Completely Quantal Treatment of the van der Waals Forces between Atoms: Application to Positronium

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The attractive interaction between atoms is described as a self-energy in which the effects of recoil and finite relative velocity are treated exactly. For systems involving positronium significant deviations from the van der Waals potential are found due to both recoil and relative motion.

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The long-range attractive interaction between two atoms, or the van der Waals force, has its origin in the mutual polarization of the two particles. For species without permanent dipole moments the force is entirely quantum mechanical in origin and was first treated by London in what is now a classical application of second-order perturbation theory.[1] London's calculation expresses the interaction as due to the exchange of virtual quanta between the two atoms while undergoing virtual excitations to excited states, and the potential is determined as a power series in the inverse distance R between the atoms, the lowest-order term being $1/R^6$. The nuclei of the atoms are taken to be infinitely massive and are treated classically thereby.

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[2] 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. Motivation for this work comes partially from the analogous problem of the interaction of an electron with a solid surface. There, the effect of recoil is to modify strongly the classical $1/z$ self-energy and to cause it to saturate to a constant near the surface,[3,4] and this saturation has been recently verified experimentally.[5] Similarly, a study of the interaction of thermal-energy positronium with a surface has shown that the effects of recoil modify the interaction in a region extending several atomic units from the surface, and very near the surface the $1/z^3$ van der Waals potential saturates to the weaker $1/z$ dependence.[6]

In this Letter, we consider the interaction between two atoms in a self-consistent many-body formalism which includes full three-dimensional recoil. The interaction potential is expressed as a self-energy and the formalism can be extended to all orders of perturbation theory. 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.

As a starting point for the calculations let us consider the interaction between two hydrogenlike atoms; the generalization to more complicated systems will become apparent shortly. We take as the unperturbed system two isolated atoms for which the corresponding eigenstate is the product of two atomic functions and two momentum functions

$$|j\rangle = u_f(\mathbf{r}_1)\exp(i\mathbf{K}_0\cdot\mathbf{R}_1)u_g(\mathbf{r}_2)\exp(i\mathbf{P}_0\cdot\mathbf{R}_2), \quad (1)$$

with corresponding unperturbed energy

$$E_j = \epsilon_f + \omega_g + \frac{K_0^2}{[2(m_1+1)]} + \frac{P_0^2}{[2(m_2+1)]}, \quad (2)$$

where ϵ_f and ω_g are the unperturbed atomic energies measured from the ground state and atomic units are used throughout. If τ and ρ are the vectors to the respective atomic nuclear cores the perturbating potential is then

$$H' = \frac{1}{|\tau-\rho|} + \frac{1}{|\tau+\mathbf{r}_1-\rho-\mathbf{r}_2|} - \frac{1}{|\tau-\rho-\mathbf{r}_2|} - \frac{1}{|\rho-\tau-\mathbf{r}_1|}. \quad (3)$$

The first contribution to the energy shift comes from second-order perturbation theory:

$$\Delta E = \textstyle\sum_j |\langle j|H'|i\rangle|^2/(E_i - E_j). \quad (4)$$

This energy shift is expressed in terms of the spatial integral over an interaction self-energy,

$$\Delta E = \int d^3R \, \langle \mathbf{0}|\mathbf{R}\rangle \Sigma(\mathbf{R}) \langle \mathbf{R}|\mathbf{0}\rangle, \tag{5}$$

where $\langle \mathbf{R}|\mathbf{0}\rangle$ is the translational eigenstate of the two-atom system in the center-of-mass reference frame. The self-energy $\Sigma(\mathbf{R})$ can be systematically generalized to all orders in perturbation theory,[4,7] and in the present case this leads to

$$\Sigma(\mathbf{R}) = \sum_j \frac{\langle \mathbf{K}|\mathbf{R}\rangle}{\langle \mathbf{0}|\mathbf{R}\rangle} \frac{\langle i|H'|j\rangle \langle f,g,\mathbf{P}|H'|0,0,0\rangle}{E_i - E_j}. \tag{6}$$

After evaluation of the matrix elements $\langle j|H'|0\rangle$ by expansion to first order in the atomic operators $\mathbf{r}_1$ and $\mathbf{r}_2$ the result is

$$\Sigma(R) = (1/4\pi^4) \sum_{f,g} \left[\int d^3K \, e^{i\mathbf{K}\cdot\mathbf{R}} \mathbf{K}\cdot\langle f|\mathbf{r}_1|0\rangle \mathbf{K}\cdot\langle g|\mathbf{r}_2|0\rangle / K^2\right]\left[\int d^3Q \, e^{i\mathbf{Q}\cdot\mathbf{R}} \mathbf{Q}\cdot\langle f|\mathbf{r}_1|0\rangle \mathbf{Q}\cdot\langle g|\mathbf{r}_2|0\rangle / Q^2\right]$$
$$\times \left\{\epsilon_f + \omega_g + \frac{1}{2(m_1+1)}[K_0{}^2 - (\mathbf{K}-\mathbf{K}_0)^2] + \frac{1}{2(m_2+1)}[P_0{}^2 - (\mathbf{K}+\mathbf{P}_0)^2]\right\}^{-1}. \tag{7}$$

If the atomic mass m_1 and m_2 are large the recoil terms in the energy denominator of (7) are negligible and the self-energy reduces to the familiar London expression[1]

$$\Sigma_L(R) = -\frac{1}{R^6} \sum_{f,g} \frac{Q_{fg}^2}{\epsilon_f + \omega_g}, \tag{8}$$

where

$$Q_{fg} = 2\langle f|z_1|0\rangle \langle g|z_2|0\rangle - \langle f|x_1|0\rangle \langle g|x_2|0\rangle - \langle f|y_1|0\rangle \langle g|y_2|0\rangle.$$

(We have also made the tacit assumption that the atomic energies are independent of azimuthal quantum number.) However, if the atomic masses are small the recoil terms can have a substantial effect for low values of R. This is most readily seen by examining Eq. (7) for the case in which the relative velocity between the two atoms is zero. The self-energy can be obtained in closed form and is

$$\Sigma(R) = -\frac{1}{R^4} \sum_{f,g} \left\{ \frac{Q_{fg}^2}{(\epsilon_f + \omega_g)} \frac{1}{R} \left[\frac{1-\exp(-aR)}{R} - a\exp(-aR) \right] - 2M\langle f|z_1|0\rangle \langle g|z_2|0\rangle Q_{fg} \exp(-aR) \right\}, \tag{9}$$

where $a^2 = 2M(\epsilon_f + \omega_g)$ and M is the reduced mass, $M = (m_1+1)(m_2+1)/(m_1+m_2+2)$. It is readily seen that $\Sigma(R)$ goes to the London expression (8) as $aR \to \infty$ (the large atomic mass limit). An interesting case which illustrates that recoil indeed causes a saturation of the self-energy is the limit as $aR \to 0$ where we obtain

$$\Sigma(R) \underset{aR \to 0}{\longrightarrow} -(2/R^4) M \langle 0|z_1^2|0\rangle \langle 0|z_2^2|0\rangle. \tag{10}$$

The effect of recoil of the atoms as they exchange virtual quanta is to weaken or saturate the attractive potential to a $1/R^4$ form. This reduction by two powers of the separation distance is the same as that noted in the atom-surface interaction.[6] The range of recoil effects in the self-energy is given by the parameter a^{-1}; and clearly for atoms even as light as hydrogen this distance is negligibly small. However, for positronium the order of magnitude of a can be estimated most readily by replacing the atomic excitation energies ϵ_f and ω_g by the ionization energy, which gives $a \simeq 2$ a.u. Thus it appears that the recoil effects can be apparent at measurable separation distances.

In the case in which there is a nonzero relative velocity between the two atomic systems Eq. (7) is again readily evaluated in terms of complete and incomplete sine integrals.[8] In the asymptotic region these velocity corrections can be expressed as a correction to the London form as a power series in $1/R^2$. Thus the velocity correction is of the same order in $1/R$ as the next term coming from the multipole expansion of the potential of Eq. (3). When there is a finite relative velocity the self-energy has an imaginary part and this is further divided into conservative and nonconservative contributions. The nonconservative imaginary part has a finite value only if there is sufficient kinetic energy to cause a real atomic excitation in one or both of the systems, i.e., it is the imaginary self-energy due to inelastic exchanges.

A complete discussion of the velocity effects is beyond the scope of this Letter but a simple illustration which generates an order-of-magnitude estimation of their range is to consider Eq. (7) for two hydrogenic atoms and approximate the atomic excitation energies ϵ_f and ω_g by the ionization energies ϵ_0 and ω_0. Then the self-energy in the asymptotic region reduces to

$$\Sigma(R) = -\frac{6}{R^6}\left[1 - \frac{12K_0^2}{R^2M^2} + \frac{22.5}{R^2} + \dots\right], \qquad (11)$$

where the term $22.5/R^2$ comes from the higher-order multipoles. The factor M^{-2} shows clearly that the velocity correction is negligible for ordinary atoms, but for two positronium atoms the ratio of the two $1/R^2$ corrections is approximately $E_i/2$ where E_i is the relative kinetic energy measured in atomic units. Thus the velocity correction can be significant over a range of R of 5 to 10 a.u., and for moderately elevated energies can cancel the other $1/R^2$ correction.

We would like to stress the importance of retaining full three-dimensional recoil in these calculations. It is considerably simpler to include recoil only in the direction transverse to the axis joining the two atoms, i.e., to retain only two-dimensional recoil. If this is done one erroneously obtains recoil corrections to the London result which can be expanded as a power series in $1/R$ in the asymptotic region. However, the correct three-dimensional treatment gives the much faster exponential decay of recoil effects as illustrated in the case of Eq. (9).

Since recoil is most important for atomic systems of small mass it is logical to search for effects in systems involving positronium. Recent advances in the development of thermal-energy positronium sources[2] suggest that experiments to measure these effects are possible in the near future. Shown in Fig. 1 is the interaction self-energy of two positronium atoms separated by a fixed distance R, and normalized to the London expression for the $1/R^6$ van der Waals potential. The polarization sums over atomic states were carried out with use of the exact expressions for the oscillator strengths of a hydrogenlike atom.[9] The saturation to a $1/R^4$ potential occurs at distances of the order of one atomic unit or less where the approximations used to obtain these results are no longer good. However, the effects are still significant even at distances as great as 6 to 10 a.u. and this indicates that recoil can make a measurable difference in the interaction energies of such systems.

Recoil can also affect the interaction between positronium and a normal atom, although in this situation the reduced mass M is twice as large as in the above case and consequently the exponential decay constant a is larger. However, in spite of the fact that recoil effects will occur at smaller separations it should be noted that most light atoms are substantially more compact than positronium and hence the approximations remain valid for smaller approach distances. Shown in Fig. 2 is the self-energy for positronium interacting with several atomic systems. For all of these systems the sums over atomic states were carried out by utilization of the Padé approximants for the atomic polarizabilities.[10] Since the Padé approximants to the polarizabilities are known for a number of systems we have carried out additional calculations for the noble gases as well as many others, including diatomic molecules such as N_2, O_2, and H_2. For all of these systems the ratio of $\Sigma(R)$ to the London potential lies between the curves for hydrogen and for neon shown in Fig. 2. It is evident that recoil can significantly lower the interaction energy out to separations of 5 a.u.

In this Letter we have demonstrated that the many-body interaction energy between two atomic systems can be represented by an effective self-energy and that this self-energy includes very naturally the effects of recoil upon exchange of virtual quanta and also includes the effects due to finite relative velocity. 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 positronium kinetic energies of less than a few electron volts.

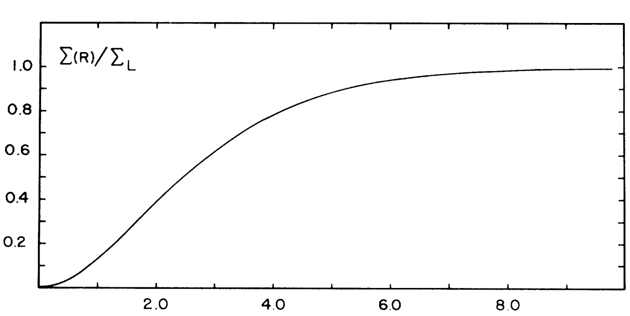

FIG. 1. The ratio of the interaction self-energy $\Sigma(R)$ to the London potential Σ_L for two positronium atoms as a function of distance R between the atomic centers.

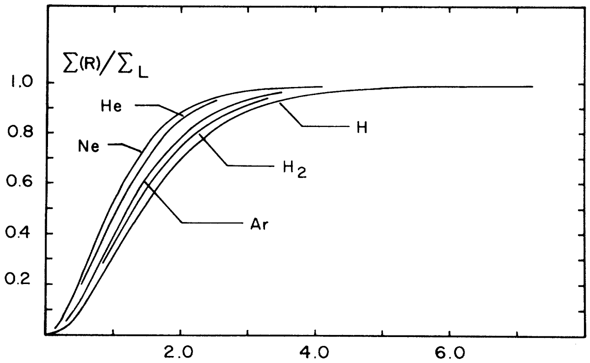

FIG. 2. The ratio of the interaction self-energy $\Sigma(R)$ to the London potential Σ_L for positronium a distance R from several different atomic or molecular species.

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