High-order corrections to the image potential

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A self-energy formalism for determining the image potential for a charge outside of a metal is generalized to include high-order corrections. In this first systematic development of the image potential in higher-order perturbation theory, the image potential is given as an asymptotic series in inverse powers of the distance of the charge from the surface.

A charged particle approaching a solid surface experiences an attractive potential arising from the polarization which it induces in the medium. The classical image potential for a particle of charge Q at fixed distance z from a metal surface is $V=-Q^2/4z$. At microscopic distances, quantum mechanics is necessary to describe the interaction between the charge and the medium. It is known[1,2] that the forces, long-range in character, experienced by a charge external to a solid surface may be considered to be due to the interaction between the charge and the virtual excitations of surface modes, i.e., surface plasmons in metals or surface optical phonons in ionic crystals, since the fields due to bulk electronic excitations extend only a few atomic units beyond the surface. Quantum theories in this simple scheme of interaction[3,4] give important dynamical corrections to the classical image potential including recoil effects due to the exchange of virtual quanta of surface excitations between the charge and the surface. It is the latter that we emphasize here.

Sunjic, Toulouse, and Lucas[3] used a method based on the canonical transformation approach of Lee, Low, and Pines[5] for the polaron problem and found a series expansion in inverse powers of z for the image potential seen by a charge moving slowly with respect to the surface. Manson and Ritchie[4] approached this problem differently. They developed a self-energy formalism based on the Rayleigh-Schrödinger (RS) perturbation theory that yields an expression for the image potential. It is the topic of this Brief Report to generalize this formalism to higher order and to present the results of the first application of this method to the image-potential problem.

We approximate the Hamiltonian for the system of a charged particle interacting with surface excitations as

$$H=H_0+H_1=p^2/2m+\sum_{\kappa}\hbar\omega_{\kappa}a_{\kappa}^{\dagger}a_{\kappa}+\sum_{\kappa}\alpha_{\kappa}e^{-\kappa|z|}e^{i\kappa\cdot\rho}(a_{\kappa}+a_{-\kappa}^{\dagger}) , \quad (1)$$

where κ is a vector parallel to the surface, and $\mathbf{p}$ is the momentum of the particle. The coupling constant for surface plasmons on metals is given by $\alpha_{\kappa}^2=Q^2\pi\hbar\omega_s/L^2\kappa$, where L^2 is the area of the surface, and $\omega_s=\omega_p/2^{1/2}$ is the surface-plasmon mode eigenfrequency. For surface optical phonons, α_{κ}^2 should be multiplied by a factor of $(\epsilon_0-1)/(\epsilon_0+1)-(\epsilon_{\infty}-1)/(\epsilon_{\infty}+1)$, where ϵ_0 and ϵ_{∞} are the dielectric constants at zero frequency and very high frequencies, respectively.[6] H_0 is the Hamiltonian of the charged particle and the surface excitations. H_1 is the interaction Hamiltonian between the charge at position (ρ,z) and the surface modes. For convenience, we consider metal surfaces only in what follows.

If a classical, massive charged particle is located at the position (ρ,z), the resulting Hamiltonian may be diagonalized exactly. The classical image potential is found to be just the shift of zero-point energy of the system due to the interaction of the charge with the surface plasmon field.[1] To see this, we make linear transformations $b_{\kappa}=a_{\kappa}+\beta_{\kappa}$ and $b_{\kappa}^{\dagger}=a_{\kappa}^{\dagger}+\beta_{\kappa}^{*}$ where β_{κ} is a c number. The system Hamiltonian can be written as

$$H=\sum_{\kappa}\hbar\omega_{\kappa}b_{\kappa}^{\dagger}b_{\kappa}+\Delta E , \quad (2)$$

if β_{κ} is taken to be $-\alpha_{\kappa}e^{-\kappa|z|}e^{-i\kappa\cdot\rho}$. Then, the zero-point energy shift is

$$\Delta E=-\sum_{\kappa}\alpha_{\kappa}^2e^{-2\kappa|z|}/\hbar\omega_{\kappa} \quad (3)$$

which is exactly the energy shift found from second-order perturbation theory. Thus in every order of RS perturbation theory beyond the second ($n=2$), the coefficients of the terms proportional to Q^n must vanish identically. Using the dispersionless approximation $\omega_{\kappa}=\omega_s$, inserting the value of α_{κ}^2 given above into Eq. (3), and converting the summation into an integration, we get

$$\Delta E=-\frac{Q^2}{2}\int_0^{\infty}d\kappa\,e^{-2\kappa z}=-\frac{Q^2}{4z} \quad (4)$$

which is identically the classical image potential.

The system Hamiltonian as given in Eq. (1) is similar in form to that for the polaron problem,[5] which has been treated by various methods.[7] It is known that RS perturbation theory is superior to Brillouin-Wigner perturbation theory in treating the binding energy of the polaron.[7] Here, we apply high-order RS perturbation theory to the system represented by Eq. (1) and find dynamical corrections depending on mass and velocity.

Second-order RS theory applied to the present problem assumes the creation by the particle of any number of virtual plasmons, neglecting plasmon-plasmon correlations. Fourth- and higher-order RS theory allows for such correlations.

We review the self-energy formalism of Ref. 4 using second-order theory first. The energy shift in this order may be written

$$\Delta E^{(2)}=\int d^3r \sum_{\mathbf{p}} \sum_{\kappa} \frac{\langle \mathbf{p}_0|\mathbf{r}\rangle\langle 0|H_1|\kappa\rangle\langle \mathbf{r}|\mathbf{p}\rangle\langle \mathbf{p}\kappa|H_1|\mathbf{p}_0 0\rangle}{E_{\mathbf{p}_0}-E_{\mathbf{p}}-\hbar\omega_\kappa+i\delta} \tag{5}$$

corresponding to one plasmon in the intermediate state (Fig. 1). Here, $|\mathbf{p}\rangle$ and $|\kappa\rangle$ are the state vectors for the particle and plasmon field, respectively, and $|\mathbf{p}\kappa\rangle$ is the product-state vector for the noninteracting system. We

FIG. 1. Diagram for the second-order contribution to the self-energy.

assume[4] that the energy shift and the spatially dependent self-energy $\Sigma^{(2)}(\mathbf{r})$ are related by the following expression:

$$\Delta E^{(2)}=\int d^3r \langle \mathbf{p}_0|\mathbf{r}\rangle \Sigma^{(2)}(\mathbf{r})\langle \mathbf{r}|\mathbf{p}_0\rangle \ . \tag{6}$$

Equating the integrands of Eqs. (5) and (6) and dividing the resulting equation by $\langle \mathbf{p}_0|\mathbf{r}\rangle\langle \mathbf{r}|\mathbf{p}_0\rangle$, we get

$$\Sigma^{(2)}(\mathbf{r})=\sum_{\mathbf{p}} \sum_{\kappa} \frac{\langle \mathbf{r}|\mathbf{p}\rangle}{\langle \mathbf{r}|\mathbf{p}_0\rangle} \frac{\langle 0|H_1|\kappa\rangle\langle \mathbf{p}\kappa|H_1|\mathbf{p}_0 0\rangle}{E_{\mathbf{p}_0}-E_{\mathbf{p}}-\hbar\omega_\kappa+i\delta} \ . \tag{7}$$

Using a similar unfolding procedure we find the self-energy as an infinite series. We assert that it is given by

$$\Sigma(\mathbf{r})=\Sigma^{(2)}(\mathbf{r})+\Sigma^{(4)}_{(a)}(\mathbf{r})+\Sigma^{(4)}_{(b)}(\mathbf{r})+\Sigma^{(4)}_{(c)}(\mathbf{r})+\cdots \ , \tag{8}$$

where

$$\Sigma^{(4)}_{(a)}=\sum_{\kappa_1}\sum_{\kappa_2}\sum_{\mathbf{p}_1}\sum_{\mathbf{p}_2}\sum_{\mathbf{p}_3} \frac{\langle \mathbf{r}|\mathbf{p}_1\rangle}{\langle \mathbf{r}|\mathbf{p}_0\rangle} \frac{\langle 0|H_1|\kappa_1\rangle\langle \mathbf{p}_1,0|H_1|\mathbf{p}_2\kappa_2\rangle\langle \mathbf{p}_2\kappa_2|H_1|\mathbf{p}_3 0\rangle\langle \mathbf{p}_3\kappa_1|H_1|\mathbf{p}_0 0\rangle}{(E_{\mathbf{p}_0}-E_{\mathbf{p}_1}-\hbar\omega_{\kappa_1}+i\delta)(E_{\mathbf{p}_0}-E_{\mathbf{p}_2}-\hbar\omega_{\kappa_1}-\hbar\omega_{\kappa_2}+i\delta)(E_{\mathbf{p}_0}-E_{\mathbf{p}_2}-\hbar\omega_{\kappa_1}+i\delta)} \ , \tag{9a}$$

$$\Sigma^{(4)}_{(b)}=\sum_{\kappa_1}\sum_{\kappa_2}\sum_{\mathbf{p}_1}\sum_{\mathbf{p}_2}\sum_{\mathbf{p}_3} \frac{\langle \mathbf{r}|\mathbf{p}_1\rangle}{\langle \mathbf{r}|\mathbf{p}_0\rangle} \frac{\langle 0|H_1|\kappa_1\rangle\langle \mathbf{p}_1,0|H_1|\mathbf{p}_2\kappa_2\rangle\langle \mathbf{p}_2\kappa_1|H_1|\mathbf{p}_3 0\rangle\langle \mathbf{p}_3\kappa_2|H_1|\mathbf{p}_0 0\rangle}{(E_{\mathbf{p}_0}-E_{\mathbf{p}_1}-\hbar\omega_{\kappa_1}+i\delta)(E_{\mathbf{p}_0}-E_{\mathbf{p}_2}-\hbar\omega_{\kappa_1}-\hbar\omega_{\kappa_2}+i\delta)(E_{\mathbf{p}_0}-E_{\mathbf{p}_3}-\hbar\omega_{\kappa_2}+i\delta)} \tag{9b}$$

and

$$\Sigma^{(4)}_{(c)}=\Sigma^{(2)}(\mathbf{r})\sum_{\mathbf{p}}\sum_{\kappa} \frac{\langle \mathbf{r}|\mathbf{p}_2\rangle}{\langle \mathbf{r}|\mathbf{p}_0\rangle} \frac{\langle 0|H_1|\kappa\rangle\langle \mathbf{p}_2\kappa|H_1|\mathbf{p}_0 0\rangle}{(E_{\mathbf{p}_0}-E_{\mathbf{p}}-\hbar\omega_\kappa+i\delta)^2} \tag{9c}$$

correspond to the three diagrams (a), (b), and (c) in Fig. 2. Figure 3 shows corresponding diagrams in sixth order.

We use a plane-wave basis set for the charged particle to evaluate the terms of Eq. (8) to sixth order. The state

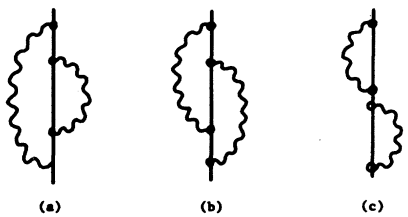

FIG. 2. The (a) nested, (b) crossing, and (c) anomalous diagrams contributing to the fourth-order self-energy correction.

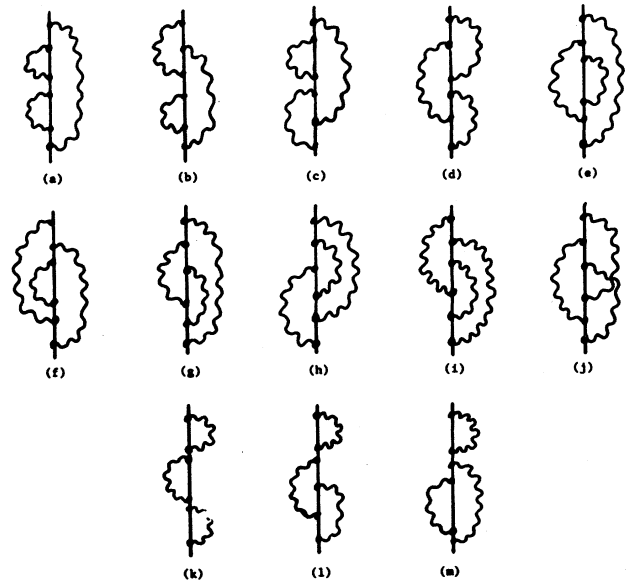

FIG. 3. Diagrams corresponding to sixth-order self-energy corrections. Diagrams (a)–(j) are self-explanatory, while diagrams (k)–(m) are anomalous.

vector $\langle \mathbf{r}|\mathbf{p}\rangle$ can be written as

$$\langle \mathbf{r}|\mathbf{p}\rangle = \frac{1}{L^{3/2}} e^{i\mathbf{P}\cdot\boldsymbol{\rho}} e^{ipz}, \tag{10}$$

where $(\mathbf{P},p)$ is the momentum of the particle resolved into components parallel and perpendicular to the surface, respectively.

The matrix elements in Eqs. (7) and (9) are evaluated by converting the summations into integrations as $L\to\infty$, assuming dispersionless plasmons ($\omega_\kappa=\omega_s$) and taking $\mathbf{P}_0=\mathbf{0}$. The result for the real part of Σ is given by

$$\mathrm{Re}[\Sigma(z)] = -\frac{Q^2}{4z}\left[1-\left[\frac{v_0^2}{2\omega_s^2 z^2}-\frac{3v_0^4}{2\omega_s^4 z^4}+\cdots\right]-\frac{\cos(p_0 z)}{\kappa_s z}\left[2-\frac{3\hbar}{m\omega_s z^2}+\frac{5mv_0^2}{2\hbar\omega_s}+\cdots\right]e^{-\kappa_s z}+\cdots\right.$$
$$\left.+\frac{Q^2}{8\hbar\omega_s z}\left[\frac{13\hbar}{4m\omega_s z^2}-\frac{9v_0^2}{\omega_s^2 z^2}+\cdots\right]+\frac{Q^4}{(\hbar\omega_s)^2(4z)^4}\frac{35\hbar}{m\omega_s}+\cdots\right], \tag{11}$$

where $v_0=\hbar p_0/m$ is the velocity of the charged particle perpendicular to the surface, m is its mass, and $\kappa_s^2=2m\omega_s/\hbar$. We omit the imaginary component of $\Sigma(z)$, which will be discussed in another publication.[8] We also omit terms of order Q^4 and higher which decrease proportionally to $\exp(-\kappa_s z)$.

This result is different from the one given in Ref. 3. The velocity-dependent terms in the first bracket agree with the corresponding ones there, but the recoil effects evinced in second order in Eq. (11) are characterized by the exponential factor $e^{-\kappa_s z}$, which is much more sensitive to the mass and the position of the particle than the corresponding inverse power function of Ref. 3. The terms in the last bracket, the fourth-order correction, are similar to the corresponding terms proportional to Q^4 that appear in Ref. 3, but differ by numerical factors, and more importantly, by signs. A possible explanation of the discrepancy in these results is that correlations among virtual surface plasmons are not included in the canonical transform method used in Ref. 3 (see Ref. 5), while the present approach accounts explicitly for such correlations. Our formalism has the advantage that higher-order corrections are readily evaluated in the model problem posed here, and are generated in a systematic way.[9]

Note that the recoil corrections given in Eq. (11) fall into two categories. Those important at points $z\sim 1/\kappa_s$, close to the surface [the term containing the factor $e^{-\kappa_s z}$ of Eq. (11)], tend to weaken the interaction. Those important in the asymptotic region tend to make the interaction potential stronger there. We should point out that this first category of recoil terms, those which decay exponentially away from the surface, should not be taken too seriously as our model becomes no longer valid at the very small displacements when such terms are appreciable. However, we have included them in Eq. (11) in order to point out that there is a class of recoil terms which are exponentially decreasing, and that analogous terms will also appear in more sophisticated models.

In conclusion, we have generalized the self-energy formalism of Ref. 4 to include high-order corrections and have given an explicit expression for the self-energy of a moving charge near a metal surface through the sixth order of perturbation theory. Comparison with the result given in Ref. 3 has been made. This approach can be applied to investigate the properties of bound positron surface states[10] and image-potential induced surface states.[11] Among other possible applications are high-order corrections to the van der Waals forces between atoms[12] and energy transfer between a moving atom and a solid surface.[13]

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