$$

Each term in (6) is a perfect square; thus we see that df/dE must be negative. Furthermore, by comparison with Eq. (10), (I), we can understand the significance of the quantity (6). That equation was the normalization relation; and we see that it can be written in the form

$$a_0^*a_0(-df/dE+\Omega)=1. \quad (7)$$

Hence we see that the contribution of the part of the wave function inside the spheres to the normalization equals $-a_0^*a_0df/dE$, and the contribution of the plane wave is $a_0^*a_0\Omega$.

Next we can prove our theorem regarding the variation properties of the solution. Let us first set up the expectation value of the energy. The contribution of the spherical part of the solution is $a_0^*a_0(-Edf/dE)$, and of the plane wave $E_0a_0^*a_0\Omega$. From Eq. (3) or (4), the contribution of the surface discontinuity is $a_0^*a_0f(E)$. If we write the total expectation value of energy, and eliminate $a_0^*a_0$ by use of (7), we have

$$\text{Energy}=(f-Edf/dE+E_0\Omega)(-df/dE+\Omega)^{-1}. \quad (8)$$

If we differentiate this expression with respect to E, denoting derivatives of f with respect to E by primes, the result is

$$f''[\Omega(E_0-E)+f](-f'+\Omega)^{-2}. \quad (9)$$

Our energy equation (5) is equivalent to setting $\Omega(E_0-E)+f=0$, so that we verify the statement that our procedure makes the expectation value of energy an extremum, when E is varied.

Finally we point out the relation between the series over n, which appear in Eqs. (8) and (9), (I), and in Eq. (4) of the present note, and Green's functions. For a given type of atom and for a given angular momentum we can subsume the two infinite series, taken over the index n, which appear in these equations, under the expression

$$(2l+1)G_{il}(x;\xi;E)/4\pi\xi x=\sum(n)u_{iml}(x)u_{inl}(\xi)/(E_{inl}-E). \quad (10)$$

This series is the expansion of a Green's function of the radial Schrödinger's equation in which the energy is to be regarded as a parameter. This Green's function $G_{il}(x;\xi;E)$ is determined through the condition that $G_{il}(x;\xi;E)/\xi x$ satisfy the same boundary conditions (for arbitrary ξ in the interval $(0,r_i)$ and for arbitrary energy) as do the u_{inl}.

As is well known, the Green's function is continuous with discontinuous slope at $x=\xi$. For the series we are interested in $\xi=r_i$ and $x=r$ is to the left of ξ. For these values, then, it can be shown that

$$G_{il}(r;r_i;E)=(r/r_i)u_{il}(E;r)[u_{il}(E;r_i)]^{-1}\times[d\ln u_{il}(E;r)/dr-d\ln j_l(kr)/dr]^{-1}. \quad (11)$$

The boundary condition at $r=r_i$ is satisfied by the value of $G_{il}(r;\xi;E)$ at $r=r_i$, and the slope of $G_{il}(r;\xi;E)$ taken with $r=r_i$ and ξ to the *right* of r. However, the function which represents our series takes on the slope of $G_{il}(r;\xi;E)$ with ξ to the *left* of r. Thus the series has the slope defined by $G_{il}'(r_i-0;r_i;E)$ which is different from $G_{il}'(r_i+0;r_i;E)$, which has the proper slope.