PHYSICAL REVIEW VOLUME 92, NUMBER 5 DECEMBER 1, 1953

Exchange Potential in the Surface Region of a Free-Electron Metal*

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(Received July 28, 1953)

The weighted average exchange charge and the average exchange potential proposed by Slater have been evaluated explicitly in the surface region of a free-electron gas bounded by an infinite barrier. It is found that in the surface the exchange hole ceases to accompany its electron and that the exchange potential beyond the surface is essentially that due to an exchange hole stationary in the surface region. This interpretation explains the failure of the statistical approximation to the exchange potential at low electron densities. At high densities, the statistical approximation agrees closely with the average exchange potential. In the surface region the normally spherically symmetrical exchange hole becomes distorted. This change of shape is discussed qualitatively for electrons in the immediate surface region and electrons very far from the surface of a distribution bounded by a finite low barrier. The exchange surface energy of this model of a metal surface is 96 ergs/cm^2 for an interior density equal to that of sodium.

I. INTRODUCTION

If the Hartree-Fock equations for the best one-electron wave functions of electrons moving in the field of atomic nuclei are written in the standard form of one-electron Schrödinger equations, the potential energy term includes an exchange energy contribution which measures the effect of a spin-dependent repulsion between electrons.[1] As a result of this interaction, the density of all other electrons of like spin is reduced in the neighborhood of a given electron. The exchange potential is essentially the potential of this local deficiency of charge at the location of the electron under consideration.[2]

The general expression for the exchange potential for an electron represented by a wave function u_i and located at $\mathbf{r}$ is given by

$$-\frac{e^2}{u_i^*(\mathbf{r})u_i(\mathbf{r})}\sum_k \int d\mathbf{r}_1 \frac{u_i^*(\mathbf{r})u_k^*(\mathbf{r}_1)u_k(\mathbf{r})u_i(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|}, \quad (1)$$

where the summation includes all wave functions with spin parallel to u_i. The expression (1) cannot be readily evaluated except for very simple wave functions. In metals in which the ion cores are small and far apart the exchange potential is usually assumed to be the same as that of a free-electron gas of the proper average density, and is independent of position. The exchange potential of such a free-electron gas of density n, averaged over all electrons, has the value

$$-3e^2(3n/8\pi)^{\frac{1}{3}}. \quad (2)$$

It has often been pointed out that this is approximately the potential at the center of a uniformly charged sphere of density $n/2$ (i.e., one kind of spin only) and radius

$$r_0=(3/2\pi n)^{\frac{1}{3}}. \quad (3)$$

However, when there are large variations in the electron density, the exchange potential becomes a complicated function of position and cannot usually be represented in this simple descriptive manner. In this paper we investigate the behavior of the exchange potential in the region of rapidly changing electron density in the surface region of a free-electron metal. For this model some explicit calculations on exchange potentials and exchange charges can be carried out and can be used to illustrate the properties of these quantities in surface regions of electron distributions. Various approximations to the surface exchange potential are compared and discussed in terms of the physical interpretation of the exchange potential. In addition, the explicit calculations are applied to evaluate the exchange energy contribution to the surface energy of such a free-electron metal.

II. APPROXIMATIONS TO THE SURFACE EXCHANGE POTENTIAL

For use in a self-consistent calculation of the surface charge distribution of a free-electron metal, Bardeen[3] has evaluated the exact exchange potential (1) of a free-electron gas bounded by an infinite and a finite step barrier, at the position of the barrier. Since the two barriers of different height are located at different positions with respect to the charge distribution, this procedure yielded two points for the potential in the surface. The potential throughout the surface region was then constructed by connecting the two calculated points by a smooth line going over into the image potential far from the surface and into the constant value obtained from (2) in the interior. This potential is a slowly varying function of the electron wave vector. Figure 1 shows a typical potential derived by Bardeen, appropriate to the average potential for all electrons. Although the two calculated points are based on slightly different electron distributions, they are representative of the exchange potential variation in the surface. However, two points are not really sufficient to construct a

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* This work has been supported by the U. S. Office of Naval Research.

[1] J. C. Slater and H. M. Krutter, Phys. Rev. 47, 559 (1935).

[2] J. C. Slater, Revs. Modern Phys. 6, 209 (1934).

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

surface potential good everywhere in this region, and this method of construction suppresses the detailed dependence of the exchange potential on a particular electron distribution. In fact, Bardeen found that the final electron distribution self-consistent with respect to the fixed exchange potential differed only slightly from the distribution on which the exchange potential was based. However, it is unlikely that consideration of the minor variations in the exchange potential in the low-density region would affect his conclusions. In the regions of higher density these variations may introduce corrections.

Recently, Slater[4] has suggested a simplification of the Hartree-Fock equations such that all electrons move in a common exchange potential. This average potential is obtained by constructing the potential due to a weighted average exchange charge for all electrons. It is given by

$$-e^2\frac{\sum_{i,k}\int d\mathbf{r}_1\frac{u_i^*(\mathbf{r})u_i(\mathbf{r}_1)u_k^*(\mathbf{r}_1)u_k(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_1|}}{\sum_i u_i^*(\mathbf{r})u_i(\mathbf{r})}. \tag{4}$$

This approximation assumes that the exchange holes for different electrons are not too different from each other, so that the dependence of the potential on the state of any one electron can be removed by substitution of the average value. For actual calculation Slater has proposed a further simplification of (4) which should be valid for slowly varying electron densities. The average exchange potential (4) is approximated by the average exchange potential of a free-electron gas of density equal to the electron density at the point in question. This is equivalent to making the density n in (2) a function of position; it corresponds, except for a numerical factor, to the Thomas-Fermi-Dirac statistical approximation. Figure 1 shows the exchange potential constructed in this manner from a distribution corresponding to a free-electron gas bounded by an infinite barrier. This electron distribution is shown in Fig. 2.

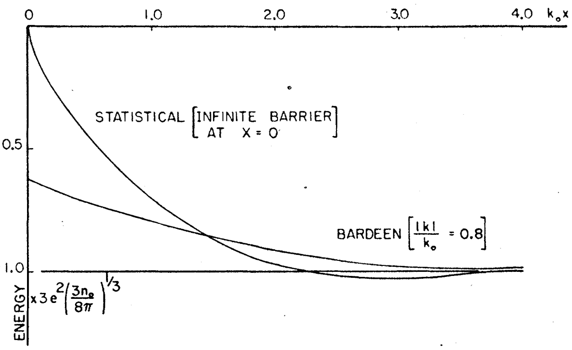

FIG. 1. Approximate exchange potentials in the surface of a free-electron metal.

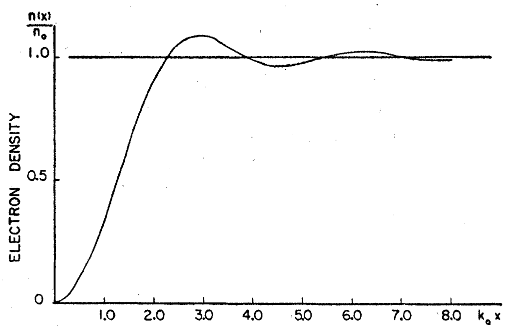

FIG. 2. Electron density distribution of free electrons bounded by an infinite barrier at $x=0$.

As to be expected, the statistical approximation is not reliable at low densities. In the regions of higher density it compares adequately with Bardeen's values. But in addition, it shows a dip in the region where the charge density has a maximum, which is not present in Bardeen's potential. The magnitude of this dip in the exchange potential will depend on the electron density, and it would be less pronounced for Bardeen's final charge distribution than for that used here. Nevertheless, this dip would reinforce the electrostatic dip in potential in the same region,[5] and a self-consistent computation of the surface charge density taking into account this variation of the exchange potential at high densities would result in a greater localization of electrons in the surface than found by Bardeen. The effective surface barrier would be more step-like and the surface would exhibit a lower electric double layer.

In the next section the Slater potential (4) will be evaluated exactly as a function of position for free electrons bounded by an infinite barrier. This allows on the one hand a comparison of the average potential with Bardeen's accurately computed points, and, on the other hand, an estimate of the accuracy of the statistical potential in regions of various electron densities and density gradients.

III. THE AVERAGE EXCHANGE POTENTIAL

Free electrons confined to the region $x>0$ by an infinite potential barrier at $x=0$ are represented by wave functions

$$u_k(x, y, z) = (2/L^3)^{\frac{1}{2}} \sin(k_x x) e^{i(k_y y+k_z z)}, \tag{5}$$

where $k_i = (2\pi/L)m_i$; m_y, m_z take on all integral values, while $m_x = \frac{1}{2}, 1, \frac{3}{2}, 2, \cdots$. The wave functions are normalized in a volume L^3. If $m = (m_x^2+m_y^2+m_z^2)^{\frac{1}{2}}$, all states (m_x, m_y, m_z) are doubly occupied by electrons up to a value $m_0 = L(3n_0/8\pi)^{\frac{1}{3}}$ where n_0 is the electron density far from the surface. The maximum $|k|$ value is given by

$$k_0 = 2\pi(3n_0/8\pi)^{\frac{1}{3}}. \tag{6}$$

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[4] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[5] See reference 3, Fig. 5.

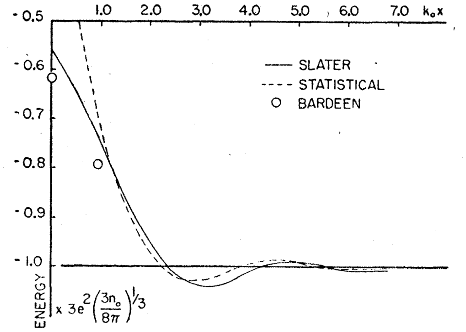

FIG. 3. Slater's exchange potential based on an average exchange charge. The statistical approximation to the exchange potential and Bardeen's calculated points are shown for comparison. The energy scale covers only half of the full range.

The electron density for one kind of spin occurring in the denominator of (4) is obtained directly from (5). It depends only on x, and in terms of $X=k_0x$ it can be written

$$\frac{n}{2}(X)=\frac{n_0}{2}\left(1-3\frac{\sin 2X}{(2X)^3}+3\frac{\cos 2X}{(2X)^2}\right). \tag{7}$$

n/n_0 is plotted in Fig. 2.

The numerator of (4) can be evaluated by first summing over i and k. By writing the $\sin(k_xx)$ as a sum of exponentials and rearranging the region of summation for k_x, the average exchange potential takes the form

$$-e^2\int\frac{d\tau_1}{r_1}\frac{\frac{1}{2}n_0}{n(k_0x)/n_0}\left\{3\frac{\sin(k_0r_1)-k_0r_1\cos(k_0r_1)}{(k_0r_1)^3}\right.$$
$$\left.-3\frac{\sin(k_0r_2)-k_0r_2\cos(k_0r_2)}{(k_0r_2)^3}\right\}^2, \tag{8}$$

where $r_1{}^2=(x-x_1)^2+(y-y_1)^2+(z-z_1)^2$ and $r_2{}^2=(x+x_1)^2+(y-y_1)^2+(z-z_1)^2$. The effect of the barrier at $x=0$ is evident in the form of the average exchange charge contained in (8). It is made up of two terms. The normal term existing in a uniform charge distribution is modified by its image with respect to the barrier.

The remaining integrations in (8) must be carried out over half-space $x_1\geq 0$. The square of the first term in the bracket of (8), if integrated over all space, gives the normal exchange integral contribution. Hence there are three correction terms in the integration over half-space; the correction when the first term is limited to $x_1\geq 0$, and the two remaining terms in the square of the bracket of (8). Since these additional terms are appreciable only in the neighborhood of $X=0$, the limits of integration are $0\leq x_1\leq\infty$, $-\infty<y_1, z_1<\infty$. Without loss of generality, the expression (8) may be evaluated for electrons located at points on the x axis.

By very careful, lengthy but elementary integration, first over angles and then over r_1, and exact evaluation of limits, one obtains for the integral (8) the expression,

$$\frac{-3e^2(3n_0/8\pi)^{\frac{1}{3}}}{n(X)/n_0}\left\{1-\left[\tfrac{1}{2}\pi-\mathrm{Si}(4X)\right]\left(\frac{2X\cos 2X-\sin 2X}{4X^4}\right)\right.$$
$$-\left[\mathrm{Ci}(4X)-\log(4\gamma X)\right]\left(\frac{\cos 2X+2X\sin 2X}{4X^4}\right)$$
$$-\left(\tfrac{1}{2}\pi-\mathrm{Si}(2X)-\frac{\cos 2X}{2X}\right)\left(\frac{2}{3X}-\frac{4X}{15}\right)$$
$$+\frac{1}{X^4}\left(\frac{2}{5}\sin^2X-\frac{1}{48}\sin^2 2X\right)$$
$$-\frac{1}{X^3}\left(\frac{7}{5}\sin 2X-\frac{1}{24}\sin 4X\right)$$
$$+\frac{1}{X^2}\left(\frac{1}{12}+\frac{11}{15}\cos 2X+\frac{1}{6}\cos 4X\right)$$
$$\left.-\frac{1}{X}\frac{\sin 2X}{15}+\frac{2}{3X}\left[\mathrm{Si}(4X)-\mathrm{Si}(2X)\right]\right\}. \tag{9}$$

$\mathrm{Si}(X)$ and $\mathrm{Ci}(X)$ are the sine and cosine integrals as defined by Jahnke and Emde,[6] $\gamma=1.781$ is Euler's constant, and $X=k_0x$. The average exchange potential (9) has been graphed in Fig. 3. This figure also includes the statistical potential derived from expressions (2) and (7) and the two points calculated by Bardeen for $|k|/k_0=0.8$, which apply very closely to the average potential for all electrons.

At the position of the barrier, the average of Bardeen's potentials has dropped to $\pi^2/16$ of its value in the interior. The Slater potential (9) has decreased to 5/9 of its interior value at the same point. The difference arises because Slater's potential is based on a weighted average favoring electrons with high wave numbers which have low exchange potentials.

Throughout most of the immediate surface region, the Slater average potential agrees quite well with that constructed by Bardeen. However, in the region where the electron density has its first maximum, the average potential shows a dip very similar to that produced by the statistical potential. It is very likely that this dip is real and will also occur in the correct exchange potential (1) if the charge distribution exhibits a maximum. Farther away from the surface the average exchange potential agrees quite well with the statistical approximation. Both follow the charge density variations closely. It should be noted, however, that the exchange potential follows with a lag, and that it tends to emphasize regions of high density, and de-emphasize regions of lower density.

One can conclude from the comparison of the curves

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[6] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), p. 1.

in Fig. 3 that the exchange potential (4) is a rather accurate description of the real average exchange potential at all densities. However, the additional simplification involved in the statistical approximation does not apply in the outer surface region. For the distribution used here, the statistical approximation becomes inaccurate when the density has dropped to about $\frac{1}{2}$ of its value in the interior.

IV. EXCHANGE CHARGE IN THE SURFACE

In Bardeen's calculation of a self-consistent surface potential the exchange potential is held fixed at the initially constructed values. Since the exchange potential is a slowly varying function in the surface region, its dependence on the actual charge distribution is probably not too critical. Nevertheless, it is of interest to understand the cause of the variation of the exchange potential in this region, in order to be able to predict possible effects of different electron distributions. For this purpose it is convenient to study the behavior of the exchange charge when the electron is in the surface region. In our model the exchange charge distribution is given by the expression contained in the integrand of (8),

$$e\frac{\frac{1}{2}n_0}{n(X)/n_0}\left\{3\frac{\sin R_1-R_1\cos R_1}{R_1^3}-3\frac{\sin R_2-R_2\cos R_2}{R_2^3}\right\}^2. \qquad (10)$$

In (10) all distances are measured in units of k_0^{-1}. R_1 is the distance from the location of the electron at (X, Y, Z) and R_2 is the distance from the image point $(-X, Y, Z)$.

Far from the surface ($X\gg 0$), only the first term in (10) is important, giving the usual exchange hole centered at the electron in question. In the surface interference between the first term and its image becomes important. As a result the exchange hole ceases to follow the electron exactly, but lags behind more and more as the electron moves into the surface. Figure 4 depicts the exchange charge density along a normal to the surface for various locations on the normal of the electron under consideration. The lag of the exchange hole is the cause of the shift of the peaks of the exchange potential with respect to the peaks of the electron density (and also of the statistical approximation) evident in Fig. 3. The interference of the two terms in (10) displaces the center of the exchange hole towards the interior of the metal. The explanation for the difference in response to peaks and valleys in the electron distribution of the statistical and the average exchange potential shown in Fig. 3 is not clear cut. One would expect in general that a potential based on an exchange hole following the actual charge density variations tends to average out local variations in density more than the statistical potential, which is based on an exchange hole in a uniform electron density. The higher peaks occurring in Slater's potential are probably due to the distortion of the exchange hole in the surface region.

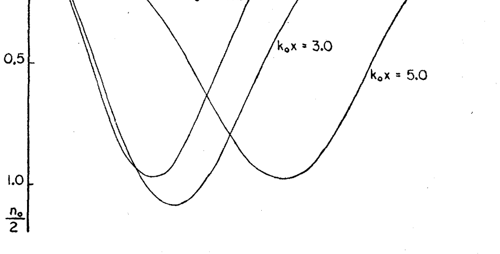

FIG. 4. Average exchange-hole density normal to the surface for various locations of an electron.

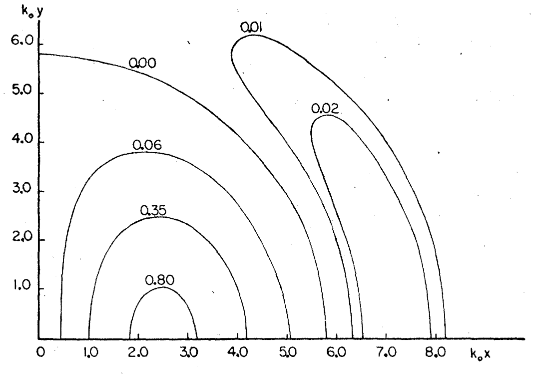

FIG. 5. Density contours of the average exchange hole associated with an electron at (0, 0). The surface is perpendicular to the x axis.

As the electron moves into the surface the exchange hole is deformed in various ways. The hole becomes more compressed in the direction normal to the surface. Thus, the first zeros of (10) measured from the center of the hole approach the value given by (3). Figure 4 shows that in the cross section considered nearly all the electrons normally in the surface are displaced by the exchange hole, so that this cross section follows the density. In addition, the hole does not remain spherically symmetrical but flattens out in the surface region. Figure 5 is a plot of the density contours of the exchange hole for an electron at $x=0$. It should be noted that in spite of these distortions most of the exchange-hole charge remains close to the electron in question. In fact, for an electron at $x=0$ a hemisphere of radius $rk_0=6$ contains nearly as much charge as a sphere of the same radius around an electron in the interior.

The exchange potential in the surface can thus be described qualitatively by observing that as soon as the electron density decreases appreciably from its interior value the exchange hole tends to stay behind. In our model this occurs at about $k_0x=2.50$. This means that for all points beyond this limit the exchange potential is not that for an electron in the center of the exchange hole, but for an electron some distance away from the center. The exchange hole can be approximated by a uniformly charged sphere of radius r_0. Since $k_0r_0=2.42$, an electron at $x=0$ is just about at the surface of the exchange hole. At that point its potential in the spherical charge distribution has decreased to $\frac{2}{3}$ of its maximum value. This is in good agreement with the potential found in expression (9). But such a description in terms of a uniform spherical charge distribution is only approximate. Actually, the exchange potential in Fig. 3 rises more rapidly than the corresponding potential of a uniformly charged sphere located at $k_0x=2.50$.

An infinite barrier is not suited for investigating the asymptotic behavior of the exchange hole, since the electron density decreases too rapidly. For this purpose it is convenient to study the exchange hole based on the wave functions proper to a finite step barrier which have been constructed by Bardeen. With these wave functions the approximate exchange hole distribution can be readily evaluated for electrons far beyond the barrier location, since the exponentially decaying wave functions in this region allow approximations in the summation over all occupied states. The result depends on the height of the barrier relative to the highest electron energy $\hbar^2k_0^2/2m$. If the relative barrier height is A, then for $A\gg 1$ the potential seen at a distance k_0x_1 from the surface approaches asymptotically $e/|x_1|$, i.e., the exchange hole remains relatively concentrated in the surface. If $A\gtrsim 1$, and the electron is not too far from the barrier, the exchange hole shows a behavior in the surface very similar to that already discussed above. But at points far away from the surface the exchange hole distribution is altered considerably. Thus, for $A\gtrsim 1$, the exchange hole distribution along the x axis due to an electron at $-k_0x_1$, ($|k_0x_1|\gg 1$) is approximately given by

$$\frac{n_0}{2}\frac{24(A-1)}{A\,(k_0x_1)^2}(\cos k_0x-(A-1)^{\frac{1}{2}}\sin k_0x)^2. \qquad (11)$$

In (11) all distances are measured from the position of the barrier. This expression is valid for $2(A-1)^{\frac{1}{2}}x\leq|x_1|$. For larger x the density oscillates with decreasing amplitude. Laterally the exchange hole is appreciable to distances up to $|x_1|^{\frac{1}{2}}$. Expression (11) shows that the single exchange hole is replaced by a series of disk-like charge distributions of equal magnitude, spaced at intervals of π/k_0 up to a distance about equal to the distance of the electron from the surface. The potential of this distribution is still essentially $e/|x_1|$, with a numerical factor smaller than unity for low barriers.

This appearance of the asymptotic exchange hole can be deduced from the general formula for the exchange hole in expression (4). Sums of the form $\sum_i u_i^*(r_1)u_i(r)$, where r is inside the metal and r_1 far away from the surface will be determined primarily by wave functions of high x wave numbers, and thus are asymptotically periodic in r with period $2\pi/k_0$. Similar behavior holds also true, although to smaller extent, for the exchange holes associated with the correct exchange potentials (1).

The basic reason why the exchange hole remains in the surface is clear; it must remove unit charge out of the existing charge distribution and thus must remain mostly in a rather dense region. Mathematically this is brought about by a correlation of phases of all wave functions in the surface region. Neither one of these two conditions is observed in the usual statistical approach to the exchange potential. Therefore, such an approach cannot lead to a good approximation in regions of low and rapidly changing charge density.

V. SURFACE EXCHANGE ENERGY

Expression (9), when multiplied by the local electron density, represents the exchange energy density in the surface region. A comparison of the energy obtained from (9), corresponding to a decaying electron density, with that of a uniform electron distribution will give the contribution to the exchange energy due to the existence of the surface. In determining surface energy contributions by such comparisons it is important to observe that (a) the density far from the surface must be the same for both distributions and (b) the comparison must be between equal total amounts of charge.[7] The charge distribution (7) on which (9) is based represents a deficit of $3\pi n_0/8k_0$ electrons per unit surface, in comparison with a uniform distribution up to the barrier.[8] If the energy based on expression (9) is corrected for this deficiency, the exchange energy per unit surface has a value $0.134e^2(3n_0/8\pi)$. This corresponds to 96 ergs/cm^2 for Na and compares closely with the value 75 ergs/cm^2 obtained by Huntington[8] directly from Bardeen's self-consistent potentials. Huntington's quoted value has been multiplied by $\frac{4}{5}$ to eliminate the contribution of the correlation energy.

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[7] W. J. Swiatecki, Proc. Phys. Soc. (London) **64**, 226 (1951).

[8] H. B. Huntington, Phys. Rev. **81**, 1035 (1951).