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Self-energy of a charge near a surface

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A new, general expression for the space-dependent self-energy of a projectile interacting with a many-particle target is derived. The exchange-correlation potential or image potential experienced by a charged particle exterior to, but near a surface, is calculated from this expression using a model in which the charge interacts with collective surface excitations. It is found that recoil is important near the surface and gives rise to interesting new quantum effects. Previously obtained classical and semiclassical results are shown to arise simply and readily from the formalism. The connection with surface bound states is discussed briefly.

The long-range attractive potential between a charged particle and a semi-infinite polarizable medium has been the subject of renewed interest in recent years because of its importance in the interpretations of low-energy electron diffraction (LEED) and reflection-electron energy loss (REEL) experiments and in electron energy loss spectroscopy. A detailed knowledge of this potential is important to the question of bound polaron states in ionic solids or bound positron states in metals. The potential is usually expressed in terms of a complex self-energy. The real part leads, at sufficiently large distances, to the classical picture of a charge interacting with its image in the solid, while the imaginary part can be associated with the damping or loss of scattered electrons from the incident beams.

It has been shown that outside the surface the forces on a charge are due, to a good approximation, entirely to surface electronic excitations[1–3] (i.e., surface plasmons in metals or surface optical phonons in ionic solids[4]) since the fields due to bulk excitations do not penetrate more than a few atomic units.[5,6] The problem of the external charge has been treated by a variety of classical[7–9] and semiclassical approaches,[10,11] but these methods have the inherent disadvantage of being restricted to distances far from the surface and to relatively large energies.

Near the surface it is necessary to use a quantum-mechanical approach which includes recoil effects due to exchange of virtual excitations with the surface. Models have been proposed demonstrating that the image potential becomes finite at the surface if the charge approaches with nonzero speed.[12–18] Investigations of bound surface polaron states[19,20] or bound surface states for positrons[21] have demonstrated that even for a charge moving arbitrarily slowly near the surface the potential still approaches a finite value due to recoil effects. However, we note that all of the previous calculations which included recoil allowed the particle to recoil only in directions parallel to the surface and not in the perpendicular direction.[12,20,21]

In this Communication we reexamine the problem and show that the quantal self-energy can be obtained from an exact solution of second-order perturbation theory including full three-dimensional recoil effects. The semiclassical results are recovered in the appropriate limit, while near the surface we show that inclusion of three-dimensional recoil substantially affects the self-energy, both quantitatively and qualitatively.

We begin by presenting a new, general expression for the space-dependent, complex self-energy (or optical potential) of a projectile interacting with a specified N-particle target. The expression found may be generalized easily to higher orders of perturbation theory. Suppose that $|\psi_n\rangle$ is the exact state vector of the target in its nth excited state with energy E_n. Let the state vector of the projectile be $|\phi_k\rangle$ when it has the energy ϵ_k. In ordinary second-order perturbation theory the energy shift due to the projectile-target interaction may be written

$$\Delta E_0 = \int d^3r \sum_n \sum_k \frac{\langle 00|V|nk\rangle}{E_0+\epsilon_0-E_n-\epsilon_k+i\delta} \times \langle \phi_k|\vec{r}\rangle \langle \psi_n|V|\psi_0\rangle \langle \vec{r}|\phi_0\rangle \ . \tag{1}$$

Here $V=\sum_{i=1}^{N} V(\vec{r}-\vec{r}_i)$ is the interaction energy, $\vec{r}$ is the projectile coordinate, and $\vec{r}_i$ is the coordinate of the ith target particle. The state vector of the noninteracting system is $|00\rangle=|\psi_0\rangle|\phi_0\rangle$ and $|nk\rangle=|\psi_n\rangle|\phi_k\rangle$. Mixed representation is used in

Eq. (1) and it is assumed that the order of the integral over $\vec{r}'$ and the sums over intermediate states may be inverted from the usual sequence.

We assert that ΔE may also be written as the integral of a spatially dependent self-energy $\Sigma_0(\vec{r})$, weighted by the probability density of the projectile in its original state, viz.,

$$\Delta E_0 = \int d^3r \, \langle \phi_0 | \vec{r} \rangle \Sigma(\vec{r}) \langle \vec{r} | \phi_0 \rangle \ . \tag{2}$$

Equating the integrands of Eqs. (1) and (2) and dividing the resulting equation by $\langle \phi_0 | \vec{r} \rangle \langle \vec{r} | \phi_0 \rangle$ we find

$$\Sigma_0(\vec{r}) = \sum_n \sum_k \frac{\langle \phi_k | \vec{r} \rangle}{\langle \phi_0 | \vec{r} \rangle} \times \frac{\langle 00 | V | nk \rangle \langle \psi_n | V | \psi_0 \rangle}{E_0 + \epsilon_0 - E_n - \epsilon_k + i\delta} \ , \tag{3}$$

a result that may be obtained from the definition of the exchange and correlation potential,[18,22] but whose derivation is considerably more transparent. It is important to note, however, that our approach leads directly to a systematic generalization of the space-dependent self-energy to arbitrarily high orders of perturbation theory.

The problem of an external charge interacting with the surface modes can be represented by the Hamiltonian $H = H_0 + V$ where

$$V = \sum_{\vec{Q}} \Gamma_Q \exp(-Q|Z| + i\vec{Q}\cdot\vec{R})(a_{\vec{Q}} + a_{-\vec{Q}}) \ , \tag{4}$$

and where H_0 describes noninteracting surface modes and an incident charge. This model of the surface response is adopted for simplicity, but should be accurate up to distances $\gtrsim 1$ Å from the surface. In this paper we focus on effects arising from the quantal properties of the incident particle. Capital letters are used for vectors parallel to the surface $(\vec{Q}, \vec{R})$ and lower case is used for perpendicular components (q,z). The constant Γ_Q for surface plasmons on metals is given by $\Gamma_Q^2 = e^2\pi\hbar\omega_s/AQ$, where A is the area of the surface and e is the charge. For surface optical phonons it is multiplied by the factor

$$(\epsilon_0 - 1)/(\epsilon_0 + 1) - (\epsilon_\infty - 1)/(\epsilon_\infty + 1) \ ,$$

where ϵ_0 is the static dielectric constant of the lattice and ϵ_∞ is the same at very high frequencies. For a plane-wave basis set Eq. (3) becomes

$$\Sigma(z) = -\frac{e^2 Q_s^2}{(2\pi)^2} \int dk \int \frac{d\vec{Q}}{Q} \frac{e^{ikz} e^{-Q|z|}}{Q^2 + k^2} \frac{1}{Q^2 + k^2 + 2\vec{Q}\cdot\vec{K}_0 + Q_s^2 + 2kk_0} \ , \tag{5}$$

where for compactness we consider a metal surface and $Q_s^2 = 2m\omega_s/\hbar$ with m the particle mass and $\omega_s = \omega_p/\sqrt{2}$ is the surface plasmon frequency which is assumed dispersionless for the remainder of this paper. Equation (5) is the complex self-energy of a charge moving with respect to the surface at velocity $\vec{u} = \hbar(\vec{K}_0, k_0)/m$, the factor of k^2 as well as Q^2 in the energy denominator being the manifestation of full three-dimensional recoil. The solution has two regimes depending upon whether or not the particle has sufficient energy to excite a surface excitation. In the above-threshold case $(k_0 > Q_s)$ we have for a charge moving perpendicular to the surface $(\vec{K}_0 = 0)$

$$\mathrm{Re}\Sigma(z) = -(e^2\omega_s/2v)\{f(2\omega_s|z|/v) + \cos(k_0 z)[\Lambda_a(\zeta) - \Gamma_a(\zeta)] + \sin(k_0 z)[\mathrm{sgn}(z) H(\zeta) + \Phi_a(\zeta)]\} \ , \tag{6}$$

$$\mathrm{Im}\Sigma(z) = (e^2\omega_s/2v)\{\mathrm{sgn}(z) g(2\omega_s|z|/v) - \cos(k_0 z)[\mathrm{sgn}(z) H_a(\zeta) - \Phi_a(\zeta)] + \sin(k_0 z)[\Lambda_a(\zeta) - \Gamma_a(\zeta)]\} \ , \tag{7}$$

where $f(x)$ and $g(x)$ are the auxiliary functions to the exponential integral,[23]

$$\Phi_a(x) = \int_0^1 \frac{du \cos xu}{a - \mathrm{sgn}(z) u} \exp[-x(1-u^2)^{1/2}] \ , \quad \Gamma_a(x) = \int_0^1 \frac{du \sin xu}{a - \mathrm{sgn}(z) u} \exp[-x(1-u^2)^{1/2}] \ , \tag{8}$$

$$\Lambda_a(x) = c \int_0^\infty \frac{du \exp[-xu - x(u^2+1)^{1/2}]}{a^2 + u^2} \ , \quad H_a(x) = \int_0^\infty \frac{du\, u \exp[-xu - x(u^2+1)^{1/2}]}{a^2 + u^2} \ , \tag{9}$$

and $a = (\alpha + 1/\alpha)^{1/2}$, $\zeta = k_0\alpha|z|$ with $\alpha = (1 - Q_s^2/k_0^2)^{1/2}$. Although we have shown in Eqs. (6) and (7) the self-energy contributions for both $z > 0$ and $z < 0$ it must be understood that the present treatment is not complete inside the solid since bulk plasmon contributions will become important there. The interior problem will be discussed elsewhere.[24]

We note that the imaginary parts of the self-energy divide neatly into conservative and dissipative parts.[11] The dissipative parts appear only above the threshold, while the conservative parts are those energy losses which are recovered again as the particle leaves the surface and appear as the antisymmetric parts of (7). A typical plot of the self-energy for the above-threshold case is shown in Fig. 1.

Physical insight on the meaning of these expressions for $\Sigma(z)$ can be obtained by looking at the relevant limiting cases. In the limit $k_0|z| \to \infty$ and $k_0/Q_s \to \infty$ we recover the well-known semiclassical results for the real[10–15] and imaginary[10] parts

$$\mathrm{Re}\Sigma(z) \to -(e^2\omega_s/2v)[f(2\omega_s|z|/v) + 2g(\omega_s|z|/v)\sin(\omega_s|z|/v)\Theta(z)] \ , \tag{10}$$

$$\mathrm{Im}\Sigma(z) \to (e^2\omega_s/2v)[\mathrm{sgn}(z)g(2\omega_s|z|/v) - 2g(\omega_s|z|/v)\cos(\omega_s|z|/v)\Theta(z)] \ . \tag{11}$$

Not included in Eqs. (10) and (11) are terms which are oscillating in $e^{\pm ik_0 z}$ and which decay away from the surface at least as fast as $(k_0 z)^{-2}$. Oscillatory behavior near the surface of this type is a manifestation of the quantum nature of the interaction and is analogous to similar complex behavior found in the generalized pair distribution function of Van Hove as applied to neutron scattering theory.[25]

The terms multiplied by the Heaviside function $\Theta(z)$ are nonvanishing inside the surface only and have been discussed previously.[10,15] It is particularly satisfying to note that the quantum-mechanical calculation gives the result for $\Sigma(z)$ directly without the need to resort to supplementary arguments to obtain extra factors of $\frac{1}{2}$.[9,10]

Of particular interest is the limit that $\Sigma(z)$ approaches near the surface. Although this method is not strictly valid for $z=0$, since we would need to introduce a maximum cutoff on Q and also take account of the bulk electron cloud which extends out a distance given approximately by the Thomas-Fermi wavelength, we find $\Sigma(0)$ is finite always. This saturation of the image potential at the surface has recently been demonstrated directly.[26] For a particle with velocity above the threshold ($k_0 > Q_s$)

$$\Sigma(z \to 0^{\pm}) = -\frac{\pi e^2 \omega_s}{2v}\left[1 \mp \frac{i}{\pi}\ln\left[1 \mp \frac{(1-2\hbar\omega_s/mv^2)^{1/2}}{1-\hbar\omega_s/mv^2}\right]\right] . \tag{12}$$

The real part of (12) is exactly twice the value obtained previously.[12–15] The usual value arises from the limit of the function $f(x)$ in Eq. (6); however, an identical contribution comes from the $\Lambda(x)$ function which can be directly attributed to the three-dimensional recoil.

A further limiting case is the situation of very small velocity, which is relevant to the question of bound states at the surface. In the limit $v \to 0$ the self-energy is entirely real and can be written for all z in terms of tabulated functions

$$\Sigma(z) = -(e^2/4|z|)[1 - \exp(-Q_s|z|) + Q_s|z|E_2(Q_s|z|)] \ , \tag{13}$$

where $E_n(x)$ is the associated exponential integral.[27] The self-energy approaches a finite value at the surface, $\Sigma(0) = -e^2 Q_s/2$, a value exactly $2/\pi$ times the previously obtained limit[20,21] based on inclusion of two-dimensional recoil only. This calculation indicates that the effect of recoil perpendicular to the surface further weakens the attractive potential at the surface. Such a conclusion has bearing on the question of bound positron surface states[21] and surface polarons.[19,20] The existence of such states has been shown to be somewhat marginal, and the present calculations would indicate that the inclusion of a full recoil treatment would make such states even more weakly bound.

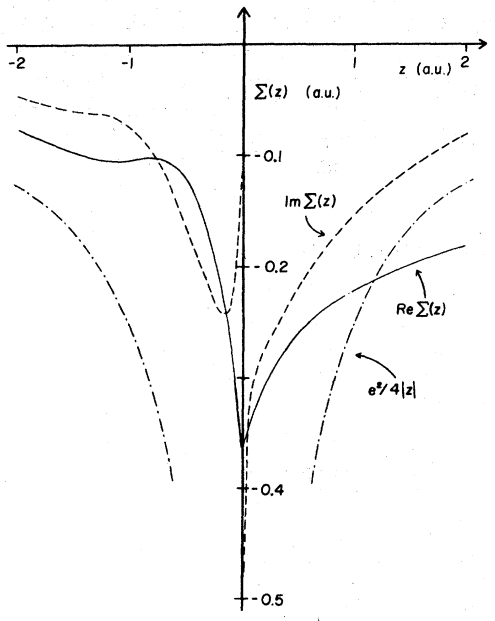

FIG. 1. Real and imaginary parts of the electron self-energy $\Sigma(z)$ are compared to the classical image potential for the above-threshold case of Eqs. (6) and (7) with $\omega_s = 0.5$ a.u. and $v = 2.0$ a.u.

Equation (13) also illustrates that far from the surface the correction terms to the classical $e^2/4|z|$ result decay faster than any inverse power of z. This is at variance with the results of the approximate calculation retaining only parallel recoil in which the corrections to classical behavior appear as inverse powers of $(Q_s z)$.[12]

We now turn to the question of the form taken by the self-energy when the particle is bound to the surface. Evans and Mills[20] have given an heuristic derivation of an expression for the self-energy of an electron in a surface polaron state on an ionic crystal. This expression accounts for recoil of the electron in virtual transitions to states of different momentum parallel to the surface, but does not include the effect of virtual transitions to states in which excitation perpendicular to the surface can occur. Nieminen and Hodges[21] have considered the error incurred by this approximation in their study of the binding of positrons at metal surfaces. They find the self-energy to be more negative by $\sim$10% than predicted by the Evans-Mills recipe. Since these estimates were made by invoking closure to sum approximately over intermediate states we have decided to employ a complete basis set that allows an exact summation to be carried out, namely, the eigenstates of an attractive δ-function potential. In fact the bound state of such a potential has an exponential form similar to the trial function used in the previous work.

We find that the z-dependent self-energy for the bound state divides nicely into two contributions, the first corresponds to virtual transitions in which the z component of motion remains unchanged (the Evans-Mills approximation) and the second comes from transitions in which the z-component of motion changes. We find that the total $\Sigma(z)$ differs substantially from the first term at all distances from the surface. Typically the total energy shift can easily by 50% or more greater than that calculated from the first contribution involving no perpendicular recoil.[24]

We have illustrated our discussion of the self-energy with the example of a charge moving perpendicular to the surface. The case of parallel motion leads to similar results but is somewhat more involved. It suffices here to state that all previous semiclassical results[7,10,16] can be readily reproduced. A more detailed treatment, the extension of this approach to higher orders in perturbation theory, a discussion of the interior problem (bulk effects) and the effects of dispersion will be presented elsewhere.

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