Corrections to van der Waals Forces

In a recent Letter[1] Au and Drachman have reconsidered the problem of the effective potential between atoms in the regime where nonadiabatic effects are important, such as the case where one of the atoms is positronium. They claim to have found a term which did not appear in our earlier treatment.[2] We would like to take this opportunity to point out that the term in question does appear quite naturally in our very straightforward formulation, to clarify several other points, and to indicate the differences in the two approaches.

The central result of our Letter is Eq. (7) of Ref. 2 where we present a general result for the interaction self-energy of two atoms separated by the displacement $\mathbf{R}$. The asymptotic form is obtained by developing an expansion in terms of inverse powers of $\epsilon_f+\omega_g$, the sum of excitation energies of the two atoms. For example, if the two atoms are identical and moving towards each other we obtain

$$\Sigma(R)=-\frac{1}{R^6}\sum_{f,g}\frac{Q_{fg}^2}{\epsilon_f+\omega_g}\left\{1+\frac{6iK_0}{R(m+1)(\epsilon_f+\omega_g)}-\frac{48K_0^2}{R^2(m+1)^2(\epsilon_f+\omega_g)^2}+\cdots\right\}. \quad (1)$$

As a result of limited space, the asymptotic expansion appeared only in an approximate form in Eq. (11) of our original Letter[2] and the conservative imaginary contribution, although discussed, was not exhibited.

Au and Drachman obtain a single-body Schrödinger equation for the two-atom system, valid only in the asymptotic region, which has the following effective potential operator (expressed here in their center-of-mass coordinates):

$$V(R)=-\frac{C_6}{R^6}+\frac{6D}{\mu R^7}\frac{\partial}{\partial R}-\frac{C_8}{R^8}+\frac{48GK^2}{\mu^2R^8}. \quad (2)$$

In comparing the two forms of Eqs. (2) and (1), the corrections in K^2/R^8 are identical. The C_8/R^8 term in (2) would appear in Eq. (1) if we included higher-order multipoles. The term in question is the $1/R^7$ contribution which appears in both Eqs. (1) and (2). A simple and transparent illustration of the equivalence of the two expansions is provided by the example of two atoms moving toward each other. (Demonstration of the equivalence in general is similarly straightforward.) The wave function for relative motion $\psi(\mathbf{R})$ associated with Eq. (2), since it is valid only in the asymptotic region, then will be nearly plane wave in character. Thus we would have

$$\frac{\partial}{\partial R}\psi(\mathbf{R})=-iK\psi(\mathbf{R})+\text{small terms}, \quad (3)$$

and it is seen that the $1/R^7$ term of Eq. (2) is essentially the same as that in Eq. (1) except for small corrections. Consequently, the $1/R^7$ term of Au and Drachman is neither new nor fundamentally different from the corresponding term discussed in Ref. 2.

Both methods are essentially equivalent in the sense that they are based on perturbation theory. Our method produces a reduced transition operator for the system with the initial unperturbed state projected out, and hence the natural and appropriate states for expansion are the unperturbed states. To lowest nonvanishing order in perturbation theory the transition and potential operators are the same, and this is reflected in the similarity of Eqs. (1) and (2). The expansion of the dipolar contributions in $1/R$ is an asymptotic series. However, our general expression shows that the self-energy is well defined and can be written in closed form.[2]

We would also like to clarify our usage of the terms "recoil effects" and "nonadiabatic corrections." Both of these result from contributions beyond the Born-Oppenheimer approximation. We would call all such corrections appearing in the large-separation region "nonadiabatic" in keeping with previous terminology from the charge-atom problem. What we call "recoil effects" are due to the "kickback" of the atoms due to the conservation of momentum during an exchange of virtual quanta. These arise primarily from the factor K^2, the square of the transferred momentum in the virtual state, appearing in the energy denominators of the perturbation expansion [see, for example, Eq. (7) of Ref. 2]. The short-range nature of the recoil contributions is essentially a reflection of the fact that the atomic electrostatic potential obeys the Laplace equation outside of the atom. We note however, that terms arising from the recoil effect are present even when there is no relative motion between the atoms.

J. R. Manson
Department of Physics and Astronomy
Clemson University
Clemson, South Carolina 29634

R. H. Ritchie
Health and Safety Research Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

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