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Attractive atom-surface interaction: Saturation effects in positronium

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The attractive interaction between an atom and a surface is examined within the general framework of a self-energy formalism. Considered in detail are deviations from the van der Waals force due to recoil effects and finite velocity of the particle. Calculations for positronium moving near a metal surface show that for such systems recoil and velocity effects are significant even at very low energies.

The dispersion force or van der Waals attraction between an atom or molecule and a surface is the dominant interaction at large separation. Near the surface there are velocity-dependent correction terms but these are generally non-negligible for atoms only if the speed is very high, corresponding to a light atom with energy in the keV range.[1] In this paper we consider the attractive interaction between an atom and a surface using a general self-energy formalism and one result is to obtain the velocity-dependent corrections for a particle moving parallel or perpendicular to the surface.

However, if one considers the similar problem of a bare charge q, where the analog of the van der Waals force is the classical image potential $q^2/4z$, it is known that the potential saturates to a constant near the surface. This saturation, which has recently been experimentally observed for electrons,[2] is due to two effects; the finite velocity of the charge coupled with the consequent inability of the surface excitations to follow this motion,[3] and recoil of the charge as it exchanges virtual quanta with the surface.[4] Even for a very slow electron the recoil effects cause saturation of the potential, and deviations from the classical image behavior for an electron persist several angstroms away from the surface.[5]

The importance of finite velocity and recoil effects in charge-surface interactions suggests that it would be of interest to consider similar effects in a very-low-mass atomic system, namely positronium, which has been the object of much recent experimental activity.[6] Of particular interest are the recent experiments demonstrating the production of thermal energy positronium as a result of the interaction of low-energy positrons with surfaces.[7] Using a general self-energy approach we have considered the interaction of positronium with a surface and find deviations from the van der Waals potential that extend to a separation of several angstroms even for thermal energies. Quantum-mechanical recoil saturation effects appear near the surface.

The energy shift due to an atom interacting with a surface is given to lowest nonvanishing order in perturbation theory by

$$\Delta E_0=\sum_{\gamma}(\langle 0|V|\gamma\rangle\langle\gamma|V|0\rangle)/(E_0-E_\gamma+i\delta) \ . \qquad (1)$$

A state vector $|\gamma\rangle$ of the noninteracting system is written as the product $|n\rangle|l\rangle|\phi_{\vec{k}}|\rangle$, of a surface state vector of energy E_n, an atomic state vector with energy $\epsilon_0+\epsilon_l$, and the translational state vector with energy $e_{\vec{k}}$, respectively. The total energy shift can also be written as the integral of the spatially dependent self-energy $\Sigma_0(\vec{r})$ weighted by the probability density of the atom in its original state,

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

A comparison of this form with the perturbation expansion leads directly to a systematic generalization of the space-dependent self-energy to all orders of perturbation theory,[5] and from Eq. (1) the lowest nonvanishing term is

$$\Sigma_0(\vec{r})=\sum_n\sum_l\sum_{\vec{k}}\frac{\langle\phi_{\vec{k}}|\vec{r}\rangle}{\langle\phi_0|\vec{r}\rangle}\times\frac{\langle\phi_0,0,0|V|n_1l_1\phi_{\vec{k}}\rangle\langle l,n|V|0,0\rangle}{E_0+\epsilon_0+e_0-E_n-(\epsilon_0+\epsilon_l)-e_{\vec{k}}+i\delta} \ . \qquad (3)$$

The interaction operator V is developed by starting from the Hamiltonian Φ for an element of charge q interacting with the surface modes,

$$\Phi(\vec{r})=\sum_{\vec{Q}}\Gamma_Q\exp(-Q|z|+i\vec{Q}\cdot\vec{R})(a^\dagger_{\vec{Q}}+a_{-\vec{Q}}) \ . \qquad (4)$$

This model neglects interactions of the charge with the bulk but such effects have been demonstrated to be non-negligible only very near (~ 1 Å) to the surface.[8] Capital letters $(\vec{Q},\vec{R})$ are used for vectors parallel to the surface and lower case is used for perpendicular components (q,z). The coupling constant $\Gamma_Q^2=Ze^2\pi\hbar\omega_Q/L^2Q$, where L^2 is the surface area. 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 and ϵ_∞ is the dielectric constant at high frequencies.

An atom can be considered as a charge density $\rho(\vec{r})$ consisting of a nuclear charge Ze and an electron cloud. The atomic interaction Hamiltonian V becomes

$$V(\vec{r})=\int d\vec{r}\,'\rho(\vec{r}\,')\Phi(\vec{r}+\vec{r}\,') \ . \qquad (5)$$

The multipole expansion of Eq. (5) begins with the dipole term

$$V=\sum_{\vec{Q}}\Gamma_Q[\vec{p}\cdot\vec{\mu}(\vec{Q})]\exp(-Q|z|+i\vec{Q}\cdot\vec{R})(a^\dagger_{\vec{Q}}+a_{-\vec{Q}}) \ , \qquad (6)$$

where $\vec{\mathrm{p}}$ is the atomic displacement operator.

For a plane-wave basis set the self-energy of Eq. (3) becomes

$$\Sigma_0(z) = -\sum_n \sum_l \sum_{\vec{Q},k} \frac{2Q\Gamma_Q^2 |\langle 0|\vec{\mathrm{p}}|l\rangle \cdot \vec{\mu}(\vec{\mathrm{Q}})|^2 \exp[-Q|z| + i(k-k_0)z]}{[Q^2+(k-k_0)^2][\hbar^2(K_0^2+k_0^2-(\vec{\mathrm{Q}}+\vec{\mathrm{K}}_0)^2-\vec{\mathrm{k}}^2)/2m - \hbar\omega_Q - \epsilon_l]} \langle 0|a^\dagger_{\vec{Q}} + a_{-\vec{Q}}|n\rangle \langle n|a_{\vec{Q}} + a^\dagger_{-\vec{Q}}|0\rangle \ , \tag{7}$$

where conservation of parallel momentum requires $\vec{\mathrm{Q}} = \vec{\mathrm{K}} - \vec{\mathrm{K}}_0$. For simplicity we consider a metal surface with a surface plasmon frequency $\omega_s = \omega_p/\sqrt{2}$ assumed dispersionless for the remainder of the paper. With the surface temperature equal to zero, the self-energy reduces to the following integral form:

$$\Sigma_0(z) = -\frac{Ze^2Q_s^2 e^{-ik_0z}}{6\pi^2} \sum_l |\langle l|\vec{\mathrm{p}}|0\rangle|^2 \int_{-\infty}^{\infty} dk \int_0^\infty dQ \int_0^{2\pi} d\phi \frac{Q^3 \exp(-Q|z| + ikz)}{Q^2+(k-k_0)^2}$$

$$\times (Q^2 + 2QK_0\cos\phi + k^2 - k_0^2 + Q_s^2 + q_l^2 - i\delta)^{-1} \ , \tag{8}$$

where $Q_s^2 = 2m\omega_s/\hbar$, $q_l^2 = 2m\epsilon_l/\hbar^2$ and we have made the assumption that the atomic excitation energies ϵ_l are independent of the azimuthal quantum number. Equation (8) is the self-energy of an atom a distance z from the surface, originally moving with a velocity $\vec{v} = \hbar(\vec{\mathrm{K}}_0, k_0)/m$. The factors Q^2 and k^2 in the denominator are the manifestation of full three-dimensional recoil.

A general solution to Eq. (8) in terms of tabulated functions is not a simple matter but there are a number of special cases which illustrate quite nicely the behavior of the self-energy. First we consider an atom moving perpendicularly toward the surface, i.e., $\vec{\mathrm{K}}_0 = 0$ and $k_0 = mv_\perp/\hbar$. The integral over azimuthal angles is trivial and the integral over k can be carried out as a contour integral in the complex plane. The final result is

$$\Sigma_0(z) = (-Ze^2Q_s^2/3)(d^2/dz^2) \sum |\langle l|\vec{\mathrm{p}}|0\rangle|^2 [f(|z|(Q_s^2+q_l^2)/k_0) - i\,\mathrm{sgn}(z) g(|z|(Q_s^2+q_l^2)/k_0)] + \Sigma'(z) \ , \tag{9}$$

where

$$f(x) = \int_0^\infty dt\, e^{-xt}/(t^2+1), \quad g(x) = \int_0^\infty dt\, te^{-xt}/(t^2+1) \tag{10}$$

are the auxiliary functions to the sine and cosine integrals.[9] The additional term $\Sigma'(z)$ decays exponentially away from the surface as $z^{-4}\exp[-(Q_s^2+q_l^2-k_l^2)^{1/2}|z|]$ and is given explicitly by

$$\Sigma'(z) = -\frac{Ze^2Q_s^2 e^{ik_0z}}{3} \sum_l |\langle l|\vec{\mathrm{p}}|0\rangle|^2 \int_0^\infty dQ\, Q^3 \frac{\exp[-zQ - z(Q^2+Q_s^2+q_l^2-k_0^2)^{1/2}]}{(Q^2+Q_s^2+q_l^2-k_0^2)^{1/2}}$$

$$\times [2k_0^2 + Q_s^2 + q_l^2 - 2ik_0(Q^2+Q_s^2+q_l^2-k_0^2)^{1/2}]^{-1} \ . \tag{11}$$

In the asymptotic region we have

$$\mathrm{Re}\Sigma_0(z) \underset{z\to\infty}{\longrightarrow} (Ze^2Q_s^2/12|z^3|) \sum_l |\langle l|\vec{\mathrm{p}}|0\rangle|^2/(Q_s^2+q_l^2) \{1 - [12k_0^2/z^2(Q_s^2+q_l^2)^2] + \cdots\} \ , \tag{12}$$

$$\mathrm{Im}\Sigma_0(z) \underset{z\to\infty}{\longrightarrow} \mathrm{sgn}(z)(Ze^2Q_s^2k_0/4z^4) \sum_l |\langle l|\vec{\mathrm{p}}|0\rangle|^2/(Q_s^2+q_l^2)^2 \{1 - [20k_0^2/z^2(Q_s^2+q_l^2)^2] + \cdots\} \ . \tag{13}$$

The first term of Eq. (12) is the well known Lifshitz expression for the van der Waals potential[10] and the correction term varies as the square of the velocity. These expressions are good for either low or high energy, with a high-energy particle being defined as one with sufficient speed to create a surface excitation. At low energies, the imaginary part of $\Sigma_0(z)$ is conservative, and even at high energies the asymptotic expression is conservative since the inelastic contributions decay exponentially away from the surface.[11]

To obtain the case of an atom moving parallel to the surface we set $k_0 = 0$ and $\vec{\mathrm{K}}_0 = m\vec{v}_\parallel/m$. The final result can be expressed in terms of the modified Bessel function $I_0(p)$ and modified Struve function $L_0(p)$ (Ref. 12) as

$$\Sigma_0(z) = -(Ze^2Q_s^2\pi/48K_0)(d^2/dz^2) \sum_l |\langle l|\vec{\mathrm{p}}|0\rangle|^2 [I_0(|z|(Q_s^2+q_l^2)/K_0) - L_0(|z|(Q_s^2+q_l^2)/K_0)] + \Sigma''(z) \ , \tag{14}$$

where $\Sigma''(z)$ is a term which decays exponentially away from the surface as $\exp[-|z|(Q_s^2+q_l^2)^{1/2}]z^{-4}$,

$$\Sigma''(z)=\frac{Ze^2Q_s^2}{6\pi}\sum_l |\langle l|\vec{p}|0\rangle|^2\int_0^\infty dQ\int_0^{2\pi}d\phi\, Q^3\exp[-zQ-z(Q^2+2QK_0\cos\phi+Q_s^2+q_l^2)^{1/2}]$$
$$\times(Q_s^2+q_l^2+2QK_0\cos\phi)^{-1}(Q^2+2QK_0\cos\phi+Q_s^2+q_l^2)^{-1}\ . \tag{15}$$

The asymptotic form is similar to Eq. (12) above, consisting of the Lifshitz term with a correction in $(v_{\parallel}/z)^2$,

$$\Sigma_0(z)\underset{z\to\infty}{\longrightarrow}-(Ze^2Q_s^2/12|z|^3)\sum_l[|\langle l|\vec{p}|0\rangle|^2/(Q_s^2+q_l^2)]\{1+[6K_0^2/z^2(Q_s^2+q_l^2)^2]+\cdots\}\ . \tag{16}$$

The correction term for an atom with a finite speed is valid for both low and high energies. It was first obtained by Ferrell and Ritchie[1] and has the opposite sign from the correction term in the perpendicular case of Eq. (12). This implies that there is an incident angle for which this first-order correction term vanishes. A further interesting point is that all recoil effects decay exponentially away from the surface in both the perpendicular and parallel motion cases [they are included in the terms $\Sigma'(z)$ or $\Sigma''(z)$, respectively]. This shows that the Ferrell-Ritchie correction in Eq. (16), originally obtained in a recoil-free approximation, remains unchanged by recoil effects.

A final special case of interest is that of an atom moving very slowly near the surface. In the limit $k_0=K_0\to 0$ the self-energy can be expressed exactly in terms of incomplete Γ functions and exponential integrals,

$$\Sigma_0(z)=-(Ze^2Q_s^2/12|z|^3)\sum_l[|\langle l|\vec{p}|0\rangle|^2/(Q_s^2+q_l^2)]$$
$$\times\{1-\tfrac{1}{2}\Gamma[3,|z|(Q_s^2+q_l^2)^{1/2}]+(3z^2/2)(Q_s^2+q_l^2)\exp[-|z|(Q_s^2+q_l^2)^{1/2}]$$
$$-\tfrac{1}{2}|z|^3(Q_s^2+q_l^2)^{3/2}[E_2(|z|(Q_s^2+q_l^2)^{1/2})-E_4(|z|(Q_s^2+q_l^2)^{1/2})]\}\ . \tag{17}$$

The separation between the Lifshitz term and the exponentially decaying recoil effects is clearly seen in the asymptotic form

$$\Sigma_0(z)\underset{z\to\infty}{\longrightarrow}-(Ze^2Q_s^2/12|z|^3)\sum_l[|\langle l|\vec{p}|0\rangle|^2/(Q_s^2+q_l^2)]\{1-4!\exp[-|z|(Q_s^2+q_l^2)^{1/2}]/[(Q_s^2+q_l^2)^{1/2}|z|]\}\ . \tag{18}$$

A result of further interest is the limit near the surface,

$$\Sigma_0(z)\underset{z\to 0}{\longrightarrow}=-(Ze^2Q_s^2/8)\sum_l|\langle l|\vec{p}|0\rangle|^2[1/|z|-16(Q_s^2+q_l^2)^{1/2}/9]\ . \tag{19}$$

The classical $1/z^3$ surface singularity saturates to the weaker $1/z$ behavior as a result of the recoil motion due to the exchange of virtual quanta with the surface.

The same velocity-independent $1/z$ term of Eq. (19) is obtained near the surface even if the atom is moving with a finite speed, as can be shown from Eqs. (9) or (14). This contrasts with the analogous problem of charge-surface interaction where the saturation value of the potential at the surface is velocity dependent.[5]

In order to get an idea of the importance of these finite velocity and recoil effects near the surface, we plot in Fig. 1 the ratio of $\mathrm{Re}\,\Sigma_0(z)$ from Eq. (9) to the asymptotic or Lifshitz term for slowly moving positronium. The polarization sums over atomic quantum states were carried out using the oscillator strengths for a hydrogen-like atom given by Sugiura.[13] The remaining parameter is the surface plasmon frequency and two curves are shown for the widely varying cases of Al and Cs, where $\hbar\omega_s$ is 11.2 and 2.5 eV, respectively. It is seen that deviations from the semiclassical behavior start several angstroms from the surface at distances where the positronium electron cloud is not substantially overlapping the surface region; in fact, for 2-eV positronium near a Cs surface the ratio is still 0.99 at a separation of 10 Å.

The effects due to recoil are dominated mainly by the decaying exponential with separation, with a range given by

$$(Q_s^2+q_l^2)^{1/2}=[2m(\hbar\omega_s+\epsilon_l)]^{1/2}/\hbar\ ,$$

which in this case has a value of approximately 2 Å^{-1}. The range parameter is decreased somewhat by the finite velocity as seen in Fig. 1 but clearly recoil saturation to a $1/z$ dependence for $\Sigma_0(z)$ occurs very near to the surface. However, very near the surface the present calculation is not valid for a variety of reasons, notably bulk electron interactions become non-negligible, higher-order multipoles

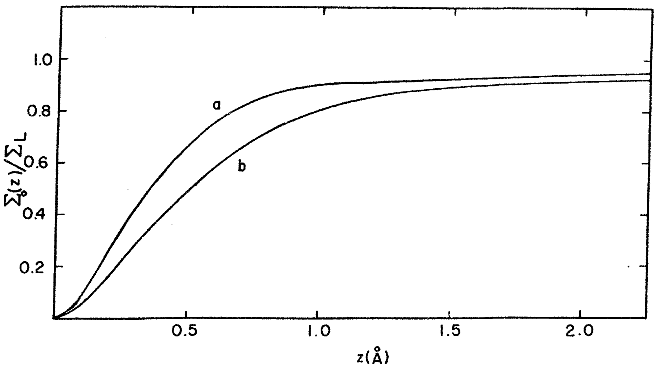

FIG. 1. Ratio of the total atom-surface self-energy $\Sigma_0(z)$ to the semiclassical Lifshitz term Σ_L as a function of distance z from the surface. Shown are two cases of slow positronium moving perpendicularly to a metal surface. Curve a, 4-eV Ps and Al with $\hbar\omega_s=11.2$ eV, and curve b, 2-eV Ps and Cs with $\hbar\omega_s=2.5$ eV.

become important, and eventually the multipole expansion itself breaks down. Nevertheless, regardless of where the present approximations break down the particle-surface interaction is the ultimate result of the exchange of virtual quanta, and with each exchange the atom must recoil. The effect of this recoil is to weaken the potential interaction. The calculations presented have demonstrated the range of such recoil saturation effects and Fig. 1 shows that they can begin to become apparent when the approximations used here are still reasonably valid.

It is perhaps surprising that the corrections for finite velocity are clearly important even for very-low-energy positronium. Since these corrections remain of the same form for all incident energies, high-velocity positronium will exhibit considerable deviation from the van der Waals $1/z^3$ attraction.

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