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Arctangent Approximation to the Intermolecular Potential*

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The form $\overline{V}^{AB}(R) = -(C^{AB}/R^6)\,[2\pi^{-1}\tan^{-1}(d/R)]$ is proposed as an approximation to the retarded van der Waals potential $V^{AB}(R)$ acting between atoms or molecules A and B. Here C^{AB} is the London–van der Waals constant and $d = 23\alpha_E{}^A\alpha_E{}^B\hbar c/8C^{AB}$, with the α_E's denoting static electric polarizabilities. $\overline{V}^{AB}$ is shown to be in excellent agreement with available numerical calculations of $V^{AB}(R)$ based on the Casimir–Polder formula, which requires infinite summation over excited atomic states. A heuristic explanation for the validity of the formula is given.

I. INTRODUCTION

The effective potential V^{AB}, describing the low-energy interaction of an atom or molecule A, with a similar system B, has been the object of theoretical and experimental study for many years. As first shown by London,[1] the electrostatic interaction between the constituents of A and B leads, via second-order perturbation theory, to

$$V^{AB} \approx -C^{AB}/R^6, \qquad R \gg a; \tag{1}$$

here a is a length of the order of atomic dimensions. The effects of the interaction of the atomic electrons with the transverse radiation field were first considered by Casimir and Polder,[2] who showed (neglecting electron spin and using the electric dipole approximation for virtual photon emission) that

$$V^{AB} \sim -\hbar c(23/4\pi)\alpha_E{}^A\alpha_E{}^B/R^7, \qquad R \gg b; \tag{2}$$

here b is of the order of the maximum wavelength of light emitted by the systems and α_E denotes the static electric polarizability, as it would be computed within the same approximations. Since $a \sim a_0$ and $b \sim 2\pi\alpha^{-1}a_0$ [a_0 = Bohr radius, $\alpha = e^2/\hbar c$] there is a substantial region where neither (1) nor (2) are good approximations. Although Casimir and Polder[2] have derived, under the above-mentioned restrictions, an expression for V^{AB} valid at such intermediate values of R, its exact evaluation requires a double summation over the excited states of A and B involving unknown dipole matrix elements, or, alternatively, knowledge of the dynamic polarizabilities for pure imaginary frequencies.

In recent years, the study of the interaction of atoms and molecules at low energies has been greatly intensified.[3] It seems, therefore, that it would be highly desirable to have available, if possible, a good approximation to V^{AB} whose complete specification requires a minimal amount of information concerning excited atomic states. It is the purpose of this paper to put forward a formula with just such properties, which is, moreover, remarkably simple. The formula agrees very well with the results of several numerical calculations based on the expression given by Casimir and Polder; a theoretical explanation of its validity is given which suggests that it may be used with confidence for many-electron atoms, in which case reliable calculations of this type would become increasingly difficult.

II. INTERMOLECULAR POTENTIAL

For the sake of clarity, we note first that the techniques of covariant dispersion theory can be applied to study not only the asymptotic form of the long-range forces arising from the exchange of mass-zero quanta[4–6] but also to find the force at any distance. A general analysis[7] of the potential $V_{2\gamma}(R)$ arising from two-photon exchange between any two systems A and B, both of which are neutral and spinless, leads to the following result. Let M denote the Feynman amplitude for the elastic scattering of a photon with momentum q and polarization ϵ by a neutral spin-zero system of mass m and momentum p. M may be written in the form

$$M = \epsilon_\mu \epsilon'_\nu M^{\mu\nu},$$

where $M^{\mu\nu} = F_E(\sigma, t)T_E{}^{\mu\nu} + F_M(\sigma, t)T_M{}^{\mu\nu}$,

with $T_E{}^{\mu\nu} = -(q\cdot Pq'\cdot Pg^{\mu\nu} + q\,.\,q'P^\mu P^\nu$

$$-q\cdot Pq'^{\mu}P^{\nu}-q'\cdot Pq^{\nu}P^{\mu})/2m^2,$$

$$T_M^{\mu\nu}=T_E^{\mu\nu}+2(q'\cdot qg^{\mu\nu}-q'^{\mu}q^{\nu})$$

and $\sigma=(p+q)^2,\quad t=(p-p')^2,\quad P=p+p'$.

The tensors T_E and T_M are such that the invariants F_E and F_M have the property

$$F_E(m^2,0)=4\pi\alpha_E,\quad F_M(m^2,0)=4\pi\alpha_M,$$

where α_E and α_M are, respectively, the static electric and magnetic polarizability of the system. Then[7]

$$V_{2\gamma}(R)=V_{EE}(R)+V_{EM}(R)+V_{ME}(R)+V_{MM}(R), \tag{3}$$

where, if the t dependence of the F's is neglected[8]

$$V_{EE}(R)\rightarrow C_{EE}(R)/R^6\ , \tag{4}$$

with

$$C_{EE}(R)=\frac{1}{4\pi^5}\int_0^\infty\int_0^\infty dk_A dk_B k_A k_B \rho_E^A(k_A)\rho_E^B(k_B)$$

$$\times\int_0^\infty d\zeta\, e^{-2\zeta R}P_{EE}(\zeta R)/(\zeta^2+k_A^2)(\zeta^2+k_B^2). \tag{5}$$

Here, e.g., $k_A=(\sigma_A-M_A^2)/2M_A$, $\rho_E^A(k_A)$ is the absorptive part of $F_E^A(\sigma_A,0)$ and $P_{EE}(\eta)=\eta^4+2\eta^3+5\eta^2+6\eta+3$. [$C_{EM}$ is similarly defined with $\rho_E B$ replaced by $\rho_M B$, etc; $P_{MM}=P_{EE}$, but $P_{ME}=P_{ME}=-(\eta^4+2\eta^3+\eta^2)$]. If A and B are both atoms or molecules and $\rho_E A$ and $\rho_E B$ are approximated by the values obtained by considering only the interaction of the transverse radiation field with nonrelativistic electrons and making the dipole approximation, (5) becomes identical with the formula of Casimir and Polder. Although there are cases where the magnetic terms in (3) become important,[9] we confine ourselves to the normally dominant, purely electric term $V_{EE}(R)$ or, equivalently, to $C_{EE}(R)$. The latter may also be written in the form

$$C_{EE}(R)=\frac{1}{\pi}\int_0^\infty d\zeta\,\alpha_E^A(i\zeta)\alpha_E^B(i\zeta)$$

$$\times\ e^{-2\zeta R}P_{EE}(\zeta R)\ , \tag{6a}$$

where $\alpha_E(\omega)=\frac{1}{2\pi}\int_0^\infty\frac{dk}{\pi}\frac{k\rho_E(k)}{k^2-\omega^2}$ (6b)

is the frequency-dependent polarizability.

III. ARCTANGENT APPROXIMATION

We now propose as a good approximation to $C_{EE}(R)$ the function

$$\tilde{C}_{EE}(R)=C^{AB}\cdot(2/\pi)\tan^{-1}d/R\ , \tag{7}$$

where $d=23\alpha_E^A\alpha_E^B\hbar c/8C^{AB}$. (8)

That the arctangent function might enter into a simple approximation to $V_{EE}(R)$ is suggested by previous experience with the dispersion-theoretic analysis of dispersion forces.[5] Once the form (7) is adopted, the length d is conveniently chosen to guarantee that $V_{EE}(R)$ has the correct asymptotic form (2).

To test the validity of (7) at intermediate values of R, we have compared it with the results of numerical calculations based on (5) (for the case $A=B=$ H atom) and on (6) (for the cases $A=B=$ He and $A=$ H, $B=$ He).[10] As can be seen from Fig. 1, the agreement is very good, especially in view of the simplicity of (7), which involves no new constants beyond those already entering (1) and (2). The difference between $C_{EE}(R)$ and $\tilde{C}_{EE}(R)$ is in no case larger than a few percent, for any value of R.

The accuracy of (7) may perhaps be understood as follows. We put $\zeta=\eta/R$ in (5) and integrate by parts to rewrite (5) in the form

$$C_{EE}(R)=\frac{1}{8\pi^2}\int_0^\infty\int_0^\infty\frac{dk_A}{\pi}\frac{dk_B}{\pi}\frac{\rho_E^A(k_A)\rho_E^B(k_B)}{k_A+k_B}$$

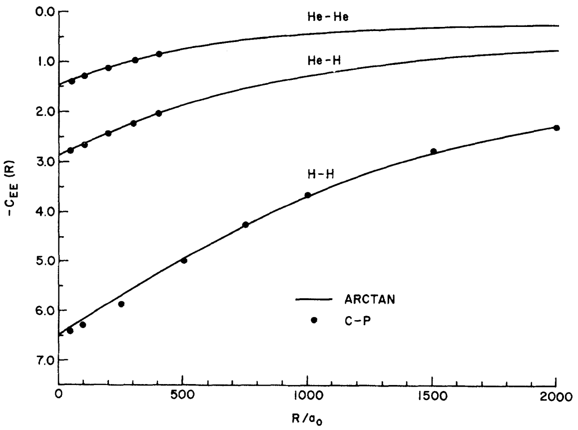

FIG. 1. Comparison of the arctangent formula [Eq. (7)], with the results of numerical calculations based on the Casimir-Polder formula. The plotted points were obtained from Eq. (5) for the H-H case, and from Eq. (6) for the other cases (Ref. 10).

$$\times \int_0^\infty d\eta\, N \frac{d}{d\eta}\left[P_{EE}(\eta) e^{-2\eta}\right], \qquad (9)$$

where

$$N = \frac{2}{\pi}\, \frac{k_B \tan^{-1}(\eta/k_A R) - k_A \tan^{-1}(\eta/k_B R)}{k_B - k_A}. \qquad (10)$$

Thus, enter the arctangent. To arrive at (7), note first that if N is replaced by unity the right-hand side of (9) reduces to $C_{EE}(0) = C^{AB}$ so that (9) may be written in the form

$$C_{EE}(R) = C^{AB} \overline{N}(R), \qquad (11)$$

where $\overline{N}(R)$ is a weighted average of $N = N(k_A, k_B; \eta; R)$. Note further that N is a slowly varying function of the integration variables and also that for $R \to \infty$, $N \to (2/\pi)(\xi/R$, where $\xi = \eta/k_{AB}$, with $k_{AB} = k_A k_B/(k_A + k_B)$. These facts and the form (10) suggest that if we define a mean value $\overline{\xi} = \overline{\xi}(R)$ of ξ by writing

$$\overline{N}(R) = (2/\pi) \tan^{-1}[\overline{\xi}(R)/R], \qquad (12)$$

then $\overline{\xi}(R)$ will be a slowly varying function of R. [Additional support for this form of $\overline{N}(R)$ comes from the observation that the function $\tilde{N} = (2/\pi) \times \tan^{-1}(\xi/R)$ is a good approximation to N for all values of k_A, k_B, and η. $\tilde{N}$ coincides with N for $k_A/k_B \gg 1$ or $k_B/k_A \gg 1$, and when both k_A and k_B are small or large relative to η/R; the maximum error (~20%) occurs for $k_A = k_B = \eta/\sqrt{2}\, R$.] On approximating $\overline{\xi}(R)$ by $\overline{\xi}(\infty)$ in (12) and noting that (2), (11), and (12) imply that $\overline{\xi}(\infty) = d$, defined by (8), we obtain Eq. (7).

It should be emphasized that our discussion is heuristic and by no means constitutes a derivation of the validity of the approximation – $C_{EE}(R) \approx \tilde{C}_{EE}(R)$. A general statement about the validity certainly cannot be made without imposing some restrictions on the spectral functions $\rho_E{}^A(k)$ and $\rho_E{}^B(k)$, e.g., that they be slowly varying in relevant regions of k space. The agreement with the numerical calculations shows that the $\rho_E(k)$ for both H and He satisfy these restrictions. We should also remark that attempted fits with other simple functions, such as $d(d + \frac{1}{2}\pi R)^{-1}$ or $d[d^2 + (\frac{1}{2}\pi R)^2]^{-1/2}$, which, like $(2/\pi)\tan^{-1}(d/R)$, involve no additional parameters and behave as $(2/\pi)(d/R)$ for $R \to \infty$ but which have no corresponding theoretical support, turn out to be much less satisfactory.

In conclusion, we believe that Eq. (7) can be used with considerable confidence in the planning and analysis of atomic scattering experiments at very low energies. We hope that the availability of a simple but apparently quite accurate expression for the dominant part of the retarded van der Waals potential[11] will help stimulate experimental efforts to measure these forces in elementary scattering processes.

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[1] F. London, Z. Physik 63, 245 (1930).

[2] H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).

[3] See, e.g., Atomic Physics, edited by B. Bederson, V. W. Cohen, and F. M. J. Pichanik (Plenum Press, New York, 1969). A review is given by E. A. Power in Advan. Atomic Mol. Phys. 12, 167 (1967).

[4] G. Feinberg and J. Sucher, Phys. Rev. 139, B1619 (1965); 166, 1638 (1968).

[5] J. Soffer and J. Sucher, Phys. Rev. 161, 1664 (1967).

[6] G. Feinberg and J. Sucher, J. Chem. Phys. 48, 3333 (1968).

[7] G. Feinberg and J. Sucher (unpublished).

[8] This neglect is valid if A and B are both atomic systems and $R \gg a_0$. Some terms of order t/m^2, which originate in the relativistic kinematics, must also be dropped in order to arrive at (4) and (5). See Ref. 7.

[9] As described in Ref. 6 and shown in Ref. 7, the exact asymptotic form of (3) is $V_{2\gamma} = -D/R$ Ref. 7, where $D = 23(\alpha_E{}^A \alpha_E{}^B + \alpha_M{}^A \alpha_M{}^B) - 7(\alpha_E{}^A \alpha_M{}^B + \alpha_M{}^A \alpha_E{}^B)/4\pi$. This implies, for $A = \mathrm{H}$, $B = \mathrm{He}$, that $V_{2\gamma}$ is repulsive at large R.

[10] The points for the latter two cases are based on the calculations of P. Getzin and M. Karplus, who used Eq. (5). {P. M. Getzin [Columbia University, Ph. D. thesis, 1967 (unpublished)]; P. Getzin and M. Karplus (unpublished)}. We thank Professor G. Feinberg for bringing this work to our attention. Before becoming aware of it, we computed $C_{EE}(R)$ for $A = B = \mathrm{H}$ directly from (5), using results obtained during the exact computation of $C_{EE}(0)$ [M. O'Carroll and J. Sucher, Phys. Rev. Letters 21, 1143 (1968)]. This case is also treated by these authors, who used (6) and the exact values of $\alpha_E{}^H(\omega)$ obtained by M. Karplus and M. Kolker, J. Chem. Phys. 39, 1493 (1963). The two calculations are in complete agreement.

[11] Approximations for the other $C_{XY}(R)$, analogous to Eq. (7) for $C_{EE}(R)$, are considered in Ref. 7.