son, *ibid.*, p. 444.

[7] Early attempts to detect V^- centers in neutron-irradiated MgO gave negative results. This may have been due either to a high transition-ion content or to the elevated temperatures of uncooled samples in various reactors.

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[12] The nonappearance of Mn^{2+} lines in Fig. 1(a) and their appearance in 1(b) for the same crystal is partially due to their greater saturation at the lower temperature, at which their relaxation time T_1 is greatly increased; the spectrometer gain is also higher in Fig. 1(b) than in 1(a).

[13] In the time required for the decay of induced radioactivity of MgO crystals to a level where they may be handled conveniently, the V_{Al} centers which have been populated by accompanying γ radiation will have decayed at room temperatures. They are easily regenerated by any ionizing radiation.

[14] If one were able to distinguish $^{25}\mathrm{Mg}$ ENDOR lines from the V_{Al} and V^- centers, discrimination could be made, but a far greater effort is involved.

Charge Densities and Binding Energies in Hydrogen Chemisorption

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The chemisorption of hydrogen on metals is treated by a self-consistent calculation. Three-dimensional charge densities, interaction energies, and dipole moments are given as a function of position of the hydrogen adatoms. The results are compared with experiment. The experimental picture of a dissociated adsorbate of small dipole moment is substantiated, and the calculations are consistent with the observation that hydrogen field desorbs together with the surface atoms of the substrate.

Hydrogen chemisorption on metal surfaces is well studied experimentally.[1-5] Any theoretical description must be in accord with experimental heats of adsorption, changes in work function, adsorbate structure, and desorption-kinetics data. We have completed a three-dimensional self-consistent calculation of hydrogen chemisorption from which many properties can be obtained and compared with experiment. In addition, the calculated charge densities and potentials allow visualization of the chemisorption process for the first time.

Earlier theoretical work has been thoroughly reviewed by Schrieffer.[6] The theoretical advance here stems from our requirement that Poisson's equation be satisfied point by point. That is, there is complete self-consistency between the electrostatic potential used and the charge density obtained. Such self-consistency is now established as essential in metal-surface calculations.[7,8] It has also been shown to be important in the screening of impurities in metal surfaces.[9]

The calculation proceeds from the linear response formulation for a metal surface.[9] The unperturbed metallic surface is treated in the jellium model, the ion-core distribution of the solid being represented by the charge density $\rho_0^{\mathrm{ex}}(\vec{r}) = \rho_+ \theta_-(x)$, where x is the coordinate perpendicular to the surface and $\theta(x)$ is the Heaviside (step) function. The x coordinate of the nuclei for the surface plane is $-\frac{1}{2}d$, where d is the distance between planes parallel to the surface.

The unscreened (or zeroth order) configuration of the chemisorbed hydrogen is taken as a proton situated in the surface region plus an extra electron in the conduction band of the metal. The actual electronic density $n(\vec{r})$ is then found self-consistently by minimizing the energy functional[7] (atomic units are used in this paper, unless noted otherwise):

$$E_{v^{\mathrm{ex}}}[n]=\iint\frac{[n(\vec{r})/2-\rho^{\mathrm{ex}}(\vec{r})]n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r\,d^3r'+\frac{3}{10}(3\pi^2)^{2/3}\int n^{5/3}\,d^3r-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n^{4/3}\,d^3r+\frac{1}{72}\int\frac{(\nabla n)^2}{n}\,d^3r, \qquad (1)$$

where $\int[n(\vec{r})-\rho^{\mathrm{ex}}(\vec{r})]\,d^3r=1$.

An Euler's equation is obtained on minimizing the energy functional. Let u be the cylindrical coordinate in the plane parallel to the surface measured from an axis through the proton, and x' is the coordinate of the proton. We now write $n(u,x;x')=n_0(x)+n_1(u,x;x')$ and keep terms in the Euler equation up to order n_1/n_0 only, where $n_0(x)$ is the electron density of the "bare" surface (without the chemisorbed hydrogen), and $n_1(u,x;x')$ is then the screening charge density. Taking the Fourier transform in the plane parallel to the surface,[9] we obtain the following linearized Euler equation[10] [scaled units[9] are used in Eqs. (2) and (3) in order to make the r_s dependence explicit; $n_1(Q,x;x')$ is the Fourier transform of the screening charge density, while $V_1(Q,x;x')$ is the Fourier transform of the electrostatic potential produced by the proton and its screening charge]:

$$\frac{d^2n_1(Q,x;x')}{dx^2}-\frac{1}{n_0(x)}\frac{dn_0(x)}{dx}\frac{dn_1(Q,x;x')}{dx}+[F(n_0)-Q^2]n_1(Q,x;x')+(2/K)n_0(x)V_1(Q,x;x')=0, \qquad (2)$$

which is to be solved self-consistently with Poisson's equation,

$$\frac{d^2V_1(Q,x;x')}{dx^2}-Q^2V_1(Q,x;x')-n_1(Q,x;x')=\delta(x-x'), \qquad (3)$$

where $\vec{Q}=(0,Q_y,Q_z)$, $Q\equiv|\vec{Q}|$, $K=2^{11/3}3^{-11/3}\pi^{-4/3}r_s$, $r_s=(3/4\pi\rho_+)^{1/3}$, and

$$F(n_0)\equiv\left[\frac{1}{n_0(x)}\frac{dn_0(x)}{dx}\right]^2-\frac{1}{n_0(x)}\frac{d^2n_0(x)}{dx^2}+\frac{9}{2}n_0^{\,1/3}(x)-\frac{4}{3K}n_0^{\,2/3}(x). \qquad (4)$$

$n_0(x)$ is a known function of position, and therefore Eqs. (2) and (3) are coupled linear differential equations for the functions $V_1(Q,x;x')$ and $n_1(Q,x;x')$. The boundary conditions are[10]

$$\lim_{x\to\pm\infty}V_1(Q,x;x')=0,\quad \lim_{x\to\pm\infty}n_1(Q,x;x')=0.$$

For $n_0(x)$, we use the results of Lang and Kohn.[8,11] The solution of Eqs. (2) and (3) is greatly facilitated by fitting $n_0^{\,1/3}(x)$ with

$$\sum_{m=0}^{2}a_m t^m,$$

where $t=\exp(-\beta_Rx)$, $x>0$; $t=\exp(\beta_Lx)$, $x\leqslant 0$. Equation (2) has a regular singular point at $t=0$, and series solutions can be found in the usual way for the homogeneous equations. $V_1(Q,x;x')$ and $n_1(Q,x;x')$ are then given by the appropriate linear combinations of these independent solutions which obey the boundary conditions and the joining conditions at $x=x'$, the location of the proton.

We now present the main results obtained by applying the above formalism to hydrogen chemisorption. We choose $r_s=1.5$ for ρ_+ in an effort to approximate[12,7] the closest-packed surface plane [(110) for bcc] for a refractory transition metal like tungsten. First, we determine the interaction energy between the hydrogen ion and the metal substrate as a function of the coordinates of the proton ($u=0$, x'). This is given, according to the Hellmann-Feynman theorem, by

$$W(x')=V_0(x')+\tfrac{1}{2}\overline{V}_1(x=x',u=0), \qquad (5)$$

where $V_0(x')$ is the electrostatic potential of the "bare" surface and $\overline{V}_1(x=x',u=0)$ is the potential of the screening charge evaluated at the proton location. The latter can be obtained from $V_1(x,x';u)$, since

$$\overline{V}_1(x,x';u)=V_1(x,x';u)-[(x-x')^2+u^2]^{-1/2}.$$

The results are shown in Fig. 1. We found that for large x', $W(x')$ tends to the image potential. That is,

$$W(x')\xrightarrow[x'\to+\infty]{}1/[4(x'-x_0)],$$

where $x_0=\int xn_1(u,x;x'=\infty)\,d^3r$. Thus the image plane is located at the center of mass of the screening charge,[13] and it is shown on Fig. 1 for the case at hand. As x' approaches the surface region ($x'\lesssim 5$ a.u.), the interaction energy begins to deviate significantly from the image potential. Finally, a minimum in $W(x')$ is reached at $x'\simeq 1.08$ a.u. While the position of the minimum

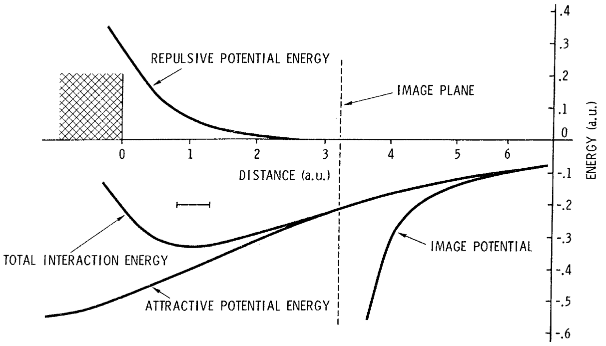

FIG. 1. Hydrogen-ion–metal interaction energy versus separation distance. The nuclei of the surface plane of the metal are located at $-\frac{1}{2}d$, where d is the distance between planes parallel to the surface.

can be used to locate the nucleus of chemisorbed hydrogen (at least at low temperatures), the curve is rather broad near the minimum. Thus we have included a reasonable error bar. The depth of the minimum gives the ionic desorption energy, $E_I = 9$ eV. The experimental value[14-16] for hydrogen on tungsten is $E_I \simeq 11.3$ eV. This gives one a measure of the accuracy of the calculation. For a first-principles calculation with no adjustable parameters, this sort of agreement is encouraging. It should be added that hydrogen is singular in that its ionic desorption energy is much larger than that of other chemisorbed species. This is borne out by our calculation. There is something else that is very interesting about Fig. 1. Note that the image plane is calculated to be on the vacuum side of the hydrogen adatom. This means that the effect of external fields on the chemisorbed hydrogen would be reduced as a result of screening by the metal electrons. The substrate atoms also benefit from this cooperative screening effect. This provides some insight into the experimental result[17] that the fields necessary to desorb hydrogen are essentially the same as those fields used to evaporate the substrate.

Next let us consider the dipole moment of the chemisorbed hydrogen, $P = \int (x' - x) n_1(\vec{r})\, d^3r$, shown in Fig. 2 as a function of x', the location of the hydrogen nucleus. At large separations, since the screening charge remains in the metal,

$$P \xrightarrow[x' \to \infty]{} (x' - x_0).$$

As the ion approaches the metal, it becomes immersed in its screening charge, and it is most interesting to note that the dipole moment changes sign as the ion moves into the surface. This is expected experimentally, as hydrogen increases the work function (negative dipole moment) for most low-index planes. Note that the change in sign occurs at $x' \simeq 1.2$ a.u., which is near the rather broad minimum in the interaction energy at $x' = 1.08$ a.u. This may shed some light on the current disagreement among experimentalists as to the sign of the dipole moment for hydrogen on W(110) (see Ref. 1 for a discussion of this). For the higher-index planes, one would expect the hydrogen to penetrate further into the surface. Thus for these planes we would predict a negative dipole moment whose magnitude is of order 10^{-2} a.u. This is in agreement with experiment,[4] although our prediction is perhaps a factor of 3 to 4 too small.

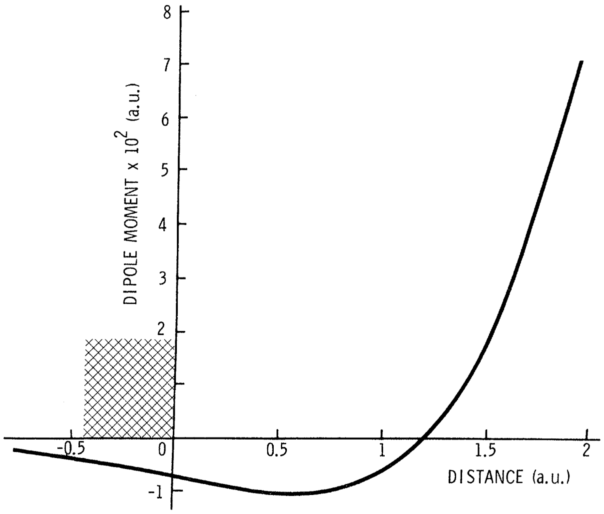

FIG. 2. Hydrogen adatom dipole moment versus the distance between the proton and the metal substrate.

The screening charge densities are plotted for two different positions of the proton in Fig. 3. This affords one a picture of the chemisorption process (scaled units[9] are used—the unit of length is 0.51 Å). In Fig. 3(a) the proton is at $x' = -1.5$; in Fig. 3(b) $x' = +1.5$. In Figs. 3(a) and 3(b), the screening charge is rather symmetric around the proton, consistent with the small dipole moments obtained earlier. It was found that as the ion was moved to still larger x', the screening charge was being left behind, leading to an increased dipole moment. Note that $n_1(u, x; x')$ is a strong function of x', the densities at the peaks varying by a factor of $\simeq 30$ for $1.5 \leqslant x' \leqslant 4.5$. This means that the potential due to the screening charge will change as the proton position is varied. This should be impor-

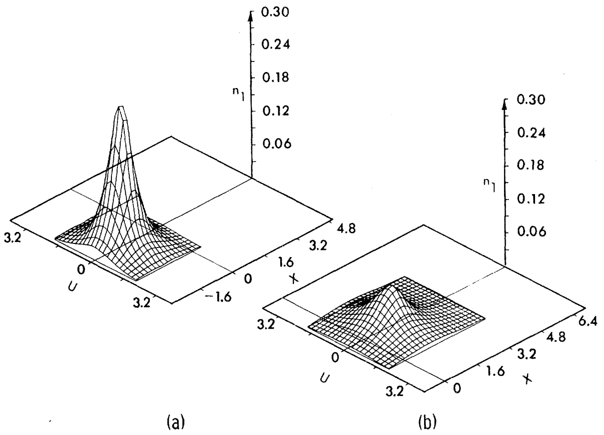

FIG. 3.. Screening charge density $n_1(u,x;x')$ for two positions of the proton: (a) $u=0$, $x'=-1.5$; (b) $u=0$, $x'=+1.5$. Scaled units (Ref. 9) are used—the unit of length is 0.51 Å.

tant in the attempt to determine the position of adsorbed particles via electron scattering.[18] Indeed Duke *et al.*[19] have shown that low-energy electron diffraction intensity profiles can be quite sensitive to scattering phase shifts. Here we see that the screening potential and hence the phase shifts will depend on the position of the chemisorbed hydrogen.

Finally, let us consider the interaction energy between hydrogen adatoms. One can again use the Hellmann-Feynman theorem to show that $V_1(x,x',u)$ is the interaction energy between adatoms whose nuclei are located at (x,u) and at $(x',0)$, respectively. We found that for the two x' values of Fig. 3, the short-range ($\lesssim 2$ a.u.) interaction energy is repulsive. This supports the numerous experimental contentions (see, e.g., Ref. 3) that hydrogen dissociates upon adsorption in the first adlayer on tungsten and certain other metals.

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[10] This equation is strictly true only for $Q\neq 0$. For $Q=0$ there is an additional term in Eq. (2), which arises from the nonzero dipole moment of the chemisorbed hydrogen. This need not concern us here, for it is only necessary to solve for $Q\neq 0$. One can then make use of the continuity of $n_1(Q,x;x')$ in Q to find $n_1(0,x;x')$.

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[13] This result has been derived more generally by N. D. Lang and W. Kohn, to be published.

[14] The experimental E_I is obtained from the atomic desorption energy E_a, the hydrogen ionization potential I, the electron work function φ_e, and the Born-Haber cycle: $E_I=E_a+I-\varphi_e$.

[15] See, e.g., T. E. Madey and J. T. Yates, Jr., *Structure et Properties des Surface des Solides* (Editions du Centre National de la Recherche Scientifique, Paris, 1970), No. 187, p. 155; T. W. Hickmott, J. Chem. Phys. 32, 810 (1960).

[16] As mentioned earlier, the model is most appropriate to the (110) plane, and therefore we took $\varphi_e=5.3$ eV. E_a appears not to be very sensitive to the surface plane, and we used a representative value of 70 kcal/mole (see Ref. 15).

[17] See, e.g., E. W. Muller *et al.*, Surface Sci. 23, 112 (1970).

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