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Potential energy of atoms near a metal surface

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The dependence of the atom-metal surface interaction potential on the response time of the metal electron gas is discussed. For an atom in its ground state, it is shown that the mirror-image potential of classical electrostatics can be retrieved if the metal response time in the Lifshitz formula is much shorter than the characteristic fluctuation time of the atom, whereas, for the opposite limit, the interaction potential of an atom in a spherically symmetric state is vanishingly small. For an atom in an excited state the interaction potential has additional terms that have the same dependence on the atom-surface separation, but it displays a resonant, dispersive character and may lead to attraction as well as repulsion of the atom.

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I. INTRODUCTION

The potential energy of a charge distribution placed in the vicinity of a metal surface can be evaluated by means of the image method of classical electrostatics [1], and relies essentially upon the assumptions that (i) the charged particle is far enough from the metal surface so that its wave function does not overlap with the metal electrons' wave function, and, (ii), the particle is at rest. If the latter condition is not satisfied, one may still use classical electrostatics, provided that the metal electrons respond very rapidly to any change of the external electrical perturbation.

The assumption of zero response time for the electron gas in the metal may not be valid in many experimental situations, such as the case of impact of very fast electrons on the metal surface or the photoelectric effect induced by high-frequency fields. Thus the problem of how to include the effects of a finite response time of the electrons in the metal arises. Extensive calculations of the dynamic response of electrons have been carried out by Feibelman [2] for the case of an external electrical perturbation $\mathcal{E}(t,\mathbf{r})=\mathcal{E}_0\exp[i(\omega t-\mathbf{q}\cdot\mathbf{r})]$ which varies rapidly in time ($\omega>\omega_p$) but slowly in space ($q_\parallel<k_F$) (here, ω_p is the plasma oscillation frequency and k_F is the Fermi wave vector), and by Persson and co-workers [3,4] for the low-frequency range ($\omega\ll\omega_p$). For a particle of moderate speed it is often possible to replace the static potential with a "spatially retarded" potential in which the finite response time of the metal electrons is accounted for in a simple way [5,6].

Although several authors (see, e.g., Ref. [1]) include the interaction potential as part of the total work function of the metal surface, it would be preferable to consider it separately, since this potential depends not only on the shape of the metal-vacuum interface and on the presence of impurities or adsorbed atoms [7], but also on the kinetics of the particle being ejected from the metal. However, in a calculation of the work function for electrons that pass from the bulk to the vacuum through a series of stationary states, the correct $1/4R$ behavior at large enough distances from the metal surface must emerge. This has been done in a series of papers by Ossicini, Bertoni, and Gies [8,9], who employed the Hohenberg-Kohn-Sham density-functional formalism [10,11] in the nonlocal formulation proposed by Gunnarsson and Jones [12] to describe the exchange and correlation effects on the particle at the boundary. Nonlocal theories are necessary [13], since use of a local-density approximation, as in an earlier paper by Lang and Kohn [14], leads to an electron potential energy in the vacuum that decays exponentially to zero when its distance from the metal surface increases.

The same problem arises when the external electrical perturbation is provided by more complex charge distributions, such as atoms. Nordlander and Tully [15] have evaluated the lifetimes of excited states of a hydrogen atom placed near a metal surface, using the Ossicini-Bertoni-Gies formulation to determine the interaction potential of the bound electron with its mirror image. At large distances from the metal surface, this is equivalent to assuming a zero response time of the metal electron gas.

However, when the adiabatic approximation is not valid and the dynamics of the electron gas inside the metal has to be taken into account, the potential energy, in regions far enough from the surface, does not follow the simple mirror-image law of classical electrostatics.

This article addresses this problem for the case of an electron bound to an atom close to a metal surface. The dependence of the mirror-image potential on the response time of the metal surface is discussed for the jellium model of the metal, in which the metal ion cores that form the crystal lattice are replaced by a homogeneously distributed positive background that terminates suddenly at the metal-vacuum interface. Moreover, the metal surface is assumed to be clean (i.e., with no impurities), and perfectly planar.

To clarify the effect of the electrons' response time on the interaction potential, we begin our discussion by evaluating the potential for an atom in the ground state in two different ways that yield apparently contradictory results. We show that the two cases apply to quite different and extreme situations, with actual interaction potentials lying somewhere in between. The relevant parameter here is the product of the surface-plasmon frequency and the atomic characteristic fluctuation time.

We next consider the interaction potential of an excited atom. The potential in this case has the same dependence on the atom-surface separation as in the previous case, but additional terms emerge. These have a resonant, dispersionlike character when the excitation energy of the atom is increased, with resonance at the surface-plasmon surface frequency. They may also lead to attractive or repulsive behavior, depending on whether the atomic transition frequency is smaller or larger than the plasmon frequency. This behavior is similar to the one found for the van der Waals interaction potential of two excited atoms.

II. THE van der WAALS POTENTIAL OF ATOMS CLOSE TO A METAL SURFACE

We start by considering two simplified ways of calculating the interaction potential of an atom with a metal surface. For simplicity, we shall consider here the case of a neutral, single-electron atom in the ground state.

According to Margenau and Kestner [16], the interaction potential of a dipole with a metal surface is evaluated by using the method of images as

$$V_{a\text{-}s}=-\frac{e^2}{16R_0^3}(\xi_0^2+\eta_0^2+2\zeta_0^2) \tag{1}$$

where ξ_0, η_0, and ζ_0 are the coordinates of the negative charge (the electron) relative to the positive charge (the nucleus), and R_0 is the distance of the dipole from the surface. Equation (1) is the classical expression for the interaction potential. To find its quantum-mechanical counterpart we must replace the coordinates of the charge by the corresponding operators, and take the expectation value in the quantum-mechanical state $|\psi\rangle$ which applies to the atom. We have

$$V_{a\text{-}s}(R_0)=-\frac{e^2}{16R_0^3}\langle\psi|(\hat{\xi}_0^2+\hat{\eta}_0^2+2\hat{\zeta}_0^2)|\psi\rangle \tag{2}$$

(R_0 need not be quantized because of the large mass of the nucleus).

It should be noted that Eq. (2) gives a potential energy that is different from zero even if the atomic state is spherically symmetric (e.g., the atom is in an S state), and has an R_0^{-3} dependence on the atom-surface separation.

We now evaluate the interaction potential of an atom close to a metal surface from another point of view. Consider an atom in an S state, with eigenfunction $\psi(\mathbf{r})$ that is spherically symmetric.

We may think of an atom as a classical distribution of charges with density $\rho(\mathbf{r})$,

$$dQ=\rho(\mathbf{r})dV=-[-|e||\psi(\mathbf{r})|^2+|e|\delta(\mathbf{r})]dV \tag{3}$$

in which the last term of the right-hand side is the charge density of the nucleus. At sufficiently large distances, the charge distribution (3) creates an electrostatic potential $\Phi(\mathbf{x})$ that can be expressed in terms of spherical harmonics $Y_{\lambda\mu}(\theta,\varphi)^{(1)}$

$$\Phi(\mathbf{x})=\sum_{\lambda=0}^{\infty}\sum_{\mu=-l}^{l}\frac{4\pi}{2\lambda+1}q_{\lambda\mu}Y_{\lambda\mu}(\theta,\varphi) \tag{4}$$

with $q_{\lambda\mu}$ given by

$$q_{\lambda\mu}=\int Y_{\lambda\mu}^{*}(\theta,\varphi)r^{\lambda}\rho(\mathbf{r})d\mathbf{r}\ . \tag{5}$$

For an atom in a spherically symmetric state, the only coefficient $q_{\lambda\mu}$ different from zero in (5) is the one with $\lambda=0$, $\mu=0$. Hence the two terms of the charge distribution in (3) generate an electrostatic potential given by

$$\Phi(\mathbf{x})=-\frac{|e|}{r}+\frac{|e|}{r}\equiv 0\ . \tag{6}$$

Thus the contribution of the electron charge distribution cancels exactly the contribution of the nuclear charge, and the resulting electrostatic potential from the whole atom is zero. This also means that no charge will be induced on the metal surface, or, equivalently, that no mirror image need be considered in the bulk. Accordingly, the interaction potential of the atom with the metal surface is zero. [A nonzero contribution to the electrostatic potential (4) created by an atom in a stationary state would arise only for states with orbital angular momentum different from zero, for which the ensuing interaction potential has a power-law dependence on the atom-surface separation of the type $1/R^n$, but with n larger than 3.]

This result seems to contradict the previous one of Eq. (2). As we will show, however, the contradiction does not actually exist, since the two formulations make implicit use of quite different assumptions on the metal-surface response time.

Indeed, when we evaluate the potential energy from Eq. (2), we assume that the metal surface responds immediately to the electrical perturbation of the atom in which the electron is in (ξ_0,η_0,ζ_0) so that the virtual image of the electron in that configuration forms instantaneously. On the other hand, when we evaluate the potential energy from the charge distribution of the stationary state $|\psi\rangle$, Eq. (3), we assume that the metal surface is unable to follow the sudden change in electron position, and reacts only to the time averaged distribution of charges in the atom.

The actual situation is somewhere in between the two limiting cases. The metal surface does react with a finite response time; thus only the highest frequencies of the electrical perturbation will be cut out, but the lowest ones survive in the metal-surface response function.

The true picture of the atom is one in which there are fluctuations; that is, the atom is not quite in a stationary state of the unperturbed Hamiltonian. Fluctuations are the quantum remnants of the dynamic motion of the electron around the nucleus in the classical description. States with higher energy may be reached for small intervals of time as allowed by the Heisenberg uncertainty principle. The instantaneous dipoles that form in this way may give rise to image charges, if the metal surface responds sufficiently fast to that perturbation. . Thus we may expect the interaction energy of a real atom near a metal surface to maintain the same power-law dependence on the surface-atom separation, but with a different overall factor.

III. THE LIFSHITZ FORMULA

The problem of finding the potential energy of an atom in its ground state when it is placed near a metal surface was addressed by Zaremba and Kohn [17]. They used linear response theory to evaluate the response function of the metal electron to the external electrical perturbation induced by the atomic charges. For a jellium model, they found the potential energy at lowest order in $1/R_0$ to be given by

$$E^{(2)}=-\frac{\hbar^2}{4\pi R_0^3}\int_0^\infty du\,\alpha(iu)\left[\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\right] \tag{7}$$

where $\alpha(iu)$ and $\epsilon(iu)$ are the atomic polarizability and the bulk dielectric function of the metal at the imaginary frequency iu. A proper definition of the metal-surface plane, where the origin of the R_0 coordinate is placed, makes the coefficient of next term $1/R_0^4$ of the expansion to vanish. The expression (7) is a special case of the polarization force found by Lifshitz [18].

Equation (7) contains both results of the preceding section, as will be shown below. The atomic polarizability of the ground state can be expressed in terms of the oscillator strength f_{0n} and frequency ω_{0k} of the transition from the ground to the kth excited state as

$$\alpha(\omega)=\frac{e^2}{m_e}\sum_{k=1}^{N}\frac{f_{0k}}{\omega_{0k}^2-\omega^2} \tag{8}$$

where the sum is carried out over all allowed transitions, e is the electron charge, and m_e is the electron mass.

The jellium model, on the other hand, allows for a single oscillation frequency, namely, the plasma frequency ω_p. The Drude model of metals brings the following dependence of the dielectric function on ω_p:

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}\ . \tag{9}$$

Replacing $\epsilon(iu)$ in (7) by Eq. (9), we find

$$E^{(2)}-\frac{\hbar^2}{4\pi R_0^3}\int_0^\infty du\,\alpha(iu)\left[\frac{\omega_{\rm SP}^2}{u^2+\omega_{\rm SP}^2}\right] \tag{10}$$

in which the surface-plasmon frequency $\omega_{\rm SP}=\omega_p/\sqrt{2}$ has been introduced. If we compare Eq. (10) with the expression for the van der Waals potential that gives rise to the London dispersion force between two atoms in their ground state,

$$E_L^{(2)}=-\frac{3\hbar}{\pi R^6}\int_0^\infty \alpha_1(iu)\alpha_2(iu)du \tag{11}$$

where $\alpha_i(iu)$ represents the polarizability of the ith atom evaluated at the imaginary frequency iu, we see that $\omega_{\rm SP}^2/(\omega_{\rm SP}^2+u^2)$ plays the role of the metal-surface polarizability.

Let us consider now the contribution of a single transition ω_{0k} to the atomic polarizability. The integral in (10) may be carried out to get

$$E_k^{(2)}=-\frac{\hbar^2e^2}{4\pi m_eR_0^3}\int_0^\infty du\frac{f_{0k}}{\omega_{0k}^2+u^2}\frac{\omega_{\rm SP}^2}{u^2+\omega_{\rm SP}^2}$$

$$=-\frac{\hbar^2e^2}{8m_eR_0^3}\frac{\omega_{\rm SP}}{\omega_{0k}}\frac{f_{0k}}{\omega_{0k}+\omega_{\rm SP}}\ . \tag{12}$$

Since $f_{0k}=2m_e\omega_{0k}|\langle\mathbf{r}_0\rangle_{0k}|^2/(3\hbar^2)$, where $\langle\mathbf{r}_0\rangle_{0k}$ is the matrix element of the separation $\mathbf{r}_0$ between the positive and negative charges in the dipole, the term $E_k^{(2)}$ can also be written as

$$E_k^{(2)}=-\frac{e^2}{12R_0^3}\frac{\omega_{\rm SP}/\omega_{0k}}{1+\omega_{\rm SP}/\omega_{0k}}|\langle\mathbf{r}_0\rangle_{0k}|^2\ , \tag{13}$$

so that we get the potential energy $E^{(2)}$

$$E^{(2)}=\sum\nolimits_k E_k^{(2)}=-\frac{e^2}{12R_0^3}\sum_k\frac{\omega_{\rm SP}/\omega_{0k}}{1+\omega_{\rm SP}/\omega_{0k}}|\langle\mathbf{r}\rangle_{0k}|^2\ . \tag{14}$$

We now take the limit $\omega_{\rm SP}/\omega_{0k}\to\infty$ in (14), and use the closure relation

$$\sum_k|\langle\mathbf{r}_0\rangle_{0k}|^2=\sum_k\langle\mathbf{r}_0\rangle_{0k}\cdot\langle\mathbf{r}_0\rangle_{k0}=\langle r_0^2\rangle_{00} \tag{15}$$

(which holds true since $\langle\mathbf{r}_0\rangle_{00}=0$ for a spherically symmetric ground state or for a state with definite parity) to find

$$E^{(2)}=-\frac{e^2}{12R_0^3}\langle r_0^2\rangle_{00}\ . \tag{16}$$

On the other hand, using the relations

$$\langle\xi_0^2\rangle_{00}=\langle\eta_0^2\rangle_{00}=\langle\zeta_0^2\rangle_{00}=\tfrac{1}{3}\langle r_0^2\rangle_{00} \tag{17}$$

for the expectation values of ξ_0^2, η_0^2, ζ_0^2 in the ground state, we find that Eq. (2) may also be cast in the form

$$\langle V_{a\text{-}s}\rangle=-\frac{e^2}{12R_0^3}\langle r_0^2\rangle_{00}\ . \tag{18}$$

Thus Eq. (10) reduces to (16) and becomes identical with (2), in the limit $\omega_{\rm SP}/\omega_{0k}\to\infty$, i..e., when the surface plasma oscillation frequency is much larger than the frequency of any atomic transition that enters Eq. (7) with an appreciable oscillator strength, so that the metal surface can respond instantaneously to the electrical perturbation caused by quantum fluctuations. The ratio $\omega_{\rm SP}/\omega_{0k}$ can also be written as τ_k/τ_s, where τ_s is the response time of the metal surface to external electrical perturbations and τ_k is the characteristic fluctuation time during which the atom may access the kth excited state, as allowed by the Heisenberg uncertainty principle.

If, on the contrary, the metal surface reacts slowly to any perturbation, then $\omega_{\rm SP}/\omega_{0k}$ is vanishingly small, and the coefficient of the $1/R_0^3$ term goes to zero, according to the result obtained from Eq. (6).

The surface-plasmon frequency usually lies in the ultraviolet, but may be in the visible region for metals with large Wigner-Seitz radius r_s. Thus the assumption $\omega_{\mathrm{SP}}/\omega_{0k} \to \infty$ does not hold in many instances; for these the full dynamical behavior of the electron gas must be taken into account.

IV. THE INTERACTION ENERGY FOR AN EXCITED ATOM

The interaction between a metal surface and an atom in a stationary state (not necessarily the ground state) causes the energy level of the latter to be shifted. These level shifts were studied in the past by several authors [19–21]. We address this problem from a somewhat different point of view, by extending the procedure followed by Zaremba and Kohn [17] to treat the interaction energy of excited atoms with metal surfaces, within the framework of the jellium model. Our treatment, however, does not include effects from the radiation field emitted by the atom.

We derive now the interaction energy of an excited atom located near a metal surface, under the assumption that the separation of the atom from the surface is too large for the electronic wave functions to overlap. Denoting the initial states of the atomic and metallic electrons by $|\psi_0^a\rangle$ and $|\psi_0^m\rangle$, respectively, and the interaction potential by V_{am}, we write the interaction energy in second-order perturbation theory as

$$E^{(2)}=-\sum_{\substack{i\neq 0,\\ j\neq 0}}\frac{|\langle\psi_0^a\psi_0^m|V_{am}|\psi_i^a\psi_j^m\rangle|^2}{(E_i^a-E_0^a)+(E_j^m-E_0^m)}\,, \tag{19}$$

where the sum is over all atomic (ψ_i^a) and metallic (ψ_j^m) states, excluding the respective initial states, and E_i^a (E_j^m) is the energy of the ith (jth) atomic (metallic) state.

If both ψ_0^a and ψ_0^m referred to ground states, the two terms in the denominator of (19) would always be positive. Then, one could use the formula

$$\frac{1}{A_i+B_j}\equiv\frac{1}{\pi}\int_{-\infty}^{+\infty}du\,\frac{A_i}{u^2+A_i^2}\,\frac{B_j}{u^2+B_j^2} \tag{20a}$$

with $A_i=E_i^a-E_0^a$, $B_j=E_j^m-E_0^m$, to factor (19) into a product of two terms, one dependent only on the atomic parameters, and the other on the metallic parameters. This procedure has been followed by Zaremba and Kohn [17] to derive the interaction energy (7) reported above. This second-order energy is always negative for the composite ground state. There are positive contributions at small distances [15], which are first-order effects. We are not considering these. In our case, at least one of the A_i's is negative, because of our choice of the atomic initial state. Let i_0 denote an atomic state for which A_{i_0} is negative. Then Eq. (20a) changes to

$$\frac{1}{A_{i_0}+B_j}=\frac{1}{\pi}\int_{-\infty}^{+\infty}du\,\frac{A_{i_0}}{u^2+A_{i_0}^2}\,\frac{B_j}{u^2+B_j^2}+\frac{2B_j}{B_j^2-A_{i_0}^2}\,. \tag{20b}$$

This can be seen either by evaluating the integral in (20b), or by considering $1/(A_{i_0}+B_j)$ as a complex function of the complex variable A_{i_0}. When $\mathrm{Re}\,A_{i_0}>0$, this function is given by the integral (20a). When $\mathrm{Re}\,A_{i_0}<0$, the function is still given by the integral

$$\frac{1}{A_{i_0}+B_j}=\frac{1}{\pi}\int_C du\,\frac{A_{i_0}}{u^2+A_{i_0}^2}\,\frac{B_j}{u^2+B_j^2} \tag{20c}$$

but the integration path must be distorted as shown in Fig. 1. The last term in Eq. (20b) is the sum of the contributions to the integral (25c) coming from the poles at iA_{i_0} and $-iA_{i_0}$.

The first term on the right-hand side of Eq. (20b) leads to the same formula for the interaction energy as given by (7), with the ground-state polarizability $\alpha(iu)$ replaced by the $\alpha_e(iu)$ polarizability of the excited state in which the atom was initially prepared.

The second term on the right-hand side of Eq. (20b) adds a contribution to the interaction energy for each atomic state whose energy is lower than the energy of the initial state. For simplicity, we assume the atom to be prepared in the first excited state, so that one term only need be considered. Moreover, we assume that the excited state is coupled to the ground state through electric dipole interaction. Then the interaction energy reads

$$\begin{aligned}E^{(2)}&=-\frac{\hbar^2}{4\pi R_0^3}\int_0^\infty du\,\alpha_e(iu)\left[\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\right]\\&\quad-2\sum_{j\neq 0}\frac{B_j}{B_j^2-A_0^2}|\langle\psi_0^a\psi_0^m|V_{am}|\psi_i^a\psi_j^m\rangle|^2\\&\equiv-\frac{\hbar^2}{4\pi R_0^3}\int_0^\infty du\,\alpha_e(iu)\left[\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\right]+E_e^{(2)}\,,\end{aligned} \tag{21}$$

where $A_0=E_0-E_g$ is the excitation energy of the initial state relative to the ground state. The interaction potential V_{am} is expressed in terms of the electron density operators $n^a(\mathbf{r})$ and $n^m(\mathbf{r})$ for the atomic and metallic electron density distribution, respectively, defined by

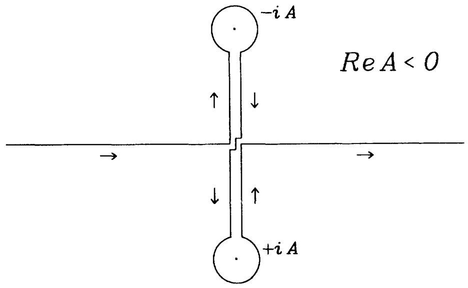

FIG. 1. The integral in Eq. (25c) must be performed along this path in the complex domain to get the correct result $1/(A_i+B_j)$ when $\mathrm{Re}\,A_i<0$.

$$n^{a,m}(\mathbf{r})|\mathbf{r}_{a,m}\rangle = e\delta(\mathbf{r}-\mathbf{r}_{a,m})|\mathbf{r}_{a,m}\rangle \ . \tag{22}$$

The two distributions are coupled by the Coulomb interaction

$$V_{am} = \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r}-\mathbf{r}') n^a(\mathbf{r}) n^m(\mathbf{r}') \tag{23}$$

with

$$v(\mathbf{r}-\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{24}$$

We shall denote by **x** the position of the atomic electron relative to the (fixed) atomic nucleus position **R**, so that $\mathbf{r}_a = \mathbf{R}+\mathbf{x}$, and drop **R** from the expressions when not needed. Then we have

$$E_e^{(2)} = -2 \sum_{j\neq 0} \frac{B_j}{B_j^2 - A_0^2} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{x} \int d\mathbf{x}' v(\mathbf{R}+\mathbf{x}-\mathbf{r}) v(\mathbf{R}+\mathbf{x}'-\mathbf{r}') \langle \psi_0^a | n^a(\mathbf{x}) | \psi_g^a \rangle \\ \times \langle \psi_g^a | n^a(\mathbf{x}') | \psi_0^a \rangle \langle \psi_0^m | n^m(\mathbf{r}) | \psi_j^m \rangle \langle \psi_j^m | n^m(\mathbf{r}') | \psi_0^m \rangle \ . \tag{25}$$

By using the identity

$$\frac{B_j}{B_j^2 - A_0^2} = \frac{i}{2} \left[\frac{1}{i(A_0+B_j)} - \frac{1}{i(A_0-B_j)} \right] \tag{26}$$

one finds

$$\frac{B_j}{B_j^2 - A_0^2} \langle \psi_0^m | n^m(\mathbf{r}) | \psi_j^m \rangle \langle \psi_j^m | n^m(\mathbf{r}') | \psi_0^m \rangle = \frac{i}{2\hbar} \int_0^\infty dt\, e^{-i\omega_{0g}t} [e^{-i\omega_j t} \langle \psi_0^m | n^m(\mathbf{r}) | \psi_j^m \rangle \langle \psi_j^m | n^m(\mathbf{r}') | \psi_0^m \rangle \\ + e^{i\omega_j t} \langle \psi_0^m | n^m(\mathbf{r}') | \psi_j^m \rangle \langle \psi_j^m | n^m(\mathbf{r}) | \psi_0^m \rangle] \tag{27}$$

where the dummy variables **r** and **r**′ have been exchanged in the last term in square brackets. The energies $\hbar\omega_j$ and $\hbar\omega_{0g}$ are given by $E_j^m - E_g^m$ and $E_0^a - E_g^a$.

By introducing the operator $n^m(\mathbf{r},t)$ in the interaction representation

$$n^m(\mathbf{r},t) = e^{iH_0^m t/\hbar} n^m(\mathbf{r}) e^{-iH_0^m t/\hbar} \tag{28}$$

with H_0^m denoting the unperturbed Hamiltonian of the metal electron system, we may also carry out the summation over the intermediate states $|\psi_j^m\rangle$ to get

$$-2 \sum_j \frac{B_j}{B_j^2 - A_0^2} \langle \psi_0^m | n^m(\mathbf{r}) | \psi_j^m \rangle \langle \psi_j^m | n^m(\mathbf{r}') | \psi_0^m \rangle \\ = -\frac{i}{\hbar} \int_0^\infty dt\, e^{-i\omega_{0g}t} \langle \psi_0^m | [n^a(\mathbf{r},t), n^a(\mathbf{r}')] | \psi_0^m \rangle \ , \tag{29}$$

where [,] indicates the commutator of two operators. The summation over j in Eq. (29) has been extended to include the ground state, $j=0$, since it does not contribute to the expectation value of the commutator. The right-hand side of Eq. (29) is the linear susceptibility of the metal system at the frequency ω_{0g}, and will be denoted by $\chi(\mathbf{r},\mathbf{r}',\omega_{0g})$.

We now expand the Coulomb potential (24) in the two-dimensional Fourier series

$$v(\mathbf{r}-\mathbf{r}) = \frac{1}{L^2} \sum_{\mathbf{K}_h} \left[\frac{2\pi}{K_h} \right] e^{i\mathbf{K}_h\cdot(\mathbf{r}-\mathbf{r}')} e^{-K_h|z-z'|} \tag{30}$$

valid for periodic boundary conditions with spatial periodicity L in both x and y directions. The vector $\mathbf{K}_n$ in Eq. (30) has nonzero components only along the x and y axes, and assumes discrete values

$$\mathbf{K}_h \equiv \left[\frac{2\pi n_{h,x}}{\pi}, \frac{2\pi n_{h,y}}{\pi}, 0 \right] \tag{31}$$

with $n_{x,x}$ and $n_{y,x}$ integers.

Then, using (29) and (30), the interaction energy (25) becomes

$$E_e^{(2)} = \frac{1}{L^4} \sum_{\mathbf{K},\mathbf{K}'} \left[\frac{2\pi}{K} \right] \left[\frac{2\pi}{K'} \right] e^{i\mathbf{R}\cdot(\mathbf{K}-\mathbf{K}')} e^{-R_0(K+K')} \int d\mathbf{x} \int d\mathbf{x}' G(\mathbf{x},\mathbf{x}') e^{i(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathbf{x}} e^{-i(\mathbf{K}'+i\hat{\mathbf{k}}K')\cdot\mathbf{x}'} \\ \times \int d\mathbf{r} \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega_{0,g}) e^{-i(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathbf{r}} e^{i(\mathbf{K}'-i\hat{\mathbf{k}}K')\cdot\mathbf{r}'} \tag{32}$$

where we have introduced the function $G(\mathbf{x},\mathbf{x}')$ defined as

$$G(\mathbf{x},\mathbf{x}') = e^2 [\psi_0^a(\mathbf{x}) \psi_g^a(\mathbf{x}')]^* \psi_g^a(\mathbf{x}) \psi_0^a(\mathbf{x}') \tag{33}$$

where $\hat{\mathbf{k}}$ is the unit vector along the z axis.

In the jellium model of the metal all physical parameters display translational invariance for any displacement parallel to the metal surface. Therefore we may write

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi(\rho-\rho', z_m, z_m', \omega) \tag{34}$$

with $\boldsymbol{\rho}\equiv\mathbf{r}_{\perp}$, $\boldsymbol{\rho}'\equiv\mathbf{r}'_{\perp}$. Then we have

$$\int d\mathbf{r}\int d\mathbf{r}'\chi(\mathbf{r},\mathbf{r}',\omega_{0,g})e^{-i(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathbf{r}}e^{i(\mathbf{K}'-i\hat{\mathbf{k}}K')\cdot\mathbf{r}'}$$

$$=4\pi^2\int_{-\infty}^{+\infty}dz_m\int_{-\infty}^{+\infty}dz'_m e^{K(z_m+z'_m)}\int d(\boldsymbol{\rho}-\boldsymbol{\rho}')e^{-i\mathbf{K}\cdot(\rho-\rho')}\chi(\boldsymbol{\rho}-\boldsymbol{\rho}',z_m,z'_m,\omega_{0,g})\delta(\mathbf{K}-\mathbf{K}') \qquad (35)$$

and the interaction energy becomes

$$E_e^{(2)}=\frac{1}{L^2}\sum_{\mathbf{K}}\left[\frac{2\pi}{K}\right]^2 e^{-2KR_0}|(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathcal{P}|^2\int_{-\infty}^{+\infty}dz_m\int_{-\infty}^{+\infty}dz'_m e^{K(z_m+z'_m)}\int d(\boldsymbol{\rho}-\boldsymbol{\rho}')e^{-i\mathbf{K}\cdot(\rho-\rho')}\chi(\boldsymbol{\rho}-\boldsymbol{\rho}',z_m,z'_m,\omega_{0,g})\ , \qquad (36)$$

where we have performed the integration over the atomic electron coordinates $\mathbf{x}$ and $\mathbf{x}'$ in the electric dipole approximation and indicated the atomic dipole moment by $\mathcal{P}$,

$$\mathcal{P}=|e|\int d\mathbf{x}\langle\psi_0^a|\mathbf{x}|\psi_g^a\rangle\ . \qquad (37)$$

The integrals over the metal electron coordinates may be given a simple physical interpretation. To this aim, let us suppose that a planar charge distribution is placed at a distance R_0 from the metal surface, and consider its Fourier component

$$\rho^{\text{ext}}(\mathbf{r},t)=\theta_{q,\omega}\delta(z-R_0)e^{i\mathbf{q}\cdot\rho}e^{i\omega t}\ , \qquad (38)$$

where $\theta_{q,\omega}$ is a constant and $\mathbf{q}\equiv(q_x,q_y,0)$. This charge distribution produces an electrical perturbation whose potential is given by

$$\Phi^{\text{ext}}(\mathbf{r},t)=\frac{2\pi}{q}\theta_{q,\omega}e^{-q|z-R_0|}e^{i\mathbf{q}\cdot\rho}e^{i\omega t} \qquad (39)$$

as can be seen immediately, since (39) satisfies the Poisson equation $\nabla^2\Phi^{\text{ext}}=-4\pi\rho^{\text{ext}}$. In turn, the electrostatic potential couples to the charge distribution in the metal via the interaction potential

$$\hat{V}=\int d\mathbf{r}\, n^m(\mathbf{r})\Phi^{\text{ext}}(\mathbf{r},t)\ . \qquad (40)$$

The variation of the charge distribution inside the metal can be calculated by means of linear response theory. We obtain

$$\begin{aligned}\Delta\langle n^m(\mathbf{r},t)\rangle&\equiv\langle n^m(\mathbf{r})\rangle_{V\neq0}-\langle n^m(\mathbf{r})\rangle_{V=0}\\&=-\frac{i}{\hbar}\int d\mathbf{r}\,\Phi^{\text{ext}}(\mathbf{r}',t)\int_0^t d\tau\langle[n^m(\mathbf{r},\tau),n^m(\mathbf{r}')]\rangle e^{-i\omega\tau}\\&\equiv\int d\mathbf{r}'\Phi^{\text{ext}}(\mathbf{r}',t)\chi(\mathbf{r},\mathbf{r}',\omega)\ .\end{aligned} \qquad (41)$$

Because of the spatial invariance of the metal wave functions for any displacement parallel to the metal surface, Eq. (41) can also be written as

$$\Delta\langle n^m(\mathbf{r},t)\rangle=\delta\bar{n}_0(z,\mathbf{q},\omega)(\theta_{q,\omega}e^{-qR_0}e^{i\mathbf{q}\cdot\rho+i\omega t}) \qquad (42)$$

with

$$\delta\bar{n}_0(z,\mathbf{q},\omega)=\frac{2\pi}{q}\int_{-\infty}^{+\infty}dz'e^{qz'}\int d\mathbf{u}\,e^{-i\mathbf{q}\cdot\mathbf{u}}\chi(\mathbf{u},z,z',\omega)\ . \qquad (43)$$

The change of the metal electron distribution due to the external electrical perturbation (41) has the same spatial and time dependence as the inducing charge, vanishes exponentially for large distances of the inducing charge (as long as $q\neq0$), and depends on the metal parameters through the factor $\delta\bar{n}_0(z,\bar{q},\omega)$.

In terms of $\delta\bar{n}_0(z,\mathbf{q},\omega)$, Eq. (41) may be written as

$$E_e^{(2)}=\frac{1}{L^2}\sum_{\mathbf{K}}\left[\frac{2\pi}{K}\right]^2 e^{-2KR_0}|(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathcal{P}|^2$$

$$\times\frac{K}{2\pi}\int_{-\infty}^{+\infty}dz_m e^{Kz_m}\delta\bar{n}_0(z_m,\mathbf{K},\omega_{0,g})\ . \qquad (44)$$

The charge distribution (42) induced by the external charge is concentrated on the metal surface, i.e., in a tiny region δz of space around $z_m=0$. The exponential function e^{Kz_m} in Eq. (44) may be approximated by 1 in this interval, unless $K\sim1/\delta z$ or larger. Now the contribution to $E_e^{(2)}$ is vanishingly small for K large, provided that $Z\gg\delta z$. Thus, in this limit, we may replace the integral in Eq. (44) by $\int dz_m\delta\bar{n}_0(z_m,0,\omega_{0,g})$. On the other hand, from the continuity equation

$$\frac{\partial\Delta\langle n^m(\mathbf{r},t)\rangle}{\partial t}+\nabla\cdot\mathbf{j}=0 \qquad (45)$$

in the limit $K\rightarrow0$, we obtain

$$j_0(z,0,\omega)=-i\omega\int_{-\infty}^{z}dz\,\delta\bar{n}_0(z,0,\omega)+j_0(-\infty,0,\omega) \qquad (46)$$

where $j_0(z,0,\omega)$ is the z component of the current $\mathbf{j}$, defined by

$$\mathbf{j}(z,t)=\theta_{0,\omega}j_0(z,0,\omega)e^{i\omega t}\hat{\mathbf{k}}\ . \qquad (47)$$

Since at $z=+\infty$, i.e., well outside the metal, the current is zero, we get

$$j_0(-\infty,0,\omega)=i\omega\int_{-\infty}^{+\infty}dz\,\delta\bar{n}_0(z,0,\omega)\ . \tag{48}$$

The mean electric field also has the form

$$\mathbf{E}(z,t)=\theta_{0,\omega}E_0(z,0,\omega)e^{i\omega t}\hat{\mathbf{k}} \tag{49}$$

and its value in the bulk is related to the charge distribution by Gauss's law,

$$E_0(-\infty,0,\omega)=-2\pi\left[\int_{-\infty}^{+\infty}dz\,\delta\bar{n}_0(z,0,\omega)+1\right]\ . \tag{50}$$

Notice that the last term in Eq. (50) comes from the external charge distribution (41), evaluated in the $q\rightarrow 0$ limit.

Ohm's law provides the link between the current and the mean electric field in the bulk,

$$j_0(z,0,,\omega)=\sigma(0,\omega)E_0(z,0,\omega) \tag{51}$$

where $\sigma(0,\omega)$ is the bulk conductivity at frequency ω.

Using (48), (50), and (51), we find

$$\int_{-\infty}^{+\infty}dz\,\delta\bar{n}_0(z,0,\omega)=-\frac{2\pi\sigma(0,\omega)}{i\omega+2\pi\sigma(0,\omega)}\ . \tag{52}$$

The bulk conductivity $\sigma(0,\omega)$ and the dielectric constant $\epsilon(0,\omega)$ are related by

$$\epsilon(0,\omega)=1-\frac{4\pi i\sigma(0,\omega)}{\omega}\ . \tag{53}$$

Using Eqs. (53) and (9), we find

$$\int_{-\infty}^{+\infty}dz\,\delta\bar{n}_0(z,0,\omega)=\frac{\omega_{\mathrm{SP}}^2}{\omega^2-\omega_{\mathrm{SP}}^2} \tag{54}$$

where once more the surface-plasmon frequency is $\omega_{\mathrm{SP}}=\omega_p/\sqrt{2}$.

The integral on the left-hand side of Eq. (54), multiplied by $\theta_{0,\omega}e^{i\omega t}$, represents the total amount of charge induced by the external perturbation at or near the metal surface. The integral may be either negative or positive, depending on the sign of the denominator in (54). In particular, if the oscillator frequency ω is lower than the surface-plasmon frequency ω_{SP}, the total induced charge is of opposite sign to the inducing charge. In the limit $\omega\rightarrow 0$, the integral in Eq. (54) tends to -1, so that the total induced charge is equal in magnitude and opposite in sign to the inducing charge, as expected from classical electrostatics. On the other hand, if $\omega>\omega_{\mathrm{SP}}$, the total induced charge has the same sign as the inducing charge, and tends to 0 when the oscillator frequency grows to very large values. These conclusions agree well with the discussion in Sec. III of the role played by ω_{SP} in determining the interaction potential of charged particles with metal surfaces.

We may now evaluate the interaction energy (44) by evaluating the summation over $\mathbf{K}$. Since $|(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathcal{P}|^2$ is of the order of K^2, we may approximately set

$$|(\mathbf{K}+i\hat{\mathbf{k}}K)\cdot\mathcal{P}|^2\sim K^2|\bar{\mathcal{P}}|^2\ . \tag{55}$$

Replacing the summation by integration over K_x and K_y, we find

$$E_e^{(2)}=\frac{1}{4R_0^3}|\bar{\mathcal{P}}|^2\frac{\omega_{\mathrm{SP}}^2}{\omega_{0,g}^2-\omega_{\mathrm{SP}}^2}\ . \tag{56}$$

A similar expression was derived in Ref. [21] for the atomic frequency shift induced by surface polaritons, by using a different method based on a two-level model. The $E_e^{(2)}$ term in the interaction energy (21) appears if the atom is prepared in an excited state. It keeps the same $1/R_0^3$ dependence on the atom-surface separation, but has two novel features. First, it may be either negative or positive, depending on whether the atomic transition frequency is lower or greater than the plasmon oscillation frequency; thus the atom may be attracted or repelled by the metal surface. This feature is also common to the van der Waals potential of two interacting atoms: while the two atoms attract each other if they are in the ground state, they may mutually repel if they are excited. The second feature is that the extra term (56) is resonant in character, and has a dispersive behavior. This means that the extra term may become dominant if the atomic transition frequency is close to the plasmon frequency, and a net repulsion of the atom from the metal surface may occur.

Notice, however, that Eq. (56) is not valid at resonance, $\omega_{0,g}=\omega_{\mathrm{SP}}$, since we have neglected the relaxation rate of the plasma oscillation in deriving Eq. (54) from Eq. (53).

V. CONCLUSIONS

We have discussed the interaction energy of an atom with a metal surface, in the simplifying assumption that the metal charge distribution may be described by the jellium model. The atom is assumed to be prepared in a stationary state, which may be the ground state or an excited state. The interaction energy differs in the two cases by a term that displays a resonant character and has a dispersive behavior as the energy of the initial atomic state is increased.

The interaction energy depends on the atom-metal surface separation R_0 with an inverse power law, $1/R_0^3$. For atoms in the ground state, the interaction is always attractive in character, and may go from a dipole–virtual-dipole interaction, if the response time of the metal electrons is fast compared to any characteristic time of the atomic transitions, down to low values for slow response time. For atoms in an excited state, the interaction energy is expressed by the same formula as for the ground, except for an extra term for each energy level lower than, and dipole coupled to, the initial state. In this case, repulsion as well as attraction may set in, depending on whether the atomic transition frequency is close to or far from the plasmon frequency.

The relevant parameter of the metal system is in both cases the surface-plasmon frequency, whose inverse characterizes the response time of the metal electrons to the external perturbation produced by the atom located near the metal surface.

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