Particles, and Surfaces

R. H. RITCHIE

Health and Safety Research Division, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37831, and Department of Physics, University of Tennessee, Knoxville, Tennessee 37996

J. R. MANSON

Department of Physics, Clemson University, Clemson, South Carolina 29631

Abstract

A brief review is given of some applications of a novel form of self-energy theory. These include the image force experienced by an electron near a metal, the van der Waals interaction between two molecules, and the polarization potential of atomic scattering theory.

Introduction

In this review we will cover some of the basic ideas about the way a probe, which, for example, could be an electron or an atom in arbitrary motion, interacts with a polarizable body such as a condensed matter surface or another particle with internal structure. The approach is straightforward and unconventional. We will focus on the way the quantal properties of the probe affect these long-range interactions. The linear response function of the condensed matter system is assumed to be known. We employ an unfolding procedure [1] to obtain a spatial representation of the proper self-energy of the interacting probe.

Application of this straightforward formalism to describe the image potential of an electron approaching a surface and an electron tunneling through a barrier is made. A new treatment of the van der Waals interaction between two molecules and of the polarization potential in atomic scattering theory will be given. Finally, other applications of the formalism are discussed briefly.

Classical Long-range Interactions

A point charge Q located at distance z from a plane-bounded semiinfinite dielectric experiences an attractive force derivable from the electrostatic potential

$$V_{self} = -\left(\frac{\varepsilon - 1}{\varepsilon + 1}\right)\frac{Q^2}{4z} \tag{1}$$

Of course this potential arises because the charge polarizes the dielectric. This polarization charge reacts with the applied charge to yield the self-energy V_{self}.

CCC 0360-8832/87/210363-13$04.00

Similarly, a charge Q located at distance R from a molecule with isotropic polarizability α induces charge separation in the molecule and gives rise to a self-energy

$$V_{self}^{mol} = -\frac{\alpha Q^2}{R^4} \qquad (2)$$

in the asymptotic region.

Two molecules separated by a distance R interact with the asymptotic self-energy

$$V_{self}^{vdW} = -\frac{C}{R^6} \qquad (3)$$

where the constant C is determined by the molecular properties of the interacting systems. It is interesting that, although the R^{-6} dependence of V_{self}^{vdW} may be inferred by a simple classical argument, the value of the constant C must be found using quantum arguments.

The Self-energy of a Particle Interacting with a Target

Consider a projectile incident on a many-particle target. Suppose that in the absence of interactions with the target the projectile is described by the basis set $\{|\phi_n\rangle\}$ with eigenenergies $\{E_n\}$ and that a typical many-particle state vector of the target is $|\psi_n\rangle$ with eigenenergy E_n. The projectile may possess internal degrees of freedom. For simplicity, we write the interaction energy between the target and the projectile as $V = \Sigma\Sigma V(\mathbf{r}_i, \rho_j)$, where $\mathbf{r}_i$ is the coordinate of the ith particle making up the projectile, and ρ_j is the coordinate of the jth target particle.

Consider the Green function $G(\mathbf{r}, \mathbf{r}', E)$ of the projectile. As Feynman has shown [2], this is the probability amplitude for finding it at $\mathbf{r}$ if it is originally at $\mathbf{r}'$ and if it has energy E. The development of the Green function due to repeated scatterings on the target is represented in Figure 1a and symbolically as

$$G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \cdots \qquad (4)$$

where G_0 is the noninteracting Green function, and matrix multiplications are indicated. If we include purely elastic interactions in G_0 and hence account only for inelastic interactions in a perturbation series for G, then it may be represented as in Figure 1b. A Dyson summation [3] involving only proper self-energy diagrams may be carried out as indicated in Figure 1b and 1c, resulting in an explicit form for the exact Green function of a projectile interacting with a many-particle target, viz.,

$$G_k(E) = \{E - \varepsilon_k - \Sigma_k(E)\}^{-1} \qquad (5)$$

where $G(\mathbf{r}, \mathbf{r}', E) = \Sigma_k G_k(E)\phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')$ is the exact nonlocal Green function. For simplicity, we assume here that the projectile has no internal structure, and that exchange between the projectile and target may be neglected.
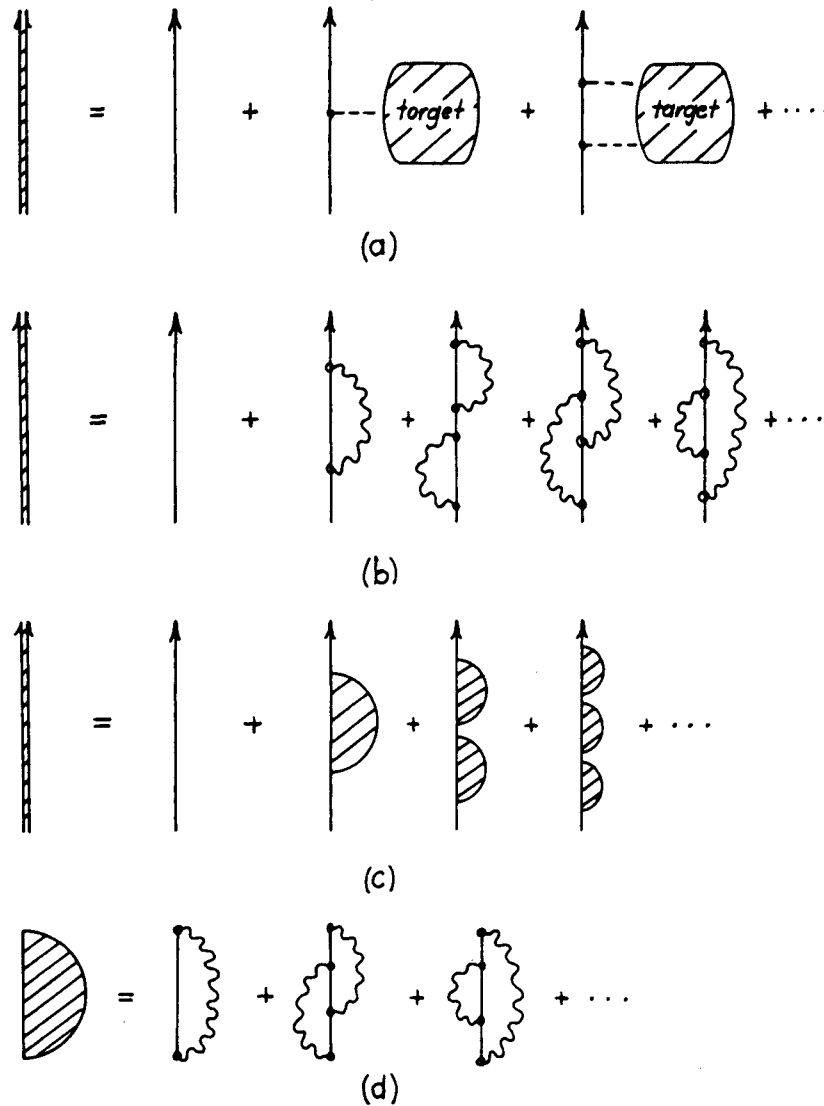
Figure 1. Feynman diagrams representing the interaction of a projectile with a many-particle target. For a detailed description, see the text.

One may show [1,4] that the spatial dependence of the projected (or local) self-energy may be written

$$
\Sigma_k(\mathbf{r}) = \sum_{nl} \frac{\langle 0|V|l\rangle \langle ln|V|k0\rangle}{(\varepsilon_k + E_0 - \varepsilon_n - E_l + i\delta)} \frac{\phi_n(\mathbf{r})}{\phi_k(\mathbf{r})} + \sum_{nl} \sum_{n'l'} \sum_{n''l''}
$$

$$
\cdot \frac{\langle 0|V|l\rangle \langle nl|V|n'l'\rangle \langle n'l'|V|n''l''\rangle \langle n''l''|V|k0\rangle}{(\varepsilon_k + E_0 - \varepsilon_n - E_l + i\delta)(\varepsilon_k + E_0 - \varepsilon_{n'} - E_{l'} + i\delta)(\varepsilon_k + E_0 - \varepsilon_{n''} - E_{l''} + i\delta)}
$$

$$
x \frac{\phi_n(\mathbf{r})}{\phi_k(\mathbf{r})} + \cdots \qquad (6)
$$

where only proper self-energy diagrams are to be included in the infinite sum represented in Eq. (6). The obvious abbreviation $|nl\rangle = |\phi_n\rangle |\psi_l\rangle$ is used and $|\phi_k\rangle |\psi_0\rangle$ is taken to be the state vector of the noninteracting system. The unfolding procedure

used to obtain this equation may be employed in a straightforward generalization to derive [4] an expression for the nonlocal self-energy.

The Classical Image Potential for a Model Solid

It was early recognized [5] that the image potential of a classical point charge located at a fixed distance from a metallic surface can be thought of as arising from a shift in the zero-point energy of the surface plasmon field. As is well-known, one represents the Hamiltonian of the noninteracting surface plasmon oscillators as

$$H_s = \sum_\kappa \hbar\omega_\kappa (b_\kappa^+ b_\kappa + \tfrac{1}{2}) \tag{7}$$

where b_κ is the annihilation operator for a surface plasmon with wave vector κ and frequency ω_κ. A perturbing charge Q located at distance z outside of the surface gives rise to the perturbation energy

$$H' = Q \sum_\kappa \Gamma_\kappa e^{i\kappa \cdot q - \kappa|z|}(b_\kappa + b_{-\kappa}^+) \tag{8}$$

where Q is located at (ρ, z), and $\Gamma_\kappa^2 = \pi\hbar\omega_s^2/Ak\omega_\kappa$. The surface area is A, and $\omega_\kappa = \omega_s$ as $\kappa \to 0$.

As is well known, a linear transformation of the operators b_κ and b_κ^+ puts the total Hamiltonian in the form $H_0 + H' = \sum_k \hbar\omega_\kappa (C_\kappa^+ C_\kappa + \tfrac{1}{2}) + \Delta E$, with the resulting shift in the zero point energy

$$\Delta E = -Q^2/4z \tag{9}$$

if dispersion of the surface plasmon eigenenergy is neglected. One may show that this expression is asymptotically correct even when dispersion is included. By choosing $\omega_\kappa^2 = \omega_s^2 + \alpha\kappa + \beta\kappa^2 + \hbar^2\kappa^4/4m^2$, Echenique et al. [6] have shown that the divergence displayed by ΔE in Eq. (9) is removed and that results are obtained that are equivalent to the use of a surface dielectric function that contains the effect of both surface plasmon modes and single-particle excitations. Mahan [7] has shown that the Hamiltonian H' of Eq. (8) may be generalized to describe interactions with surface optical phonons by multiplying Γ_κ^2 given in the line following Eq. (8) by the factor $(\varepsilon_0 - 1)/(\varepsilon_0 + 1) - (\varepsilon_\infty - 1)/(\varepsilon_\infty + 1)$, where $(\varepsilon_0, \varepsilon_\infty)$ is the (static, optical) dielectric constant of the insulator and by taking $\omega_\kappa = \omega_0$, the surface optical phonon frequency. Mahan [7] has also shown that interactions with bulk plasmon or optical phonon modes may be represented by the Hamiltonian

$$H' = \theta(z) \sum_k \Gamma_k e^{ik \cdot q} \sin(zk_z)(b_k + b_{-k}^+) \tag{10}$$

where $\Gamma_k^2 = 4\pi e^2\hbar\omega_p^2/\Omega_0 k^2\omega_k$ with an additional factor $(1/\varepsilon_\infty) - (1/\varepsilon_0)$, and $\omega_p^2 \to \omega_k \cdot \omega_{LO}$ in the case of bulk optical phonons. Also the sum over k_z is restricted to $k_z \geq 0$; $\theta(z)$ is the Heaviside step function, and Ω is the volume of the half space.

The Self-energy of an Electron Interacting with a Condensed Matter Surface

To lowest order.

$$\sum(\mathbf{r}) = \sum_{k,n} \frac{\langle\psi_0|V|\psi_n\rangle\langle nk|V|00\rangle}{(\varepsilon_0 + E_0 - \varepsilon_k - E_n + i\delta)} \frac{\phi_k(r)}{\phi_0(r)} \tag{11}$$

In general Σ is complex. The real part is just the exchange-correlation potential at large distances from the surface. The imaginary part contains the effects of real transitions (energy exchange between the probe and the target) and, except when a completely self-consistent projectile basis set is used, also consists of a portion describing energy transfers that are overall conservative.

There have been many papers dealing with the dynamic interaction of electrons with condensed matter surfaces. References 5–8 lists some that are pertinent to this topic

For purposes of orientation, we may employ a plane-wave basis set, i.e., $\phi_k(r) = e^{ik\cdot r}/\sqrt{\Omega}$, where Ω is the normalization volume. This allows one to examine the effects of projectile recoil in its most transparent aspect. One finds

$$\Sigma(z) = -\frac{e^2\bar\omega}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ikz} \int_0^{\infty} Q\, dQ \frac{e^{-Q|z|}}{k^2 + Q^2} \frac{1}{k^2 + Q^2 + 2Q\cdot\mathbf{\kappa}_0 + \bar\omega + 2kk_0} \tag{12}$$

where $\bar\omega = 2m\omega_s/\hbar$, and the state of the electron interacting with the surface is specified by the vector $(\mathbf{\kappa}_0, k_0)$. The integral over k may be carried out straightforwardly, and the integral over Q may be done numerically. The results may be written, for the case $\mathbf{\kappa}_0 = 0$, $k_0 = mv/\hbar$,

$$\mathrm{Re}\,\Sigma(z) = -\frac{e^2\omega_s}{2v}\left\{f\left(\frac{2\omega_s}{v}|z|\right) + \text{quantal correction}\right\} \tag{13}$$

$$Im\,\Sigma(z) = \frac{e^2\omega_s}{2v}\left\{g\left(\frac{2\omega_s}{v}|z|\right)\mathrm{sgn}(z) + \text{quantal correction}\right\} \tag{14}$$

Here $f(x) = \int_0^{\infty} dt\, e^{-xt}/(1 + t^2)$ and $g(x) = -df/dx$ are tabulated functions. When $k_0|z| \gg 1, k_0/\bar\omega^{1/2} > 1$

$$\mathrm{Re}\,\Sigma(z) = -\frac{e^2}{4|z|}(1 - v^2/2\omega_s^2 z^2) \tag{15}$$

$$\mathrm{Im}\,\Sigma(z) = \frac{e^2 v}{8\omega_s z^2}(1 - 3v^2/2\omega_s^2 z^2)\,\mathrm{sgn}(z) \tag{16}$$

and near the surface $k_0|z| \ll 1, k_0/\omega^{1/2} > 1$

$$\Sigma(z) = -\frac{\pi e^2\omega_s}{2v}\left\{1 - \frac{i}{\pi}\ln\left[1 - \frac{(1 - 2\hbar\omega_s/mv^2)^{1/2}}{1 - \hbar\omega_s/mv^2}\right]\mathrm{sgn}(z)\right\} \tag{17}$$

In the low-velocity limit $|k_0|/\omega_s^{1/2} \ll 1$

$$\Sigma(z) = -\frac{e^2}{4|z|}\{1 - \exp(-\bar{\omega}^{1/2}|z|) + \bar{\omega}^{1/2}|z|E_2(\bar{\omega}^{1/2}|z|)\}$$

$$\rightarrow -e^2\bar{\omega}^{1/2}/2 \quad \text{as} \quad z \rightarrow 0 \qquad (18)$$

showing that the divergence of the classical image potential at the surface is removed by quantal recoil of the electron.

In the case $k_0 = 0$, $\kappa_0 z \gg 1$, $\kappa_0/\omega^{1/2} \gg 1$, one recovers the expression [9]

$$\text{Im } \Sigma(z) = -\frac{e^2\omega_s}{2v}K_0\left(\frac{2\omega_s}{v}|z|\right)$$

The original paper of Manson and Ritchie [1] considered only the interaction with dispersionless surface plasmons. This is known to be a good approximation for non-relativistic particles and for points not too close to the surface. Recently Mahanty et al. [10] have used the Manson–Ritchie formalism, together with a hydrodynamical representation of the response function of a metal, to obtain results for the self-energy both interior and exterior to the metal. Figure 2 shows a plot of Re $\Sigma(z)$ for two different values of $k_0(\kappa_0 = 0)$ for an electron incident on the surface from vacuo.

Results for $\Sigma(z)$ from higher-order perturbation theory are under development [4].

It is of some interest to see how dependent the self-energy is on the form of the basis set used to represent the electron. In particular, an analytically manageable set
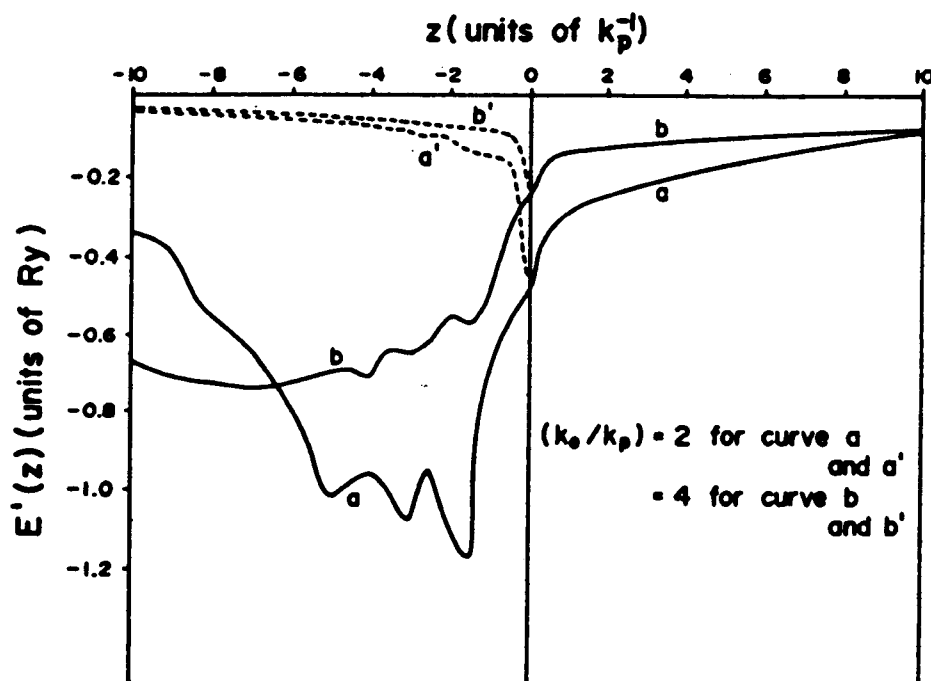

Figure 2. Real part of the self-energy, $E'(z) = \text{Re}\,\Sigma(z)$, for incident particle speeds far above the threshold speed. Here k_0 is the wave number of the incident particle, and k_p is the wave number of a particle with energy equal to the energy of the volume plasmon. The dashed curves represent the surface contributions to $E'(z)$, whereas the solid curves show the total $E'(z)$ functions.

with one or more bound states would be very useful. For simplicity and convenience, then, we choose the set having a single bound state with the form

$$\phi_0(\mathbf{r}) = \sqrt{p_0}\, e^{-p_0|z|} e^{i\kappa_0 \cdot \mathbf{q}}/\sqrt{A} \tag{20}$$

and whose other members lie in the continuum. The binding energy of this state is $\varepsilon_0 = \hbar^2 p_0^2/2m$, and, of course, the state has plane wave character for motion parallel with the surface. The surface itself is taken to lie in the plane $z = 0$. The continuum eigenfunctions are analytically very simple, can be shown to form a complete set with the bound state eigenfunctions, and facilitate all calculations.

The self-energy of an electron in the bound state may be derived in a straightforward manner. One finds [11] for the self-energy due to interaction with the surface modes, if $\kappa_0 = 0$,

$$\Sigma_0(z) = -\frac{m\omega_s e^2}{\pi\hbar} e^{p_0 z} \int_0^\infty \kappa e^{-\kappa z}\, d\kappa$$

$$\int_{-\infty}^\infty \cdot \frac{(p + ip)e^{ip|z|} p\, dp}{(p^2 + p_0^2)([p_0 + \kappa]^2 + p^2)(p^2 + p_0^2 + \kappa^2 + \bar{\omega} + i\delta)} \tag{21}$$

In a sense we may regard this as the self-energy of an electron tunneling through a barrier. Jonson [12] has approached the problem of the self-energy of a tunnelling electron from a different viewpoint.

Carrying out the integration over k we find,

$$\Sigma_0 = -\frac{e^2 \bar{\omega}}{2} \int_0^\infty \frac{d\kappa}{(\bar{\omega} - 2p_0\kappa)} \left\{ e^{-2\kappa|z|} - \frac{\kappa}{s - p_0} e^{-(\kappa+s-p_0)|z|} \right\} \tag{22}$$

where $s^2 = p_0^2 + \bar{\omega} + \kappa^2$. The second integral is due to recoil of the tunneling electron, decays exponentially away from the surface, and may be expressed as an exponential integral. The first term yields the classical image potential at large distances, viz., as $z \to \infty$.

$$\Sigma_0(z) = -\frac{e^2}{4|z|} \left\{ 1 + \frac{p_0}{|z|\bar{\omega}} + \frac{p_0^2}{z^2\bar{\omega}^2} + \cdots \right\} \tag{23}$$

As one expects, $\text{Im}(\Sigma_0) = 0$. Figure 3 shows a plot of the ratio of Re $\Sigma_0(z)$ to the classical limit $V_{Cl} = -e^2/4z$ as it depends on z for two different values of ω_s and for $p_0 = 1$ a.u. One sees that the correction may be important at fairly large distances when the surface plasmon energy is appropriate to, e.g., the alkali metals.

When $\kappa_0 \neq 0$, one may look for the contribution of the surface plasmon field to the effective mass of the bound particle. This is of current interest in the theory of image potential-induced surface states on solids. We find [11] that $m^*/m - 1 = \delta m/m \approx$ a few percent for $p_0 = 1$ a.u. Furthermore, it is interesting to evaluate the error incurred in invoking closure in the present calculation. Closure is invoked frequently, e.g., to determine the binding energy of a positron at a metal surface [13]. In the calculation of the energy shift of the bound state [11], the closure approximation leads to an error or $\sim 30\%$.
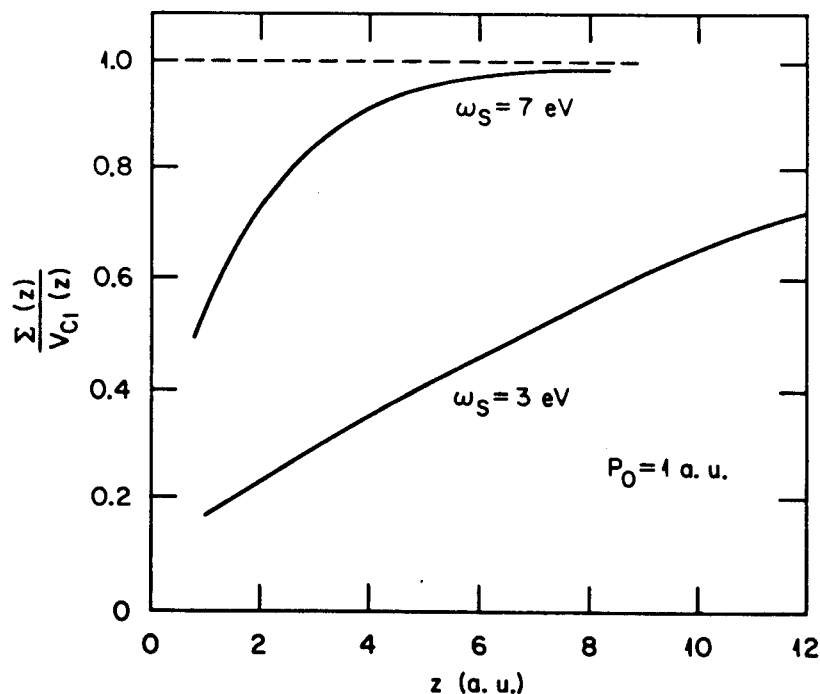
Figure 3. The image potential appropriate to a tunneling electron. $\Sigma(z)$ is the self-energy for an electron tunneling into vacuum from a metal characterized by the surface plasmon energy $\hbar\omega_s$. The attenuation length appropriate to the electron was taken to be 1 a.u. The classical image potential $V_{Cl}(z) = -1/4z$ in atomic units.

The formalism described above has also been used [14] to determine the self-energy of a positronium atom near a metal surface. We have shown [14] that for the dispersionless surface plasmon model of the metal, the self-energy of an atom moving parallel with the surface may be written

$$\text{Re} \sum(z) = -\frac{e^2\bar{\omega}}{12|z|^3} \sum_l \frac{|\langle l|\mathbf{r}|0\rangle|^2}{\bar{\omega} + q_l^2}\left[1 - \frac{6k_0^2}{z^2(\bar{\omega} + q_l^2)^2} + \cdots\right] \tag{24}$$

where $q_l^2 = 2m\epsilon_l/\hbar^2$, and ϵ_l is the excitation energy of the lth atomic state. The first term of Eq. (24) is the well-known Lifschitz [15] expression for the van der Waals potential between an atom and a metal, and the correction term agrees with that obtained by Ferrell and Ritchie [16] using a semiclassical approach. Figure 4 shows a plot of the ratio of $\Sigma(z)$ to the semiclassical Lifschitz term $\Sigma_L(z)$ as a function of distance from the surface for a positronium atom.

Interactions with Atomic Systems

The present self-energy approach has been used to study the polarization potential between an electron and an atom [17] and the van der Waals interaction between two atoms [18].

The long-range attractive interaction between an electron and an atom or molecule has its origin in the polarization of the collective system by the approaching electron. For atoms or molecules without permanent dipole moments, the force is entirely quantum mechanical in nature and is usually calculated in a development based
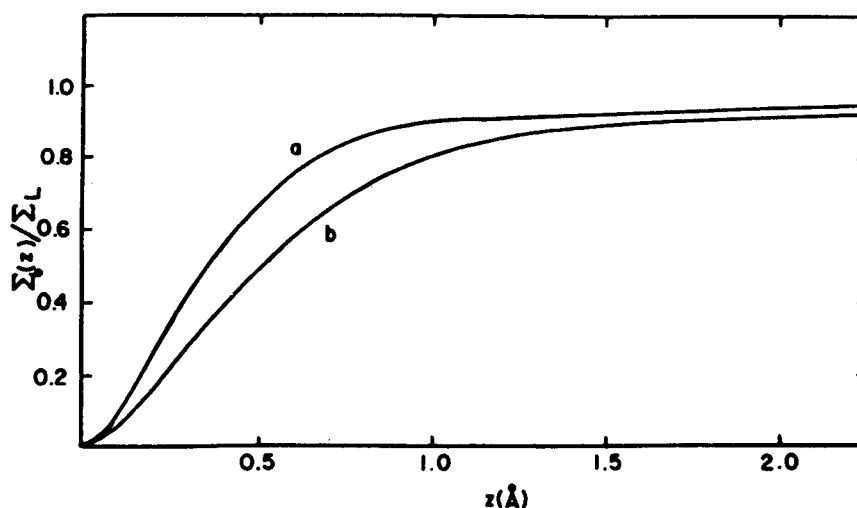
Figure 4. Ratio of the total atom-surface self-energy $\Sigma_0(z)$ to the semiclassical Lifshitz term Σ_L as a function of distance z from the surface. Shown are two cases of slow positronium moving perpendicularly to a metal surface: (a) 4 eV Ps and Al with $\hbar\omega_s = 11.2$ eV; (b) 2 eV Ps and Cs with $\hbar\omega_s = 2.5$ eV.

on perturbation theory. The potential is determined as a power series in the inverse distance $1/R$ between the electron and the atom, the lowest-order term being $1/R^4$ and the next term being $1/R^6$ and containing, in part, the nonadiabatic correction due to the inability of the atomic electron cloud to follow faithfully the motion of the electron.

When a virtual quantum is exchanged, both the atom and electron must recoil in order to conserve momentum. Even for the lightest atoms such as hydrogen or helium, the effect is negligibly small, but for the electron which has a very small mass, the recoil may cause measurable changes in the interaction. To lowest order in our formalism, the nonadiabatic effects appear as the velocity-dependent $1/R^6$ correction to the leading $1/R^4$ term. The effect of recoil of the scattering electron is to reduce the strength of the interaction, and, for small separation, it causes the $1/R^4$ interaction to saturate to a $1/R^2$ form. For simplicity, consider the interaction between an electron and a hydrogen atom, neglecting exchange interactions. Take the unperturbed system to be an isolated atom and an electron for which the corresponding eigenstate is the product of an atomic function and two momentum functions.

$$|j\rangle = u_f(\mathbf{r}) \frac{e^{i\kappa_0 \cdot \mathbf{R}_1}}{\sqrt{\Omega}} \frac{e^{i\mathbf{p}_0 \cdot \mathbf{R}_2}}{\sqrt{\Omega}} \tag{25}$$

with corresponding unperturbed energy

$$E_j = \epsilon_f + \kappa_0^2/2(m_1 + 1) + p_0^2/2 \tag{26}$$

where ϵ_f is the unperturbed atomic energy measured from the ground state, and atomic units are used throughout. If τ_1 and τ_2 are the vectors from the origin to the atomic nucleus and to the scattering electron, respectively, and if ρ_1 is the vector to the atomic electron, the perturbing potential is then

$$H' = \frac{1}{|\tau_1 - \tau_2|} + \frac{1}{|\rho_1 - \tau_2|} \tag{27}$$

The first nonvanishing contribution to the self-energy may be written

$$\sum (\mathbf{R}) = \sum_j \frac{\langle \mathbf{R} \mid \kappa \rangle}{\langle \mathbf{R} \mid 0 \rangle} \frac{\langle i|H'|j\rangle \langle f, \kappa|H'|0, 0\rangle}{\epsilon_i - \epsilon_j} \tag{28}$$

Evaluating the matrix elements by expanding to first order in the variable $\mathbf{r} = \rho_1 - \tau_1$ and neglecting terms in the velocity and recoil of the electron, we recover the familiar $1/R^4$ potential.

$$\sum_{Cl} (\mathbf{R}) = -\frac{1}{R^4} \sum_f \frac{|\langle f|z|i\rangle|^2}{\epsilon_f} \tag{29}$$

where z is the polarization operator parallel to the direction of $\mathbf{R}$.

However, because of the light mass of the electron, the neglect of its recoil in the denominator is valid only for asymptotically large values of R. This is most readily seen for the case in which the relative velocity of the system is small, i.e., $P_1 \to 0$. The self-energy can then be obtained in closed form and is

$$\sum (R) = -\frac{1}{R^2} \sum_f \frac{|\langle f|z|a\rangle|^2}{\epsilon_f} \left[\frac{1}{R^2} - \left(\frac{1}{R^2} + \frac{a}{R} \right) e^{-aR} \right] \tag{30}$$

where

$$a^2 = \frac{2(m_1 + 1)}{(m_1 + 2)} \epsilon_f$$

An interesting case that illustrates that recoil indeed causes a saturation of the self-energy is the limit $aR \to 0$ where we recover

$$\sum (R) \xrightarrow[aR \to 0]{} -\frac{1}{2R^2} \langle i|z^2|i\rangle \frac{2(m_1 + 1)}{m_1 + 2} \tag{31}$$

The effect of recoil as the system exchanges virtual quanta is to weaken or saturate the interaction to a $1/R^2$ form. The range of the effect is given by the parameter $a = \sqrt{2\epsilon_f}$, which can be several atomic units, as noted by estimating ϵ_f to be a typical atomic excitation energy. Although the limit of zero separation distance $(R = 0)$ is certainly beyond the range of validity of the approximations used to develop the general formula for $\epsilon(R)$, this is more than a mere academic exercise. It demonstrates that the inclusion of electronic recoil weakens the leading $1/R^4$ term (and will also act similarly on the high-order terms as well) at separation distances where the effect can become noticeable. Furthermore, this effect is not expressible in terms of a power series in $1/R$.

We have also studied Σ when the system has finite relative velocity. It is found that

$$\text{Re} \sum (R) = -\frac{1}{R^4} \sum_f \frac{|\langle f|z|i\rangle|^2}{\epsilon_f} \left\{ 1 - \frac{6P_i^2}{R^3\epsilon_f^2} + \cdots \right\} \tag{32}$$

The correction term, proportional to the initial energy, is recognized as the first velocity-dependent nonadiabatic contribution [19]. The leading term in the low-energy conservative imaginary part is proportional to the electron velocity and is given by

$$\text{Im} \sum (R) = \frac{2P_i}{R^5} \sum_f \frac{|\langle f|z|i\rangle|^2}{\epsilon_f^2} + \cdots \tag{33}$$

We should emphasize the importance of keeping full three-dimensional recoil in these calculations. It is considerably simpler to neglect the longitudinal component and retain only the two-dimensional recoil in the directions transverse to the axis of relative motion. If this is done, one obtains erroneous recoil corrections to the $1/R^4$ potential that can be expanded in $1/R$ in the asymptotic region. However, the correct three-dimensional treatment gives the much faster exponential decay of recoil effects.

Our formalism carries over easily [18] to the treatment of the long-range attractive interaction between two atoms, or the van der Waals force. It is only necessary to expand in terms of eigenfunctions for each atom that depends on both the internal coordinates and the center-of-mass coordinates. The dependence on the latter is naturally expressed in terms of momentum eigenfunctions. Defining the self-energy in a manner directly comparable with Eq. (28), we find the leading term in an expansion in powers of R^{-1} to be proportional to $1/R^6$ with a coefficient that agrees with that originally found by London [20]. London's calculation assumes that the atomic nuclei are infinitely massive.

When a virtual quantum is exchanged the atom must recoil in order to conserve momentum, but even for the lightest atoms such as hydrogen or helium the effect is negligibly small and is usually completely ignored. However, recent advances in the development of high-intensity thermal-energy positronium sources have led us to investigate the interaction of positronium with an atom, or with another positronium atom, situations in which recoil must be accounted for.

We find that for the interaction between positronium atoms significant deviations from the van der Waals $1/R^6$ form extend out to separations of 10 a.u., and for small R the self-energy saturates to a $1/R^4$ form. Further deviations are due to finite relative velocity of the two atoms, and for positronium these can be substantial for energies even as small as a few electronvolts.

Figure 5 shows the dependence of the ratio of $\sum (R)/\sum_L$, on R for two positronium atoms. Here $\sum_L$ is the London expression for the interaction energy, $\sum_L = \lim_{R \to 0} \sum (R)$. One sees that the recoil effect is appreciable at rather large separations here. Recoil can also affect the interaction between a positronium atom (PS) and a normal atom, although one expects the effect to extend to smaller distances. Shown in Figure 6 is the same ratio for PS interacting with several different systems. It is evident that recoil can significantly lower the interaction energy out to separations ~ 5 a.u. Although recoil is totally unimportant for ordinary atoms, we see that it can contribute to a significant weakening of the van der Waals potential in a system involving positronium. A finite relative velocity also weakens the interaction to a noticeable degree even for PS kinetic energies of less than a few electronvolts.
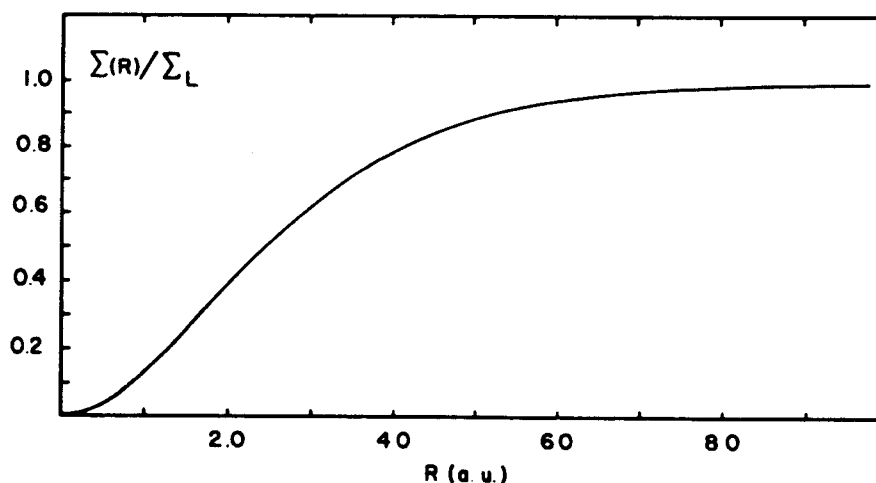
Figure 5.   The ratio of the interaction self-energy $\Sigma(R)$ to the London potential Σ_L for two positronium atoms as a function of distance R between the atomic centers.
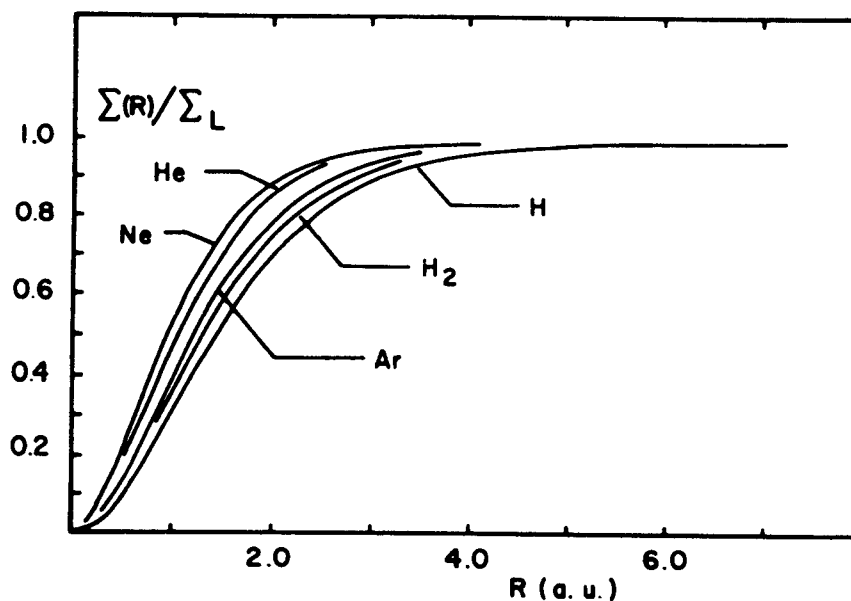

Figure 6.   The ratio of the interaction self-energy $\Sigma(R)$ to the London potential Σ_L for positronium a distance R from several different atomic or molecular species.

The formalism discussed here has been applied to a number of different physical problems in addition to those described above. For example, we have analyzed the energy loss of a slowly moving atom to surface optical phonon [21] when the lowest excitation energy of the atom is appreciably smaller than the surface optical phonon eigenenergy. We have also [22] discussed the wake potential generated in condensed matter using this approach to study quantal aspects of the potential for the first time.

Other applications presently under development include investigations of the properties of the hydrated electron in small water droplets [23], the characteristics of electrons tunneling from metals into the conduction band of insulators [24], higher-order perturbation theory contributions to the image potential of charged particles [4], and related developments.

Acknowledgments

Bibliography

[1] J. R. Manson and R. H. Ritchie, *Phys. Rev. B* **24**, 4867 (1981).

[2] R. P. Feynman, *Phys. Rev.* **84**, 108 (1951).

[3] See, e.g., T. D. Schultz, *Quantum Field Theory and the Many-Body Problem* (Gordon and Breach, New York, 1964).

[4] R. H. Ritchie, J. R. Manson, and C. L. Zheng, to be published.

[5] A. A. Lucas, *Phys. Rev. B* **4**, 2939 (1971); P. J. Feibelman, *Surf. Sci.* **27**, 438 (1971); G. D. Mahan, *Phys. Rev. B* **5**, 739 (1972); R. H. Ritchie, *Phys. Lett. A* **38**, 189 (1972).

[6] P. M. Echenique, R. H. Ritchie, N. Barberan, and J. C. Inkson, *Phys. Rev. B* **23**, 6486 (1981); M. Sunjic, G. Toulouse, and A. A. Lucas, *Solid State Comm.* **11**, 1629 (1972).

[7] G. D. Mahan, *Collective Properties of Physical Systems*, Nobel Symposium No. 24 (Academic Press, New York, 1973) p. 164.

[8] H. Takimoto, *Phys. Rev.* **146**, 366 (1966); R. Ray and G. D. Mahan, *Phys. Lett.* **42A**, 301 (1972); M. Sunjic, G. Toulouse, and A. A. Lucas, *Solid State Comm.* **11**, 1629 (1972); J. C. Inkson, *J. Phys. F* **3**, 2143 (1972); D. Chan and P. Richmond, *Surf. Sci.* **39**, 437 (1973); J. Heinrichs, *Phys. Rev. B* **18**, 1346 (1973); C. H. Hodges, J. Phys. C **8**, 1849 (1975); J. Harris and R. O. Jones, *J. Phys. C* **7**, 3751 (1974); A. Muscat and D. M. Newns, *Surf. Sci.* **64**, 641 (1977); F. Flores and F. Garcia-Molin, *J. Phys. C* **12**, 907 (1979).

[9] P. M. Echenique and J. B. Pendry, *J. Phys. C* **8**, 2488 (1976).

[10] J. Mahanty, K. N. Pathak, and V. V. Paranjape, *Phys. Rev. B* **33**, 2333 (1986).

[11] P. M. Echenique, A. Gras-Marti, J. R. Manson, and R. H. Ritchie, *Phys. Rev. B* (in press).

[12] M. Jonson, *Solid State Comm.* **33**, 743 (1980).

[13] R. Nieminen and C. H. Hodges, *Phys. Rev. B* **18**, 2568 (1978).

[14] J. R. Manson and R. H. Ritchie, *Phys. Rev. B* **29**, 1084 (1984).

[15] E. M. Lifschitz, *Zh. Eksp. Teor. Fiz.* **29**, 94 (1955) [*Sov. Phys. JETP* **2**, 72 (1956)].

[16] T. L. Ferrell and R. H. Ritchie, *Phys. Rev. A* **21I**, 1305 (1980).

[17] J. R. Manson and R. H. Ritchie, *Phys. Rev. A* **32**, 3782 (1985).

[18] J. R. Manson and R. H. Ritchie, *Phys. Rev. Lett.* **54**, 785 (1985).

[19] M. J. Seaton and Lois Steenman-Clark, *J. Phys. B* **10**, 2639 (1977).

[20] See, e.g., H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, 2nd Ed. (Pergamon, New York, 1971), p. 23.

[21] J. R. Manson, R. H. Ritchie, and T. L. Ferrell, *Phys. Rev. B* **29**, 1080 (1984).

[22] R. H. Ritchie and P. M. Echenique, *Ann. Israeli Phys. Soc.* **4**, 245 (1980); R. H. Ritchie and P. M. Echenique, *Phil. Mag. A* **45**, 347 (1982).

[23] R. H. Ritchie, K. Mo, and C. C. Sung, *Bull. Am. Phys. Soc.* **30**, 1773 (1985); K. Mo, C. C. Sung, and R. H. Ritchie, *Chem. Phys. Letters* **136**, 9 (1987); C. C. Sung, P. M. Echenique, and R. H. Ritchie, to be submitted for publication.

[24] F. Sols and R. H. Ritchie, *Solid State Comm.* **63**, 245 (1987).