Self-energy of a hydrogenic atom near a metal surface

B. Singla, V. K. Jindal, and K. N. Pathak
Department of Physics, Panjab University, Chandigarh 160 014, India

V. V. Paranjape
Department of Physics, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1
(Received 27 February 1992)

General expressions for the self-energy of hydrogenic atoms near a metal surface have been derived. It is found that the self-energy at the metal surface saturates to a finite value with the inclusion of multipolar excitations of the hydrogenic atoms. Numerical results have been presented for hydrogenic atoms moving normal to the metal surface at two speeds. It is also found that dispersion effects of surface-plasmon excitation further reduce the magnitude of the self-energy.

I. INTRODUCTION

In the past, efforts have been made to study the theoretical as well as the experimental[1] aspects of the interaction between an atom and a metal surface. The interaction between an atom and a metal surface is basically of the van der Waals type[2] and is due to induced excitations of the atom and the metal surface. Although the interaction has been examined using semiclassical approaches,[3,4] a quantum-mechanical treatment of the problem has been proposed only recently by Manson and Ritchie.[5] These authors have shown that the interaction energy near a metal surface is determined by quantum effects arising from virtual atomic excitations and surface plasmons. In their work they used a dipolar approximation to simplify the interaction Hamiltonian, thereby considering only virtual atomic excitations of simple dipoles. They have found that the interaction energy varies as $1/Z^3$ when Z, the separation between the atom and metal surface, is very large, and it varies as $1/Z$ when separation between atom and metal surface is very small. Manson and Ritchie[5] have attributed the softening of the interaction to quantum effects near the surface. These authors have also shown that this interaction also depends on the speed of the atom relative to the metal surface.

Recently, several papers[6-8] have extended the work of Manson and Ritchie to incorporate multipolar excitations of the atom. With inclusion of these excitations, they have shown that at the surface, the interaction energy saturates to a finite negative value. The numerical results for the interaction energy of a positronium atom have been obtained by Pathak, Jindal, and Paranjape.[8] It has been found that this interaction energy is smaller than the value obtained by Manson and Ritchie. In all earlier works the dispersion effects of surface and bulk plasmons have been neglected and results have been obtained with only the positronium atom kept in mind. In this paper we formulate a general theory for the calculation of the self-energy of hydrogenic atoms near a metal surface, using a hydrodynamical model[9] of metallic electrons. We incorporate the dispersion effects of surface plasmons. Our expressions for the self-energy of the atom moving normal to the surface at a speed below threshold reduce to the earlier results[4,5] in the dispersionless limits of surface plasmons.

We present a theoretical formulation in Sec. II. The numerical results and discussions for the self-energy of the positronium and hydrogen atoms are presented in Sec. III.

II. THEORETICAL FORMULATION

A. Hamiltonian

The Hamiltonian representing two charged particles with charges $\pm Q'$, momenta P_1, P_2, and masses m_1, m_2, and interacting with a metal surface is given by

$$H=\frac{P_1^2}{2m_1}+\frac{P_2^2}{2m_2}+H_{\rm met}+H_{\rm int}\ , \tag{1}$$

$$H_{\rm met}=\sum_Q \hbar\omega_Q(a_Q^\dagger a_Q+\tfrac{1}{2})\ , \tag{2}$$

$$H_{\rm int}=-\frac{Q'^2}{|\mathbf{r}_1-\mathbf{r}_2|}+\sum_{\mathbf{Q}}[\exp(i\mathbf{Q}\cdot\mathbf{R}_+)\Gamma_Q(Z_+) -\exp(i\mathbf{Q}\cdot\mathbf{R}_-)\Gamma_Q(Z_-)] \times(a_Q+a_{-Q}^\dagger)\ . \tag{3}$$

In Eqs. (2) and (3) a_λ and $a_\lambda^\dagger$ are the annihilation and creation operators of the plasmon modes of the metal electrons. $\mathbf{Q}$ represent the wave vectors of the surface plasmons. The position coordinates of the two charges are, respectively, $\mathbf{r}_1$ and $\mathbf{r}_2$, which in the cylindrical coordinates are given by $(\mathbf{R}_+, Z_+)$ and $(\mathbf{R}_-, Z_-)$, where $\mathbf{R}_\pm$ is parallel to the surface and Z is the positive distance away from the surface on the vacuum side. After making a transformation into the center of mass and relative coordinates, the positional coordinates of the two charges $(\mathbf{R}_+, Z_+)$ and $(\mathbf{R}_-, Z_-)$ become

$$\mathbf{R}_+=\mathbf{R}+\frac{\mathbf{R}'}{\nu+1}\ ,\quad Z_+=Z+\frac{Z'}{\nu+1}$$
$$\mathbf{R}_-=\mathbf{R}-\frac{\mathbf{R}'\nu}{\nu+1}\ ,\quad Z_-=Z-\frac{Z'\nu}{\nu+1}\ ,$$

where $\nu=m_1/m_2$, $(\mathbf{R},Z)$ are the coordinates of the center of mass of the atom with mass $M=m_1+m_2$, and $(\mathbf{R}',Z')$ are the relative coordinates. With this transformation the Hamiltonian in Eq. (1) can be written as

$$H=\frac{P^2}{2M}+H_{\text{atom}}+H_{\text{metal}}+H_{\text{int}}\ . \tag{4}$$

The first term represents the Hamiltonian for the motion of the center of mass of the atom and H_{atom} is given by

$$H_{\text{atom}}=\frac{P'^2}{2\mu}+\frac{-Q'^2}{|\mathbf{r}_1-\mathbf{r}_2|}\ , \tag{5}$$

where $\mu=m_1m_2/M$ and P' is the relative momentum. The Hamiltonian corresponding to the interaction of the atom with the metal surface is given by

$$H_{\text{int}}=-Q'\sum_{Q'}\left\{\exp\left[i\mathbf{Q}\cdot\left[\mathbf{R}+\frac{\mathbf{R}'}{\nu+1}\right]\right]\Gamma_Q\left[Z+\frac{Z'}{\nu+1}\right]-\exp\left[i\mathbf{Q}\cdot\left[\mathbf{R}-\frac{\mathbf{R}'\nu}{\nu+1}\right]\right]\times\Gamma_Q\left[Z-\frac{Z'\nu}{\nu+1}\right]\right\}[a_Q+a^{\dagger}_{-Q}]\ . \tag{6}$$

The coupling coefficients for the interaction of the atom with surface plasmons are defined[10] for any Z,

$$\Gamma_Q(Z)=\frac{m}{e}N_Q[\Theta(Z)Ae^{-QZ}+\Theta(-Z)(Be^{QZ}-Ce^{\gamma Z})]\ ,$$
$$A=\omega_S^2\gamma-Qw_P^2\ ,\quad B=w_s^2\gamma\ ,\quad C=Qw_P^2\ , \tag{7}$$

where $w_P^2=4\pi ne^2/m$ is the plasma frequency and m is the mass of the electron. $\Theta(Z)=1$ for $Z>0$ and 0 otherwise. The normalization factor $|N_Q|$ is given by

$$|N_Q|^2=\frac{\hbar e^2(2w_S^2-w_P^2)^2}{4\pi^2m^2Q^3w_S(2w_S^2+w_P^2)(w_S^2-w_P^2)^2}\ , \tag{8}$$

$$w_S^2=\tfrac{1}{2}[w_P^2+\beta^2Q^2+\beta Q(2w_P^2+\beta^2Q^2)^{1/2}]\ , \tag{9}$$

and

$$\gamma^2=Q^2+(w_P^2-w_S^2)/\beta^2\ . \tag{10}$$

In Eqs. (9) and (10) β is the dispersion parameter. Its value is equal to $\frac{3}{5}v_F^2$; $v_F^2=(9\pi/\mathbf{r}_S^3a_0^3)^{1/3}$ in the random-phase approximation and $(\frac{1}{3}v_F^2)$ in the Thomas-Fermi approximation. The form of the Hamiltonian given by Eqs. (1)–(3), describing the interaction between an atom and a metal surface within the hydrodynamical model of metallic electrons, is quite general. This form of the Hamiltonian differs from those of earlier workers,[3–5] who used a simplified version of Eq. (3).

B. Self-energy of the hydrogenic atom

The interaction energy of a hydrogenic atom interacting with a metal surface is given by

$$\Sigma(Z)=\sum_{n,l,k}\frac{\langle\phi_k|\mathbf{r}\rangle}{\langle\phi_0|\mathbf{r}\rangle}\times\frac{\langle\phi_0,0,0|H_{\text{int}}|n,l,k\rangle\langle l,n|H_{\text{int}}|0,0\rangle}{E_0-E_n+e_0-e_k-\varepsilon_l+i\delta}\ . \tag{11}$$

In Eq. (11) a state vector $|n,l,k\rangle$ represents the products of a surface state vector of energy E_n, atomic state vector with energy ε_l, and the translational state vector with energy e_k, respectively. $|\phi_0\rangle$ is the unperturbed state of the free atom with incident momentum $\hbar k_0/M$ where k_0 is the speed of the atom. $\mathbf{k}$ is the free atomic state with $\mathbf{K}$ and k_3 as its parallel and perpendicular components to the metal surface. After substituting the interaction Hamiltonian given by Eq. (3) into Eq. (11) and completing the summation over the parallel component $\mathbf{K}$ and plasmon intermediate state, we get

$$\Sigma(Z)=-\frac{2M}{\hbar^2}Q'^2\left[\frac{m}{e}\right]^2\sum_{l,\mathbf{Q}}|N_Q|^2\int_{-\infty}^{+\infty}\frac{dk_3}{(k_3^2+\alpha^2)}\left[\left\langle 0\left|\exp\left[i\mathbf{Q}\cdot\frac{\mathbf{R}'}{\nu+1}-iZ_+(k_3+k_{03})\right]-\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}-iZ_-(k_3+k_{03})\right]\right|l\right\rangle\times\left[\frac{A}{Q-i(k_3+k_{03})}+\frac{B}{Q+i(k_3+k_{03})}-\frac{C}{\gamma+i(k_3+k_{03})}\right]\times\left\{\left\langle l\left|\left[\Theta(Z_+)Ae^{-QZ_+}+\Theta(-Z_+)(Be^{QZ_+}-Ce^{\gamma Z_+})\right]\times\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'}{\nu+1}\right]-\exp\left[i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}\right]\times[\Theta(Z_-)Ae^{-QZ_-}+\Theta(-Z_-)(Be^{+QZ_-}-Ce^{\gamma Z_-})]\right|0\right\rangle\right\}\right], \tag{12}$$

where

$$\alpha^2=Q_s^2+Q_l^2+Q^2-k_{03}^2 \ , \tag{13}$$

$$Q_s^2=2Mw_S/\hbar \ , \tag{14}$$

$$Q_l^2=2M\varepsilon_l/\hbar \ . \tag{15}$$

Before proceeding toward the k_3 integration we make the substitution $k_3+k_{03}=t$ in Eq. (12). The limits of integration are not affected by this change and we get $\Sigma(Z)$ in a more simplified form:

$$\begin{aligned}\Sigma(Z)=&-\frac{2M}{\hbar^2}Q'^2\left[\frac{m}{e}\right]^2 \\ &\times\sum_{l,\mathbf{Q}}|N_Q|^2\int_{-\infty}^{+\infty}\frac{dt}{\alpha^2+(t-k_{03})^2} \\ &\times\left[\left\langle 0\left|\exp\left[i\mathbf{Q}\cdot\frac{\mathbf{R}'}{\nu+1}-iZ_+t\right]-\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}-iZ_-t\right]\right|l\right\rangle\right. \\ &\times\left[\frac{A}{Q-it}+\frac{B}{Q+it}-\frac{C}{\gamma+it}\right] \\ &\times\left\{\left\langle l\left|\left[[\Theta(Z_+)Ae^{-QZ_+}+\Theta(-Z_+)(Be^{QZ_+}-Ce^{\gamma Z_+})]\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'}{\nu+1}\right]\right.\right.\right. \\ &\left.\left.\left.-\exp\left[i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}\right][\Theta(Z_-)Ae^{-QZ_-}+\Theta(-Z_-)(Be^{+QZ_-}-Ce^{\gamma Z_-})]\right|\right|0\right\rangle\right\}\Bigg] .\end{aligned} \tag{16}$$

Now integration over t in Eq. (16) can be done by methods of complex variables for speeds of an atom below threshold. After integrating over t for $Z>0$ and $Z<0$, Eq. (16) becomes

$$\begin{aligned}\Sigma(Z)=&-\left[\frac{m}{e}\right]^2\frac{2M}{\hbar^2}\frac{Q'^2}{2} \\ &\times\sum_{l,\mathbf{Q}}|N_Q|^2\left[\left\langle 0\left|\exp\left[i\mathbf{Q}\cdot\frac{\mathbf{R}'}{\nu+1}\right][T_1\Theta(Z_+)+T_2\Theta(-Z_+)]\right.\right.\right. \\ &\left.\left.-\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}\right][T_3\Theta(Z_-)+T_4\Theta(-Z_-)]\right|l\right\rangle \\ &\times\left\langle l\left|\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}\right][A\Theta(Z_+)e^{-QZ_+}+\Theta(-Z_+)(Be^{QZ_+}-Ce^{\gamma Z_+})]\right.\right. \\ &\left.\left.-\exp\left[-i\mathbf{Q}\cdot\frac{\mathbf{R}'\nu}{\nu+1}\right][Ae^{-QZ_-}\Theta(Z_-)+\Theta(-Z_-)(Be^{QZ_-}-Ce^{\gamma Z_-})]\right|0\right\rangle\Bigg] .\end{aligned} \tag{17}$$

In Eq. (16) T_1, T_2, T_3, and T_4 are defined as follows:

$$T_1=\frac{A}{\alpha}\frac{e^{-\alpha Z_+-ik_{03}Z_+}}{Q-\alpha-ik_{03}}+\frac{2Ae^{-QZ_+}}{\alpha^2+(k_{03}+iQ)^2}+\frac{B}{\alpha}\frac{e^{-\alpha Z_+-ik_{03}Z_+}}{Q+\alpha+ik_{03}}-\frac{C}{\alpha}\frac{e^{-\alpha Z_+-ik_{03}Z_+}}{\alpha+\gamma+ik_{03}} \ , \tag{18}$$

$$T_2=\frac{Ae^{-\alpha Z_++ik_{03}Z_+}}{\alpha(Q+\alpha-ik_{03})}+\frac{2Ae^{-QZ_+}}{\alpha^2+(k_{03}-iQ)^2}+\frac{B}{\alpha}\frac{e^{-\alpha Z_++ik_{03}Z_+}}{Q-\alpha+ik_{03}}-\frac{Ce^{-\alpha Z_++ik_{03}Z_+}}{\alpha(\gamma-\alpha+ik_{03})}-\frac{2Ce^{-\gamma Z_+}}{\alpha^2+(k_{03}-i\gamma)^2} \ , \tag{19}$$

$$T_3=\frac{A}{\alpha}\frac{e^{-\alpha Z_--ik_{03}Z_-}}{Q-\alpha-ik_{03}}+\frac{2Ae^{-QZ_-}}{\alpha^2+(k_{03}+iQ)^2}+\frac{B}{\alpha}\frac{e^{-\alpha Z_--ik_{03}Z_-}}{(Q+\alpha+ik_{03})}-\frac{C}{\alpha}\frac{e^{-\alpha Z_--ik_{03}Z_-}}{\alpha+\gamma+ik_{03}} \ , \tag{20}$$

$$T_4=\frac{A}{\alpha}\frac{e^{-\alpha Z_-+ik_{03}Z_-}}{Q+\alpha-ik_{03}}+\frac{2Ae^{-QZ_-}}{\alpha^2+(k_{03}-iQ)^2}+\frac{B}{\alpha}\frac{e^{-\alpha Z_-+ik_{03}Z_-}}{(Q-\alpha+ik_{03})}-\frac{C}{\alpha}\frac{e^{-\alpha Z_-+ik_{03}Z_-}}{(\gamma-\alpha+ik_{03})}-\frac{2Ce^{-\gamma Z_-}}{(\alpha^2+k_{03}-i\gamma)^2} \ . \tag{21}$$

Equation (17) represents the self-energy of a hydrogenic atom interacting with a metal surface when dispersion effects of surface plasmons are included. It is valid for an atom moving with any arbitrary speed k_0. Here summation over $\mathbf{Q}$ can be replaced by integration and the angle of vector $\mathbf{Q}$ can be integrated out to yield

$$\Sigma(Z)=-\left[\frac{m}{e}\right]^2\frac{2M}{\hbar^2}\pi Q'^2$$
$$\times\sum_l\int_0^\infty dQ\,Q|N_Q|^2\int d\mathbf{r}'\int d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l(\mathbf{r}')\psi_l^*(\mathbf{r}'')$$
$$\times\left\{\left[J_0\left[\frac{Q}{\nu+1}|R'-R''|\right][Ae^{-QZ''_+}\Theta(Z''_+)+\Theta(-Z''_+)(Be^{QZ''_+}-Ce^{\gamma Z''_+})]\right.\right.$$
$$\left.-J_0\left[\frac{Q}{\nu+1}|R'+R''\nu|\right][Ae^{-QZ''_-}\Theta(Z''_-)+\Theta(-Z''_0)(Be^{QZ''_-}-Ce^{\gamma Z''_-}]\right]$$
$$\times[T_1\Theta(Z'_+)+T_2\Theta(-Z'_+)]$$
$$+\left[J_0\left[\frac{Q\nu}{\nu+1}|R'-R''|\right][Ae^{-QZ''_-}\Theta(Z''_-)+\Theta(-Z''_-)(Be^{QZ''_-}-Ce^{\gamma Z''_-})]\right.$$
$$\left.\left.-J_0\left[\frac{Q}{\nu+1}|R'\nu+R''|\right][Ae^{-QZ''_+}\Theta(Z''_+)+\Theta(-Z''_+)(Be^{QZ''_+}-Ce^{\gamma Z''_+})]\right.\right.$$
$$\left.\left.\times[T_3\Theta(Z'_-)+T_4\Theta(-Z'_-)]\right]\right\}. \tag{22}$$

In Eq. (22), J_0 is a Bessel function of the first kind and Z'_+, Z''_+, Z'_-, and Z''_- are given as

$$Z'_+=Z+Z'/(\nu+1)\,, \tag{23a}$$
$$Z''_+=Z+Z''/(\nu+1)\,, \tag{23b}$$
$$Z'_-=Z-Z'\nu/(\nu+1)\,, \tag{23c}$$
$$Z''_-=Z-Z''\nu/(\nu+1)\,. \tag{23d}$$

Equation (22) is applicable to any arbitrary atom (i.e., hydrogen, positronium, and muonium). If $\nu=1$, one gets results for the self-energy of the positronium atom and if $\nu=1836$ one gets results for the self-energy of the hydrogen atom. In the $\beta=0$ limit our results agree with those obtained by earlier authors.[6–8]

It is of interest to obtain the self-energy given by Eq. (22) in the limits of $Z\to 0$ and $Z\to\infty$. The expression for $\Sigma(Z)$ can be easily worked out from Eq. (22). For $Z\to 0$, the self-energy of a stationary hydrogen atom is given as

$$\Sigma(Z\to 0)=-\frac{M}{\hbar^2}Q'^2\sum_l\int_0^\infty dQ\int d\mathbf{r}'\int d\mathbf{r}''\frac{\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l^*(\mathbf{r}'')(2w_S^2-w_P^2)^2}{Q^2(2w_S^2-w_P^2)w_S(w_S^2-w_P^2)^2}$$
$$\times\left[\left[J_0\left[\frac{Q}{\nu+1}|R'-R''|\right]\left\{A\exp\left[-Q\frac{Z''}{\nu+1}\right]\Theta\left[\frac{Z''}{\nu+1}\right]+\Theta\left[-\frac{Z''}{\nu+1}\right]\left[B\exp\left[Q\frac{Z''}{\nu+1}\right]\right.\right.\right.\right.$$
$$\left.\left.\left.\left.-C\exp\left[\gamma\frac{Z''}{\nu+1}\right]\right]\right\}\right.$$
$$\left.-J_0\left[\frac{Q}{\nu+1}|R'+R''\nu|\right]\left\{A\exp\left[Q\frac{Z''\nu}{\nu+1}\right]\Theta\left[-\frac{Z''\nu}{\nu+1}\right]+\Theta\left[+\frac{Z''\nu}{\nu+1}\right]\left[B\exp\left[-Q\frac{Z''\nu}{\nu+1}\right]\right.\right.\right.$$
$$\left.\left.\left.\left.-C\exp\left[-\gamma\frac{Z''\nu}{\nu+1}\right]\right]\right\}\right]$$
$$\times\left[\Theta\left[\frac{Z'}{\nu+1}\right]\left[\frac{A}{\alpha}\frac{\exp\left[-\alpha\frac{Z'}{\nu+1}\right]}{Q-\alpha}+\frac{2A\exp\left[-Q\frac{Z'}{\nu+1}\right]}{\alpha^2-Q^2}\right.\right.$$
$$\left.\left.+\frac{B}{\alpha}\frac{\exp\left[-\alpha\frac{Z'}{\nu+1}\right]}{Q+\alpha}-\frac{C}{\alpha}\frac{\exp\left[-\alpha\frac{Z'}{\nu+1}\right]}{(\gamma+\alpha)}\right]\right.$$

$$+\Theta\left[-\frac{Z'}{\nu+1}\right]\left[\frac{A}{\alpha}\frac{\exp\left[\alpha\frac{Z'}{\nu+1}\right]}{Q-\alpha}+\frac{2B\exp\left[Q\frac{Z'}{\nu+1}\right]}{\alpha^2-Q^2}+\frac{B\exp\left[+\alpha\frac{Z'}{\nu+1}\right]}{\alpha(Q-\alpha)}\right.$$
$$\left.-\frac{C}{\alpha}\frac{\exp\left[\alpha\frac{Z'}{\nu+1}\right]}{(\gamma-\alpha)}-\frac{2C\exp\left[\gamma\frac{Z'}{\nu+1}\right]}{\gamma^2-\alpha^2}\right]\Bigg]$$
$$+\left[J_0\left[\frac{Q\nu}{\nu+1}|R'-R''|\right]\left\{A\exp\left[-Q\frac{Z''\nu}{\nu+1}\right]\Theta\left[\frac{Z''\nu}{\nu+1}\right]+\Theta\left[-\frac{Z''\nu}{\nu+1}\right]\left[B\exp\left[-Q\frac{Z''\nu}{\nu+1}\right]\right.\right.\right.$$
$$\left.\left.\left.-C\exp\left[-\gamma\frac{Z''\nu}{\nu+1}\right]\right]\right\}$$
$$-J_0\left[\frac{Q}{\nu+1}|R''+R'\nu|\right]\left\{A\exp\left[-Q\frac{Z''}{\nu+1}\right]\Theta\left[\frac{Z''}{\nu+1}\right]+\left[B\exp\left[Q\frac{Z''}{\nu+1}\right]-C\exp\left[\gamma\frac{Z''}{\nu+1}\right]\right]\right.$$
$$\left.\left.\times\Theta\left[-\frac{Z''}{\nu+1}\right]\right\}\right]$$
$$\times\left[\Theta\left[-\frac{Z'\nu}{\nu+1}\right]\left[\frac{A}{\alpha}\frac{\exp\left[\alpha\frac{Z'\nu}{\nu+1}\right]}{Q-\alpha}+\frac{2A\exp\left[Q\frac{Z'\nu}{\nu+1}\right]}{Q_S^2+Q_l^2}\right.\right.$$
$$\left.+\frac{B}{\alpha}\frac{\exp\left[\alpha\frac{Z'\nu}{\nu+1}\right]}{Q+\alpha}-\frac{C\exp\left[\alpha\frac{Z'\nu}{\nu+1}\right]}{\alpha(\gamma+\alpha)}\right]$$
$$+\Theta\left[\frac{Z'\nu}{\nu+1}\right]\left[\frac{A}{\alpha}\frac{\exp\left[-\alpha Z'\frac{\nu}{\nu+1}\right]}{Q+\alpha}+\frac{2B\exp\left[-Q\frac{Z'\nu}{\nu+1}\right]}{Q_S^2+Q_e^2}+\frac{B}{\alpha}\frac{\exp\left[-\alpha\frac{Z'\nu}{\nu+1}\right]}{Q-\alpha}\right.$$
$$\left.\left.-\frac{C}{\alpha}\frac{\exp\left[-\alpha\frac{Z'\nu}{\nu+1}\right]}{\gamma-\alpha}-\frac{2C\exp\left[-\gamma\frac{Z'\nu}{\nu+1}\right]}{\gamma^2-\alpha^2}\right]\right]\Bigg]. \tag{24}$$

In the presence of the dispersion effects of surface plasmons, the expression for the self-energy is somewhat lengthy even for an atom of zero speed. However, in the dispersionless limit we obtain a simple expression, given as

$$\Sigma(Z)=-\frac{Q_S^2e^2}{2}\sum_l\int_0^\infty dQ\int d\mathbf{r}'\int d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(\mathbf{r}'')\psi_l^*(\mathbf{r}'')$$
$$\times\left[\mathrm{Re}\left\{\frac{\exp\left[-Q\left|\frac{Z'}{\nu+1}\right|\right]}{D_1}+\frac{Q}{\alpha}\frac{\exp\left[-(\alpha+ik_{03})\left|\frac{Z'}{\nu+1}\right|\right]}{D_2}\right\}\right.$$
$$\times\left\{J_0\left[\frac{Q}{\nu+1}|R'-R''|\right]\exp\left[-Q\left|\frac{Z''}{\nu+1}\right|\right]\right.$$
$$\left.\left.-J_0\left[\frac{Q}{\nu+1}|R'+R''\nu|\right]\exp\left[-Q\left|\frac{Z''}{\nu+1}\right|\right]\right\}\right]$$

$$+\mathrm{Re}\left\{\frac{\exp\left[-Q\left|\frac{Z'\nu}{\nu+1}\right|\right]}{D_1}+\frac{Q}{\alpha}\frac{\exp\left[-(\alpha+ik_{03})\left|\frac{Z'\nu}{\nu+1}\right|\right]}{D_2}\right\}$$
$$\times\left\{J_0\left[\frac{Q}{\nu+1}|R'-R''|\nu\right]\exp\left[-Q\frac{|Z''|\nu}{\nu+1}\right]\right.$$
$$\left.-J_0\left[\frac{Q}{\nu+1}|R'\nu+R''|\right]\exp\left[-Q\frac{|Z''|}{\nu+1}\right]\right\}\Bigg], \tag{25}$$

where $D_1=Q_S^2+Q_l^2+2ik_{03}Q$; $D_2=2k_{03}^2-Q_S^2-Q_l^2-2ik_{03}\alpha$. On the other hand, in the limit of $Z\to\infty$ dispersion effects play no role and the expression for $\Sigma(Z)$ reduces to

$$\Sigma(Z)=-\frac{Q_S^2e^2}{2}\sum_l\int_0^\infty dQ\int d\mathbf{r}'\int d\mathbf{r}''\psi_0^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_0(r'')\psi_l^*(\mathbf{r}'')\left[\frac{e^{-2QZ}}{D_1}+\frac{Q}{\alpha}\frac{e^{-(\alpha+ik_{03}+Q)Z}}{D_2}\right]$$
$$\times\left\{J_0\left[\frac{Q}{\nu+1}|R'-R''|\right]+J_0\left[\frac{Q\nu}{\nu+1}|R'-R''|\right]\right.$$
$$\left.-J_0\left[\frac{Q}{\nu+1}|R'\nu+R''|\right]-J_0\left[\frac{Q}{\nu+1}|R'+R''\nu|\right]\right\}. \tag{26}$$

The dominant Z dependence of self-energy can be obtained from Eq. (26) by expanding the integral in the small-Q limit. We thus obtain

$$\Sigma(Z\to\infty)=-\frac{2Q_S^2e^2}{3}\sum_l|\langle 0|r'|l\rangle|^2\int_0^\infty dQ\left[\frac{Q^2e^{-2QZ}}{D_1}+\frac{Q}{\alpha}\frac{e^{-\alpha Z-ik_{03}Z-QZ}}{D_2}\right]. \tag{27}$$

It can easily be seen that Eq. (27) reduces to a well-known Lifshiftz result whose real part is given as

$$\Sigma(Z\to\infty)=-\frac{Q_S^2e^2}{12Z^3}\sum_l\frac{1}{Q_S^2+Q_l^2}\left[|\langle 0|r'|l\rangle|^2\left[1-\frac{12k_{03}^2}{Z^2(Q_S^2+Q_l^2)}+\cdots\right]\right]. \tag{28}$$

In obtaining the result in Eq. (28) we have omitted some correction to the Lifshitz result arising from the speed of the atom. It may be mentioned that Eqs. (25) and (28) for $\nu=1$ reduce to results obtained by Pathak and Paranjape.

III. RESULTS AND DISCUSSIONS

We present the result for the self-energy of the positronium and hydrogen atom using Eq. (22). We measure the self-energy in Rydbergs ($Q'^2/2a_0$) where a_0 is Bohr's radius (i.e., $a_0=\hbar^2/me^2$, where m is the mass of the electron). The unit of length is taken to be a_0. w_S is measured in the units of plasma frequency w_P. The multiplying constant for the numerical calculation of Eq. (22) contains $\mathbf{r}_s$ which arises from the definition of ω_P (i.e., $w_P^2=4\pi ne^2/m$; $n=3/4\pi r_s^3a_0^3$). The value of $\mathbf{r}_s$ lies in the range 2–6 for various metals.

Using the hydrogenic wave functions, seven-dimensional integration is done using a Monte Carlo technique. For the summation over l in Eq. (22), the first five excited states of the hydrogen atom have been taken. The sum is found to be sufficiently convergent up to the fifth excited state of the atom. A study of the variation of the integral with respect to the number of random points choosen for the Monte Carlo method is done and is shown in Fig. 1. It is clear from Fig. 1 that the integral is fairly stable if we select nearly 15 000 random points. We have also checked our integration routine for a known six-dimensional integral.[11] Our computed results with the Monte Carlo method was found to be in very close agreement with the known results.

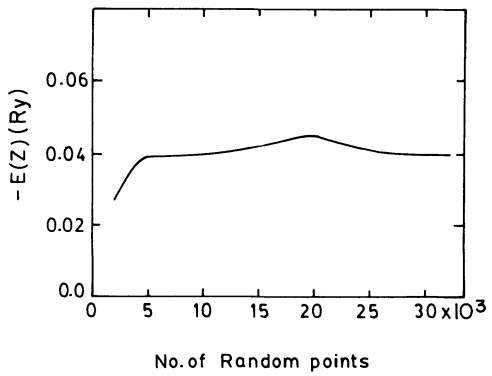

FIG. 1. Variation of the self-energy with respect to a set of random points chosen for the Monte Carlo method.

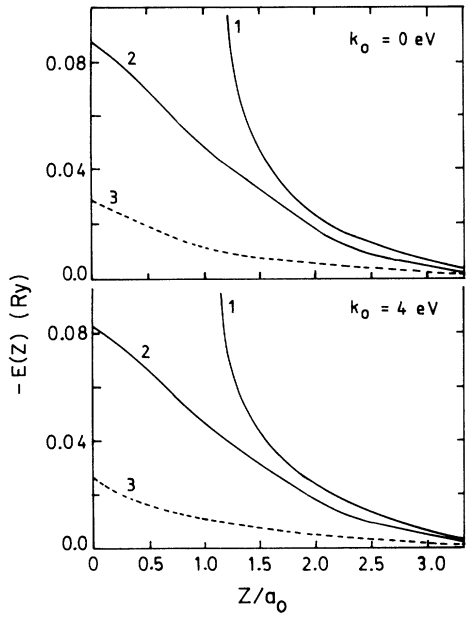

FIG. 2. Variation of the self-energy with respect to the distance between the center of mass of the positronium atom and metal surface for 0- and 4-eV speeds. Curves 2 and 3 represent the dispersion-effects-excluded and -included cases, respectively. Curve 1 represents the asymptotic result.

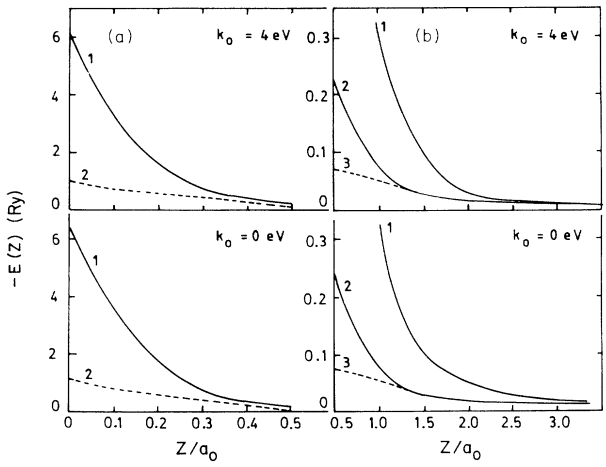

FIG. 3. (a) Variation of the self-energy of a hydrogen atom for distance $Z < 0.5a_0$ for 0- and 4-eV speeds. Curves 1 and 2 represent the dispersion-effects-excluded and -included cases, respectively. (b) Variation of the self-energy of a hydrogen atom for distance $Z > 0.5a$ for 0- and 4-eV speeds. Curves 2 and 3 represent the self-energy for the dispersion-effects-excluded and -included cases, respectively. Curve 1 represents the asymptotic result.

Numerical calculations have been done for the aluminum surface corresponding to $r_s = 2.1$ and these are plotted in Figs. 2 and 3. In Fig. 2, results for the self-energy of the positronium atom (i.e., $\nu = 1$) are presented for the two normal speeds. Curves 2 and 3 represent the results of self-energy obtained by excluding and including the dispersion effects of surface plasmons. Curve 1 gives the asymptotic behavior of the self-energy obtained from Eq. (28). It is seen from Fig. 2 that the self-energy of the positronium atom attains a finite value of -0.086 Ry. This finite value is due to inclusion of multipolar excitations of the positronium atom. The self-energy further reduces to -0.029 Ry when the dispersion effects of surface plasmons are included. This decrease is due to electron-screening effects. The speed of the positronium atom, which is below threshold, has very small effects on the self-energy. It can be seen that for the distances around a_0 to $2a_0$ there is an appreciable difference between the Lifshitz result and that obtained by us. It is only around a distance of $Z > 3a_0$ that the difference between our result and the Lifshitz result becomes very small.

In Figs. 3(a) and 3(b) we plot the self-energy of the hydrogen atom (i.e., $\nu = 2000$). Figure 3(a) represents the behavior of the self-energy for distance $Z < a_0/2$. Here the values plotted on curve 3 are multiplied by a factor of 25 to present the result in the same figure. The value of the self-energy at the surface is -6.74 and -0.042 Ry for the dispersion-excluded and -included cases, respectively. There is a significant decrease in the value of the self-energy with the inclusion of dispersion effects of surface plasmons. It may be noted that here we have considered the contribution to the self-energy from the surface plasmons only. Bulk-plasmon contribution to the self-energy is known to be very small. In Fig. 3(b) we have plotted the self-energy for the distances $Z > a_0/2$. Curves 2 and 3 represent the self-energy of a hydrogen atom for the dispersion-effects-excluded and -included cases, respectively. Curve 3 is multiplied by a factor of 5 to represent the result of self-energy in the same figure. Curve 1 represents the asymptotic value of the self-energy obtained from Eq. (28). Here again there is appreciable difference between our result and that obtained from the Lifshitz formula, even for distances of a_0 to (1.5) a_0. As the center of mass of the atom moves away from the surface, the difference between the two (curves 2 and 3) decreases. For $Z > 2a_0$ there is practically no difference between our results and the Lifshitz results.

On the basis of the numerical results as described above it is clear that as the atom approaches the surface, the range of Q's contributing to the self-energy increases, as is evident from Eqs. (12) and (17). The self-energy is therefore affected by the range of Q's and the dispersion effects of increasing range. For large Z, the plasmon modes, with only small value of Q, are important and the dispersion effects over this range are negligible. Thus the dispersion effects will be large as Z is decreased. On the other hand, the difference between the self-energy with and without dispersion decreases as Z is increased. This result is clearly seen in Figs. 2 and 3. Small effects of the speed of the positronium and hydrogen atom on the self-energy are also understandable from Eq. (13), where α is much larger than k_{03}.

We conclude that our work provides a complete description of the self-energy of the hydrogenic atoms

near a metal surface. The metal surface is treated within the hydrodynamical model and dispersion effects of the surface plasmon in this model are completely taken into account. The theory takes care of the multipolar excitations of the atom. It is found that multipolar excitation of the atom and dispersion effects of surface plasmons provides a finite value of the self-energy at the metal surface.

ACKNOWLEDGMENTS

The major part of this work was supported by University Grant Commission, New Delhi, through a Research Grant. One of us (B.S.) gratefully acknowledges the Council of Scientific and Industrial Research for providing partial financial support. We are also thankful to Dr. K. Dharamvir for several helpful discussions with her.

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