ЖЭТФ, 2003, том 124, вып. 3 (9), стр. 670–679

STABILITY OF NEGATIVE IONS NEAR THE SURFACE OF A SOLID

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Submitted 4 February 2003

Stationary states of molecular negative ions (anions) near the surface of a solid are investigated. The lone electron is assumed to interact with a diatomic molecule and the surface of the solid. The energies of electron levels are determined by solving the $2D$ Schrödinger equation. It is shown that its stable solutions exist at distances from the surface greater than some critical distance, otherwise the electron is detached from the anion. In the case of attraction between the electron and the solid, the interaction potential between the anion and the solid appears to have the Lennard–Jones form and the ion is separated from the surface by some equilibrium distance.

PACS: 34.50.Dy, 32.10.Hq, 31.15.Fx

1. INTRODUCTION

The interaction of electronegative molecules and negative molecular ions (anions) with surfaces of condensed state is extensively studied within the last decades. One of the problems most interesting to us is the formation and evolution of negative ion resonances (NIRs) on surfaces [1–4]. As in the gas phase, NIRs can also be generated at surfaces by the attachment of free electrons to absorbed molecules at a defined energy [1–3]. It has been recognized that the photochemical behavior of adsorbed molecules can effectively be governed by the photoinduced electron transfer from the substrate to the adsorbed molecule [5–7]. In some systems, NIRs thus formed are considered as the driving force for the respective photochemical reaction.

The formation and evolution of NIRs are usually appreciably modified when passing from the gas phase to the surface [8, 9]. This concerns the energy of the temporary negative ion, its lifetime (with respect to the electron loss and dissociation), and the branching ratios between the dissociative attachment channels.

Some electron scattering experiments have been performed on molecules deposited on cold noble gas substrates (solids). Here, a noble gas layer of variable thickness can be used to study the influence of the metallic substrate on the particular process, e.g., the (dissociative) attachment cross section or the energy shift of the negative ion resonance [8–10]. In addition, substrate-induced electron transfer reactions via the initial formation of an electron exciton precursor in the noble gas layer could be observed [3, 13].

The stability of molecular negative ions at or near the surface is an essential point in the investigation of low-energy electron-driven reactions on adsorbed and condensed molecules [14]. In addition to its importance from the standpoint of basic science, the stability of negatively charged particles at or near a solid surface is an important issue in many technological processes like photocopying, laser printing, etc.

In [15], it was shown that the interaction of a negative ion with a nonpolar liquid results in a considerable shift of its photodetachment threshold. Apparently, noticeable shifts can be expected in the interaction of an anion and the surface of a solid. In [16–18], the dynamics of the processes of charge transfer and production of molecular anions in the vicinity of a surface were investigated. It was recognized that an accurate calculation of electron energies requires solving the $2D$ Schrödinger equation, because the spherical symmetry for the lone electron is broken at a short distance from

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the surface [18]. Consequently, on the basis of a one-dimensional perturbation theory, sufficiently accurate values of the electron energy cannot be found at short distances from the surface because higher-order terms require nonspherical corrections to the wave function.

The objective of this paper is to calculate the stationary state energy of the lone electron of a molecular anion near the surface of a solid by solving the stationary $2D$ Schrödinger equation. The interaction of the lone electron with the diatomic molecule is described by a polarization pseudopotential; the interaction with the solid is characterized by a single parameter, the effective energy of the electron inside the solid, V_0.

In this formulation, the problem has a two-dimensional axial symmetry with the axis perpendicular to the surface, and we must therefore solve the $2D$ Schrödinger equation. Solutions of the multidimensional Schrödinger equation are known in the cases where spatial variables can be separated (as in the theory of the Stark effect). In the case of unseparable variables, due to the complexity of the general mathematical formulation, no regular methods, either analytic or numerical, have been developed up to date. As a rule, the multidimensional Schrödinger equation is reduced to a quasi-one-dimensional one, specific for the problem under consideration. There are several approaches to the treatment of multidimensional equations. Among them, the split-step Fourier scheme [19] was used in [20] for the investigation of white noise in the $2D$ nonlinear Schrödinger equation. The $3D$ wave packet propagation method was used in [21] to describe the propagation of an electron near the surface of a solid.

We propose a solution of this problem assuming that the electron state is in fact a superposition of states with different values of the angular momentum in the corresponding effective spherically symmetric potentials. The state with zero angular momentum is assumed to dominate. An exact solution of the Schrödinger equations is then sought as a linear combination of the wave functions corresponding to different values l of the angular momentum. Thus, the $2D$ Schrödinger equation is reduced to an infinite set of one-dimensional equations for the radial wave functions. It can be shown that its solution can be approximated to a very good accuracy by the truncation of the infinite set to two equations for $l = 0$ (zero approximation) and $l = 1$ (first approximation). The latter is easily solved numerically by the iteration method. This allows calculating the lone electron energy as a function of the parameters characterizing its total interaction potential.

Two cases must be distinguished, the repulsive surface (potential barrier) and the attractive surface (potential well). Repulsion of the electron from the surface causes pure repulsion of the anion from the surface; there is the minimum distance at which a stationary state is possible. At shorter distances, nonstationary states emerge, which prove to have the decay times too short to be detected experimentally. Thus, detachment of the electron from a diatomic molecule occurs, and the electron is removed into vacuum.

In the case of an attractive surface, the existence of an electron stationary state depends on the values of potential parameters. If the potential well in a solid is too deep, no stationary state is possible, and the electron is detached from the anion at the distance where the anion decay time becomes shorter than its residence time near the surface of the solid. If the well depth is moderate, there is a finite range with some minimum and maximum distances from the surface where a stationary solution exists. If the potential well is shallow, there is only the minimum distance, as in the case of a potential barrier. In the case of surface attraction, detachment of the lone electron implies its tunneling into the potential well of a solid. If stationary states exist, the curve of interaction between the anion and the surface of the solid has the form characteristic of the interatomic interaction (the Lennard–Jones potential). As is known, this potential has an equilibrium distance. Hence, a molecule-like equilibrium state of the anion near the surface emerges. This makes it possible to predict not only the shift of the electron level (of the electron photodetachment threshold), but also the distance from the surface at which the anion can be found.

This paper is organized as follows. In Sec. 2, the interaction potential for the lone electron and the Schrödinger equation to be solved are written; in Sec. 3, its asymptotically exact solution is found and the first-order approximation to this solution is considered. Potential curves for anions near the surface are calculated in Sec. 4; the results obtained are analyzed in Sec. 5.

2. PROBLEM FORMULATION

We consider a system consisting of a highly polarizable diatomic molecule, the surface of a solid, and a lone electron. The interactions between the molecule and the surface are assumed to be negligibly small, and we can therefore take only the interactions between the lone electron and molecule, and between the electron and the surface into account. We let V_p and V_s denote the respective interaction potentials.

We introduce the spherical coordinate system with the origin at the point of location of the molecule and with the polar axis perpendicular to the surface. The polar axis is directed toward the surface. The corresponding spherical coordinates are denoted by r and θ. The distance between the molecule and the surface is z_0. The half-space $r\xi < z_0$ ($\xi = \cos\theta$) is the vacuum and the other half-space $r\xi \geq z_0$ is occupied by the solid; the surface is defined by the equation $r\xi = z_0$. At sufficiently large distances from the molecule in the vacuum, $r \geq r_c$, where r_c is the molecule hard-core radius, the lone electron polarizes core electrons of the molecule, and the interaction can be described by the polarization potential

$$V_p = -\alpha r^{-4},$$

where α is the molecule polarization in the units of a_0^3 (and a_0 is the Bohr radius) [22]; the length and energy are measured in the units of a_0 and in Ry, respectively (in contrast to the atomic units, we measure the energy in Ry). At small distances $r < r_c$, due to the Pauli principle, a short-range repulsion occurs, and we can therefore set

$$V_p = +\infty \quad \text{at} \quad r < r_c$$

(see [22]). Thus, we use a spherically symmetric pseudopotential to describe a lone electron. Because a real diatomic molecule is not spherically symmetric, this assumption is made for simplicity. We also assume that the electron charge is screened inside the solid and does not therefore interact with the molecule, which allows us to set $V_p = 0$ for $r\xi \geq z_0$.

The lone electron polarizes the surface of the solid, and the arising electrostatic image force is responsible for the interaction between the electron and the surface at large distances. At short distances and inside the solid, the electron experiences attraction caused by polarization of surrounding molecules by its charge and the Pauli repulsion. For simplicity, we do not take the details of this interaction into account and use its simplest form instead.

We note that the characteristic length of variation of the image force potential is given by several a_0, whereas the characteristic length of the lone electron localization (the width of the electron wave function) is about $10a_0$. Obviously, V_s must be uniform inside the solid. This enables approximating V_s by a simple «step» potential $V_s = 0$ for $r\xi < z_0$ and $V_s = V_0$ for $r\xi \geq z_0$. The interaction between the electron and the surface is therefore allowed by a single parameter V_0. This parameter characterizes the interaction as a whole and is essentially an effective one. Its sign depends on the ratio between the strengths of the attractive electrostatic image force outside the solid and the Pauli repulsion inside it. This ratio is defined by constants characterizing the molecule and the solid. In some cases (e.g., the surface of a metal), the image force dominates, and $V_0 < 0$. In this case, a potential well occurs, which causes attraction, at large distances at least. If $V_0 > 0$, the solid is represented by a potential barrier, and the net effect is repulsion.

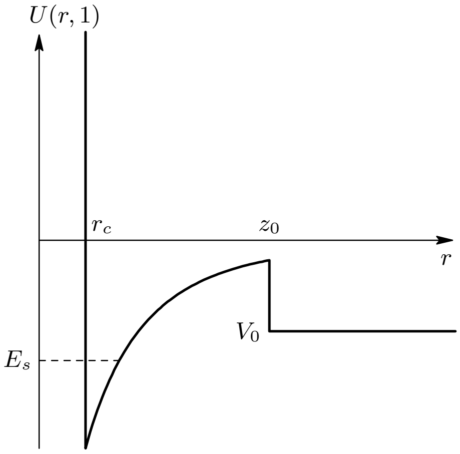

Fig. 1. Interaction potential for the attractive surface along the polar axis

Although the details of the potential V_s can be included (as, e.g., in Ref. [21]), this can considerably complicate the analysis of the results obtained and mask the nature of the effects that we want to demonstrate. At the same time, any complicated form of the electron–surface interaction potential can be included in our formalism if necessary.

Thus, the total electron interaction potential

$$U = V_p + V_s$$

is given by

$$U(r,\xi) = \begin{cases} +\infty, & r < r_c, \\ -\alpha r^{-4}, & \xi r_c \leq \xi r < z_0, \\ V_0, & \xi r \geq z_0. \end{cases} \tag{1}$$

It is shown in Fig. 1. Because potential (1) has the axial symmetry, the electron energy is found from the $2D$ stationary Schrödinger equation

$$\hat{H}\psi = E_s\psi, \tag{2}$$

where $\psi(r,\,\xi)$ is the electron wave function and E_s is the energy. In the spherical coordinates, the Hamiltonian $\hat{H}$ is given by

$$\hat{H} = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \\ -\frac{1}{r^2}\left[\left(1-\xi^2\right)\frac{\partial^2}{\partial \xi^2} - 2\xi\frac{\partial}{\partial \xi}\right] + U(r,\,\xi). \quad (3)$$

The boundary conditions for the wave function are

$$\psi(r_c,\,\xi) = \psi(\infty,\,\xi) = 0. \quad (4)$$

3. THE METHOD OF SOLUTION

To solve Eq. (2), we have to additionally assume that its solution has the same symmetry as the potential $U(r,\,\xi)$ in Eq. (1), i.e., the axial symmetry. This is correct for the ground state, which is a single state for most of diatomic anions in the approximation of the simplified electron–molecule interaction potential V_p.

A solution of Eq. (2) can be represented as an expansion in any complete set of functions of ξ. Similarly to the quantum scattering theory, we use the Legendre polynomials $P_l(\xi)$. But in contrast to scattering, we seek a stationary bound state localized in a finite spatial region with the real energy E_s less than the minimum value of potential (1) at $r \to \infty$. Thus, we can represent the solution as a series in the Legendre polynomials

$$\psi(r,\,\xi) = \frac{1}{r}\sum_{l=0}^{\infty}\varphi_l(r)P_l(\xi). \quad (5)$$

The wave function ψ is normalized to unity,

$$2\pi\int_0^\infty r^2 dr\int_{-1}^{1}|\psi(r,\,\xi)|^2\,d\xi = 1. \quad (6)$$

It follows from the discussion above and condition (6) that $\varphi_l(r)$ are real functions. Substituting (5) in (6) and recalling the normalization and orthogonality condition for the Legendre polynomials,

$$\int_{-1}^{1}P_l^2(\xi)\,d\xi = \frac{2}{2l+1}, \quad \int_{-1}^{1}P_l(\xi)P_k(\xi)\,d\xi = 0, \quad l \neq k,$$

we obtain the normalization condition for the functions $\varphi_l(r)$,

$$4\pi\sum_{l=0}^{\infty}\left[\frac{1}{2l+1}\int_0^\infty \varphi_l^2(r)\,dr\right] = 1. \quad (7)$$

Because the Legendre polynomials are eigenfunctions of the square angular momentum operator,

$$\left(\xi^2-1\right)\frac{d^2P_l}{d\xi^2} + 2\xi\frac{dP_l}{d\xi} = l(l+1)P_l, \quad (8)$$

substitution of expansion (5) in Schrödinger equation (2) yields

$$-\sum_{k=0}^{\infty}P_k\frac{d^2\varphi_k}{dr^2} + \frac{1}{r^2}\sum_{k=0}^{\infty}k(k+1)P_k\varphi_k + \\ + U\sum_{k=0}^{\infty}P_k\varphi_k = E_s\sum_{k=0}^{\infty}P_k\varphi_k. \quad (9)$$

We multiply both sides of Eq. (9) with $P_l(\xi)$ and integrate over ξ from -1 to 1 to derive

$$\frac{d^2\varphi_l}{dr^2} + \left[E_s - \frac{l(l+1)}{r^2}\right]\varphi_l - \sum_{k=0}^{\infty}\bar{V}_{lk}\varphi_k = 0, \quad (10)$$

where the matrix elements

$$\bar{V}_{lk}(r) = \left(l+\frac{1}{2}\right)\int_{-1}^{1}U(r,\,\xi)P_l(\xi)P_k(\xi)\,d\xi \quad (11)$$

are the effective spherically symmetric potentials; they are related by the ratio

$$\bar{V}_{lk} = \frac{2l+1}{2k+1}\bar{V}_{kl}. \quad (12)$$

The boundary conditions for the set of equations (10) are

$$\varphi_l(r_c) = \varphi_l(\infty) = 0. \quad (13)$$

Thus, we have reduced the $2D$ Schrödinger equation to an infinite set of ordinary differential equations (10), each of which corresponds to a certain value of the angular momentum.

Solution of Eqs. (10) makes sense only if series (5) converges fast. This means that some state must dominate superposition (5). Because the increase of the hard-core parameter r_c of the potential V_p by few per cent leads to the disappearance of the bound state of an isolated anion, we can assume that if the lone electron is localized on the molecule, the deviation of its wave function from the spherically symmetric form is moderate. Hence, the s-state ($l = 0$) must dominate, and we can truncate the set of equations (10) at some finite value of l. The error involved in this truncation can easily be estimated by inclusion of a higher-order equation. Thus, (10) can be regarded as a key to obtain an asymptotically exact solution.

In the zero approximation ($l = 0$), Eqs. (10) are reduced to the one-dimensional Schrödinger equation for the radial wave function $\varphi_0(r)/r$ in the spherically averaged interaction potential $\bar{V}_{00}(r)$ in Eq. (1),

$$\frac{d^2\varphi_0}{dr^2} + [E_s - \bar{V}_{00}(r)]\varphi_0 = 0, \tag{14}$$

where

$$\bar{V}_{00}(r) = \frac{1}{2}\int\limits_{-1}^{1} U(r,\,\xi)\,d\xi = V_p(r) + \frac{1}{2}\int\limits_{-1}^{1} V_s(r,\,\xi)\,d\xi = \begin{cases} +\infty, & r < r_c, \\ -\alpha r^{-4}, & r_{hc} \le r < z_0, \\ \dfrac{V_0}{2}\left(1 - \dfrac{z_0}{r}\right) - \dfrac{\alpha}{2r^4}\left(1 + \dfrac{z_0}{r}\right), & r \ge z_0. \end{cases} \tag{15}$$

In the zero approximation, nonsphericity is obviously not allowed. Far from the surface, the lone electron wave function can be approximated by that of an isolated anion $\varphi_\infty(r)/r$. By definition,

$$\frac{d^2\varphi_\infty}{dr^2} + [E_0 - V_p(r)]\varphi_\infty = 0, \tag{16}$$

where

$$E_0 = \lim_{z_0\to\infty} E_s$$

is the electron energy of an isolated anion ($-E_0$ is the electron affinity of an isolated molecule), and we can therefore obtain the electron energy from (14) as

$$E_s \approx E_0 + 2\pi \int\limits_{-1}^{1} \varphi_\infty^2(r) V_s(r,\,\xi)\,d\xi.$$

This coincides exactly with the result of the perturbation theory if V_s is treated as a small perturbation.

At the surface (small distance z_0), V_s is not small, and the first order of the perturbation theory does not therefore provide high accuracy. Calculation of higher-order corrections of the perturbation theory is impossible, because the nonsphericity effect is not included. But we can handle small distances z_0 even in the first approximation on the basis of the set of equations (10). In this approximation, (10) is truncated to two equations for $l = 0$ and 1,

$$\frac{d^2\varphi_0}{dr^2} + [E_s - \bar{V}_{00}(r)]\varphi_0 - \bar{V}_{01}(r)\varphi_1 = 0, \tag{17}$$

$$\frac{d^2\varphi_1}{dr^2} + \left[E_s - \frac{2}{r^2} - \bar{V}_{11}(r)\right]\varphi_1 - 3\bar{V}_{01}(r)\varphi_0 = 0, \tag{18}$$

where relation (12) is used,

$$\bar{V}_{01}(r) = \frac{1}{2}\int\limits_{-1}^{1} U(r,\,\xi)\xi\,d\xi = \begin{cases} 0, & r < z_0, \\ \left(1 - \dfrac{z_0}{r^2}\right)\left(\dfrac{\alpha}{4r^4} + \dfrac{V_0}{4}\right), & r \ge z_0, \end{cases} \tag{19}$$

$$\bar{V}_{11}(r) = \frac{3}{2}\int\limits_{-1}^{1} U(r,\,\xi)\xi^2\,d\xi = \begin{cases} +\infty, & r < r_c, \\ -\alpha r^{-4}, & r_{hc} \le r < z_0, \\ \dfrac{V_0}{2}\left(1 - \dfrac{z_0^3}{r^3}\right) - \dfrac{\alpha}{2r^4}\left(1 + \dfrac{z_0^3}{r^3}\right), & r \ge z_0, \end{cases} \tag{20}$$

and the wave function is the sum of two terms

$$\psi(r,\,\xi) \approx \frac{1}{r}[\varphi_0(r) + \xi\varphi_1(r)] \tag{21}$$

normalized by the condition

$$4\pi \int\limits_0^\infty \left[\varphi_0^2(r) + \varphi_1^2(r)/3\right]\,dr = 1.$$

We can estimate the accuracy of this approximation by comparison of electron energy $E_s^{(0)}$ obtained from (14) with that calculated using (17) and (18), $E_s^{(1)}$.

The set of equations (17) and (18) can be solved numerically using the iteration method. First, we set

$$\varphi_1(r) \equiv 0,$$

and (17) becomes a one-dimensional equation. This equation is solved with the boundary conditions

$$\varphi_0(r_c) = 0, \quad \left(\frac{d\varphi_0}{dr}\right)_{r=r_c} = C_0,$$

where C_0 is an arbitrary number; the parameter E_s appearing in the equation is adjusted to satisfy the boundary condition

$$\varphi_0(\infty) = 0.$$

The obtained value of E_s and the calculated function $\varphi_0(r)$ are then substituted in Eq. (18), which is solved with the boundary conditions

$$\varphi_1(r_c) = 0, \quad \left(\frac{d\varphi_1}{dr}\right)_{r=r_c} = C_1.$$

The value of C_1 is then varied to satisfy the boundary condition

$$\varphi_1(\infty) = 0.$$

For the next iteration, the calculated function $\varphi_1(r)$ is substituted in Eq. (17), etc. This iteration procedure terminates when the difference in the values of E_s obtained from successive iterations, $E_s^{(0)} - E_s^{(1)}$, is sufficiently small. Obviously, the procedure described can also be used for a set containing more than two equations.

4. CALCULATION RESULTS

For numerical calculations, we considered two molecules, O_2 with a moderate polarizability and highly polarizable Br_2. The molecule O_2 was selected because it is widely used in experiments. In addition, in spite of the obvious internal asymmetry, the excess electron can be approximately treated as a lone one, which allows solving the one-electron problem. Br_2 is an example of a dimer with a very high polarizability. Polarizabilities α and electron affinities $-E_0$ for these molecules [23] are listed in the Table. The values of hard-core radii r_c of the potential V_p were adjusted to fit the corresponding experimental electron affinities by the values of $-E_0$ obtained from the ground state solution of Eq. (16).

The set of equations (17) and (18) was solved numerically using the procedure discussed in the previous section for different values of the interaction potential parameter V_0. We first consider positive V_0. Figure 2 illustrates the solution of Eqs. (17) and (18) for Br_2^- at $V_0 = 1$ eV and $z_0 = 2a_0$. In this figure, wave function (21) is plotted in the XZ plane ($Y = 0$) of the Cartesian coordinate system whose Z axis is parallel to the polar axis of the spherical coordinate system used in the foregoing. The spherical coordinates are related to the Cartesian ones as follows:

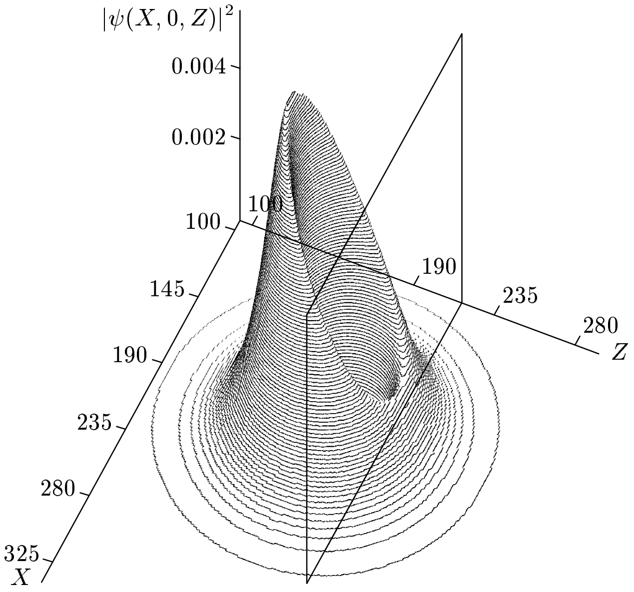

Fig. 2. Wave function for Br_2^- in the XZ plane (repulsive surface, $V_0 = 1$ eV). The plane $Z = 227$ ($z_0 = 2a_0$) indicates the location of the surface of the solid

$$r = \sqrt{x^2 + z^2}, \quad \xi = z/r,$$

$$x = 0.075(X - 200), \quad z = 0.075(Z - 200).$$

It is seen in Fig. 2 that the front of the wave function is lowered near the repulsive surface. This is indicative of a considerable repulsion of the wave function from the surface. The ratio

$$\frac{E_s^{(1)} - E_s^{(0)}}{E_0} = 0.17$$

is moderate, however.

The lone electron energy as a function of the distance from the solid surface is shown in Fig. 3. It is seen that the results are similar for O_2^- and Br_2^-, although the differences in polarizabilities and electron affinities for these molecules are about an order of magnitude. Each curve drops abruptly at some small distance and E_0 vanishes, which is indicative of the existence of the minimum distance at which a stable state of the anion is possible (at this distance, $E_s = 0$). At shorter distances, the electron is detached from the anion and is removed to infinity in the vacuum, which means the electron detachment. Fast vanishing of the effect of the surface as the anion moves away from the surface is also

Parameters of diatomic molecules

Molecule	Polarizability α, a_0^3	Electron affinity E_0, eV	Cutoff radius r_c, a_0
O_2	10.6	0.46	0.909
Br_2	43.6	2.6	1.457

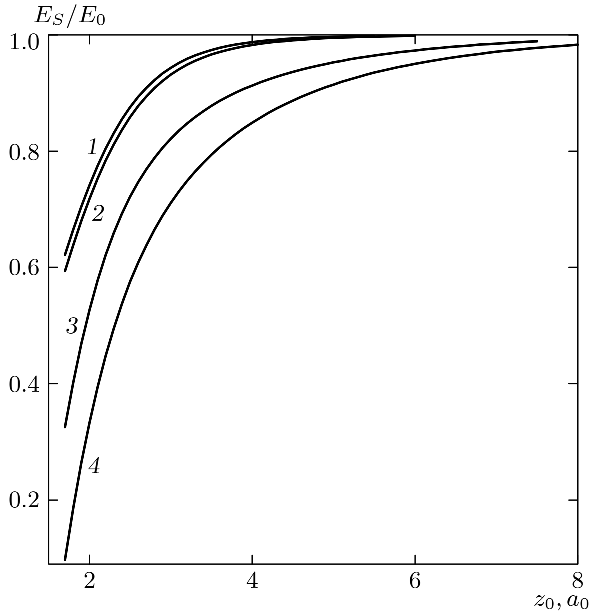

Fig. 3. Lone electron energy as a function of the distance from a repulsive surface. *1* — Br_2^- for $V_0 = 0.5$ eV; *2* — Br_2^- for $V_0 = 1$ eV; *3* — O_2^- for $V_0 = 0.5$ eV; *4* — O_2^- for $V_0 = 1$ eV

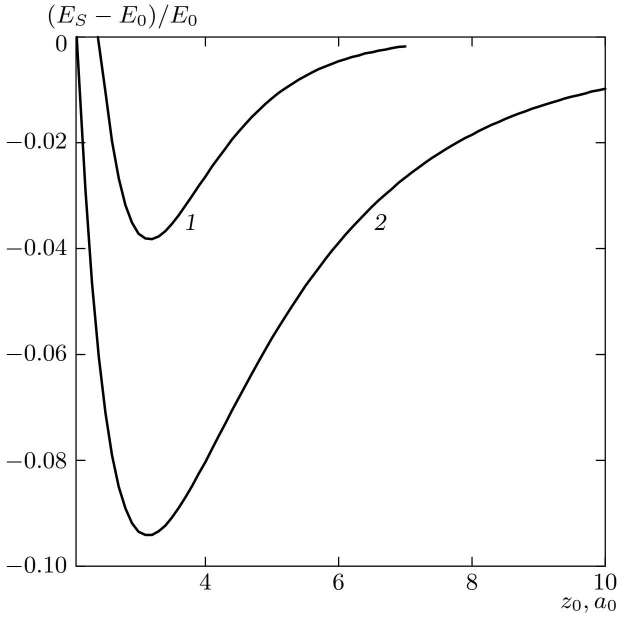

Fig. 4. Relative electron energy shifts as functions of the distance from an attractive surface at $V_0 = E_0$. *1* — Br_2^-; *2* — O_2^-

seen in this figure. We note that the electron energy at a short distance from the surface cannot be calculated on the basis of perturbation theory; at moderate distances, the results of the latter are not of interest because of this vanishing.

In the case of an attractive surface, the form of the wave function is qualitatively similar to the previous case, but the front of the wave function is raised near the attractive surface, which is indicative of the attraction of the wave function. The potential curve $E_s(z_0)$ is more complicated, however. In Fig. 4, the relative energy shifts are shown for the values of V_0 that coincide with the corresponding energies E_0 of isolated anions. For both molecules, potential curves have the form of the Lennard–Jones interatomic potential with a short-range repulsion and vanishing long-range attraction. This behavior of a potential curve holds for any negative value of V_0. The reason of such behavior is as follows. At a large separation z_0 from the surface, $|V_p(z_0)| < |V_0|$, and the effect of the surface amounts to lowering the energy E_s. Because $|V_p(r_c)| \gg |E_0|$, the inequality $|V_p(z_0)| > |V_0|$ holds at sufficiently short distances (interaction of the electron with the molecule is stronger than with the surface), which results in the increase of E_s due to the confinement of space available for the electron and in the consequent increase in its kinetic energy.

A stable electron state is realized only if the energy E_s is less than the minimum value $\lim\limits_{r\to\infty} U(r, \xi)$; otherwise, the tunneling to the region of lower potential must lead to the electron detachment. In the previously considered case of a repulsive potential ($V_0 > 0$), this minimum is equal to zero at $\xi = -1$. If $V_0 < 0$, it is equal to V_0 at $\xi = 1$. In the latter case, the region of stable states is therefore limited by the condition $E_s < V_0$.

In the case of an attractive surface, the existence of a stable state depends on the ratio of parameters E_0

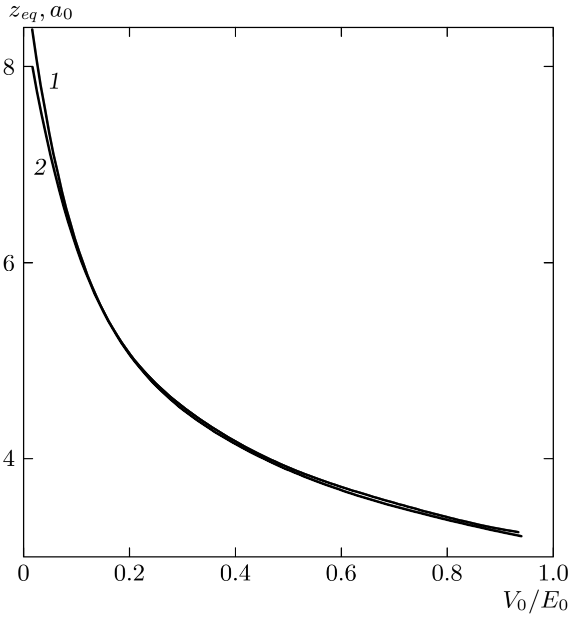

Fig. 5. Equilibrium distance as a function of V_0 for an attractive surface. *1* — Br_2^-; *2* — O_2^-

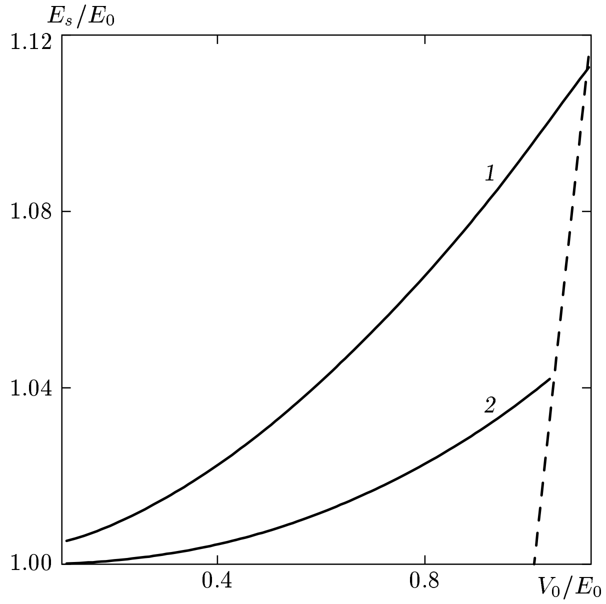

Fig. 6. Equilibrium energies as functions of V_0 for an attractive surface. *1* — Br_2^-; *2* — O_2^-; dashed curve indicates the line $E_s = V_0$

and V_0. If $|E_0| > |V_0|$, a bound state is possible at $z_0 \to \infty$ at least, where $E_s = E_0$. Therefore, a bound state exists at a sufficiently large distance $z_0 > z_{min}$, where z_{min} is a single root of the equation $E_s(z_0) = V_0$. If $|E_0| < |V_0|$, electron detachment occurs at large distances, and the region of possible bound states is finite, $z_{min} < z_0 < z_{max}$, where z_{min} and z_{max} are two roots of the equation $E_s(z_0) = V_0$. As V_0 increases, $z_{min} \to z_{max}$, and at some value $V_0 = V_{min}$, $z_{min} = z_{max}$. Obviously, this case corresponds to the bottom of the potential curve $E_s(z_0)$. At $|V_0| > |V_{min}|$, no stable state is realized; in this case, only electron detachment is possible.

We note that independently of z_0 and the sign of V_0, the interaction with a surface leads to the decrease of anion stability, $|E_s(V_{min}) - V_{min}| < |E_0|$ due to broken spherical symmetry of the lone electron state in an isolated anion.

If we neglect the interaction between the molecule and the surface, which is most likely a hard-core attraction at small distances, then the energy $E_s - E_0$ is that of the anion as a whole. The condition

$$\left(\frac{dE_s}{dz_0}\right)_{z=z_{eq}} = 0$$

defines some distance z_{eq} at which the energy $E_s(z_0)$ reaches the minimum and an equilibrium bound state of the anion at solid surface is realized. We note that the interaction between the molecule and the metal surface may noticeably contribute to the total energy of the anion, especially in the region of short distances z_0, but we can expect that this does not change the situation qualitatively. Equilibrium distances z_{eq} and the corresponding equilibrium state energies $E_{eq} = E_s(z_{eq})$ are shown in Figs. 5 and 6 as functions of the potential well depth V_0. It is seen in Fig. 5 that the equilibrium distance increases sharply as $V_0 \to 0$, and the curves for O_2^- and Br_2^- almost coincide. The quantities $|E_{eq}(V_0)|$ increase with $|V_0|$ until the condition $E_s = V_0$ (dashed curve in Fig. 6) is satisfied. In Fig. 6, the intersection points of solid curves with the dashed curve indicate the maximum well depths at which bound states can occur. For O_2^-, the maximum value of V_0/E_0 is 1.04; for Br_2^-, it is 1.12.

5. DISCUSSION

In this paper, we have solved the $2D$ Schrödinger equation for the lone electron interacting with a diatomic molecule and the surface of a solid. Our solution allows calculating electron energies of an anion at the surface. In the case of an attractive surface, we predict molecule-like bound states of the anion, which are realized if the potential well depth $|V_0|$ characterizing the interaction with the surface does not exceed some threshold value. We have determined this value, above which the electron detachment occurs and the lone electron is removed either into the vacuum or into the solid.

Molecule-like states of the system under consideration can exist only if the vibrational energy quantum $\hbar\omega_v$ is much smaller than the well depth $E_0 - E_s$. For the potential curves shown in Fig. 4, the estimate

$$\hbar\omega_v \sim \frac{\hbar}{z_{eq} - z_{min}} \sqrt{\frac{2(E_0 - E_{eq})}{M}},$$

is valid, where M is the mass of a diatomic molecule. Because the ratio m/M is small, the resulting condition

$$\frac{4m}{M} a_0^2 (z_{eq} - z_{min})^{-2} \mathrm{Ry} (E_0 - E_{eq})^{-1} \ll 1$$

is satisfied for both Br_2^- and O_2^- (the product in the left-hand side is of the order 10^{-3} for Br_2^- and 10^{-2} for O_2^-). We note that similar phenomenon of levitation above the surface is known for liquid helium [24].

The objective of introducing potential (1) was to qualitatively include all possible cases of the interaction between the lone electron and the solid. For some particular anion and a surface, the interaction potential may not be reduced to its simplest form (1). A rigorous answer to the question concerning the existence of an equilibrium state for given experimental conditions implies the calculation of a real interaction potential between the lone electron and the surface. This complicated problem (see, e.g., [21]) requires additional investigation.

It is natural to discuss the lifetimes of transient anion states near the surface. The lifetime of an anion above the electron detachment threshold can be estimated as the time of tunneling under the barrier with the height $-E_0$ and width z_0,

$$\tau \sim \frac{2\pi\hbar}{E_0} \exp\left(\frac{z_0}{a_0} \sqrt{\frac{E_0}{\mathrm{Ry}}} \right).$$

For typical values used in our calculations, τ reaches the minimum time necessary for experimental detection of an anion (10^{-3} s) at $z_0 > 60a_0$, i.e., at mesoscopic distances, where its interaction with the surface is negligibly small. Therefore, it is impossible to observe an anion in the instability region: the electron detachment is very fast.

It is clear that the higher the value of l is at which the set of equations (10) is truncated, the higher the accuracy of the calculated electron energy. Because (5) is an exact solution of (10), the sequence of approximations $E_s^{(0)}$, $E_s^{(1)}$, $E_s^{(2)}$, ... converges to the exact energy E_s. From the standpoint of the variational principle, the higher the approximation order, the closer the «trial» wave function

$$\psi^{(k)}(r, \xi) = r^{-1} \sum_{l=0}^{k} \varphi_l(r) P_l(\xi)$$

is to the exact solution for which the energy reaches the minimum. Therefore,

$$E_s \le E_s^{(k+1)} \le E_s^{(k)},$$

and the accuracy of $E_s^{(k+1)}$ can be roughly estimated as $|E_s^{(k+1)} - E_s^{(k)}|$. In our calculations, this accuracy depends primarily on the relative energy shift $(E_s - E_0)/E_0$, and the accuracy is better than 4 % for an attractive surface. If necessary, higher values of l can be included. The iteration method discussed above can also be applied for the solution of the corresponding set of equations.

It is interesting to note that for the truncated set of equations (17) and (18) for an attractive potential, a stable solution disappears at some threshold value of E_s somewhat higher than V_0; that is, the limit condition $E_s = V_0$ does not hold automatically. However, the threshold value of E_s converges to V_0 as l increases. Thus, for O_2^- in the zero approximation, this threshold value is $E_s \approx 1.4$ eV; in the first approximation, $E_s \approx 0.8$ eV; the exact value is 0.52 eV.

One can expect that the accuracy of the method described in this paper is very high and that it is compatible with the accuracy of spectroscopic measurements. Thus, calculation results could be directly compared with, e.g., measurements of electron photodetachment threshold shifts.

We now discuss possible experimental realization of the effects proposed in this paper. Layers of noble gases are frequently used as simple model surfaces to study the effect of a condensed environment [25]. In a typical experiment, O_2^- anions are deposited on a metal surface covered with approximately 10 monolayers of a noble gas (krypton). Because the energy of the electron inside the solid (relative to the vacuum) can range from -2 to -1 eV, the case of attraction would be realized in such an experiment. The case of repulsion could occur when the metal is coated with a polyethylene film. If this film is sufficiently thick, the energy of the electron inside the solid can vary from 0.5 to 1 eV. The problems of possible experimental investigation are also generally related to the photochemistry of adsorbed molecules via phototransfer of substrate electrons to the adsorbate molecules. Such problems can be treated experimentally by charging experiments.

We hope that the solution of the $2D$ Schrödinger equation proposed in this paper is sufficiently universal to be used in other applications where the effect of the wave function nonsphericity is not negligibly small.

A more detailed investigation of the stability of anions requires solution of the time-dependent Schrödinger equation, because the electron detachment occurs as a tunnel process. In addition, the effect of the image force has to be included more accurately in the calculation of the overall interaction potential.

This paper was supported by a joint program of the Deutsche Forschungsgemeinschaft (DFG, grant №436 RUS 113/433/0-2(R)) and the RFBR (grant №01-02-04008).

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