THE ATTRACTIVE INTERACTION BETWEEN AN ATOM AND A SURFACE

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Using a general self-energy formalism, we examine the interaction between an atom and a surface. Considered in detail are deviations from the Van der Waals force due to recoil and finite velocity of the particle. Calculations for positronium near a metal surface show that for such systems, recoil and velocity effects are significant even at very low energies. We also examine the mechanisms for energy exchange with the surface and calculations show that single quantum events do not always dominate the exchange rates.

The dispersion force or Van der Waals attraction between an atom or molecule and a surface is the dominant interaction at large separation. In this work we consider this interaction using a general self-energy formalism. As a result, we are able to obtain the velocity dependent corrections to the force on a particle moving parallel or perpendicular to the surface; we investigate saturation effects on the interaction potential due to recoil upon exchange of virtual surface quanta, and we calculate the probability of energy loss of the particle due to creation of surface optical phonons or surface plasmons.

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

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

A state $|\gamma\rangle$ of the noninteracting system is written as the product $|n\rangle|l\rangle|\phi_k|\rangle$ 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_k, respectively. The total energy shift can also be written as the integral of the spatially dependent self-energy $\Sigma_0(r)$ weighted by the probability density of the atom in its original state

$$\Delta E_0 = \int dr\langle\phi_0|r\rangle\Sigma(r)\langle r|\phi_0\rangle. \tag{2}$$

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 [1], and from eq. (1) the lowest non-vanishing term is

$$\Sigma_0(r) = \sum_n \sum_l \sum_k \frac{\langle\phi_k|r\rangle}{\langle\phi_0|r\rangle} \frac{\langle\phi_0,0,0|V|n,l,\phi_k\rangle\langle l,n|V|0,0\rangle}{E_0 + \epsilon_0 + e_0 - E_n - (\epsilon_0 + \epsilon_l) - e_k + i\delta}. \tag{3}$$

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

$$\Phi(r) = \sum_Q \Gamma_Q \exp(-Q|z| + iQR)(a_Q^+ + a_Q). \tag{4}$$

This model neglects interactions of the charge with the bulk, but such effects have been demonstrated to have non-negligible effects only very near (~ 1 Å) to the surface [2]. Capital letters (Q,R) are used for

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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

$$\beta = \left[(\epsilon_0 - 1)/(\epsilon_0 + 1)\right] - \left[(\epsilon_\infty - 1)/(\epsilon_\infty + 1)\right],$$

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 $\rho(r)$ consisting of a nuclear charge Ze and an electron cloud. The atomic interaction Hamiltonian V becomes

$$V(r) = \int dr' \rho(r')\Phi(r + r'). \tag{5}$$

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

$$V = \sum_Q \Gamma_Q [\hat{p} \cdot \mu(Q)] \exp(-Q|z| + iQ \cdot R)(a_Q^+ + a_{-Q}), \tag{6}$$

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

For a plane wave basis set, and assuming a metal surface with a dispersionless surface plasmon frequency $\omega_s = \omega_p/\sqrt{2}$, the self-energy of eq. (3) becomes

$$\Sigma_0(z) = -\frac{Ze^2 Q_s^2 e^{-ik_0 z}}{6\pi^2} \sum_l |\langle l|\hat{p}|0\rangle|^2 \int_\infty^\infty dk \int_0^\infty dQ \int_0^{2\pi} d\phi \frac{Q^3 \exp(-Q|z| + ikz)}{Q^2 + (k - k_0)^2}$$

$$\times \left\{ Q^2 + 2QK_0\cos\phi + k^2 - k_0^2 + Q_s^2 + q^2 - i\delta \right\}^{-1}, \tag{7}$$

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. Eq. (7) is the self-energy of an atom at distance z from the surface, originally moving with a velocity $v = \hbar(K_0, k_0)/m$. The factors Q^2 and q^2 in the denominator are the manifestation of full three-dimensional recoil.

A general solution to eq. (7) 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. As an example we consider an atom moving perpendicularly toward the surface, i.e. $K_0 = 0$, 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

$$\Sigma_0(z) = (-Ze^2 Q_s^2/3)(d^2/dz^2)\Sigma_l|\langle l|\hat{p}|0\rangle|^2\left\{ f(|z|[Q_s^2 + q_l^2]/k_0) \right.$$

$$\left. - i\,\text{sgn}(z)g(|z|[Q_s^2 + q_l^2]/k_0)\right\} + \Sigma'(z), \tag{8}$$

where

$$f(x) = \int_0^\infty dt\, e^{-tx}/(t^2 + 1); \quad g(x) = \int_0^\infty dt\, t\, e^{-xt}/(t^2 + 1), \tag{9}$$

are the auxiliary functions to the sine and cosine integrals [3]. The additional term $\Sigma'(z)$ decays exponentially away from the surface as $Z^{-4} \exp[-\sqrt{Q_s^2 + q_l^2 - k_0^2}|z|]$. In the asymptotic region we have

$$\text{Re}\Sigma_0(z) \underset{z \to \infty}{\to} -(Ze^2 Q_s^2/12|z^3|)\sum_l|\langle l|\hat{p}|0\rangle|^2/(Q_s^2 + q_l^2)$$

$$\times \left\{ 1 - [12k_0^2/z^2(Q_s^2 + q_l^2)^2] + \cdots \right\}, \tag{10}$$

$$\text{Im}\Sigma_0(z) \underset{z \to \infty}{\to} \text{sgn}(z)(Ze^2 Q_s^2 k_0/4z^4)$$

$$\times \sum_l|\langle l|\hat{p}|0\rangle|^2/(Q_s^2 + q_l^2)^2\left\{ 1 - [20k_0^2/z^2(Q_s^2 + q_l^2)^2] + \cdots \right\}. \tag{11}$$

The first term of eq. (10) is the well known Lifshitz expression for the Van der Waals potential [4] and the correction term varies as the sqaure 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 [5].

For the case of an atom moving parallel to the surface, we obtain similar expressions to eqs. (10) and (11) which contain the velocity dependent corrections obtained earlier by Ferrell and Ritchie [6].

A final special case of interest is that of an atom moving very slowly near the surface. In the limit $k_0 = K_0 \rightarrow 0$ the self-energy can be expressed exactly in terms of incomplete Γ functions and exponential integrals. For simplicity we exhibit here only the limiting cases.

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

$$\Sigma_0(z) \underset{z \rightarrow \infty}{\rightarrow} -\left(Ze^2 Q_s^2 / 12|z|^3 \right) \sum_l \left[|\langle l|\hat{p}|0\rangle|^2 / \left(Q_s^2 + q_l^2 \right) \right]$$

$$\times \left\{ 1 - 4! \, \exp\left(-|z|\sqrt{Q_s^2 + q_l^2} \right) / \left[\sqrt{Q_s^2 + q_l^2} \, |z| \right] \right\}. \tag{12}$$

A result of further interest is the limit near the surface

$$\Sigma_0(z) \underset{z \rightarrow 0}{\rightarrow} = -\left(Ze^2 Q_s^2 / 8 \right) \sum_l |\langle l|\hat{p}|0\rangle|^2 \left\{ 1/|z| - 16\sqrt{Q_s^2 + q_l^2}/9 \right\}. \tag{13}$$

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 and is independent of velocity.

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 Re $\Sigma_0(z)$ from eq. (8) 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 [7]. 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 $\sqrt{Q_s^2 + q_l^2} = \sqrt{2m(\hbar\omega_s + \epsilon_l)}/\hbar$, which in this case has a value of approximately 2 Å. 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
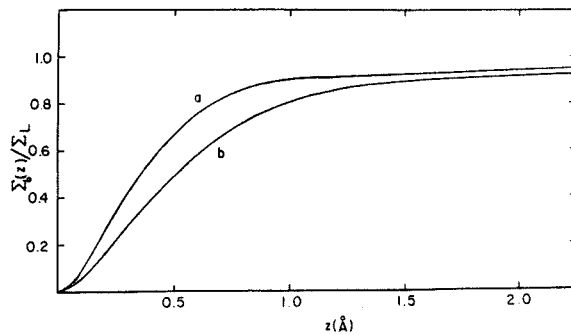

Fig. 1. Ratio of the total atom–surface self-energy $\Sigma_0(z)$ to the semi-classical Lifshitz term Σ_L as a function of distance z from the surface. Two cases of slow positronium moving perpendicularly to a metal surface are shown: (a) 4 eV Ps and Al with $\hbar\omega_s = 11.2$ eV and (b) 2 eV Ps and Cs with $\hbar\omega_s = 2.5$ eV.

calculation is not valid for a variety of reasons, notably bulk electron interactions become non-negligible, higher order multipoles 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 in the same form for all incident energies, high velocity positronium will exhibit considerable deviation from the Van der Waals $1/z^3$ attraction.

To obtain the total inelastic transition rates one can start from the generalized golden rule formula

$$R_i = (2\pi/\hbar)\sum_f |T_{fi}|^2 \delta(E_f - E_i). \tag{14}$$

However, this can also be related to the spatially dependent self-energy as above in eq. (2)

$$R_i = \int \langle i|r\rangle R_i(r)\langle r|i\rangle \mathrm{d}r, \tag{15}$$

where $R_i(r) = 2\,\mathrm{Im}\,\Sigma_0(r)/\hbar$ and $\mathrm{Im}\,\Sigma_0(r)$ is the non-conservative imaginary part of the spatial self-energy.

We have carried out extensive calculations for the exchange of surface optical phonons or surface plasmons using the same atom–surface interaction model as in eqs. (5) and (6). Since the atom is assumed to have a kinetic energy below the atomic excitation level, the lowest order contribution coming from the dipole potential of eq. (6) is a two phonon process. this corresponds to the T matrix of eq. (14) calculated to second order in the Born series, or equivalently to the $\mathrm{Im}\,\Sigma_0(r)$ coming from the fourth order term. If we again make the simplifying assumption that the surface optical phonon ω_Q is independent of Q we obtain a general expression for the total energy transfer, and the leading term in its asymptotic expansion is

$$R_2^D(z) \underset{z\to\infty}{\to} \beta^2\bigl(3Z^2 e^4 \pi m Q_s^{12}/128\hbar^3 K_0^5\bigr)\left|\sum_l |z_{l0}|^2/(Q_s^2 + q_l^2)\right|^2 \exp(-4|z|\delta)/|z|, \tag{16}$$

where $\delta = Q_s^2/2K_0$.

It is also possible to have a single phonon exchange process when the atom is very near the surface, so that its charge density actually begins to overlap. This is the monopole contribution, so called because it gives a contribution in the first order Born approximation just as in the case of a bare charge. To obtain this contribution we treat the atom as a point charge Ze surrounded by an electron cloud, $\rho(r) = \delta(r) - \rho_{el}(r)$ and each element of charge interacts with the potential of eq. (4) as shown in eq. (5). Using a hydrogen-like wave function with decay range $\alpha/2 = Z_{eff}/a_0$ (with Z_{eff} the effective charge and a_0 the Bohr radius), we obtain for the leading term in the monopole contribution

$$R_0(z) \underset{z\to\infty}{\to} \beta Z e^2 \alpha^4 Q_s^4 \sqrt{\pi} /\bigl(32\hbar K_0^2\bigr)\bigl(\delta^2 + \alpha^2\bigr)^{-7/4}|z|^{3/2}\exp\bigl(-2|z|\sqrt{\delta^2 + 4\alpha^2}\bigr). \tag{17}$$

The decay constant for this single quantum process $2\sqrt{\delta^2 + 4\alpha^2}$ includes the decay range α of the charge distribution. This indicates that the monopole process will be most important at small separation where the atomic charge density actually begins to overlap the surface.

The monopole process also contributes to the two quantum exchange rate through higher order terms in the perturbation series, but these contributions, as well as higher order single phonon events, are found to be negligible.

We have carried out a number of calculations for light atoms moving near ionic as well as metallic surfaces. The summation over atomic states appearing in eq. (16) can be related directly to the atomic polarizability and was evaluated using Pade approximants [8]. For example, a comparison of the single phonon transition rate R_0 to the two phonon rate as a function of distance between atom and surface leads

to the following observations. Except for the very smallest separations, the two quantum rate is always dominated by the dipole contribution of eq. (16). At distances in the neighborhood of 1 Å the single phonon exchange dominates the scattering, but at larger separation it is the dipole two-quantum process which is larger. This interesting result is characteristic of all energies except the smallest. Only when the atomic energy is comparable to the surface optical phonon energy is the single quantum exchange the largest term for all separation distances. However, under these conditions the exponential decay range parameter $\delta = Q_s^2/2K_0 = \omega_s/v_0$ is large and all transfer rates become negligibly small as z becomes appreciable.

The conclusions that we can draw from these inelastic calculations are similar for the exchange of surface optical phonons at ionic surfaces or surface plasmons at metal surfaces. The major contributors to the inelastic exchange rates are the single quantum monopole mechanism and the double quantum dipole process. All other processes examined seem to be reltively unimportant, and in particular, single quantum transfers arising from higher order terms in the perturbation expansion are totally negligible. The exchange rates decay exponentially with the separation z between surface and atom. As a function of particle energy there is a maximum in the exchange rate at approximately 5 or 10 times the surface optical phonon energy, or in the keV range for the exchange of surface plasmons.

An interesting result pertaining to both ionic and metal surfaces is that the single quantum process is not always dominant. At metal surfaces, the single plasmon process is the most important only in the low keV range and below, and the single quantum process is almost negligible at higher energies, where the transfer rates are at their maximum. For the exchange of surface optical phonons at ionic surfaces the effect is not so clear cut, but at particle energies which give the maximum inelastic transfer rates the single quantum process is most important near the surface, but for $z > 1.2-1.6$ Å, it is the two quantum process which dominates.

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