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# Plasmon model for image-potential-induced surface states with an application to positrons at metal surfaces

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A variational method is presented to calculate dynamic corrections to the image potential of a charged particle at a metal-vacuum interface and hence to calculate its binding energy. The response of the metal is treated within the plasmon approximation. As an application, a model for positron surface states on simple metals is studied. It predicts the existence of bound positron surface states in Al, Ga, Zn, Cd, and possibly other high-density simple metals. Further, the resulting localized positron state would have a lifetime 2 to 3 times longer than in the bulk.

## I. INTRODUCTION

The long-range attraction between a charged particle and a semi-infinite medium may in some cases lead to a bound or resonant state localized at the vacuum-medium interface. This sort of surface state has been described as "image-potential-induced" to distinguish it from surface states associated with energy gaps in the bulk band structure. Examples are provided by electrons trapped at a liquid-helium surface[1] or more generally by surface polarons, electrons bound to the surface region of a dielectric by coupling to the phonon fields.[2,3]

The existence of such states at a void-metal interface has also been proposed[4,5] to account for the observed sensitivity of thermalized positrons to voids in irradiated materials.[6] Thus the anomalous annihilation characteristics of positrons in such metals may be due to annihilation from a trapped state localized close to a metal-void boundary rather than one extending throughout the volume of the void.

Calculations of the characteristics of such positron surface states have up to now concentrated on using the classical electrostatic form of the image potential, which assumes the medium to respond macroscopically and instantaneously to a time varying perturbation. The problem of including dynamic and microscopic corrections to the image potential was not considered in any detail. As pointed out by Sak,[2] the binding energies of electrons on a liquid-helium surface (~1 meV) are so much smaller than the electron excitation energies (~1 eV) responsible for generating the image potential that the electrostatic form must be a very good approximation. For the case of a surface polaron, however, the particle binding energies may be of the order or even greater than the excitation energies of the medium lattice. Thus the use of the classical form for the part of the image potential generated by coupling to the lattice vibrations will not in general be valid. The situation for a positron on a metal is similar to that for a surface polaron except that now all of the image potential is generated by electronic excitations. The most important of these are the surface plasmons, whose energy is only slightly greater than the estimated positron binding energy of a few eV. Thus it is clear that for a positron surface state one is in a regime where dynamic image potential effects may be of some importance; how much so is not clear without further investigation, which is the object of this paper.

We assume a trial wave function for the particle localized at the surface region, and minimize the energy expectation value at the ground state. This involves the one-particle kinetic and potential energies and the interaction self-energy arising from the correlation between the particle and the metal electrons. The latter will be described by the plasmon approximation: we account for it in terms of (virtual) excitations of surface and bulk plasmons. Our theory is reminiscent of using variational[7] methods for a polaron-type linear model Hamiltonian. The theory for calculating the self-energy is presented in Chap. 2. As an application, we describe in Chap. 3 the results of a calculation for the positron surface states on simple metals. For these, the one particle potential is approximated by a pseudopotential[8] that mimics the effects of the electrostatic surface dipole and the repulsion from the ionic cores in the metal (see Fig. 1).

For this model, we conclude that the dynamic and recoil effects are by no means negligible: they

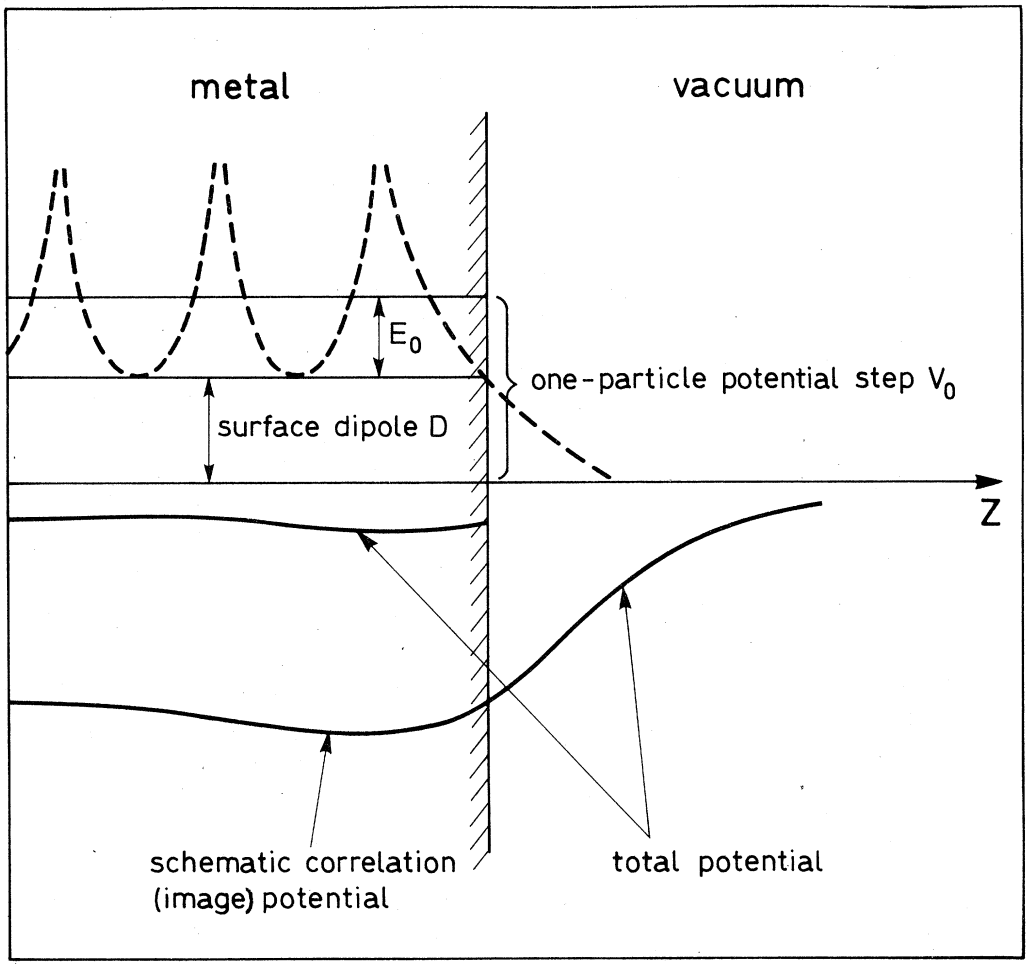


FIG. 1. Schematic one-particle presentation of the surface potentials for a positively charged particle on a metal. Note that the image potential in reality is nonlocal. The total potential may have a bound state below both vacuum and bulk levels. This is what we call a surface state.

decrease the binding energy by as much as a third. In Chap. 3, we also estimate the annihilation rates for stable surface states. The resulting lifetimes are 2 to 3 times longer than for bulk positron states.

Before proceeding to the theory, one or two remarks about the plasmon approximation should be made. Because the positron is in a relatively tightly bound state it is also quite close to the metal surface, say within a few Å. The particle potential perturbing the medium will have Fourier components with wavelengths parallel to the surface of this order of magnitude, comparable with the interatomic spacing. The microscopic dielectric properties of the medium should thus in principle be taken into account. This would mean considering the dispersion of the plasmons and also the coupling of the particle to single-particle excitations. The response of a metal to a perturbation with a finite wave vector $\vec{Q}$ parallel to the surface is, however, still a matter of debate. We have therefore studied a simple model in which the microscopic nature of the medium is taken into account by a cutoff wave vector $Q_c = \omega_p/v_F$ ($\omega_p$ is the plasma frequency and $v_F$ the Fermi velocity of the bulk electron gas) to the plasmons, the coupling to the single-particle excitations being neglected altogether. It should be noted that the coupling to plasmons contributes the major part of the random-phase approximation (RPA) correlation potential for a positron in the bulk.[9] Our assumption of a dispersionless surface plasmon is consistent with the neglect of particle-hole excitations. Furthermore, the asymptotic limit of the image potential is correctly given by the long-wavelength surface plasmons only.[10]

## II. THEORY

Following the approach of Sak[2] and Evans and Mills[3] to the surface polaron problem the coupling of the particle to surface plasmons of frequency $\omega_s = \omega_p/\sqrt{2}$ on the metal can be represented by the Hamiltonian (a.u.)

$$H = H_0 + H_s\,, \tag{2.1a}$$

$$H_0 = -\tfrac{1}{2}\nabla^2 + V(z) + \sum_{Q<Q_c} \omega_s (a^\dagger_{\vec{Q}} a_{\vec{Q}} + \tfrac{1}{2})\,, \tag{2.1b}$$

$$H_s = \sum_{Q<Q_c} \left(\frac{\pi\omega_s}{QA}\right)^{1/2} e^{-Q|z|} e^{i\vec{Q}\cdot\vec{\rho}} (a_{\vec{Q}} + a^\dagger_{-\vec{Q}})\,, \tag{2.1c}$$

where the particle (effective mass unity) is located at $\vec{r} = (\vec{\rho}, z)$, $z$ being the coordinate perpendicular to the surface (surface plane at $z=0$, area $A$). The operator $a^\dagger_{\vec{Q}}$ creates a surface plasmon of wave vector $\vec{Q}$ parallel to the surface with an associated electric potential $e^{-Q|z|}e^{i\vec{Q}\cdot\vec{\rho}}$. The one-particle potential $V(z)$ represents the Hartree field of ions and electrons acting on the particle when it is inside the metal ($z<0$). This type of Hamiltonian has been widely used in connection with surface problems, e.g., multiple plasmon excitation in thin films,[10] core level shifts[11] and satellite structure[12] in x-ray photoemission from absorbed atoms, and also to evaluate the dynamic image potential for a recoilless particle moving along a classical trajectory.[13] The Hamiltonian (2.1) can be straightforwardly generalized to include bulk-plasmon excitations; we will do this later and for the moment discuss the surface-plasmon part, which in our case is by far the more important one.

Solutions of Hamiltonians of the polaron type (2.1) have been reviewed for the bulk case by Fröhlich[14] and discussed for the surface case by Sak[2] and Evans and Mills.[3] By analogy with the bulk polaron the different types of solution may be classified by a dimensionless coupling constant which is $\alpha_s = e^2(m/2\hbar^3\omega_s)^{1/2}$ for the surface Hamiltonian (2.1). Values of the surface-plasmon frequency $\omega_s$ and the coupling constant $\alpha_s$ are given in Table I for some simple metals. The weak coupling solution, appropriate when $\alpha_s \ll 1$, has been considered by Sak.[2] Although our values of $\alpha_s$ are of the order of unity, we discuss the weak coupling solution in short because it enables us to make a connection with an approach to the problem of dynamic corrections to the image potential used by Hodges.[15] That approach uses diagrammatic methods and the RPA and is therefore exact only in the weak coupling limit. In this limit the ground state of (2.1) is described by a wave function including at most zero- and one-plasmon excitations. Its most general form is

TABLE I. Values of the surface plasmon energy $\hbar\omega_s$ and the associated coupling constant $\alpha_s$ for simple metals.

| | $\hbar\omega_s$ (eV) | $\alpha_s$ |
|---|---|---|
| Li | 5.7 | 1.55 |
| Na | 4.3 | 1.78 |
| K | 3.1 | 2.09 |
| Rb | 2.8 | 2.20 |
| Cs | 2.5 | 2.33 |
| Mg | 7.7 | 1.32 |
| Zn | 9.6 | 1.17 |
| Cd | 8.0 | 1.30 |
| Hg | 7.7 | 1.33 |
| Al | 11.2 | 1.10 |
| Ga | 10.2 | 1.15 |
| In | 8.9 | 1.24 |
| Tl | 8.5 | 1.26 |
| Sn | 10.1 | 1.16 |
| Pb | 9.6 | 1.19 |

$$|\psi\rangle = \left[\phi(z) + \sum_{Q<Q_c} c_{\vec{Q}}\, \phi_{\vec{Q}}(z) e^{i\vec{Q}\cdot\vec{\rho}} a^\dagger_{\vec{Q}}\right]|0\rangle\,. \tag{2.2}$$

Here we have taken the ground state with zero total momentum parallel to the surface; $|0\rangle$ represents the plasmon vacuum. Equation (2.2) is analogous to the use of first-order perturbation theory for the bulk polaron wave function.[14] Sak[2] substituted (2.2) into the Schrödinger equation for Hamiltonian (2.1) and for the case of weak binding (the binding energy $E_B$ is much less than the medium excitation energies, see Introduction) derived the classical image potential and a dynamic correction term proportional to $1/\omega_s$. In fact this latter term is the first in a series of corrections ascending in powers of $1/\omega_s$ derived in the RPA.[15]

In the present work we estimate the ground-state energy *variationally* using (2.1) and (2.2). The weak coupling condition corresponds to assuming (2.2) to be already normalized, i.e.,

$$\sum_{Q<Q_c} |c_{\vec{Q}}|^2 \ll 1\,.$$

In this case minimization of the expectation value of the Hamiltonian (2.1) with respect to $c_{\vec{Q}}$, keeping $\phi(z)$ and $\phi_{\vec{Q}}(z)$ constant, leads to

$$c_{\vec{Q}} = -(\pi\omega_s/QA)^{1/2} M_{\vec{Q}}/(\omega_s + \tfrac{1}{2}Q^2 + \epsilon_{\vec{Q}} - \epsilon_0)\,, \tag{2.3}$$

and the estimated ground-state energy is

$$\tilde{E}_0 = \epsilon_0 - \sum_{Q<Q_c} \left(\frac{\pi\omega_s}{QA}\right) \frac{|M_{\vec{Q}}|^2}{\omega_s + \tfrac{1}{2}Q^2 + \epsilon_{\vec{Q}} - \epsilon_0} = \epsilon_0 - \Sigma_s\,, \tag{2.4}$$

where

$$M_{\vec{Q}} = \langle \phi | e^{-Q|z|} | \phi_{\vec{Q}} \rangle , \tag{2.5a}$$

$$\epsilon_{\vec{Q}} = \langle \phi_{\vec{Q}} | h(z) | \phi_{\vec{Q}} \rangle , \tag{2.5b}$$

$$\epsilon_0 = \langle \phi | h(z) | \phi \rangle , \tag{2.5c}$$

and

$$h(z) = -\frac{1}{2}\frac{\partial^2}{\partial z^2} + V(z) . \tag{2.5d}$$

The matrix elements in (2.5) involve integrals over the coordinate $z$ perpendicular to the surface. In principle one should now continue with the variational procedure by varying $\phi(z)$ and $\phi_{\vec{Q}}(z)$ independently. In fact we have found it to be a good approximation to take $\phi_{\vec{Q}}(z) = \phi(z)$ and then vary $\phi$ (see below). It should be noted that this procedure leads to the same results as Evans and Mills[3] obtained for the ground-state energy using a wave function containing multiple plasmon excitation. They use the method of Lee, Low, and Pines[7] which is valid beyond the weak coupling limit and in fact provides a reasonable approximation for the ground state in the bulk up to coupling constants $\alpha_s$ considerably greater than unity.[14] In this approximation the surface-plasmon contribution to the self-energy is

$$\Sigma_s^0 = -\frac{1}{2}\int_0^{Q_c} dQ \, \frac{|\langle \phi | e^{-Q|z|} | \phi \rangle|^2}{1 + Q^2/2\omega_s} . \tag{2.6}$$

We now proceed to discuss another way to derive (2.6) and to generalize it. This starts from the Hedin-Lundqvist[16] expression for the self-energy operator

$$\Sigma(\vec{r}', \vec{r}, E) = \frac{i}{2\pi}\int_c d\omega \, G(\vec{r}', \vec{r}, E - \omega)\frac{\delta V_{\text{ind}}(\vec{r}', \omega)}{\delta n(\vec{r}, \omega)} , \tag{2.7}$$

where $E$ is the energy of the state under consideration, $G$ is the one-particle Green's function, and $\delta V_{\text{ind}}/\delta n$, the space and frequency dependent response function. The Green's function for the surface state may be written

$$G(\vec{r}', \vec{r}, \omega) = \frac{1}{(2\pi)^2}\int d^2\vec{k}_{\parallel} \sum_{n\geq 0} \frac{\phi_n^*(z')\phi_n(z)}{E_n + k_{\parallel}^2/2 - (\omega + i\delta)} \times e^{i\vec{k}_{\parallel}\cdot(\vec{\rho} - \vec{\rho}')} , \tag{2.8}$$

where translational invariance parallel to the surface has been used to factorize the eigenfunctions; $E_n$ is the energy eigenvalue of the $n$th state. The response function $\delta V_{\text{ind}}/\delta n$ can be expressed via the surface dielectric function $\epsilon_{\vec{Q}}(\omega)$[17] as

$$\frac{\delta V_{\text{ind}}(\vec{r}', \omega)}{\delta n(\vec{r}, \omega)} = \frac{1}{2\pi}\int d^2\vec{Q} \, \frac{1 - \epsilon_{\vec{Q}}(\omega)}{1 + \epsilon_{\vec{Q}}(\omega)} e^{i\vec{Q}\cdot(\vec{\rho} - \vec{\rho}')} \times e^{-Q(|z| + |z'|)} . \tag{2.9}$$

If (2.8) and (2.9) are inserted in (2.7) and the resulting $\Sigma(\vec{r}', \vec{r}, E)$ is applied to a surface state with a wave vector $\vec{q}_{\parallel}$ parallel to the surface, the $\vec{\rho}'$ integration can be performed and sets $\vec{Q} = \vec{k}_{\parallel} + \vec{q}_{\parallel}$. As above, we confine ourselves to states at the bottom of the two-dimensional band, i.e., $\vec{q}_{\parallel} \approx 0$. In that case we find

$$\Sigma(z', z, E) = \frac{i}{(2\pi)^2}\int_c d\omega \int d^2\vec{Q} \, \frac{1 - \epsilon_{\vec{Q}}(\omega)}{1 + \epsilon_{\vec{Q}}(\omega)} \frac{e^{-Q(|z| + |z'|)}}{Q} \times \sum_{n\geq 0} \frac{\phi_n^*(z')\phi_n(z)}{E_n + Q^2/2 - E + \omega - i\delta} . \tag{2.10}$$

To proceed one has to invoke an approximation for the surface dielectric function $\epsilon_{\vec{Q}}(\omega)$, a matter of continuing interest. In the semiclassical infinite barrier model of a metallic surface, $\epsilon_{\vec{Q}}(\omega)$ is related to the bulk dielectric function through the Ritchie-Marusak[18] relation. For the latter we use the Drude formula $1 - \omega_p^2/\omega^2$, i.e., in the spirit of (2.1) assume the bulk medium to have single dispersionless excitation frequency $\omega_p$ up to a cutoff wave vector $Q_c$. The contour integral in (2.10) may now be evaluated, and one just picks up the surface plasmon pole to get

$$\Sigma_s(z', z, E) = -\frac{1}{2}\int_0^{Q_c} dQ e^{-Q(|z| + |z'|)} \times \sum_{n\geq 0} \frac{\phi_n^*(z')\phi_n(z)}{1 + Q^2/2\omega_s + (E_n - E)/\omega_s} . \tag{2.11}$$

Taking the expectation value at the ground state $E = E_0$ gives the self-energy estimate

$$\Sigma_s = -\frac{1}{2}\int_0^{Q_c} dQ \sum_{n\geq 0} \frac{|\langle \phi_n | e^{-Q|z|} | \phi_0 \rangle|^2}{1 + Q^2/2\omega_s + (E_n - E_0)/\omega_s} . \tag{2.12}$$

Upon comparison, [making the identification $\phi_0(z) = \phi(z)$] the Evans-Mills expression (2.6) is seen to be the first term of expansion (2.12).

In a full application of this theory, $\Sigma_s$ would have to be evaluated self-consistently with a number of states $\phi_n(z)$ and energies $E_n$. In the present case we have, however, found it to be a good approximation to consider only the ground state $\phi_0(z)$ in the actual calculation; we shall estimate the contribution from states $n > 0$ in (2.12) to the ground state by noticing that $|E_n| \ll |E_0|$. Thus $E_n$ can be omitted from the denominator for $n > 0$ and the sum over matrix elements can be performed, since $\{\phi_n\}$ is a complete set of states.

Omission of higher states from (2.12) is equivalent to setting $\phi_{\vec{Q}}(z) = \phi(z)$ in the variational wave function (2.2). The wave-number integral of the

self-energy in (2.6) is limited not only by the cutoff $Q_c$, but also by the matrix elements, which decay from unity for $Q$ values greater than the decay parameters of the localized state $\phi$. Thus the magnitudes of $\Sigma_s$ will be less than $\frac{1}{2}\pi\alpha_s\omega_s$, which would be obtained by integrating just the denominator up to $Q$ equals infinity.[2] However, since the self-energy will still be a substantial fraction of $\omega_s$, it cannot be said that we are truly in the weak coupling regime. The correction to the normalization of the wave function (2.2) $\sum_{Q<Q_c}|c_Q|^2$ is of the order of $\Sigma_s/\omega_s$ and not necessarily negligible (in the application below, $\sum_{Q<Q_c}|c_Q|^2 = 0.2 \ldots 0.5$). In fact for a finite coupling a rigorous application of the variational principle using (2.2) requires us to reduce the self-energy (2.6) in magnitude by approximately the normalization factor $1+\sum_{Q<Q_c}|c_Q|^2$. On the other hand, the generalization of the weak coupling wave function used by Evans and Mills[3] (see also Ref. 14, Sec. IV B) allows a simple extrapolation of the weak coupling result (2.4) to finite coupling constants, provided one imposes the restriction $\phi_{\vec{Q}}(z) = \phi(z)$.

We complete the theory by considering the bulk-plasmon contribution to the energy functional. The fields of the bulk plasmons do not extend into the vacuum, but if the surface state has an appreciable overlap with the interior medium, the possibility of exciting a bulk plasmon must certainly be considered. From various analysis[19,20] we know that a substantial compensation exists between the contributions of surface and bulk plasmons to the self-energy just inside the surface. A particle well outside the surface layer couples only to the surface plasmons. The strength of the bulk modes, which are suppressed near the surface region, where surface modes dominate, gradually take over deeper inside the metal.

The Hamiltonian linear in bulk-plasmon operators $b_{\vec{q}}^\dagger, b_{\vec{q}}$ is readily written as

$$H_b = \sum_{q<Q_c}\left(\frac{4\pi\omega_p}{q^2\Omega}\right)^{1/2} e^{i\vec{Q}\cdot\vec{\rho}}\sin q_z z\,\Theta(-z)(b_{\vec{q}}^\dagger + b_{-\vec{q}}), \tag{2.13}$$

$\Omega$ being the crystal volume. The analysis presented above could be repeated for the bulk term; the dependence of (2.13) on the perpendicular momentum $q_z$ somewhat complicates the algebra. However, as it turns out, the bulk-plasmon contribution to the total binding energy is small and we may do the $q_z$ integration in the self-energy by neglecting the "perpendicular" cutoff $(Q_c^2 - Q^2)^{1/2}$. This leads to a self-energy formula, which also could be obtained from an expression for the weak coupling vertex given by Feibelman *et al.*[19] An analysis analogous to that leading to (2.11) gives the bulk-plasmon contribution to the self-energy, and the lowest-order approximation yields the expectation value at the ground state as

$$\Sigma_b^0 = -\int_0^{Q_c} dQ \int_{-\infty}^0 dz \int_{-\infty}^0 dz' |\phi(z)|^2 |\phi(z')|^2 \times \frac{e^{-Q|z-z'|} - e^{-Q(|z'|+|z|)}}{1+Q^2/2\omega_p}. \tag{2.14}$$

Summarizing, the total energy functional to be minimized with respect to the ground-state wave function $\phi(z)$ is, from (2.5c), (2.6), and (2.14),

$$E[\phi] = \epsilon_0 + \Sigma_s^0 + \Sigma_b^0. \tag{2.15}$$

This will be done in Sec. III for the special case of positron surface states on metals.

## III. APPLICATION TO POSITRON SURFACE STATES

### A. Binding energies

Following the positron pseudopotential idea,[8] the Hartree potential $V(z)$ in (2.1) may be modeled by a potential step, which we shall place at the image potential plane $z=0$, i.e., $V(z) = V_0\Theta(-z)$. The height of the step may be determined from positron work-function calculations.[21,22] This step mimics the effects of electrostatic surface dipole and of the kinetic energy of the positron in the interior metal due to the repulsive ion cores (see Fig. 1):

$$V_0 = D + E_0, \tag{3.1}$$

where $D$ is the surface dipole, measured from the electrostatic potential at a Wigner-Seitz cell boundary, and $E_0$ is the kinetic energy of the positron in the discrete lattice. It would be wrong to add the bulk correlation potential to $V(z)$ because of the compensation between bulk- and surface-plasmon contribution to the correlation just inside the metal, as discussed above. Instead the correlation, in terms of the coupling to bulk plasmons, must be considered explicitly as was indicated in Sec. II. We minimize (2.15) using a two-parameter trial function

$$\phi(z) = \begin{cases} Ae^{\gamma z} & (z<0) \\ B(z+z_0)e^{-\beta z} & (z>0), \end{cases} \tag{3.2}$$

and impose normalization and continuity conditions. In Table II, we give the one-particle energy $\epsilon_0$ (2.5b), the surface-plasmon self-energy $\Sigma_s^0$ (2.6), and the bulk-plasmon self-energy $\Sigma_b^0$ (2.14) corresponding to the optimum parameters $\beta$ and $\gamma$ for a number of simple metals. The contribution $\Sigma_s^{n>0}$ from the states $n>0$ has been evaluated by keeping $\beta$ and $\gamma$ fixed and approximating $E_{n>0} \approx 0$ in (2.12). No higher-order corrections to $\Sigma_b$ have been con-

TABLE II. Values of the Hartree potential step $V_0$, the optimum wave-function parameters $\beta$ and $\gamma$, the one-particle energy $\epsilon_0$ [Eq. (2.5c)], and various contributions to the self-energy from variational calculations. $\Sigma_s^0$ is the first-order surface plasmon contribution [Eq. (2.6)], $\Sigma_b^0$ the bulk plasmon contribution [Eq. (2.14)], and $\Sigma_s^{n>0}$ the estimate of higher-order corrections to $\Sigma_s$ [Eq. (2.12)]. $E_B = -E_{\rm tot}$ is the total binding energy and $\phi_p$ is the positron work function (Ref. 21). All energies are in eV. A stable surface state is predicted for metals with $E_B > \phi_p$.

| | $V_0$ | $\beta$ [a.u.] | $\gamma$ [a.u.] | $\epsilon_0$ | $\Sigma_s^0$ | $\Sigma_s^{n>0}$ | $\Sigma_b^0$ | $E_B$ | $\phi_p$ | Stable surface states |
|---|---|---|---|---|---|---|---|---|---|---|
| Li | 3.0 | 0.766 | 0.225 | 2.56 | −3.86 | −0.39 | −1.11 | 2.8 | 4.4 | No |
| Na | 2.4 | 0.749 | 0.200 | 2.23 | −3.47 | −0.34 | −1.10 | 2.7 | 4.6 | No |
| K | 1.8 | 0.755 | 0.166 | 1.82 | −3.00 | −0.28 | −1.17 | 2.6 | 5.2 | No |
| Rb | 1.5 | 0.771 | 0.153 | 1.65 | −2.84 | −0.27 | −1.22 | 2.7 | 5.4 | No |
| Cs | 1.2 | 0.831 | 0.132 | 1.32 | −2.58 | −0.26 | −1.37 | 2.9 | 5.7 | No |
| Mg | 5.2 | 0.634 | 0.351 | 2.86 | −4.24 | −0.46 | −0.47 | 2.3 | 2.7 | No |
| Zn | 7.5 | 0.536 | 0.503 | 2.59 | −3.93 | −0.56 | −0.15 | 2.0 | 0.9 | Yes |
| Cd | 6.3 | 0.561 | 0.432 | 2.63 | −3.99 | −0.49 | −0.23 | 2.1 | 1.8 | Yes |
| Hg | 5.0 | 0.644 | 0.342 | 2.87 | −4.26 | −0.45 | −0.51 | 2.4 | 2.9 | No |
| Al | 8.2 | 0.540 | 0.532 | 2.69 | −4.02 | −0.62 | −0.14 | 2.1 | 0.7 | Yes |
| Ga | 6.5 | 0.616 | 0.424 | 3.02 | −4.43 | −0.56 | −0.34 | 2.3 | 2.0 | Yes |
| In | 5.6 | 0.644 | 0.368 | 3.01 | −4.41 | −0.50 | −0.47 | 2.4 | 2.6 | No |
| Tl | 4.5 | 0.732 | 0.297 | 3.11 | −4.48 | −0.48 | −0.85 | 2.7 | 3.5 | No |
| Sn | 5.8 | 0.664 | 0.375 | 3.17 | −4.50 | −0.54 | −0.51 | 2.5 | 2.7 | No |
| Pb | 4.6 | 0.759 | 0.300 | 3.27 | −4.65 | −0.52 | −0.94 | 2.8 | 3.8 | No |

sidered. The total binding energies $E_B = -(\epsilon_0 + \Sigma_s + \Sigma_b)$ are also given. Surface states can only occur if the binding energy $E_B$ relative to the vacuum is larger than the positron work function $\phi_p$. In Table II, we give values of $\phi_p$ calculated by Hodges and Stott.[21] Comparing our results with those of the simple static potential model[23] we find that including corrections to the classical image potential reduces the binding energy relative to vacuum by 15 to 30%. According to this calculation, surface states would be stable in Zn, Cd, Al, Ga, and possibly In and Sn of the simple metals.

### B. Lifetimes

It is clear that if the positron really annihilates from the surface state of this sort, characteristics such as the lifetime should show a saturation effect becoming constant for void sizes larger than a few Å. We have estimated the lifetime corresponding to a large void limit in two different ways. The positron annihilation rate is for the surface state

$$\lambda = \pi\alpha^3 \int d\vec{r}\,|\phi(\vec{r})|^2 [n_0(z) + \Delta n(\vec{\rho}, z)]\,, \qquad (3.3)$$

where $\alpha$ is the fine-structure constant, $n_0(z)$ is the static electron density profile at the surface,[24] and $\Delta n(\vec{\rho}, z)$ is the screening charge density due to the presence of the positron.

Within the plasmon model, $\Delta n(\vec{\rho}, z)$ can be written in terms of the surface- and bulk-plasmon fluctuations as

$$\Delta n(\vec{\rho}, z) = \sum_{Q<Q_c} e^{i\vec{Q}\cdot\vec{\rho}} \Bigg[ \left(\frac{\omega_s Q}{4\pi A}\right)^{1/2} U_{sp}(z)(a_{\vec{Q}} + a_{-\vec{Q}}^{\dagger}) + \sum_{q_z} \left(\frac{\omega_p(Q^2+q_z^2)}{4\pi\Omega}\right)^{1/2} \times U_{bp}(q_z, z)(b_{\vec{q}} + b_{-\vec{q}}^{\dagger}) \Bigg]\,, \qquad (3.4)$$

where $b_{\vec{q}}^{\dagger}$ creates a bulk plasmon with an associated density oscillation $U_{bp}(q_z, z) = \Theta(-z)\sin q_z z$, $U_{sp}(z)$ is the surface-plasmon density fluctuation. Inserting (3.4) into (3.3) together with the wave function including surface- and bulk-plasmon excitations yields the weak coupling result

$$\lambda = \lambda_0 + \lambda_{sp} + \lambda_{bp}\,, \qquad (3.5)$$

where $\lambda_0$ is the rate due to the static profile in (3.2), and

$$\lambda_{sp} = \frac{\alpha^3}{2} \int_{-\infty}^{\infty} dz\,|\phi(z)|^2 U_{sp}(z) \int_0^{Q_c} dQ\, \frac{QM(Q)}{1 + Q^2/2\omega_s} \qquad (3.6)$$

and

$$\lambda_{bp} = \frac{\alpha^3}{\pi} \int_0^{Q_c} dQ\, Q \int_0^{(Q_c^2 - Q^2)^{1/2}} dq_z\, \frac{|W(q_z)|^2}{1 + (Q^2 + q_z^2)/2\omega_p} \qquad (3.7)$$

TABLE III. Estimates of lifetime enhancement factors for surface states. $\lambda_{sp}$ and $\lambda_{bp}$ are the surface- and bulk-plasmon contributions to the total annihilation rate $\lambda$ within the random-phase approximation [Eq. (3.5)], and $S_p$ is the corresponding lifetime enhancement for a surface state. $S_{LD}$ is the enhancement from the local density approximation (3.11) for the annihilation rate.

| | $\lambda_{sp}/\lambda$ | $\lambda_{bp}/\lambda$ | $S_p$ | $S_{LD}$ |
|---|---|---|---|---|
| Zn | 0.49 | 0.02 | 3.0 | 2.3 |
| Cd | 0.52 | 0.03 | 2.3 | 1.9 |
| Al | 0.45 | 0.02 | 3.2 | 1.8 |
| Ga | 0.46 | 0.03 | 2.5 | 2.0 |
| In | 0.48 | 0.04 | 2.7 | 2.2 |
| Sn | 0.42 | 0.04 | 2.1 | 1.8 |

are the surface- and bulk-plasmon contributions to the annihilation rate. Above, $M(Q)$ is given in (2.4), and

$$W(q_z)=\langle\phi\,|\,e^{iq_z z}\sin q_z z\,\Theta(-z)|\,\phi\rangle\,. \tag{3.8}$$

It may be recalled that the bulk-plasmon coupling vertex[19] used above to derive (2.14) corresponds to neglecting the cutoff $(Q_c^2-Q^2)^{1/2}$ in the $q_z$ integration of the self-energy integral. We keep the cutoff here because the annihilation rate may be more sensitive to it. The density oscillation $U_{sp}(z)$ of a surface plasmon is localized at the surface region; we choose to approximate it as

$$U_{sp}(z)=\left|\frac{dn_0(z)}{dz}\right|\frac{1}{n_0(-\infty)}\,. \tag{3.9}$$

All the metals which we, according to the energetic considerations, expect to have surface states have fairly high electron densities and thus the plasmon approximation underestimates the absolute annihilation rate $\lambda_{bulk}$ in the bulk by a factor of roughly 2. Thus it is more appropriate to consider the *relative* lifetime enhancement for a surface state, defined as

$$S_p=\lambda_{bulk}/\lambda\,. \tag{3.10}$$

In Table III, we give estimates of the enhancement factor $S_p$ for Zn, Cd, Al, Ga, In, and Sn computed from Eqs. (3.5)–(3.10). We also give the relative contributions of surface and bulk plasmons to $\lambda$ in Eq. (3.5). As for the self-energy, the bulk-plasmon contribution is again seen to be clearly the smaller one.

The above estimates of the lifetime enhancement ignore the nonlinear response effects, which become very important at the density range of interest, and also the core electron contribution to the annihilation rate, which may be quite sizeable. Furthermore, the approximation (3.9) to the surface-plasmon field is quite arbitrary. Thus we have thought it advisable to obtain another estimate of $S$ using a local density formula

$$\lambda_{LD}=\int_{-\infty}^{\infty}dz\,\Gamma(n_0(z))\,|\,\phi(z)\,|^2\,, \tag{3.11}$$

where $\Gamma(n)$ is the annihilation rate[25] in a homogeneous electron gas of density $n$. To account for the core electrons, we have used the recipe of West[26] by renormalizing the static profile $n_0(z)$[24] in (3.11) to

$$n_0'(z)=\begin{cases} n_0(z) & (z>0) \\ n_0(z)+(\Gamma_c/\Gamma_v)n_0(-\infty) & (z<0)\,, \end{cases} \tag{3.12}$$

where $\Gamma_c/\Gamma_v$ is the probability ratio of core and valence annihilations.[27]

The bulk $\lambda_{bulk}$ is calculated from an analogous formula, and the enhancement estimates, denoted by $S_{LD}$, are given in Table III. It must be noted that the expression (3.11) corresponds to the case where the positron carries its screening cloud across the surface, the lifetime going the spin-averaged positronium limit with decreasing electron density.

The experimental data on lifetime enhancement is still scarce: of the metals considered here Petersen *et al.*,[28] report $S=3.0$ for Al. For the transition metal Mo, $S=4.0$.[29]

## IV. DISCUSSION

One of the motivations for this work was the question whether dynamic and microscopic corrections to the classical image potential could make the particle surface binding much weaker than an adiabatic calculation would suggest. We have, therefore, tried to obtain a lower bound to the degree of binding to the surface. For example, the variational principle has been used throughout and any coupling to the single-particle excitations which could only increase the binding energy have been neglected. The question of a possible displacement of the effective image potential plane into the vacuum,[30] which would also lower the energy,[5] has again been disregarded. A variational upper bound on the ground-state energy is provided by an analog of the formalism of Evans and Mills,[3] which neglects the response of the medium to particle motion perpendicular to the surface, but takes into account the multiple plasmon excitations important at finite coupling constants. It should be noted that although the Evans-Mills formalism goes beyond the weak coupling wave function (2.2), it still gives an energy linear in the coupling constant. It therefore does not include any of the effects on nonlinear response, which are known to be important for the positron annihilation rate and correlation potential in the bulk.[21] According to

Fröhlich,[14] terms nonlinear in the coupling constant $\alpha_s$ only become important for polaron Hamiltonians of the type (2.1) at values of $\alpha_s > 6$, i.e., much larger than those that apply to the present case. For positrons, however, the nonlinear response is provided by coupling terms quadratic and higher order in the plasmon operators $a_{\vec{Q}}^{\dagger}$ and $b_{\vec{q}}^{\dagger}$,[31] which are neglected when one attempts to treat the positron electron gas coupling by a linearized interaction as in (2.1) or (2.13). Once again, the inclusion of nonlinear response could, as in the bulk, only serve to increase the positron metal binding. Also it may be noted that nonlinear effects are likely to be less important at the surface than in the bulk because the interaction there is, on the average, weaker.

For positron surface states, the proper evaluation of the image interaction is important. Our results suggest that a simple static approximation overestimates the binding energy by up to a third. There is good evidence for positron surface states in Al[28,32] and in Mo.[29] On the basis of our calculations we would expect similar states to exist in Zn, also in Ga and Cd, and possibly in Mg, In, and Sn, but not in the alkalis or Hg, Tl, and Pb. If the present model was extended to the transition metals, some of which have fairly well-defined surface plasmons, we would expect to find a whole host of materials where positron surface states exist. This comes about mainly because the transition metals have generally low and in some cases even negative positron work functions.[22]

Much of the basic evidence of positron surface states comes from the huge lifetime increase which clearly distinguishes these states from any other defect-induced levels. Using two different ways of estimating the annihilation rate, we predict the localized surface state on the simple metals mentioned above to have a lifetime 2–3 times longer than a bulk propagating state.

Some words concerning the reliability of the numerical results obtained are in order. Although we do not find the binding energies or lifetime enhancements to be very sensitive to the plasmon cutoff $Q_c$ (another "natural" cutoff is provided by the spatial extent of the state), the basic crudeness of the model must be kept in mind, and any numbers should not be taken too literally. The stable surface states predicted are fairly localized, and thus, details of the electronic and ionic structure at the surface region may become important.

We have concentrated on assessing the importance of nonadiabatic effects within a simple approximation for the responding electron gas. The underlying lattice and the static surface properties are included in a very approximate manner. Also our plasmon approximation is questionable for a very localized state. A better theory should incorporate a more realistic description of the surface structure and of the excitation spectrum of the metallic electrons. The latter can, in principle, be included in the present theory by using a better surface dielectric function in calculating the self-energy.

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