PHYSICAL REVIEW A, VOLUME 64, 064902

Electron near a helium liquid surface

S. H. Patil
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073, Göttingen, Germany
and Department of Physics, Indian Institute of Technology, Bombay 400 076, India

(Received 25 July 2001; published 19 November 2001)

The energies of an electron above a liquid-helium surface are analyzed in terms of an electron-atom polarizability potential with an infinite barrier. An integration over a layer, and a summation over different layers, leads to a one-dimensional Coulomb potential with a $1/x^2$ correction. This potential provides an accurate description of the observed one-dimensional Rydberg energies with a quantum defect.

DOI: 10.1103/PhysRevA.64.064902 PACS number(s): 34.50.Dy, 03.65.Ge

I. INTRODUCTION

It was suggested some time ago that isolated electrons resting on a helium surface have [1–3] a spectrum of one-dimensional Coulomb potential in half space. The electron induces an image charge in the helium surface, leading to a potential [4]

$$\begin{aligned} V(x) &= -\frac{Ze^2}{x}, \quad x>0, \quad Z=\frac{\epsilon-1}{4(\epsilon+1)} \\ &= \infty, \quad \text{for } x<0 \end{aligned} \tag{1.1}$$

where ϵ is the dielectric constant of liquid He. For helium, one has [5,6]

$$\epsilon = 1.057\,23, \quad Z=0.006\,955. \tag{1.2}$$

This leads to the usual hydrogenic spectrum. The spectrum has been observed experimentally [6,7] though with some deviations.

Recently, Nieto [8] has analyzed the spectrum of the electron near the surface in terms of the one-dimensional Coulomb potential in half space with a quantum defect. He has suggested an additional potential of the angular momentum barrier form,

$$V_\delta = \frac{\hbar^2}{2m}\frac{(-\delta)(-\delta+1)}{x^2} \quad \text{for } x>0, \tag{1.3}$$

which leads to a simple and elegant description of the quantum defect δ. However, there are two related questions that need to be considered. One has to do with the singular behavior of the potential at the origin that needs to be handled with great care. The second point is about the physical origin of such a potential term. These points need to be analyzed carefully.

Here, we analyze the electron-He surface interaction in terms of the electron-He atom interaction potential. This potential is summed over the atoms in different layers of the half space to deduce the electron-surface potential. This approach leads to an accurate representation of the Coulomb potential in Eq. (1.1) and the quantum defect term in Eq. (1.3). What is even more important is that it provides a clear insight into the properties of different potential terms and their physical origin. In particular, it emphasizes the point that one needs to carry out a careful summation over the contributions from different layers of the liquid.

We will use atomic units $e=\hbar=m_e=1$, unless stated otherwise.

II. EFFECTIVE ELECTRON-SURFACE POTENTIAL

We first obtain the potential for an electron interacting with a helium atom, and then use it to deduce the interaction potential for an electron near the surface of atoms in a liquid state.

A. Electron-atom potential

The basic interaction of an electron with an atom is given by the potential

$$U(\vec{r},\vec{r}_i)=\sum_i \left(\frac{1}{|\vec{r}-\vec{r}_i|}-\frac{1}{r}\right), \tag{2.1}$$

where $\vec{r}$ is the position of the electron and $\vec{r}_i$ are the positions of the electrons in the atom, with respect to the nucleus. In the adiabatic approximation, the effective electron-atom potential is developed by treating the electron as an observer. With the potential in Eq. (2.1) as a perturbation, one obtains an effective potential for the interaction of the electron with the atom,

$$V(r)=U_{00}+\sum_{i\neq 0}\frac{U_{0i}U_{i0}}{E_0-E_i}+\cdots, \tag{2.2}$$

where the matrix elements are taken with respect to the unperturbed states of the atom.

Now for the helium atom in the ground state, because of the spherical symmetry of the density, the first term is exponentially small [9] for large r,

$$U_{00}\to e^{-(2E_I)^{1/2}r} \quad \text{for } r\to\infty, \tag{2.3}$$

where E_I is the ionization energy of the atom, and therefore, will not be important in our considerations. The dominant term for large r comes from the second-order term in Eq. (2.2). Using the Legendre polynomial expansion in Eq. (2.1) to calculate the second-order term in Eq. (2.2), one obtains the polarization potential [10],

$$V_{pol}(r) = -\frac{1}{2}\sum_{l=1} \alpha_l \frac{1}{r^{2l+2}} f_l(r). \tag{2.4}$$

Here, α_l are the usual multipolar polarizabilities and $f_l(r)$ are the damping functions [9]. At large values of r, the damping functions differ from one by exponentially small quantities, but ensure that potential is nonsingular at the origin. Since in our analysis, large r region is the important domain, we will take $f_l(r) = 1$.

There are two significant components that have been left out in our consideration with the electron as an observer. One component corresponds to including the changes in the states of the external electron. This leads to additional terms [11] in the summation over the intermediate states in Eq. (2.2), described as nonadiabatic terms. However, these terms go to zero faster than the polarizability terms in Eq. (2.4) by a factor or $1/r^2$ for large r, and therefore will be left out. The other important component corresponds to the exchange effect between the external electron and the electrons in the atom. It essentially generates a strong repulsion [9] for the external electron to be found in the region of the atomic electrons. We will represent this short-range repulsive potential by an infinite potential barrier. Combining the essential components, one has for the electron-He potential,

$$\begin{aligned} V(r) &= -\tfrac{1}{2}\alpha_1 \frac{1}{r^4} \quad \text{for} \quad r > a, \\ &= \infty \quad \text{for} \;\; r \leqslant a, \end{aligned} \tag{2.5}$$

where we have included only the leading dipolar polarizability term. The barrier radius will be determined by requiring that the predicted scattering length is equal to the experimental scattering length [12] of 1.19. One has an exact analytical expression [13] for the scattering length for this potential,

$$A = \alpha_1^{1/2} \cot[\alpha_1^{1/2}/a]. \tag{2.6}$$

Using the accurate value [14] of 1.383 for α_1 of He and $A = 1.19$ for the scattering length, one obtains

$$a = 1.51. \tag{2.7}$$

It is interesting to note that the Born approximation modified to take into account the vanishing of the wave function at $r = a$ leads to [13,15]

$$A = a - \frac{\alpha_1}{3a}. \tag{2.8}$$

With $\alpha_1 = 1.383$ and $A = 1.19$, this gives $a = 1.50$, which is quite close to the value of 1.51 from the exact relation in Eq. (2.6).

B. Electron-He surface potential

For deducing the potential for the electron near the He liquid surface, the electron-atom potential is integrated over a layer. Using Eq. (2.5), one then gets for the electron-single-layer potential, with the electron at a distance x from the layer,

$$\begin{aligned} V_0(x) &= -\tfrac{1}{2}\alpha_1 N_s \int_0^\infty \frac{2\pi\rho d\rho}{(\rho^2 + x^2)^2} \\ &= -\tfrac{1}{2}\pi\alpha_1 N_s \left(\frac{1}{x^2}\right) \quad \text{for} \;\; x > a \\ &= \infty \qquad \text{for} \;\; x \leqslant a, \end{aligned} \tag{2.9}$$

where N_s is the number of atoms per unit area in the layer. It may be noted that if d is the interparticle or interlayer distance,

$$N_s = N_v d, \qquad N_v = 1/d^3, \tag{2.10}$$

where N_v is the number of atoms per unit volume. The total potential for the electron near the liquid surface is then obtained by summing over the different layers,

$$\begin{aligned} V(x) &= -\tfrac{1}{2}\pi\alpha_1 N_s \sum_{n=0}^{\infty} \frac{1}{(x+nd)^2} \quad \text{for} \;\; x > a \\ &= \infty \qquad \text{for} \;\; x \leqslant a. \end{aligned} \tag{2.11}$$

Usually, the summation is converted into an integral that then gives the leading $1/x$ term correctly. However, from the analysis of Nieto [8] it follows that $1/x^2$ term is important in determining the quantum defect. Therefore, one has to carry out a more careful analysis of the summation. For this, we first separate out the leading term

$$\sum_{n=0} \frac{1}{(x+nd)^2} = \frac{1}{x^2} + \sum_{n=1} \frac{1}{(x+nd)^2}, \tag{2.12}$$

The second term tends to $1/(xd)$ for $x \to \infty$. Therefore, we consider a representation

$$\begin{aligned} \sum_{n=1} \frac{1}{(x+nd)^2} &= \frac{1}{xd} + f(x) \\ &= \int_0^\infty \frac{du}{(x+ud)^2} + f(x). \end{aligned} \tag{2.13}$$

for obtaining a suitable form for $f(x)$, one starts with

$$\begin{aligned} f(x) &= \sum_{n=1} \frac{1}{(x+nd)^2} - \int_0^\infty \frac{du}{(x+ud)^2} \\ &= \sum_{n=1} \frac{1}{(x+nd)^2} - \sum_{n=1} \int_{n-1}^{n} \frac{du}{(x+ud)^2}. \end{aligned} \tag{2.14}$$

Carrying out the integration leads to

$$f(x)=\sum_{n=1}\frac{1}{(x+nd)^2}-\sum_{n=1}\frac{1}{(x+nd)(x+nd-d)}$$

$$=-\sum_{n=1}\frac{d}{(x+nd)^2(x+nd-d)}. \tag{2.15}$$

For $x \gg d$, this can be converted into an integral, and one gets

$$f(x)\to-\frac{1}{2x^2}+O\left(\frac{1}{x^3}\right) \qquad \text{for } x\to\infty. \tag{2.16}$$

Combining Eqs. (2.12)–(2.16) then leads to

$$\sum_{n=0}\frac{1}{(x+nd)^2}=\frac{1}{xd}+\frac{1}{2x^2}, \qquad \text{for } x\to\infty, \tag{2.17}$$

correct to order $(1/x^3)$. Finally, one has for the total potential, with the two leading asymptotic terms,

$$V(x)=-Z\left[\frac{1}{x}+\frac{d}{2x^2}\right] \qquad \text{for } x>a$$

$$=\infty \qquad \text{for } x\leqslant a, \tag{2.18}$$

where

$$Z=\tfrac{1}{2}\pi\alpha_1N_v\,. \tag{2.19}$$

For the liquid helium at a temperature between 1 and 2 K, one has a density of about 0.150 g/ml which is equivalent (in a.u.)

$$N_v=3.3\times10^{-3},$$

$$d=6.7. \tag{2.20}$$

Together with the value of dipolar polarizability $\alpha_1=1.383$ for He, one gets

$$Z=7.17\times10^{-3}, \tag{2.21}$$

which is quite close to the value of 0.006 955 obtained [5,6] from the dielectric constant relation in Eq. (1.1). The small difference could be due to some variation in the polarizability of helium atom in the liquid state.

III. RESULTS

For obtaining the results in the Coulombic form, it is more appropriate to use the variable

$$x'=x-a, \tag{3.1}$$

so that our potential is

$$V(x')=-Z\left[\frac{1}{x'+a}+\frac{d/2}{(x'+a)^2}\right] \qquad \text{for } x'>0$$

$$=\infty \qquad \text{for } x'\leqslant 0. \tag{3.2}$$

In the second term, only the leading asymptotic term will be retained. To analyze the solutions, we separate out the Coulombic part and write

$$V(x')=-\frac{Z}{x'}+V_{\text{pert}}(x') \qquad \text{for } x'>0$$

$$=\infty \qquad \text{for } x'\leqslant 0, \tag{3.3}$$

where the perturbative term is

$$V_{\text{pert}}=Z\left(\frac{1}{x'}-\frac{1}{x'+a}\right)-\frac{Zd}{2(x'+a)^2}. \tag{3.4}$$

For large values of x', which is the domain of interest, one has

$$V_{\text{pert}}=-\frac{Z}{2x'^2}(d-2a). \tag{3.5}$$

Finally, substitution of the values of Z=0.006 955, $d=6.7$, and $a=1.51$ leads to

$$V_{\text{pert}}=-\frac{0.0256}{2x'^2}. \tag{3.6}$$

To deduce the corresponding quantum defect, we compare this expression with

$$V_{\text{orbital}}=\frac{-\delta(-\delta+1)}{2x'^2}, \tag{3.7}$$

which gives to leading order,

$$\delta\approx0.0256. \tag{3.8}$$

The corresponding hydrogenic energies are

$$E_n=-\frac{Z^2}{2(n-\delta)^2}, \tag{3.9}$$

with the quantum defect $\delta=0.0256$. This is quite close to the experimentally determined value [8] of $\delta=0.0237$.

It should be noted that our potential is nonsingular at $x=a$ or $x'=0$. Therefore, there are no technical difficulties at $x'=0$. In effect, what we have done is to treat the asymptotic form of the deviation from the Coulombic term perturbatively, for which the perturbed energies are given correctly by the expansion of the energy in Eq. (3.9) in powers of δ. What is really striking is that the deviations from the Coulombic energies are to be analyzed in terms of the discreteness of the layers. A careful analysis of the potential due to the discrete layers provides a good description of the quantum defect in the one-dimensional Rydberg energies of an electron near a liquid-helium surface.

[1] W. T. Sommer, Ph. D. thesis, Stanford University, 1964.
[2] M. W. Cole and M. H. Cohen, Phys. Rev. Lett. **23**, 1238 (1969); M. W. Cole, Phys. Rev. B **2**, 4239 (1970).
[3] V. B. Shilkin, Zh. Eksp. Teor. Fiz. **58**, 1748 (1970) [Sov. Phys. JETP **31**, 936 (1970)].
[4] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Oxford, 1960), p. 40.
[5] R. F. Harris-Lowe and K. A. Smee, Phys. Rev. A **2**, 158 (1970).
[6] T. R. Brown and C. C. Grimes, Phys. Rev. Lett. **29**, 1233 (1972); C. C. Grimes, T. R. Brown, M. L. Burns, and C. L. Zipfel, Phys. Rev. B **13**, 140 (1976).
[7] D. K. Lambert and P. L. Richards, Phys. Rev. Lett. **44**, 1427 (1980); Phys. Rev. B **23**, 3282 (1981).
[8] M. M. Nieto, Phys. Rev. A **61**, 034901 (2000).
[9] S. H. Patil, Phys. Scr. **51**, 465 (1995).
[10] J. E. Mayer and M. G. Mayer, Phys. Rev. **43**, 605 (1933).
[11] H. H. Eissa and U. Öpik, Proc. Phys. Soc. London **92**, 556 (1967).
[12] R. W. Crompton, M. T. Elford, and A. G. Robertson, Aust. J. Phys. **23**, 667 (1970); J. Ferch, W. Raith, and K. Schröder, J. Phys. B **3**, 1481 (1980).
[13] R. Szmythowski, Phys. Rev. A **51**, 853 (1995).
[14] A. Koide, W. J. Meath, and A. R. Allnatt, J. Phys. Chem. **86**, 1222 (1982).
[15] G. Reisfeld and U. Asaf, Phys. Rev. A **49**, 348 (1994); **50**, 4428 (1994).