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The Classical Surface in Modern Theories of Solid Surface: Positronium in Front of a Surface

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We have reviewed the image potential of a charge from the classical and the solid surface aspects. The coulombic potential of a charge in front of a surface is not itself a classical subject. We find that in such an environment the parallel displacement law of a vector is incompatible. We find also that the cylindrical coordinate system is not usable for the solutions. It is the bispherical coordinate system which can be used so that a positionium or an exciton can be confined in the semi-infinite space. The electron in such a coordinate system neither enters the electron sea of the solid nor pierces one of the barriers of a quantum well.

I. INTRODUCTION

An atom or charge in front of a solid or metal surface has attracted much attentions.[1-9] Physicists have solved problems of this kind according to various models. Nearly all of models as well as their originators have taken into account that the image potential in the classical electrodynamics is the standard (reduced) result. The implication or inherent nature of this approach has scarely been discussed or even clearly delineated. We shall discribe a few aspects in the following.

Let the solid be $0 \leqslant z < \infty$ with a surface located at $z = 0$. When there is a charge Q at (0,0,-z,) outside the solid surface, the image potential in classical electrodynamics can be found from any electrodynamics textbook to be

$$\Phi_{+} = \frac{2KQ}{K+1} \frac{1}{|\vec{r}+z_0\hat{k}|} \qquad z>0 \tag{1.1}$$

$$\Phi_{-} = \frac{Q}{|\vec{r}+z_0\hat{k}|} - \frac{Q(K-1)/(K+1)}{|\vec{r}-z_0\hat{k}|} \qquad z<0 \tag{1.2}$$

at the field point $\vec{r}$; K is the dielectric constant of the solid. Following the definition of electrostatic potential in classical electrodynamics we put an infinitesimal test charge ϵ at $\vec{r}$, the potential energy at 3 outside the surface is

$$p.e. = \epsilon\Phi_{-} = \frac{\epsilon Q}{|\vec{r}+z_0\hat{k}|} - \frac{\epsilon Q(K-1)/(K+1)}{|\vec{r}-z_0\hat{k}|} \tag{1.3}$$

Now let the test charge ϵ approach Q and combine with Q. viz, $\vec{r}\to -z_0\hat{k}$. We thus obtain finally a potential energy which is exactly the so-called image potential in solid surface theory. for metals in particular. in cgs esu units

$$V_{\mathrm{I}} = -\frac{(Q+\epsilon)^2}{2z_0} \sim \frac{Q^2}{2z_0} \tag{1.4}$$

It is easily seen that V_{I} in (1.4) can never be obtained from (1.3). Even if we make a renormalization to eliminate the infinity in the first term of (1.3) as $\vec{r}\to -z_0\hat{k}$, the "self charge" Q of the charge Q itself is not able to become Q^2 in the numerator in (1.3). A second point of interest in (1 .1) and (1.2) is that we are not able to determine an unique space charge distribution to comply with both (1.1) and (1.2). Then what is the charge distribution to comply with V_I in (1.4) is a challenge in most thoeries of solid surface.[7,10-12]

II. PECULIARITY OF THE COULOMBIC POTENTIAL IN CHARGE-SURFACE INTERACTION PICTURE

For a charge Q located at $-z_0\hat{k}$ the coulombic potential written in vector notations is

$$\Phi^{(0)}_{coul} = Q\,|\vec{r}+z_0\hat{k}|^{-1} \tag{2.1}$$

In classical electrodynamics, if there is a spherical entity, such as a dielectric sphere nearby, with radius a and centered at $(0,0,a\hat{k})$, as given in Fig. 1(a), we need shift the origin from Q

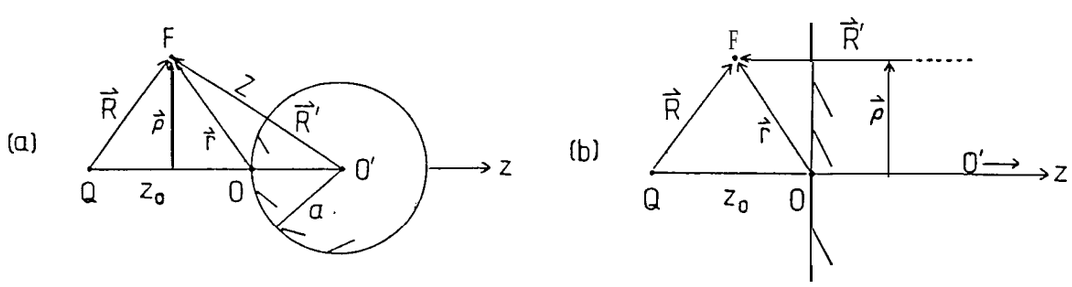

FIG. 1. The coulombic potential due to a charge Q is expressed with the origin at a sphere of radius a.
(a) The origin of the potential expression is shifted from Q to 0'. The position $\boldsymbol{F}$ is the field point.
(b) The limit figure for $a\to\infty$ is given with the origin 0 on the surface of the sphere remaining at rest.

to the center 0' of the sphere.[13] The potential in (2.1) is rewritten as

$$\Phi^{(11)}_{coul} = Q\,|(z_0 + a)\hat{k} + R'\hat{R}'\,|^{-1} \tag{2.2}$$

or in components of the two-dimensional vector $\vec{\rho} = (\rho, \psi)$ and $\vec{r} = (\vec{\rho}, z\hat{k})$, for z < 0,

$$\begin{aligned}\Phi^{(12)}_{coul} &= Q\,|(z_0 + a)\hat{k} - (a - z)\hat{k} + \vec{\rho}\,|^{-1} \\ &= Q\,|(z_0 + z)\hat{k} + \vec{\rho}\,|^{-1} \\ &= Q\,|z_0\hat{k} + \vec{r}\,|^{-1}\end{aligned} \tag{2.3}$$

The result $\Phi^{(12)}_{coul}$ in (2.3) reconciles the routine result $\Phi^{(0)}_{coul}$ in (2.1). Now let a $\to\infty$ to produce a surface at z = 0 and Fig. 1 (a) tends to Fig. 1 (b) as a limit. We see from the figures the quantities in this limit

$$\hat{R}' \to -\hat{k} \tag{2.4a}$$

$$Z \equiv |R' - a| \to -z \tag{2.4b}$$

The potential

$$\begin{aligned}\Phi^{(11)}_{coul} &= Q\,|(z_0 + a)\hat{k} + Z\hat{R}' + a\hat{R}'\,|^{-1} \\ &\to Q\,|(z_0 + z)\hat{k}\,|^{-1}\end{aligned} \tag{2.5}$$

It is clear that the limits $\Phi^{(12)}_{coul}$ and $\Phi^{(11)}_{coul}$ from the same simple coulombic potential are different by a vector $\vec{\rho}$. Pictorially we believe the correctness of $\Phi^{(12)}_{coul}$ as if there were no limit a $\to\infty$. $\Phi^{(11)}_{coul}$ is however derived from (2.4), and both equations in (2.4) are rigorous in limiting senses. Intuitatively, (2.5) is also a rigorous result. At a glance we draw the following conclusions:

First, mathematically the limiting process a $\to\infty$ destroys the parallel displacement law of the vector $\vec{R}'$ in the usage of the vector geometry. The parallel displacement law of vectors arises in the theory of relativity;[14] we will not discuss it here. This law is noticeably destroyed as shown from Fig. 1 in comparison Fig. l(a) and Fig. 1 (b). In Fig. 1 (a), $\vec{R}'$ is decomposed by

$$\vec{R}' = \vec{\rho} - (a - z)\hat{k} \tag{2.6a}$$

no matter what is the value of a. After the limiting process a $\to\infty$ in Fig. 1 (b) we see that

$$\vec{R}' = (a + Z)\hat{R}' \to (a - z)(-\hat{k}) \tag{2.6b}$$

in which $\vec{\rho}$ vanishes rigorously. We conclude incidentally that our vector $\vec{R}'$ can slide along its own line but permits no displacement in a parallel way.

Secondly the astonishing result (2.5) of $\Phi^{(11)}_{coul}$ inherently appears in the mathematics of surface sciences. Because this result $\Phi^{(11)}_{coul}$ has a two-dimensional symmetry even though it is only a point charge at Q. it is consistent with the field-theoretic insight;[15-18] thus it verifies the many-body theory.[19] This result is even more profound in relation to experiments. According to the kinetics of physisorption, the sample consists of many pouches. In order to verify the van der Waals force, actions in terms of molecular vibrations[15-18,20] and some other adsorption processes are considered to be the average result out of the so-called "master equation". In other words, a model gives a result for an event of only one atom or only one molecule. This result is used to interpret experimental data. These data are actually taken with or after an averaged process. For an isolated system, the one atom event and the averaged data are the same thing without conceptual contradiction. For systems with induction, it is possible to be misled. For instance, a charge induces an image inside the solid. For one charge, it is a pair of charges problem, one real charge and one induced image charge. For two real charges in front of a surface, there are two induced image charges; a 4-body problem arises instead of two separated problems consisting of isolated pairs. If the model calculations are for one "typical" isolated pair, as commonly considered, they are definitely inapplicable to such a 4-body problem. To reconcile this contradiction, we investigate a pair of charge layer-image charge layer. Again the model calculation is applicable. A(charge) layer is mathematically expressed as only one-dimension. As an instance, $\Phi^{(11)}_{coul}$ in (2.5) is one of them. It indicates not only a property of a charge located at Q, as we have shown above, but also an expression for a charge layer located at $z = -z_0$ (for all $\vec{\rho}$). Evidently $\Phi^{(11)}_{coul}$ in (2.5) recovers or overcomes, at least, part of this trouble in description. Of course, the field-theoretic treatments[16-18] represent this kind of many-body features. Careful and clear pictures for this direction of interpretation need further investigated.

A further step to solve a charge Q outside the dielectric sphere is the expansion in the Bessel function of order zero J_0 (kp); explicitly[13,21]

$$\frac{1}{R} = \frac{1}{\sqrt{\rho^2 + (z_0 - z)^2}} = \int_0^\infty e^{\pm k(z_0 - z)} J_0(k\rho) dk \tag{2.7}$$

in which the exponential is positive for $z_0 - z < 0$ and negative for $z_0 - z > 0$. In the solid surface, this expansion is unacceptable mathematically. The surface here is described by the Heaviside step function $\theta(z)$. For example the background positive charges in the jellium model are denoted by $n_b\theta(z)$ for the bulk charge density n_b. From mathematical tables we find that

$$e(z) = (\rho + z)\int_0^\infty J_1[q(\rho + z)]\, J_0(q\rho) dq \tag{2.8}$$

in the three-dimensional cylindrical coordinate system. It is obvious that the expansion coefficients here is p-dependent. For this reason. the expansion is totally unacceptable. Then what mathematics is usable for the system of a solid with surfaces? We shall *figure* a possible solution for a positronium in front of a surface.

III. A POSITRONIUM IN FRONT OF A SURFACE

The positron physics has been investigated intensively.[10,22,23] A positronium (Ps) in front of a surface is a favorable subject to investigate for the behavior of a positive charge interacting with a surface. For Ps placed very near the surface, it belongs to be a chemisorption case: the electron inside Ps is mixed with the Fermi sea of electrons in solid. But if Ps is placed about 2.5 Å outside the surface it is however considered totally isolated;[10] the electron inside Ps seems unable to enter or join the electrons in the solid. This behavior is also met for the exciton inside a quantum well; in this case the exciton is confined inside the well unable to penetrate or pierce the barriers.

From the above investigations we understand that the vectors in these (2+1)-dimensional cases here are not able to displace in a parallel way; but it can slide along its own line. Second, the cylindrical coordinate system is somehow unable to be used. Third, Ps is totally outside the surface when it is located farther away than 2.5 Å.

We formulate the problem in quantum mechanics for the positron coordinate $\vec{r}_+$ and the electron coordinate $\vec{r}_-$ in Ps. The Schrodinger equation is, in atomic units,

$$(-\nabla^2_{\vec{r}} - \frac{1}{r})\psi_n = E_n \psi_n \tag{3.1}$$

for the relative coordinate $\vec{r} = \vec{r}_- - \vec{r}_+$ and the reduced mass $\mu = 1/2$. It is noted that $\vec{r}$ is translation-invariant and without any particular origin *in laboratory* in quantum mechanics. The familiar H-atom or exciton solutions are

$$E_n = \frac{1}{4n^2} \tag{3.2}$$

since the "bohr radius" here is $a_0 = \hbar^2/(\mu e^2) = 2$ bohrs and eigenstates of they-part

$$\psi_n(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \psi)$$

with the ground state

$$\psi_1(\vec{r}) = \frac{1}{\sqrt{8\pi}} e^{-r/2} \tag{3.3}$$

For such a Ps in front of a surface located $\geqslant 2.5$ Å apart, it is entirely beyond the solid. We must confine it in the left half-infinite space in the laboratory. It is noted that the bispherical coordinates[24]

$$u^2 \equiv (z - z_0 \coth\upsilon)^2 + \rho^2 = z_0^2 \operatorname{csch}^2 \upsilon \tag{3.4}$$

$$\upsilon \equiv \tanh^{-1} \frac{2z_0 z}{z_0^2 + z^2 + \rho^2} \tag{3.5}$$

satisfy this requirement for the semi-infinite space $z = 0$ to $-\infty$ and $\upsilon = 0$ to $-\infty$ and have the

"floating origin" in the laboratory at $z = z_0 \coth u$, $\rho = 0$ outside the surface. The bispherical coordinate system is drawn in Fig. 2 in which the spheres are of radii $|z_0 \operatorname{csch} v|$. It is also noted that the center of mass coordinate in this positronium problem according to quantum

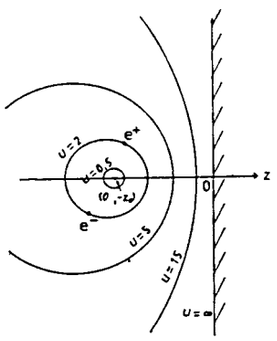

FIG. 2. The bispherical coordinate system is drawn outside the surface. The three-dimensional situation is a revolution about the z-axis. Here z_0 is equal to 5.

mechanics is an independent variable, entirely independent of $\vec{r}$. We identify the classical center of mass i.e. $\vec{r}/2$ as the origin of u defined in (3.4); then $u = r/2$ is thus identified. The e^+e^- pair in Ps locates at the opposite sides on the sphere with the classical center of mass as "floating origin". Thus our wave function becomes,

$$\psi_{nlm}(r, \theta, \psi) = R_{nl}(r) Y_{lm}(\theta, \psi)$$

$$\Rightarrow R_{nl}(2u) Y_{lm}(\theta, \psi)$$

In particular for the ground state in (3.3) it becomes

$$\psi_1(\vec{r}) \sim e^{-u} \tag{3.6}$$

For such a "floating origin" solution the question arises here is where is the location vector $\vec{L}$ of Ps. In quantum mechanics it should be an expectation value. It is obvious here that

$$\vec{L} = (\rho = 0, z = -\langle z_0 \coth v \rangle) = (0, -\langle \sqrt{z_0^2 + u^2} \rangle) \tag{3.7}$$

Since the volume element of integration in th bispherical coordinate system is

$$\int f(u) dv = \int f(u) z_0^{-1} (z_0^2 + u^2)^{-1/2} \pi u^4 du$$

the ground state expectation

$$\langle \sqrt{z_0^2 + u^2} \rangle_1 = \int_0^\infty u^4 e^{-2u} du / \int_0^\infty u^4 e^{-2u} du (z_0^2 + u^2)^{-1/2} \tag{3.8}$$

We obtain the result by numerical integration for Ps at $z_0 = 2.5$ Å ≈ 5 bohrs

$$-\langle\sqrt{z_0^2+u^2}\rangle_1 = 5\text{X}\ \ 1.1250$$

We see that there is only 12.5% deviation from the free space calculation for Ps.

We may need to know the square deviation, for instance, in the dipole calculation for the van der Waals-London force. We calculate it here as for $z_0 = 5$ bohrs

$$\begin{aligned}\langle r^2\rangle_1 &= \langle 4u^2\rangle_1 \\ &= 27.65\ bohr^2\end{aligned} \tag{3.9}$$

Apart from this possible dipole-images interaction, we have Ps totally outside the surface and with zero charge density. Thus it should have no influences in the theory of solid surfaces. Further investigations of nature of Ps-surface interaction treated here are intensively proceeded. The main point is that Ps itself is not considered as a whole; but Ps-surface is a quantum mechanical system. The approach is still in the chemisorption side.

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