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High-Order Dispersion Coefficients for Alkali-metal Atoms*

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Abstract *High-order dispersion coefficients C_9, C_{11}, C_{12}, and C_{13} for the ground-state alkali-metals were calculated by combining the l-dependent model potential of alkali-metal atoms and linear variation method based on B-spline basis functions. The results were compared.*

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1 Introduction

The long-range interactions among atoms play an important role in the study of cold atom collision processes. A variety of physical processes, such as atomic beam experiments,[1] laser trapping technologies,[2] Bose–Einstein condensation[3] and photoassociation,[4] depend on the knowledge of these interactions. Most of the theoretical studies focused on the dispersion coefficients C_6, C_8, and C_{10}, which are produced in the second order of perturbation with the perturbing potential limited to dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and dipole-octapole interactions.[5−23] However, for the needs and the most important advances of modern physics, the pairwise potential is insufficient, and the higher-order dispersion coefficients and nonadditive terms among atoms, such as the "triple-dipole" terms, should be considered.

A number of nonadditive terms of dispersion coefficients for alkali-metal atoms, which are the subject in this study, have been discussed since Axilrod *et al.* investigated these "triple-dipole" terms by applying a third-order perturbation theory to a special atomic model.[24−25] Bade has developed the Drude model calculation of dispersion forces.[26−27] Midzuno and Kihara[28] have studied the third-order perturbation under less restrictive assumptions. Ayres and Tredgold[29] have investigated the dipole-dipole-quadrupole three-body terms using third-order perturbation theory. The combined rules for three-body dispersion coefficients were investigated by Diaz Peña *et al.*[31] Power *et al.*[31] deduced systematically the dispersion energy among the neutral molecules.

In this paper, the following conditions are investigated: the higher-order dispersion coefficients of C_{12} between homonuclear and heteronulear alkali-metal atom pairs; the triplet nonadditive terms C_9, C_{11}, and C_{13} among three homonuclear and heteronulear alkali-metal atoms; and the quadruplet nonadditive terms C_{12} among four homonuclear and heteronulear alkali-metal atoms. The long-range interactions among atoms can be calculated based on the dynamic polarizabilities and hyperpolarizabilities at imaginary frequencies. To calculate the higher-order dispersion coefficients, we present a method for computing the wavefunctions for ground-state alkali-metal with linear variation based on B-splines basis functions, in which the valence electron for the alkali-metal atom is described by l-dependent model potential.[32] Atomic units are used throughout the paper.

2 Theory and Method

In the Born-Oppenheimer picture, the Hamiltonian of the three interacting atoms is given by

$$H = H_a + H_b + H_c + V_{ab} + V_{ac} + V_{bc} + V_{\rm dis}\,, \quad (1)$$

where H_j, for $j = a$, b, and c, is the Hamiltonian of the j atom, V_{ij} is the Coulomb interaction between the atomic charge distributions of the i and j atoms, and $V_{\rm dis}$ is the long-range dispersion potential. The unperturbed state is described by the sum of the atomic Hamiltonians

$$H_0 = H_a + H_b + H_c\,. \quad (2)$$

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In the long-range limit, the first nonzero contribution to $V_{\rm dis}$ appears in the second order of the perturbation with the following well-known expression in terms of the pair-interaction dispersion coefficients:[5,23]

$$\begin{aligned} V_2 = & -\frac{C_6^{ab}}{R_{ab}^6}-\frac{C_8^{ab}}{R_{ab}^8}-\frac{C_{10}^{ab}}{R_{ab}^{10}}-\frac{C_{12}^{ab}}{R_{ab}^{12}}-\cdots \\ & -\frac{C_6^{bc}}{R_{bc}^6}-\frac{C_8^{bc}}{R_{bc}^8}-\frac{C_{10}^{bc}}{R_{bc}^{10}}-\frac{C_{12}^{ab}}{R_{ab}^{12}}-\cdots \\ & -\frac{C_6^{ca}}{R_{ca}^6}-\frac{C_8^{ca}}{R_{ca}^8}-\frac{C_{10}^{ca}}{R_{ca}^{10}}-\frac{C_{12}^{ca}}{R_{ab}^{12}}-\cdots , \end{aligned} \tag{3}$$

where R_{ab}, R_{bc}, and R_{ca} are the internuclear distances. The C_6 coefficients describe the dipole-dipole interaction between two atoms, the C_8 coefficients, the dipole-quadrupole interaction, and the C_{10} coefficients of the sum of the dipole-octapole and quadrupole-quadrupole interactions. The C_{2n}^{ab} coefficients can be expressed as[8,23]

$$C_{2n}^{ab}(R)=\sum_{l=1}^{n-2}\begin{pmatrix}2n-2\\2l\end{pmatrix}\frac{1}{2\pi}G_{ab}(l,n-l-1)\,, \tag{4}$$

where

$$G_{ab}(l_a,l_b)=\int_0^\infty \alpha_{l_a}^a(\mathrm{i}\omega)\alpha_{l_b}^b(\mathrm{i}\omega)\mathrm{d}\omega\,, \tag{5}$$

where $\alpha_l^a(\mathrm{i}\omega)$ is the dynamic 2^l polarizability for atom a at imaginary frequency ω,[8,23] where the dynamic polarizability can be expressed as a sum of all intermediate states.

$$\alpha_l(\mathrm{i}\omega)=\sum_n{}' \frac{f_{nk}^{(l)}}{E_{nk}^2-\omega^2}\,, \tag{6}$$

where $f_{nk}^{(l)}$ is the 2^l-pole oscillator strength between the initial Ψ_k and the intermediate Ψ_n states.

Using the identity

$$\frac{2}{\pi}\int_0^\infty \frac{\mathrm{d}\omega}{(a^2+\omega^2)(b^2+\omega^2)}=\frac{1}{ab(a+b)}\,,\quad a,b>0\,. \tag{7}$$

Equation (5) can be expressed as

$$G_{ab}(l_a,l_b)=\frac{\pi}{2}\sum_{nn'}\frac{f_{nk}^{(l_a)}f_{n'k'}^{(l_b)}}{|E_{nk}^a||E_{n'k'}^b|(|E_{nk}^a|+|E_{n'k'}^b|)}\,, \tag{8}$$

where $E_{nk}^i=E_n^i-E_k^i$, $i=a,b$ is the excitation energy difference between the initial Ψ_k and intermediate Ψ_n states of atom i.

Generally, the long-range part of the interaction among multi-atoms is not exactly equal to the interaction energies taken in pairs. Thus, the nonadditive term that comes from the high-order perturbation should be considered. In this paper, we would consider the interaction among three- and four-atoms. The lowest order nonadditive contribution in inverse powers of the internuclear distances would appear in the third order of perturbation, which may be written as[31]

$$\begin{aligned} V_3 = & -\frac{C_9^{(ddd)}}{R_{ab}^3R_{bc}^3R_{ca}^3}-\frac{C_{11}^{(ddq)}}{R_{ab}^3R_{bc}^4R_{ca}^4}-\frac{C_{11}^{(dqd)}}{R_{ab}^4R_{bc}^4R_{ca}^3} \\ & -\frac{C_{11}^{(qdd)}}{R_{ab}^4R_{bc}^3R_{ca}^4}-\frac{C_{13}^{(dqq)}}{R_{ab}^4R_{bc}^5R_{ca}^4} \\ & -\frac{C_{13}^{(qdq)}}{R_{ab}^4R_{bc}^4R_{ca}^5}-\frac{C_{13}^{(qqd)}}{R_{ab}^5R_{bc}^4R_{ca}^4}\cdots , \end{aligned} \tag{9}$$

while the terms of the interaction among four atoms is[31]

$$\begin{aligned} V_4 = & -\frac{C_{12}^{(abcda)}}{R_{ab}^3R_{bc}^3R_{cd}^3R_{da}^3}-\frac{C_{12}^{(acbda)}}{R_{ac}^3R_{bc}^3R_{bd}^3R_{da}^3} \\ & -\frac{C_{12}^{(adbca)}}{R_{ad}^3R_{bd}^3R_{bc}^3R_{ca}^3}\cdots , \end{aligned} \tag{10}$$

where the coefficients of triplet nonadditive term $C_9^{(ddd)}$ is the triple-dipole constant defined by Axilrod,[24−25] the coefficients $C_{11}^{(ddq)}$, $C_{11}^{(dqd)}$, and $C_{11}^{(qdd)}$ are the dipole-dipole-quadrupole terms, and the coefficients $C_{13}^{(dqq)}$, $C_{13}^{(qdq)}$, and $C_{13}^{(qqd)}$ are dipole-quadrupole-quadrupole terms. For the homonuclear three alkali-metal atom dimers, $C_{11}^{(ddq)}=C_{11}^{(dqd)}=C_{11}^{(qdd)}$, and $C_{13}^{(qqd)}=C_{13}^{(qdq)}=C_{13}^{(dqq)}$, while for the heteronuclear alkali-metal atom dimers, $C_{11}^{(ddq)}\neq C_{11}^{(dqd)}\neq C_{11}^{(qdd)}$, and $C_{13}^{(qqd)}\neq C_{13}^{(qdq)}\neq C_{13}^{(dqq)}$. These coefficients can be expressed as

$$C_{abc}=Z_{abc}(l_a,l_b,l_c)W_{abc}(l_a,l_b,l_c)\,, \tag{11}$$

where

$$Z_{abc}(l_a,l_b,l_c)=\frac{3}{\pi}\int_0^\infty \alpha_{l_a}^a(\mathrm{i}\omega)\alpha_{l_b}^b(i\omega)\alpha_{l_c}^c(\mathrm{i}\omega)\mathrm{d}\omega \tag{12}$$

and W_{abc} are the geometric factors with $\vec{R}_{ab}$, $\vec{R}_{bc}$ and $\vec{R}_{ac}$. For the nonadditive constant $C_9^{(ddd)}$, the corresponding geometric factor is[24−25,31]

$$W_{abc}(1,1,1)=1+3\cos\theta_a\cos\theta_b\cos\theta_c\,. \tag{13}$$

For the nonadditive constant $C_{11}^{(ddq)}$, the corresponding geometric factor is[22,31]

$$\begin{aligned} W_{abc}(1,1,2)=\frac{1}{16}[&9\cos\theta_c-25\cos 3\theta_c+6\cos(\theta_a-\theta_b) \\ &\times(3+5\cos 2\theta_c)]\,. \end{aligned} \tag{14}$$

Changing the indices of Eq. (14), we obtain the geometric factors of $C_{11}^{(dqd)}$ and $C_{11}^{(qdd)}$. For the nonadditive constant $C_{13}^{(dqq)}$, the corresponding geometric factor is[22,31]

$$W_{abc}(1,2,2)=\frac{15}{64}[3(\cos\theta_a+5\cos 5\theta_a)+20\cos(\theta_b-\theta_c)(1-3\cos 2\theta_a)+70\cos(\theta_b-\cos\theta_c)\cos\theta_a]\,. \tag{15}$$

Changing the indices of Eq. (15), we obtain the geometric factors of $C_{13}^{(qqd)}$ and $C_{13}^{(qdq)}$.

Using the identity

$$\frac{2}{\pi}\int_0^\infty \frac{\mathrm{d}\omega}{(a^2+\omega^2)(b^2+\omega^2)(c^2+\omega^2)}=\frac{a+b+c}{abc(a+b)(b+c)(c+a)}\,,\quad a,b,c>0\,. \tag{16}$$

Equation (12) can be expressed as

$$Z_{abc}(l_a,l_b,l_c)=\frac{2}{3}\sum_{n_an_bn_c}\frac{f^{(l_a)}_{n_ak_a}f^{(l_b)}_{n_bk_b}f^{(l_c)}_{n_ck_c}(|E^a_{n_ak_a}|+|E^b_{n_bk_b}|+|E^c_{n_ck_c}|)}{|E^a_{n_ak_a}||E^b_{n_bk_b}||E^c_{n_ck_c}|(|E^a_{n_ak_a}|+|E^b_{n_bk_b}|)(|E^b_{n_bk_b}|+|E^c_{n_ck_c}|)(|E^a_{n_ak_a}|+|E^c_{n_ck_c}|)}\,, \tag{17}$$

where $E^i_{nk}=E^i_n-E^i_k$, ($i=a,b$, and c) is the excitation energy difference between the initial Ψ_k and the intermediate Ψ_n states of atom i.

The quadruplet nonadditive term $C_{12}^{(ijkli)}$ can also be expressed as[31]

$$C_{abcd}=Z_{ijkli}(l_a,l_b,l_c,l_d)W_{ijkli}(l_a,l_b,l_c,l_d)\,,\quad i,j,k,l=a,b,c,d\,, \tag{18}$$

where

$$Z_{ijkli}(l_a,l_b,l_c,l_d)=\frac{3}{\pi}\int_0^\infty\alpha^a_{l_a}(\mathrm{i}\omega)\alpha^b_{l_b}(\mathrm{i}\omega)\alpha^c_{l_c}(\mathrm{i}\omega)\alpha^d_{l_d}(\mathrm{i}\omega)\,\mathrm{d}\omega\,. \tag{19}$$

For the quadruple-dipole constant $C_{12}^{(abcda)}$, the geometric factors W_{abcda} changed with $\vec{R}_{ab}$, $\vec{R}_{ac}$, $\vec{R}_{ad}$, $\vec{R}_{bc}$, $\vec{R}_{bd}$, and $\vec{R}_{cd}$.[31]

$$\begin{aligned}W_{abcda}=&\{-4+3\{(\hat{R}_{ab}\cdot\hat{R}_{bc})^2+(\hat{R}_{ab}\cdot\hat{R}_{cd})^2+(\hat{R}_{ab}\cdot\hat{R}_{da})^2+(\hat{R}_{bc}\cdot\hat{R}_{cd})^2+(\hat{R}_{bc}\cdot\hat{R}_{da})^2+(\hat{R}_{cd}\cdot\hat{R}_{da})^2\}\\&-9\{(\hat{R}_{bc}\cdot\hat{R}_{cd})(\hat{R}_{cd}\cdot\hat{R}_{da})(\hat{R}_{bc}\cdot\hat{R}_{da})+(\hat{R}_{cd}\cdot\hat{R}_{da})(\hat{R}_{da}\cdot\hat{R}_{ab})(\hat{R}_{ab}\cdot\hat{R}_{cd})+(\hat{R}_{ab}\cdot\hat{R}_{bc})(\hat{R}_{bc}\cdot\hat{R}_{da})(\hat{R}_{da}\cdot\hat{R}_{ab})\\&+(\hat{R}_{bc}\cdot\hat{R}_{cd})(\hat{R}_{cd}\cdot\hat{R}_{ab})(\hat{R}_{ab}\cdot\hat{R}_{bc})\}+27\{(\hat{R}_{ab}\cdot\hat{R}_{bc})(\hat{R}_{bc}\cdot\hat{R}_{cd})(\hat{R}_{cd}\cdot\hat{R}_{da})(\hat{R}_{da}\cdot\hat{R}_{ab})\}\}\,.\end{aligned} \tag{20}$$

where $\hat{R}$ is the unit vector of $\vec{R}$.

Using the identity

$$\begin{aligned}I(a,b,c,d)&=\frac{2}{\pi}\int_0^\infty\frac{\mathrm{d}\omega}{(a^2+\omega^2)(b^2+\omega^2)(c^2+\omega^2)(d^2+\omega^2)}\\&=\frac{[a^2(b+c+d)+b^2(a+c+d)+c^2(a+b+d)+d^2(a+b+c)+2(abc+bcd+abd+acd)]}{abcd(a+b)(a+c)(a+d)(b+c)(c+d)(c+d)}\,,\\&\quad a,b,c,d>0\,,\end{aligned} \tag{21}$$

Equation (19) can be expressed as

$$Z_{abc}(l_a,l_b,l_c,l_d)=\frac{2}{3}\sum_{n_an_bn_cn_d}f^{(l_a)}_{n_ak_a}f^{(l_b)}_{n_bk_b}f^{(l_c)}_{n_ck_c}f^{(l_d)}_{n_dk_d}I(|E^a_{n_ak_a}|,|E^b_{n_bk_b}|,|E^c_{n_ck_c}|,|E^d_{n_dk_d}|)\,, \tag{22}$$

where $E^i_{nk}=E^i_n-E^i_k$, $i=a,b,c$, and d, is the excitation energy difference between the initial Ψ_k and the intermediate Ψ_n states of atom i.

In this paper we considered the many-body atomic structure calculations of long-range interactions for system of alkali-metal atoms, where the motion of the valence electron for the alkali-metal atom is described by l-dependent model potential method.[32] The model potentials can be expressed in the form of

$$V_l(r)=-\frac{Z_l(r)}{r}-\frac{\alpha_c}{2r^4}[1-\mathrm{e}^{-(r/r_c)^6}]\,, \tag{23}$$

where α_c is the polarizability of the positive ion core. The radial charge $Z_l(r)$ is expressed as

$$Z_l(r)=1+(z-1)\,\mathrm{e}^{-a_1r}-r(a_3+a_4r)\,\mathrm{e}^{-a_2r}\,, \tag{24}$$

where z is the nuclear charge of the neutral atom and r_c is the cut-off radius introduced to truncate the unphysical short-range contribution of the polarization potential near the origin. For a given atom, a_1, a_2, a_3, a_4, α_c, and r_c are parameters. The l-dependent model potential parameters of alkali-metal atoms are given in Ref. [32].

In our calculation for the valence electron of alkali-metal atom, the radial wavefunctions are expanded using the B-spline basis set given in Refs. [33] and [34]. In our early work, this method has been proven effective.[35−38]

3 Result

We calculated the long-range dispersion coefficients C_6, C_8 and C_{10} of the homonuclear alkali-metal atom pairs before calculating the high-order dispersion coefficients for alkali-metal atoms to check the validity and the efficiency of the proposed B-spline method combined with the l-dependent potential method. Table 1 shows the agreement of our results compared with those of previous studies. All the coefficients C_6, C_8 and C_{10} of the homonuclear alkali-metal atom pairs, except C_8 for Cs-Cs, have only a 0.5% difference between our values and the results of Marinescu.[32] The difference of coefficients C_8 for Cs-Cs is approximately 3%. The difference between our results on most of C_6, C_8, and C_{10} and those of the pseudopotential calculations of Maeder and Kuzelning[15] and the simple analytic wave functions calculation of Patil and Tang[23] is also less than 3%. Large difference exists compared with the results of Bussery *et al.*[18] These comparisons illustrate the effectiveness of our method for the alkali-metal atom pairs using linear variation based on the B-splines basis function combined with the l-dependent model potential.

Table 1 The long-range dispersion coefficients C_6, C_8, and C_{10} for homonuclear alkali-metal atom pairs.

	Source	Li-Li	Na-Na	K-K	Rb-Rb	Cs-Cs
10^3C_6	[15]	1.389	1.540	3.945	4.768	6.855
	[16]	1.386	1.518	3.574		
	[18]	1.383	1.698	4.721	5.726	9.469
	[17]	1.360	1.330	3.780	4.7006	6.500
	[32]	1.388	1.472	3.813	4.426	6.331
	[23]	1.388	1.500	3.796	4.531	6.651
	Present	1.388	1.473	3.808	4.421	6.317
10^5C_8	[15]	0.8089	1.098	3.834	5.244	9.025
	[18]	0.7578	1.028	3.894	6.115	12.910
	[32]	0.8324	1.119	4.096	5.506	9.630
	[23]	0.8183	1.090	3.892	5.256	9.546
	Present	0.8322	1.119	4.087	5.496	9.395
10^7C_{10}	[15]	0.6901	1.036	4.522	6.836	13.010
	[18]	0.4817	0.6939	4.069	6.316	14.510
	[32]	0.7365	1.107	5.248	7.665	15.200
	[23]	0.7289	1.068	4.789	6.833	13.58
	Present	0.7362	1.106	5.235	7.648	14.933

The dispersion coefficient C_{12} for alkali-metal atom pairs is shown in Table 2. Our calculated results were compared with the values of Patil *et al.*,[23] where a good agreement was found for the case of Li-Li. For the case of Li-Na and Na-Na, the differences are not more than 2%. However, for the others, the differences are more than 10%. For the case of Cs-Cs, the difference reached 16%. We considered our calculated results to be realistic since we checked the validity and the efficiency of the proposed method.

The triple-dipole dispersion coefficients Z^{ddd}, dipole-dipole-quadrupole coefficients Z^{ddq}, and dipole-quadrupole-quadrupole dispersion coefficients Z^{dqq} for homonuclear alkali-metal atom dimers are shown in Tables 3. For the triple-dipole dispersion coefficients Z^{ddd}, our numerical results agree with those of Marinescu[5] and Midzuno.[28] Some considerable differences are found between our results for homonuclear alkali-metal atom dimers, except for Li dimers, and those of several authors.[19−21,23,30] For the dispersion coefficients of Z^{ddq} and Z^{dqq}, our results are consistent with those of the simple analytic wavefunction calculation of Patil and Tang *et al.*,[23] and the differences between our values and theirs are approximately 5% and 10%, respectively.

Table 2 The long-range dispersion coefficients C_{12} for alkali-metal atom pairs.

10^9	Li	Na	K	Rb	Cs
Li	0.900(0.903)[a]	1.157(1.143)[a]	3.044(2.86)[a]	3.912(3.57)[a]	6.161(5.41)[a]
Na		1.472(1.43)[a]	3.755(3.49)[a]	4.795(4.33)[a]	7.438(6.50)[a]
K			8.888(7.99)[a]	11.128(9.78)[a]	16.732(14.4)[a]
Rb				13.854(11.19)[a]	20.631(17.4)[a]
Cs					30.262(25.3)[a]

[a]The values in the brackets are results of S.H. Patil and K.T. Tang.[23]

Table 3 The triple-dipole dispersion coefficients Z^{ddd}, dipole-dipole-quadrupole coefficients Z^{ddq}, and dipole-quadrupole-quadrupole dispersion coefficients Z^{dqq} for homonuclear alkali-metal atom dimers.

	Source	Li-Li-Li	Na-Na-Na	K-K-K	Rb-Rb-Rb	Cs-Cs-Cs
10^5Z^{ddd}	[28]	1.707	1.758	8.373	10.60	19.10
	[19]	1.7010	1.8246	8.373	11.34	21.35
	[21]	1.69	2.09	8.24	10.6	13.5
	[30]	1.6982	1.8810	8.4787	11.56	22.00
	[20]	1.70	1.76	8.61	11.0	19.9
	[5]	1.701	1.758	8.375	10.60	19.10
	[23]	1.689	1.788	8.16	10.74	20.01
	Present	1.701	1.758	8.382	10.61	19.12
10^6Z^{ddq}	[23]	1.742	2.349	15.33	23.25	54.9
	Present	1.780	2.413	16.439	24.389	52.873
10^8Z^{dqq}	[23]	0.192	0.327	2.979	5.13	15.21
	Present	0.199	0.345	3.332	5.749	14.942

Table 4 The triple-dipole dispersion coefficients Z^{ddd} for heteronuclear alkali-metal atom dimers.

Dimers	$Z^{ddd}(10^5)$					Dimers	Source				
	[28]	[19]	[30]	[5]	Present		[28]	[19]	[30]	[5]	Present
Li-Li-Na	1.721	1.7376	1.7566-1.742	1.716	1.717	Rb-Rb-Cs	12.87	13.99	13.98-14.31	12.88	12.90
Li-Li-K	2.891	2.8881	2.8949-2.8978	2.884	2.886	Cs-Cs-Li	8.448	9.138	9.134-9.341	8.442	8.451
Li-Li-Rb	3.124	3.195	3.197-3.216	3.116	3.119	Cs-Cs-Na	8.443	9.276	9.350-9.648	8.447	8.459
Li-Li-Cs	3.775	3.933	3.932-3.977	3.768	3.771	Cs-Cs-K	14.48	15.62	15.62-16.01	14.48	14.493
Na-Na-Li	1.737	1.7784	1.7823-1.8176	1.735	1.736	Cs-Cs-Rb	15.67	17.27	17.27-17.74	15.67	15.688
Na-Na-K	2.928	3.0060	3.0215-3.0976	2.928	2.929	Li-Na-K	2.907	2.9439	2.9523-2.9957	2.904	2.905
Na-Na-Rb	3.161	3.327	3.349-3.440	3.161	3.163	Li-Na-Rb	3.140	3.258	3.273-3.326	3.136	3.137
Na-Na-Cs	3.806	4.083	4.117-4.249	3.808	3.810	Li-Na-Cs	3.788	4.005	4.023-4.110	3.785	3.787
K-K-Li	4.192	4.914	4.908-4.955	4.908	4.911	Li-K-Rb	5.311	5.436	5.433-5.495	5.305	5.310
K-K-Na	4.928	4.998	5.022-5.119	4.929	4.935	Li-K-Cs	6.433	6.696	6.696-6.803	6.249	6.434
K-K-Rb	9.056	9.261	9.260-9.405	9.057	9.066	Li-Rb-Cs	6.958	7.410	7.410-7.542	6.952	6.959
K-K-Cs	11.00	11.430	11.435-11.657	11.00	11.01	Na-K-Rb	5.326	5.532	5.559-5.679	5.327	5.330
Rb-Rb-Li	5.742	6.012	6.017-6.096	5.735	5.748	Na-K-Cs	6.442	6.807	6.851-7.027	6.444	6.449
Rb-Rb-Na	5.756	6.120	6.157-6.301	5.756	5.761	Na-Rb-Cs	6.965	7.533	7.581-7.793	6.967	6.972
Rb-Rb-K	9.796	10.248	10.244-10.424	9.796	9.806	K-Rb-Cs	11.90	12.642	12.641-12.915	11.90	11.912

Table 5 The dipole-dipole-quadrupole dispersion coefficients Z^{ddq} for heteronuclear alkali-metal atom dimers.

Dimers	$Z^{ddq}(10^6)$			Dimers			
	ddq	dqd	qdd		ddq	dqd	qdd
Li-Li-Na	2.317	1.816		Rb-Rb-Cs	36.055	29.459	
Li-Li-K	5.776	2.978		Cs-Cs-Li	8.433	23.706	
Li-Li-Rb	7.319	3.210		Cs-Cs-Na	11.018	23.857	
Li-Li-Cs	10.758	3.845		Cs-Cs-K	27.964	40.350	
Na-Na-Li	1.857	2.362		Cs-Cs-Rb	35.651	43.622	
Na-Na-K	5.964	3.942		Li-Na-K	5.863	3.881	3.027
Na-Na-Rb	7.534	4.249		Li-Na-Rb	7.418	4.182	3.262
Na-Na-Cs	11.029	5.079		Li-Na-Cs	10.881	5.016	3.897
K-K-Li	5.004	9.725		Li-K-Rb	12.345	10.495	5.399
K-K-Na	6.527	9.842		Li-K-Cs	18.193	12.626	6.485
K-K-Rb	20.901	17.752		Li-Rb-Cs	19.646	16.051	7.001
K-K-Cs	30.875	21.409		Na-K-Rb	12.477	10.612	7.044
Rb-Rb-Li	5.826	13.325		Na-K-Cs	18.353	12.742	8.467
Rb-Rb-Na	7.602	13.464		Na-Rb-Cs	19.814	16.180	9.142
Rb-Rb-K	19.173	22.577		K-Rb-Cs	33.363	27.259	23.132

The triple-dipole dispersion coefficients Z^{ddd} for heteronuclear alkali-metal atom dimers case in Table 4, our results are also in agreement with those of Marinescu[5] and Midzuno,[28] but not with the results from other authors.[19,30] The dipole-dipole-quadrupole dispersion coefficients Z^{ddq}, Z^{dqd}, and Z^{dqd} and dipole-quadrupole-quadrupole dispersion coefficients Z^{dqq}, Z^{qdq}, and Z^{qqd} for the case of heteronuclear alkali-metal atom dimers are shown in Tables 5 and 6, respectively.

The dispersion coefficients of quadruplet nonadditive term C_{12} for four alkali-metal atom dimers were also investigated. The corresponding four-dipole dispersion coefficients Z^{dddd} are shown in Table 7. For Li-Li-Li-Li case, our value of $Z^{dddd} = 2.322 \times 10^7$ is in agreement with the result of Cvitaš *et al.*,[22] $Z^{dddd} = 2.319 \times 10^7$ with the deviation of 0.1%. The comparative results show that our calculations for quadruplet nonadditive term C_{12} are also effective. No data can be referenced for the other cases. Table 7 shows that the value of Z^{dddd} changes only a little to exchange the atom of Li and Na in any way. For example, the Z^{dddd} of Li-Li-Li-Li, Li-Li-Li-Na, Li-Li-Na-Na, Li-Na-Na-Na, and Na-Na-Na-Na case are 2.322×10^7, 2.320×10^7, 2.321×10^7, and $Z^{dddd} = 2.332 \times 10^7$ respectively, with a difference of no more than 0.5%. The differences among Z_{ddd} for Li-Li-Li, Li-Li-Na, Li-Na-Na, and Na-Na-Na from Tables 3 and 4 are also very small. These results can be attributed to the close polarizabilities of Li and Na, which are 164.01 and 159.02 a.u., respectively.

Table 6 The dipole-quadrupole-quadrupole dispersion coefficients Z^{dqq} for heteronuclear alkali-metal atom dimers.

Dimers	$Z^{dqq}(10^8)$			Dimers			
	dqq	qqd	Source qdq		dqq	qqd	qdq
Li-Li-Na	0.258	0.206		Rb-Rb-Cs	8.439	6.891	
Li-Li-K	0.626	0.326		Cs-Cs-Li	2.446	6.823	
Li-Li-Rb	0.786	0.351		Cs-Cs-Na	3.187	6.919	
Li-Li-Cs	1.141	0.415		Cs-Cs-K	7.987	11.500	
Na-Na-Li	0.267	0.334		Cs-Cs-Rb	10.138	12.414	
Na-Na-K	0.834	0.549		Li-Na-K	0.812	0.423	0.643
Na-Na-Rb	1.047	0.590		Li-Na-Rb	1.021	0.455	0.807
Na-Na-Cs	1.518	0.699		Li-Na-Cs	1.484	0.538	1.168
K-K-Li	1.035	1.997		Li-K-Rb	2.519	1.115	1.304
K-K-Na	1.346	2.041		Li-K-Cs	3.679	1.325	1.901
K-K-Rb	4.212	3.591		Li-Rb-Cs	4.653	1.672	2.048
K-K-Cs	6.172	4.292		Na-K-Rb	2.570	1.449	1.696
Rb-Rb-Li	1.404	3.182		Na-K-Cs	3.745	1.724	2.475
Rb-Rb-Na	1.827	3.240		Na-Rb-Cs	4.729	2.178	2.667
Rb-Rb-K	4.541	5.330		K-Rb-Cs	7.822	5.436	6.658

Table 7 The four-dipole dispersion coefficients Z^{dddd} for alkali-metal atom dimers.

				10^7					
Dimers	Z^{dddd}	Dimers	Z^{dddd}	Dimers	Z^{dddd}	Dimers	Z^{dddd}	Dimers	Z^{dddd}
Li-Li-Li-Li	2.322	Li-Li-Cs-Cs	12.043	Li-K-Rb-Rb	13.900	Na-Na-Rb-Rb	7.993	K-K-K-Rb	22.167
Li-Li-Li-Na	2.320	Li-Na-Na-Na	2.325	Li-K-Rb-Cs	17.008	Na-Na-Rb-Cs	9.747	K-K-K-Cs	27.157
Li-Li-Li-K	3.990	Li-Na-Na-K	3.974	Li-K-Cs-Cs	20.837	Na-Na-Cs-Cs	11.900	K-K-Rb-Rb	24.022
Li-Li-Li-Rb	4.319	Li-Na-Na-Rb	4.301	Li-Rb-Rb-Rb	15.056	Na-K-K-K	11.781	K-K-Rb-Cs	29.435
Li-Li-Li-Cs	5.269	Li-Na-Na-Cs	5.234	Li-Rb-Rb-Cs	18.431	Na-K-K-Rb	12.760	K-K-Cs-Cs	36.105
Li-Li-Na-Na	2.321	Li-Na-K-K	6.841	Li-Rb-Cs-Cs	22.585	Na-K-K-Cs	15.595	K-Rb-Rb-Rb	26.033
Li-Li-Na-K	3.980	Li-Na-K-Rb	7.407	Li-Cs-Cs-Cs	27.704	Na-K-Rb-Rb	13.820	K-Rb-Rb-Cs	31.906
Li-Li-Na-Rb	4.308	Li-Na-K-Cs	9.039	Na-Na-Na-Na	2.332	Na-K-Rb-Cs	16.896	K-Rb-Cs-Cs	39.144
Li-Li-Na-Cs	5.249	Li-Na-Rb-Rb	8.020	Na-Na-Na-K	3.974	Na-K-Cs-Cs	20.680	K -Cs-Cs-Cs	48.070
Li-Li-K-K	6.867	Li-Na-Rb-Cs	9.790	Na-Na-Na-Rb	4.299	Na-Rb-Rb-Rb	14.970	Rb-Rb-Rb-Rb	28.213
Li-Li-K-Rb	7.437	Li-Na–Cs-Cs	11.966	Na-Na-Na-Cs	5.225	Na-Rb-Rb-Cs	18.306	Rb-Rb-Rb-Cs	34.586
Li-Li-K-Cs	9.086	Li-K-K-K	11.842	Na-Na-K-K	6.822	Na-Rb-Cs-Cs	22.411	Rb-Rb-Cs-Cs	42.441
Li-Li-Rb-Rb	8.055	Li-K-K-Rb	12.829	Na-Na-K-Rb	7.384	Na-Cs-Cs-Cs	27.465	Rb-Cs-Cs-Cs	52.128
Li-Li-Rb-Cs	9.843	Li-K-K-Cs	15.696	Na-Na-K-Cs	9.001	K-K-K-K	20.457	Cs-Cs-Cs-Cs	64.841

4 Summary

In this paper, with the nondegenerating perturbation theory up to the fourth order, we deduced the high-order dispersion coefficients C_9 C_{11}, C_{12}, and C_{13} for the ground-state alkali-metals. Then, we calculated high-order dispersion coefficients for alkali-metal atoms combined with the l-dependent model potential and linear variation based on B-spline basis function. The results for the long-range dispersion coefficients C_6, C_8, and C_{10} of pair alkali-metal atoms were compared. The dispersion coefficients C_{12} for alkali-metal atom pairs were calculated based on their polarizabilities and hyperpolarizabilities. The dispersion coefficients of triplet nonadditive term C_9, C_{11}, and C_{13} among three atoms and those of the quadruplet nonadditive term C_{12} among four atoms were also calculated.

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