Long range intermolecular forces in triatomic systems: connecting the atom-diatom and atom-atom-atom representations

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The long-range forces that act between three atoms are analysed in both atom-diatom and atom-atom representations. Expressions for atom-diatom dispersion coefficients are obtained in terms of 3-body nonadditive coefficients. The anisotropy of atom-diatom $C_6$ dispersion coefficients arises primarily from nonadditive triple-dipole and quadruple-dipole forces, while pairwise-additive forces and nonadditive triple-dipole and dipole-dipole-quadrupole forces contribute significantly to atom-diatom $C_8$ coefficients. The resulting expressions are applied to dispersion coefficients for Li + Li$_2$ (triplet) and recommendations are made for the best way to obtain global triatomic potentials that dissociate correctly both to three separated atoms and to an atom and a diatomic molecule.

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INTRODUCTION

There is great current interest in forming diatomic molecules in cold gases of alkali metal atoms, by photoassociation spectroscopy, by magnetic tuning through atom-atom Feshbach resonances and through 3-body recombination. In most current experiments, the diatomic molecules are formed in vibrational states near dissociation and spend most of their time at large internuclear separations. Once formed, the fate of the molecules depends on collisional processes which in turn depend on atom-atom and atom-diatom potential energy surfaces.

The potential energy surfaces for alkali metal trimers are strongly nonadditive, even for spin-polarized atoms (quartet electronic states). In all cases both linear and equilateral configurations of the M$_3$ collision complex lie below the asymptotic atom-diatom energy, so that barrierless atom exchange reactions can occur. We have carried out quantum dynamics calculations including reactive channels for spin-polarized Na + Na$_2$, Li + Li$_2$, and K + K$_2$. In Na + Na$_2$, nonadditivity increases the well depth by about 60% and increases the low-energy cross sections for vibrational quenching by a factor of 10. For the other alkali metals the nonadditive contributions to the potential are even larger.

Low-energy collisions are particularly sensitive to long-range potentials. In developing triatomic potential energy surfaces for collision calculations, it is thus highly desirable to use global functional forms that include nonadditivity and have the correct physical behaviour both for three-body dissociation (to separated atoms) and for two-body dissociation (to an atom and a diatomic molecule). However, although there has been a considerable amount of work on both these limits, the connection between them has not been fully explored. This paper sets out to establish the connection and to suggest functional forms that are correct in both limits.

ATOM-DIATOM LIMIT

An atom-diatom system is conveniently described in terms of Jacobi coordinates $R$, $r$ and $\theta$. In this case, “long range” is usually interpreted to mean that the atom-diatom distance $R$ is large but that the diatom internal distance $r$ can be either large or small. For an atom interacting with a homonuclear diatom the long-range forces for $R \gg r$ (neglecting retardation and damping) can be written to order $R^{-10}$.

$$V(R, r, \theta) = -C_6(r, \theta)R^{-6} - C_8(r, \theta)R^{-8} - C_{10}(r, \theta)R^{-10},$$  

where

$$C_6(r, \theta) = C_6^0(r) + C_6^2(r)P_2(\cos \theta)$$
$$C_8(r, \theta) = C_8^0(r) + C_8^2(r)P_2(\cos \theta) + C_8^4(r)P_4(\cos \theta)$$
$$C_{10}(r, \theta) = C_{10}^0(r) + C_{10}^2(r)P_2(\cos \theta) + C_{10}^4(r)P_4(\cos \theta).$$

The $r$-dependence of the dispersion coefficients $C_n^m(r)$ is central to the present work.

Rérat and Bussery-Hovvalt have calculated isotropic and anisotropic dispersion coefficients $C_n^m(r)$ and $C_n^m$ for Li and Na interacting with triplet Li$_2$ and Na$_2$. They fitted the results to empirical functional forms based on the known asymptotic behaviour of diatomic polarizabilities. However, they stated that the proper asymptotic functional form for atom-diatom dispersion coefficients was unknown. Mérara et al. extended parts of this work (not including the $r$-dependence of the dispersion coefficients) to systems containing K and triplet K$_2$.

SEPARATED ATOM LIMIT

A system of three well-separated atoms is more conveniently described in terms of atom-atom distances $r_{12},$
of the inverse powers. The interaction energy for such a system is conventionally represented in terms of pairwise additive and nonadditive terms,

\[ V(r) = \sum_{i<j} V_{\text{dimer}}(r_{ij}) + V_3(r), \]

where we use the shorthand \((r)\) to indicate \((r_{12}, r_{23}, r_{31}, \phi_1, \phi_2, \phi_3)\). For a pair of S-state atoms the long-range energy is

\[ V_{\text{dimer}}(r) = -C_6 r^{-6} - C_8 r^{-8} - C_{10} r^{-10} + \mathcal{O}(r^{-11}). \]

The nonadditive energy has several long-range contributions that need careful consideration. The best-known is the Axilrod-Teller-Muto (ATM) triple-dipole (DDD) term, which has the form

\[ V_{3\text{DDD}}(r) = Z_{111} W_{111}(r), \]

where

\[ W_{111}(r) = 3(1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3) r_{12}^{-3} r_{23}^{-3} r_{31}^{-3}. \]

The triple-dipole term is one of several that arise in third-order perturbation theory from terms of the type

\[ \frac{\langle 000| H_{12}^I |lm0 \rangle \langle lm0| H_{23}^I |00n \rangle \langle 00n| H_{31}^I |000 \rangle}{(\Delta E_l^I + \Delta E_m^I + \Delta E_n^I)}, \]

where the ket \(|lmn\rangle\) indicates a product wavefunction with atoms 1, 2 and 3 in states \(l, m\) and \(n\) respectively and \(\Delta E_l^I\) is the excitation energy for state \(l\) of atom \(i\). The interaction Hamiltonian \(H_{ij}^I\) is usually expanded at long range in terms of multipole-multipole interactions. The triple-dipole term arises when each of the three operators \(H_{ij}^I\) is a dipole-dipole interaction of the form

\[ H_{ij}^I(\text{DD}) = \mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij}), \]

where \(\hat{r}_{ij}\) is a unit vector along \(r_{ij}\). The triple-dipole term will be referred to below as a third-order (3,3,3) contribution to indicate the powers of the three distances involved.

There are additional third-order terms that arise when one or more of the dipole operators is replaced by a quadrupole or higher-order moment. The low-order terms and their resulting contributions for 3 identical atoms are

\[ V_{3\text{DDQ}}(r) = Z_{112} W_{112}(r), \]

\[ V_{3\text{DQQ}}(r) = Z_{122} W_{122}(r), \]

\[ V_{3\text{DDO}}(r) = Z_{113} W_{113}(r), \]

\[ V_{3\text{QQQ}}(r) = Z_{222} W_{222}(r), \]

where \(Q\) stands for quadrupole and \(O\) for octopole. The coefficients \(Z_{l_1 l_2 l_3}\) are related to polarizabilities of rank \(l_1, l_2\) and \(l_3\) at imaginary frequencies,

\[ Z_{l_1 l_2 l_3} = (1/\pi) \int_0^\infty \alpha^{l_1}(i\omega)\alpha^{l_2}(i\omega)\alpha^{l_3}(i\omega) \, d\omega. \]

The corresponding geometric factors are

\[ W_{112}(r) = \frac{3}{16} [9 \cos \phi_3 - 25 \cos 3 \phi_3 + 6 \cos(\phi_1 - \phi_2)(3 + 5 \cos 2 \phi_3)] r_{12}^{-3} r_{23}^{-4} r_{31}^{-4} + \text{c.p.} \]

\[ W_{122}(r) = \frac{15}{64} [3(\cos \phi_1 + 5 \cos 5 \phi_3) + 20 \cos(\phi_2 - \phi_3)(1 - 3 \cos 2 \phi_1)] r_{12}^{-4} r_{23}^{-5} r_{31}^{-5} + \text{c.p.} \]

\[ W_{113}(r) = \frac{5}{32} [9 + 8 \cos 2 \phi_3 - 49 \cos 4 \phi_3 + 6 \cos(\phi_1 - \phi_2)(9 \cos \phi_3 + 7 \cos 3 \phi_3)] r_{12}^{-3} r_{23}^{-5} r_{31}^{-5} + \text{c.p.} \]

\[ W_{222}(r) = \frac{15}{128} [-27 + 220 \cos \phi_1 \cos \phi_2 \cos \phi_3 + 490 \cos 2 \phi_1 \cos 2 \phi_2 \cos 2 \phi_3]
+ 175 \left[ \cos 2(\phi_1 - \phi_2) + \cos 2(\phi_2 - \phi_3) + \cos 2(\phi_3 - \phi_1) \right] r_{12}^{-5} r_{23}^{-5} r_{31}^{-5}, \]

where c.p. indicates summation of all cyclic permutations of indices. It may be noted that the multipole operator on each atom appears in two terms in Eq. (17), so that changing one dipole operator into a higher-order one affects two of the inverse powers.

In addition to these third-order terms, there are terms arising from fourth and higher-order perturbation theory that make important contributions to the long-range atom-diatomic coefficients. In principle, any combination of interaction operators could produce a 4th-order term, although only those that involve excitations on all three atoms produce a contribution to the 3-body nonadditive energy. In addition, any odd-order operators (dipoles and octopoles) must
occur an even number of times on each atom to satisfy parity constraints. Thus there are terms such as

$$\langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |ql0\rangle \langle ql0| H_{12}^{(DD)} |000\rangle,$$

which gives rise to a (6,6,0) contribution, and

$$\langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |q0p\rangle \langle q0p| H_{31}^{(DD)} |000\rangle,$$

which gives rise to a (8,3,3) contribution. However, terms such as

$$\langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |q0p\rangle \langle q0p| H_{31}^{(DD)} |000\rangle,$$

are forbidden by parity, so that there is no (6,3,3) contribution. The fourth-order dipole energy (15) has been given within a Drude oscillator model by Bade (27). We adopt the definition $Z_{1111} = (5/32)V\alpha^3$, which corresponds to

$$Z_{1111} = (1/\pi) \int_0^\infty [\alpha^1(i\omega)]^5 d\omega.$$

In the 5th-order case, Eq. (10) of ref. 27 then reduces to

$$V_3^{DDDD}(r) = Z_{1111}W_{1111}(r),$$

with

$$W_{1111}(r) = -\frac{9}{2} \left(1 + \cos^2\phi_1\right) r_{12}^{-6} r_{13}^{-6} + \text{c.p.}$$

In addition, there are fourth-order terms like Eq. (15) but with one pair of the dipole-dipole operators replaced with dipole-quadrupole operators. These give terms with powers (8,6,0), (8,3,3), (7,7,0), (7,4,3) and (6,4,4). The angular factors have been given to within overall scaling factors by Lotrich and Szalewicz (29) (though the (6,3,3) term that they describe is in fact zero and there are several typographical errors in their equations). There is also a fourth-order term involving a single octopole-dipole operator (with all the rest dipole-dipole) that also contributes to (8,6,0) but is not mentioned in ref. 29.

There are also analogous terms arising from fifth-order perturbation theory, which are also constrained by the requirement that odd-order operators must occur an even number of times for each atom. The leading such term (DDDDD) has powers (9,3,3), but its explicit angular form has not been given previously. We have evaluated

it within the Drude model of ref. 27. We adopt the definition $Z_{1111} = (35/256)V\alpha^3$, which corresponds to

$$\langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |ql0\rangle \langle ql0| H_{12}^{(DD)} |000\rangle, \quad \langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |q0p\rangle \langle q0p| H_{31}^{(DD)} |000\rangle, \quad \langle 000| H_{12}^{(DD)} |lm0\rangle \langle lm0| H_{23}^{(DD)} |lnp\rangle \langle lnp| H_{12}^{(DD)} |q0p\rangle \langle q0p| H_{31}^{(DD)} |000\rangle.$$

CONNECTING THE ATOM-DIATOM AND SEPARATED ATOM LIMITS

To make an explicit connection between the atom-atom additive and nonadditive dispersion terms and the atom-diatom dispersion formulae (22), we must collect terms in the $(r_{12}, r_{23}, r_{31})$ representation that contribute to individual powers of the Jacobi distance $R$. Let us consider the case in which a diatom made up of atoms 1 and 2 is separated from atom 3. For simplicity, we will assume that the three atoms are identical. The atom-atom distances may be written in terms of Jacobi coordinates $R$, $r$ and $\theta$,

$$r_{12} = r,$$

$$r_{23} = \sqrt{R^2 + \frac{r^2}{4} + Rr \cos \theta},$$

$$r_{31} = \sqrt{R^2 + \frac{r^2}{4} - Rr \cos \theta},$$

and the cosines of $\phi_1$, $\phi_2$ and $\phi_3$ are given by the cosine rule. The approach we take is to express the different contributions to 3-body energies in Jacobi coordinates.
using these equations and then to expand the results as power series in \( r/R \).

We consider first the additive terms \( V_{\text{dimers}}(rij) \). For \( R \gg r \) the atom-atom \( C_6 \) term makes contributions to the atom-diatom coefficients of Eq. (2) given by

\[
C_{\text{add},6}^{C_6}(r, \theta) = 2C_6; \\
C_{\text{add},6}^{C_8}(r, \theta) = C_8 \left( \frac{5}{2} + 8P_2(\cos \theta) \right) r^2; \\
C_{\text{add},6}^{C_{10}}(r, \theta) = C_{10} \left( \frac{7}{4} + \frac{50}{7} P_2(\cos \theta) + \frac{48}{7} P_4(\cos \theta) \right) r^4.
\]

Similarly, the atom-atom \( C_8 \) and \( C_{10} \) terms contribute

\[
C_{\text{add},8}^{C_8}(r, \theta) = 2C_8; \\
C_{\text{add},10}^{C_{10}}(r, \theta) = 2C_{10}.
\]

It may be seen that the atom-atom pair potential contributes no anisotropy to the longest-range \((R^8)\) term in the atom-diatom potential. All such anisotropy must come from 3-body nonadditive terms in the potential. The only third-order 3-body term that contributes to \( C_6(r, \theta) \) is the triple-dipole term. Its geometric factor may be expanded at large \( R \),

\[
W_{111}(R, r, \theta) = -6P_2(\cos \theta)r^{-3}R^6 + \left( \frac{3}{2} - \frac{6}{7} P_2(\cos \theta) - \frac{36}{7} P_4(\cos \theta) \right) r^{-1}R^8 + O(rR^{-10}).
\]

Similarly, the geometric factors for the third-order DDQ, DQQ and DDO terms may be expanded

\[
W_{112}(R, r, \theta) = -\frac{120}{7} \left[ P_2(\cos \theta) - P_4(\cos \theta) \right] r^{-3}R^8 + O(r^{-1}R^{10}) \\
W_{122}(R, r, \theta) = 30P_4(\cos \theta)r^{-5}R^8 + O(r^{-3}R^{10}) \\
W_{113}(R, r, \theta) = -40P_4(\cos \theta)r^{-5}R^8 + O(r^{-3}R^{10}),
\]

where any contributions from cyclic permutations are now included. These three terms thus contribute to the atom-diatom \( C_4(r) \) and its anisotropy but not to \( C_6(r, \theta) \).

As noted above, the fourth-order DDDDD term does not have a \((6,3,3)\) contribution but does have a \((6,6,0)\) contribution. It can thus contribute to the atom-diatom \( C_6 \) coefficient. Its geometric factor \(^{24}\) may be expanded at large \( R \),

\[
W_{1111}(R, r, \theta) = -6 \left[ 2 + P_2(\cos \theta) \right] r^{-6}R^6 \\
- \left( \frac{33}{2} + \frac{402}{7} P_2(\cos \theta) + \frac{144}{7} P_4(\cos \theta) \right) r^{-4}R^8 + O(r^{-2}R^{10}).
\]

Collecting these equations together provides expressions for the behaviour of the atom-diatom dispersion coefficients \( C_n^\lambda(r) \) at large \( r \),

\[
C_6^0(r) = 2C_6 + 12Z_{1111}r^{-6} + O(r^{-8}); \\
C_6^2(r) = 6Z_{1111}r^{-3} + 6Z_{111}r^{-6} + O(r^{-8}); \\
C_8^0(r) = \frac{5}{2}C_6r^2 + 2C_8 - \frac{3}{2}Z_{111}r^{-1} + \frac{33}{2}Z_{1111}r^{-4} + O(r^{-6}); \\
C_8^2(r) = 8C_6r^2 + \frac{6}{7}Z_{1111}r^{-1} + \frac{120}{7}Z_{112}r^{-3} + \frac{402}{7}Z_{1111}r^{-4} + O(r^{-6}); \\
C_{10}^0(r) = \frac{36}{7}Z_{1111}r^{-1} - \frac{120}{7}Z_{112}r^{-3} + \frac{144}{7}Z_{1111}r^{-4} + (40Z_{113} - 30Z_{122}) r^{-5} + O(r^{-6}).
\]

The \( O(r^{-8}) \) terms in Eqs. \(^{12}\) and \(^{13}\) come from the \((8, 6, 0)\), \((8, 3, 3)\) and \((6, 4, 4)\) contributions to the fourth-order energy, while the \( O(r^{-6}) \) terms in Eqs. \(^{14}\) to \(^{16}\) come from both these and the \((7, 7, 0)\) and \((7, 4, 3)\) con-
tributions. The fifth-order term (Eq. (27)) does not contribute until \( O(r^{-9}R^{-6}) \).

**FITTING DISPERSION COEFFICIENTS FOR Li + Li₂**

The equations above apply when all three of \( r_1 \), \( r_2 \) and \( r_3 \) are large. However, when any of them is small, the power series is insufficient. We therefore use Eqs. (12) to (16) as the long-range limits of more general expressions, constructed by (i) multiplying the individual inverse power terms by damping functions \( D_n(r) \) and (ii) adding a short-range exponential term to allow for the effects of orbital overlap.

As described above, Rérat and Bussery-Honvault \[21\] have calculated isotropic and anisotropic dispersion coefficients for Li + Li₂ (\( ^4 \Sigma_u^+ \)) as a function of \( r \) and have fitted them to long-range expansions. They stated that “no asymptotic form of the coefficients \( C_6 \) exists to our knowledge”, but found empirically that \( C_6^0(r) \) required both \( r^{-3} \) and \( r^{-6} \) terms, while \( C_6^3(r) \) required only \( r^{-6} \). Our expressions (12) and (16) above provide the explanation for this. However, our results also show that there should be relationships among the coefficients of the fit, and the resulting constraints were not included in ref. \[21\]. In particular, the coefficient of \( r^{-6} \) in \( C_6^0 \) should be half that in \( C_6^0 \) and \( Z_{1111} \) can be related at least approximately to \( Z_{111} \) and \( C_6 \) as described below.

In devising functional forms for \( C_6^0(r) \) and \( C_6^3(r) \) it is important to consider damping of the inverse power terms. For the two-body interaction energy, the most popular approach is to use Tang-Toennies damping functions \[31\] of the form

\[
D_n(R) = 1 - e^{-bR} \sum_{k=0}^{n} \frac{(bR)^k}{k!}.
\]  

When damping 3-body terms such as Eqs. (13) and (14) to (17), a damping function is required for each \( r_i^6 \). We have chosen to use \( \sqrt{D_{2n}(r_i)} \) rather than \( D_n(r_i) \) for this purpose, because this recovers the correct \( D_n(R) \) in the 2-body energies. Thus we damp 3-body terms according to prescriptions such as

\[
r_1^3 r_2^3 r_3^4 \rightarrow r_1^3 r_2^3 r_3^3 \sqrt{D_6(r_1)} D_6(r_2) D_6(r_3); \quad (48)
\]

\[
r_1^3 r_2^3 r_3^4 \rightarrow r_1^3 r_2^3 r_3^3 \sqrt{D_6(r_1)} D_6(r_2) D_6(r_3). \quad (49)
\]

When damping is introduced in this way, the \( r^{-6} \) terms in the expressions for dispersion coefficients are damped with \( D_6(r) \), but the \( r^{-3} \) term in \( C_6^3(r) \) is damped with \( \sqrt{D_6(r)} \) rather than \( D_3(r) \). The expressions that we fit to are therefore

\[
C_6^0(r) = 2C_6 + 12Z_{1111} r^{-6} D_6(r) + A \exp(-Cx);
\]

\[
C_6^3(r) = 6Z_{1111} r^{-3} \sqrt{D_6(r)} + 6Z_{1111} r^{-6} D_6(r) + B \exp(-Cx),
\]

where \( x = (r - r_0)/r_0 \) and \( r_0 = 7.0 \) Å.

We have fitted the values of \( C_6^0(r) \) and \( C_6^3(r) \) in ref. \[21\] to the functional forms \[30\] and \[31\]. [Our \( C_6^0(r) \) are \( C_n^{\lambda \lambda}(r)/\sqrt{\lambda(\lambda + 1)} \) in the notation of ref. \[21\].] The triple-dipole coefficient was fixed at a value taken from variational calculations with Hylleraas basis sets by Yan et al. \[31\]. \( Z_{1111} = \nu_{abc}/3 = 5.687 \times 10^4 E_a a_0^3 \) (where \( a_0 \) is the Bohr radius and \( E_a \) is the Hartree energy). There is no \( ab \) initio value available for the quadrupole-dipole coefficient, but in a Drude model \( Z_{1111} = (5/32)VA^2 \) as described above, where \( V \) is a characteristic excitation energy and \( a \) is the atomic dipole polarizability. Within the same model, \( C_6 = (3/4)VA^2 \) and \( Z_{1111} = (3/16)VA^3 \). Combining these results gives an estimate

\[
Z_{1111} \approx \frac{10(Z_{111})^2}{3C_6}.
\]

For Li₃ with \( C_6 \) and \( Z_{111} \) values from ref. \[31\], this gives \( Z_{1111} = 7.73 \times 10^6 E_a a_0^{12} \). The \( C_6 \) coefficient in Eq. \[30\] could not be fixed at the value \( C_6 = 1393 E_a a_0^6 \) from ref. \[31\], because the results for \( C_6(r) \) in ref. \[21\] converge on a slightly asymptotic value, so \( C_6 \) was allowed to vary in our fit.

Meath and coworkers \[32\] have calculated dispersion damping functions for Li₂ and found that the \( r^{-6} \) damping function is around 0.45 at the diatomic minimum, \( r_e \approx 4.2 \) Å. With the Tang-Toennies form of \( D_6(r) \), this requires \( b \approx 1.5 \) Å⁻¹. We found that the exponent \( C \) needed to fit the short-range part of \( C_6(r) \) was very different from \( b r_0 \), so we allowed \( b r_0 \) and \( C \) to be different and fixed \( b \) at 1.5 Å⁻¹. The remaining parameters were then determined by a weighted least-squares fit, giving values \( C_6 = 1414.8 E_a a_0^6 \), \( A = 17.2 \pm 2.6 E_a a_0^6 \), \( B = 35.2 \pm 3.9 E_a a_0^6 \) and \( C = 5.13 \pm 0.25 \). The quality of the resulting fit is shown in Fig. 1 together with the contributions of the individual terms in Eqs. \[30\] and \[31\].

Rérat and Bussery-Honvault \[21\] have also given values of \( C_6^0(r) \), \( C_6^3(r) \) and \( C_8^4(r) \) for the single distance \( r = 4.2 \) Å, which is near the equilibrium distance for
explore the onset of long-range behaviour. It is interesting to calculate $C_r$ from Eqs. (44) to (46) at the Bohr radius. Evaluating the long-range expressions for $C_r$ and $C_0$, respectively, we find that the exponential contributions to long-range contributions, and indeed it may be seen from Fig. 1 that the exponential contributions to $C_0(r)$ and $C_0(r)$ are quite large at this distance. It would be very interesting to calculate $r$-dependent $C_8$ coefficients and explore the onset of long-range behaviour.

**GLOBAL FUNCTIONAL FORMS FOR POTENTIAL ENERGY SURFACES**

The results obtained above have important implications for the choice of functional forms to represent potential energy surfaces for triatomic systems. For low-energy scattering calculations, it is highly desirable to have an interaction potential that dissociates correctly both to three atoms and to an atom and a diatomic molecule. This is especially important for processes such as 3-body recombination and collisions of long-range diatomic molecules with atoms, which are of current interest in studies of cold molecule formation.

A global potential energy surface for a homonuclear triatomic system must be symmetric in the atom indices if it is to reproduce the full symmetry of the system. The simplest coordinate system that achieves this is a set of 3 bond length coordinates ($r_{12}, r_{23}, r_{31}$). Jacobi coordinates cannot easily describe the full symmetry.

Our approach is to obtain a potential energy surface from high-quality ab initio calculations on a grid of values ($r_{12}, r_{23}, r_{31}$). Once this has been done, we need to interpolate and extrapolate it in a way that incorporates the correct long-range behaviour. In one dimension, reciprocal power - reproducing kernel Hilbert space (RKHS) interpolation [18, 35] provides an attractive way to obtain a potential with desired inverse power behaviour at long range. However, multidimensional RKHS interpolation [15, 35] at best gives a potential that extrapolates beyond the points as a simple product of inverse powers in the different coordinates. None of the long-range 3-body terms have this form, so a more sophisticated approach is required.

Two different cases may be distinguished. For systems such as spin-polarized Na$_3$ or K$_3$, the nonadditive forces are substantial at short range but do not dwarf the additive forces [13, 19]. Under these circumstances, we have found it best to transform the potential to a form that does behave as a simple product of inverse powers at long range and then interpolate in that form. The first stage in this process is to subtract the (assumed known) sum of pair potentials from the ab initio points according to Eq. (4) to obtain the nonadditive contribution to the interaction, $V_3(r)$. The leading terms in the long-range expansion of $V_3(r)$ are the DDD and DDQ terms. However, it may be noted that the DDD term of Eq. (5) vanishes on a seam in the angular space and the DDQ term of Eq. (14) vanishes at all linear configurations. It is therefore not adequate to divide $V_3(r)$ by an angular factor in order to obtain a form that depends only on inverse powers. Fortunately, the coefficients $Z_{111}$ and $Z_{112}$ are known for all the homonuclear alkali metal atom systems [34], so that damped versions of these terms can be subtracted from the total nonadditive energy $V_3$ to give...
a quantity $V''_3$,

$$V'_3(r) = V_3(r) - \left[ V_{3,damp}^{DDD}(r) + V_{3,damp}^{DDQ}(r) \right]. \quad (53)$$

In our work on $K_3$ [12], we used a single damping function for both terms. However, the present work has shown that it would be better to choose separate damping functions for each inverse power term as in Eqs. (18) and (19), and to define (for example)

$$V_{3,damp}^{DDQ}(r) = \frac{3}{16} Z_{112} \left[ 9 \cos \phi_3 - 25 \cos 3\phi_3 \
+ 6 \cos (\phi_1 - \phi_2)(3 + 5 \cos 2\phi_3) \right].$$

The leading asymptotic term of the function $V''_3$ now has the form $-\text{constant} \times r^{-3}$. An RP-RKHS interpolation with respect to ab initio at the correct long-range form. We thus have

$$V_{3,damp}^{LR}(r) = \frac{r_3^3}{r_1^3 r_2^3} \left[ 1 + \cos^2 \phi_1 \right] + \frac{r_3^3}{r_1^3} \left[ 1 + \cos^2 \phi_2 \right] + \left[ 1 + \cos^2 \phi_3 \right]. \quad (55)$$

The leading term in the asymptotic multipole expansion of $V''_3$ is the fourth-order dipole-dipole-dipole term (DDDD), which has the more complicated (unfactorizable) form of Eq. (21) above, with powers (6,6,0). If $Z_{1111}$ is known, this too could be subtracted out. However, this term is negative at all geometries, so a satisfactory alternative is to eliminate it by defining $V''_3(r) = g(r) \times V'_3(r)$, where

$$g(r) = \frac{r_3^3}{r_1^3 r_2^3} \left[ 1 + \cos^2 \phi_1 \right] + \frac{r_3^3}{r_1^3} \left[ 1 + \cos^2 \phi_2 \right] + \left[ 1 + \cos^2 \phi_3 \right]. \quad (56)$$

A system such as quartet Li$_3$ requires a different approach [17]. In this case the nonadditive forces are so large that at short range it does not make sense to decompose the potential into additive and nonadditive parts at all. The nonadditive potential is many times larger than the additive potential [11], and the decomposition would require the full short-range potential to be expressed as the difference of two large numbers. Nevertheless, at long range a decomposition according to Eq. (28) is essential. Under these circumstances, we found it best to carry out an unconstrained fit to the ab initio points at short range, without imposing the correct long-range behaviour, to obtain a short-range function $V_{3SR}(r)$. We then use a switching function $S(r)$ to join this onto the correct long-range form. We thus have

$$V(r) = S(r) V_{3SR}(r) + [1 - S(r)] V_{3LR}(r). \quad (57)$$

The long-range form must be valid when any of the atom-atom distances is large. In our work on Li$_3$ [17], we used

$$V_{3LR}(r) = \sum_{i<j} V_{\text{dimer}}(r_{ij}) + V_{3,LR}(r), \quad (58)$$

where

$$V_{3,LR}(r) = V_{3,damp}^{DDD}(r) + V_{3,damp}^{DDQ}(r) + V_{3,damp}^{DD}(r) + V_{3,rep}(r). \quad (59)$$

The function of the term $V_{3,rep}(r)$ is to ensure that the atom-atom dispersion coefficients $C_6^0(r)$ and $C_6^2(r)$ have the correct values (given by Eqs. (50) and (51)) even when one of the atom-atom distances is small. When $R \gg r$, this is achieved by defining

$$V_{3,rep}^{DD}(r) = -[A + BP_2(\cos \theta)] \times \exp(-Cx r_3^{-3} r_2^{-3} \sqrt{\sum_{23} D_4(r_{23}) D_4(r_{31})}) + \text{c.p.}, \quad (60)$$

where $x = (r_{12} - r_0)/r_0$ as before and the parameters $A$, $B$, and $C$ come from fits to numerical values of $C_6^0(r)$ and $C_6^2(r)$ as described above. In evaluating Eq. (60) it is convenient to use an approximate form of $P_2(\cos \theta)$ that is valid for $R \gg r$ but is well-behaved at all geometries,

$$P_2(\cos \theta) \approx -\frac{1}{2} \left( 1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3 \right). \quad (61)$$

This is already evaluated as part of $W_{111}(r)$, and since it is symmetric the cyclic permutations required in Eq. (60) involve no extra geometric calculations.

Finally, the switching function $S(r)$ must become zero when any of the three atom-atom distances is large. For Li$_3$ we chose to use

$$S(r) = \frac{1}{2} \tanh[1 - s_1 (r_1 + r_2 + r_3 - s_2)], \quad (62)$$
with the parameters $s_1$ and $s_2$ determined in such a way that the switching takes place in a region where both functional forms give reasonably accurate energies.

**CONCLUSIONS**

We have investigated the relationship between long-range intermolecular forces for triatomic systems in the atom-diatom and atom-atom-atom representations. We have obtained expressions relating the dispersion coefficients in the two representations. We have shown that the anisotropy of the atom-diatom $C_6$ dispersion coefficient arises entirely from nonadditive terms in the 3-body expansion. The most significant contributions at long range arise from the third-order triple-dipole term and the fourth-order quadruple-dipole term. The leading contributions to the atom-diatom $C_8$ coefficient arise from the additive atom-atom $C_6$ and $C_8$ coefficients and the third-order nonadditive triple-dipole and dipole-dipole-quadrupole coefficients.

There is great current interest in the formation of diatomic molecules in cold atomic gases, and the collisional properties of such molecules are of great importance. Calculations on these collisions need triatomic intermolecular forces for triatomic systems in the fourth-order quadruple-dipole term. The leading contributions to the atom-diatom $C_8$ coefficient arise from nonadditive terms in the 3-body expansion. The most significant contributions at long range arise entirely from nonadditive terms in the 3-body expansion. The most significant contributions at long range arise entirely from nonadditive terms in the 3-body expansion.

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