Long-range interaction of Li(2^{2}S)-Li(2^{2}S)-Li^{+}(1^{1}S)

Pei-Gen Yan, Li-Yan Tang, Zong-Chao Yan, and James F. Babb

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The long-range interaction of Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$)

Pei-Gen Yan[1,2], Li-Yan Tang[2,*] , Zong-Chao Yan[1,2,3], and James F Babb[4]
[1]*Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B5A3, Canada*
[2]*State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, People's Republic of China*
[3]*Center for Cold Atom Physics, Chinese Academy of Sciences, Wuhan 430071, People's Republic of China*
[4]*ITAMP, Center for Astrophysics | Harvard & Smithsonian, MS 14, 60 Garden St., Cambridge, Massachusetts 02138, USA*
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Abstract

The long-range interactions among two- or three-atom systems are of considerable importance in the cold and ultracold research areas for many body systems. For an ion and an atom, the long-range interaction potential is dominated by the induction (or polarization) potential resulting from the (classical) effect of the ion's electric field on the atom and the leading term of the induction potential is much stronger than the (quantum mechanical) dispersion (or van der Waals) interaction. The present paper focuses on the long-range interaction of the Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$) system, to see what changes this induction effect (originating in the electric field of the Li$^+$ ion) yields in the long-range additive and nonadditive interactions of this three-body system. Using perturbation theory for energies, we evaluate the coefficients C_n in the potential energy for the three well-separated constituents, where n refers to the corresponding order in inverse powers of distance, obtaining the additive interaction coefficients C_4, C_6, C_7, C_8, C_9 and the nonadditive interaction coefficients C_7, C_9. The obtained coefficients C_n are calculated with highly accurate variationally-generated nonrelativistic wave functions in Hylleraas coordinates. Our calculations may be of interest for the study of three-body recombination and for constructing precise potential energy surfaces. We also provide precise evaluations of the long-range potentials for the two-body Li($2\,^2S$)-Li$^+$($1\,^1S$) system. For both the two-body and three-body cases, we provide results for the like-nuclei cases of ^{6}Li and ^{7}Li.

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*Email: lytang@wipm.ac.cn

I. INTRODUCTION

Considerable attention has been given to the study of the Axilrod-Teller-Muto interaction between three S-state atoms [1–7], for which the leading nonadditive (not expressible as a sum of pairs) term in the mutual potential energy occurs in third-order perturbation theory and contains a geometrical factor depending on the relative orientation of the three atoms. This kind of nonadditive interaction has shown its importance recently in, for example, the study of cold collisions [8–14], three-body recombination [3, 15, 16], and Efimov effects [17–19].

Experimentally, the multi-body interactions have been observed as inelastic loss resonances in three- and four-body recombinations of atom-atom and atom-molecule collisions [20, 21]. With recent experimental advances in manipulating ultracold atoms and ions, there is a growing interest in studying such a few-body hybrid system containing an ion [22, 23]. The long-range part of the ion-atom interaction is well-known to be especially important for cold and ultracold physics and chemistry, see, for example, Refs. [24, 25]. The highly successful use of a single ion in three-body reaction in an ultracold atomic gas has renewed theoretical interest in studying long-range interactions of many-body systems with cold trapped ions [26]. Recently, three-body recombination rates were measured for Rb^+-Rb-Rb [26] and for Ba^+-Rb-Rb [27].

Theoretically, long-range additive and nonadditive interactions for two- or three-neutral-atom system, including ground states [1, 2, 5, 6] and excited states [28, 29], have been fully characterized and given very clear explanations. The long-range interactions for two-body atom-ion systems have also been widely studied and deeply analyzed [22, 23]. The interaction between ionic and neutral particles is dominated by the induction component, which can be understood in terms of the interaction of the charge of an ion with the electronic cloud of a neutral partner [30, 31]. For example, recently a method of utilizing Rydberg molecules to initialize the ultracold ion-atom scattering event for the lithium ion-atom ($^6Li^+$-^6Li, $^7Li^+$-^7Li) system has been proposed by Schmid *et al.* [32]; further improvement may need a highly accurate calculation of the long-range interactions for these two systems, which we will describe below.

The main purpose of the present paper is to investigate the influence of an ion on the long-range interaction in a three-body system. Indeed, we find that the presence of an ion will lead to new types of nonadditive induction interactions in the third- or higher-order energy corrections. In the present work, we will start with the second-order induction and dispersion forces. Also, we will demonstrate the third-order additive and nonadditive interactions.

Using perturbation theory up to fourth-order, we derive the formulas for the long-range interaction coefficients for the Li($2\,^2S$)-Li($2\,^2S$)-Li^+($1\,^1S$) system, and evaluate these coefficients with highly accurate, variationally determined wave functions in Hylleraas coordinates. Defining "additive" to mean pairwise amongst the three particles, and "nonadditive" to mean collectively amongst the three particles, we present the second-order additive interaction coefficients $C_4^{(IJ)}$, $C_6^{(IJ)}$, $C_8^{(IJ)}$; the third-order additive interaction coefficients $C_7^{(23)}$, $C_7^{(31)}$, $C_9^{(23)}$, $C_9^{(31)}$ and the fourth-order additive interaction coefficents $C_8^{(23)}$, $C_8^{(31)}$. The nonadditive interaction coefficients $C_9^{(12,23)}$, $C_9^{(31,12)}$, $C_7^{(12,23,31)}$ and $C_9^{(12,23,31)}$ contain dependencies on the geometrical arrangement of these three particles. We will give general formulas, which can be used to evaluate their numerical values in any geometrical configuration. The numerical values of these nonadditive coefficients for an equilateral triangle configuration

will be given as an example. We also give, as a consequence of our accounting for additive effects, a highly accurate result for the long-range potential of the Li($2\,^2S$)-Li$^+$($1\,^1S$) system.

II. THEORETICAL FORMULATION

In this section, the expressions for the long-range interactions coefficients are given specifically for the Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$) system. The detailed derivation of these coefficients is given in the supplemental materials; the formulas given there are readily applicable to other ion-atom A($n_0\,S$)-A($n_0\,S$)-A$^+$($n_0'\,S$) systems as well.

A. Hamiltonian and the zeroth-order wavefunction

The total Hamiltonian for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system can be written as

$$H = H_1 + H_2 + H_3^+ + H' \,, \tag{1}$$

where H_1 and H_2 are the unperturbed Hamiltonian of the two neutral atoms, H_3^+ is the unperturbed Hamiltonian of the ion, and H' is the perturbation Hamiltonian,

$$H' = V_{123} = V_{12} + V_{23} + V_{31} \,, \tag{2}$$

where V_{12}, V_{23}, and V_{31} represent the mutual electrostatic interactions among the atom 1, 2 and the ion 3. We label the particles by I, J, and K, respectively. When the labels I, J or K appear, it is understood that cyclic permutation would be used.

The zeroth-order wavefunction for the non-degenerate Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system is written as

$$\left|\Psi^{(0)}\right\rangle = |n_0 0; n_0 0; n_0' 0\rangle \ , \tag{3}$$

where $|n_0 0\rangle$ and $|n_0' 0\rangle$ represent the wave functions of the initial states for the Li atoms and Li$^+$ ion, respectively.

B. The perturbation theory

According to the perturbation theory, the energy correction for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system,

$$\Delta E \ = \ \Delta E^{(1)} + \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)} + \cdots \,, \tag{4}$$

where

$$\Delta E^{(1)} \ = \ \langle \Psi^{(0)} | V_{123} | \Psi^{(0)} \rangle = 0 \,, \tag{5}$$

$$\Delta E^{(2)} \ = \ - \sum_{n_s n_t n_u}{}' \sum_{L_s L_t L_u} \sum_{M_s M_t M_u} \frac{|\langle \Psi^{(0)} | V_{123} | \Psi_{stu} \rangle|^2}{E_{n_s n_t n_u} - E_{n_0 n_0 n_0'}} \,, \tag{6}$$

$$\Delta E^{(3)} = \sum_{\substack{n_s n_t n_u \\ n_s' n_t' n_u'}}{}' \sum_{\substack{L_s L_t L_u \\ L_s' L_t' L_u'}} \sum_{\substack{M_s M_t M_u \\ M_s' M_t' M_u'}} \frac{\mathbb{D}_1}{(E_{n_s n_t n_u} - E_{n_0 n_0 n_0'})(E_{n_s' n_t' n_u'} - E_{n_0 n_0 n_0'})} + \sum_{n_s n_t n_u}{}' \sum_{L_s L_t L_u} \sum_{M_s M_t M_u} \frac{\mathbb{D}_2}{(E_{n_s n_t n_u} - E_{n_0 n_0 n_0'})^2}\,, \tag{7}$$

$$\Delta E^{(4)} = \sum_{\substack{n_s n_t n_u \\ n_s' n_t' n_u' \\ n_s'' n_t'' n_u''}}{}' \sum_{\substack{L_s L_t L_u \\ L_s' L_t' L_u' \\ L_s'' L_t'' L_u''}} \sum_{\substack{M_s M_t M_u \\ M_s' M_t' M_u' \\ M_s'' M_t'' M_u''}} (\frac{\mathbb{C}}{\mathbb{F}_1} - \delta(n_s', n_0)\delta(n_t', n_0)\delta(n_u', n_0')\frac{\mathbb{C}}{\mathbb{F}_2})\,, \tag{8}$$

where $\mathbb{D}_1$, $\mathbb{D}_2$, $\mathbb{C}$, $\mathbb{F}_1$ and $\mathbb{F}_2$ are expressed as

$$\mathbb{D}_1 = \langle\Psi^{(0)}|V_{123}|\Psi_{stu}\rangle\langle\Psi_{stu}|V_{123}|\Psi_{s't'u'}\rangle\ \langle\Psi_{s't'u'}|V_{123}|\Psi^{(0)}\rangle\,, \tag{9}$$

$$\mathbb{D}_2 = -\langle\Psi^{(0)}|V_{123}|\Psi^{(0)}\rangle|\langle\Psi^{(0)}|V_{123}|\Psi_{stu}\rangle|^2 = 0\,, \tag{10}$$

$$\mathbb{C} = \langle\Psi^{(0)}|V_{123}|\Psi_{stu}\rangle\langle\Psi_{stu}|V_{123}|\Psi_{s't'u'}\rangle\langle\Psi_{s't'u'}|V_{123}|\Psi_{s''t''u''}\rangle\langle\Psi_{s''t''u''}|V_{123}|\Psi^{(0)}\rangle\,, \tag{11}$$

$$\mathbb{F}_1 = (E_{n_0;n_0;n_0'} - E_{n_s;n_t;n_u})(E_{n_0;n_0;n_0'} - E_{n_s';n_t';n_u'})(E_{n_0;n_0;n_0'} - E_{n_s'';n_t'';n_u''})\,, \tag{12}$$

$$\mathbb{F}_2 = (E_{n_0;n_0;n_0'} - E_{n_s;n_t;n_u})(E_{n_0;n_0;n_0'} - E_{n_s'';n_t'';n_u''})^2\,, \tag{13}$$

where the first-order energy correction is zero. $\mathbb{D}_2 = 0$ is because $\langle\Psi^{(0)}|V_{123}|\Psi^{(0)}\rangle = 0$. $E_{n_0 n_0 n_0'} = E_{n_0} + E_{n_0} + E_{n_0'}$ is the total energy for the initial state of three-body system. $\Psi_{stu} = |n_s L_s M_s; n_t L_t M_t; n_u L_u M_u\rangle$, $\Psi_{s't'u'} = |n_s' L_s' M_s'; n_t' L_t' M_t'; n_u' L_u' M_u'\rangle$ and $\Psi_{s''t''u''} = |n_s'' L_s'' M_s''; n_t'' L_t'' M_t''; n_u'' L_u'' M_u''\rangle$ represent the intermediate states with the energy eigenvalues $E_{n_s;n_t;n_u} = E_{n_s} + E_{n_t} + E_{n_u}$, $E_{n_s';n_t';n_u'} = E_{n_s'} + E_{n_t'} + E_{n_u'}$ and $E_{n_s'';n_t'';n_u''} = E_{n_s''} + E_{n_t''} + E_{n_u''}$, respectively. The prime in the summation indicates that the terms with $E_{n_s;n_t;n_u} = E_{n_0 n_0 n_0'}$, $E_{n_s';n_t';n_u'} = E_{n_0 n_0 n_0}$ and $E_{n_s'';n_t'';n_u''} = E_{n_0 n_0 n_0'}$ should be excluded.

C. Choice of coordinates

In this work, the selection of coordinates for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system is shown in Fig. 1. We set the two Li atoms as particles 1 and 2 and the Li$^+$ ion as particle 3. Specifically, we choose atom 1 as the origin of our coordinate system and the plane formed by the three-body system is taken as the x-y plane. We set the x-axis to be $\mathbf{R}_{12}$ and the z-axis perpendicular to the x-y plane by the right-hand convention. The interior angles of the triangle formed by the three particles are denoted as α, β, and γ.

D. Coulomb interaction potential energy expansion

V_{IJ} can be expanded according to Refs. [2, 28, 33],

$$V_{IJ} = \sum_{l_I l_J} \sum_{m_I m_J} T_{l_I\,-m_I}(\boldsymbol{\sigma}) T_{l_J m_J}(\boldsymbol{\rho}) W_{l_I l_J}^{m_I - m_J}(IJ)\,. \tag{14}$$

The geometry factor $W_{l_I l_J}^{m_I-m_J}(IJ)$ is expanded as [28, 29]

$$W_{l_I l_J}^{m_I-m_J}(IJ) = \frac{4\pi(-1)^{l_J}}{R_{IJ}^{l_I+l_J+1}} \frac{(l_I+l_J-m_I+m_J)!(l_I,l_J)^{-1/2}}{[(l_I+m_I)!(l_I-m_I)!(l_J+m_J)!(l_J-m_J)!]^{1/2}} \times P_{l_I+l_J}^{m_I-m_J}(\cos\theta_{IJ}) \exp[i(m_I-m_J)\Phi_{IJ}], \quad (15)$$

where $R_{IJ} = R_J - R_I$ is the relative position from particle I to particle J, the notation $(a, b, \ldots) = (2a+1)(2b+1)\cdots$. Noting that $\theta_{12} = \theta_{23} = \theta_{31} = \pi/2$ in Fig. 1, the associated Legendre functions can be simplified according to

$$P_l^m(0) = \frac{1}{2^{l+1}}[1+(-1)^{l+m}](-1)^{\frac{l+m}{2}}(l+m)!\left[\left(\frac{l+m}{2}\right)!\right]^{-1}\left[\left(\frac{l-m}{2}\right)!\right]^{-1}. \quad (16)$$

The angles Φ_{12}, Φ_{23}, and Φ_{31} satisfy $\Phi_{12} = 0$, $\Phi_{23} = \pi - \beta$, and $\Phi_{31} = \pi + \alpha$, which can be used to simplify the exponential function $\exp[i(m_I - m_J)\Phi_{IJ}]$ of the geometry factor.

$T_{l_I-m_I}(\boldsymbol{\sigma})$ and $T_{l_J m_J}(\boldsymbol{\rho})$ are the multipole tensor operators, which are defined by

$$T_{l_I-m_I}(\boldsymbol{\sigma}) = \sum_i Q_i \sigma_i^{l_I} Y_{l_I-m_I}(\hat{\boldsymbol{\sigma}}_i), \quad (17)$$

$$T_{l_J m_J}(\boldsymbol{\rho}) = \sum_j q_j \rho_j^{l_J} Y_{l_J m_J}(\hat{\boldsymbol{\rho}}_j). \quad (18)$$

In the Eqs.(17) and (18), if $l_I = 0$ or $l_J = 0$, we have

$$T_{00} = \frac{1}{\sqrt{4\pi}} \sum_i Q_i, \quad (19)$$

where $\sum_i Q_i$ represents the total charge of the system. For a neutral atom, $T_{00} = 0$. However for an ion, the nonzero T_{00} results in the occurrence of induction interaction for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system.

E. The second-order energy correction

According to the perturbation theory, the nonzero energy correction for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n_0'\,^1S$) system starts from the second-order,

$$\Delta E^{(2)} = -\left[\frac{C_{6,disp}^{(12)}}{R_{12}^6} + \frac{C_{8,disp}^{(12)}}{R_{12}^8}\right] - \left[\frac{C_{4,ind}^{(23)}}{R_{23}^4} + \frac{C_{6,ind}^{(23)}+C_{6,disp}^{(23)}}{R_{23}^6} + \frac{C_{8,ind}^{(23)}+C_{8,disp}^{(23)}}{R_{23}^8}\right] - \left[\frac{C_{4,ind}^{(31)}}{R_{31}^4} + \frac{C_{6,ind}^{(31)}+C_{6,disp}^{(31)}}{R_{31}^6} + \frac{C_{8,ind}^{(31)}+C_{8,disp}^{(31)}}{R_{31}^8}\right] - \cdots, \quad (20)$$

where the terms $C_{2n,disp}^{(12)}$ in the first square bracket are the additive two-body long-range dispersion interaction coefficients between two Li atoms, which have been reported in the Ref. [34]. The terms in the second and third square brackets represent the long-range interaction between one Li atom and the Li$^+$ ion. Because the Li($2\,^2S$)-Li$^+$($1\,^1S$) long-range interaction of itself is of interest for ultra-cold atom-ion applications, we will discuss it in

some detail in Sec. III A. The terms of $C^{(IJ)}_{2n,ind}$ appear in Eq.(20), are the induction interaction coefficients [30, 31], which can be interpreted as the interaction between the charge of the Li^+ ion and the induced dipole moment of the Li atom

$$C^{(23)}_{2n,ind} = C^{(31)}_{2n,ind} = \frac{4\pi Q^2}{(2\ell+1)^2} \sum_{n_s}{}' \frac{|\langle n_0 0 \| T_\ell \| n_s L_s \rangle|^2}{E_{n_s} - E_{n_0}} = \frac{1}{2} Q^2 \alpha_\ell \,, \tag{21}$$

where Q is the charge of the ion (here $Q = 1$ for the Li^+ ion), α_ℓ are the 2^ℓ-pole static polarizabilities α_ℓ of the Li atom.

The $C^{(IJ)}_{2n,disp}$ terms, which involve the label 3, represent the additive two-body dispersion interaction coefficients between the Li atom and the Li^+ ion. They can be expressed as

$$C^{(23)}_{6,disp} = C^{(31)}_{6,disp} \;=\; \frac{32\pi^2}{27} \sum_{n_s n_t}{}' \frac{|\langle n_0 0 \| T_1 \| n_s 1 \rangle|^2 |\langle n_0' 0 \| T_1 \| n_t 1 \rangle|^2}{(E_{n_s} - E_{n_0}) + (E_{n_t} - E_{n_0'})} \,, \tag{22}$$

$$C^{(23)}_{8,disp} = C^{(31)}_{8,disp} \;=\; \frac{16\pi^2}{15} \sum_{n_s n_t}{}' \left\{ \frac{|\langle n_0 0 \| T_2 \| n_s 2 \rangle|^2 |\langle n_0' 0 \| T_1 \| n_t 1 \rangle|^2}{(E_{n_s} - E_{n_0}) + (E_{n_t} - E_{n_0'})} + \frac{\langle n_0 0 \| T_1 \| n_s 1 \rangle|^2 |\langle n_0' 0 \| T_2 \| n_t 2 \rangle|^2}{(E_{n_s} - E_{n_0}) + (E_{n_t} - E_{n_0'})} \right\}. \tag{23}$$

F. The third-order energy correction

The third-order energy correction for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li^+($n_0'\,^1S$) system can be written as

$$\begin{aligned}
\Delta E^{(3)} \;=\; & -\left[\frac{C^{(23)}_{7,ddq}}{R_{23}^7} + \frac{C^{(31)}_{7,ddq}}{R_{31}^7}\right] - \left[\frac{C^{(23)}_{9,dqo} + C^{(23)}_{9,qqq} + C^{(23)}_{9,rind}}{R_{23}^9} + \frac{C^{(31)}_{9,dqo} + C^{(31)}_{9,qqq} + C^{(31)}_{9,rind}}{R_{31}^9}\right] \\
& - \frac{C_7^{(12,23,31)}(1,1,0)}{R_{12}^3 R_{23}^2 R_{31}^2} - \frac{C_9^{(12,23,31)}(1,1,1)}{R_{12}^3 R_{23}^3 R_{31}^3} - \frac{C_9^{(12,23,31)}(1,2,0)}{R_{12}^4 R_{23}^3 R_{31}^2} - \frac{C_9^{(12,23,31)}(2,1,0)}{R_{12}^4 R_{23}^2 R_{31}^3} \\
& - \frac{C_9^{(12,23)}(1,1,2,1,1,2)}{R_{12}^6 R_{23}^3} - \frac{C_9^{(12,23)}(1,1,1,2,2,1) + C_9^{(12,23)}(1,2,1,1,1,1)}{R_{12}^7 R_{23}^2} \\
& - \frac{C_9^{(31,12)}(1,1,2,1,1,2)}{R_{12}^6 R_{31}^3} - \frac{C_9^{(31,12)}(1,1,1,2,2,1) + C_9^{(31,12)}(1,2,1,1,1,1)}{R_{12}^7 R_{31}^2} - \cdots \,,
\end{aligned} \tag{24}$$

From the Eq. (24), we can find that the third-order correction include both additive and nonadditive interaction terms. Among them, the nonadditive interaction term $C_9^{(12,23,31)}(1,1,1)/R_{12}^3 R_{23}^3 R_{31}^3$ is the dispersion term; the rest are all induction interaction terms.

1. The additive interaction

The additive two-body induction interaction coefficients $C^{(23)}_{7,ddq}$ and $C^{(31)}_{7,ddq}$, which can also be interpreted as the interaction of the charge of the ion and the moment of the Li atom,

are expanded as

$$
\begin{aligned}
C^{(23)}_{7,ddq} = C^{(31)}_{7,ddq} &= -\frac{8\pi\sqrt{6\pi}}{125}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_2\|n'_t 1\rangle\langle n'_t 1\|T_1\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})} \\
&- \frac{16\pi\sqrt{10\pi}}{225}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_1\|n'_t 2\rangle\langle n'_t 2\|T_2\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})} \\
&= -\frac{1}{2}Q^3 B\,, \qquad (25)
\end{aligned}
$$

where B is the static dipole-dipole-quadrupole polarizability [35, 36] of the Li atom.

The additive two-body induction coefficients $C^{(23)}_{9,dqo}$ and $C^{(31)}_{9,dqo}$, which are related to the dipole-quadrupole-octopole polarizability, include three terms

$$
\begin{aligned}
C^{(23)}_{9,dqo} = C^{(31)}_{9,dqo} &= \frac{16\pi\sqrt{15\pi}}{525}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_3\|n'_t 2\rangle\langle n'_t 2\|T_2\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})} \\
&+ \frac{16\pi\sqrt{21\pi}}{735}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_2\|n'_t 3\rangle\langle n'_t 3\|T_3\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})} \\
&+ \frac{16\pi\sqrt{35\pi}}{1225}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_2\|n_t 2\rangle\langle n_t 2\|T_1\|n'_t 3\rangle\langle n'_t 3\|T_3\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})}\,, \qquad (26)
\end{aligned}
$$

The additive two-body induction coefficients $C^{(23)}_{9,qqq}$ and $C^{(31)}_{9,qqq}$, which are related to the quadrupole-quadrupole-quadrupole polarizability, include one term,

$$
C^{(23)}_{9,qqq} = C^{(31)}_{9,qqq} = \frac{8\pi\sqrt{14\pi}}{875}Q^3 {\sum_{n_t n'_t}}' \frac{\langle n_0 0\|T_2\|n_t 2\rangle\langle n_t 2\|T_2\|n'_t 2\rangle\langle n'_t 2\|T_2\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})}\,, \qquad (27)
$$

and the rest of the induced (denoted by "rind") interaction coefficients, $C^{(23)}_{9,rind}$ and $C^{(31)}_{9,rind}$, include the following five terms,

$$
\begin{aligned}
C^{(23)}_{9,rind} = C^{(31)}_{9,rind} &= -\frac{96\pi^2\sqrt{2\pi}}{1215}Q {\sum_{n_t n'_t n_u}}' \frac{|\langle n'_0 0\|T_1\|n_u 1\rangle|^2\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_2\|n'_t 1\rangle\langle n'_t 1\|T_1\|n_0 0\rangle}{(E_{n'_t}+E_{n_u}-E_{n_0}-E_{n'_0})(E_{n_t}+E_{n_u}-E_{n_0}-E_{n'_0})} \\
&- \frac{64\pi^2\sqrt{30\pi}}{675}Q {\sum_{n_t n_u n'_t}}' \frac{|\langle n'_0 0\|T_1\|n_u 1\rangle|^2\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_1\|n'_t 2\rangle\langle n'_t 2\|T_2\|n_0 0\rangle}{(E_{n'_t}+E_{n_u}-E_{n_0}-E_{n'_0})(E_{n_t}+E_{n_u}-E_{n_0}-E_{n'_0})} \\
&- \frac{64\pi^2\sqrt{6\pi}}{135}Q {\sum_{n_t n'_t n'_u}}' \frac{|\langle n'_0 0\|T_1\|n'_u 1\rangle|^2\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_2\|n'_t 1\rangle\langle n'_t 1\|T_1\|n_0 0\rangle}{(E_{n'_t}+E_{n'_u}-E_{n_0}-E_{n'_0})(E_{n_t}-E_{n_0})} \\
&- \frac{64\pi^2\sqrt{10\pi}}{225}Q {\sum_{n_t n'_t n'_u}}' \frac{|\langle n'_0 0\|T_1\|n'_u 1\rangle|^2\langle n_0 0\|T_1\|n_t 1\rangle\langle n_t 1\|T_1\|n'_t 2\rangle\langle n'_t 2\|T_2\|n_0 0\rangle}{(E_{n'_t}+E_{n'_u}-E_{n_0}-E_{n'_0})(E_{n_t}-E_{n_0})} \\
&- \frac{192\pi^2\sqrt{10\pi}}{2025}Q {\sum_{n_t n'_t n'_u}}' \frac{|\langle n'_0 0\|T_1\|n'_u 1\rangle|^2\langle n_0 0\|T_2\|n_t 2\rangle\langle n_t 2\|T_1\|n'_t 1\rangle\langle n'_t 1\|T_1\|n_0 0\rangle}{(E_{n'_t}+E_{n'_u}-E_{n_0}-E_{n'_0})(E_{n_t}-E_{n_0})}\,. \qquad (28)
\end{aligned}
$$

2. The nonadditive interaction

There are two types of nonadditive interations terms in the Eq. (24): Some of them are related to $R_{12}R_{23}R_{31}$, the rest are related to $R_{12}R_{23}$ or $R_{12}R_{31}$. The nonadditive three-body coefficients that are related to $R_{12}R_{23}R_{31}$ can be expanded respectively as

$$C_7^{(12,23,31)}(1,1,0) = -\frac{256\pi^3}{81}Q^2\Big[\cos\alpha\cos\beta+\cos(\alpha-\beta)\Big]\mathbb{T}_3(1,1,0)\,, \tag{29}$$

$$C_9^{(12,23,31)}(1,2,0) = -\frac{64\pi^3}{75}Q^2\Big[\cos\alpha+\cos\alpha\cos2\beta+2\cos(\alpha-2\beta)\Big]\mathbb{T}_3(1,2,0)\,, \tag{30}$$

$$C_9^{(12,23,31)}(2,1,0) = -\frac{64\pi^3}{75}Q^2\Big[\cos\beta+\cos2\alpha\cos\beta+2\cos(2\alpha-\beta)\Big]\mathbb{T}_3(2,1,0)\,, \tag{31}$$

$$C_9^{(12,23,31)}(1,1,1) = -\frac{256\pi^3}{243}\Big[3\cos\alpha\cos\beta\cos\gamma+1\Big]\mathbb{T}_3(1,1,1)\,, \tag{32}$$

where $C_9^{(12,23,31)}(1,1,1)$ is the long-range dispersion coefficient, which originates in the instantaneous dipole moment of the two Li atoms and Li^+ ion. The rest are the induction coefficients, which result from the induced effect of the Li^+ ion. The reduced matrix element $\mathbb{T}_3(L_s,L_t,L_u)$ is expressed as

$$\begin{aligned}\mathbb{T}_3(L_s,L_t,L_u) &= {\sum_{n_sn_tn_u}}' |\langle n_00\|T_{L_s}\|n_sL_s\rangle|^2|\langle n_00\|T_{L_t}\|n_tL_t\rangle|^2|\langle n_0'0\|T_{L_u}\|n_uL_u\rangle|^2 \\ &\times \frac{(E_{n_s}+E_{n_t}+E_{n_u}-2E_{n_0}-E_{n_0'})}{(E_{n_s}+E_{n_t}-2E_{n_0})(E_{n_t}+E_{n_u}-E_{n_0}-E_{n_0'})(E_{n_s}+E_{n_u}-E_{n_0}-E_{n_0'})}\,,\end{aligned} \tag{33}$$

where the energy factor of the above formula is same with that of the triple-dipole (Axilrod-Teller-Muto) interaction terms [1, 2, 5, 37–39]. The nonadditive three-body coefficients that are related to $R_{12}R_{23}$ or $R_{12}R_{31}$, can be expanded as

$$C_9^{(12,23)}(1,1,1,2,2,1) = -\frac{96\pi^2\sqrt{2\pi}}{405}Q\cos\beta\Big[2\sqrt{3}\mathbb{D}_3(1,1,2,1)+\frac{3\sqrt{5}}{5}\mathbb{D}_3'(1,1,1,2)\Big]\,, \tag{34}$$

$$C_9^{(12,23)}(1,1,2,1,1,2) = -\frac{8\pi^2\sqrt{2\pi}}{405}Q(3\cos2\beta+1)\Big[\frac{6\sqrt{5}}{5}\mathbb{D}_3(1,1,1,2)+\sqrt{3}\mathbb{D}_3'(1,1,2,1)\Big]\,, \tag{35}$$

$$C_9^{(12,23)}(1,2,1,1,1,1) = -\frac{96\pi^2\sqrt{10\pi}}{675}Q\cos\beta\Big[2\mathbb{D}_3(1,2,1,1)+\mathbb{D}_3'(1,2,1,1)\Big]\,, \tag{36}$$

where the $\mathbb{D}_3(L_s,L_t,l_1,L_t')$ and $\mathbb{D}_3'(L_s,L_t,l_1,L_t')$ are

$$\mathbb{D}_3(L_s,L_t,l_1,L_t') = {\sum_{n_sn_tn_t'}}' \frac{|\langle n_00\|T_{L_s}\|n_sL_s\rangle|^2\langle n_00\|T_{L_t}\|n_tL_t\rangle\langle n_tL_t\|T_{l_1}\|n_t'L_t'\rangle\langle n_t'L_t'\|T_{L_t'}\|n_00\rangle}{(E_{n_s}+E_{n_t}-2E_{n_0})(E_{n_t'}-E_{n_0})}\,, \tag{37}$$

$$\mathbb{D}_3'(L_s,L_t,l_1,L_t') = {\sum_{n_sn_tn_t'}}' \frac{|\langle n_00\|T_{L_s}\|n_sL_s\rangle|^2\langle n_00\|T_{L_t}\|n_tL_t\rangle\langle n_tL_t\|T_{l_1}\|n_t'L_t'\rangle\langle n_t'L_t'\|T_{L_t'}\|n_00\rangle}{(E_{n_s}+E_{n_t}-2E_{n_0})(E_{n_s}+E_{n_t'}-2E_{n_0})}\,.$$

(38)

The expansion of $C_9^{(31,12)}(L_s, L_t, L_u, L'_s, L'_t, L'_u)$ can be obtained by replacing the interior angle β with α in Eqs. (34), (35), and (36).

Compared with a three-body system consisting of three ground-state S atoms, the leading-terms of the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n'_0\,^1S$) system in Eq.(24) are the additive two-body induction interaction coefficients $C^{(23)}_{7,ddq}$, $C^{(31)}_{7,ddq}$ and the nonadditive three-body coefficients $C_7^{(12,23,31)}(1,1,0)$ due to the induction effect of Li$^+$ ion. For the C_9 coefficients, the new types of the additive induction coefficients of $C^{(23)}_{9,dqo}$, $C^{(31)}_{9,dqo}$, $C^{(23)}_{9,qqq}$, $C^{(31)}_{9,qqq}$, $C^{(23)}_{9,rind}$, $C^{(31)}_{9,rind}$, and the nonadditive induction coefficients of $C_9^{(12,23)}(L_s, L_t, L_u, L'_s, L'_t, L'_u)$ and $C_9^{(31,12)}(L_s, L_t, L_u, L'_s, L'_t, L'_u)$ appear.

G. The fourth-order energy correction

The fourth-order energy correction for the Li($n_0\,^2S$)-Li($n_0\,^2S$)-Li$^+$($n'_0\,^1S$) system contains many more intermediate states and the detailed derivation is complicated. Therefore, since the leading term of the fourth-order correction is related to the eighth power of the distance between particles, we deduce the leading term of the fourth-order energy correction, in order to guarantee the completeness of the expansion for the interaction potential in the present paper. Thus,

$$\Delta E^{(4)} \;=\; -\frac{C^{(23)}_{8,hyp}}{R^8_{23}} - \frac{C^{(31)}_{8,hyp}}{R^8_{31}} - \cdots\,, \tag{39}$$

where the induction interaction coefficients of $C^{(23)}_{8,hyp}$ and $C^{(31)}_{8,hyp}$ are related to the static hyperpolarizability γ_0 [34, 40–42] of the ground-state Li atom,

$$C^{(23)}_{8,hyp} \;=\; C^{(31)}_{8,hyp} = \frac{16\pi^2}{9}Q^4\left[\frac{1}{9}\mathbb{T}_4(1,0,1) + \frac{2}{45}\mathbb{T}_4(1,2,1)\right] = \frac{1}{24}Q^4\gamma_0\,, \tag{40}$$

with the expression of $\mathbb{T}_4$ is [34]

$$\begin{aligned}\mathbb{T}_4(L_t, L'_t, L''_t) \;=\; & {\sum_{n_t n'_t n''_t}}' \frac{\langle n_0 0\|T_1\|n_t L_t\rangle\langle n_t L_t\|T_1\|n'_t L'_t\rangle\langle n'_t L'_t\|T_1\|n''_t L''_t\rangle\langle n''_t L''_t\|T_1\|n_0 0\rangle}{(E_{n_t}-E_{n_0})(E_{n'_t}-E_{n_0})(E_{n''_t}-E_{n_0})} \\ & -\; \delta(L_t,0)(-1)^{L_t+L''_t}{\sum_{n_t n''_t}}' \frac{|\langle n_0 0\|T_1\|n_t 1\rangle|^2|\langle n_0 1\|T_1\|n''_t\rangle|^2}{(E_{n_t}-E_{n_0})(E_{n''_t}-E_{n_0})^2}\,.\end{aligned} \tag{41}$$

III. RESULTS AND DISCUSSION

In the present work, using accurate variational wave functions for the Li atom and Li$^+$ ion in Hylleraas coordinates [34], we evaluate the additive second-order, additive and nonadditive third-order, and part of additive fourth-order coefficients for the Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$) system. As part of the analysis, we also obtain the terms that correspond to the Li($2\,^2S$)-Li$^+$($1\,^1S$) long-range interaction potential. Finite mass effects are treated as in Refs. [34, 43], see for example Eq. (1) of [34]. In the present calculations, we used the nuclear mass 10961.8977 for ^{6}Li and 12786.3916 for ^{7}Li in units of the electron mass.

A. The additive dispersion interaction coefficients

For the newly generated polarization terms under the second-order energy correction of the Li($2\,^2S$)-Li($2\,^2S$)-Li^+($1\,^1S$) system, since the additive long-range dispersion coefficients of the $C^{(12)}_{6,disp}$ and $C^{(12)}_{8,disp}$ terms between two Li atoms are listed in the Ref. [34], we will not repeat these values for simplicity. Also, for these additive interaction terms, this three-body system can be seen as three two-body systems and we have $C^{(23)}_n = C^{(31)}_n$. Moreover, as we will show, these coefficients give an accurate representation of the long-range Li($2\,^2S$)-Li^+($1\,^1S$) interaction potential.

Table I lists the additive long-range coefficients of the $C^{(23)}_4$, $C^{(23)}_6$, $C^{(23)}_8$ terms between the Li atom interacting with the Li^+ ion, and their each components: the induction interaction terms $C^{(23)}_{4,ind}$, $C^{(23)}_{6,ind}$, $C^{(23)}_{8,ind}$, the dispersion interaction terms $C^{(23)}_{6,disp}$, $C^{(23)}_{8,disp}$ and the hyperpolarizability terms $C^{(23)}_{8,hyp}$. The induction interactions can be seen as the interaction between the induced electric dipolar, quadrupole, octupole moment of the Li atom and the charge of the Li^+ ion, which are related to the static polarizability of the atom. They always give the biggest contribution to the total corresponding interactions. The dispersion interaction terms describe the interaction between instantaneous dipole-dipole, dipole-quadrupole moment of the ion and atom, which give the next biggest contribution. The hyperpolarizability terms result from the induced hyperpolarizability of the atoms and the charge of the ion and give the smallest contribution to the corresponding total interaction.

Table II lists the third-order additive interaction coefficients $C^{(23)}_{7,ddq}$, $C^{(23)}_{9,dqo}$, $C^{(23)}_{9,qqq}$, $C^{(23)}_{9,rind}$ and the total numerical values $C^{(23)}_{9,dqo}$+$C^{(23)}_{9,qqq}$+$C^{(23)}_{9,rind}$. The induction interaction coefficient $C^{(23)}_{7,ddq}$ is related to the dipole-dipole-quadrupole polarizability [35, 40]; $C^{(23)}_{9,dqo}$ is related to the dipole-quadrupole-octupole polarizability; $C^{(23)}_{9,qqq}$ is related to the quadrupole-quadrupole-quadrupole polarizability; $C^{(23)}_{9,rind}$ is the rest of the induced (denoted "rind") interaction terms. For these terms of $C^{(23)}_9$ in Table II, we can find that $C^{(23)}_{9,dqo}$ gives the biggest contribution; $C^{(23)}_{9,qqq}$ gives the next biggest contribution; and $C^{(23)}_{9,rind}$ gives the smallest contribution.

Table III shows the comparison of the dipole-dipole-quadrupole polarizability B between our calculations and other available results. Our calculation shows good agreement, to within 0.026%, with the result of Pipin and Bishop [40]. For the hyperpolarizability γ_0 a comparison of our calculations with other available ones was presented in Ref. [34].

Using the data in Tables I–II, we can write down the long-range interaction potential for the $^\infty$Li($2\,^2S$)-$^\infty Li^+$($1\,^1S$), ^{6}Li($2\,^2S$)-$^6Li^+$($1\,^1S$), and ^{7}Li($2\,^2S$)-$^7Li^+$($1\,^1S$) systems, which are applicable to scattering calculations at ultra-low energies [25, 44, 45]. For example, with R the internuclear distance, we have, taking the "(23)" terms in Eqs. (20), (25), (26), (27), (28), and (39), the result for $^\infty$Li nuclei:

$$V_{^\infty\mathrm{Li}\text{-}^\infty\mathrm{Li}^+}(R) \sim -82.056/R^4 - 714.951/R^6 - 27143.0/R^7 - 20105.0/R^8 - 1080753.2/R^9. \quad (42)$$

This result is expected to be substantially more accurate than the form given in Ref. [25], where the dispersion coefficient (our $C^{(23)}_{6,disp}$ in Table I) was estimated to be 263.5 by fitting to an *ab initio* potential energy curve calculated in Ref. [44]. We note that a recent density functional theory calculation of the dispersion coefficient [46] is in good agreement with our calculation, yielding a value 3.37 (obtained using the benchmark set `ModelPGG_Scaled.dat` provided in the supplementary data of [46]). We note that the long-range potential used

in Ref. [45] does not account for the dispersion interaction at $\mathcal{O}(R^{-6})$. While there has been little systematic work on the contribution of higher-order terms to ultra-cold energy ion-atom scattering—conventionally terms beyond $\mathcal{O}(R^{-6})$ are considered unimportant—it has been shown in the case of quantum defect theory for Na-Na^+ that an important length scale is set by the ratio of the coefficients of the $1/R^4$ and $1/R^6$ terms [24, 47]. In addition, in Ref. [48], Li and Gao carried out calculations on H-H^+ using a long-range potential accurate to $\mathcal{O}(R^{-9})$. Our result, Eq. (42), might enable similar calculations for Li-Li^+, especially given recent advances in calculations of the Li_2^+ potential curve [44, 49]. We now leave aside the particular case of the Li($2\,^2S$)-Li^+($1\,^1S$) interactions, and complete the discussion on the evaluation of the three-body terms.

B. The nonadditive interaction coefficients

Similarly to the triple-dipole (Axilrod-Teller-Muto) interaction terms, the nonadditive interaction coefficients contain a dependence on the geometrical structure of these three particles. Table IV lists the values of $\mathbb{T}_3(1,1,0)$, $\mathbb{T}_3(1,2,0)$, $\mathbb{T}_3(2,1,0)$, $\mathbb{T}_3(1,1,1)$; $\mathbb{D}_3(1,1,1,2)$, $\mathbb{D}_3(1,1,2,1)$, $\mathbb{D}_3(1,2,1,1)$, $\mathbb{D}'_3(1,1,1,2)$, $\mathbb{D}'_3(1,1,2,1)$ and $\mathbb{D}'_3(1,2,1,1)$ of the Li($2\,^2S$)-Li($2\,^2S$)-Li^+($1\,^1S$) system. With these values and the formulas shown in the Section II F, we can evaluate the nonadditive interaction coefficients of Li($2\,^2S$)-Li($2\,^2S$)-Li^+($1\,^1S$) system in any configurations. For example, in the case of the three nuclei forming an equilateral triangle, we have $\alpha = \beta = \gamma = \pi/3$. Thus, with these given interior angles, we can obtain all the nonadditive interaction coefficients, which are shown in the table V.

IV. CONCLUSION

We theoretically investigated the long-range interactions between a ground state Li^+ ion and two ground state neutral Li atoms with highly accurate variationally-generated wave functions in Hylleraas coordinates. Using perturbation theory for the energies up to the third-order and partially to the fourth-order, we evaluated the long-range additive interaction coefficients C_4, C_6, C_7, C_8 and C_9, and the nonadditive interaction coefficients C_7 and C_9 for the three-body system. For these additive coefficients C_4, C_6, C_8, we also showed each contributor to these coefficients: the induction interaction terms $C^{(IJ)}_{4,ind}$, $C^{(IJ)}_{6,ind}$, $C^{(IJ)}_{8,ind}$; the dispersion interaction terms: $C^{(IJ)}_{6,disp}$, $C^{(IJ)}_{8,disp}$; and the hyperpolarizability terms $C^{(IJ)}_{8,hyp}$, which enter in the fourth-order correction. In addition, some different new types of nonadditive interactions that are related to $R_{12}R_{23}$, $R_{12}R_{31}$ and $R_{12}R_{23}R_{31}$ were found to appear in the third-order energy correction. In this paper, we give the universal formulas to calculate these nonadditive coefficients and demonstrate their applications using the example of an equilateral triangle configuration. All the nonadditive interaction coefficients depend on the geometrical configurations of three particles. Our calculation may be useful in the study of cold collisions, the three-body recombination of an ion and two neutral atoms, and in constructing accurate three-body potential curves. We also, as a consequence of accounting for additive terms, give a precise result for the long-range interactions of the Li($2\,^2S$)-Li^+($1\,^1S$) system.

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TABLE I: The additive interaction coefficients $C_4^{(23)}$, $C_6^{(23)}$ and $C_8^{(23)}$ of the Li($2\,^2S$)-Li$^+$($1\,^1S$) system in atomic units. The numbers in parentheses represent the computational uncertainties.

Coefficient[a]	$^\infty$Li	^{7}Li	^{6}Li
$C_{4,ind}^{(23)} = \alpha_1/2$	82.056(5)	82.080(5)	82.084(5)
$C_{6,ind}^{(23)} = \alpha_2/2$	711.631(1)	711.706(1)	711.718(1)
$C_{6,disp}^{(23)}$	3.3208(5)	3.3227(5)	3.3229(4)
$C_{6,ind}^{(23)} + C_{6,disp}^{(23)}$	714.951(1)	715.028(1)	715.041(1)
$C_{8,ind}^{(23)} = \alpha_3/2$	19824.64(1)	19826.85(1)	19827.22(1)
$C_{8,disp}^{(23)}$	152.884(3)	152.948(2)	152.960(3)
$C_{8,hyp}^{(23)} = \gamma_0/24$	127.5(9)	117.5(9)	115.8(9)
$C_{8,ind}^{(23)} + C_{8,disp}^{(23)} + C_{8,hyp}^{(23)}$	20105.0(9)	20097.3(9)	20096.0(9)

[a]The polarizabilities α_1, α_2, α_3, and the hyperpolarizability γ_0, are taken from Tang *et al.* [34].

TABLE II: The additive interaction coefficients $C_7^{(23)}$ and $C_9^{(23)}$ of the Li($2\,^2S$)-Li$^+$($1\,^1S$) system in atomic units. The numbers in parentheses represent the computational uncertainties.

Coefficient	$^\infty$Li	^{7}Li	^{6}Li
$C_{7,ddq}^{(23)}$	27143.0(2)	27153.8(1)	27155.4(2)
$C_{9,dqo}^{(23)}$	995387.75(6)	995678.23(2)	995726.60(2)
$C_{9,qqq}^{(23)}$	81722.20(1)	81738.36(1)	81741.05(1)
$C_{9,rind}^{(23)}$	3643.2(1)	3645.7(1)	3646.1(1)
$C_{9,dqo}^{(23)}+C_{9,qqq}^{(23)}+C_{9,rind}^{(23)}$	1080753.2(1)	1081062.4(1)	1081113.9(1)

TABLE III: Comparison of the dipole-dipole-quadrupole polarizability B for the ground state $2\,^2S$ of $^\infty$Li, in atomic units.

Reference	$B = -2C_7^{(23)}$
Maroulis & Thakkar [35](1989)	−54930
Pipin & Bishop [40](1992)	−54300
This work	−54286.0(4)

TABLE IV: Values of $\mathbb{T}_3(1,1,0)$, $\mathbb{T}_3(1,2,0)$, $\mathbb{T}_3(2,1,0)$, $\mathbb{T}_3(1,1,1)$; $\mathbb{D}_3(1,1,1,2)$, $\mathbb{D}_3(1,1,2,1)$, $\mathbb{D}_3(1,2,1,1)$, $\mathbb{D}'_3(1,1,1,2)$, $\mathbb{D}'_3(1,1,2,1)$ and $\mathbb{D}'_3(1,2,1,1)$ of the Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$) system, in atomic units. The numbers in parentheses represent the computational uncertainties.

Coefficient	$\mathbb{T}_3(1,1,0)$	$\mathbb{T}_3(1,2,0)$	$\mathbb{D}_3(1,1,1,2)$	$\mathbb{D}_3(1,1,2,1)$	$\mathbb{D}_3(1,2,1,1)$
	$\mathbb{T}_3(1,1,1)$	$\mathbb{T}_3(2,1,0)$	$\mathbb{D}'_3(1,1,1,2)$	$\mathbb{D}'_3(1,1,2,1)$	$\mathbb{D}'_3(1,2,1,1)$
$^{\infty}Li$	274.840(4)	6620.95(6)	−21486.0(1)	−35427.2(5)	−29332.6(5)
	8.2033(3)	6620.95(6)	−14674.2(3)	−17785.61(2)	−14674.2(3)
^{7}Li	275.002(4)	6623.60(6)	−21497.6(1)	−35447.6(6)	−29348.6(4)
	8.2103(3)	6623.60(6)	−14682.5(2)	−17795.82(1)	−14682.5(2)
^{6}Li	275.029(4)	6624.04(6)	−21499.4(1)	−35450.8(5)	−29351.3(4)
	8.2115(3)	6624.04(6)	−14683.7(3)	−17797.50(1)	−14683.7(3)

TABLE V: The nonadditive interaction coefficients of the Li($2\,^2S$)-Li($2\,^2S$)-Li$^+$($1\,^1S$) system, where the three nuclei form an equilateral triangles, in atomic units. The numbers in parentheses represent the computational uncertainties.

Coefficient	$^{\infty}$Li	^{7}Li	^{6}Li
$C_7^{(12,23,31)}(1,1,0)$	−33666.2(5)	−33686.1(5)	−33689.4(5)
$C_9^{(12,23,31)}(1,1,1)$	−368.45(2)	−368.77(2)	−368.82(2)
$C_9^{(12,23,31)}(1,2,0)$	−218977(2)	−219064(2)	−219079(2)
$C_9^{(12,23,31)}(2,1,0)$	−218977(2)	−219064(2)	−219079(2)
$C_9^{(12,23)}(1,1,1,2,2,1)$	417562(5)	417800(5)	417840(5)
$C_9^{(12,23)}(1,1,2,1,1,2)$	−21613.97(6)	−21625.91(6)	−21627.99(4)
$C_9^{(12,23)}(1,2,1,1,1,1)$	288502(2)	288661(2)	288687(2)
$C_9^{(31,12)}(1,1,1,2,2,1)$	417562(5)	417800(5)	417840(5)
$C_9^{(31,12)}(1,1,2,1,1,2)$	−21613.97(6)	−21625.91(6)	−21627.99(4)
$C_9^{(31,12)}(1,2,1,1,1,1)$	288502(2)	288661(2)	288687(2)

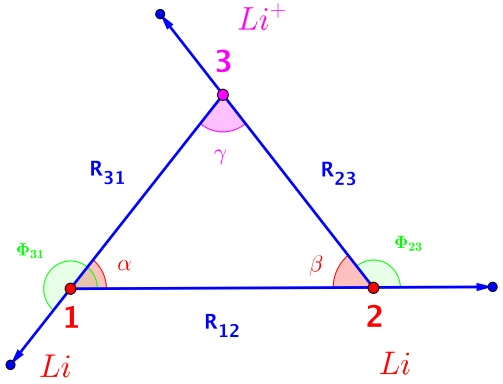

FIG. 1: Coordinate for atoms 1, 2 and ion 3: the z-axis is perpendicular to the plane of the three nuclei and the x-axis is parallel to $\mathbf{R}_{12}$. The angles satisfy $\Phi_{12} = 0$, $\Phi_{23} = \pi - \beta$, $\Phi_{31} = \pi + \alpha$. The nuclei lie in the x-y plane.