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Use of Surface States to Explain Activated Adsorption

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A theory is advanced connecting activated adsorption with electron surface states in solids. The theory is constructed for H_2 but the suggested mechanism would work equally well for other molecules. It is supposed that H atoms interact with surface electron states of the solid when the atom gets close enough to make the latter stable. The stability condition for surface states and its relation to the position of the visiting H atom is investigated in some detail. If the energy of the surface state is low enough, the atom will on reaching the critical distance for stability transfer its electron to the surface state with considerable reduction in total energy. At close distances, exchange sets in. The energy of the various interactions is calculated approximately on the basis of a simplified model of the surface potential field and the surface state wave function. By using a reasonable form for the repulsion between the H nucleus and the positive cores in the metal, total energy curves whose minima lie at depths up to 2.5 volts are obtained. An H_2 molecule with sufficient energy may get close enough to the surface to come into the range of interaction of the H atoms with surface states. When this happens the molecule can split into atoms and be bound as such to the surface. The present theory of this interaction seems to be capable of properly accounting for the observed heats of activated adsorption of H_2.

A TENTATIVE theory of activated adsorption has been proposed by Lennard-Jones.[1] It is assumed that the adsorption of systems with unsaturated valencies is accomplished through a lowering of the surface potential of the solid in the immediate neighborhood of the visiting atom. This would give rise to a localized potential hole in which electrons would be caught and enter into normal exchange binding with the visitor. The forces involved would be large and the binding energy of the same order as in diatomic molecules. For molecules with completed bonds an activation energy is involved. The process in the case of H_2 on a metal is best described in terms of Fig. 1 (which is very similar to Fig. 3 in Lennard-Jones' paper[1]). The curve (m) represents qualitatively the normal interaction through van der Waals or polarization forces of an H_2 molecule with a metal M. The other curve (a) represents the much stronger interaction discussed above between two H atoms and the metal. The separation of the two curves at infinity is the dissociation energy D of the molecule. Consider a molecule approaching the metal with total energy W. If W is sufficient for it to reach the intersection G of the curves (m) and (a) (i.e., $W=A$), it can dissociate without changing its total energy. The individual H atoms would then follow the atomic curve (a) to their respective minima where they take up vibrational energy W'. The observed heat of adsorption will be $E=Q+W-W'$ or simply $Q+A$ when the vibrational energy W' is neglected. The combined binding of the two H atoms must be $Q+D$. In order to give a satisfactory explanation of activated adsorption, therefore, any theory of the interaction between the atom and the surface must account for a binding of the order of $\frac{1}{2}(D+E-A)$. The mechanism by which the H_2 bond is broken and bonds between the separate H atoms and the surface are substituted for it has been discussed by Sherman and Eyring[2] from the standpoint of the latter's theory of activation energy in chemical reactions.

It is the purpose of this paper to investigate the nature of possible interactions between monatomic hydrogen and metal surfaces with a view to determining the mechanism which gives rise to the curve (a) in Fig. 1. We begin with a general consideration of electronic surface states in solids.

In the periodic potential field of a crystal lattice the solutions of Schroedinger's equation for an electron are the well-known Bloch functions

$$\psi(\mathbf{r})=u(\boldsymbol{\mu},\mathbf{r})\exp[\boldsymbol{\mu}\cdot\mathbf{r}], \tag{1}$$

where $\boldsymbol{\mu}$ is in general complex and $u(\boldsymbol{\mu},\mathbf{r})$ is periodic with the lattice period. The total energy of the electron with this wave function is a function of $\boldsymbol{\mu}$. For an infinite crystal there are a number of ranges or bands of the total energy

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[1] J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 341 (1932).

[2] A. Sherman and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

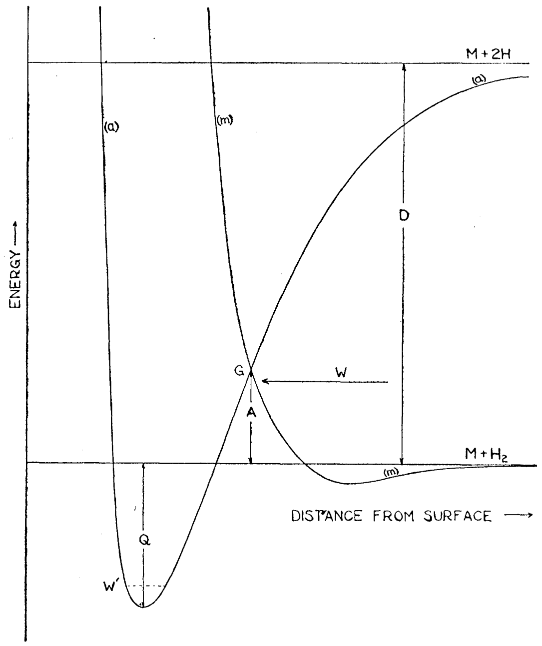

FIG. 1. Schematic representation of the proposed mechanism of activated adsorption.

for which all three components of $\boldsymbol{\mu}$ are pure imaginary so that $\boldsymbol{\mu}=i\mathbf{k}$ with $\mathbf{k}$ real. In these solutions the function $u(\mathbf{k}, \mathbf{r})$ represents the atomic wave function of the electron around each lattice point and goes into the corresponding isolated atom wave function upon infinite separation of the lattice points. The function $\exp [i\mathbf{k}\cdot\mathbf{r}]$ represents a modulation of the function $u(\mathbf{k}, \mathbf{r})$ and is associated with the continual transfer of electrons from one lattice point to another. These solutions make up the totality of stationary states in the interior of crystalline solids.

When, however, the crystal is regarded as being of finite size and its surface is taken into account, stationary solutions involving one real component of $\boldsymbol{\mu}$ are possible. This was first pointed out by Tamm.[3] These solutions represent a state of motion in which the electron is confined to the surface with its wave function exponentially damped both into and out from the surface but free to move over it. They are obtained from the family of solutions (1) by choosing the component of $\boldsymbol{\mu}$ normal to the surface real, taking the other two pure imaginary, and fitting the resulting function smoothly across the boundary to the exterior solution.

Tamm employed a semi-infinite periodic potential of the Kronig and Penny type. Let E be the energy of the surface state, V_s the rise in potential at the surface, and p the Kronig and Penny parameter measuring the magnitude of potential fluctuations in the lattice. The essential features of his solution may be stated as follows: (a) Surface states exist only for those values of the energy which satisfy

$$E \geqslant V_s - \hbar^2 p^2/2ma^2, \qquad (2)$$

where a is the lattice period. (b) For all energies satisfying (2), there exists one and only one surface state in each "forbidden" region or energy gap between allowed bands of the interior states.

These states have since been studied by several investigators,[4] and it has been shown that the second property (b) above has to be altered for a finite lattice with a surface at each end to make the surface states occur in pairs. Recently Shockley[5] has made quite a detailed study of these states, and has described the manner in which they originate from the atomic levels of the isolated atoms as the lattice distance is continuously decreased from very large values. The energy minimum (a) imposed on the surface states is formulated in a much more general and precise way. As the atoms composing the lattice approach each other, the isolated atom levels broaden and finally intersect. The electronic bands on either side of the intersection are separated with forbidden regions between. The levels associated with surface states, however, can originate only after the point of intersection has been reached. In actual crystals at their equilibrium configuration the bands above a certain energy will have intersected and all below will not. This energy corresponds to the minimum imposed by condition (2).

In the application to adsorption with which this paper is concerned, the condition (2) is of considerable importance, and it is desirable to associate it as closely as possible with actual

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[3] Ig. Tamm, Physik. Zeits. Sowjetunion **1**, 733 (1932).

[4] R. H. Fowler, Proc. Roy. Soc. **A141**, 56 (1933); S. Rijanow, Zeits. f. Physik **89**, 806 (1934); A. W. Maue, Helv. Phys. Acta **7**, supp. 2, 68 (1934), Zeits. f. Physik **94**, 717 (1935); E. T. Goodwin, Proc. Camb. Phil. Soc. **35**, 205 (1939). The reader is referred to the accompanying paper of Shockley's for a discussion of this work.

[5] W. Shockley, Phys. Rev. This issue. The author is greatly indebted to Dr. Shockley for the privilege of seeing his paper before publication.

solids. For this purpose the treatment presented in the appendix to this paper is useful. An approximate solution for the surface state wave functions is obtained there in the form

$$\begin{aligned}\psi(\boldsymbol{\kappa},\gamma;\mathbf{r})&=u(\boldsymbol{\kappa},\gamma;\mathbf{r})\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}+\gamma z]\quad\text{inside the lattice }(z\leqslant 0)\\&=\sum_n c_n(\gamma)f_n(z)Q_n(\boldsymbol{\kappa},\boldsymbol{\rho})\quad\text{outside the lattice }(z\geqslant 0)\end{aligned}\tag{3}$$

with

$$Q_n(\boldsymbol{\kappa},\boldsymbol{\rho})=v_n(\boldsymbol{\kappa},\boldsymbol{\rho})\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}].$$

Here z is measured normal to the surface, $\boldsymbol{\rho}$ is the radius vector parallel with the surface, $\boldsymbol{\kappa}$ a momentum vector parallel with the surface, and the functions $u(\boldsymbol{\kappa},\gamma;\mathbf{r})$ and $v_n(\boldsymbol{\kappa},\boldsymbol{\rho})$ are periodic with the lattice period. The energy of the surface state is obtained by choosing the coefficients $c_n(\gamma)$ so that the interior and exterior solutions join at the surface, and then determining γ to make them join smoothly. It is shown that this process leads to a condition similar to (2).

The parameter σ in Shockley's treatment may be associated with Tamm's $[2m(V_s-E)]^{\frac{1}{2}}/\hbar$. Any mechanism which would lower V_s (such as, e.g., an H^+ ion close to the surface) would also lower σ. An inspection of Figs. 4(d) and 4(e) in Shockley's paper makes it clear that this would also improve the chances for an intersection of the σ/μ curve with the others in regions II and III where the surface states originate. This gives rise to a dependence of the minimum energy for surface states on the surface potential V_s which is qualitatively similar to that in (2). The other factor in (2) involving the parameter p would depend on Shockley's γ and μ but the connection between them is not evident.

Application to Adsorption

Consider the approach of an ion of charge Ze to a solid surface. If the solid is a dielectric the region of its surface immediately below the ion becomes polarized; if it is a metal, this region becomes negatively charged in such a way as to reduce the electric field in the interior of the metal to zero. The net effect in either case is an accumulation of electrons on the surface immediately below the visitor. Denote by β the normal distance between the surface and the ion. If for the moment we regard the "induced" surface charge as removed, it is clear that the surface potential V_s is reduced at the point immediately below the ion by an amount Ze/β. This creates a localized potential pocket in the part of the surface below the ion. The way in which this pocket is formed is discussed in detail in Lennard-Jones' paper.[6] One can picture how it arises by thinking of the superposition of the surface potential curve (drawn asymptotic to zero energy and rapidly falling near the surface) and the characteristic horn-shaped potential curve of a proton. The total potential formed by this superposition is reduced near the proton by the ordinate of the surface curve, and in the neighborhood of the surface by the ordinate of the proton curve. The latter reduction forms the pocket. If an electron were now placed on the ion it would distribute itself between the potential hole around the ion and the potential pocket in the surface. The amplitude of its wave function would be large around the ion, small between the ion and the surface, and large again in the neighborhood of the pocket. Since the depth, Ze/β, of the pocket increases with β, the amplitude of the wave function around the ion would decrease with β and that at the surface increase with β.

As measured by the amplitude of the wave function at the surface, it is evident that in this process a type of surface state gradually grows as the ion approaches. At large β this state would be negligible since the electron would remain almost entirely with the ion. The amplitude at the surface would not become appreciable until the depth of the surface hole became comparable with that of the ion. Thus the growth of the surface state would take place in a comparatively narrow range of β.

It is useful to consider the development of this type of state in terms of the surface states of an isolated solid discussed in the previous section. As the visiting core approaches the surface, a position β_0 will eventually be reached at which V_s will be lowered enough to satisfy (2) for a low-lying surface state. β_0 should be regarded as lying in the above narrow range of β. The character of the surface state formed in this way will, however, be quite different from those already con-

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[6] Reference 1, p. 344.

sidered because the stability condition (2) will now hold only locally in a small region of the surface below the ion. This will have the effect of altering the character of the functions $Q_n(\boldsymbol{\kappa}, \boldsymbol{\rho})$ in Eqs. (3). Instead of being of the type $v_n(\boldsymbol{\kappa}, \boldsymbol{\rho}) \exp [i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}]$ corresponding to free transmission over the surface, they must now be large only in a circle directly below the visiting ion with exponentially decreasing character outside. They will form a discrete set $Q_{nl}(\boldsymbol{\rho})$ with integral l and have eigen energies

$$E_{il}=\sum_n c_n{}^2(\gamma_i)(W_n(l)+\epsilon_n)$$

associated with them rather than the $E_i(\boldsymbol{\kappa})$ of Eq. (29) in the appendix. In order to account for adsorption it is necessary to have one of these energies close to, or lower than, the lowest level of the visiting core. For hydrogen this means a surface state at -13 volts or lower which places it well below the conduction band.

These states are true surface states and would arise whenever the Eqs. (28) of the appendix could be satisfied for functions $Q_{nl}(\boldsymbol{\rho})$ of the above type. They cannot, however, be very well interpreted in terms of those obtained by Shockley for an isolated crystal. The reason is that the local broadening of the bands caused by the visiting ion is of equal importance with the broadening arising from the degree of packing of the atoms in the crystal.

In what follows all energies are expressed in units of $Z^2e^2/2a_0$ and all lengths in units of a_0/Z where a_0 is the radius of the first Bohr orbit in hydrogen. Application is made only to the adsorption of H for which $Z=1$ but the results are given in terms of an ion of charge Ze for generality. In the presence of the visiting ion, condition (2) becomes

$$E \geqslant V_s - Ze^2/\beta - \hbar^2 p^2/2ma^2.$$

Expressed in the above units with E measured on the basis that the potential energy of an electron far from the solid is zero (instead of the interior of the lattice as in Tamm's model), this condition for all points of the surface within a circle of radius ρ' becomes

$$E \geqslant -2(\beta^2+\rho'^2)^{-\frac{1}{2}}-(p/a)^2$$

or

$$(\beta^2+\rho'^2)^{\frac{1}{2}} \leqslant -2/[E+(p/a)^2]. \tag{4}$$

The greatest value β_0 of β for which the surface state could exist is

$$\beta_0=-2/[E+(p/a)^2] \tag{5}$$

and the radius of the circle on the surface within which the stability condition is satisfied is

$$\rho'=(\beta_0{}^2-\beta^2)^{\frac{1}{2}}. \tag{6}$$

The part $Q_{nl}(\boldsymbol{\rho})$ of the surface wave function would be large within this circle and exponentially decreasing outside. This circle would have some limiting radius ρ_1 attained for $\beta=\beta_1<\beta_0$ below which no stationary solutions would exist. The surface state would not become possible then until the visiting core came as close as β_1 to the surface.

As the positive core approaches the surface it is attracted to it by a force whose potential at large distances is

$$\Phi_1(\beta)=-Z/2\beta. \tag{7}$$

There is an accumulation of electrons in the surface immediately below the visiting core with density (number not charge) as given by classical electrostatics,

$$\sigma=Z\beta/[4\pi(\beta^2+\rho^2)^{\frac{3}{2}}]. \tag{8}$$

This surface charge is in general contributed by the conduction band to reduce the internal electric field to zero. For large β, it has nothing to do with the surface states already discussed. The way in which it arises in quantum mechanics may be seen as follows. In the undisturbed metal the density of charge at any point is given by Fermi statistics as $8\pi[2m(H_0-U)]^{\frac{3}{2}}/3h^3$ where U is the self-consistent periodic potential in the lattice calculated from this charge density.[7] In the neighborhood of the surface this density falls off very rapidly. With a visiting positive charge near the surface, however, the potential U is reduced in the part of the surface nearest the charge. This automatically increases the density through the increase of the term $(H_0-U)^{\frac{3}{2}}$ in it.

When the visiting ion gets sufficiently close to the surface to have $\beta \leqslant \beta_1$, the surface state of low energy whose properties we have been considering becomes stable. If now a transition from the conduction band to this state were possible, it would become populated and the analog of the

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[7] J. C. Slater, Rev. Mod. Phys. 6, 238 (1934).

classical induced charge in the conduction band would become very small. It seems reasonable to identify $\int|\psi|^2dz$ for the surface state with the charge density (8). In the most important case $Z=1$, both integrate to just one electron and both peak at the same point. The local accumulation of charge in the surface state would behave electrically like the image of the visiting core in the metal. The result of a transition to this surface state on the interaction (7) would therefore be very slight.

With this behavior of the ion in mind, consider next the approach of a neutral atom. This is also attracted to the surface but with a force whose potential is[8]

$$\Phi_2(\beta)=-\langle r^2\rangle_{\mathrm{Av}}/3Z\beta^3, \tag{9}$$

where $\langle r^2\rangle_{\mathrm{Av}}$ is the average value of the square of the radius vector over the whole electron cloud in the visiting atom. The potential arises from interaction with the images in the metal of the dipoles formed by the electrons and nucleus of the visiting atom. In this case, however, a deficiency rather than an excess of electrons exists in the surface immediately below the visitor. When the value β_1 is reached so that the surface state in the field of the core is stable, the whole system can in general materially reduce its energy by transferring its outer electron across the potential barrier between atom and metal into the surface state of the metal. If the surface state has approximately the same energy as the vacated state in the atom, this electron can go into normal exchange between the two states. If the surface state has appreciably lower energy than the atom, the latter will remain ionized. In either case a one electron bond is formed similar to that in H_2^+ or NaCl, respectively.

A question which suggests itself here is whether by approaching closer the ion could not pick up another electron from the conduction band in the metal and so form a two-electron bond as in H_2 with further reduction in total energy. Except in very rare cases this would not happen for the following reasons. The surface state electron is held to the surface by the presence of the ion. In neutralizing the ion, the condition for the stability of the surface state would be destroyed. Even if this condition is ignored, there would be left on the surface a strong local concentration of negative charge in the surface state representing a considerable excess over the local *deficiency* normal for the neutral atom. This highly unstable distribution of charge would doubtless constitute an energy gain for the solid which would more than outweigh the decrease resulting from the neutralization of the ion.

It is important to point out here that these considerations apply only when the binding is dependent on the formation and preservation of the surface state. In cases where no localized surface state is present, such transfers often occur. Neutral atoms or molecules whose ionization potentials are smaller than the energy depth of the top of the conduction band or whose electron affinity is larger than this depth can, respectively, either transfer an electron to the conduction band or receive one from it. The atom or molecule is then converted into either a positive or negative ion and can be bound to its mirror image in the metal. Such processes have been observed experimentally[9] and they have been discussed theoretically by Gurney.[10] The interaction of an H atom with a surface state is similar to the interaction of an atom of small ionization potential with the conduction band. After the H atom has transferred its electron to the surface state, however, the system is similar to an atom of large electron affinity near the surface. The reason that no transfer from the conduction band takes place here lies in the screening of the positive ion by the surface state electron. Insofar as the latter fulfills the function of the classical induced charge, its screening is perfect since it everywhere raises the potential at the surface to the value it had in the absence of the ion.

Calculations with a simplified model

Let ψ_s represent the surface state wave function and ψ_a the wave function of the outer electron in the visiting atom. The wave function of the combined system may be taken to be

$$\psi=C\psi_s+D\psi_a. \tag{10}$$

For $\beta>\beta_1$ the surface state does not exist, the amplitude ψ around the surface pocket is very

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[8] Reference 1, p. 334.

[9] See for example, J. A. Becker, Trans. Faraday Soc. **28**, 148 (1932).

[10] R. W. Gurney, Phys. Rev. **47**, 479 (1935).

small, and $C \cong 0$ and $D \cong 1$. When $\beta \to \beta_1$ and ψ_s becomes stable, the electron will transfer itself from the atom to the surface state so that after the transfer the coefficients will be $C \cong 1$ and $D \cong 0$. As the ion comes closer to the surface, the stability condition (4) becomes less stringent. Provided the two states have nearly the same energy, it will be possible for exchange to take place between them to a limited extent. At still closer distances, the stability of ψ_s is no longer a consideration and the electron will distribute itself between the two states in a manner which leads to the lowest energy. The coefficients C and D will then be determined by minimizing the energy.

As a rough approximation it seems reasonable to regard the limitations imposed by condition (4) as a measure of the degree to which free exchange may take place between the two states, i.e., the degree to which C may differ from unity. This may be accomplished by regarding the positive charge on the ion as $Ze(1-|D|^2)=Ze|C|^2$ instead of Ze as in (4). Inserting this in Eq. (4) and making use of the quantities β_0, and β_1 as introduced in Eqs. (5) and (6) there follows

$$(\beta^2+\rho_1{}^2)^{\frac{1}{2}} \leqslant \beta_0|C|^2$$

or

$$|C| \geqslant [1-(\beta_1{}^2-\beta^2)/\beta_0{}^2]^{\frac{1}{4}}. \tag{11}$$

There will be some sufficiently small value of β which makes this lower limit on C equal to the value of C for which the energy is a minimum. For all smaller values of β, Eq. (11) will no longer be important and C will be determined by the energy minimum.

If $-V(\mathbf{r}_s)$ is the potential energy of an electron in the self-consistent field of the solid, the Hamiltonian for the electron in the field of solid and ion is

$$H=-\nabla^2+U_c-V(\mathbf{r}_s)-2/r_a,$$

where r_a is measured from the nucleus of the ion, and U_c is the interaction between the atomic core and what remains of the solid after exclusion of the surface state electron. The energy of the distribution (10) with this Hamiltonian becomes

$$E=[|C|^2H_{ss}+C^*DH_{sa}+CD^*H_{as}+|D|^2H_{aa}]/[1+2|C||D|\Delta], \tag{12}$$

where Δ and the matrix elements of H have their usual meaning. They cannot be evaluated explicitly without introducing some assumptions about the form of the wave functions ψ_s and ψ_a, and the potential $V(\mathbf{r}_s)$. For ψ_a the simplest case to consider is that in which the atomic function is the $1s$ function $e^{-r_a}/\sqrt{\pi}$. For ψ_s we assume no more at present than that the surface state function is a solution of the equation

$$\nabla^2\psi_s+(E_s+V(\mathbf{r}_s))\psi_s=0.$$

The diagonal matrix elements then become

$$H_{ss}=E_s+U_c-\int(2|\psi_s|^2/r_a)d\mathbf{r}_a,$$

$$H_{aa}=E_a+U_c-(1/\pi)\int V(\mathbf{r}_s)\exp[-2r_a]d\mathbf{r}_s.$$

The integral in H_{ss} is the Coulomb interaction J_1 between the surface state electron and the visiting core. Inasmuch as we have identified the surface state charge density with the classical induced charge this is merely the interaction of the core with its image. It does not include the interaction U_c between the core and the metal exclusive of this image. Hence the classical expression (7) should be a fair approximation to it even for small β. Thus

$$\begin{aligned} H_{ss}&=E_s+U_c-J_1,\\ J_1&=Z/2\beta. \end{aligned} \tag{13}$$

The interaction J_2 represented by the integral in the expression for H_{aa} is the Coulomb interaction between the distribution $|\psi_a|^2$ and the solid exclusive of the surface state charge. Its evaluation requires an explicit assumption for the form of $V(\mathbf{r}_s)$. This interaction with exchange has been discussed by Bardeen[11] for electrons in the conduction band. Outside the metal it approaches the classical image potential of the electron $-1/2Z\xi$ in the units used here. Inside it is fairly constant but depends on the momentum of the electron. The presence of the ion near the surface does not matter since $V(\mathbf{r}_s)$ is the interaction with the solid after the image of the ion has been removed. The simplest form with the right properties is

$$\begin{aligned} V(\mathbf{r}_s)&=V(\xi)=V_0 && \xi\leqslant 0,\\ V(\xi)&=(1-e^{-\alpha\xi})/2Z\xi && \xi\geqslant 0,\\ \alpha&=2ZV_0. \end{aligned} \tag{14}$$

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

The interaction J_2 may then be expressed as

$$J_2=\tfrac{1}{2}\int_{-\infty}^{+\infty} V(\xi)(1+2|\beta-\xi|)e^{-2|\beta-\xi|}d\xi,$$

which may be evaluated without much difficulty. The result is

$$H_{aa}=E_a+U_c-J_2,$$

$$\begin{aligned}J_2=\frac{1}{4Z}\bigg\{&\frac{4\alpha}{4-\alpha^2}e^{-\alpha\beta}+\alpha\left(\frac{1-\alpha}{2-\alpha}+\beta\right)e^{-2\beta}\\&+(1+2\beta)e^{-2\beta}[\overline{Ei}(2\beta)-Ei(-(\alpha-2)\beta)]\\&+(1-2\beta)e^{2\beta}\\&\times[Ei(-(\alpha+2)\beta)-Ei(-2\beta)]\bigg\}^{*}.\end{aligned}\quad(15)$$

The exchange terms H_{as} and H_{sa} require for their calculation an explicit knowledge of the form of the surface state function ψ_s. Their evaluation is under any conditions quite difficult. The simplest case mathematically is that in which $\psi_s=\psi_a$. Unfortunately this does not give a very good approximation. The surface state function falls off exponentially both into the surface and out from it. In Shockley's solution the wave function outside the surface is approximately exp $[-\sigma z]$ which, in our units and in case the surface state has the same energy as the visitor, becomes exp $[-z]$. This is the same as exp $[-r_s]$ along the normal to the surface through the visiting core. It is fortunately along this line that the integrand of the exchange integrals is a maximum. In this sense the approximation is good. But the variations parallel to the surface do not seem to be properly given by it. As we have seen ψ_s exhibits exponentially decreasing character outside a circle of radius ρ_1 in the surface. But if we are to judge the rate of this decrease by the classical expression for the induced charge density it is not nearly as large as $e^{-\rho}$. The fraction of an electron to be found in a cylinder of unit radius normal to the surface whose axis passes through the origin is 0.53 for the 1s function $e^{-r}/\sqrt{\pi}$. The corresponding fraction computed from the classical density, Eq. (8), with $Z=1$ is 0.05 when $\beta=2$, 0.15 when $\beta=1$, and 0.55 when $\beta=\frac{1}{2}$. Thus in the range of importance $1<\beta<4$ the approximation gives too strong a local concentration of charge parallel with the surface.

TABLE I. *Values of the Coulomb, exchange, and overlap integrals in Rydberg units $e^2/2a_0$ for the case $Z=1$ and $\alpha=4$ tabulated as functions of β in units of the first Bohr orbit radius a_0.*

β	J_1	J_2	K	J	H	Γ	Δ
0.5	1.000	1.078	1.244	1.039	0.039	1.001	0.960
1.0	.500	.750	.970	.625	.125	1.011	.858
1.5	.333	.514	.676	.423	.090	1.014	.725
2.0	.250	.360	.470	.305	.055	1.012	.586
3.0	.167	.202	.210	.185	.018	1.007	.348
4.0	.125	.138	.086	.131	.006	1.005	.189

In the absence of detailed knowledge of the form and properties of ψ_s and the potential $V(\mathbf{r}_s)$, it seems useless to try for anything beyond a rough idea of the magnitude of the results. For this purpose, the fact that $\psi_s=(1/\pi)^{\frac{1}{2}}\exp[-r_s]$ is best in the region which contributes most to the integral is sufficient. The only case of importance in the exchange terms is $E_s\cong E_a$. When $E_s<E_a$ the important term is H_{ss}. When $E_s>E_a$ the atom is unaffected by the presence of the surface state and no adsorption from this source would result anyway. With these approximations and limitations, the result is

$$H_{sa}=H_{as}=(E_a+U_c)\Delta-K,$$

where

$$K=(1/\pi)\int V(\mathbf{r}_s)\exp[-(r_s+r_a)]d\mathbf{r}_s.\quad(16)$$

The integral for K is best evaluated by transforming to elliptic coordinates. Introducing the expressions (14) for $V(\mathbf{r}_s)$, the integral is written

$$\begin{aligned}K=(\beta^2/4Z)\int_1^{\infty}e^{-\beta\xi}d\xi\bigg\{&(\alpha\beta/2)\int_{-1}^{-1/\xi}(\xi^2-\eta^2)d\eta\\&+\int_{-1/\xi}^{+1}[1-e^{-\frac{1}{2}\alpha\beta(1+\xi\eta)}]\\&\times[(\xi^2-\eta^2)/(1+\xi\eta)]d\eta\bigg\}.\end{aligned}$$

The second integral in {} may be simplified by the substitution $y=\frac{1}{2}\alpha\beta(1+\xi\eta)$. The evaluation from here on is complicated but straightforward. The result is

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* A definition and tabulation of the functions $\overline{Ei}(x)$ and $Ei(-x)$ may be found in Jahnke and Emde, *Tables of Functions* (Teubner, Second Edition, 1933), pp. 78–86.

$$\begin{aligned}K=\frac{1}{4Z}\bigg\{\bigg[&\left(1+\alpha+\frac{2}{\alpha^2}\right)+\left(\frac{\alpha^2-4}{2\alpha}-\frac{2}{\alpha^2}\right)\beta\\&+\left(\frac{7}{4}+\frac{12-\alpha^2}{6\alpha}\right)\beta^2+\frac{\alpha-9}{12}\beta^3-\frac{\alpha}{12}\beta^4\bigg]e^{-\beta}\\&+\left[\frac{\alpha^2-4}{2\alpha^2}+\frac{\alpha+2}{\alpha}\beta-\frac{3}{4}\beta^2-\frac{\alpha}{12}\beta^3\right]\beta^2Ei(-\beta)\\&-\beta^2P(\alpha,\beta)+(1+\beta)e^{-\beta}(\ln\gamma\alpha\beta-Ei(-\alpha\beta))\\&+e^{\beta}[Ei(-(\alpha+2)\beta)-(1-\beta)Ei(-2\beta)]\\&-\frac{\alpha\beta^2(2+\alpha)+4(1-\beta)}{2\alpha^2}e^{-(1+\alpha)\beta}\\&-\frac{\alpha\beta(2+\alpha)-2(2-\alpha)}{2\alpha^2}(1+\tfrac{1}{2}\alpha)\beta^2e^{-\frac{1}{2}\alpha\beta}\\&\times Ei(-(1+\tfrac{1}{2}\alpha)\beta)\bigg\},\end{aligned}\tag{17}$$

where

$$P(\alpha,\beta)=\int_1^\infty[\ln\tfrac{1}{2}\gamma\alpha\beta(1+\xi)-Ei(-\tfrac{1}{2}\alpha\beta(1+\xi))]e^{-\beta\xi}d\xi/\xi^3.$$

This function was evaluated by numerical integration. γ is Euler's constant.

The electronic part of the energy exclusive of E_a and the interaction U_c of the cores of solid and atom is

$$W_e=E-E_a-U_c.$$

This becomes on substitution of Eqs. (13), (15), and (16) in Eq. (12) for real C and D

$$W_e=-\frac{C^2J_1+D^2J_2+2CDK}{1+2CD\Delta}.\tag{18}$$

In minimizing this expression with respect to C and D it is convenient to introduce the following quantities

$$\begin{aligned}J&=\tfrac{1}{2}(J_1+J_2),\\H&=\tfrac{1}{2}(J_2-J_1),\\\Gamma&=[1+H^2(1-\Delta^2)/(K-J\Delta)^2]^{\frac{1}{2}}.\end{aligned}\tag{19}$$

In terms of these the minimum value of W_e is

$$W_e=\frac{J-K\Delta+(K-J\Delta)\Gamma}{1-\Delta^2}.\tag{20}$$

The percent ionization, χ, of the visiting core is

$$\chi=100(1-D^2)=100C^2.$$

When C is given its limiting value in Eq. (11) and for simplicity β_1 is taken equal to β_0, this is

$$\chi=100\beta/\beta_0.\tag{21}$$

For the case in which C is determined to give W_e its minimum value, however, the percent ionization is given by

$$\chi=\frac{50(K-J\Delta)(1-\Gamma\Delta)^2}{(\Gamma-\Delta)[(K-J\Delta)(\Gamma-\Delta)+H(1-\Delta^2)]}.\tag{22}$$

Computations were made for the special case $Z=1$ and $\alpha=4(V_0=2)$. In this case the visitor is a hydrogen atom, the energy is in the usual Rydberg unit $e^2/2a_0$, and β is in units of a_0. In Table I, the values of the various interactions computed from Eqs. (13), (15), (17), and (19) with these values of the parameters are given as functions of β.

In the upper part of Fig. 2 the percent ionization of the visiting atom is plotted against β. The full curve is a plot of Eq. (22) for the case giving minimum energy. The broken curves are plots of Eq. (21) for $\beta_0=1.5$, 2, 3, and 4. In the figure χ is shown to rise discontinuously from 0 to 100. Actually the rise would take place rapidly in a short interval of β around the value β_0, and would, doubtless not go all the way to $\chi=100$. However, the energy curves are not particularly sensitive to this behavior and the energy minima obtained later would not be appreciably affected by it. In the lower part of Fig. 2 the energy W_e is plotted as a function of β under various conditions. The upper full curve represents the interaction J' of the neutral atom, Eq. (9), before the surface state becomes stable. In this case it is simply $-1/\beta^3$. The lower full curve gives the minimum value of W_e, Eq. (20), in the presence of the surface state, and with $E_s=E_a$. The dotted curve represents the energy $W_e=-J_1$ for the case $E_s<E_a$. The broken curves are plots of Eq. (18) with C given by its minimum value in Eq. (11) (when $\beta_1=\beta_0$) for the same values of β_0 above. Each curve is joined to the minimum energy curve when the corresponding value of C is reached. For comparison the corresponding contribution for H_2^+

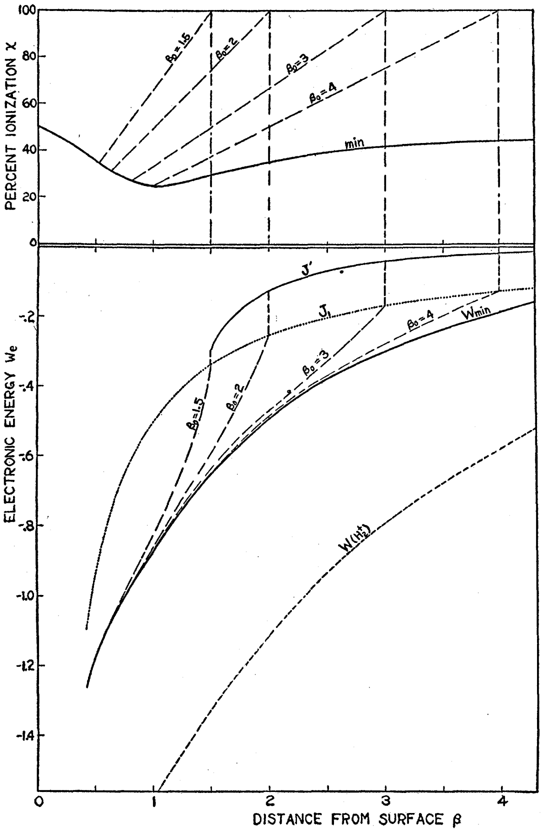

FIG. 2. Upper part: Percent ionization of the hydrogen atom as a function of its distance from the surface. Full curve for minimum energy and broken curves determined by the stability condition. Lower part: Upper full curve J' is classical image interaction of a neutral H atom with the metal and the dotted curve J_1 the corresponding interaction of an H ion. The lower full curve is the minimum electronic energy and the upper broken curves are this energy determined by the stability condition. The lower broken curve is the corresponding term for the hydrogen molecular ion.

$$W(H_2^+) = -2[(1/\beta)-(1+(1/\beta))e^{-2\beta} + (1+\beta)e^{-\beta}]/[1+(1+\beta+(1/3)\beta^2)e^{-\beta}]$$

is shown in the dashed curve.

At first sight it appears that the binding energy is considerably less than in H_2^+. But this may not at all be the case. In H_2^+ there is superposed on the electronic energy W_e a strong repulsion of the two nuclei. In this case no such repulsion exists at large distances. The interaction is given entirely by the electronic energy W_e until the visiting core actually penetrates the electron clouds of the surface atoms. The character of the repulsion due to this penetration depends also on whether the adsorption occurs above a lattice point or on a space intermediate between lattice points. Thus the repulsive term U_c is of much shorter range in this case than in H_2^+ where it is $2/\beta$. From the standpoint of its source in the penetration by the ion of the electron clouds extending from the surface, U_c for this case would presumably be of the approximate form $(2/\beta)\exp[-\beta/b]$. Without attempting to determine a particular value of b, the depths and positions of the minima formed by the superposition of the W_e curves in Fig. 2 and this term were obtained for different β_0. The values so obtained are plotted as functions of b in Fig. 3. For convenience, the equilibrium energy and separation are given in kilogram calories per mol and angstroms, respectively, as well as in the units used here.

COMPARISON WITH EXPERIMENT

Activated adsorption of H_2 on Cu and Ni has been observed by Benton and White[12] with heat of adsorption from 10,000 to 30,000 calories. Beebe *et al.*[13] give 11,000 to 12,000 calories for the heat of adsorption of H_2 and D_2 on Cu. For H_2 on zinc oxide, Taylor and Sickman[14] give a heat of adsorption of 21,000 calories with activation energies ranging from 7000 calories to 15,000 calories depending on the temperature and the fraction of surface covered. The heat of the low temperature molecular adsorption represented by the minimum in curve (m), Fig. 3, is in this case 1100 calories. Taylor and Williamson[15] have examined H_2 on manganous oxide and manganous-chromic oxide. The heat of adsorption on the latter at low temperatures is 1900 calories while at high temperatures the heat of activated adsorption is 20,000 calories per mol. The activation energies are respectively 19,000 and 10,000 calories on the two adsorbates. Kingman[16] obtained 30,000 calories activation energy for H_2 on charcoal.

The theory in the form presented here cannot hope to account for the specific properties of activated adsorption of H_2 on particular

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[12] A. F. Benton and T. A. White, J. Am. Chem. Soc. **52**, 2325 (1930).

[13] R. A. Beebe *et al.*, J. Am. Chem. Soc. **57**, 2531 (1935).

[14] H. S. Taylor and D. V. Sickman, J. Am. Chem. Soc. **54**, 611 (1932).

[15] H. S. Taylor and A. T. Williamson, J. Am. Chem. Soc. **53**, 2177 (1931).

[16] F. E. T. Kingman, Trans. Faraday Soc. **28**, 269 (1932).

adsorbates. It should, however, be capable of accounting for heats of adsorption between 10,000 and 30,000 calories per mol and for activation energies between 5000 and 30,000 calories. The latter are easily accounted for by Lennard-Jones' proposed mechanism since the intersection G of curves (a) and (m), Fig. 3, is subject to considerable variation. It could easily occur for values of the activation energy A between, say, 0 and $\frac{1}{2}D$ which for H_2 gives it a range of 50,000 calories. To account for the former, use is made of the result obtained at the outset that the required binding per mol of atomic hydrogen adsorbed in the activated state is $\frac{1}{2}(D+E-A)$. The above ranges of E and A mean a maximum range in $E-A$ of $-20{,}000$ to $+25{,}000$ calories. Since D is 103,000 for H_2, this means that a binding between 40,000 and 65,000 calories per mol of H is needed to account for the observed activated adsorptions of H_2. An inspection of Fig. 3 shows that for $\beta_0 \geqslant 3$ this range of binding energy is obtained for values of b between 1.5 and 2.0. This is a highly probable range for the parameter b.

The model employed here is of course a rather crude representation of the actual conditions and the form assumed for the repulsive term U_c is only a very rough approximation to the truth. It would be unwise, therefore, to draw any conclusions from the curves of Fig. 3 as to the actual values or ranges of values of the parameters β_0 and b to be associated with observed adsorptions.

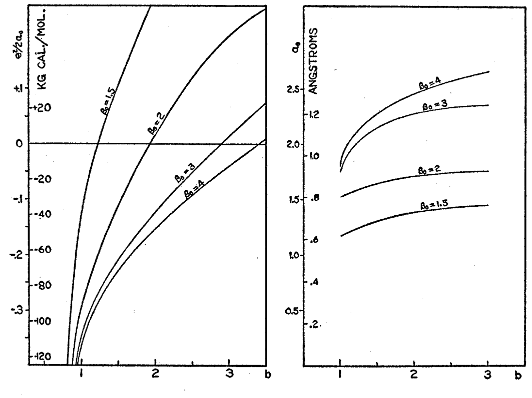

FIG. 3. Left: Value of the energy minimum in Rydberg units $e^2/2a_0$ and kilogram calories per mol as a function of the parameter b in the assumed repulsive potential $U_c=(2/\beta)\exp[-\beta/b]$. Right: Position of the energy minimum in atomic units a_0 and in angstroms as a function of b.

But it does seem possible to conclude that the proposed scheme of binding to surface states leads to the right order of magnitude of binding energy and gives enough flexibility to account for the wide range in the observed values of E and A.

In conclusion the author wishes to express his gratitude to Dr. William Shockley for the priviledge of seeing and using his paper on surface states before publication and for his several helpful criticisms of this paper.

APPENDIX

In the interior of a crystal lattice the potential may be expressed in the usual Fourier series and the solution has the general form (1). If the surface of the solid is regarded as lying in the x, y plane with the origin in the surface, then the wave function analogous to Shockley's one-dimensional case may be written for the interior

$$\psi_i(\mathbf{r})=u(\mathbf{r})\exp[\gamma z+ik_x x+ik_y y]; \quad z\leqslant 0. \tag{23}$$

Outside the solid, the potential may be expanded as

$$V(\mathbf{r})=V_{00}(z)+\sum_{\mathbf{g}} V_{\mathbf{g}}(z)\exp[2\pi i\mathbf{g}\cdot\boldsymbol{\rho}], \tag{24}$$

where $\boldsymbol{\rho}$ is the vector (x, y) and $\mathbf{g}$ is a two-component vector drawn to points of the reciprocal lattice of the surface. The Schroedinger equation for this potential function is not separable and hence its solutions are rather difficult to discuss even approximately.

We denote by $\boldsymbol{\kappa}$ the vector (k_x, k_y) and by $\psi_e(\mathbf{r})$ the solution of Schroedinger's equation in the region exterior to the surface. The fitting at the surface where $z=0$ is performed by making

$$\psi_e(\boldsymbol{\rho}, 0)=u(\boldsymbol{\kappa}, \gamma; \boldsymbol{\rho}, 0)\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}]$$

and

$$\gamma=[(\partial/\partial z)\ln(\psi/u)]_{z=0}. \tag{25}$$

The second of these conditions means that in the neighborhood of $z=0$, $\psi_e(\mathbf{r})$ must have the form

$$\psi_e(\mathbf{r})=f(z)h(\boldsymbol{\rho})u(\mathbf{r})$$

in order to make the fitting possible for all $\boldsymbol{\rho}$. By comparison with the first of the conditions (25), this means that

$$\lim_{z\to 0}\psi_e(\mathbf{r})=f(z)u(\boldsymbol{\kappa}, \gamma; \mathbf{r})\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}]$$

with

$$f(0)=1.$$

It is possible to introduce an alteration of the potential (24) which makes the Schroedinger equation separable. The basis for the alteration is the observation that the periodic variations with $\boldsymbol{\rho}$ of the potential of an electron in the surface field must be fairly rapidly damped out with increasing distance from the surface. As a first approximation it is therefore quite proper to neglect all terms in (24) except the first $V_{00}(z)$. The electron wave function in this field is then quite simple being given by

$$\psi_e(\mathbf{r})=f_n(z)\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}]$$

with

$$\frac{d^2f_n}{dz^2}+\frac{2m}{\hbar^2}(E_n{}^0-\hbar^2|\boldsymbol{\kappa}|^2/2m-V_{00}(z))f_n=0. \tag{26}$$

It is convenient to denote the eigenvalues of this equation by $\epsilon_n=E_n{}^0-\hbar^2|\boldsymbol{\kappa}|^2/2m$. The subscript n enumerates a set of solutions of Eq. (26) which are regular at infinity and appropriate for the fitting involved in Eqs. (28).

As a second approximation we regard the neglected terms in the potential (24) as a perturbation. The first-order correction to the energy is then $\sum_{\mathbf{g}}V_n(\mathbf{g})$ where

$$V_n(\mathbf{g})=\int f_n{}^*(z)\,V_{\mathbf{g}}(z)f_n(z)dz.$$

In view of this the substitute potential

$$U_n(\mathbf{r})=V_{00}(z)+\sum_{\mathbf{g}}V_n(\mathbf{g})\exp[2\pi i\mathbf{g}\cdot\boldsymbol{\rho}]$$

will give the same energies for an electron in the exterior field of the solid as the true potential (24) to the extent of first-order perturbation theory. This potential makes the Schroedinger equation separable and leads to the solution

$$\psi_e(\mathbf{r})=f_n(z)Q_n(\boldsymbol{\kappa},\boldsymbol{\rho}), \tag{27}$$

where

$$\frac{\partial^2Q}{\partial x^2}+\frac{\partial^2Q}{\partial y^2}+\frac{2m}{\hbar^2}\{W-\sum_{\mathbf{g}}V_n(\mathbf{g})\exp[2\pi i\mathbf{g}\cdot\boldsymbol{\rho}]\}Q=0$$

and

$$\frac{d^2f}{dz^2}+\frac{2m}{\hbar^2}(E-W-V_{00}(z))f=0.$$

The solutions of the equation for Q with the proper physical behavior are of the well-known form

$$Q_n(\boldsymbol{\kappa},\boldsymbol{\rho})=v_n(\boldsymbol{\kappa},\boldsymbol{\rho})\exp[i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}]$$

while the equation for $f(z)$ has the same solutions as before with the same eigenvalues ϵ_n. The energies E_n are therefore given by $\epsilon_n=E_n-W_n(\boldsymbol{\kappa})$ or by

$$E_n=W_n(\boldsymbol{\kappa})+\epsilon_n=E_n{}^0+W_n(\boldsymbol{\kappa})-\hbar^2|\boldsymbol{\kappa}|^2/2m.$$

The eigenvalues $W_n(\boldsymbol{\kappa})$ of the equation for Q are functions of both n and $\boldsymbol{\kappa}$ since the coefficients of the substitute potential depend on n. W_n plotted against k_x, k_y would give the usual discontinuous bands around a paraboloid-like surface.

In order to perform the fitting of the interior and exterior wave functions, generalize the exterior solution by taking a linear combination of the solutions (27) with respect to n,

$$\psi_e(\mathbf{r})=\sum_n c_nf_n(z)Q_n(\boldsymbol{\kappa},\boldsymbol{\rho}).$$

Smooth fitting of this at the boundary $z=0$ with the interior wave function (23) is performed by taking

$$u(\boldsymbol{\kappa},\gamma;\boldsymbol{\rho},0)=\sum_n c_nf_n(0)v_n(\boldsymbol{\kappa},\boldsymbol{\rho})$$

and

$$[(\partial/\partial z)u(\boldsymbol{\kappa},\gamma;\boldsymbol{\rho},z)]_{z=0}=\sum_n c_n(f_n{}'(0)-\gamma f_n(0))v_n(\boldsymbol{\kappa},\boldsymbol{\rho}). \tag{28}$$

The solution of these equations implies the determination of the c_n's as functions of γ, $c_n(\gamma)$, to satisfy the first equation in whatever range or ranges of γ it is possible to do so. Then a particular value or values of γ must be found if possible for which the second of the equations is satisfied. This would in general be possible only for discrete values γ_i. For these values, stable surface states would exist and their energy would be given by

$$E_i(\boldsymbol{\kappa})=\sum_n c_n{}^2(\gamma_i)(\epsilon_n+W_n(\boldsymbol{\kappa})). \tag{29}$$

As a practical attack on the problem of surface states, this particular method is probably out of the question. The functions $v_n(\boldsymbol{\kappa},\boldsymbol{\rho})$ are not orthogonal for different n so that the determination of the coefficients c_n would be most difficult. To make matters worse, γ appears implicitly in the functions $u(\mathbf{r})$ as indicated in

Eqs. (28) so that the determination of the particular values which satisfy the equations would be extremely difficult.

Certain general conclusions can, however, be drawn from this treatment. If the energies E_i are plotted against k_x and k_y, the resulting surface would show the usual characteristics of continuous bands with forbidden regions between. This must be the case since the behavior of the solution in any plane parallel with the surface is identical with that of the interior solutions. In the corresponding plot of energy (but not now of E_i) against k_z (not γ) at constant k_x and k_y, the bands obtained represent possible energies for the interior electrons and form the spectrum of the totality of solutions for which μ_z is pure imaginary. If there is no degeneracy between surface states and interior states, this spectrum will not overlap the spectrum of E_i as a function of γ. This places the surface states in the energy gaps between allowed bands of the interior states.

Now introduce the energies

$$E_i' = E_i - \sum_n c_n^2(\gamma_i) W_n(\boldsymbol{\kappa}) = \sum_n c_n^2(\gamma_i)\epsilon_n,$$

which may be regarded as the contribution to the total energy E_i by the z dependent part of the wave function. They are therefore directly comparable to the energy in the one-dimensional solutions of Tamm and of Shockley. None of the energies E_i' can be smaller than the lowest eigenvalue ϵ_1 of Eq. (26). This in turn together with all the other eigenvalues ϵ_n is determined by the form and magnitude of the potential $V_{00}(z)$. A decrease in the surface potential would decrease all the ϵ_n's and so the surface state energies E_i'. It would seem, however, that as a result of the complicated dependence of the ϵ_n's on the form as well as magnitude of $V_{00}(z)$, the relation (2) for actual solids might involve V_s in a much more complicated manner. The other factor which limits the energies E_i' is the set of coefficients $c_n(\gamma)$. As the coefficients for large n become larger at the expense of those for small n, the lower limit to the energies E_i' increases. Since these coefficients arise from the fitting of the functions $v_n(\boldsymbol{\kappa}, \boldsymbol{\varrho})$ and $u(\boldsymbol{\kappa}, \gamma; \boldsymbol{\varrho}, 0)$, this dependence may be associated with the term involving p in (2). The actual dependence is, however, very complex. It is on the whole far better to interpret the energy above which surface states appear in terms of the intersection of the bands as described in Shockley's paper. The other alternative of expressing it in terms of parameters associated with the surface and interior potentials as in (2) would seem to lead to considerable complexity. At the same time the use of (2) which is made in this paper is probably justifiable as a simplification of the same order as the others employed.

As a particular example, we may chose $V_{00}(z)$ equal to the image potential, $-e^2/4z$, for $z \geqslant z_0$ and equal to the mean potential energy, $-e^2/4z_0$, in the interior for $0 \leqslant z \leqslant z_0$. Eq. 26 then possesses solutions which are regular at infinity and also at $z=0$ even for $z_0=0$ as follows

$$\begin{aligned} f_n(z) &= [2n!(na_0)^{\frac{1}{2}}]^{-1} \exp[-z/4na_0] \\ &\quad \times [L_n(z/2na_0) - nL_{n-1}(z/2na_0)]; \quad z \geqslant z_0 \\ &= [4n!(na_0)^{\frac{1}{2}}]^{-1} \exp[-z_0/4na_0] \\ &\quad \times \{A_n \exp[ip_n(z_0-z)] \\ &\quad + A_n^* \exp[-ip_n(z_0-z)]\}; \quad z \leqslant z_0 \end{aligned}$$

with

$$\begin{aligned} A_n &= (1 - i/4np_na_0)L_n(z_0/2na_0) \\ &\quad - n(1 + i/4np_na_0)L_{n-1}(z_0/2na_0), \end{aligned}$$

$$p_n = 1/2z_0 - 1/16n^2a_0.$$

These functions are normalized for $z_0 \rightarrow 0$. The functions $L_n(x)$ are Laguerre polynomials of degree n. The eigen energies associated with these functions are $\epsilon_n = -e^2/32a_0n^2$, so that the lowest state ϵ_1 corresponds to only about 0.85 volt.

In addition solutions regular at infinity exist for all $\epsilon < 0$ which are highly singular at $z=0$ if $z_0=0$. These solutions are

$$\begin{aligned} f(z) = e^{-\alpha z/a_0}\Bigg[\frac{a_0}{z} &- \frac{4}{(8\alpha+1)}\left(\frac{a_0}{z}\right)^2 \\ &+ \frac{48}{(12\alpha+1)(8\alpha+1)}\left(\frac{a_0}{z}\right)^3 - \cdots\Bigg]; \quad z \geqslant z_0 \end{aligned}$$

with $\epsilon = -e^2\alpha^2/2a_0$. When $z_0 > 0$ these solutions can be made everywhere finite by setting

$$\begin{aligned} f(z) &= B \exp[ip_0(z_0-z)] \\ &\quad + B^* \exp[-ip_0(z_0-z)]; \quad z \leqslant z_0 \end{aligned}$$

and fitting continuously to the above at $z=z_0$. If now this solution is denoted by $f_0(z)$ and the associated energy by $\epsilon_0=-e^2\alpha^2/2a_0$, a sufficiently general linear combination of solutions for use in Eqs. (28) is probably obtained by taking

$$\psi_e(\mathbf{r})=\sum_{n=0}^{\infty} c_n f_n(z) v_n(\boldsymbol{\kappa}, \boldsymbol{\varrho}).$$

The coefficient c_0, the energy ϵ_0, and the function $v_0(\boldsymbol{\kappa}, \boldsymbol{\varrho})$ will all be functions of the adjustable parameter α. The corresponding quantities for all other values of n will be independent of α. The energy E_i' is

$$E_i'=-(e^2/2a_0)[c_0^2\alpha^2+\sum_{n=1}^{\infty} c_n^2/16n^2].$$

The fitting is performed by choosing the c_n's including c_0 and the parameters α and γ to satisfy both Eqs. (28) and the condition that α and γ shall lead to the same total energy.

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The Structure of Liquid Potassium

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The method of Wall for calculating the free volume per atom in a liquid has been applied to liquid potassium, using the atomic distribution curves for potassium at 70°C and at 395°C given by Thomas and Gingrich. From the free volumes at these temperatures, the entropies of the liquid at its melting point and at its boiling point are obtained. These values, together with the entropy of solid potassium at its melting point and the entropy of potassium vapor at its boiling point, supply the entropies of fusion and of vaporization. Hence the latent heat of fusion is calculated as 2.06 *kj*/mol, and the latent heat of vaporization is calculated as 87.5 *kj*/mol. These values are to be compared with the observed values 2.38 *kj*/mol and 84.0 *kj*/mol, respectively.

THE atomic distribution curves, as obtained from x-ray diffraction patterns of liquid elements, have been used in the determination of certain characteristics of the liquid state. Wall[1] has made use of the atomic distribution curves for liquid sodium at two temperatures to obtain the free volume of the liquid, and the dependence of this free volume upon temperature. These quantities were used to calculate numerical values of the latent heats of fusion and vaporization, which values compared favorably with the corresponding experimental values. Hildebrand[2] used a somewhat different method to calculate the ratio of the energies of vaporization of liquid potassium at two temperatures from the results of Thomas and Gingrich.[3] The experimental value of this ratio was nearly identical with the calculated value. De Boer and Michels[4] use the liquid potassium results[3] in a qualitative comparison with their theoretical calculation of atomic distribution functions at various temperatures. In the present work, the method of Wall is used to calculate the free volume and its temperature dependence in the case of liquid potassium. These quantities are then used to calculate the latent heat of fusion and the latent heat of vaporization for comparison with the corresponding experimental values.

In developing an analytical expression for the atomic distribution function, Wall has adopted a quasi-solid model for the liquid. This model is essentially equivalent to that proposed by Lennard-Jones and Devonshire,[5] i.e., each atom in the liquid is assumed to be trapped (at least

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