Interaction energy between a positronium atom and a metal surface

V. V. Paranjape
Department of Physics, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1

K. N. Pathak
Department of Physics, Panjab University, Chandigarh 160014, India
(Received 30 May 1985)

The interaction energy of a positronium atom interacting with a metal surface is obtained as a function of the speed of the positronium atom and the separation from the metal surface. It is shown that the energy saturates to a finite value at the surface and follows the Lifshitz relation for large separations. The treatment is based on the consideration of the virtual excitations of the multipoles of the atom, while in the earlier work by Manson and Ritchie only the dipolar excitations were considered. The divergence of the interaction energy obtained by the earlier authors arises due to incomplete consideration of multipolar effects.

I. INTRODUCTION

Although there has been, over the last twenty-five years, considerable interest both in the theoretical and experimental aspects of the interaction between an atom and a metal surface, recent experiments on the scattering of very-low-mass atomic systems (such as positronium) by a metal surface have generated increased activity in the field.[1,2]

The interaction between an atom and a metal surface is basically of the van der Waals type and is known to be due to the induced polarizations of the atom and the surface. Although the interaction has been examined extensively within a semiclassical framework,[3,4] a quantum-mechanical treatment of the problem has been proposed recently by Manson and Ritchie.[5] These authors show that the interaction energy near the metal surface is determined by quantum effects arising from the virtual excitation of the atom and the surface plasmons. Their calculations are performed under a dipolar approximation in which the virtual excitations of the atom are restricted to simple dipoles. They find that for a large separation between the atom and the surface, the interaction varies according to the well-known $1/Z^3$ dependence, while near the surface the interaction varies as $1/Z$. Manson and Ritchie[5] attribute the weakening of the interaction near the surface (compared to its large separation behavior), to the importance of the quantum effect near the surface. These authors also show that the interaction is affected by the speed of the atom relative to the surface.

It is the purpose of the present paper to extend the work of Manson and Ritchie to include the multipole excitations of the atom. By such inclusions we are able to show that at the surface the interaction energy saturates to a finite value and consequently the interaction potential close to the surface is smaller than the values of the potential obtained by Manson and Ritchie. Asymptotic expressions for the interaction energy as a function of atomic speed are obtained near and far away from the surface. As a special case the interaction energy in the limit of infinite mass of the nucleus is also derived. This situation corresponds to the semiclassical case where the recoil effects are automatically excluded.

It may be remarked that the saturation of the interaction energy in the atom-surface system due to the multipolar excitation of the atom is similar to the saturation of the interaction between two atoms as shown by Paranjape and Mahanty.[6] In the latter case the saturation resulted by inclusion of multipolar excitations of the two atoms. The two problems, although dissimilar, have indeed a common feature.

II. THEORY

The Hamiltonian for a hydrogenlike atom and a metal surface is given by

$$H=\frac{P^2}{2M}+H_{\text{atom}}+\sum_{\mathbf{Q}}\hbar\omega(a^\dagger_{\mathbf{Q}}a_{\mathbf{Q}}+\tfrac{1}{2})+H' , \quad (1)$$

with

$$H'=\sum_{\mathbf{Q}}\Gamma_Q[\exp(-Q\mid Z_+\mid+i\mathbf{Q}\cdot\mathbf{R}_+) -\exp(-Q\mid Z_-\mid+i\mathbf{Q}\cdot\mathbf{R}_-)](a^\dagger_{\mathbf{Q}}+a_{-\mathbf{Q}}) ,$$

where the first term is the kinetic energy of the atom with mass M, the second term is the Hamiltonian of the atom given in terms of the relative coordinates of the two charges, the third term is the Hamiltonian of the surface plasmons, the fourth term is the interaction term between the surface plasmons and the charges forming the atom, the coupling constant $\Gamma_Q^2=e^2\pi\hbar\omega/L^2Q$ with the surface area given by L^2 and $(R_\pm,Z_\pm)$ are the position coordinates of the $+ve$ and the $-ve$ charges in cylindrical coordinates with the Z axis normal to the surface.

The potential energy of the atom due to the metal surface is derived by Manson and Ritchie[5] using a self-energy analysis. Up to second order in the interaction Hamiltonian, the potential energy $E(\mathbf{r})$ of the atom at a position $\mathbf{r}$ is given by

$$E(\mathbf{r})=\sum_n\sum_l\sum_{\mathbf{k}}\frac{1}{(8\pi^3)}\exp[-i\mathbf{r}\cdot(\mathbf{k}_0+\mathbf{k})]\times\frac{\langle\phi_0,0,0\,|\,H'\,|\,n,l,\phi_{\mathbf{k}}\rangle\langle l,n\,|\,H'\,|\,0,0\rangle}{(E_0-E_n)+(e_0-e_{\mathbf{k}})-(\epsilon_l)+i\delta}\,, \tag{2}$$

where the free-atom state is denoted by

$$|\,\phi_{\mathbf{k}}\rangle=(2\pi)^{-3/2}\exp(i\mathbf{k}\cdot\mathbf{r})$$

with energy $e_{\mathbf{k}}=(\hbar^2k^2/2M)$, $|\,n\,\rangle$ is the quantum state of the surface plasmon with energy $E_n=\hbar\omega(n+\frac{1}{2})$, $|\,l\,\rangle$ is the internal state of the atom with energy $(\epsilon_0+\epsilon_l)$, and the unperturbed free state of the atom is taken to be

$$|\,\phi_0\rangle=(2\pi)^{-3/2}\exp(-i\mathbf{k}_0\cdot\mathbf{r})\,.$$

For convenience we will consider henceforth the atom to be normally incident onto the surface so that the component of the vector $\mathbf{k}_0$ parallel to the surface is assumed to be zero.

We denote the free atomic state wave vector $\mathbf{k}$ in terms of its components parallel and perpendicular to the surface by $\mathbf{k}\equiv(\boldsymbol{\kappa},k_3)$ and the position coordinates of the $+ve$ and $-ve$ charges of the hydrogenlike atom which we assume for simplicity to be a positronium atom accordingly as $Z_\pm=Z\pm(Z'/2)$ and $\mathbf{R}_\pm=\mathbf{R}\pm(\mathbf{R}'/2)$. $(\mathbf{R},Z)$ are the coordinates for the center of mass of the positronium. With this notation the sum over the parallel component $\boldsymbol{\kappa}$ can be completed easily. Also, the summation over the plasmon intermediate states is easily realized to give

$$E(\mathbf{r})=\sum_l\sum_{\mathbf{Q}}\left[\frac{-2M}{\hbar^2}\right]\int\frac{dk_3}{2\pi}\frac{2Q\exp[-i(k_3+k_{03})Z]}{[Q^2+(k_{03}+k_3)^2](\alpha^2+k_3^2)}\langle 0\,|\exp[-i(k_{03}+k_3)(Z'/2)+i\mathbf{Q}\cdot(\mathbf{R}'/2)]-\exp[i(k_{03}+k_3)(Z'/2)-i\mathbf{Q}\cdot(\mathbf{R}'/2)]\,|\,l\rangle$$
$$\times\langle l\,|\exp[-Q\,|\,Z+(Z'/2)\,|\,-i\mathbf{Q}\cdot(\mathbf{R}'/2)]-\exp[-Q\,|\,Z-(Z'/2)\,|\,+i\mathbf{Q}\cdot(\mathbf{R}'/2)]\,|\,0\rangle\,, \tag{3}$$

where $\alpha^2=Q_s^2+Q_l^2+Q^2-k_{03}^2$, $Q_s^2=(2\omega_sM/\hbar)$, and $Q_l^2=(2M\epsilon_l/\hbar^2)$.

The integration over k_3 in Eq. (3) can be performed by contour integration. The poles of the integrand occur at $k_3=\pm i\alpha$ and $k_3=-k_{03}\pm iQ$. By selecting a semicircle as a contour above or below the x axis as appropriate, the integration can be completed to give

$$\begin{aligned}E(\mathbf{r})=-\left[\frac{2M}{\hbar^2}\right]\sum_l\sum_Q\Gamma_Q^2\Bigg[&\langle 0\,|\exp[-Q\,|Z_+|\,+i\mathbf{Q}\cdot(\mathbf{R}'/2)]\left[\frac{\Theta(Z_+)}{D_1}+\frac{\Theta(-Z_+)}{D_1^*}\right]\\&+\frac{Q}{\alpha}\exp[-\alpha\,|Z_+|\,+i\mathbf{Q}\cdot(\mathbf{R}'/2)]\left[\frac{\exp(-ik_0\,|Z_+|)\Theta(Z_+)}{D_2}+\frac{\exp(ik_0\,|Z_+|)\Theta(-Z_+)}{D_2^*}\right]\\&-\exp[-Q\,|Z_-|\,-i\mathbf{Q}\cdot(\mathbf{R}'/2)]\left[\frac{\Theta(Z_-)}{D_1}+\frac{\Theta(-Z_-)}{D_1^*}\right]\\&-\frac{Q}{\alpha}\exp[-\alpha\,|Z_-|\,-i\mathbf{Q}\cdot(\mathbf{R}'/2)]\left[\frac{\exp(-ik_0\,|Z_-|)\Theta(Z_-)}{D_2}+\frac{\exp(ik_0\,|Z_-|)\Theta(-Z_-)}{D_2^*}\right]|\,l\rangle\Bigg]\\&\times\langle l\,|\exp[-Q\,|Z_+|\,-i\mathbf{Q}\cdot(\mathbf{R}'/2)]-\exp[-Q\,|Z_-|\,+i\mathbf{Q}\cdot(\mathbf{R}'/2)]\,|\,0\rangle\,,\end{aligned} \tag{4}$$

where $\Theta(x)=1$ for $x>0$ and zero otherwise,

$$D_1=[\alpha^2+(k_0+iQ)^2]\quad\text{and}\quad D_2=[Q^2+(k_0-i\alpha)^2]\,. \tag{5}$$

The angular integration of the vector Q can be performed to produce the result

$$E(\mathbf{r})=-\frac{Q_s^2e^2}{2}\sum_l \int_0^\infty dQ\, d\mathbf{r}'d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l^*(\mathbf{r}'')$$
$$\times\left[J_0\left[\frac{Q}{2}|\mathbf{R}'-\mathbf{R}''|\right]\right]\left\{\exp(-Q|Z''_+|)\left[\exp(-Q|Z'_+|)\left[\frac{\Theta(Z'_+)}{D_1}+\frac{\Theta(-Z'_+)}{D_1^*}\right]+\frac{Q}{\alpha}\exp(-\alpha|Z'_+|)\left[\frac{\Theta(Z'_+)\exp(-ik_0|Z'_+|)}{D_2}+\frac{\Theta(-Z'_+)\exp(ik_0|Z'_+|)}{D_2^*}\right]\right]\right.$$
$$\left.+\exp(-Q|Z''_-|)\left[\exp(-Q|Z'_-|)\left[\frac{\Theta(Z'_-)}{D_1}+\frac{\Theta(-Z'_-)}{D_1^*}\right]+\frac{Q}{\alpha}\exp(-\alpha|Z'_-|)\left[\frac{\Theta(Z'_-)\exp(-ik_0|Z'_-|)}{D_2}+\frac{\Theta(-Z'_-)\exp(ik_0|Z'_-|)}{D_2}\right]\right]\right\}$$
$$-J_0\left[\frac{Q}{2}|R'+R''|\right]\left\{\exp(-Q|Z''_-|)\left[\exp(-Q|Z'_+|)\left[\frac{\Theta(Z'_+)}{D_1}+\frac{\Theta(-Z'_+)}{D_1^*}\right]+\frac{Q}{\alpha}\exp(-\alpha|Z'_+|)\left[\frac{\Theta(Z'_+)\exp(-ik_0|Z'_+|)}{D_2}+\frac{\Theta(-Z'_+)\exp(ik_0|Z'_+|)}{D_2^*}\right]\right]\right.$$
$$\left.+\exp(-Q|Z''_+|)\left[\exp(-Q|Z'_-|)\left[\frac{\Theta(Z'_-)}{D_1}+\frac{\Theta(-Z'_-)}{D_1^*}\right]+\frac{Q}{\alpha}\exp(-\alpha|Z'_-|)\left[\frac{\Theta(Z'_-)\exp(-ik_0|Z'_-|)}{D_2}+\frac{\Theta(-Z'_-)\exp(ik_0|Z'_-|)}{D_2^*}\right]\right]\right\}\Bigg], \tag{6}$$

where we have used $Z'_\pm=[Z\pm(Z'/2)]$ and $Z''_\pm=[Z\pm(Z''/2)]$ and J_0 is the Bessel function of the first kind.

The expression (6) for $E(\mathbf{r})$ is exact. It can be written as a power series in Z, assuming that Z is much smaller than the spread in the ground-state wave function:

$$E(\mathbf{r})=E_0(\mathbf{r})+E_1(\mathbf{r})+E_2(\mathbf{r})+\cdots, \tag{7}$$

where E_0 is independent of Z, and E_1 and E_2 are proportional to Z and Z^2, respectively. A straightforward calculation, using (6), gives

$$E_0=-Q_s^2e^2\sum_l \int_0^\infty dQ\int d\mathbf{r}'d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l^*(\mathbf{r}'')$$
$$\times\exp\left[-\frac{Q}{2}|Z''|\right]\left[\exp\left[-\frac{Q}{2}|Z'|\right]\mathrm{Re}\left[\frac{1}{D_1}\right]+\frac{Q}{\alpha}\exp\left[-\frac{\alpha}{2}|Z'|\right]\mathrm{Re}\left[\frac{\exp(-ik_0|Z'|)}{D_2}\right]\right]$$
$$\times\left[J_0\left[\frac{Q}{2}|\mathbf{R}'-\mathbf{R}''|\right]-J_0\left[\frac{Q}{2}|\mathbf{R}'+\mathbf{R}''|\right]\right], \tag{8}$$

$$E_1=-iQ_s^2e^2Z\sum_l\int_0^\infty dQ\int\int d\mathbf{r}'d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l(\mathbf{r}'')$$

$$\times\exp\left[-\frac{Q}{2}|Z''|\right]\left[\left\{\exp\left[-\frac{Q}{2}|Z'|\right]\operatorname{Im}\left[\frac{4\delta(Z')-Q}{D_1}\right]+\frac{Q}{\alpha}\exp\left[-\frac{\alpha|Z'|}{2}\right]\right.\right.$$

$$\left.\times\operatorname{Im}\left[\exp\left[\frac{-ik_0|Z'|}{2}\right]\left[\frac{(4\delta(Z')-ik_0-\alpha)}{D_2}\right]\right]\right\}\left[J_0\left[\frac{Q|R'-R''|}{2}\right]-J_0\left[\frac{Q|R'+R''|}{2}\right]\right]$$

$$-\left\{\exp\left[-\frac{Q}{2}|Z'|\right]\operatorname{Im}\left[\frac{Q}{D_1}\right]+\frac{Q}{\alpha}\exp\left[-\frac{\alpha|Z'|}{2}\right]\operatorname{Im}\left[\exp\left[\frac{-ik_0|Z'|}{2}\right]\frac{Q}{D_2}\right]\right\}$$

$$\left.\times\left\{\operatorname{sgn}(Z')\operatorname{sgn}(Z'')\left[J_0\left[\frac{Q|\mathbf{R}'-\mathbf{R}''|}{2}\right]+J_0\left[\frac{Q|\mathbf{R}'+\mathbf{R}''|}{2}\right]\right]\right\}\right] \tag{9}$$

and

$$E_2=-\frac{Q_s^2e^2}{2}Z^2\sum_l\int_0^\infty dQ\int d\mathbf{r}'d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l^*(\mathbf{r}'')$$

$$\times\exp\left[-\frac{Q}{2}|Z''|\right]\left[\left\{\exp\left[-\frac{Q}{2}|Z'|\right]\operatorname{Re}\left[\frac{2Q^2}{D_1}\right]+\frac{Q}{\alpha}\exp\left[-\frac{\alpha}{2}|Z'|\right]\right.\right.$$

$$\left.\times\operatorname{Re}\left[\exp\left[\frac{-ik_0|Z'|}{2}\right](\alpha^2-k_0^2+Q^2-2ik_0\alpha)\right]\right\}\left[J_0\left[\frac{(Q|\mathbf{R}'-\mathbf{R}''|}{2}\right]-J_0\left[\frac{Q|\mathbf{R}'+\mathbf{R}''|}{2}\right]\right]$$

$$+\left[\exp\left[-\frac{Q}{2}|Z'|\right]\operatorname{Re}\left[\frac{2Q^2}{D_1}\right]+\frac{Q}{\alpha}\exp\left[-\frac{\alpha|Z'|}{2}\right]\operatorname{Re}\left[\exp(-ik_0|Z'|)\frac{(2ik_0Q+2Q\alpha)}{D_2}\right]\right]$$

$$\left.\times\left\{\operatorname{sgn}(Z')\operatorname{sgn}(Z'')\left[J_0\left[\frac{Q|\mathbf{R}'-\mathbf{R}''|}{2}\right]+J_0\left[\frac{Q|\mathbf{R}'+\mathbf{R}''|}{2}\right]\right]\right\}\right]. \tag{10}$$

For the ground state of the atom each term in the expansion (7) is finite. The interaction energy at the surface is provided by E_0 while for small Z the approximate value of the energy is given by the sum of E_0, E_1, and E_2.

The general expression for $\mathbf{E}(\mathbf{r})$ given by (6) can be approximated for large Z also. Writing the real part of $\mathbf{E}(\mathbf{r})$ for large Z, we obtain

$$\operatorname{Re}E(Z)=-\frac{Q_s^2e^2}{12Z^3}\sum_l\frac{1}{Q_s^2+Q_l^2}\left[|\langle 0|\mathbf{r}'|l\rangle|^2\left[1-\frac{12k_0^2}{Z^2(Q_s^2+Q_l^2)^2}+\cdots\right]\right.$$

$$+\left[\frac{9}{64}\right]\left[\frac{1}{Z^2}\right][\langle 0|(r'^2+3Z')\mathbf{R}'|l\rangle\cdot\langle l|\mathbf{R}'|0\rangle$$

$$\left.-\langle 0|(4r'^2+5Z'^2)Z'|l\rangle\langle l|Z'|0\rangle]+\cdots\right]. \tag{11}$$

The corresponding imaginary part of $E(Z)$ is

$$\operatorname{Im}E(Z)=\operatorname{sgn}(Z)\frac{Q_s^2e^2k_0}{4Z^4}\sum_l\frac{1}{(Q_s^2+Q_l^2)^2}\left[|\langle 0|\mathbf{r}'|l\rangle|^2\left[1-\frac{20k_0^2}{Z^2(Q_s^2+Q_l^2)^2}+\cdots\right]\right.$$

$$-\frac{15}{64Z^2}[\langle 0|(4r'^2-22Z'^2)\mathbf{R}'|l\rangle\cdot\langle l|\mathbf{R}'|0\rangle$$

$$\left.+\langle 0|(18r'^2+47Z'^2)Z'|l\rangle\langle l|Z'|0\rangle]\right]. \tag{12}$$

III. CLASSICAL LIMIT

In the limit of large atomic mass, the recoil effects drop out and the result for E, valid for all Z and all speeds, can be written but the result is lengthy. The result is relatively simpler for $k_0=0$. In this case we obtain

$$E=-\frac{Q_s^2e^2}{2}\sum_l \frac{1}{(Q_s^2+Q_l^2)}\int\int d\mathbf{r}'d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(r'')\psi_l^*(r'')$$
$$\times\Bigg[\Bigg[\frac{1}{\{(|Z'_+|+|Z''_+|)^2+[(\mathbf{R}'-\mathbf{R}'')/2]^2\}^{1/2}}+\frac{1}{\{(|Z'_-|+|Z''_-|)^2+[(\mathbf{R}'-\mathbf{R}'')/2]^2\}^{1/2}}$$
$$-\frac{1}{\{(|Z'_+|+|Z''_-|)^2+[(\mathbf{R}'+\mathbf{R}'')/2]^2\}^{1/2}}-\frac{1}{\{(|Z'_-|+|Z''_+|)^2+[(\mathbf{R}'+\mathbf{R}'')/2]^2\}^{1/2}}\Bigg]$$
$$+\Bigg[\frac{\exp[-(Q_s^2+Q_l^2)^{1/2}|Z'_+|]|Z''_+|}{(Q_s^2+Q_l^2)^{1/2}\{|Z''_+|+[(\mathbf{R}'-\mathbf{R}'')/2]^2\}^{3/2}}+\frac{\exp[-(Q_s^2+Q_l^2)^{1/2}|Z'_-|]|Z''_-|}{(Q_s^2+Q_l^2)^{1/2}\{|Z''_-|^2+[(\mathbf{R}'-\mathbf{R}'')/2]^2\}^{3/2}}$$
$$-\frac{\exp[-(Q_s^2+Q_l^2)^{1/2}|Z'_+|]|Z''_-|}{(Q_s^2+Q_l^2)^{1/2}\{|Z''_-|^2+[(\mathbf{R}'+\mathbf{R}'')/2]^2\}^{3/2}}-\frac{\exp[-(Q_s^2+Q_l^2)|Z'_-|]|Z''_+|}{(Q_s^2+Q_l^2)^{1/2}\{|Z''_+|^2+[(\mathbf{R}'+\mathbf{R}'')/2]^2\}^{3/2}}\Bigg]\Bigg], \quad (13)$$

where due to the differences in the masses of the nuclei and the electron $Z'_+=Z$ and $Z'_-=Z-Z'$. Equation (13) for $Z=0$ can be seen to be finite.

IV. CONCLUDING REMARKS

It is shown that the interaction energy between an atom and a metal surface saturates to a finite value at the surface if multipolar excitations of the atom are included. This result differs from the treatment by Manson and Ritchie who consider only the dipolar excitations and therefore neglect the contributions of the higher-order multipolar excitations of the atom. In the limit of large atomic mass an exact expression for the interaction energy valid for all the separations is also obtained.

For the case of large separations the asymptotic expressions for the potential energy contain the result of Manson and Ritchie,[5] but in addition include the contributions from the higher-order multipoles. These additions can be seen to be comparable in magnitude to the effects produced by the speed of the atom when $|k_0|$ is small.

ACKNOWLEDGMENT

The authors gratefully acknowledge the partial support of the Natural Sciences and Engineering Research Council of Canada towards this research.

[1]K. G. Lynn and D. O. Welch, Phys. Rev. B 22, 99 (1980).
[2]A. P. Mills, Jr. and Loren Pfeiffer, Phys. Rev. Lett. 43, 1961 (1979).
[3]P. R. Rao and G. Mukhopadhyay, Solid State Commun. 52, 697 (1984).
[4]J. Mahanty and B. V. Paranjape, Solid State Commun. 24, 651 (1977).
[5]J. R. Manson and R. H. Ritchie, Phys. Rev. B 29, 1084 (1984).
[6]V. V. Paranjape and J. Mahanty, Phys. Rev. A 19, 2466 (1979).