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A New Method for Calculating Wave Functions in Crystals

CONYERS HERRING*
Massachusetts Institute of Technology, Cambridge, Massachusetts

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For many problems in the electron theory of metals none of the methods hitherto used to calculate the eigenfunctions and energy values of an electron in a crystal lattice is satisfactory. It is here proposed that these wave functions and energies be calculated by solving a secular equation with wave functions χ_k which are simply plane waves made orthogonal to the core eigenfunctions. The rapidity of convergence to be expected for such a procedure is discussed. Some methods for practical computation are suggested, and expressions are given for the matrix elements occurring in the secular equation.

1. INTRODUCTION

THE problem of calculating explicitly the eigenfunctions and energy values for an electron in the periodic field of a crystal is one which has not yet been satisfactorily solved. The method of Wigner and Seitz[1] is simple and gives good results for the lower states of the valence electron band of a metal, but the natural extension of this method to states of higher energy[2] becomes rapidly more unreliable as the energy increases.[3] Another method, proposed by Slater,[4] is better adapted to high energy states, but has the disadvantage that the fluctuations in potential in the outer region of each atomic cell are disregarded. The method to be described in the present paper, while not entirely satisfactory, possesses advantages which make it applicable to numbers of problems which cannot be treated safely by the other methods. The principal disadvantage of the procedure to be described is that it is rather laborious. It is nevertheless practicable, and some successful applications to simple metals have already been made.[5]

One of the earliest methods of approximating to the electron energies in a crystal consisted in starting from plane waves and treating the periodic variation of potential as a perturbation.[6] This method has been considered futile for accurate work, however. For if we set up the matrix of the Hamiltonian relative to some number n of plane waves, and solve the secular equation, we find that for small values of n the lowest root approximates a valence electron eigenvalue, but that as $n \rightarrow \infty$ the lowest root approaches the energy of the lowest state of an atomic core, and it is only one of the higher roots which approaches a valence electron eigenvalue.[7] And to get a good final approximation to the valence electron energy, we would have to use a very large value of n, so that the solution of the secular equation would be prohibitively difficult. This corresponds to the fact that in the Fourier expansion of a valence electron eigenfunction there is a great contribution from waves of short wave-length. However, if we set up instead the matrix of the Hamiltonian relative to a set of n functions which are all orthogonal to the eigenfunctions of the core bands of the crystal, and solve the secular equation for this matrix, the lowest root must approach a valence electron eigenvalue as $n \rightarrow \infty$, and it is more reasonable to expect that the convergence will be rapid.

Two principles are involved in the procedure to be described. The first is that the statement at the end of the preceding paragraph is approximately true if we work with wave functions which are orthogonal, not to the true core eigenfunctions φ_{jk}, but to functions φ_{jk}' which closely approximate the φ_{jk}. Let χ_k be the wave function obtained by orthogonalizing a plane wave of wave vector $\mathbf{k}$ to all the functions φ_{jk}'

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* National Research Fellow, 1937–39.

[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

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

[3] W. Shockley, Phys. Rev. **52**, 866 (1937).

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

[5] C. Herring and A. G. Hill, Phys. Rev., to appear later.

[6] See the article of Sommerfeld and Bethe, *Handbuch der Physik* (2nd ed., Berlin, 1933), Vol. 24/2, p. 385.

[7] Cf. J. C. Slater, Rev. Mod. Phys. **6**, 250–258 (1934).

having the same reduced wave vector.[8] Let φ_k' be the wave function of lowest average energy which can be constructed from the functions $\chi_{k+2\pi g}$, where **k** is a given vector and **g** runs over all vectors of the reciprocal lattice of the crystal. The average energy E_k' of φ_k' is of course the limit, as $n \rightarrow \infty$, of the smallest root of the secular equation constructed with the n functions χ of smallest wave vectors. This E_k' is slightly less than the eigenvalue E_k of the lowest valence electron state with the same reduced wave vector.

If we use the abbreviation

$$(\varphi_{sk}, \varphi'_k) = \int \varphi_{sk}^* \varphi_k' d\tau$$

we may write

$$\varphi_k' = \sum_s (\varphi_{sk}, \varphi_k')\varphi_{sk},$$

$$E_k' = \sum_s |(\varphi_{sk}, \varphi_k')|^2 E_{sk},$$

where the φ_{sk} and E_{sk} are the true eigenfunctions and energies of all the core and valence electron states with reduced wave vector **k**. Since φ_k' is orthogonal to any φ_{jk}' we have by Bessel's inequality

$$|(\varphi_{sk}, \varphi_k')|^2 + |(\varphi_{sk}, \varphi_{jk}')|^2 \leqslant 1,$$

so

$$E_k - E_k' = \sum_s |(\varphi_{sk}, \varphi_k')|^2 (E_k - E_{sk}) \leqslant \sum_{j\,\mathrm{core}} |(\varphi_{jk}, \varphi_k')|^2 (E_k - E_{jk}) \leqslant \sum_{j\,\mathrm{core}} [1 - |(\varphi_{jk}, \varphi_{jk}')|^2](E_k - E_{jk}). \quad (1)$$

This tells us how much we can allow φ_{jk}' to deviate from the corresponding true eigenfunction φ_{jk} of the core band, when an allowable error $(E_k - E_k')$ has been specified. Moreover, φ_k can be obtained from φ_k' by adding multiples of the true core functions and renormalizing. So if the right of (1) is sufficiently small, it is reasonable to expect that we can get a much better approximation to φ_k, and hence to E_k, by adding to φ_k' a small multiple of each φ_{jk}'; i.e., we can treat the matrix elements of the Hamiltonian connecting φ_k' with the φ_{jk}' as small perturbations.

The second of the principles mentioned has to do with the fact that in the troublesome region near a nucleus, the solutions of the wave equation do not depend very much on the energy, because the negative potential is very large. Thus for example the s part of a valence electron eigenfunction φ_k can be approximated near a nucleus by an s solution of the wave equation for a somewhat different energy, the p part by a p solution for a different energy, etc. So by subtracting off from φ_k a suitable multiple of some s solution of the wave equation we can obtain a function which no longer has a sharp maximum at the nucleus, and which accordingly can be much better represented by a few terms of its Fourier series than could the original φ_k. This suggests that it would be practical to try to approximate φ_k by a linear combination of a few plane waves, plus a linear combination of a few functions u_j localized about each nucleus and obeying wave equations of the form

$$\nabla^2 u_j + (E_j - V_j)u_j = 0 \quad (2)$$

(distances to be measured in Bohr units and energies in rydbergs), where E_j and V_j are such that within a reasonable radius from the nucleus

$$(E_j - V_j) - (E_k - U) \ll (E_k - U),$$

U being the actual potential in the crystal. By considering the case where V_j is nearly the same as U and the u_j are atomic core functions it is possible to show that the lowest root of the secular equation mentioned in the preceding paragraphs ought to converge fairly rapidly toward E_k'. For definiteness let us suppose V_j to be spherically symmetrical, and the u_j to be $1s$, $2s$, and $2p$ functions. Then near the nucleus we can represent the s part of φ_k fairly well by a linear combination of the $1s$ and $2s$ functions and the p part by a multiple of the $2p$ function. The d part of φ_k will vary rather smoothly with position near the nucleus, if the atomic number is reasonably small. Thus we can choose coefficients $\alpha_{j\nu}$ so that

$$\varphi_k - \sum_{j\nu} \alpha_{j\nu} u_j(\mathbf{r} - \mathbf{R}_\nu) \quad (3)$$

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[8] For the conception of "reduced wave vector" see Sommerfeld and Bethe, reference 6, p. 394.

varies much more gradually near each nuclear position than does φ_k. The Fourier series for the function (3) will then converge rapidly, and so φ_k can be fairly well approximated by a linear combination of a few plane waves plus the sum $\sum_{j\nu}\alpha_{j\nu}u_j(\mathbf{r}-\mathbf{R}_\nu)$. Now if the V_j resemble U sufficiently closely, the Bloch waves[9] constructed from the $u_j(\mathbf{r}-\mathbf{R}_\nu)$ will be good approximations to the core eigenfunctions φ_{jk}, and can be used for the φ_{jk}' mentioned in the preceding paragraph. In such case let us write

$$\varphi_k=\sum_{j\nu}\alpha_{j\nu}u_j(\mathbf{r}-\mathbf{R}_\nu)+\sum_{\mathbf{g}}\frac{\beta_g}{\Omega^{\frac{1}{2}}}\exp i(\mathbf{k}+2\pi\mathbf{g})\cdot\mathbf{r},$$

where Ω is the volume of the crystal. Then from the fact that φ_k is approximately orthogonal to each u_j we may conclude that

$$\varphi_k\approx\sum_{\mathbf{g}}\beta_g\chi_{k+2\pi g},$$

where each χ is simply a plane wave made orthogonal to all the $u_j(\mathbf{r}-\mathbf{R}_\nu)$. From what has been said above this series will converge rapidly. It is thus to be expected that the lowest root of the secular equation formed using the first n χ's will converge rapidly toward E_k' as n is increased.

In many cases it will be sufficient to work with a secular equation formed from the χ's, and Sections 2 and 3 will be concerned exclusively with such cases. It should be mentioned, however, that it may sometimes be desirable to use one or more functions u_i which do not resemble core functions, and to set up a secular equation using these u_i together with χ-functions which are orthogonal to the other u_j. Consider for example a crystal (such as Li or Be) for which there is only one core band, derived from the 1*s* atomic levels. First assume the u_{1s} to be the 1*s* eigenfunction in a central field V which is the spherical average of the true field U. If near a nucleus

$$V(r)=-2Z/r+a+br\cdots,$$

we have

$$u_{1s}\propto 1-Zr+\left(\frac{Z^2}{3}+\frac{a-E_{1s}}{6}\right)r^2+\cdots,$$

while, to a high degree of accuracy,

$$s\text{ part of }\varphi_k\propto 1-Zr+\left(\frac{Z^2}{3}+\frac{a-E_k}{6}\right)r^2+\cdots.$$

Thus with properly chosen coefficients the *s* part of the function (3) will vanish with its radial derivative at each nucleus, and even the second radial derivative will be small. The *p* part of φ_k, on the other hand, has quite a large gradient at a nucleus, whereas the *p* part of a sum of a few χ-functions (which is the same as the *p* part of a sum of plane waves) cannot have a very large gradient unless waves of short wave-length are included.[10] Thus if we use only a few χ-functions we can approximate the *s* part of φ_k much more closely than the *p* part. The situation could be improved by inventing a *p* function u_p obeying near the nucleus a wave equation resembling that for the *p* part of φ_k, and dying off smoothly to zero in the outer regions of an atomic cell. A combination of a few χ-functions (or plane waves) with a suitable multiple of u_p should then give a much closer approximation to the *p* part of φ_k. Our final wave function need not be even approximately orthogonal to u_p, however, since there is no *p* band in the core.

2. General Theory

Consider a crystal of volume Ω, containing N identical unit cells each of volume Ω_0. For simplicity assume that all atoms of the crystal are of the same kind, even though there may be more than one atom per unit cell. Let $U(\mathbf{r})$ be the potential energy of an electron at the point $\mathbf{r}$. Let $V(r)$ be a more or less arbitrary spherically symmetric potential field, chosen, however, so as to resemble U as closely as possible in the region near a nucleus. When calculations are made for several values of the lattice constant or of other parameters, U will be a different function in each case, whereas V is best kept fixed to avoid repetition of the labor of computing core functions and quantities which depend on them. Let one or more real functions u_{nlm} be core eigenfunctions in the field $V(r)$, with

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[9] See Sommerfeld and Bethe, reference 6, p. 394.

[10] Cf. Fig. 4 of the following paper.

energies E_{nlm}. The Bloch waves formed from these "atomic" functions will play the part of the functions which were called φ_{jk}' in the preceding section.

In the following it will be assumed that energies are measured in rydbergs and distances in units of the Bohr radius. The functions χ_k we shall use will be defined by

$$N^{\frac{1}{2}}\chi_k(\mathbf{r})=\frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}-\sum_{\nu}\sum_{nl}\exp(i\mathbf{k}\cdot\mathbf{R}_\nu)A_{nl}(k)u_{nl;\,k}(\mathbf{r}-\mathbf{R}_\nu), \tag{4}$$

where ν runs over all atoms of the crystal, $u_{nl;\,k}$ is the function u_{nl0} when the axis to which m refers is chosen in the direction of $\mathbf{k}$, and where

$$A_{nl}(k)=\int_{\infty}\frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}u_{nl;\,k}d\tau. \tag{5}$$

It is easily verified that each χ_k is orthogonal to all the $u_{nlm}(\mathbf{r}-\mathbf{R}_\nu)$ if one neglects the fact that core functions about different atoms may overlap and thus fail to be exactly orthogonal to one another.

Before writing down the accurate expressions for the matrix elements of the Hamiltonian between the functions (4), which are rather lengthy, it may be worth while to see what they look like if one makes the approximations that the $u_{nlm}(\mathbf{r}-\mathbf{R}_\nu)$ are true eigenfunctions in the crystal field and that the functions on different atoms do not overlap. Noting that

$$\int_{\infty}u_{nl;\,k}(\mathbf{r})u_{nl;\,k'}(\mathbf{r})d\tau=P_l(\cos\theta_{kk'}),$$

where $\theta_{kk'}$ is the angle between $\mathbf{k}$ and $\mathbf{k}'$, we have in the approximation mentioned

$$(\chi_k,\chi_{k'})=\delta_{kk'}-\sum_{nl}A_{nl}(k)A_{nl}(k')P_l(\cos\theta_{kk'})\sum_{\nu}^{\text{cell}}\exp\left[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu\right], \tag{6}$$

if $(\mathbf{k}-\mathbf{k}')$ is 2π times a vector of the reciprocal lattice, and $=0$ otherwise. The summation in (6) is over all atoms ν in a single unit cell. Also, since in our present approximation the Hamiltonian H applied to each $u_{nl;\,k}$ merely multiplies it by E_{nl},

$$(\chi_k,H\chi_{k'})=k^2\delta_{kk'}+U[\mathbf{k}'-\mathbf{k}]-\sum_{nl}E_{nl}A_{nl}(k)A_{nl}(k')P_l(\cos\theta_{kk'})\sum_{\nu}^{\text{cell}}\exp\left[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu\right], \tag{7}$$

if $(\mathbf{k}'-\mathbf{k})$ is 2π times a vector of the reciprocal lattice, and $=0$ otherwise. Here

$$U[\mathbf{K}]=\frac{1}{\Omega_0}\int_{\Omega_0}\exp(i\mathbf{K}\cdot\mathbf{r})U(\mathbf{r})d\tau \tag{8}$$

is a Fourier coefficient of the potential.

Numerical calculations have shown that solution of a secular equation obtained from a few χ-functions from (6) and (7) gives a fair approximation to the energy of a valence electron eigenfunction for a metal, such as an alkali, for which the u_{nlm} are confined quite closely around the nuclei. However, the derivatives of energy with respect to lattice constant, as obtained from (6) and (7), approximate the true derivatives very poorly. This is not surprising, for a small change in lattice constant has a large effect on the validity of the assumption that U and V are identical, and of the assumption that core functions on different atoms do not overlap. We therefore need exact expressions for $(\chi_k,\chi_{k'})$ and $(\chi_k,H_{k'})$. When $(k'-k)$ is 2π times a vector of the reciprocal lattice, we have

$$(\chi_k, H\chi_{k'})=k^2\delta_{kk'}+U[\mathbf{k}'-\mathbf{k}]-\frac{1}{N}\sum_{\nu'}\sum_{nl}\int_{\Omega}\Big[\frac{\exp(-i\mathbf{k}\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}\exp(i\mathbf{k}'\cdot\mathbf{R}_{\nu'})A_{nl}(k')Hu_{nl;\,k'}(\mathbf{r}-\mathbf{R}_{\nu'})$$

$$+\frac{\exp(i\mathbf{k}'\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}\exp(-i\mathbf{k}\cdot\mathbf{R}_{\nu'})A_{nl}(k)Hu_{nl;\,k}(\mathbf{r}-\mathbf{R}_{\nu'})\Big]d\tau$$

$$+\frac{1}{N}\sum_{\nu,\nu'}\sum_{nl,n'l'}\int_{\Omega}\exp(-i\mathbf{k}\cdot\mathbf{R}_\nu+i\mathbf{k}'\cdot\mathbf{R}_{\nu'})A_{nl}(k)A_{n'l'}(k')u_{nl;\,k}(\mathbf{r}-\mathbf{R}_\nu)Hu_{n'l';\,k'}(\mathbf{r}-\mathbf{R}_{\nu'})d\tau. \quad (9)$$

In (9) we may put $H=[-\nabla^2+V(\mathbf{r}-\mathbf{R}_{\nu'})]+[U(\mathbf{r})-V(\mathbf{r}-\mathbf{R}_{\nu'})]$. To simplify the resulting expression, three new symbols will be introduced:

$$I_{nl}(\mathbf{k};\mathbf{k}';\nu)=\int_\infty\frac{\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_\nu)]}{(\Omega_0)^{\frac{1}{2}}}[U(\mathbf{r})-V(\mathbf{r}-\mathbf{R}_\nu)]u_{nl;\,k'}(\mathbf{r}-\mathbf{R}_\nu)d\tau, \quad (10)$$

$$S(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu')=\int_\infty u_{nl;\,k}(\mathbf{r}-\mathbf{R}_\nu)u_{n'l';\,k'}(\mathbf{r}-\mathbf{R}_{\nu'})d\tau, \quad (11)$$

$$F(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu')=\int_\infty u_{nl;\,\mathbf{k}}(\mathbf{r}-\mathbf{R}_\nu)[U(\mathbf{r})-V(\mathbf{r}-\mathbf{R}_{\nu'})]u_{n'l';\,k'}(\mathbf{r}-\mathbf{R}_{\nu'})d\tau. \quad (12)$$

Inserting (10), (11), and (12) into (9) gives finally

$$(\chi_k, H\chi_{k'})=k^2\delta_{kk'}+U[\mathbf{k}'-\mathbf{k}]-\sum_{nl}E_{nl}A_{nl}(k)A_{nl}(k')P_l(\cos\theta_{kk'})\sum_{\nu}^{\text{cell}}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu]$$

$$-\sum_{nl}\sum_{\nu}^{\text{cell}}[(A_{nl}(k')I_{nl}^*(\mathbf{k};\mathbf{k}';\nu)+A_{nl}(k)I_{nl}(\mathbf{k}';\mathbf{k};\nu)]\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu]$$

$$+\sum_{nl,n'l'}A_{nl}(k)A_{n'l'}(k')\sum_{\nu}^{\text{cell}}F(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu)\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu]$$

$$+\sum_{nl,n'l'}A_{nl}(k)A_{n'l'}(k')\sum_{\nu'\neq\nu}\sum_{\nu}^{\text{cell}}[E_{nl}S(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu')$$

$$+F(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu')]\exp[-i\mathbf{k}\cdot\mathbf{R}_\nu+i\mathbf{k}'\mathbf{R}_{\nu'}], \quad (13)$$

if $(\mathbf{k}-\mathbf{k}')$ is 2π times a vector of the reciprocal lattice, and $=0$ otherwise. Similarly

$$(\chi_k, \chi_{k'})=\delta_{kk'}-\sum_{nl}A_{nl}(k)A_{nl}(k')P_l(\cos\theta_{kk'})\sum_{\nu}^{\text{cell}}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_\nu]$$

$$+\sum_{nln'l'}A_{nl}(k)A_{n'l'}(k')\sum_{\nu'\neq\nu}\sum_{\nu}^{\text{cell}}S(nl\mathbf{k}\nu,\ n'l'\mathbf{k}'\nu')\exp(-i\mathbf{k}\cdot\mathbf{R}_\nu+i\mathbf{k}'\cdot\mathbf{R}_{\nu'}), \quad (14)$$

if $(\mathbf{k}'-\mathbf{k})$ is 2π times a vector of the reciprocal lattice, and $=0$ otherwise. When there are core functions with $l>0$, the S integrals and the F integrals for $\nu\neq\nu'$ become very difficult to evaluate, so in such cases it will be convenient to choose core functions which become zero at a value of r less than half the distance between neighboring atoms. If this is done the last terms of (13) and (14) disappear.

The matrix elements (13) and (14) determine the wave function $\varphi_k'=\sum_g a_g\chi_{k+2\pi g}$ mentioned in Section 1, whose average energy E_k' is less than, but nearly equal to, the eigenvalue E_k we are seeking. If the correction bounded by (1) is sufficiently small, it will be a good approximation to set

$$E_k = E_k' + \sum_{nlm\nu} \frac{|[\varphi_k', \{H - E_k'\} u_{nlm}(\mathbf{r} - \mathbf{R}_\nu)]|^2}{E_k' - E_{nl}}. \tag{15}$$

For brevity only matrix elements of the form $[\chi_k, Hu_{nl;k'}(\mathbf{r}-\mathbf{R}_\nu)]$ will be given here; the summation on m in (15) is easily expressed in terms of these when $l=0$ or 1:

$$\exp(i\mathbf{k}'\cdot\mathbf{R}_\nu) N^{\frac{1}{2}} [\chi_{k'}, Hu_{nl;\,k}(\mathbf{r}-\mathbf{R}_\nu)] = I_{nl}^*(\mathbf{k}'; \mathbf{k}; \nu) - \sum_{n'l'} A_{n'l'}(k') F(n'l'\mathbf{k}'\nu, nl\mathbf{k}\nu)$$

$$- \sum_{n'l'} A_{n'l'}(k') \sum_{\nu' \neq \nu} [E_{nl} S(n'l'\mathbf{k}'\nu', nl\mathbf{k}\nu) + F(n'l'\mathbf{k}'\nu', nl\mathbf{k}\nu)] \exp[i\mathbf{k}'\cdot(\mathbf{R}_\nu - \mathbf{R}_{\nu'})] \tag{16}$$

$$\exp(i\mathbf{k}'\cdot\mathbf{R}_\nu) N^{\frac{1}{2}} [\chi_{k'}, u_{nl;\,k}(\mathbf{r}-\mathbf{R}_\nu)] = -\sum_{n'l'} A_{n'l'}(k) \sum_{\nu' \neq \nu} S(n'l'\mathbf{k}'\nu', nl\mathbf{k}\nu) \exp[i\mathbf{k}'\cdot(\mathbf{R}_\nu - \mathbf{R}_{\nu'})]. \tag{17}$$

When core functions on different atoms are so constructed that they do not overlap, (17) and the last term of (16) vanish.

3. Remarks and Discussion

(1) Choice of U and evaluation of $U[\mathbf{K}]$. In metallic crystals it is convenient and accurate to assume that U is a summation of potentials $v(\mathbf{r}-\mathbf{R}_\nu)$ due to the different ions, plus the potential due to a homogeneous free electron distribution. In such case $U[\mathbf{K}]$ can be reduced for $\mathbf{K}\neq 0$ to

$$U[\mathbf{K}] = \frac{3}{Kr_s^3} \left(\frac{1}{n} \sum_{\nu}^{\text{cell}} \exp(i\mathbf{K}\cdot\mathbf{R}_\nu) \right) \left(-\frac{2X}{K} - \int_0^\infty r \left[v(r) + \frac{2X}{r} \right] \sin Kr dr \right). \tag{18}$$

where n is the number of atoms in a unit cell and X is the number of valence electrons per atom, so that $v(r) \sim -2X/r$ for large r. The most convenient choice for the zero of U is that made by Wigner and Seitz: the average value of U over a unit cell is defined to equal the average over an s sphere of the potential due to the ion at its center and an amount of negative charge sufficient to neutralize it, uniformly distributed throughout the s sphere. Thus

$$U[0] = \frac{2.4}{r_s} + \frac{3}{r_s^3} \int_0^{r_s} r^2 v(r) dr, \tag{19}$$

provided $v(r) = -2X/r$ for $r \geqslant r_s$.

(2) Choice of V. The perturbation in (15) due to the core states can be made quite small by choosing a V which resembles U very closely; for the above choice of U we might use

$$\begin{aligned} V &= v(r) + \frac{3X}{r_0} - \frac{Xr^2}{r_0^3} \quad \text{for } r \leqslant r_0, \\ &= 0 \quad \text{for } r \geqslant r_0. \end{aligned} \tag{20}$$

Thus for $r \leqslant r_0$, V coincides with the spherical average of U[11] when r_s has the value r_0. The disadvantage of such a choice is that the u_{nlm} extend to infinity, so that the overlap integrals (10), (11), and (12) are difficult to evaluate. When the only core functions are the 1s, it is not hard to evaluate the S integrals exactly, and rough approximations can be obtained to the other integrals which are adequate for many purposes (see below). But when there are core functions with $l>0$, or when the s functions are too spread out for these rough values to suffice, the evaluation of the overlap

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[11] This is strictly true only if the small correction of Appendix II, reference 1, is neglected.

integrals seems hopelessly difficult. In such cases it will probably be best to construct u_{nlm} functions which vanish at less than half the distance between neighboring atoms; this of course means that V must become infinite.

If we require $u_{nlm}(r_1, \theta, \varphi)=0$, it is desirable that $\partial u_{nlm}/\partial r$ vanish at $r=r_1$ also, since we want the Fourier expansion of (3) to converge rapidly. At the same time the right of (1) must be kept small. If $u_{nlm}^{(0)}$ are the eigenfunctions in the field (20), the Bloch waves constructed from them will resemble the true core eigenfunctions much more closely than those constructed from the present u_{nlm}. So remembering that $u_{nlm}^{(0)}$ and u_{nlm} are assumed normalized we have, for the average over the $(2l+1)$ bands arising from the atomic states of given n and l,

$$\mathrm{Av}[1-|(\varphi_{jk}, \varphi_{jk}')|^2]\approx 1-|(u_{nlm}^{(0)}, u_{nlm})|^2=\tfrac{1}{2}\int_\infty |u_{nlm}^{(0)}-u_{nlm}|^2 d\tau$$

$$=\tfrac{1}{2}\int_0^\infty (P_{nl}^{(0)}-P_{nl})^2 dr>\tfrac{1}{2}\int_{r_1}^\infty P_{nl}^{(0)2}dr, \quad (21)$$

where

$$u_{nlm}=\frac{P_{nlm}(r)\,Y_{lm}(\theta, \varphi)}{r}, \qquad \int_0^\infty P_{nl}^2 dr=1, \quad \text{etc.}$$

If P_{nl} is defined to be a multiple of $P_{nl}^{(0)}$ for $r\leqslant r_2$, and a simple analytic function of r (e.g., a polynomial) for $r_2\leqslant r\leqslant r_1$, so chosen that P_{nl} and P_{nl}' are continuous at r_2 and vanish at r_1, the left of (21) will usually come out of the order of 3 or 4 times the integral

$$\tfrac{1}{2}\int_{r_1}^\infty P_{nl}^{(0)2}dr;$$

from this and (1) one can estimate in advance whether or not (15) will suffice for the core perturbation.

(3) Evaluation of the S integrals. If the field (20) is used, we may write

$$P_{1s}(r)=(4\pi)^{\frac{1}{2}} r u_{1s}(r)=B\exp[-(-E)_{1s}^{\frac{1}{2}}r]-\gamma(r), \quad (22)$$

where $\gamma(r)$ vanishes for $r\geqslant r_0$. The average of $(1/r)\exp[-(-E)_{1s}^{\frac{1}{2}}r]$ over the surface of a sphere of radius ρ whose center is at a distance d from the origin is

$$\frac{\exp[-(-E)_{1s}^{\frac{1}{2}}d]}{d(-E_{1s})^{\frac{1}{2}}}\,\frac{\sinh(-E_{1s})^{\frac{1}{2}}\rho}{\rho}.$$

From this and by neglecting the overlapping of γ's on different atoms the S integral can be reduced to an expression containing a single radial integral:

$$S(\nu, \nu')\equiv S(1s\mathbf{k}\nu, 1s\mathbf{k}'\nu')=\frac{\exp[-(-E)_{1s}^{\frac{1}{2}}|\mathbf{R}_\nu-\mathbf{R}_{\nu'}|]}{2(-E)_{1s}^{\frac{1}{2}}}\left[B^2-\frac{2B}{|\mathbf{R}_\nu-\mathbf{R}_{\nu'}|}\int_0^\infty \gamma(r)\sinh[(-E)_{1s}^{\frac{1}{2}}r]dr\right]. \quad (23)$$

(4) The I_{nl} and F integrals. If the field (20) is used, and the field U is as described above, the contributions to I_{nl} and to the F integrals for $\nu=\nu'$ may be divided into two parts: that from inside a radius r_0 and that from outside r_0. The first of these is the more important when r_s differs appreciably from r_0. This suggests that we may approximate U by $v(r)+3X/r_s-Xr^2/r_s^3$, which is its spherical average[12] for $r\leqslant r_s$, and approximately its spherical average for somewhat greater values of r. This approximation should be very good indeed for the F integral with $\nu=\nu'$, less so for the I_{nl}.

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[12] This is strictly true only if the small correction of Appendix II, reference 1, is neglected.

If this is inserted in (10) we have, for a 1s function

$$I_{1s}(\mathbf{k})\equiv I_{1s}(\mathbf{k};\mathbf{k}';\nu)\approx\int_{\infty}\frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}u_{1s}(r)\left[3X\left(\frac{1}{r_s}-\frac{1}{r_0}\right)-Xr^2\left(\frac{1}{r_s{}^3}-\frac{1}{r_0{}^3}\right)\right]d\tau$$
$$+\int_{r>r_0}\frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(\Omega_0)^{\frac{1}{2}}}u_{1s}(r)\left[-\frac{2X}{r}+\frac{3X}{r_0}-\frac{Xr^2}{r_0{}^3}\right]d\tau. \tag{24}$$

The first integral in (24) is

$$3X\left(\frac{1}{r_s}-\frac{1}{r_0}\right)A_{1s}(k)-X\left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}}\left(\frac{1}{r_s{}^3}-\frac{1}{r_0{}^3}\right)\int_0^\infty r^2\frac{\sin kr}{k}P_{1s}(r)dr. \tag{25}$$

The second integral is small and varies less rapidly with r_s: for $\mathbf{k}=0$ it may be reduced by using (22) to

$$-6X\left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}}\frac{P_{1s}(r_0)}{(-E_{1s})^{\frac{3}{4}}r_0{}^2}\left[1+\frac{1}{r_0(-E_{1s})^{\frac{1}{2}}}\right]. \tag{26}$$

The F integrals with $\nu\neq\nu'$ are much less important than the other overlap integrals, and may for many purposes be neglected. Finally, when core functions are used which go to zero at $r=r_1$, as described above, the I_{nl} and F integrals with $\nu=\nu'$ can be calculated with any desired precision by expanding $\exp(i\mathbf{k}\cdot\mathbf{r})$ and $(U-V)u_{nl;k'}$ in spherical harmonics; if this is done they reduce to a number of radial integrals to be calculated numerically.

(5) Interpolation in the calculation of $U[\mathbf{K}]$ and $A_{nl}(k)$. When calculations are made for several values of the lattice constant, the integral occurring in (18) is needed for a great many values of K; an integral of similar form is needed also for $A_{nl}(k)$. The values of the integral are most conveniently found by interpolation between directly calculated values for a few values of K. In making interpolations or extrapolations of this sort use can often be made of an analytic function which fits the directly calculated points fairly well and has the correct asymptotic behavior. Such a function can be obtained, for example, by setting a "screened potential"

$$v(r)=-\frac{2X-2Z\exp(-\sigma r)}{r}\text{ in (18).} \tag{27}$$

This gives

$$\int_0^\infty r\left[v(r)+\frac{2X}{r}\right]\sin Kr dr=-\frac{2ZK}{K^2+\sigma^2}. \tag{28}$$

Similarly if we set $P_{1s}=2b^{\frac{3}{2}}re^{-br}$ (the form for a hydrogenic eigenfunction) we have

$$A_{1s}(k)=\left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}}\frac{4b^{5/2}}{(k^2+b^2)^2}. \tag{29}$$

(6) Simplification for eigenfunctions of certain symmetry types. It often happens that eigenfunctions occur, in or near the occupied portion of the valence electron band, which belong to symmetry types which do not occur in the core bands. For example a number of eigenfunctions φ_k occur for lithium slightly above the Fermi surface, which are odd under the operation of inversion about any nucleus. Since all functions of the corresponding reduced wave vector in the 1s band are even under inversion, each such φ_k is orthogonal to the core by virtue of its symmetry alone. Any linear combination of plane waves having the given symmetry type will thus be orthogonal to the true core functions, and also to the approximate core functions constructed from the u_{nlm}. So all we need to do is to set up a secular equation relative to combinations of plane waves belonging to this symmetry type; this secular equation will be the same as if the corresponding linear combination of χ functions had been used instead of plane waves, because the contributions from all terms in (13) beyond the first two, and from all terms in (14) beyond the first, would add up to zero. Thus to calculate energies of eigenfunctions of such symmetry types only the Fourier coefficients $U[\mathbf{K}]$ are needed. In most cases it will suffice to use the second-order Schrödinger perturbation, and it can be shown that the second-order perturbations due to successive

plane wave combinations of the given symmetry will decrease rapidly. This is most easily seen by considering a particular example. Suppose that $\chi_1^- = (2/\Omega)^{\frac{1}{2}} \sin \mathbf{k}\cdot\mathbf{r}$ is a plane wave combination of the given symmetry type (this occurs for some of the lithium eigenfunctions mentioned above). The matrix element of H connecting χ_1^- with $(1/\Omega)^{\frac{1}{2}} \exp [i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}]$ will be the difference of two Fourier coefficients of the potential; for very large K it will be of order $1/K^3$, since $U[\mathbf{K}]$ is of order $1/K^2$, and even for smaller K's it will be much less than either Fourier coefficient alone. The second-order perturbation series will thus converge extremely rapidly. This in itself is of course no guarantee that this series gives a good approximation to the eigenvalue: if we were to consider functions of the symmetry type of $\chi_1^+ = (2/\Omega)^{\frac{1}{2}} \cos \mathbf{k}\cdot\mathbf{r}$, the second-order perturbation series would converge—less rapidly than above, but still fairly rapidly—to an energy value far below that of the valence electron eigenfunction of the same symmetry type (because χ_1^+ is not orthogonal to the core functions of the $1s$ band). However, it is likely that when we are working with functions of the symmetry type of χ_1^- the off-diagonal matrix elements in the secular determinant will decrease so rapidly to zero that we can set a very small upper bound to the difference between the true eigenvalue and the energy yielded by the second-order perturbations.

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Optical and Magnetic Properties of Magnetite Suspensions

Surface Magnetization in Ferromagnetic Crystals

L. W. McKEEHAN
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

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A magneto-optic effect discovered by W. R. Grove in 1845 is suggested as explaining, in part, at least, peculiarities of ferromagnetic colloid patterns on ferromagnetic crystal surfaces.

C. W. HEAPS[1] has recently investigated the optical transparency of a suspension of magnetite in oil, as modified by magnetic fields applied parallel to the light path or at right angles thereto. He explains the effects as due to changes in the area obstructed by rectilinear rows of particles, magnetically linked, when these are turned from random directions so as to lie parallel with the applied field. A field intensity of only a few oersteds produced nearly maximal effect.

The increase in transparency of a suspension of magnetite in water when a magnetic field is applied parallel to the light path was first demonstrated by W. R. Grove at a social meeting of the Royal Institution, in London, on January 8, 1845. Since the report is short, relatively inaccessible, and ignored for so long a time, it is quoted in full.[2]

"Jan. 8, 1845.—Prof. Grove communicated to the proprietors at this their first *soirée* for the season, some of the leading discoveries in physical science during the past year. Of electrical subjects, M. Matteucci's researches were described; with experimental illustrations; as also the magnetic note. In reference to the latter, Mr. Grove detailed a curious experiment that had occurred to him, and which bore greatly on the subject. A glass tube open at the ends, but protected along its length with a copper jacket, was filled

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[1] C. W. Heaps, Phys. Rev. **57**, 528–531 (1940). See also Q. Majorana, Accad. Lincei, Rendiconti [6a] **29**, 11–14 (1939) January; Ricerca Scient. **10**, 783–789 (1939), September.

[2] C. V. Walker, Elec. Mag. **1**, 601 (1845), April.