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Nonsingular van der Waals potentials

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Universal, spherical, nonsingular van der Waals interactions including retardation effect are developed for atoms and small molecules through a semiclassical field approach. Consideration of the finite molecular size effect removes the short-distance singular behavior inherent in the widely used potentials obtained from the point-molecule approximation. Physical arguments lead to the molecular size parameter a (in atomic units) as $1/a = 1.25(I/I_{\mathrm{H}})^{1/2}$, except for a system that involves at least an atom or a molecule with very different first and second ionization potentials, and for such a system the above numerical factor 1.25 is replaced by unity. Here I and I_{H} are the first ionization potentials for the atom or molecule considered and for a hydrogen atom, respectively. The nonsingular potentials have been tested for the following representative systems: H_2 $({}^3\Sigma_u^+)$, He_2, Ar_2, NaK $({}^3\Sigma^+)$, LiHg $({}^2\Sigma^+)$, He-HF, Ne-HF, HF-HF, and Ar-HCl. Very good agreement has been found for each of the systems. Based on the above systems studied, an empirical relation has been obtained between the parameter b in the Born-Mayer repulsive potential Ae^{-bR} and the molecular size parameters (a_1 and a_2). Applying this relation to dozens of systems with known b from either self-consistent-field calculations or experiments, surprisingly good agreements have been obtained. By the same token, another empirical formula is obtained that relates the van der Waals minimum well parameter R_m to the molecular size parameters (a_1 and a_2) and the first ionization potentials (I_x and I_y) of interacting species. Again, very good agreements have been achieved in comparison with dozens of systems with known experimental R_m's.

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I. INTRODUCTION

Physical, chemical, and biological phenomena are mostly governed by the so-called van der Waals interactions in the region of separation from a few angstroms to even micrometers for neutral systems [1]. The dispersion-energy component of this interaction is usually the dominant contribution and is the only contribution for neutral nonpolar systems. However, due to its smallness (less than a few hundredths of an electron volt), the direct *ab initio* calculation of this force is very limited even with the advent of modern computers [2]. The essential difficulties arise from the errors inherent in subtracting the sum of very large energies of isolated molecules from the only slightly different total energy of the corresponding interacting molecules. In practice, the most favorable approach to study the dispersion energy is still semiempirical. Such constructed potentials have the theoretically correct behavior at long range and at short range.

The widely used semiempirical van der Waals potential is obtained simply by adding the short-range Born-Mayer repulsive potential to the long-range dispersion energy as

$$V(R) = Ae^{-bR} - C_6/R^6 - C_8/R^8 - C_{10}/R^{10}, \quad (1.1)$$

with R the intermolecular separation. The exponential repulsive term is largely due to exchange as well as electrostatic forces and can be determined fairly accurately, for example, by the self-consistent-field (SCF) calculations. However, as described in [2], the attractive part of the above potential is only asypmtotically ($R \to \infty$) correct and is usually problematic around the van der Waals minimum, the region of interest. For example, even though the above model with SCF values for A and b and theoretical values for C_6, C_8, and C_{10} was able to predict the experimentally available rare-gas dimer well parameters to within a few percent [4], it gives a purely attractive interaction with no potential minimum for alkali-atom–rare-gas systems and systems such as NaK$({}^3\Sigma^+)$ and LiHg$({}^2\Sigma^+)$. Recent beam-scattering experiments [5–7] also show that the experimentally determined interaction constant C_6 is almost 50% less than the precise theoretical values for a few systems if the London potential $-C_6/R^6$ is used. In other words, the above model satisfies the criterion of the semiempirical approach at long range and at short range, but is unable to give the correct description of the intermediate region for arbitrary atomic or molecular systems. This is entirely due to the improper application of the only asymptotically correct attractive interactions to the region around the van der Waals minimum. Our purpose is to go beyond the semiempirical approach, if not completely from first principle, to find an attractive potential that is correct at least around the van der Waals minimum and for larger intermolecular separations. Such an attractive potential can replace the attractive part in Eq. (1.1) so that the resulting potential can be used to describe the van der Waals interaction for arbitrary atomic or molecular systems.

The development of the dispersion interaction began not long after the advent of quantum mechanics. The famous London force is the fluctuating dipole-induced dipole interaction of two neutral molecules, i.e., the lowest-order contribution of the point-multipole expansion of the dispersion energy. This point-multipole expansion follows the traditional perturbation approach and is easy to handle; however, this approach presents the divergence problem as noticed first by Brooks [8], and later by Roe [9] and by Dalgarno and Lewis [10], with some improvement of Brooks's original proof. This expansion converges to the true dispersion energy (in the sense of Poincaré) only as the intermolecular separation goes to infinity. Each term in the point-multipole expansion displays singular behavior for vanishing intermolecular separation. The main reason behind these problems is the omission of effects of finite molecular size in the point-multipole expansion, which is closely related to the electronic charge overlap. Theoretically speaking, quantum mechanics tells us that the electronic wave function extends to infinity in space. Therefore, charge overlap between molecules always occurs and, strictly speaking, the point-multipole expansion may not be a valid approach in describing the dispersion energy. However, the electronic charge distribution of a molecule usually falls to vanishingly small values after some distance from its center. Therefore, if effects of molecular size are incorporated into some multipole expansion, one expects that the divergence problem and the short-range singular behavior mentioned above in the usual point-multipole expansion could be cured and a good approximation for the dispersion energy can be obtained at least around the van der Waals minimum. Based on the exponential decay of wave functions and the fact that the point-multipole expansion approaches the true dispersion energy asymptotically, Brooks made an educated guess by introducing a so-called incomplete Γ damping function to each term of the point-multipole expansion. By this artifice, the aforementioned unwanted features disappear.

Along this line, various damping functions are proposed semiempirically or from first principles. It is worth mentioning the two most widely used semiempirical damping functions, the Hartree-Fock dispersion damping functions of Douketis *et al.* [11] and the incomplete Γ-function damping function of Tang and Toennies [12], both of which ensure that the dispersion energy remains finite at short range. The latter experiences tremendous success, for example, in predicting four chemically different types of van der Waals interactions [H_2 ($^3\Sigma_u^+$), He_2, NaK ($^3\Sigma^+$), and LiHg ($^2\Sigma^+$)] to agree with either nearly exact *ab initio* potential or experimental potentials within 1% and is theoretically supported. A few analytic formulas for the damping functions have also been derived from various physical considerations. Jacobi and Csanak [13] were first able to derive the damping function for the dipole-dipole interaction by using an analytical representation of the Born amplitude in momentum space together with a general angular momentum analysis. Koide [14] derived quite general formulas for the individual nonexpanded dispersion contributions D_n [D_n representing that multipole interaction which survives at infinity as C_n/R^n and is equal to $f_n(R)C_n/R^n$ at finite intermolecular distance R, with f_n the corresponding damping function and C_n the dispersion interaction constant]. However, obtaining explicit f_n requires wave functions for the atom or molecule considered, which are not available in general except for a hydrogen atom. Applying his formula to H_2 ($^3\Sigma_u^+$), Koide obtained explicit f_6 and f_8. The result is almost the same as that of Jacobi and Csanak for f_6 and shows that f_6 and f_8 can be represented to a good approximation by the squares of appropriate incomplete Γ functions. This, to some extent, supports Brooks's conjecture. The other aspects of the development of the damping functions are discussed in review articles [12,15,16].

All the above approaches are, however, nonrelativistic, i.e., not including the retardation effects. As reported in [2], the frequency integration upper limit of the dispersion interaction can be determined only if both the retardation effect and the finite molecular size effect are considered. To calculate the nonsingular fluctuating dipole-induced dipole interaction, we adopt the semiclassical field approach, which was developed by Casimir [17,18] and by Casimir and Polder [19,20]. This approach has the advantage that the retardation effect is included automatically. Consideration of the finite molecular size effect removes the singular behavior from the London potential. The key to our calculation is the atomic or molecular polarizability density tensor. We are able to prove in general that this density tensor, to a good approximation, can be determined by the atomic or molecular ground-state wave function with a parameter characterizing the finite molecular size.

II. SPHERICALLY SYMMETRIC POLARIZABILITY DENSITY TENSOR

Mahanty and Ninham were probably the first to use the semiclassical field approach of Casimir and Polder [17–20] to consider the finite molecular size effect [21–23]. They took a Gaussian form of the polarizability density simply for mathematical convenience. As a result, their retarded potential is very complicated and it is very hard to go beyond the dipole-dipole interaction. This is probably the reason that Richardson [24] later generalized only nonretarded interactions for higher multipoles. The semiclassical field approach follows the physically intuitive description of dispersion forces. Consider the interaction between two molecules as an example. The variable electric field produced by the instantaneous dipole in one molecule acts on the other, therefore polarizing it. Using the linear quantum-mechanical response theory [25], the Fourier component of the polarizability density tensor, including the consideration of the finite molecular size effect, can be expressed [23] as

$$\alpha_N(\vec{k},\omega) = -\frac{e^2}{\hbar}\sum_Q\left(\frac{\left\langle N\left|\sum_l \vec{r}_l\right|Q\right\rangle\left\langle Q\left|\sum_l e^{i\vec{k}\cdot\vec{r}_l}\right|N\right\rangle}{\omega_{QN}-\omega} + \frac{\left\langle Q\left|\sum_l \vec{r}_l\right|N\right\rangle\left\langle N\left|\sum_l e^{i\vec{k}\cdot\vec{r}_l}\right|Q\right\rangle}{\omega_{QN}+\omega}\right)\frac{i\vec{k}}{k^2}, \tag{2.1}$$

where

$$\omega_{QN} = \frac{E_Q - E_N}{\hbar}, \tag{2.2}$$

$|N\rangle$ usually stands for the unperturbed electronic ground state of the atom or molecule, and $|Q\rangle$ is the possible unperturbed electronic states of the atom or molecule. The summation $\sum_l$ is to all the electrons of the corresponding atom or molecule.

From electrodynamics, we know that once a time-varying polarization is present, there is a current associated with it. Therefore, the electromagnetic field surrounding one molecule must be changed relative to that when the molecule is isolated. In other words, the electromagnetic wave spectrum must be shifted in some fashion. This shift can be determined by solving the corresponding Maxwell equations with this current as the source and by choosing the Lorentz gauge. As in the Drude model, the sum of the frequency shifts multiplied by the Plank constant for the entire spectrum of the two molecular system must give the dispersion interaction energy of the system. As a preliminary investigation, we focus here only on the dipole-dipole dispersion interaction. The general fluctuating dipole-induced dipole interaction, including retardation, can be written [23] as

$$V(R) = -4\pi\hbar \int_{-\infty}^{\infty} d\xi \times \mathrm{Tr}\{\boldsymbol{G}_2(\vec{R}_1, \vec{R}_2; i\xi) \cdot \boldsymbol{G}_1(\vec{R}_2, \vec{R}_1; i\xi)\}, \tag{2.3}$$

where R is the center-to-center distance of the two molecules, $\vec{R}_1$ and $\vec{R}_2$ are the center position vectors of molecule one and molecule two, respectively, and

$$\boldsymbol{G}(\vec{r}_1, \vec{r}_2; i\xi) = \frac{1}{(2\pi)^3} \int d^3k \frac{(\xi^2/c^2)\boldsymbol{I} + \vec{k}\vec{k}}{\xi^2/c^2 + k^2} e^{i\vec{k}\cdot(\vec{r}_1 - \vec{r}_2)} \times \int d^3u\, \boldsymbol{\alpha}(\vec{u}, i\xi) e^{-i\vec{k}\cdot\vec{u}}, \tag{2.4}$$

with c the speed of light and $\boldsymbol{I}$ the unit tensor. Note that the polarizability density tensor $\boldsymbol{\alpha}(\vec{r}, i\xi)$ depends on both position vector and frequency. For the point-dipole approximation [i.e., by setting $\boldsymbol{\alpha}(\vec{r}, i\xi) = \boldsymbol{I}\alpha(i\xi)\delta(\vec{r})$], Eqs. (2.3) and (2.4) give a potential whose nonretarded limit is the London dispersion energy while the retarded limit is the result of Casimir and Polder [20]. It is clear from Eqs. (2.3) and (2.4) that once the polarizability density tensor is known, the potential can be obtained simply by performing a few integrations. Our job is to find a general spherically symmetric polarizability density tensor for atoms and small molecules.

We begin with applying Eq. (2.1) to a hydrogen atom since this is the only one whose Schrödinger equation can be solved exactly and analytically. Besides, as we will see, the characteristic functional form of the spherically symmetric polarizability density tensor for other atoms and small molecules can be obtained from the study of this simple system. For a hydrogen atom, the electronic states can be represented as (nlm) in general with n the principle quantum number, l the total orbital angular momentum quantum number, and m the magnetic quantum number. The ground state is $N = (100)$. The only nonvanishing matrix elements are for $Q = (q10)$ if $\vec{k}$ is chosen along the z axis. One calculates

$$\langle q10|e^{i\vec{k}\cdot\vec{r}}|100\rangle = i\sum_{j=2}^{q} \frac{F_j(ka_0)}{[(1+1/q)^2 + (ka_0)^2]^{1+j}}, \tag{2.5}$$

where $F_j(ka_0)$ is jth-order odd polynomial if j is odd, a $(j-1)$th-order odd polynomial if j is even, and it approaches zero if $k \to 0$. a_0 is the Bohr radius. The explicit form of $F_j(ka_0)$ does not concern us; therefore, it is not given here. Denoting

$$\langle q10|\vec{r}|100\rangle = f_{1q}\hat{e}_k, \tag{2.6}$$

one has

$$\boldsymbol{\alpha}(\vec{k}, \omega) = \frac{e^2}{\hbar}\hat{e}_k\hat{e}_k \times \sum_{q\geq 2} \frac{2\omega_{q1} f_{1q}}{\omega_{q1}^2 - \omega^2} \sum_{j=2}^{q} \frac{F_j(ka_0)}{k[(ka_0)^2 + (1+1/q)^2]^{1+j}}, \tag{2.7}$$

where $\hat{e}_k$ denotes the unit vector $\vec{k}/k$. The frequency-dependent polarizability density tensor is

$$\boldsymbol{\alpha}(\vec{r}, \omega) = \frac{1}{(2\pi)^3} \int d^3\vec{k}\, \boldsymbol{\alpha}(\vec{k}, \omega) e^{-i\vec{k}\cdot\vec{r}} = \frac{e^2}{\hbar} \sum_{q\geq 2} \frac{2\omega_{q1} f_{1q}}{\omega_{q1}^2 - \omega^2} \boldsymbol{A}(\vec{r}), \tag{2.8}$$

where

$$\boldsymbol{A}(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k}\, \hat{e}_k\hat{e}_k e^{-i\vec{k}\cdot\vec{r}} \times \sum_{j=2}^{q} \frac{F_j(ka_0)}{k[(ka_0)^2 + (1+1/q)^2]^{1+j}}. \tag{2.9}$$

If the unit vector $\hat{e}_k$ is written in terms of the spherical unit vectors $(\hat{e}_\theta, \hat{e}_\phi, \hat{e}_r)$ associated with vector $\vec{r}$, Eq. (2.9) can be rewritten as

$$\boldsymbol{A}(\vec{r}) = \frac{1}{(2\pi)^3} \int_0^\infty dk \sum_{j=2}^{q} \frac{kF_j(ka_0)}{[(ka_0)^2 + (1+1/q)^2]^{1+j}} \times \int_{-1}^{+1} dx\, e^{-ikxr}[\pi(1-x^2)(\hat{e}_\theta\hat{e}_\theta + \hat{e}_\phi\hat{e}_\phi) + 2\pi x^2 \hat{e}_r\hat{e}_r], \tag{2.10}$$

where the azimuthal angle integration in k space has been performed [note that relative to k space, the unit vectors $(\hat{e}_\theta, \hat{e}_\phi, \hat{e}_r)$ are fixed]. Obtaining a spherically symmetric polarizability density tensor is equivalent to performing a directional average of Eq. (2.10). By noticing that the directional average of each of $\hat{e}_r\hat{e}_r$, $\hat{e}_\theta\hat{e}_\theta$, and $\hat{e}_\phi\hat{e}_\phi$ is equal to one-third of the unit tensor $\boldsymbol{I}$, we end with

$$\boldsymbol{A}(\vec{r}) = \frac{1}{3}\frac{1}{(2\pi)^2}\boldsymbol{I}\int_0^{\infty} dk \sum_{j=2}^{q} \frac{kF_j(ka_0)}{[(ka_0)^2 + (1+1/q)^2]^{1+j}} \times \int_{-1}^{+1} dx\, e^{-ikxr}. \tag{2.11}$$

Because the polynomial $F_j(ka_0)$ in Eq. (2.11) is an odd-function of k, the integral in the above equation can be evaluated using residue theorems (see the Appendix for detail) as

$$\boldsymbol{A}(\vec{r}) = \boldsymbol{I}G_{q-1}(r/a_0)e^{-(1+1/q)r/a_0}, \tag{2.12}$$

where $G_{q-1}(r/a_0)$ is a $(q-1)$th-order polynomial of the variable r/a_0. The spherically symmetric polarizability density tensor follows from Eqs. (2.8) and (2.12) as

$$\boldsymbol{\alpha}(\vec{r},\omega) = \frac{e^2}{\hbar}\boldsymbol{I}e^{-r/a_0}\sum_{q\geq 2}\frac{2\omega_{q1}f_{1q}G_{q-1}(r/a_0)}{\omega_{q1}^2-\omega^2}\,e^{-r/qa_0}. \tag{2.13}$$

Remarkably, Eq. (2.13) is quite simple. Every quantity there is calculable, which implies that at least within the linear response approximation, we can evaluate the corresponding potential given by Eqs. (2.3) and (2.4).

The subtle information of the hydrogen atom is contained in the polynomial G_{q-1} in Eq. (2.13). However, as discussed in [2], the distance damping effect is dominantly controlled by the exponential factor $\exp(-r/a_0)$, i.e., the one in the ground-state wave function, in front of the sum in Eq. (2.13). For example, as $r \gg a_0$, that $\boldsymbol{\alpha}(\vec{r},\omega)$ goes to zero is dominantly controlled by this exponential. As $r \sim a_0$, the polynomial $G_{q-1}(r/a_0)$ is almost a constant compared to various exponential factors in Eq. (2.13). For those exponential factors within the sum in Eq. (2.13), except for the first few q's, they can essentially be taken as one. For simplicity and universal purpose, a good approximation of Eq. (2.13) can be taken as

$$\boldsymbol{\alpha}(\vec{r},\omega) = \boldsymbol{I}\frac{e^{-\beta r/a_0}}{8\pi(a_0/\beta)^3}\alpha(\omega). \tag{2.14}$$

Here the parameter β is introduced to account for the atomic size effect from the dominant exponential $\exp(-r/a_0)$ and those within the sum of Eq. (2.13) and all the remaining r-dependent terms within the sum are set to constants. Furthermore,

$$\alpha(\omega) = \frac{e^2}{\hbar}\sum_{q\geq 2}\frac{f_{1q}g_{q1}}{\omega_{q1}^2-\omega^2}, \tag{2.15}$$

where we have set $\sqrt{2\omega_{q1}}f_{1q} \to f_{1q}$ and g_{q1} is the collection of those constants and a possible normalization factor. We will return to determine β in Sec. IV.

From the above study, we conclude that the distance damping effect to the polarizability density tensor is determined by the exponential factor $\exp(-r/a_0)$ in the ground-state wave function of the atom with a replacement of a_0, the Bohr radius, by a_0/β, the parameter characterizing the size effect. Two specific properties are essential to the above conclusion. One is that each of the wave functions must contain an exponential factor similar to $\exp(-r/a_0)$. The other is that the function $F_j(ka_0)$ in Eq. (2.11) must be an odd function with respect to k. We expect that for any atom or molecule having the above two properties, the corresponding spherically symmetric polarizability density tensor should have the same form as that in Eq. (2.14).

For the other atoms, exact or even accurately correlated wave functions are, in practice, seldom available; only the fairly accurate Hartree SCF wave functions are easily accessible. The SCF wave functions, which are essentially the extension of the radial part of the hydrogen atom wave function to all the other atoms, satisfy just our needs. Since the radial part of the SCF wave function for any atom always has an exponential function similar to $\exp(-r/a_0)$ and the angular part is the same as that of the hydrogen atom, Eqs. (2.14) and (2.15) should also hold with a proper interpretation of the quantities in these equations for the corresponding atom.

For molecules, due to the presence of many atomic nuclei, even if the Hartree SCF approximation method is applied to the motion of an electron in a molecule, under the action of the nuclei and of the remaining electrons, the resulting averaged static charge distribution is not spherically symmetrical as it would be in an atom. So, strictly speaking, the angular part of the electronic molecular wave function cannot be the spherical harmonics. In molecular-orbital theory, electrons in molecules are in orbitals that may be associated with several nuclei. Even with the simplest molecular orbital (MO), i.e., the linear combination of atomic orbitals (LCAO), either variation method or numerical method must be used for the calculation of the energy of the corresponding molecular orbital. Even if we were able to analytically obtain the polarizability density tensor by the LCAO MO, the expression must be very complicated and contains only the atomic parameters. What we really need is the molecular-orbital concept and such approximated orbital functions, which contain only molecular parameters instead of the atomic parameters. This is hardly possible in general. However, in our case, this is at least approximately feasible for small molecules. First we are interested in only the spherically symmetrical polarizability density tensor. Second, we are interested in dispersion interaction, which is important only around the van der Waals minimum and for larger intermolecular separations and is small by nature. For intermolecular separations a little less than that corresponding to the van der Waals minimum, the dispersion energy is negligible compared with the quantum mechanical first-order energy. The intermolecular separation corresponding to the van der Waals minimum is in general a few times the internuclear separations. For example, the internuclear separation for H_2 is 0.74 Å while the intermolecular separation of the van der Waals minimum between two H_2 molecules is around 3.5 Å. Finally, the outermost molecular-orbital electrons contribute most to the polarizability.

From the above consideration, we may neglect the internuclear separations for small molecules and think that all nuclei in a molecule are centered at one point, i.e., an atomlike molecule. Then, the above discussion for atoms applies to small molecules as well. However, as will be discussed in Sec. IV, the molecular size parameter is estimated by use of the experimentally determined first ionization potential of the molecule rather than that of an atom with the same number of electrons. For example, the molecular size parameter of H_2 is different from that of the He atom. For large molecules, due to the appearance of many centers of polarization and many-body effects, we postpone the study of this case to another work, even though for each center of the polarization, Eqs. (2.14) and (2.15) may also be true.

Following our recipe, one sees that Mahanty and Ninham's Gaussian form of the polarizability density tensor corresponds actually to choosing a molecular ground state as a harmonic-oscillator wave function. We emphasize that unlike the situation in the point-multipole expansion, the correct distance-damping behavior of the electronic wave function should be used to correctly account for the finite molecular size effect, as indicated in [26].

In summary, we have proved that, to a good approximation, the following expression for the polarizability density tensor is physically correct in general for atoms and small molecules:

$$\boldsymbol{\alpha}(\vec{r},\omega) = \frac{1}{8\pi a^3} e^{-r/a} \boldsymbol{I} \alpha(\omega), \tag{2.16}$$

where a is the parameter characterizing the atomic or molecular size effect and the frequency expression for $\alpha(\omega)$ looks similar to Eq. (2.15).

III. UNIVERSAL NONSINGULAR VAN DER WAALS POTENTIALS

The explicit potential including retardation follows from Eqs. (2.3), (2.4), and (2.16) as

$$V(R) = -\frac{3\hbar}{2\pi R^6} \int_0^\infty d\xi\, \mathcal{V}(R, a_1, a_2; \xi), \tag{3.1}$$

where

$$\begin{aligned} \mathcal{V}(R, a_1, a_2; \xi) = \alpha_1(i\xi)\alpha_2(i\xi) e^{-2R\xi/c} [&F(R, a_1; \xi) F(R, a_2; \xi) - F(R, a_1; \xi) G(R, a_2; \xi) \\ &-G(R, a_1; \xi) F(R, a_2; \xi) + 3G(R, a_1; \xi) G(R, a_2; \xi)], \end{aligned} \tag{3.2}$$

a_1 and a_2 are two parameters characterizing sizes of the two molecules, respectively, and

$$\begin{aligned} F(R, a; \xi) = \frac{1}{[1 - (\frac{a\xi}{c})^2]^2} &\Bigg[\left[1 + \frac{R\xi}{c} - \left(\frac{R\xi}{c}\right)^2\right] + \Bigg(\left(\frac{R\xi}{c}\right)^2 \left\{1 + \frac{R}{2a}\left[1 - \left(\frac{a\xi}{c}\right)^2\right]\right\} \\ &- \left\{1 + \frac{R}{a} + \frac{R^2}{2a^2}\left[1 - \left(\frac{a\xi}{c}\right)^2\right]\right\} \Bigg) e^{-\frac{R}{a}\left(1 - \frac{a\xi}{c}\right)} \Bigg], \end{aligned} \tag{3.3a}$$

$$\begin{aligned} G(R, a; \xi) = \frac{1}{[1 - (\frac{a\xi}{c})^2]^2} &\Bigg(\left[1 + \frac{R\xi}{c} + \frac{1}{3}\left(\frac{R\xi}{c}\right)^2\right] - \Bigg\{1 + \frac{R}{a} + \frac{R^2}{6a^2}\left[3 - \left(\frac{a\xi}{c}\right)^2\right] \\ &+ \frac{R^3}{6a^3}\left[1 - \left(\frac{a\xi}{c}\right)^2\right] \Bigg\} e^{-\frac{R}{a}\left(1 - \frac{a\xi}{c}\right)} \Bigg). \end{aligned} \tag{3.3b}$$

Looking at Eq. (3.2) as well as Eq. (3.3), one sees a common frequency factor

$$1/\left[1 - (a_1\xi/c)^2\right]^2 \left[1 - (a_2\xi/c)^2\right]^2, \tag{3.4}$$

which is almost unity if both $a_1\xi/c$ and $a_2\xi/c$ are much less than one. Equation (3.2) seems to go to infinity if both $a_1\xi/c$ and $a_2\xi/c$ approach one. However, this is not the case if one looks at Eq. (3.3) carefully. Actually, the common singular frequency factor $1/(1-a\xi/c)^2$, in either the $F(R, a; \xi)$ or $G(R, a; \xi)$ function, will be canceled out to leave both of them nonsingular as $a\xi/c \to 1$.

The above discussion implies that the factor in Eq. (3.4) does not play a role in Eq. (3.2) unless $a_1\xi/c$ and $a_2\xi/c$ are much greater than one. For example, if $a_1\xi/c$ and $a_2\xi/c$ take the value 10, the factor would be 10^{-8}, negligibly small. Therefore, it is legitimate to set the frequency-integration upper limit (FIUL) in Eq. (3.1) as

$$\xi_0 = \max\{c/a_1, c/a_2\}, \tag{3.5}$$

which is on the order of 10^{18} rad s^{-1} by noticing that $c = 3 \times 10^{10}$ cm s^{-1} and $a \sim 10^{-8}$ cm. This is entirely consistent with physically intuitive consideration that the energy involved in atomic and molecular phenomena is at most on the order of a keV, i.e., x-ray energy, giving frequency 10^{18} rad s^{-1}. Further numerical study shows that Eq. (3.2) is negligibly small if frequency ξ is greater than $0.5c/a$ regardless of the intermolecular separation R. To our knowledge, this is the first time that such fact has been taken into account explicitly in the intermolecular potential. We stress that no such conclusion can be made if either the nonretardation limit is taken ($c \to \infty$) or the molecular size parameters a_1 and a_2 are set to zero.

For simplicity and without losing generality, the numerical study has been done by setting $a_1 = a_2 = a$, $x = a\xi/c$, and $y = R/a$. The frequency dependence of Eq. (2.15) is also used and the possible maximum frequency ω_{nq} is reasonably chosen as $0.1c/a$, i.e., on the order 10^{17} rad s^{-1}, which is even one order of magnitude higher than the typical plasma frequency. Therefore, at high frequency, $\alpha_j(i\xi)$ $(j = 1,2)$ behave like $1/(1+100x^2)$. In other words, $(1+100x^2)\alpha_j(i\xi) \sim$ const as $\xi > 10^{17}$ rad s^{-1}. A few characteristic profiles of the function $\mathcal{V}$ in Eq. (3.2) vs $x = a\xi/c$ are shown in Fig. 1 for $y = R/a = 5, 10, 20$, and 60. As y increases to large values, we see that the tail of the profile shifts to the direction of lower frequency as physically expected. For example, the tail essentially ends at frequency $0.1c/a$ for $R = 60a$. These facts are very useful in calculating non-retarded interaction constants, for example, C_6 or the frequency-dependent dielectric constants in the condensed-body case.

If both a_1 and a_2 are set to zero, the resulting potential from Eqs. (3.1)–(3.3) is the usual point dipole-dipole retarded potential obtained before by many authors, except for the replacement of the FIUL from infinity to ξ_0. The nonsingular nonretarded potential can be obtained by setting $c \to \infty$ either in Eq. (2.4) from the outset or in Eqs. (3.2) and (3.3) as

$$V(R) = -\frac{C_6 f_6(R)}{R^6}, \tag{3.6}$$

where

$$C_6 = \frac{3\hbar}{\pi}\int_0^{\xi_0} d\xi \alpha_1(i\xi)\alpha_2(i\xi) \tag{3.7}$$

is the usual dipole-dipole interaction constant again with the modification of the FIUL from infinity to ξ_0 and the so-called distance damping function $f_6(R)$ is

$$f_6(R) = \frac{1}{3}\prod_{j=1}^{2}\left\{1 - \left[1 + \frac{R}{a_j} + \frac{1}{2}\left(\frac{R}{a_j}\right)^2\right]e^{-\frac{R}{a_j}}\right\} + \frac{2}{3}\prod_{j=1}^{2}\left\{1 - \left[1 + \frac{R}{a_j} + \frac{1}{2}\left(\frac{R}{a_j}\right)^2 + \frac{1}{4}\left(\frac{R}{a_j}\right)^3\right]e^{-\frac{R}{a_j}}\right\}, \tag{3.8}$$

which approaches one if either a_1 and a_2 are both set to zero or $R \gg \max(a_1, a_2)$, i.e., the corresponding potential goes to the London potential.

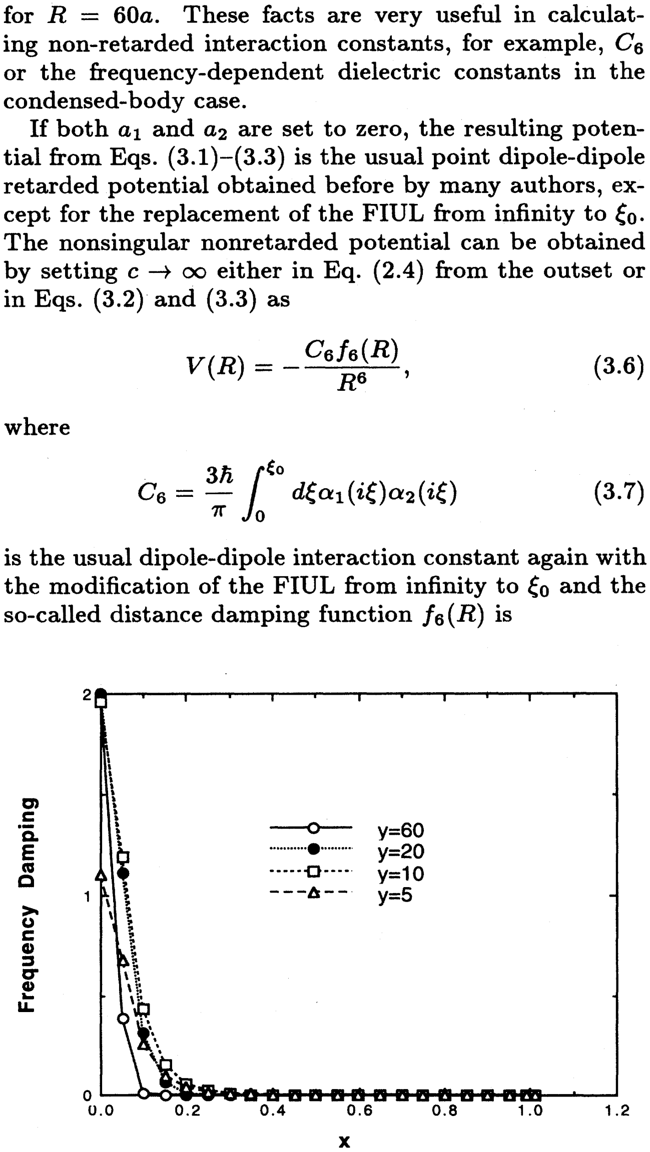

FIG. 1. Frequency damping of the function $\mathcal{V}(x,y)$ in Eq. (3.2) vs $x = a\xi/c$ for $y = R/a = 5, 10, 20$, and 60. The actual plot was drawn for the dimensionless function $\mathcal{V}(x,y)/[(1+100x^2)^2\alpha_1(i\xi)\alpha_2(i\xi)]$ vs $x = a\xi/c$ (see the text for detail).

Noticing that the maximum peak frequency in $\alpha(\omega)$ is, in general, much less than the ξ_0 given by Eq. (3.5), both the retarded potential Eq. (3.1) and the nonretarded potential Eq. (3.6), in the $R \to 0$ limit, give

$$V(R \to 0) = -\frac{C_6}{72(a_1 a_2)^3} \tag{3.9}$$

finite, as expected. As is well known, dispersion energies are small in nature and are completely negligible in short intermolecular separation compared to tremendous large repulsive energies. In reality, van der Waals phenomena never run into a distance less than the corresponding atomic or molecular size. The above $R \to 0$ limit is merely used to show that the short-distance singular behavior inherent in the London potential is removed and the potentials developed here are analytical and finite at all separations. The potentials are also small at short distance. For example, if we extrapolate the potential Eq. (3.6) physically to $R \to 0$ for the interacting system H(1S)-H(1S), the corresponding dispersion energy is the largest and is estimated as 0.3 a.u., while the repulsive energy approaches infinity.

From a practical viewpoint, the retarded potential given by Eqs. (3.1)–(3.3) is quite complicated. Numerically, the function $\mathcal{V}(R, a_1, a_2; \xi)/\alpha_1(i\xi)\alpha_2(i\xi)$ may be represented approximately by a simpler fitted function. A similar approximation procedure may also be applied to the nonretarded damping function Eq. (3.8). This assertion concerning the nonretarded damping function is supported by the evidence that our damping function can be represented, to a good approximation, by the semiempirical one of Tang and Toennies for a few representative systems, which will be demonstrated in Sec. V. We will pursue such practically useful approximations in general elsewhere.

Theoretically speaking, the potentials developed here give a definitely better description of the dispersion interaction around the van der Waals minimum than the currently widely used potentials, which are singular at short separation and are based on the point-molecule approximation. In Sec. V, we will demonstrate explicitly how good the potentials are for a few representative systems, which include four chemically different types of van der Waals interactions, giving the interactions from very weak to very strong and the potential well from very narrow to very wide. Therefore, we are able to show that our potentials describe correctly the dispersion interaction, at least down to the intermolecular separation around the van der Waals minimum. Due to the limitation of the theory used, we are not sure, at very short separations, if the potentials are still able to describe the dispersion energy correctly. However, as described above, it is in the short separations that the dispersion energy plays no role and can be completely neglected. Moreover, our potentials are analytical at all separations and remain small even at zero separation. For practical purposes, our potentials are quite adequate. We fulfill our goal given in the Introduction.

In order to compare our potentials with those from either *ab initio* calculations or experiments, we need to know both C_6 and the atomic or molecular size parameters a_1 and a_2. The dispersion coefficients C_n can be determined with either theoretical calculations or experimental information on oscillator strength distributions as described in the review article by Buckingham *et al.* [16] and the references therein. We could leave the atomic or molecular size parameters as fitted ones such that the potentials developed here are models. However, we still prefer to go one step further to estimate these size parameters through physical considerations as well as by using the first ionization potentials of the corresponding atoms or molecules. This is topic of the next section.

IV. ATOMIC OR MOLECULAR SIZE PARAMETERS

In Secs. II and III we have reached the conclusion that the spherically symmetric potentials between two interacting species (atoms or small molecules), to a good approximation, have the same function form as that for the H(1S)-H(1S) system. This confirms the belief of many authors [11,12,27,29] that for all isotropic interactions, the distance damping functions described in the Introduction, aside from scaling (or the atomic or molecular size parameters), should be very similar to that for the H(1S)-H(1S) system. This fact, plus what we have done in Sec. II, gives us the hint that if we know clearly the way to determine the atomic size parameter for a hydrogen atom, this may shed light on how to determine the atomic or molecular size parameters in general. Throughout the remainder of this study, atomic units are used. In [2], $\beta = 1.2$ has been simply introduced to account for the atomic size effect of a hydrogen atom by taking the ($q = 5$) exponential $\exp(-0.2r)$ out of the sum in Eq. (2.13) and combining it with the dominant $\exp(-r)$. In what follows, we will derive $\beta = 1.25$, less than 5% increase of the above value, by a general physical analysis.

As described in Sec. II, the distance damping effect of the hydrogen is important only as r approaches a few atomic units. Though the exponential $\exp(-r)$ dominantly controls the distance damping effect, we expect also that a small portion of this effect comes from the exponentials within the sum of Eq. (2.13). Certainly, the first term ($q = 2$) in the sum contributes the most of the small portion since it is this term that is most likely not to be a constant for r around a few atomic units. Due to the differences among these exponentials, we need to keep in mind that in extracting an exponential factor out of the sum, the remaining exponentials should be left to change as slowly as possible with respect to r. For example, taking an exponential $\exp(-r/q_0)$ out of the sum in Eq. (2.13), the remaining exponentials in the sum look like $\exp[-(q-q_0)r/qq_0]$. We expect that all of these exponentials change slowly as r changes around a few atomic units. This would require that $|q - q_0|/qq_0$ be reasonably small for all q's. This is obviously satisfied for those q's near q_0, provided q_0 by itself is reasonably large. As $q \gg q_0$, $|q - q_0|/qq_0 \sim 1/q_0$. So q_0 should be large, but it cannot be very large. Otherwise, for $q \ll q_0$, we have $|q - q_0|/qq_0 \sim 1/q$, which is not small. The best way to satisfy that $|q - q_0|/qq_0$ is small for all q's is to set the value of $|q - q_0|/qq_0$ for the allowed minimum $q = 2$ the same as its value, i.e., $1/q_0$, for $q \gg q_0$. So we have $(q_0 - 2)/2q_0 = 1/q_0$, which gives $q_0 = 4$. Therefore, the atomic size parameter $\beta = 1 + 1/q_0 = 1.25$. As will be shown in Sec. V our damping function with the choice of the above $\beta = 1.25$ agrees almost perfectly with the one from the almost exactly *ab initio* calculation [27] for the H(1S)-H(1S) system.

According to the SCF approach, the exponential factor in the one-electron ground-state wave function is similar to that of a hydrogen atom, given by $\exp(-\sqrt{-E_n}r)$, where E_n is the corresponding one-electron energy in atomic units. As a general estimation, the first ionization potential is certainly a good choice for $|E_n|$. By now, it seems that the atomic or molecular size parameter can be estimated in general as

$$\begin{aligned} 1/a_x &= \beta(I_x/I_{\rm H})^{1/2} \\ &= 1.25(I_x/I_{\rm H})^{1/2}, \end{aligned} \tag{4.1}$$

where I_x and $I_{\rm H}$ are the first ionization potentials of an atom or a molecule x and a hydrogen atom, respectively. Experimental first ionization potentials for atoms and molecules can be found, for example, from [28]. However, the above is only part of the story. Further discussion is needed.

For our purpose, the Hartree approximation is well suited. The Fourier component of the polarizability density tensor of Eq. (2.1) can be written, in terms of one-electron wave functions and energies, as

$$\begin{aligned} \boldsymbol{\alpha}(\vec{k},\omega) = -\frac{e^2}{\hbar}\sum_n\sum_m \Bigg(& \frac{\left\langle m\left|\sum_l \vec{r}_l\right|n\right\rangle\left\langle n\left|\sum_l e^{i\vec{k}\cdot\vec{r}_l}\right|m\right\rangle}{\omega_{nm}-\omega} \\ & + \frac{\left\langle n\left|\sum_l \vec{r}_l\right|m\right\rangle\left\langle m\left|\sum_l e^{i\vec{k}\cdot\vec{r}_l}\right|n\right\rangle}{\omega_{nm}+\omega}\Bigg)\frac{i\vec{k}}{k^2}, \end{aligned} \tag{4.2}$$

where $|m\rangle$ and $|n\rangle$ are the one-electron states and ω_{nm} are evaluated according to Eq. (2.2) but now by one-electron energies. We assume that the m is summed over all states occupied by electrons in the atomic or molecular ground state and n is summed over all unoccupied (excited) states. If we proceed along the same line as in Sec. II for the hydrogen atom, we end up with

$$\boldsymbol{\alpha}(\vec{r},\omega)=\frac{e^2}{\hbar}\boldsymbol{I}\sum_{m=1}^{m_0}e^{-\rho_m r}\sum_{n>m_0}\frac{f_{mn}G_{nm}(r)}{\omega_{nm}^2-\omega^2}e^{-\rho_n r},\quad(4.3)$$

where m_0 represents the highest occupied one-electron state and $\rho_n\sim\sqrt{-E_n}$, with E_n the one-electron energy. So the larger the $|E_n|$ or the smaller the n, the larger the ρ_n. Therefore, the most important contribution is from $m=m_0$, since the corresponding ρ_m is the smallest among those allowed m in the sum. This explains that the outermost-shell electrons (valence electrons) dominantly contribute to the polarizability of an atom or a molecule. In general, the smaller the ρ_{m_0}, the more important the effect of the atomic or molecular size around the van der Waals minimum. So Eq. (4.3) can be rewritten as

$$\boldsymbol{\alpha}(\vec{r},\omega)=\frac{e^2}{\hbar}\boldsymbol{I}e^{-\rho_{m_0}r}\times\sum_{m=1}^{m_0}e^{-(\rho_m-\rho_{m_0})r}\sum_{n>m_0}\frac{f_{mn}G_{nm}(r)}{\omega_{nm}^2-\omega^2}e^{-\rho_n r}.\quad(4.4)$$

Recall that the energy $-E_m$ for $1\leq m\leq m_0$ can be taken as the corresponding ionization potentials. Look at the atomic ionization potentials, for example. For all except for alkali atoms, from the second and first ionization potentials, one can estimate that $\rho_{m_0-1}-\rho_{m_0}$ is about 0.5, which looks similar to the $1/q=0.5$ for $q=2$, i.e., corresponding to the first term in the sum of Eq. (2.13) for the hydrogen atom. For the third ionization potential and beyond, the corresponding $\rho_m-\rho_{m_0}$ and ω_{mn} are generally large in comparison with those corresponding to the second ionization potential. In practice, we can neglect the contributions from those terms for $m<m_0-1$. For alkali atoms, even the second ionization potential is almost ten times that of the first. So all the terms for $m<m_0$ are negligible in Eq. (4.4). Besides, the huge difference between the first and the second ionization potentials pushes the first ionization potential to a relatively small value, which implies that the unoccupied state absolute energy $|E_n|$ is even smaller. Therefore, in comparison with all the other atoms, the effect of atomic size for an alkali atom is solely determined by the first ionization potential with no need to include the corrections from either $m<m_0$ occupied one-electron states or $n>m_0$ unoccupied one-electron states discussed above. This also implies that the effect of atomic size for an alkali atom plays the most important role around the van der Waals minimum in comparison with those for the other atoms, which will be demonstrated in Sec. V.

In general, we have

$$1/a_x=(1+\delta)(I_x/I_{\rm H})^{1/2},\quad(4.5)$$

where δ, the correction factor discussed above, is either around 0.25 or around zero, as classified in the following. For a hydrogen atom, $\delta=0.25$. For any other atoms or molecules whose first and second ionization potentials are not very different, δ is close to 0.25. For atoms or molecules whose first and second ionization potentials are very different, $\delta\sim0$. In what follows, we simply take δ as either 0.25 or 0 for the above two cases, respectively. For an interacting atomic or molecular system involving an atom or molecule with $\delta=0$, it appears to us that δ has to be set to zero for any other atom or molecule interacting with this atom or molecule. Some correlation seems to exist. We have as yet no good physical explanations for this. As will be shown in Sec. V, the above choices are very satisfactory. The choice of the atomic or molecular size has also been discussed in [30], where the size was simply given by Eq. (4.5) without the correction factor δ. In [11,31], some improvement of Ref. [30] for the size has been claimed by changing the exponent 0.5 in Eq. (4.5) to 0.66 from the consideration of obtaining good agreements with experiments for mixtures containing the alkali atoms while the molecular size for a like-pair system not involving alkali metal atoms was proposed to be inversely proportional to R_m, the position of the potential minimum. The molecular size for mixed interactions was also proposed.

V. COMPARISON WITH EXPERIMENTS

We come to test the present potentials. The comparison of our potential to those previously obtained is equivalent to that of the corresponding damping functions. The nearly exact *ab initio* calculations of damping functions for the H(1S)-H(1S) system have been performed some time ago with applications of the so-called separable pseudostate method [27]. In this calculation, the usual Coulomb interaction potential energy between the two H(1S) is not expanded in the R^{-1} multipole expansion; therefore the corresponding calculated induction and dispersion energies include the charge overlap effects and go with the name "nonexpanded" energies. In other words, the effects of atomic size are included. However, the electronic exchange effects are neglected and the separability of the nonexpanded induction and dispersion energies into properties of the isolated species is assumed. This implies that the calculated energies are possibly accurate only for reasonably large R, which was also pointed out by those authors. This applies also to the decomposition of the second-order energy into additive induction, the so-called spherical dispersion, and the remaining dispersion components. This fact, as well as other complications, has also been discussed for smaller R in [12]. In general, one expects that the smaller the R, the larger the errors for the calculated dispersion energies. As indicated in [27], the calculated results for the second-order energy are in good agreement with the exact *ab initio* correspondences of Kolos and Wolniewicz [32] for $R\geq4$, respectively, but not for the smaller values of R. Hence the *ab initio* damping functions in [27] do serve as standards for $R\geq4$ to test their correspondences obtained by other means.

Our damping function with $\beta = 1.25$ determined in Sec. IV agrees with that of Koide *et al.* [27] within 2% for $R \geq 6$. Even though the determination of the $\beta = 1.25$ descibed in Sec. IV is theoretically attractive, small errors, for example, less than 5%, are expected. For example, better agreement can be obtained, which is within 2% for $R \geq 5$, if β is reduced to 1.19. The comparisons are shown in Fig. 2. Recall that the van der Waals minimum for the H(1S)-H(1S) system happens close to $R = 7.8$ and the total interaction energy vanishes around $R = 6.8$. $R = 6$ is already in the strong repulsive region where the repulsive energy is almost 10 times the van der Waals potential well depth. With these in mind and by noticing that even the *ab initio* damping functions are expected to have small errors, the agreement is almost perfect in the region of interest. This indicates not only the correctness of our analytical damping functional form, at least in the region of interest, but also that of the way to determine the atomic or molecular size parameters given in Sec. IV. In what follows, we will provide more examples to give further support to this.

In general, it is very difficult to calculate directly the analytical damping functions, which requires analytical wave functions of the system under study. However, we do have very successful empirical damping functions, for example, those of Tang and Toennies [12]. As discussed in the Introduction, their empirical potential has been tested for each of the following representative systems: H_2 ($^3\Sigma_u^+$), He_2, and Ar_2 as well as NaK ($^3\Sigma^+$) and LiHg ($^2\Sigma^+$). The agreement with the corresponding experimental potential is within 1% in the potential well region. Since these potentials are empirical in nature, one should not expect that the corresponding damping functions are also good within 1% accuracy in the well regions. By comparing our damping function to its correspondent for each of the above systems, the agreement is always within 4% in the potential well region and for the separations extended even to the strong repulsive region. The comparisons have been shown in Figs. 3–6. The very good agreements indicate also the universality of the current potentials since the representative systems include four chemically different types of van der Waals interactions, giving the interactions from very weak to very strong and the potential wells from very narrow to very wide.

Strictly speaking, we have not yet made the comparisons for true molecular systems. The structure of a true molecule is very complicated in comparison with that of an atom. This certainly will complicate the calculation. Among other things, the basis set and convergence problems make the nearly exact *ab initio* calculation unfeasible, especially for the dispersion energy, even with

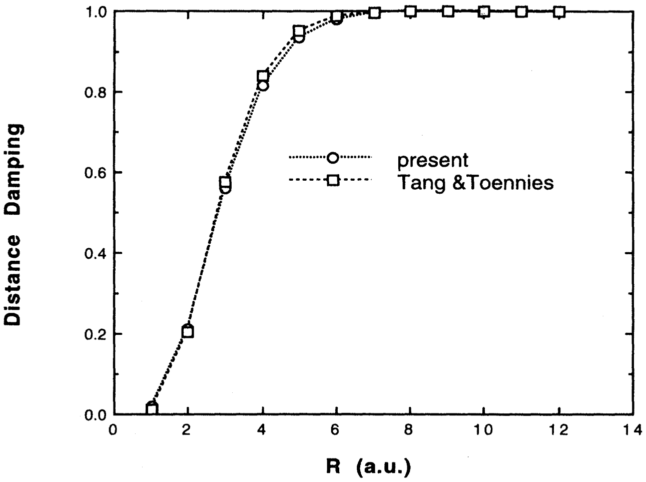

FIG. 3. Comparison of our damping function for $1/a_{He} = 1.681$ with the model damping function of Tang and Toennies (Born-Mayer parameter $b = 2.388$) [12] for the He-He system.

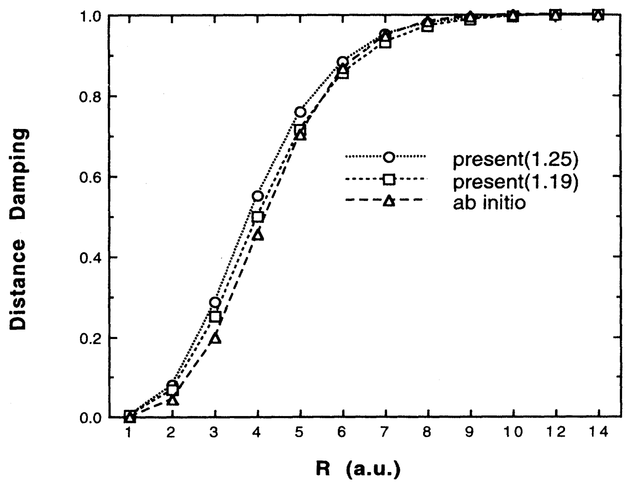

FIG. 2. Comparison of the damping function given by Eq. (3.8) for $1/a_H = 1.25$ with that from the *ab initio* calculation of Koide, Meath, and Allnatt [27] for the H(1S)-H(1S) system. A comparison is also given for $1/a_H = 1.19$.

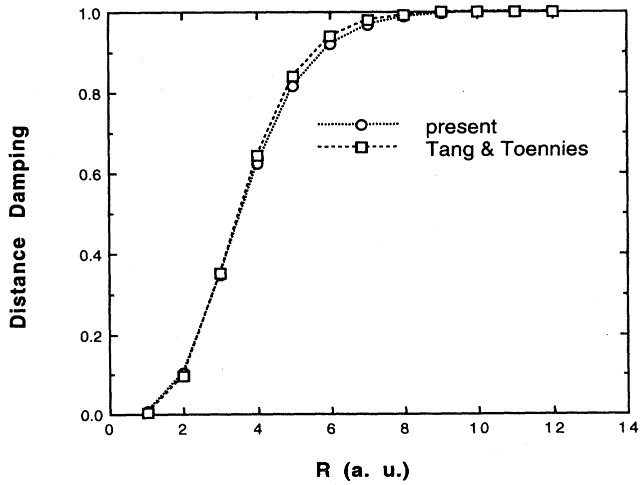

FIG. 4. Comparison of our damping function for $1/a_{Ar} = 1.346$ with the model damping function of Tang and Toennies (Born-Mayer parameter $b = 1.917$) [12] 2 for the Ar-Ar system.

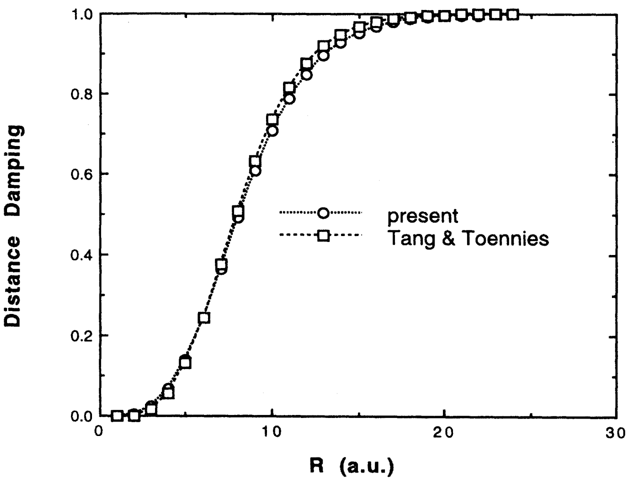

FIG. 5. Comparison of our damping function for $1/a_{\text{Na}} = 0.6147$ and $1/a_{\text{K}} = 0.565$ with the model damping function of Tang and Toennies (Born-Mayer parameter $b = 0.8414$) [12] for Na-K ($^3\Sigma^+$).

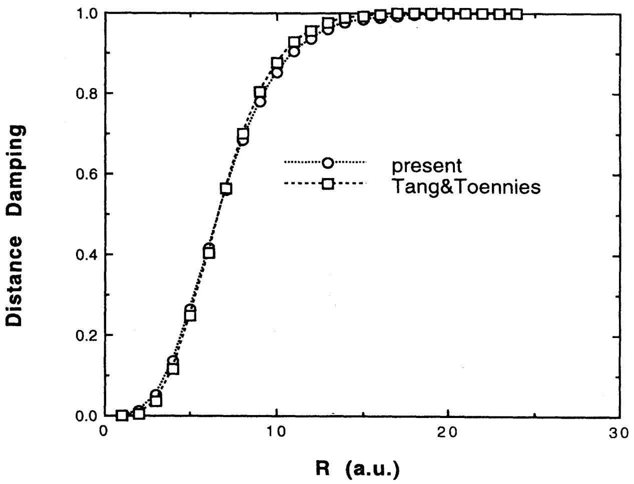

FIG. 6. Comparison of our damping function with $1/a_{\text{Li}} = 0.6297$ and $1/a_{\text{Hg}} = 0.8759$ with the model damping function of Tang and Toennies (Born-Mayer parameter $b = 1.012$) [12] for Li-Hg ($^2\Sigma^+$).

modern computers. Therefore, the damping functions extracted from such calculated energies cannot really serve as standards to test damping functions obtained by other means. Various aspects of van der Waals interaction from *ab initio* calculations for molecular systems have been discussed in the most recent review article [33]. On the empirical side, the family of accurate potentials of Hutson [36,37] is believed so far to be the best. These potentials are partitioned into the Born-Mayer repulsion, the induction contribution, and the dispersion contribution. The damping functions used in the dispersion term are those of Tang and Toennies [12]. As pointed out in [33], the dispersion contribution is adjusted to accommodate the deficiencies of the repulsion and induction contributions so that the total potential can reproduce the experimental data. Therefore, we expect that the damping functions with such fitted parameters cannot serve as standards either.

Despite so many defects of damping functions for true molecular systems, we are to test our damping function for the following typical systems: He-HF Ne-HF, HF-HF, and Ar-HCl. The first three systems have a very weak anisotropy of the total interaction energies while the Ar-HCl has a very strong anisotropy of the total interaction energy. It is believed that reasonably reliable damping functions for the first three systems have been calculated for intermolecular distances $R = 5 - 10$ by evaluating the nonexpanded dispersion energies with employing time-dependent coupled Hartree-Fock techniques [34,35]. HF is a polar molecule and the induction energy of the interacting system HF-HF is as important as its dispersion energy. The empirical damping function for the system Ar-HCl is that of Tang and Toennies but with a fitted parameter $b = 1.892$ with 95% confidence to give the so-called H(3) total potential to reproduce experimental data [36].

The comparison to our damping function for each of the above systems is given in Table I and in Fig. 7. The agreement is within 4% for the He-HF system and within 3% for the Ne-HF and HF-HF systems. The trend is that the smaller the intermolecular separation R, the larger the disagreement. Keeping in mind that certain errors are inevitable and the accuracy goes down as R becomes small in the *ab initio* calculations of the damping functions, the above agreements are again excellent. As for Ar-HCl, if $b = 1.892$ is simply taken, the agreement is not so good, which is about 5% around the van der Waals minimum $R_m = 7.2$. However, if the above b is reduced

TABLE I. Comparison of our damping function $f_6(R)$ with its *ab initio* correspondence of Knowles and Meath [34,35] for He-HF, Ne-HF, and HF-HF systems at intermolecular separations $R = 5 - 10$. The atomic or molecular size parameters used for our damping function are $1/a_{\text{He}} = 1.681, 1/a_{\text{Ne}} = 1.547$, and $1/a_{\text{HF}} = 1.346$ in atomic units.

	He-HF		Ne-HF		HF-HF	
R	Present	Knowles and Meath	Present	Knowles and Meath	Present	Knowles and Meath
5	0.8745	0.9096	0.862	0.887	0.816	0.836
6	0.9505	0.9767	0.945	0.970	0.921	0.948
7	0.9816	0.9950	0.9795	0.9931	0.9689	0.9864
8	0.9934	0.9991	0.9927	0.9987	0.9883	0.9969
9	0.9977	0.9999	0.9975	0.9998	0.9958	0.9994
10	0.9992	1.0000	0.9992	1.0000	0.9985	0.9999

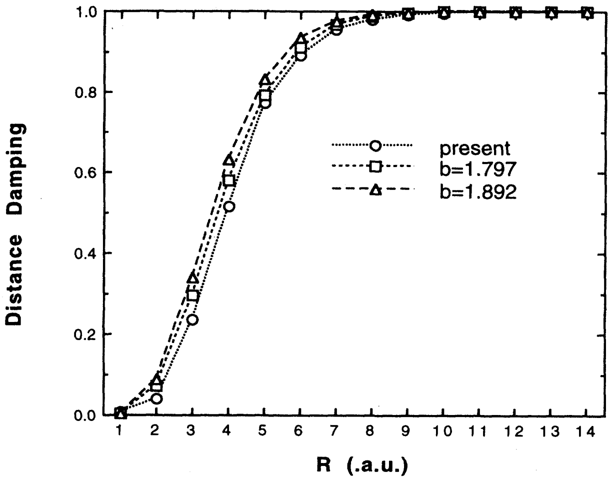

FIG. 7. Comparison of our damping function for $1/a_{\mathrm{Ar}} = 1.346$ and $1/a_{\mathrm{HCl}} = 1.21$ with the model damping function of Tang and Toennies for such fitted Born-Mayer parameters $b = 1.892, 1.797$ [36] for the Ar-HCl system.

by 5% to 1.797, the resulting agreement is within 3% down to the intermolecular separation $R = 5$. Such a reduction of b is allowable by recalling that the damping function employed here to compare with our damping function is by nature empirical and it does not purely describe the dispersion damping as discussed above.

So far we have shown that the potential Eq. (3.6) is very satisfactory. In addition, we provide the method, discussed in Sec. IV to determine the atomic or molecular size parameter a. The asymptotic constant C_6 can be obtained from many sources, also discussed in Sec. IV. As a preliminary investigation, we have as yet not given the attractive terms $C_8 f_8(R)/R^8$ and $C_{10} f_{10}(R)/R^{10}$, which are necessary to give an accurate description of van der Waals interaction for at least atomic or molecular systems. We wish to return to this elsewhere. As is well known, currently only the dipole-dipole dispersion interaction including the many-body effects is considered for the van der Waals interaction of condensed bodies. However, the effects of the atomic or molecular size as well as the short-range repulsive interaction are completely ignored in the existing treatment. In the above, we have shown how to incorporate the effects of the atomic or molecular size into the dispersion interaction. Therefore, we expect that the potential developed in this study can be applied readily to the van der Waals interaction at small separations for condensed bodies. In what follows, we try to go one step further to give empirical estimations for the parameters A and b of the Born-Mayer repulsive energy Ae^{-bR} based on physical considerations and observations to the aforementioned systems studied. If neither good experimental data nor *ab initio* calculations are available to determine these parameters, the following empirical estimations are good at least for qualitative study. Full discussions of the short-separation van der Waals interactions including the repulsive forces for neutral condensed bodies will be given in [3].

Physically speaking, the parameter b indicates at which intermolecular separation the repulsive interaction becomes important. Therefore, it must also relate to the atomic or molecular size discussed in Sec. IV. With this in mind, comparing the atomic or molecular sizes to their corresponding Born-Mayer parameters b, which are known for all systems except for He-HF, Ne-HF, and HF-HF studied above, one has the following equation, which holds for these systems within 5%:

$$b = 0.700(1/a_1 + 1/a_2), \tag{5.1}$$

where a_1 and a_2 are the atomic or molecular size parameters for the interacting species, respectively, and are determined according to Eq. (4.5). Recalling that the above systems include four very different types of van der Waals interactions, one may think that Eq. (5.1) may be true in general. This is further supported by the following evidence. Equation (5.1) is used to calculate the parameter b for 21 systems whose Born-Mayer parameters were given or collected in [38,39] either by SCF calculations and other theoretical means or from experiments. Our selection for the above systems from [38,39] is based on the following criteria: the theoretical b's should give fairly accurate experimental well parameters or the experimental b's are obtained from accurate experimental well parameters. The results, in addition to the previous six b's, are listed in Table II. The agreement is very good, either within 5% of theoretical calculations or within the experimental errors.

We need to find one more relation so that the parameter A can be determined. This turns out to be much more difficult. At present, only a partial answer is found. As before, once an interacting system consisting of atoms or molecules with very different first and second ionization potentials is considered, complication occurs. We have not yet found an answer for the interacting system, which contains such atoms or molecules but no rare-gas atoms. Except for those systems, we find the relation for interacting systems whose long-range interactions are dominated by dispersion energies as

$$R_m = 4.65 \frac{a_1 + a_2}{1 \pm \left(\frac{I_x - I_y}{I_x + I_y}\right)^2}, \tag{5.2}$$

where R_m is the intermolecular separation correponding to the van der Waals minimum, the "+" is for systems involving at most one rare-gas atom while the "−" is for systems involving only rare-gas atoms, and I_x and I_y are, as usual, the first ionization potentials of the two interacting species involved, respectively. For interacting systems involving true molecules, the above R_m should be understood as the separation corresponding to the minimum of the spherically symmetric part of the van der Waals potential.

Loosely speaking, we can take an atom or a molecule as a hard sphere with an effective radius a. By this approximation, one expects that $R_m \sim (a_1 + a_2)$ for an interacting system with atomic or molecular size parameters a_1 and a_2, respectively. If the two interacting species are different, one expects that a certain correction is needed, in comparison with the case when the two interacting species are identical, to account for the effect of asymmetry between the two interacting species. Even so, the correction needed depends also on the actual interacting species involved. It is well known that the dispersion interaction between two rare-gas atoms is very weak while the short-distance repulsive force is very strong in comparison with the case when at most one of the two interacting species is a rare-gas atom. One expects that either even weaker attractive force or even stronger short-distance repulsive force appear between two different rare-gas atoms in comparison with the case involving two identical rare-gas atoms. Therefore, R_m should be larger, which is indicated by the minus sign in Eq. (5.2). If at most one rare-gas atom is involved, one expects that a larger attractive force or a weaker repulsive force appears. Therefore, the R_m should be smaller, which is indicated by the plus sign in Eq. (5.2). The term $(I_x - I_y/I_x + I_y)^2$ quantifies the effect of asymmetry between interacting species x and y. So we qualitatively explain Eq. (5.2). This equation has been used to calculate the R_m for 29 systems. The results, along with the corresponding experimental or theoretical values for R_m, are listed in Table III. Compared to the crudeness of the above estimation, the agreement is excellent.

By employing Eqs. (5.1), (5.2), and the dipole-dipole dispersion energy (3.6) and requiring that the first derivative of the following total energy vanish at $R = R_m$:

$$V(R) = Ae^{-bR} - C_6 f_6(R)/R^6, \qquad (5.3)$$

we can estimate the parameter A as

$$A = C_6\left[f_6'(R_m) - 6R_m f_6(R_m)\right] e^{bR_m}/bR_m^7, \qquad (5.4)$$

where $f_6'(R) = df_6(R)/dR$.

By now, it seems that we can determine the van der Waals potential completely for a system if the interaction constant C_6 and the first ionization potentials of interacting species are known. However, caution must be taken by noting that both Eqs. (5.1) and (5.2) are empirical in nature and Eq. (5.3) has not yet included the $C_8 f_8(R)/R^8$ and $C_{10} f_{10}(R)/R^{10}$ terms.

TABLE II. Comparison of our Born-Mayer parameters b determined by Eq. (5.1) with those either from theoretical calculations or fitted from experimental data. Most theoretical or experimental b's are from the collection of Tang and Toennies [38,39] except for those with footnotes. All quantities are in atomic units.

System	Present	Theor. or Expt.
He-H_2	2.108	2.207[a]
He-He	2.353	2.388
He-Ar	2.118	2.022
He-Ne	2.278	2.434
He-Kr	2.064	1.905
Ne-Ar	2.044	2.148
Ne-Kr	1.990	2.037
Ne-Xe	1.928	1.963
Ar-Ar	1.884	1.917
Ar-Kr	1.830	1.969
H-H	1.750	1.670
H-Ne	1.977	1.873
H-Ar	1.817	1.815
H-Kr	1.763	1.810
Li-Kr	1.151	1.175
Na-Kr	1.141	1.175
K-Ar	1.149	1.132
K-Kr	1.106	1.164
Rb-Kr	1.098	1.132
Cs-Ar	1.128	1.058
Cs-Kr	1.085	1.080
Cs-Xe	1.036	1.067
NaK	0.826	0.841
Na-Na	0.861	0.812[b]
K-K	0.791	0.807[c]
LiHg	1.054	1.012
ArHCl	1.789	1.797[d]

[a] Reference [40].
[b] Reference [42].
[c] Reference [43].
[d] 5% reduction of the value from Ref. [36] as discussed in Sec. V.

TABLE III. Comparison of the determined van der Waals well parameters R_m from Eq. (5.2) with their correspondences determined from experiments collected in [38,39] except for those with footnotes. Again, quantities are in atomic units.

System	Present	Expt.
He-He	5.53	5.62
He-Ar	6.54	6.69
He-Ne	5.75	5.69
He-Kr	6.96	7.09
He-Xe	7.58	7.84
He-HF	5.94	5.97[a]
Ne-Ne	5.91	5.86
Ne-Ar	6.57	6.48
Ne-Kr	6.94	6.77
Ne-Xe	7.48	7.09
Ar-Ar	6.91	7.10
Ar-Kr	7.15	7.33
Ar-Xe	7.52	7.75
Ar-HCl	7.22	7.33[b]
Ar-HF	6.91	6.60[c]
Ar-HBr	7.31	7.57[c]
Kr-Kr	7.33	7.62
H-H	7.44	7.85
H-Ne	6.35	6.27
H-Ar	7.14	6.84
Li-Ar	9.44	9.35
Na-Ne	8.17	7.84
Na-Ar	9.44	9.26
K-Ar	9.49	9.73
K-Kr	10.03	10.02
Rb-Kr	10.04	10.00
Cs-Ar	9.53	10.39
Cs-Kr	10.06	10.28
Cs-Xe	10.77	10.34

[a] Reference [41].
[b] Reference [36].
[c] Reference [37].

VI. CONCLUSION

The universal polarization density tensor with spherical symmetry, to a good approximation, has been determined, which is used to calculate the nonsingular potentials for both retarded and nonretarded cases through a semiclassical field approach. The finite molecular size effect incorporated in the polarization density tensor is crucial to remove the short-distance singular behavior from the widely used potentials that are obtained from the point-molecular approximation. We are able to show that the frequency-integration upper limit of the van der Waals interaction is $0.5\,c/a$ instead of infinity. In addition to the formula used to determine the atomic or molecular size parameter a, two empirical formulas have also been proposed, that can be used to estimate the Born-Mayer parameter b and the van der Waals well parameter R_m, and therefore the Born-Mayer parameter A, respectively. The accuracy of these formulas has been tested extensively. If neither accurate *ab initio* calculations nor experimental data are available, the potential developed in this study, plus the above mentioned formulas along with the interacting constant C_6, which can be obtained from many sources as discussed before, can be used at least for qualitatively study for atomic or small molecular systems.

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APPENDIX

In this appendix we show explicitly how one can reach Eq. (2.12) from Eq. (2.11) by utilizing the fact that $F_j(ka_0)$ in Eq. (2.11) is an odd function of k. At the end, we will prove in general that $M_{n_0l_0m_0,nlm}(k) = \langle n_0l_0m_0|r\cos\theta|nlm\rangle\langle nlm|e^{ikr\cos\theta}|n_0l_0m_0\rangle$ is an odd function of k for any one-electron state $|nlm\rangle$, which is equivalent to saying that the corresponding function F_j, as for the case of a hydrogen atom, is an odd function of k for any given one-electron state $|n_0l_0m_0\rangle$. This result, plus the exponential factor $\exp(-r/a)$ in the ground-state wave function for other atoms and molecules as discussed in Sec. II, leads us, by the same token as for the hydrogen atom case, to Eq. (2.16).

Let us rewrite Eq. (2.11) as

$$\boldsymbol{A}(\vec{r}) = \frac{1}{3}\frac{1}{(2\pi)^2}\boldsymbol{I}\sum_{j=2}^{q} B(r), \qquad \text{(A1)}$$

where

$$B(r) = \int_0^{\infty} dk\, \frac{kF_j(ka_0)}{[(ka_0)^2+(1+1/q)^2]^{1+j}} \times \int_{-1}^{+1} dx\, e^{-ikrx}. \qquad \text{(A2)}$$

By noticing that $F_j(ka_0)$ is an odd function of k, Eq. (A2) can be written, by integrating over variable x, as

$$B(r) = \frac{1}{2ir}\int_{-\infty}^{+\infty} dk^2\, \frac{F_j(ka_0)/k}{[(ka_0)^2+(1+1/q)^2]^{1+j}}. \qquad \text{(A3)}$$

Since $F_j(ka_0)$ is an odd function of k, $F_j(ka_0)/k$ is an even function of k. $F_j(ka_0)/k[(ka_0)^2+(1+1/q)^2]^{1+j}$ can be written as $1/[(ka_0)^2+(1+1/q)^2]^{(3+j)/2}$ + higher order terms if j is odd or as $1/[(ka_0)^2+(1+1/q)^2]^{(4+j)/2}$ + higher order terms if j is even, where no such term $1/[(ka_0)^2+(1+1/q)^2]$ exists for allowed j values. Therefore, we can rewrite

$$dk^2\frac{F_j\ (ka_0)/k}{[(ka_0)^2+(1+1/q)^2]^{1+j}} = d\left\{\frac{g_{j-1}(ka_0)}{[(ka_0)^2+(1+1/q)^2]^{j}}\right\}, \qquad \text{(A4)}$$

where $g_{j-1}(ka_0)$ is an even polynomial of k, whose order is $j-1$ if j is odd and $j-2$ if j is even. As $k \to \pm\infty$, $g_{j-1}(ka_0)/[(ka_0)^2+(1+1/q)^2]^j$ goes to zero as $1/[(ka_0)^2+(1+1/q)^2]^{(j+1)/2}$ + higher order infinitesimal terms if j is odd or as $1/[(ka_0)^2+(1+1/q)^2]^{(j+2)/2}$ + higher order infinitesimal terms if j is even. With this in mind and performing partial integration in Eq. (A3), we have

$$B(r) = -\frac{1}{2}\int_{-\infty}^{+\infty} dk\frac{g_{j-1}(ka_0)}{[(ka_0)^2+(1+1/q)^2]^{j}}\, e^{ikr}. \qquad \text{(A5)}$$

The integration in Eq. (A5) is a very common one and can be evaluated by employing residue theorems around poles $i(1+1/q)$. The result can be cast as

$$B(r) = G_{j-1}(r/a_0)e^{-(1+1/q)\ r/a_0}, \qquad \text{(A6)}$$

where $G_{j-1}(r/a_0)$ is a $(j-1)$th-order polynomial of variable r/a_0. Returning to Eq. (A1), we have

$$\boldsymbol{A}(\vec{r}) = \frac{1}{3}\frac{1}{(2\pi)^2}\boldsymbol{I}\sum_{j=2}^{q} G_{j-1}(r/a_0)e^{-(1+1/q)\ r/a_0}, \qquad \text{(A7)}$$

which is essentially Eq. (2.12).

Since $|nlm\rangle = |nl\rangle|lm\rangle$ and $|lm\rangle \sim P_l^m(\cos\theta)\ e^{im\phi}$ up to a constant with $P_l^m(\cos\theta)$ the associated Legendre polynomial, we have first

$$\langle l_0m_0|\cos\theta|lm\rangle = \delta_{m_0,m}\langle l_0m_0|\cos\theta|lm_0\rangle. \qquad \text{(A8)}$$

By using the identity

$$x\ P_l^m(x) = (2l+1)^{-1}[(l+m)P_{l-1}^m(x) + (l-m+1)P_{l+1}^m(x)] \qquad \text{(A9)}$$

and the orthogonal relation

$$\int_{-1}^{+1} P_l^m(x)P_{l'}^m(x)d\ x = \frac{(l+m)!}{(l-m)!}\frac{2}{2l+1}\delta_{l,l'}, \qquad \text{(A10)}$$

we have

$$\langle l_0 m_0|\cos\theta|lm\rangle \sim [(l_0+m_0+1)\delta_{l_0,l-1} + (l_0-m_0)\delta_{l_0,l+1}]\delta_{m_0,m}. \quad \text{(A11)}$$

Hence the only nonvanishing matrix elements are those for $m = m_0$, $l = l_0 + 1$, or $l = l_0 - 1$. For those allowed m, l values, the matrix element $\langle n_0 l_0 m_0|e^{ikr\cos\theta}|nlm\rangle$ can be shown to be an odd function of k in the following. This can be easily done by noticing that $P_l^m(-x) = (-1)^{l+m}P_l^m(x)$ from the definitions $P_l^m(x) = (1-x^2)^{m/2}\, d^m P_l(x)/dx^m$ and $P_l(x) = 1/2^l\, l!\, d^l(x^2-1)^l/dx^l$. Since $\langle l_0 m_0|e^{ikr\cos\theta}|lm_0\rangle = -\langle l_0 m_0|e^{-ikr\cos\theta}|lm_0\rangle$ for both $l = l_0 - 1$ and $l = l_0 + 1$, we have

$$\begin{aligned} M_{n_0 l_0 m_0, nlm}(k) &= \langle n_0 l_0 m_0|r\cos\theta|nlm\rangle \\ &\quad \times\langle nlm|e^{ikr\cos\theta}|n_0 l_0 m_0\rangle \\ &= i\langle n_0 l_0 m_0|r\cos\theta|nlm\rangle \\ &\quad \times\langle nlm|\sin(kr\cos\theta)|n_0 l_0 m_0\rangle, \end{aligned} \quad \text{(A12)}$$

which is an odd function of k.

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