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Properties of a substitutional and/or interstitial surface hydrogen atom

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The ground state of a substitutional and/or an interstitial hydrogen atom at the surface of solids is studied theoretically under the half-confinement approximation. The resultant wave function is not spherically symmetric, thus resulting in a nonzero dipole moment which points toward the solid, and the binding energy of the electron of the impurity-hydrogen atom is significantly lowered. The chemical activity of the confined atom and of the surface of solids is therefore greatly enhanced.

I. INTRODUCTION

Many surface properties, such as adsorption, catalysis, and etching are related to the various defects of the surface.[1-5] In this paper, we investigate a simple but important type of surface defect, namely, the impurity atom trapped in a vacancy at the surface of solids. The results will also be applicable to a description of the impurity atom at an interstitial position of surface. We will give a quantitative discussion of the behavior of the trapped atom in the hope that it will be helpful in the understanding of some chemical and physical processes at the surface.

Obviously, the properties of a substitutional (or an interstitial) atom are determined by its mutual interaction with the neighboring substrate atoms. Such interaction changes the wave function and energy of the impurity atom. Generally speaking, the interaction is rather complicated. However, the problem may be greatly simplified for solids in which the host atom or ion has a closed-shell structure. This is particularly true for molecular crystals which are formed from inert gas atoms. Taking the solid of an inert gas such as Ar as an example, if a surface Ar atom at a lattice point is replaced by a H atom impurity, or the H atom is located in an interstitial position, the neighboring Ar atoms mainly exert Pauli repulsion, restricting the region of motion of the electron of the hydrogen atom. Similar arguments should apply to ionic crystals such as NaCl when a Na^+ ion is replaced by a H atom. As for metal crystals, minor modification may be necessary due to the free electrons.

We can formally introduce some repulsive potential to simulate the action of host atoms on the substitutional or interstitial atom. In fact, similar approximations have been successfully used to describe the properties of a trapped hydrogen atom in solid α-quartz.[6-9] In the original application by Mickels *et al.*,[6] a model of a hydrogen atom confined in a spherical box with an impenetrable wall was made by adding to the normal Hamiltonian an infinite potential at radial distance larger than the radius of the box. There is no difficulty in principle to extend such a model to describe the substitutional or interstitial surface atom if the substrate atom is closed-shell one. The main modification now is that the box is opened. Following Mickels *et al.*, we replace the infinite potential

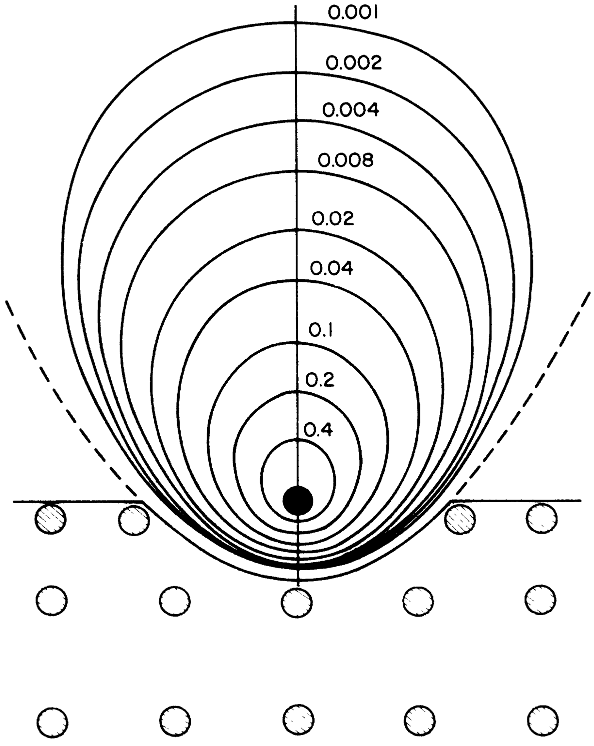

FIG. 1. The geometry of the surface vacancy and the contours of probability density of electron of the half-confined hydrogen atom in ground state in the vacancy ($\nu_1=1,\nu_2=0,m=0$). The shape of the potential wall of repulsion is approximately represented by a paraboloid of revolution. ζ_0 is approximately equal to the nearest-neighbor distance of the solid. ●, the nucleus of the impurity-hydrogen atom; ○, the host atom.

by an equivalent boundary condition of the wave function. The wave function of the electron of the impurity atom is required to vanish at the impenetrable wall of the vacancy. We prefer to use an upward-opened paraboloidal wall rather than a hemisphere one to describe the geometry of the surface vacancy (Fig. 1) because it leads to simple analytic solution of the Schrödinger equation. We note that the dashed line in Fig. 1 represents a segment of the fictitious wall which has very little effect on our calculation because the wave function is very small there.

The paper is organized as follows. In Sec. II, the Schrödinger equation of half-confined atomic hydrogen at the surface of a solid is solved. We obtain a simple wave function of the ground state and we use it to compute the dipole moment. The ground-state energy is also computed. In Sec. III some general properties of the substitutional or interstitial surface atom and their consequences are discussed.

The calculation of atomic hydrogen is not only for the sake of simplicity, but also for the following considerations: (1) a hydrogen atom exhibits high surface mobility; therefore, it may be easier for it to be trapped in a surface vacancy; (2) hydrogen atoms are particularly important in astrochemistry, due to the abundance of the element hydrogen in the universe (about 90%).

We would like to emphasize the substantial difference of the present discussion from the conventional one. Here the substitutional hydrogen atom located in a surface vacancy or the hydrogen at an interstitial position of surface is a half-confined atom which is only weakly bound. Its behavior is quite different from that of the bonding atom such as H-W, H-Si, and H-Pb at the surface of the solid. We believe such surface atoms are much more active in chemical processes than the bonding atoms.

II. BASIC FORMULAS AND CALCULATIONS

We assume the impenetrable potential wall of surface vacancy has a paraboloidal shape, as illustrated in Fig. 1. The nucleus of a hydrogen atom is located at the focus of paraboloids of revolution. To describe the motion of atomic hydrogen, it is most convenient to use the parabolic coordinates (ζ,η,ϕ):[10]

$$x=\sqrt{\zeta\eta}\cos\varphi,\quad y=\sqrt{\zeta\eta}\sin\varphi,\quad z=\tfrac{1}{2}(\eta-\zeta)\ , \tag{1}$$

where ζ and η range from zero to ∞ and φ ranges from zero to 2π. The surfaces of constant ζ (or η) are upward opened (or downward opened) paraboloids of revolution about the z axis normal to the surface of a solid. The Schrödinger equation of atomic hydrogen in parabolic coordinates is

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{4}{\zeta+\eta}\left[\frac{\partial}{\partial\zeta}\zeta\frac{\partial}{\partial\zeta}+\frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta}\right]+\frac{1}{\zeta\eta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{2e^2}{\zeta+\eta}\right\}\psi(\zeta,\eta,\varphi)=E\psi(\zeta,\eta,\varphi)\ . \tag{2}$$

According to the discussion given in Sec. I, the interaction of the electron of the hydrogen atom with the solid is represented by the requirement that the wave function vanish on the impenetrable potential wall,

$$\psi(\zeta_0,\eta,\varphi)=0\ , \tag{3a}$$

where ζ_0 is a parameter characterizing the shape of the vacancy.[11]

Another natural condition is, of course,

$$\psi(\zeta,\eta,\varphi)|_{\eta\to\infty}=0\ . \tag{3b}$$

The Schrödinger equation (2) with the boundary conditions (3a) and (3b) can be solved in a similar way as for the free hydrogen atom. We briefly outline the procedure. Inserting

$$\psi(\zeta,\eta,\varphi)=cf_1(\zeta)f_2(\eta)f_3(\varphi) \tag{4}$$

into Eq. (2), we obtain the following equations:

$$\left[-\frac{\hbar^2}{2\mu}\left[\frac{4}{\zeta}\frac{d}{d\zeta}\zeta\frac{d}{d\zeta}-\frac{m^2}{\zeta^2}\right]-\frac{4\beta_1}{\zeta}\right]f_1=Ef_1\ , \tag{5a}$$

$$\left[-\frac{\hbar^2}{2\mu}\left[\frac{4}{\eta}\frac{d}{d\eta}\eta\frac{d}{d\eta}-\frac{m^2}{\eta^2}\right]-\frac{4\beta_2}{\eta}\right]f_2=Ef_2\ , \tag{5b}$$

$$\frac{d^2f_3}{d\varphi^2}=-m^2f_3\ , \tag{5c}$$

where the parameters β_1 and β_2 satisfy

$$\beta_1+\beta_2=\tfrac{1}{2}e^2\ . \tag{6}$$

The solution of (5c) is

$$f_3(\varphi)=e^{im\varphi}\ , \tag{7}$$

with the magnetic quantum number $m=0,\pm1,\pm2,\ldots$.

For bound states $E<0$, we introduce the dimensionless variables

$$\nu=\frac{e}{\sqrt{-2a_0E}},\quad \rho_1=\frac{\zeta}{2a_0\nu},\quad \rho_2=\frac{\eta}{2a_0\nu}\ , \tag{8}$$

where $a_0\equiv h^2/\mu e^2\simeq0.53$ Å is the Bohr radius. ν corresponds to the principal quantum number n of a free hydrogen atom.

Equations (5b) and (5c) can now be written as

$$\frac{d^2f_i}{d\rho_i^2}+\frac{1}{\rho_i}\frac{df_i}{d\rho_i}+\left[\frac{2}{\rho_i}\left[\frac{|m|+1}{2}+\nu_i\right]-\frac{m^2}{4\rho_i^2}-1\right]f_i=0,\quad i=1,2 \tag{9a}$$

with

$$\nu_i=\frac{2}{e^2}\nu\beta_i-\tfrac{1}{2}(|m|+1),\quad i=1,2 \tag{9b}$$

and

$$\nu_1+\nu_2+|m|+1=\nu\ . \tag{9c}$$

The asymptotic solution of Eq. (9) behaves like $e^{-\rho_i}$ at large ρ_i and like $\rho_i^{|m|/2}$ at small ρ_i. Therefore, we assume

$$f_i(\rho_i)=e^{-\rho_i}\rho_i^{|m|/2}w_i(\rho_i)\ . \tag{10}$$

The equation for $w_i(\rho_i)$ is obtained by combining (9) and (10),

$$\rho_i\frac{d^2w_i}{d\rho_i^2}+(|m|+1-2\rho_i)\frac{dw_i}{d\rho_i}+2\nu_i w_i=0\ . \tag{11}$$

The solution of Eq. (11) is the well-known confluent hypergeometric function[12]

$$w_i(\rho_i)=F(-\nu_i,\ |m|+1,\ 2\rho_i)\ , \tag{12}$$

where

$$F(\alpha,\beta,z)\equiv 1+\frac{\alpha}{\beta}\frac{z}{1!}+\frac{\alpha(\alpha+1)}{\beta(\beta+1)}\frac{z^2}{2!}+\cdots\ . \tag{13}$$

Therefore, the solution of the Schrödinger equation is

$$\begin{aligned}\psi(\zeta,\eta,\varphi)=&\,C(\rho_1\rho_2)^{|m|/2}\\ &\times e^{-\rho_1-\rho_2}F(-\nu_1,\ |m|+1,\ 2\rho_1)\\ &\times F(-\nu_2,\ |m|+1,\ 2\rho_2)e^{im\varphi}\ .\end{aligned} \tag{14}$$

The boundary condition (3b) demands that ν_2 take only non-negative integers $\nu_2=0,1,2,\ldots$.

The boundary condition (3a) is equivalent to

$$F(-\nu_1,\ |m|+1,\ 2\rho_1)\big|_{\rho_1=\rho_1^0}=0\ . \tag{15}$$

$2\rho_1^0\equiv\zeta_0/(a_0\nu)$ are therefore the zeros of the function F. Only positive ν_1 is possible to satisfy Eq. (15). This is because when $\nu_1<0$, each term of the function F in (15) is positive [see Eq. (13)].

We summarize the above results as follows. The eigenfunctions of the Schrödinger equation (2) are expressed in Eq. (14). Each state is labeled by three quantum numbers (ν_1,ν_2,m). $m=0,\pm1,\pm2,\ldots$; $\nu_2=0,1,2,\ldots$; for a given focal distance ζ_0, ν_1 is obtained by solving (15), $\nu_1>0$. The solutions of Eq. (15) form an increasing monotonic series $\nu_1=\nu_1^1,\nu_1^2,\ldots$. The energy of state (ν_1,ν_2,m) is given by $E=e^2/[2a_0(\nu_1+\nu_2+|m|+1)^2]$. ν_1 is in general not an integer.

Our main interest here is the ground state of the half-confined hydrogen atom. It corresponds to $\nu_2=m=0$, and ν_1 is such that $2\rho_1$ is the first positive zero of function F in (15). In practice it is easier to determine ζ_0 for a given ν_1. After obtaining the first positive zero $(2\rho_1^0)$ of Eq. (15), the focal distance $\zeta_0=\nu a_0(2\rho_1^0)$ and the energy are determined.

The wave function of a half-confined hydrogen atom is no longer spherically symmetric but pushed out of the surface somewhat. As an example, the ground-state wave function for $\nu_1=1$ is shown in Fig. 1. With such a wave function, a dipole moment is induced,

$$P=P_z=\frac{\int\psi^* ez\psi\,dv}{\int\psi^*\psi\,dv}\ , \tag{16a}$$

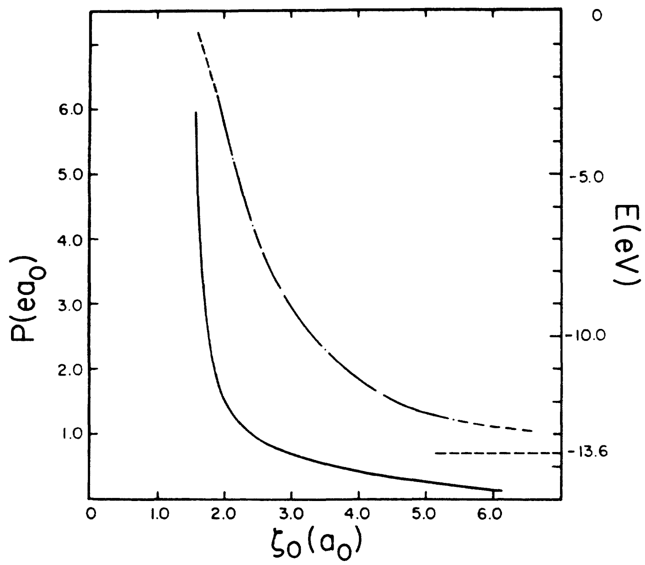

FIG. 2. The dipole moment P and the ionization energy E of the half-confined hydrogen atom in the ground state at the surface as a function of the focal distance ζ_0. ——, the relation of P vs ζ_0; — · — · —, the relation of E vs ζ_0.

with

$$dv=\tfrac{1}{4}(\zeta+\eta)d\zeta\,d\eta\,d\varphi\ . \tag{16b}$$

Note in (16a) the integration limits in variable ζ are from zero to ζ_0.

The ground-state energy and the dipole moment are presented in Table I (Ref. 12), and in Fig. 2. As the focal distance from the large value of the free hydrogen atom limit decreases, the energy is increased, and so is the dipole moment.

III. DISCUSSION AND CONCLUSIONS

Unlike the spherical symmetric wave function of a free hydrogen atom, the ground-state wave function of a half-confined substitutional or interstitial atom is lengthened in the direction normal to the solid's surface. The first consequence of this deformed wave function is the appearance of the dipole moment. The existence of the dipole moment increases considerably the possibility of the interaction of the surface hydrogen with other atoms in the ambient atmosphere. Positive charged ions such as N^{2+} and O^{3+} are particularly attractive to the confined hydrogen atom.

The second consequence of the deformed wave function is the lowering of the binding energy of the electron. Therefore, a half-confined atom is more easily ionized than a free atom. From Table I we see that a more confined atom has a smaller binding energy. We expect experimental verification of this. In the discussion of the chemical reaction at the surface of solids, the energy as well as the change in the wave function should be taken into consideration. Therefore, a greatly enhanced chemical activity of the surface hydrogen is expected.

Strictly speaking, the vacancy at the surface of a solid

TABLE I. Energy E and dipole moment P of the ground state of the half-confined surface hydrogen atom as a function of the parameter ζ_0.

ν_1	ζ_0/a_0	E (eV)	P/ea_0
0.04	5.32	−12.57	0.238
0.2	1.13	−9.44	0.607
0.4	2.53	−6.94	0.893
0.6	2.26	−5.31	1.14
0.8	2.11	−4.20	1.36
1.0	2.00	−3.40	1.58
1.5	1.84	−2.18	2.11
2.0	1.76	−1.51	2.63
3.0	1.66	−0.85	3.64
4.0	1.61	−0.54	4.65

is not electric neutral, but with a weak excess of negative charge which is neglected in the Hamiltonian in Eq. (2). This negative charge tends to adsorb atoms with dipole. The Coulomb force will cause a half-confined hydrogen atom with the dipole pointing toward the surface to be fixed in the vacancy rather tightly. Therefore, our model of the surface hydrogen is quite realistic. Taking the ionic crystal, e.g., NaCl, as an example, the estimation of the order of magnitude of the interaction energy of the impurity hydrogen with its surroundings (i.e., adsorption energy) can be made as follows. When a surface Na^+ is replaced by a H atom, the neighboring Cl^- ions provide a net charge $-e$ (charge of an electron). Under the approximation of homogeneous charge distribution on the surface of a hemisphere with radius ζ_0, the order of the strength of electric field at the center of the sphere is $e/\zeta_0^2 \simeq e/12a_0^2$. (The radius of Na^+ is $\zeta_0 \simeq 3.5a_0$; a_0 is the Bohr radius. Detailed calculation gives $\sim e/2\zeta_0^2$, i.e., only a difference of a factor of 2.) The dipole of the surface H atom corresponding to $\zeta_0 = 3.5a_0$ is $P \simeq 0.5ea_0$ (Fig. 2). Therefore, the adsorption energy is $-\mathbf{p}\cdot\mathbf{E} \simeq e^2/12a_0 \simeq 1$ eV. As for the metal crystals (e.g., Na), the electric field induced by the dipole $\mathbf{p}$ of the confined H atom at surface can be estimated by the mirror-image method. The order of image dipole is $\mathbf{p}' \simeq \mathbf{p}$. Therefore, the adsorption energy ($\mathbf{p}'$-$\mathbf{p}$ interaction) is also of the order of $\sim$eV. The magnitude of the average adsorption force pointing to the inside of the solid is $F_z = -d/dz\,(-\mathbf{p}\cdot\mathbf{E}) \simeq pEz/\zeta_0 \simeq 10^{-4}$ dyn. Here the approximation is due to the fact that the energy $-\mathbf{p}\cdot\mathbf{E} = -pE_z$ is nearly zero at a lattice distance $\sim \zeta_0$ above the solid's surface. The microscopic pressure applied to the surface vacancy would be $p \simeq F_z/2\pi\zeta_0^2 \simeq 10^{11}$ dyn/cm$^2 \simeq 10^5$ atmospheric pressure, which may be helpful to understand the strong body adsorption of some metals (e.g., Pd crystal) to the hydrogen and/or deuterium atoms.

Except for the vacancy, there are also other kinds of defects such as the ledge and kink, etc., at the surface of solids. Although the quantitative treatment of the impurity atoms in these locations is comparatively more complicated, the qualitative behavior remains the same. We expect the deformation of the electron cloud, nonzero dipole moment, and lowering of the ionization energy in general.

Finally, the study of surface atoms may be potentially important for astrochemistry. There is evidence suggesting the existence of small solid particles in the interstellar medium.[13] It seems to us that the surface atoms should play an important role in the formation of molecules.

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