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Atom-surface interaction: Zero-point energy formalism

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The interaction energy between an atom and a surface formed by a polar medium is derived with use of a new approach based on the zero-point energy formalism. It is shown that the energy depends on the separation Z between the atom and the surface. With increasing Z, the energy decreases according to $1/Z^3$, while with decreasing Z the energy saturates to a finite value. It is also shown that the energy is affected by the velocity of the atom, but this correction is small. Our result for large Z is consistent with the work of Manson and Ritchie [Phys. Rev. B **29**, 1084 (1984)], who follow a more traditional approach to the problem.

I. INTRODUCTION

The van der Waals interaction energy between an atom and a solid surface is well known to follow $1/Z^3$ dependence where the separation Z between the atom and the surface is assumed to be sufficiently large. The interaction at short separations, which has not received as much attention, is considerably different from its large separation behavior. It is the object of this paper to calculate the interaction for small Z and to show that it saturates as Z approaches zero, and to show that it depends on the relative velocity of the atom with respect to the surface. These considerations are particularly relevant to the recent experimental work involving atoms of low mass and metal surfaces.[1] They would also apply to the case of an atom interacting with a surface formed by an ionic crystal.

The interaction is derived in this paper using the approach[2] based on the calculation of the zero-point energy of the radiation field. The energy given by the sum of the energies of all the modes of the electromagnetic field is obtained when the interaction between the atom and the surface is present and when it is absent. The difference between the two energies provides the value of the interaction.

This procedure for obtaining the interaction energy between two atoms is well known in molecular physics. The extension of the method to the present problem is natural if we recognize that the interaction energy between an atom and a surface is equivalent to calculating the interaction energy between the atom and its image formed by the surface.

The method followed in this paper is not expected to produce results different from the method used by Manson and Ritchie[3] to calculate the energy of interaction between an atom and a surface. These authors make use of the interaction Hamiltonian for the atom and the polarization waves of the surface while we obtain the interaction from first principles. To some readers, our method may appear more lengthy, but this may be partly due to its unfamiliarity. Our object in writing this paper is to provide an alternative procedure to calculate the interaction energy with the hope that the procedure might lead to improved understanding of the present problem. To avoid unnecessary numerical evaluations we will restrict ourselves to calculating the interaction energy in the limits of small and large separations. Although our method and the method used by Manson and Ritchie give the interaction energy in a similar form, for small Z, our method provides a saturation value while such saturated value is not obtained by the earlier authors. This difference, however, is likely to be due to differences in the approximations used in the two methods.

The plan of the paper is as follows. In Sec. II the zero-point energy approach is given and a formal result for the interaction energy between an atom and a surface is obtained. In Sec. III the result of our model is used to obtain explicitly the interaction energy of an atom and a surface. Finally, in Sec. IV, the main conclusions of the paper are presented.

II. ZERO-POINT ENERGY FORMALISM

In this section a sketch of the zero-point energy formalism is presented, while a more detailed analysis is available in literature.[2] Consider a system consisting of an atom and a surface formed by an ionic crystal (or by a metal with some minor changes in the analysis). When these are coupled and uncoupled, the zero-point energy of the system is given by

$$E=\sum_i \tfrac{1}{2}\hbar\omega_i \quad \text{and} \quad E_0=\sum_i \tfrac{1}{2}\hbar\omega_i^0 , \tag{2.1}$$

respectively, where ω_i's are the frequencies of the electromagnetic field when the system is coupled and ω_i^0's are the frequencies when it is uncoupled. The interaction energy E_I of the system is given by the difference between E and E_0 and can be written as

$$E_I=\frac{\hbar}{4\pi i}\oint \ln\left[\frac{D(\omega)}{D_0(\omega)}\right]d\omega , \tag{2.2}$$

where $D(\omega)$ and $D_0(\omega)$ are, respectively, the determinants giving frequencies of the electromagnetic field for the coupled and uncoupled system. In (2.2), the contour encloses the real ω axis. Once $D(\omega)$ and $D_0(\omega)$ are obtained for our system, the interaction energy is determined using (2.2).

To obtain the secular determinants we proceed as follows. Let the electromagnetic field potential at point $\mathbf{x}'$ be given by $\phi(\mathbf{x}',\omega)$. As a consequence of the polarization of the system and the interaction, the potential $\phi(\mathbf{x},\omega)$ at any point $\mathbf{x}$ is connected to the potentials at other points $\mathbf{x}'$ by the relation

$$\phi(\mathbf{x},\omega)=\int G_n(\mathbf{x},\mathbf{x}',\omega)\phi(\mathbf{x}',\omega)d^3x' \;, \tag{2.3}$$

where the kernel G_n depends on the state of the system. Taking the Fourier components of (2.3), we get

$$\phi(\mathbf{k},\omega)=\sum_{\mathbf{k}'} G_n(\mathbf{k},\mathbf{k}',\omega)\phi(\mathbf{k}',\omega) \;. \tag{2.4}$$

The secular determinant $D(\omega)$ can be written, using (2.4), according to

$$D(\omega)=|\,\delta_{\mathbf{k},\mathbf{k}'}-G_n(\mathbf{k},\mathbf{k}',\omega)\,| \;. \tag{2.5}$$

If the interaction of the system is neglected then the corresponding secular determinant can be given by

$$D_0(\omega)=|\,\delta_{\mathbf{k},\mathbf{k}'}-G_n^0(\mathbf{k},\mathbf{k}',\omega)\,| \;. \tag{2.6}$$

The expressions for G's occurring in (2.5) and (2.6) can be obtained using the first-order time-dependent perturbation theory. If we denote the position coordinates of the particle forming the atom by $\mathbf{x}_l$ and the charge associated with the particles by q_l, then the potential energy of the atom in the presence of the electromagnetic field is given by

$$\mathscr{H}(t)=H'\exp(-i\omega t)=\sum_l q_l\phi(\mathbf{x}_l)\exp(-i\omega t) \;. \tag{2.7}$$

The change in the atomic wave function $|\,n\,\rangle$ due to the perturbation (2.7) can be obtained using the standard method of the perturbation theory. These changes in turn gives rise to changes in any physical quantity A associated with the atom. The change ΔA_n in the average value of A in the nth atomic state can be written as

$$\Delta A_n=\sum_m \frac{\langle n\,|\,A\,|\,m\,\rangle\langle m\,|\,H'\,|\,n\,\rangle}{E_n-E_m+\hbar\omega}+\frac{\langle m\,|\,A\,|\,n\,\rangle\langle n\,|\,H'\,|\,m\,\rangle}{E_n-E_m-\hbar\omega} \;, \tag{2.8}$$

where E_m is the energy of the mth atomic state.

If we now set in (2.8)

$$A=\sum_j \frac{q_j^*}{|\,\mathbf{x}-\mathbf{x}_j^*\,|}=\sum_j \frac{q_j\Delta(\omega)}{|\,\mathbf{x}-\mathbf{x}_j^*\,|} \;, \tag{2.9}$$

then A is the potential energy at $\mathbf{x}$ due to image charge q_j^* produced by the q_jth particle of the atom. The position of the image is denoted by $\mathbf{x}_j^*$. The potential energy A is therefore produced by the surface through the use of the image atom. If we now identify the induced potential at $\mathbf{x}$ by the surface with the perturbing potential $\phi(\mathbf{x},\omega)$ then a self-consistency condition is realized,

$$\phi(\mathbf{x},\omega)=\sum_m \frac{\langle n\,|\,A\,|\,m\,\rangle\langle m\,|\,H'\,|\,n\,\rangle}{E_n-E_m+\hbar\omega}+\frac{\langle m\,|\,A\,|\,n\,\rangle\langle n\,|\,H'\,|\,m\,\rangle}{E_n-E_m-\hbar\omega} \;. \tag{2.10}$$

If we now write (2.10) in terms of Fourier components using the following identities:

$$\phi(\mathbf{x},\omega)=\sum_k \phi(\mathbf{k},\omega)\exp(i\mathbf{k}\cdot\mathbf{x}) \;, \tag{2.11}$$

$$|\,\mathbf{x}-\mathbf{x}_j^*\,|^{-1}=\frac{1}{2\pi^2}\int \frac{\exp[i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}_j^*)]}{k^2}d^3k \;, \tag{2.12}$$

and

$$\sum_{\mathbf{k}}=\frac{V}{8\pi^3}\int d^3k \;, \tag{2.13}$$

where V is the periodic volume used in the transformation (2.13), we get

$$\phi(\mathbf{k},\omega)=\sum_{\mathbf{k}} G_n(\mathbf{k},\mathbf{k}',\omega)\phi(\mathbf{k}',\omega) \;, \tag{2.14}$$

with

$$G_n(\mathbf{k},\mathbf{k}',\omega)=\sum_{l,j,m}\frac{(-1)q_lq_j^*4\pi}{Vk^2}\left[\frac{\langle n\,|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)\,|\,m\,\rangle\langle m\,|\exp(i\mathbf{k}\cdot\mathbf{x}_l)\,|\,n\,\rangle}{E_n-E_m+\hbar\omega}+\frac{\langle m\,|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)\,|\,n\,\rangle\langle n\,|\exp(i\mathbf{k}\cdot\mathbf{x}_l)\,|\,m\,\rangle}{E_n-E_m-\hbar\omega}\right] . \tag{2.15}$$

If we neglect the coupling between the atom and the surface modes the G_n^0 arises by replacing q_j^* by $q_j\Delta(\infty)$ in (2.15). Thus

$$G_n^0(\mathbf{k},\mathbf{k}',\omega)=G_n(\mathbf{k},\mathbf{k}',\omega)\frac{\Delta(\infty)}{\Delta(\omega)} \;. \tag{2.16}$$

Substituting the expressions for G_n's obtained in (2.15) and (2.16) into (2.5) and (2.6), we are able to rewrite E_I given by (2.2) according to

$$E_I=\frac{\hbar}{4\pi i}\oint \mathrm{tr}\left[\frac{\Delta(\infty)}{\Delta(\omega)}-1\right]G_n(\mathbf{k},\mathbf{k}',\omega)d\omega \;, \tag{2.17}$$

where the ln term in (2.2) is expanded in powers of the coupling and only the linear term in the coupling is considered. This completes our sketch of the zero-point energy method. Explicit expressions for E_I are obtained in Sec. III.

III. CALCULATIONS

To apply the result of Sec. II to the present problem, we define our system as follows. Let the surface be denoted by $Z=0$ with an empty space for $Z>0$ and an ionic medium for $Z<0$. An atom is assumed to move in the empty space and is prevented from entering the $Z<0$ zone.

The frequency-dependent dielectric constant $\epsilon(\omega)$ of the medium is assumed to be of the simple form

$$\epsilon(\omega)=\epsilon(\infty)+\frac{\epsilon(0)-\epsilon(\infty)}{1-(\omega/\omega_T)^2}, \tag{3.1}$$

where ω_T is the transverse optical frequency of the medium. The longitudinal optical frequency ω_0 is related to ω_T by the well-known Lyddane-Sachs-Teller[4] result:

$$\frac{\omega_T^2}{\omega_0^2}=\frac{\epsilon(\infty)}{\epsilon(0)}. \tag{3.2}$$

For a charged particle q_j the image charge q_j^* produced by the surface polarization is given by

$$q_j^*=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}q_j, \tag{3.3}$$

so that $\Delta(\omega)$, introduced in (2.9), is defined by

$$\Delta(\omega)=-\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}. \tag{3.4}$$

The relevant properties of the atom are as follows. The wave function consisting of the localized and the free parts is given by

$$\Psi_n\equiv|n\rangle=U_n(r,z)\sin(k_{Zn}Z)\exp(i\mathbf{k}_{Rn}\cdot\mathbf{R}), \tag{3.5}$$

where (r,z) and (R,Z) are, respectively, the internal coordinates and the coordinates of the center of mass of the atom written in the cylindrical coordinate system. For simplicity we have considered a two-particle hydrogenlike atom. The energy E_n associated with the atom is given by

$$E_n=\epsilon_n+\frac{\hbar^2k_n^2}{2M}, \tag{3.6}$$

where M is the atomic mass.

The positions $\mathbf{x}_j$ of the particles forming the atom and the positions of the images x_j^* can be written in terms of (r,z) and (R,Z) as follows:

$$\begin{aligned} x_1&=\mathbf{R}+\eta Z-\frac{m_2}{M}(\mathbf{r}+\eta z),\\ x_2&=\mathbf{R}+\eta Z+\frac{m_1}{M}(\mathbf{r}+\eta z),\\ x_1^*&=\mathbf{R}-\eta Z-\frac{m_2}{M}(\mathbf{r}-\eta z),\\ x_2^*&=\mathbf{R}-\eta Z+\frac{m_1}{M}(\mathbf{r}-\eta z), \end{aligned} \tag{3.7}$$

where m_1 and m_2 are the masses of the particles.

With the properties of our system defined, the contour integration in (2.17) can now be performed. Using (3.1), (3.2), and (3.4) we obtain

$$\Delta(\infty)-\Delta(\omega)=\frac{\Delta(\infty)-\Delta(0)}{1-(\omega^2/\omega_s^2)}, \tag{3.8}$$

where ω_s is the frequency of the surface excitations and is given by

$$\omega_s^2=\omega_0^2\frac{\epsilon(\infty)}{\epsilon(0)}\frac{\epsilon(0)+1}{\epsilon(\infty)+1}. \tag{3.9}$$

The poles of the integrand in (2.17) occur at $\omega=\omega_s$ and $\omega=|E_n-E_m|/\hbar$. The evaluation of the residues produces the result

$$E_I=\frac{(-1)}{2}\sum_{l,j,m,\mathbf{k}}\frac{(4\pi)q_lq_j}{Vk^2}[\Delta(\infty)-\Delta(0)]\frac{\hbar\omega_s\langle n|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)|m\rangle\langle m|\exp(i\mathbf{k}\cdot\mathbf{x}_l)|n\rangle}{(E_m-E_n+\hbar\omega_s)}. \tag{3.10}$$

The result (3.10) is exact but the evaluation E_I from it requires considerable computations. Approximations are possible and these are made to obtain results which are easy to calculate and analyze.

Approximations. We may express the energy denominator in Eq. (3.10) in a descending series following the procedure introduced by Platzman,[5]

$$\frac{1}{E_m-E_n+\hbar\omega_s}=\frac{1}{\hbar\omega_s+\alpha}-\frac{E_m-E_n-\alpha}{\hbar\omega_s+\alpha}\frac{1}{E_m-E_n+\hbar\omega_s}=\frac{1}{\hbar\omega+\alpha}-\frac{E_m-E_n-\alpha}{(\hbar\omega_s+\alpha)^2}+\frac{(E_m-E_n-\alpha)^2}{(\hbar\omega_s+\alpha)^3}+\cdots, \tag{3.11}$$

where α is chosen in such a way that when the series (3.11) is substituted into (3.10) the term arising from the second term of (3.11) vanishes. Use of (3.11) allows us to write

$$\sum_m\frac{\langle n|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)|m\rangle\langle m|\exp(i\mathbf{k}\cdot\mathbf{x}_l|n\rangle}{E_m-E_n+\hbar\omega_s}=\sum_{t=1}^{\infty}\frac{\langle n|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)(\hat{\mathbf{H}}-E_n-\alpha)^{t-1}\exp(i\mathbf{k}\cdot\mathbf{x}_l)|n\rangle}{(\hbar\omega_s+\alpha)^t}, \tag{3.12}$$

where $\hat{H}$, the Hamiltonian of the atom, is given by

$$\hat{H}=\frac{\hat{P}^2}{2M}+\frac{\hat{p}^2}{2\mu}+v(r)\ . \tag{3.13}$$

$\hat{P}$ and $\hat{p}$ are the momentum operators of the center of mass and relative motion, μ is the relative mass, and $v(r)$ is the Coulombic potential between the particles forming the atom. We now use the identities

$$e^{-i\mathbf{k}\cdot(\mathbf{r}+\eta\mathbf{z})}\hat{\mathbf{p}}\,e^{i\mathbf{k}\cdot(\mathbf{r}+\eta\mathbf{z})}=\hat{\mathbf{p}}+\hbar\mathbf{k} \tag{3.14}$$

and

$$e^{-i\mathbf{k}\cdot(\mathbf{R}+\eta Z)}\hat{\mathbf{P}}\,e^{i\mathbf{k}\cdot(\mathbf{R}+\eta Z)}=\hat{\mathbf{P}}+\hbar\mathbf{k} \tag{3.15}$$

in (3.12) to evaluate each term in the series. For $t=1$, the term in (3.12) represents the lowest-order effect produced by the interaction; higher-order contributions to the energy arise from higher values of t. In this paper we restrict ourselves to the first three terms.

Consideration of the term $t=2$ in (3.12) would allow us to determine α occurring in (3.11). Using the relation (3.7) with $\mathbf{x}_l=\mathbf{x}_1$, (3.14) and (3.15), we write

$$\begin{aligned}&\langle n\,|\exp(-i\mathbf{k}\cdot\mathbf{x}_j^*)(\hat{H}-E_n-\alpha)\exp(i\mathbf{k}\cdot\mathbf{x}_1)\,|\,n\,\rangle\\&\qquad=\left\langle n\left|\exp[-i\mathbf{k}\cdot(\mathbf{x}_j^*-\mathbf{x}_1)]\left[\frac{\hbar^2k^2}{2m_1}-\alpha\right]\right|n\right\rangle\ ,\end{aligned} \tag{3.16}$$

where the atomic part of the state $|\,n\,\rangle$ is assumed to be symmetric. The expression (3.16) vanishes for $\alpha=(\hbar^2k^2/2m_1)$ and, likewise for $\mathbf{x}_l=\mathbf{x}_2$, the term equivalent to (3.16) vanishes for $\alpha=(\hbar^2k^2/2m_2)$. Thus, depending on the value for $\mathbf{x}_l$, appropriate α can be selected so that the term in (3.16) is zero.

With α so defined, we now substitute the term $t=1$ in (3.12) into the result (3.10) to get

$$\begin{aligned}E_I(t=1)=\frac{(-4\pi)(\hbar\omega_s)q^2[\Delta(\infty)-\Delta(0)]}{2(8\pi^3)}\int\Bigg[&\frac{\langle n\,|\exp[i\mathbf{k}\cdot(\mathbf{x}_1-\mathbf{x}_1^*)]-\exp[i\mathbf{k}\cdot(\mathbf{x}_1-\mathbf{x}_2^*)]\,|\,n\,\rangle}{k^2[\hbar\omega_s+(\hbar^2k^2/2m_1)]}\\&+\frac{\langle n\,|\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1^*)]-\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_2^*)]\,|\,n\,\rangle}{k^2[\hbar\omega_s+(\hbar^2k^2/2m_2)]}\Bigg]d^3k\ ,\end{aligned} \tag{3.17}$$

where the summation over $\mathbf{k}$ is changed to integration using the result (2.13) and $q=|\,q_j\,|$. The term $E_I(t=3)$ which is of a lower order than $E_I(t=1)$ can also be written but its form is more complex. Nevertheless, the term is important since it contains the effect of the atomic velocity on the interaction energy. We write this term only partly by considering its portion which is dependent on the velocity. The rest of the term is not of particular significance to this paper. Substituting (3.12) with $t=3$ into (3.10) and selecting the velocity-dependent parts of the term, we write

$$\begin{aligned}E_I(t=3)\simeq\frac{(-4\pi)(\hbar\omega_s)q^2[\Delta(\infty)-\Delta(0)]}{2(8\pi^3)}\int\Bigg[&\frac{\langle n\,|\exp[i\mathbf{k}\cdot(\mathbf{x}_1-\mathbf{x}_1^*)]-\exp[i\mathbf{k}\cdot(\mathbf{x}_1-\mathbf{x}_2^*)]\,|\,n\,\rangle}{k^2[\hbar\omega_s+(\hbar^2k^2/2m_1)]^3}\\&+\frac{\langle n\,|\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1^*)]-\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_2)]\,|\,n\,\rangle}{k^2[\hbar\omega_s+(\hbar^2k^2/2m_2)]^3}\Bigg]\left[\frac{\hbar^2\mathbf{k}_n\cdot\mathbf{k}}{M}\right]^2d^3k\ .\end{aligned} \tag{3.18}$$

Terms $E_I(t)$ for t greater than 4 will not be considered because of their lack of intrinsic value to this paper.

If we now express the interaction energy E_I as a matrix element of a variable $\mathscr{E}_I(r,z,R,Z)$ between the same state $|\,n\,\rangle=|\,R,Z,r,z,n\,\rangle$ according to

$$E_I=\langle n,R,Z,r,z\,|\,\mathscr{E}_I(r,z,R,Z)\,|\,n,R,Z,r,z\,\rangle\ , \tag{3.19}$$

then the integration over the r, z, and R gives

$$E_I=\langle Z\,|\,\mathscr{E}_I(Z)\,|\,Z\,\rangle\ , \tag{3.20}$$

where $\mathscr{E}_I(Z)$ is the energy of interaction between the atom and the surface at the separation Z. Using $E_I(t)$ for $t=1$ and 3 we can obtain the corresponding contributions to $\mathscr{E}_I(Z)$.

IV. CONCLUSION

We integrate (3.17) over $d^3\mathbf{k}$ to write $\mathscr{E}_I(Z,t=1)$ as

$$\begin{aligned}\mathscr{E}_I(Z,t=1)=\frac{q^2[\Delta(0)-\Delta(\infty)]}{2}\Bigg\langle n\Bigg|&\frac{[1-\exp(\,|\,\mathbf{x}_1-\mathbf{x}_1^*\,|\,/a_1)]}{|\,\mathbf{x}_1-\mathbf{x}_1^*\,|}-\frac{[1-\exp(\,|\,\mathbf{x}_1-\mathbf{x}_2^*\,|\,/a_1)]}{|\,\mathbf{x}_1-\mathbf{x}_2^*\,|}\\&+\frac{[1-\exp(\,|\,\mathbf{x}_2-\mathbf{x}_1^*\,|\,/a_2)]}{|\,\mathbf{x}_2-\mathbf{x}_2^*\,|}-\frac{[1-\exp(\,|\,\mathbf{x}_2-\mathbf{x}_2^*\,|\,/a_2)]}{|\,\mathbf{x}_2-\mathbf{x}_1^*\,|}\Bigg|n\Bigg\rangle\ ,\end{aligned} \tag{4.1}$$

where a_1 and a_2 are the polaron radii given by $(\hbar/2m_1\omega_s)^{1/2}$ and $(\hbar/2m_2\omega_s)^{1/2}$, respectively. To obtain $\mathscr{E}_I(Z,t=1)$ in the asymptotic limit we substitute (3.7) into (4.1). For large Z

$$\lim_{Z\to\infty} \mathscr{E}_I(Z,t=1)=\frac{q^2[\Delta(0)-\Delta(\infty)]}{16Z^3}[\langle r,z\,|\,(2z^2+r^2)\,|\,r,z\rangle]\;, \tag{4.2}$$

while for small Z

$$\lim_{Z\to 0} \mathscr{E}(Z,t=1)=\frac{q^2[\Delta(0)-\Delta(\infty)]}{2}\left[\langle r,z\,|\;|(2\eta Z-2(m_2/M)\eta z\,|-|\,2\eta Z-[(m_2-m_1)/M]\eta\mathbf{z}-\mathbf{r}\,|\;|\,r,z\rangle\frac{1}{a_1^2}\right.$$
$$\left.+\langle r,z\,|\;|\,2\eta Z+(2m_1/M)\eta z\,|-|\,2\eta Z-[(m_2-m_1)/M]\eta\mathbf{z}+\mathbf{r}\,|\;|\,r,z\rangle\frac{1}{a_2^2}\right]. \tag{4.3}$$

In the limit of Z approaching zero but keeping $Z>z$, the interaction term saturates and the saturated value is obtained from (4.3) by putting $Z=0$. The result is, however, unphysical since at $Z=0$ the atomic wave function would spread into the surface, a situation precluded by the assumption that the atom is in the free space (i.e., $Z>0$).

The velocity dependence of the interaction energy is contained in $E_I(t=3)$ which can be obtained by integration over k in the expression (3.18). The integration is somewhat involved but can be done by using integration tables.[6] The resulting expression gives $\mathscr{E}(Z)$ which for large Z can be written as

$$\lim_{Z\to\infty} \mathscr{E}(Z,t=3)=-\left[\frac{3}{4}\right]\frac{q^2[\Delta(\infty)-\Delta(0)]}{Z^5}\times\left[\frac{\hbar K_n}{2M\omega_s}\right]^2\langle z,\mathbf{r}\,|\,z^2+r^2\,|\,z,\mathbf{r}\rangle\times\left[\frac{\sin^2\theta_n}{2}-\cos^2\theta_n\right], \tag{4.4}$$

where θ_n is the angle made by the incident direction of the atom with the Z axis..

V. DISCUSSION

The interaction energy between an atom and a surface formed by an ionic crystal is derived using the zero-point energy formalism. The method was used earlier by Ritchie[7] in another closely related problem.

The derived results can be extended to the case of a metal surface by replacing (3.1) by the frequency-dependent dielectric constant for a metal

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}\;, \tag{5.1}$$

where ω_p is the plasma frequency of the electron gas. Using Eq. (5.1) in (3.4) and (3.9), we obtain $\Delta(0)=-1$, $\Delta(\infty)=0$, and $\omega_s=(\omega_p^2/2)$. Making use of these changes, the expressions for the interaction energy derived in the previous section can be used for a metal surface if we replace $[\Delta(\infty)-\Delta(0)]$ by unity and ω_s by the surface plasmon frequency.

Apart from differences in the approaches, there are also differences in approximations made in this paper and in the work of Manson and Ritchie. Manson and Ritchie obtain the interaction energy using the dipolar interaction between an atom and a surface. This approximation is expected to hold relatively better for large Z than for small Z. Although we do not use the dipolar approximation, we have utilized Platzman's[5] expansion in deriving our results. This expansion is useful if the unperturbed energy E_n is smaller than $\hbar\omega_s$. Alternately if $\hbar\omega_s>|\,E_n-E_m\,|$ for those states which are coupled sufficiently strongly by the interaction then Platzman's[5] expansion is known to produce reliable results. Thus if $\hbar\omega_s$ is sufficiently large then our results are expected to be reasonably accurate even when only the first term in Platzman's expansion is utilized.

The use of Platzman's expansion is known to produce results which are many times difficult to interpret, as is the case with our calculations. If we consider the first term in Platzman's expansion, the interaction energy, given by (4.1), has the dominant $1/Z^3$ dependence for large Z. Unfortunately higher terms in Platzman's expansion would also contain $1/Z^3$ dependent terms, so that the behavior of the interaction energy for large Z is given by the sum of all these contributions. The interaction energy given by (4.1) is therefore incomplete and cannot be meaningfully compared with the corresponding result of Manson and Ritchie. A similar difficulty arises when comparing the results given by (4.3) and (4.4) with the corresponding results obtained by Manson and Ritchie.[3] Specifically, the saturation of the interaction energy found in (4.3) is also subject to a correction, should higher-order terms in Platzman's expansion produce a divergent term. We intend to examine this issue in a later publication. In addition we wish to point out the result (4.4) is smaller than the result obtained earlier by Manson and Ritchie[3] and by Ferrell and Ritchie.[8]

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