ues by Natale and Rudnick[2] and by Dugdale and Gugan.[18] There is a significant discrepancy between the two sets of experimental values. In Fig. 4, we plot ρ_2 obtained, as described above, from the ultrasonic attenuation at three different frequencies and compare it with the measured ρ. Here, we have used the value of the conversion factor C [Eq. (9)] in Table II under the column "Expt." In Table III, we list the ratio of τ_2/τ_1 from experimental measurements.

The temperature dependence of the measured τ_2/τ_1 roughly follows the theoretical prediction. It is small at low temperature, rises to a maximum in the neighborhood of about 8 °K and then diminishes slightly. However, even taking the largest calculated set of τ_2/τ_1, which comes from Bardeen's electron-phonon matrix element, and allowing for the uncertainty in the experimental values due to the uncertainty in the elastic constants of the polycrystal, we find that there is significant disagreement. This discrepancy cannot be ascribed to many-body effects since the attenuation formula which we have used correctly includes all such effects, nor can the discrepancy be ascribed to uncertainties in the phonon spectrum since we have used the phonon frequencies measured at 9 °K by Cowley *et al.*[19] It would clearly be desirable to have more measurements of the ultrasonic attenuation and electrical resistivity at low temperatures, preferably on single crystals, in a number of simple metals. Should the discrepancy persist between the calculated and experimental values, we may have to question the validity of our Kohler solution of the transport equation and the concomitant Matthiessen's rule and, perhaps, also the equivalence of the pseudopotentials needed to fit the Fermi surface and the transport coefficients.

---

*Work supported in part by the National Science Foundation, Grant No. GP-14912.

[1] M. S. Steinberg, Phys. Rev. 109, 1486 (1958); A. B. Bhatia and R. A. Moore, *ibid.* 121, 1075 (1961).

[2] G. G. Natale and I. Rudnick, Phys. Rev. 167, 687 (1968).

[3] For more details, see L. J. Sham, *Modern Solid State Physics, Vol. II, Phonons and their Interactions*, edited by R. H. Enns and R. R. Haering (Gordon and Breach, London, 1969), p. 189.

[4] T. M. Rice, Phys. Rev. 175, 858 (1968).

[5] J. Bardeen, Phys. Rev. 52, 688 (1937).

[6] A. Hasegawa, J. Phys. Soc. Japan 19, 504 (1964).

[7] There is some discrepancy between our results for the resistivity as a function of temperature and Hasegawa's. This is due to a different and more realistic treatment of the phonon spectrum by us.

[8] N. W. Ashcroft, Phys. Letters 23, 48 (1966).

[9] M. J. G. Lee and L. M. Falicov, Proc. Roy. Soc. (London) A314, 319 (1968).

[10] J. C. Garland and R. Bowers, Phys. Rev. Letters 21, 1007 (1968).

[11] For a review of various averaging methods used, see H. G. Huntington, Solid State Phys. 7, 317 (1958).

[12] E. Kroner, Z. Physik 151, 504 (1958).

[13] Actually, Kroner gave two methods, both of which yield the same values for potassium.

[14] W. R. Marquardt and J. Trivisonno, J. Phys. Chem. Solids 26, 273 (1965).

[15] D. H. Filson, Phys. Rev. 115, 1516 (1959).

[16] It is obtained by a method given by J. L. Davis, Trans. Soc. Rheol. 10, 449 (1966). We are grateful to Dr. N. C. Huang for this reference.

[17] M. J. Rice and L. J. Sham, Phys. Letters 28A, 481 (1969).

[18] J. S. Dugdale and D. Gugan, Proc. Roy. Soc. (London) A270, 186 (1962).

[19] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. 150, 487 (1966).

PHYSICAL REVIEW B VOLUME 1, NUMBER 12 15 JUNE 1970

One-Electron Potential-Energy Functions for Calculating Wave Functions at Solid Surfaces*

D. S. Boudreaux

Department of Physics, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

(Received 25 August 1969)

An expression is given for the potential energy seen by an electron near a crystal surface including both potential periodicity and exchange and correlation effects among electrons. The possible usage of such a function for determining wave functions and charge distributions is discussed.

I. INTRODUCTION

The solution to the wave mechanical problem describing electrons near solid surfaces has been sought for a number of years. For semiconductors and a few problems dealing with metals, the concept of the step truncation of the bulk potential-energy function has become a useful approximation in discussion of interface and surface effects.[1] Most surface properties of metals, however, are considerably more complicated. Bardeen[2] was the first to discuss the quantum-mechanical details of the solution to this problem. Other authors[3,4] share with Bardeen the assumption that the solid is adequately represented by a model with free electrons in a smeared-out background of positive charge, which background simply disappears at the surface. All of these authors have recognized the importance of the many-electron exchange and correlation contributions to the surface potential-energy function. Smith,[5] Lang,[6] and Bennett and Duke[7] have recently published a self-consistent calculation of the charge distribution at a metallic interface; they also use the "jellium" model for the metals.

There is a class of problems for which previous models are of limited use. For example, the electronic charge "redistribution" responsible for the formation of surface double layers is very dependent upon the arrangement of positive charge centers in the surface planes.[8] It is also clear that the potential periodicity in the surface plane will be critically important in discussing the bonding or interaction of a foreign atom with that plane. It is not obvious, at the present time, how to carry out a complete calculation of surface charge distributions including fully both crystallinity (i. e., potential periodicity over a half-space) and exchange and correlation effects. Thus this paper takes the following viewpoint: An expression is sought for the potential energy that an electron sees at a surface; it is desirable to include fully the effect of solid crystallinity and to include, in the best way possible, the effects of electron-electron exchange and correlation. This is exactly opposite from the viewpoint taken by others[2-7] who include the electron-electron effects in the best way possible and approximate the effects of the periodic lattice by ignoring them completely.

II. SURFACE MODEL AND ITS POTENTIAL-ENERGY FUNCTION

Consider a solid made up of $N+1$ layers, each of which is infinite in extent. Suppose the set of potential-energy functions describing the interactions of an electron with each lattice site are given. The problem is to compute an expression for the total potential-energy function which is valid throughout all space. Although not required, the discussion is simplified by restricting attention to a set of identical, attractive potential wells centered on each site with a given number of electrons per site in the solid. Further, consider that the spacing of ion sites is the same near the surface as in the bulk; removal of this restriction will be discussed later.

The total interaction of an electron with the ion cores can be written as

$$V_i(\vec{R}) = \sum_s V(\vec{R} - \vec{R}_s), \tag{1}$$

where $\vec{R}_s$ is the position vector of the sth site and the sum is over potentials centered at each site in the solid. The Fourier transform of this is

$$V_i(\vec{K}) = \Omega^{-1} \int d\vec{R} \sum_s V(\vec{R} - \vec{R}_s)\, e^{-i\vec{K}\cdot\vec{R}}, \tag{2}$$

where Ω is the volume of a box in which the Fourier transformation is done. Rewritting,

$$V_i(\vec{K}) = \Omega^{-1} \sum_s e^{-i\vec{K}\cdot\vec{R}_s} \int d(\vec{R} - \vec{R}_s) \times V(\vec{R} - \vec{R}_s)\, e^{-i\vec{K}\cdot(\vec{R}-\vec{R}_s)}. \tag{3}$$

And using the fact that each V is the same,

$$V_i(\vec{K}) = \Omega^{-1} \sum_s e^{-i\vec{K}\cdot\vec{R}_s}\, V(\vec{K}) \tag{4}$$

$$\equiv \Omega^{-1} S(\vec{K})\, V(\vec{K})\,; \tag{5}$$

$S(\vec{K})$ is called a structure factor.

It is in this representation that one usually seeks to include the effects of the other conduction electrons by means of a static dielectric function.[9] The total potential energy is written

$$V_T(\vec{K}) = \Omega^{-1} S(\vec{K})\, V(\vec{K}) / \epsilon(\vec{K})\,; \tag{6}$$

such an approximation has been very useful and successful in solid-state physics. There are many different approximations to ϵ, and one could conceivably use the "best" one.[10]

It is desired to compute

$$V_T(\vec{R}) = [\Omega/(2\pi)^3] \int d\vec{K}\, e^{i\vec{K}\cdot\vec{R}}\, V_T(\vec{K})\,. \tag{7}$$

First consider

$$S(\vec{K}) = \sum_s e^{i\vec{K}\cdot\vec{R}_s}\,. \tag{8}$$

Let reciprocal space be spanned by unit vectors such that two of them lie in the plane of the surface and one is normal to it. Breaking the sum into two parts

$$S(\vec{K}) = \sum_{l=0}^{N} e^{-i\vec{K}\cdot Z_l \hat{n}} \sum_a e^{-i\vec{K}\cdot\vec{R}_a(l)}\,; \tag{9}$$

Z_l is the depth of the lth layer, $\hat{n}$ is the normal to the surface, $\vec{r}_a(l)$ describes the position of the ath atom in the lth layer. For the most common crystal types and for the low rational-index faces of these, it is sufficient to write

$$\vec{r}_a(l) = \vec{r}_a + l\vec{d}\,; \tag{10}$$

here $\vec{d}$ is the displacement of a given atom in going from the $(l-1)$th to lth layer plane. This simplifies and makes definite the mathematics to follow, although there is no requirement that a crystal be of this type. Substituting

$$S(\vec{K}) = \sum_{l=0}^{N} e^{-i\vec{K}\cdot(\vec{Z}_l + l\vec{d})} \sum_{a} e^{-i\vec{K}\cdot\vec{r}_a}, \tag{11}$$

it is well known[11] that

$$\begin{aligned} \textstyle\sum_a e^{-i\vec{K}\cdot\vec{r}_a} &= N_a\,, && \text{if } \vec{K}=\vec{q}_{\parallel} \\ &= O(1/N_a), && \text{otherwise} \end{aligned} \tag{12}$$

where $\vec{q}_{\parallel}$ is a reciprocal-lattice vector of the two-dimensional net planes of N_a atoms,

$$S(K_z, \vec{q}_{\parallel}) = N_a \sum_{l=0}^{N} e^{-i(K_z Z_l + l\vec{q}_{\parallel}\cdot\vec{d})}\,. \tag{13}$$

For layers equally spaced with spacing c,

$$Z_l = l\,c, \tag{14}$$

so that

$$S(K_z, \vec{q}_{\parallel}) = N_a \sum_{l=0}^{N} e^{-il(K_z c + \vec{q}_{\parallel}\cdot\vec{d})}\,, \tag{15}$$

$$S(K_z, \vec{q}_{\parallel}) = N_a \frac{1-e^{-iN(K_z c + \vec{q}_{\parallel}\cdot\vec{d})}}{1-e^{-i(K_z c + \vec{q}_{\parallel}\cdot\vec{d})}}\,. \tag{16}$$

Thus Eq. (7) becomes

$$V_T(\vec{R}) = \textstyle\sum_{\vec{q}_{\parallel}} \displaystyle\frac{L}{2\pi}\int_{-\infty}^{+\infty} dK_z\, e^{i(K_z Z + \vec{q}_{\parallel}\cdot\vec{r})} \times \frac{1}{LA}\,\frac{1-e^{-iN(K_z c + \vec{q}_{\parallel}\cdot\vec{d})}}{1-e^{-i(K_z c + \vec{q}_{\parallel}\cdot\vec{d})}}\,\frac{V(\vec{K})}{\epsilon(\vec{K})}\,. \tag{17}$$

The integral over $d\vec{K}_{\parallel}$ has been converted into a sum on discrete $\vec{q}_{\parallel}$; A is the area of the unit two-dimensional mesh, and L is the length of the crystal. K_z is not quantized by periodic boundary conditions so the integral must be performed.

Examining the integrand for poles one finds the structure factor to contain none, for its largest value is $N_a(N+1)$ when the denominator vanishes. Poles of $V(\vec{K})/\epsilon(\vec{K})$ depend on the precise analytical expression but suffice it to say at this point that correct expressions contain no poles on the real K_z axis. One is then free to displace the path of integration infinitesimally downward from the real axis. Rewritting the integral as the sum of two parts and rationalizing the denominator,

$$V_T(\vec{R}) = \frac{-i}{4\pi A}\left(\sum_{\vec{q}_{\parallel}} e^{i\vec{q}_{\parallel}\cdot(\vec{r}+\vec{d}/2)} \times\int_{-\infty-i\delta}^{+\infty-i\delta} dK_z\,\frac{e^{iK_z(z+c/2)}}{\sin(\frac{1}{2}(K_z c + \vec{q}_{\parallel}\cdot\vec{d}))}\right.$$

$$\left.\times\frac{V(\vec{K})}{\epsilon(\vec{K})} + \sum_{\vec{q}_{\parallel}} e^{i\vec{q}_{\parallel}\cdot(\vec{r}+\vec{d}/2-N\vec{d})} \times\int_{-\infty-i\delta}^{+\infty-i\delta} dK_z\,\frac{e^{iK_z(z+c/2-Nc)}}{\sin(\frac{1}{2}(K_z c + \vec{q}_{\parallel}\cdot\vec{d}))}\,\frac{V(\vec{K})}{\epsilon(\vec{K})}\right)\,. \tag{18}$$

Now besides the poles of $V(K)/\epsilon(K)$ there are poles in each integrand along the real axis at

$$K_z = (1/c)(2\pi n - \vec{q}_{\parallel}\cdot\vec{d}), \tag{19}$$

where n is an integer.

The integration contour can be closed in the upper half-plane for $z > -\frac{1}{2}c$ in the first integral and for $z > (N-\frac{1}{2})c$ in the second. The contour can be closed in the lower half-plane for $z > \frac{1}{2}c$ in the first and for $z < (N-\frac{1}{2})c$ in the second. Call the poles on the real axis B type (B for bulk) and other poles S type (S for surface); the reason being that complex K_z poles will correspond to exponentially decaying contributions to the sum of residues, decaying from the surface at $z = -\frac{1}{2}c$ (S_0 type) or at $z = (N-\frac{1}{2})c$ (S_L type).[12]

Consider three regions, and the contributions to the integral in each: (i) $Z < -\frac{1}{2}c$, S_0- and S_L-type contributions only; (ii) $-\frac{1}{2}c < Z < (N+\frac{1}{2})c$, S_0-, S_L-, and B-type contributions; (iii) $Z > (N+\frac{1}{2})c$, S_0- and S_L-type contributions (the B type cancel). Being interested in the form of the potential in the neighborhood of one surface at a time, it is possible to ignore the S_L-type contributions near the surface at $Z = -\frac{1}{2}c$. This is equivalent to ignoring the second of the integrals in Eq. (18).

We have thus been successful in exhibiting a surface in the model which occurs naturally at a plane halfway between atom layers. The shape of the potential-energy function near this plane is determined wholly by the poles of $V(\vec{K})/\epsilon(\vec{K})$. In fact, since $V(\vec{K})$ itself has only a pole at $K=0$ which is effectively eliminated by $\epsilon(\vec{K})$, all of the structure of the surface barrier through a given point $\vec{r}$ in the surface plane can be seen to arise from the analytic form of $\epsilon(\vec{K})$. This is important, for ϵ carries all of the information about exchange and correlation effects which, it has been agreed,[2-7] are responsible for the shape of the barrier.

III. USAGE AND DISCUSSION

The representation in which the above expression is most useful results from substituting the expansion

$$\psi_{\vec{k}}(\vec{R}) = \textstyle\sum_{\vec{q}_{\parallel}} \psi_{\vec{k}}^{\vec{q}_{\parallel}}(z)\, e^{i(\vec{k}+\vec{q}_{\parallel})\cdot\vec{r}} \tag{20}$$

into the Schrödinger equation. The resulting expression is

$$\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi_{\vec{k}}^{\vec{q}_{\parallel}}(z) = \left(\frac{\hbar^2}{2m}(\vec{k}+\vec{q}_{\parallel})^2 - E\right)\psi_{\vec{k}}^{\vec{q}_{\parallel}}(z)$$

$$+\sum_{\vec{q}_{\parallel}'} V_T^{\vec{q}-\vec{q}_{\parallel}'}(z)\psi_{\vec{k}}^{\vec{q}_{\parallel}}(z). \tag{21}$$

Here $\vec{k}$ is the wave vector characterizing the electron's momentum state parallel to the surface, E is the energy, and

$$V_T^{\vec{q}_{\parallel}}(z) = (1/\mathcal{A}) \int d\vec{r}\; V_T(\vec{R})e^{-i\vec{q}_{\parallel}\cdot\vec{r}} \;; \tag{22}$$

$\mathcal{A}$ is the area of the surface plane and $\vec{r}$ is the projection of $\vec{R}$ on that plane.

A numerical integration will produce the solution of the set of Eqs. (21); for this purpose it is convenient to think of the $\psi_{\vec{k}}^{\vec{q}_{\parallel}}(z)$ as forming a column vector $\vec{\psi}_{\vec{k}}(z)$. The Schrödinger equation can then be written (in a.u.) as

$$\frac{d^2}{dz^2}\,\vec{\psi}_{\vec{k}} = A\vec{\psi}_{\vec{k}} \;, \tag{23}$$

a form which has been studied,[13] and for which numerical methods exist.[14] It remains to discuss the boundary conditions. If integration is begun at a point inside the crystal where the surface terms make practically no contribution to the potential, the correct starting wave function will be the Bloch state (or linear combination of Bloch states) at the particular $\vec{k}$ and E of interest; there are always at least two of them at $\pm k_{\perp}$. It is necessary to note further that the relative phase of the starting Bloch functions is important, for the remaining boundary condition is that the wave function go to zero outside the crystal; thus the choice of phase is not arbitrary. It should be recognized that when using a perfect crystal as a model, the Bloch wave state is only an approximation to the correct boundary condition, for the presence of a crystal surface causes mixing among Bloch states; however this mixing is proportional to the surface area to volume ratio and is usually neglected; in a realistic model of a solid an electron approaching a surface has no "memory" of its last sojourn in that region and is correctly represented by a single Bloch wave.

The ideal way of proceeding would be to use a given potential to determine the conduction electron wave functions, and consequently the charge density. Compute an $\epsilon(\vec{K})$ based on this charge distribution, then recompute the wave functions, and cycle to self-consistency. Calculations with this in mind are now in progress.

It remains to comment on the possibility that (i) the lattice spacing may be different from the bulk in the last few atomic layers and (ii) that the potential-energy functions centered at such sites may be different. In such a situation, it would be possible to sum the last few layers under discussion as two-dimensional arrays and add them appropriately to a term such as Eq. (18) for the rest of the crystal. There may, however, exist more convenient methods of handling this problem.

Note added in proof. One can effect the same many-body approximations as Refs. 6 and 7 by choosing in Eq. (6)

$$[\epsilon(\vec{K})]^{-1} = 1 + [V_{es}(\vec{K}) + V_{xc}(\vec{K})]/V_T(\vec{K});$$

$V_{es}(\vec{K})$ and $V_{xc}(\vec{K})$ are Fourier transforms of functions defined by Lang.[6]

---

*Work supported by the U. S. Air Force, Office of Scientific Research Grant No. AFOSR-1709-69.

[1] A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965), Chaps. 4 and 5.

[2] J. Bardeen, Phys. Rev. 49, 653 (1936).

[3] T. L. Loucks and P. H. Cutler, J. Phys. Chem. Solids 25, 105 (1964).

[4] R. W. Davies, Surface Sci. 11, 419 (1968).

[5] J. R. Smith, Phys. Rev. 181, 522 (1969).

[6] N. D. Lang, Solid State Commun. 7, 1047 (1969).

[7] A. J. Bennett and C. B. Duke, Phys. Rev. 160, 541 (1967); 162, 578 (1967); and *Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969).

[8] R. Smoluchowski, Phys. Rev. 60, 661 (1941).

[9] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U. P., New York, 1964), Chap. 5.

[10] L. J. Sham [thesis, Cambridge University, 1963 (unpublished)] has attempted to include exchange in the dielectric function. See also V. Heine and I. Aberenkov, Phil. Mag. 9, 451 (1964).

[11] Reference 9, p. 55.

[12] Others have used similar methods of simulating a surface, e.g., see P. P. Ewald and H. J. Juretschke, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer (University of Chicago Press, Chicago, 1953), p. 82; also C. H. Hodges, Phil. Mag. 15, 371 (1967).

[13] P. M. Marcus and D. W. Jepsen, Phys. Rev. Letters 20, 925 (1968).

[14] P. M. Marcus and D. W. Jepsen (unpublished).