Long-range additive and nonadditive potentials in a hybrid system: Ground state atom, excited state atom, and ion

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We report a theoretical study on the long-range additive and nonadditive potentials for a three-body hybrid atom-atom-ion system composed of one ground $S$ state Li atom, one excited $P$ state Li atom and one ground $S$ state Li$^+$ ion, Li($2^2S$)-Li($2^2P$)-Li$^+$(1$^1S$). The interaction coefficients are evaluated with highly accurate wave functions calculated variationally in Hylleraas coordinates. For this hybrid system the three-body nonadditive interactions (appearing in second-order) induced by the energy degeneracy and enhanced by the induction effect of the Li$^+$ ion through the internal electric field can be strong and even stronger than the two-body additive interactions at the same order. We find that for particular geometries the two-body additive interactions of the system sum to zero leaving only three-body nonadditive interactions thus making the present system potentially a platform to explore quantum three-body effects. We also extract by first-principles the leading coefficients of the long-range electrostatic, induction, and dispersion energies of Li$^+_2$ electronic states correlating to Li$^+$($1^1S$)-Li($2^2P$), which until now were not available in the literature. The results should be especially valuable for the exploration of schemes to create trimers with ultracold atoms and ions in optical lattices.

Keywords: Long-range interactions; Van der Waals interaction; First-principles calculations

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I. INTRODUCTION

This paper provides detailed results for the long-range interactions between three atomic systems, specifically, a ground state atom, a (low-lying) excited state atom, and a ground state ion, for the particular case of lithium, specifically, Li$(2^2S)$-Li$(2^2P)$-Li$^+(1^1S)$. Most studies of hybrid systems consisting of ground or low-lying state atoms have been concerned with pair-wise cases, \textit{i.e.}, an atom and an ion (reviewed in Ref. [1]), or a diatomic molecule and an ion [2–4]. Recently, properties of low-lying states of triatomic cations were systematically studied [5]. And, some studies, while considering excitation of atoms, do not consider ions. For three atoms, with at least one atom in a Rydberg state, there are a number of studies, such as Refs. [6, 7]. Other studies have considered three-body interactions of diatomic molecules in a trapping potential [8, 9].

We explore another possibility—three atomic systems that are in the long-range domain (sufficiently separated such that electron exchange is small) with one constituent charged and one constituent \textit{electronically excited}. There are two main results: First, we give expressions for the long-range potentials as expansions in inverse-powers of separation distances and corresponding precisely evaluated coefficients for two-body (dipole-dipole and van der Waals) and three-body (van der Waals) long-range additive and nonadditive interactions, in a manner similar to, but extending our previous work on three atoms [10, 11] and on two atoms and a ground state ion [12]. While in the present work the derived formulas are generally applicable to the hybrid $A(n_0S)-A(n'_0L)-A^{Q+}(n''_0S)$ systems, even involving Rydberg states, we choose the particular states of lithium because we can evaluate the coefficients precisely using accurate wave functions. We discuss applications for quantum chemical studies of Li$_3^+$ and, as a consequence of our formulation, for long-range potential energies of Li$_2^+$ electronic states correlating to Li$^+(1^1S)$–Li$(2^2P)$. Second, different from previous studies on the weak nonadditive interactions for three-body systems composed of atoms [10, 11, 13–19] or of two atoms and an ion [12], here we find theoretical evidence of a new pure quantum three-body effect that might have influence on constructing accurate potential surfaces. Specifically, for the Li$(2^2S)$-Li$(2^2P)$-Li$^+(1^1S)$ system, we find that at particular geometries the two-body additive interactions disappear leaving only three-body nonadditive interactions. These net effects of two- and three-body interactions are quite similar to those for two- and three-body interactions in the case of polar molecules confined in lattice traps [8, 9] or three Rydberg atoms under the influence of an external electric field [7], where the same goal—removal of two-body interactions—was pursued. To provide necessary context we begin with some general contextual background from molecular (chemical) physics and from ultra-cold science.

A. General aspects of triatomic systems

The intrinsic complexity of triatomic molecules\footnote{A widely-known aphorism (from 1981), attributed to Schawlow, warns atomic physicists that, “a diatomic molecule is one atom too many” [20], but it may be predated by an earlier observation (from 1971) attributed to Herschbach: “The trouble with triatomic molecules is, they have one atom too many!” [21]. Recently, Gao [22] emphasized the emergence of chemical complexity beginning with three atoms.} produces interesting phenomena such as conical intersections and geometric phases [23, 24] and the Renner-Teller effect [25], while...
consideration of three atoms at ultra-low energies leads to Efimov \[26, 27\], Borromean \[9\], and Pfaffian \[8, 28\] states and makes the description of collisional processes, such as atom-diatom collisions \[29, 30\] and three-body recombination loss \[31–33\] challenging. The demands for understanding the spectroscopy and collisional processes of specific important triatomic molecules at thermal collisional energies also continue to drive progress. For example, ozone (O$_3$) is a vital atmospheric constituent of the planet, with quantum-mechanical collisional cross sections recently reported (see Ref. \[34\] and references therein), tricarbon (C$_3$) is prominent in comets and other astrophysical \[35\] and laboratory realms \[36\], and H$_3$, H$_3^+$, and their isotopologues, serve as long-standing theoretical benchmark systems \[23, 37\] and are important in astrophysical applications such as, for example, to the cooling of hydrogen gas in molecular clouds \[38\] and in the evolution of the early Universe \[39\].

Detailed procedures for calculating and constructing potential energy surfaces (and other properties) of triatomic systems have been developed, exemplified (for the representative molecules discussed above) by recent works such as for tricarbon \[40\], for ozone \[41–43\], and for H$_3$ \[44\]. A successful strategy to construct three-atom potential energy surfaces using semi-empirical methods requires input calculations of atom-dimer and three-atom long-range potentials \[45–47\]. To understand the dynamics of low-energy (ultra-cold) collisions, consideration of the long-range potentials is paramount, see, for example, for atom-molecule systems \[2, 3, 48–50\] and for atom-molecular-ion systems \[51–53\]. Next, we provide an overview of the lithium dimer and trimer cations.

### B. Homonuclear lithium dimer and trimer cations: Excited electronic states

We provide a brief overview of relevant work on the lithium homonuclear systems Li$_2^+$ and Li$_3^+$ in order to demonstrate that the present work provides data previously not available in the literature.

For the diatomic lithium cation Li$_2^+$, four electronic states (ignoring fine-structure) correlate to the separated pair Li$^+$ (1$^1$S)–Li(2$^2$P), namely, 2$^2$Σ$_g$, 2$^2$Σ$_u$, 1$^2$Π$_g$, and 1$^2$Π$_u$. Model potential method calculations were given by Magnier et al. \[54\] and by Rabli and McCarroll \[55\]; a CASSCF/MRCI calculation was reported in Ref. \[56\] (and references therein for earlier work). Magnier et al. \[54\] calculated long-range potential curves as functions of internuclear distance \( R \), including the exchange energies and electrostatic, induction, and dispersion terms up to \( O(R^{-8}) \), but did not give the long-range potential coefficients. The emphasis of the present paper is on the three-body system, but because the two-body interactions are available from our calculations, as will be shown in Secs. II G–II I, we will extract the values of the long-range potential coefficients of the four states of Li$_2^+$.

For the triatomic lithium cation Li$_3^+$, because we have found no previous quantum chemical studies of the excited electronic states corresponding to those reported here, we present a summary of calculations on the ground electronic state of Li$_3^+$. In a series of works, Searles, Dunne, and von Nagy-Felsobuki \[57–60\] calculated the ground state potential energy and dipole moment surfaces, which were utilized to calculate ro-vibrational spectra \[61, 62\]. Surprisingly, we have found few subsequent studies on the Li$_3^+$ ground electronic state \[63\]; although, very recently as part of a systematic study exploring alkali-metal and alkali-earth-metal hybrid ion-atom diatomic and triatomic systems, Śmiałkowski and Tomza \[5\] calculated equilibrium properties of the ground $^1A_1$ and lowest triplet $^3B_2$ states of Li$_3^+$. Our
previous paper \cite{12} supplies the long-range interactions for the ground and lowest triplet
states of $\text{Li}_3^+$. In advance of awaited \textit{ab initio} quantum chemical calculations, in the present
work, we calculate the long-range interaction potentials of $\text{Li}_3^+$ when one Li atom is $\text{Li}(2^2P)$.

C. Similarity to lattice studies

B"uchler \textit{et al.} derived a Hubbard model for cold polar molecules trapped in an optical
lattice \cite{64}, with the intent of realizing a system that could be used to model Hamiltonians
that exhibit exotic ground state properties \cite{8, 9}. In terms of the intermolecular interactions
within the lattice, they write

\begin{equation}
U_{ij} = U_0 a^3 |\mathbf{R}_i - \mathbf{R}_j|^{-3} + U_1 a^6 |\mathbf{R}_i - \mathbf{R}_j|^{-6} \tag{1}
\end{equation}

and

\begin{equation}
W_{ijk} = W_0 a^6 |\mathbf{R}_i - \mathbf{R}_j|^{-3} |\mathbf{R}_i - \mathbf{R}_k|^{-3} , \tag{2}
\end{equation}

where $U_0$, $U_1$, and $W_0$ are certain energy scales, $a$ is a length scale, $(i, j, k)$ label the
particles, the indices $i, j, k$ are cyclically permuted, and $\mathbf{R}_i$ are certain position vectors of
the lattice site (see Ref. \cite{64} for the complete definitions). By appropriate “dressing” of the
cold molecules by an external static electric field and a microwave field, they show that the
two-body interactions may be tuned “from repulsive to attractive, and even switched off,
while the three-body terms remain repulsive and strong.” We will derive two equations for
the present system, Eqs. (21) and (33), respectively, that are of the same form—but with
additional terms—as Eqs. (1) and (2). We will show that at specific geometries we recover
exactly Eqs. (1) and (2). The anisotropies of the interactions in the present system due
to the ion charge and the excited $\text{Li}(2^2P)$ atom are similar to the anisotropies due to the
intermolecular dipole-dipole interactions in the optical-lattice-trapped cold polar molecular
system \cite{65–68}. Further discussion will be given in Sec. \text{III E}.

II. THEORETICAL FORMULATION

The geometry of the three-body system is shown in Fig. \text{I} in which the three particles
define a plane with the two neutral atoms labeled as 1 and 2 and the ion labeled as 3. It is
important to note that due to the degeneracy of atoms 1 and 2 we can’t specify which one
is in the ground state or excited state. The interior angles of the configuration are $\alpha, \beta$ and
$\gamma$.

A. Coulomb potential expansion

In the present work, we take the electrostatic interaction $V_{123}$ between pairs of particles
for the $\text{Li}(n_0 S)\text{-Li}(n_0 L)\text{-Li}^+(n_0^* S)$ system as a perturbation,

\begin{equation}
H’ = V_{123} = V_{12} + V_{23} + V_{31} , \tag{3}
\end{equation}
FIG. 1. Configuration of the Li(2\textsuperscript{2}S)-Li(2\textsuperscript{2}P)-Li\textsuperscript{+}(1\textsuperscript{1}S) system. The three particles define the $x$--$y$ plane with the two neutral atoms labeled as 1 and 2 and the ion labeled as 3, $R_{IJ}$ are the internuclear distances, and $\alpha$, $\beta$ and $\gamma$ are the interior angles.

where $V_{12}$, $V_{23}$ and $V_{31}$ are the two-body mutual electrostatic interactions between atoms 1 and 2 and ion 3. For three well-separated atoms or ions, the mutual interaction energy $V_{IJ}$ can be expanded with the same method as used in Refs. [10–12], thus,

$$V_{IJ} = \sum_{l_{I}l_{J}} \sum_{m_{I}m_{J}} T_{l_{I}-m_{I}}(\sigma)T_{l_{J}m_{J}}(\rho)W_{l_{I}l_{J}}^{m_{I}-m_{J}}(IJ),$$

(4)

where the geometry factor is

$$W_{l_{I}l_{J}}^{m_{I}-m_{J}}(IJ) = \frac{4\pi(-1)^{l_{J}}}{R_{I}^{l_{I}+l_{J}}+1} \frac{(l_{I}+l_{J}-m_{I}+m_{J})!(l_{I},l_{J})^{-1/2}}{[(l_{I}+m_{I})!(l_{I}-m_{I})!(l_{J}+m_{J})!(l_{J}-m_{J})!]^{1/2}} P_{l_{I}l_{J}}^{m_{I}-m_{J}}(\cos \theta_{IJ}) \times \exp[i(m_{I} - m_{J})\Phi_{IJ}],$$

(5)

where $R_{IJ} = R_{J} - R_{I}$ is the relative position vector from particle $I$ to particle $J$, the notation $(l_{I},l_{J},\ldots) = (2l_{I}+1)(2l_{J}+1)\ldots$, and $P_{l_{I}l_{J}}^{m_{I}-m_{J}}(\cos \theta_{IJ})$ is the associated Legendre function with $\theta_{IJ}$ representing the angle between $R_{IJ}$ and the $z$-axis. The $2\ell$-pole transition operator of an atom consisting of $n+1$ charged particles, in the laboratory frame is defined as in Ref. [69],

$$T_{\ell m} = \sum_{i=0}^{n} q_{i}\rho_{i}^{\ell}Y_{\ell m}(\hat{\rho}_{i}),$$

(6)
where \( q_i \) is the charge of the \( i \)-th sub-particle of the atom. In the center of mass frame \[69\], \( \rho_i \) becomes

\[
\rho_i = \sum_{j=1}^{n} \epsilon_{ij} r_j ,
\]

(7)

where \( r_i = \rho_i - \rho_0 \), \( \epsilon_{ij} = \delta_{ij} - m_j/M_T \), \( i = 0, 1, 2, \ldots, n \), \( j = 1, 2, \ldots, n \), and \( M_T \) represents the total mass of the system. Using the formula

\[
Y_{\ell m}(\mathbf{r}) = \sqrt{\frac{3}{4\pi}} \prod_{i=1}^{\ell-1} \left( \frac{2i+3}{i+1} \right) \left( \mathbf{\hat{r}} \otimes \mathbf{\hat{r}} \otimes \cdots \mathbf{\hat{r}} \right)_{\ell m}^{(\ell)},
\]

(8)

where \( \otimes \) denotes the coupling between two irreducible tensor operators, the \( 2^\ell \)-pole transition operator can be simplified as

\[
T_\ell = \sqrt{\frac{3}{4\pi}} \prod_{m=1}^{\ell-1} \left( \frac{2m+3}{m+1} \right) \sum_{j_1, \ldots, j_\ell} \left( \sum_{i=0}^{n} q_i \epsilon_{ij_1} \epsilon_{ij_2} \cdots \epsilon_{ij_\ell} \right) \left( \mathbf{\hat{r}}_{j_1} \otimes \mathbf{\hat{r}}_{j_2} \otimes \cdots \mathbf{\hat{r}}_{j_\ell} \right)_{m}^{(\ell)}.
\]

(9)

For a four-body system, the explicit forms of transition operators \( T_\ell \) with \( \ell \) up to 3 can be found in Ref. \[70\].

**B. The Hylleraas basis set**

The nonrelativistic Hamiltonian of the Li atom in the centre of mass frame \[71\] can be written as

\[
H = -\frac{1}{2\mu} \sum_{i=1}^{3} \nabla_i^2 - \frac{1}{m_0} \sum_{i>j \geq 1} \nabla_i \cdot \nabla_j + q_0 \sum_{i=1}^{3} \frac{q_i}{r_i} + \sum_{i>j \geq 1} \frac{q_i q_j}{r_{ij}},
\]

(10)

where \( \mu = m_e m_0/(m_e + m_0) \) is the reduced mass between an electron \( m_e \) and the nucleus \( m_0 \). The basis set is constructed in Hylleraas coordinates,

\[
\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} Y^{(LM)}_{(\ell_1 \ell_2) \ell_{12} \ell_3} (\mathbf{\hat{r}}_1, \mathbf{\hat{r}}_2, \mathbf{\hat{r}}_3) \mathcal{X}(1, 2, 3),
\]

(11)

where

\[
Y^{(LM)}_{(\ell_1 \ell_2) \ell_{12} \ell_3} (\mathbf{\hat{r}}_1, \mathbf{\hat{r}}_2, \mathbf{\hat{r}}_3) = \sum_{m_{123}} \langle \ell_1 m_1; \ell_2 m_2; \ell_{12} m_{12}; \ell_3 m_3 | \ell_{12} m_{12}; \ell_3 m_3 | \ell_{12} \ell_3; L M_L \rangle
\]

\[
\times Y_{\ell_1 m_1} (\mathbf{\hat{r}}_1) Y_{\ell_2 m_2} (\mathbf{\hat{r}}_2) Y_{\ell_3 m_3} (\mathbf{\hat{r}}_3)
\]

(12)

is a vector-coupled product of spherical harmonics to form an eigenstate of the total angular momentum \( L \) and component \( M_L \), and \( \mathcal{X}(1, 2, 3) \) is the three-electron spin-1/2 function. The variational wave function of the Li atom is a linear combination of basis functions \( \phi \) antisymmetrized. With some truncations to avoid the numerical linear dependence, all terms in Eq. \[11\] are included such that

\[
j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega,
\]

(13)
where $\Omega$ is an integer, and the convergence for the energy eigenvalue is studied by increasing $\Omega$ progressively. The reduced matrix elements for various transition operators can be evaluated with the following basic integral

$$
\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}
\times Y^{*}_{\ell_1 m_1}(\mathbf{r}_1) Y^{*}_{\ell_2 m_2}(\mathbf{r}_2) Y^{*}_{\ell_3 m_3}(\mathbf{r}_3) Y_{\ell_1 m_1}(\mathbf{r}_1) Y_{\ell_2 m_2}(\mathbf{r}_2) Y_{\ell_3 m_3}(\mathbf{r}_3).
$$

The details of computational method for this integral are developed in Refs. [71, 72]. Similarly, for the Li$^+$ ion, we also use the Hylleraas variational method to obtain the energies, wavefunctions and transition matrix elements. The detailed Hylleraas method for a two-electron atom is given in Ref. [73].

C. The zeroth-order wave function

For the degenerate Li($n_0$S)-Li($n_0$L)-Li$^+$(n$'_0$S) system with energy $E^{(0)}_{n_0 n_0 n'_0} = E^{(0)}_{n_0 S} + E^{(0)}_{n_0 L} + E^{(0)}_{n'_0 S}$, the zeroth-order wave function can be written as

$$
|\Psi^{(0)}\rangle = a |n_0 L; n_0 0; n'_0 0\rangle + b |n_0 0; n_0 L; n'_0 0\rangle,
$$

where $a$ and $b$ are the expansion coefficients of the zeroth-order wave function in the basis set $\{|n_0 L; n_0 0; n'_0 0\rangle, |n_0 0; n_0 L; n'_0 0\rangle\}$ with $|n_0 0\rangle, |n_0 L\rangle$, and $|n'_0 0\rangle$, respectively, being the initial states for Li($n_0$S), Li($n_0$L) and Li$^+$(n$'_0$S). The corresponding zeroth-order wave functions (or the values of $a$ and $b$) depend on the geometrical configuration formed by the three particles and are determined by diagonalizing the perturbation in this basis set. Then using the degenerate perturbation theory, we can obtain the long-range part of the interaction potential for the Li(2$^2$S)-Li(2$^2$P)-Li$^+(1^1S)$ system, which can be written as

$$
\Delta E = \Delta E_{add}^{(1)} + \Delta E_{add}^{(2)} + \Delta E_{non}^{(2)},
$$

where $\Delta E_{add}^{(1)}$ and $\Delta E_{add}^{(2)}$ are, respectively, the first-order and second-order additive interactions and $\Delta E_{non}^{(2)}$ is the second-order nonadditive interaction.

D. The first-order additive interactions

The first-order additive interaction $\Delta E_{add}^{(1)}$ is given by

$$
\Delta E_{add}^{(1)} = -\frac{C_3^{(12)}(1, M)}{R_{12}^3} - \frac{C_3^{(23)}(1, M)}{R_{23}^3} - \frac{C_3^{(31)}(1, M)}{R_{31}^3},
$$

where $C_3^{(12)}(1, M)$ describes the dipole-dipole interaction between two neutral atoms. $C_3^{(23)}(1, M)$ and $C_3^{(31)}(1, M)$, respectively, describe the electrostatic interaction between the charge of the ion labeled as 3 and the quadrupole moments of atom 2 and atom 1; the quadrupole moment comes from the excited Li(2$^2$P) atom, which can be atom 1 or atom.
due to the degeneracy of the three-body system. These leading long-range interaction coefficients are given by

\[ C_{3}^{(12)}(1, M) = (a^*b + b^*a) \frac{4\pi(-1)^{1+M}}{9(1-M)!(1+M)!} |\langle n_00||T_1||n_01 \rangle|^2, \]  
(18)

\[ C_{3}^{(23)}(1, M) = |b|^2 Q(-1)^{1+M} \sqrt{\frac{\pi}{5}} \left( \begin{array}{ccc} 1 & 2 & 1 \\ -M & 0 & M \end{array} \right) \langle n_01||T_2||n_01 \rangle, \]  
(19)

\[ C_{3}^{(31)}(1, M) = |a|^2 Q(-1)^{1+M} \sqrt{\frac{\pi}{5}} \left( \begin{array}{ccc} 1 & 2 & 1 \\ -M & 0 & M \end{array} \right) \langle n_01||T_2||n_01 \rangle, \]  
(20)

where \( Q \) is the charge of the ion, \( M \) represents the magnetic quantum number of the excited \( \text{Li}(2^2P) \) atom, and \( T_\ell \) is the \( 2^\ell \)-pole transition operator, which is defined in Sec. II A.

### E. The second-order additive interactions

The second-order additive interaction \( \Delta E_{\text{add}}^{(2)} \) is given by

\[ \Delta E_{\text{add}}^{(2)} = - \frac{C_{4}^{(23)}(1, M)}{R_{23}^4} - \frac{C_{4}^{(31)}(1, M)}{R_{31}^4} - \frac{C_{6}^{(12)}(1, M)}{R_{12}^6} - \frac{C_{6}^{(23)}(1, M)}{R_{23}^6} - \frac{C_{6}^{(31)}(1, M)}{R_{31}^6} - \ldots, \]  
(21)

where \( C_{4}^{(23)}(1, M) \) and \( C_{4}^{(31)}(1, M) \), respectively, describe the induction interactions between the ion 3 and the neutral atoms 2 and 1. The dispersion interaction coefficient between the neutral atoms 1 and 2 is given by \( C_{6}^{(12)}(1, M) \), while \( C_{6}^{(23)}(1, M) \) and \( C_{6}^{(31)}(1, M) \), respectively, describe the interactions between the ion 3 and the two neutral atoms 2 and 1, including both the induction and the dispersion interaction coefficients. The corresponding expressions for the additive coefficients are

\[ C_{4}^{(23)}(1, M) = |a|^2 T_1 + |b|^2 T_3(M), \]  
(22)

\[ C_{4}^{(31)}(1, M) = |a|^2 T_3(M) + |b|^2 T_1, \]  
(23)

\[ C_{6}^{(12)}(1, M) = |a|^2 T_4(M) + |b|^2 T_4(M), \]  
(24)

\[ C_{6}^{(23)}(1, M) = |a|^2 T_2 + |b|^2 T_5(M), \]  
(25)

\[ C_{6}^{(31)}(1, M) = |a|^2 T_5(M) + |b|^2 T_2, \]  
(26)

where

\[ T_1 = \frac{4\pi Q^2}{9} \sum_{n_2} |\langle n_00||T_1||n_11 \rangle|^2 \frac{E_{n_{11}} - E_{n_{00}}^{(0)}}{E_{n_{11}} - E_{n_{00}}^{(0)}}, \]  
(27)
\[ T_2 = \frac{4\pi Q^2}{25} \sum_{n_t} \frac{\langle n_0|T_2|n_t2\rangle^2 + 32\pi^2}{E_{n_t2} - E_{n_0}^{(0)}} + \frac{1}{27} \sum_{n_m} \frac{\langle n_0|T_1|n_t1\rangle^2}{E_{n_t1} - E_{n_m}^{(0)}} = (E_{n_m} - E_{n_0}^{(0)}) \],

\[ T_3(M) = \frac{Q^2}{4\pi} \sum_{n_{tLt}} G_1(L_t, 0; 1, 1; 1, M) \langle n_0|T_1|n_tL_t\rangle^2 \frac{1}{E_{n_{tL_t}} - E_{n_0}^{(0)}} + (E_{n_{t1}} - E_{n_0}^{(0)}) \],

\[ T_4(M) = \sum_{n_{tLt}} G_1(L_t, 1; 1, 1; 1, M) \langle n_0|T_1|n_tL_t\rangle^2 \frac{1}{E_{n_{tL_t}} - E_{n_0}^{(0)}} + (E_{n_{t1}} - E_{n_0}^{(0)}) \]

\[ T_5(M) = \sum_{n_{tLt}} G_1(L_t, 0; 2, 2; 1, M) \langle n_0|T_2|n_tL_t\rangle^2 \frac{1}{E_{n_{tL_t}} - E_{n_0}^{(0)}} + (E_{n_{t1}} - E_{n_0}^{(0)}) \]

\[ + \frac{Q^2}{4\pi} \sum_{n_{tLt}} \left\{ G_1(L_t, 0; 1, 3; 1, M) \langle n_0|T_3|n_tL_t\rangle^2 \frac{1}{E_{n_{tL_t}} - E_{n_0}^{(0)}} + (E_{n_{t1}} - E_{n_0}^{(0)}) \right\} \],

where \( G_1 \)-function is defined by

\[ G_1(L_i, L_j, \ell_k, \ell_k', M; L, M) = \frac{16\pi^2(\ell_k, \ell_k')^{-1/2}}{(2L_j + 1)^2} \sum_{M_i, M_j, m_k} \left( \begin{array}{ccc} L & \ell_k & L_i \\ -M & m_k & M_i \end{array} \right) \left( \begin{array}{ccc} L & \ell_k' & L_i \\ -M & m_k & M_i \end{array} \right) \]

\[ \times \frac{(L_j + \ell_k - M_j + m_k)!(L_j + \ell_k' - M_j + m_k)!P_{L_j+\ell_k}^{M_j-m_k}(0)P_{L_j+\ell_k'}^{M_j-m_k}(0)}{(L_j + M_j)!(L_j - M_j)!((\ell_k + m_k)!((\ell_k' + m_k)!(\ell_k' - m_k)!)^{1/2}}. \]

The detailed derivations are given in the Supplemental Material [74]. We note that these formulas can also be used to calculate long-range interaction coefficients for other two-body or three-body systems such as the two-body Li(2\(^2\)S)-Li(2\(^2\)P) system, the two-body Li(2\(^2\)S)-Li\(^+\)(1\(^1\)S) system, the two-body Li(2\(^2\)P)-Li\(^+\)(1\(^1\)S) system, and the three-body Li(2\(^2\)S)-Li(2\(^2\)S)-Li\(^+\)(1\(^1\)S) system. We will provide specific examples below in Secs. [II G][II H]

**F. The second-order nonadditive potentials**

Due to the degeneracy of the three-body system, the nonadditive potential \( \Delta E^{(2)}_{\text{non}} \) starts at the second-order, and is given by

\[ \Delta E^{(2)}_{\text{non}} = - \frac{C_{3,3}^{(12,23)}(1, M)}{R_{12}^3 R_{23}^3} - \frac{C_{3,3}^{(23,31)}(1, M)}{R_{23}^3 R_{31}^3} - \frac{C_{3,3}^{(31,12)}(1, M)}{R_{31}^3 R_{12}^3} - \frac{C_{4,2}^{(12,23)}(1, M)}{R_{12}^4 R_{23}^4} - \frac{C_{2,4}^{(31,12)}(1, M)}{R_{31}^4 R_{12}^4} - \ldots, \]
where \( C_{3,3}^{(23,31)}(1, M) \) represents the dispersion nonadditive interaction coefficient. The remaining terms are the nonadditive induction interactions. The detailed expressions are given by

\[
C_{3,3}^{(23,31)}(1, M) = \sum_{M} (-1)^{M_u} G_4(1, M; 1, M) \left\{ (a^*b) \exp \left[ i(M_u - M) \gamma \right] + (b^*a) \exp \left[ -i(M_u - M) \gamma \right] \right\} \\
\times \sum_{n_u} \left[ \frac{|\langle n_0 1 || T_1 || n_0 1 \rangle |^2 \langle n_0 0 || T_1 || n_u 1 \rangle |^2}{(E_{n_u 1} - E_{n_u 0}) + (E_{n_0 0} - E_{n_0 1})} + \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 0 || T_1 || n_u 1 \rangle |^2}{(E_{n_u 1} - E_{n_u 0}) + (E_{n_0 0} - E_{n_0 1})} \right], \tag{34}
\]

\[
C_{4,2}^{(12,23)}(1, M) = |a|^2 \sum_{M_t} (-1)^{M_t} G_5(1, M; 2; 1, M; Q) \cos(M_t \beta) \\
\times \sum_{n_t} \frac{|\langle n_0 1 || T_2 || n_0 1 \rangle |^2 \langle n_0 0 || T_1 || n_t 1 \rangle |^2}{E_{n_t 1} - E_{n_0 0}} \sum_{n_t} \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 0 || T_2 || n_t 1 \rangle |^2}{E_{n_t 2} - E_{n_0 1}} \\
- \sum_{M_t} G_7(1, M; 2; 1, M; Q) \left\{ (a^*b) \exp \left[ i(M_t) \beta \right] + (b^*a) \exp \left[ -i(M_t) \beta \right] \right\} \\
\times \sum_{n_t} \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 0 || T_2 || n_t 1 \rangle |^2}{E_{n_t 1} - E_{n_0 0}}, \tag{35}
\]

\[
C_{2,4}^{(31,12)}(1, M) = |b|^2 \sum_{M_s} (-1)^{M_s} G_5(1, M; 2; 1, M; Q) \cos(M_s \alpha) \\
\times \sum_{n_s} \frac{|\langle n_0 1 || T_2 || n_0 1 \rangle |^2 \langle n_0 0 || T_1 || n_s 1 \rangle |^2}{E_{n_s 1} - E_{n_0 0}} \sum_{n_s} \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 0 || T_2 || n_s 1 \rangle |^2}{E_{n_s 2} - E_{n_0 1}} \\
- \sum_{M_s} G_7(1, M; 2; 1, M; Q) \left\{ (a^*b) \exp \left[ i(M_s) \alpha \right] + (b^*a) \exp \left[ -i(M_s) \alpha \right] \right\} \\
\times \sum_{n_s} \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 1 || T_2 || n_s 1 \rangle |^2}{E_{n_s 1} - E_{n_0 0}} \sum_{n_s} \frac{|\langle n_0 0 || T_1 || n_0 1 \rangle |^2 \langle n_0 1 || T_2 || n_s 1 \rangle |^2}{E_{n_s 0} - E_{n_0 0}}, \tag{36}
\]

\[
C_{3,3}^{(12,23)}(1, M) = \sum_{M_1 m_2} G_6(1, M; 2; m_2; 1, M; Q) \left\{ (a^*b) \exp \left[ -i(m_2') \beta \right] + (b^*a) \exp \left[ i(m_2) \beta \right] \right\} 
\]



\[ \times \sum_{n_2} \frac{\langle n_0 || T_1 || n_0 \rangle \langle n_0 || T_1 || n_1 \rangle^* \langle n_0 || T_2 || n_1 \rangle}{E_{n_1} - E_{n_0}} \]

\[- \sum_{M_t} G_7(2, M_t; 1, 1; M; Q) \left\{ (a^* b) \exp[i(M_t)\beta] + (b^* a) \exp[-i(M_t)\beta] \right\} \]

\[ \times \sum_{n_2} \frac{\langle n_0 || T_1 || n_0 \rangle^* \langle n_0 || T_1 || n_2 \rangle^* \langle n_0 || T_2 || n_2 \rangle}{E_{n_2} - E_{n_0}}, \quad (37) \]

and

\[ C_{3,3}^{(31, 12)}(1, M) = \sum_{M_s m'_1} G_6(1, M_s; 2, m'_1; 1, M; Q) \left\{ (a^* b) \exp[i(m'_1)\alpha] + (b^* a) \exp[-i(m'_1)\alpha] \right\} \]

\[ \times \sum_{n_s} \frac{\langle n_0 || T_1 || n_0 \rangle \langle n_0 || T_1 || n_s \rangle^* \langle n_0 || T_2 || n_s \rangle}{E_{n_1} - E_{n_0}} \]

\[- \sum_{M_s} G_7(2, M_s; 1, 1; M; Q) \left\{ a^* b \exp[i(M_s)\alpha] + b^* a \exp[-i(M_s)\alpha] \right\} \]

\[ \times \sum_{n_s} \frac{\langle n_0 || T_1 || n_0 \rangle^* \langle n_0 || T_1 || n_s \rangle^* \langle n_0 || T_2 || n_s \rangle}{E_{n_2} - E_{n_0}}, \quad (38) \]

where the functions \( G_4, G_5, G_6, \) and \( G_7 \) are defined by

\[ G_4(L_i, M_i; L, M) = 16\pi^2 \frac{[P_{L_i + L}^M(0)(L_i + L - M_i + M)! (L_i, L)^{-1}]}{(L_i + M_i)!(L_i - M_i)!(L + M)!(L - M)!}, \quad (39) \]

\[ G_5(L_i, M_i; \ell_k, L, M; Q) = \frac{8\sqrt{\pi^3} Q P_{\ell_k + L_i}^{M_i}(0) P_{L_i}^M(0) (\ell_k + L_i - M_i)!}{(2L_i + 1)^2 \sqrt{2\ell_k + 1} (L_i + M_i)!} \begin{pmatrix} L & \ell_k & L \\ -M & 0 & M \end{pmatrix}, \quad (40) \]

\[ G_6(L_i, M_i; \ell_k, m_k, L, M; Q) = \frac{8\sqrt{\pi^3} Q (\ell_k)^{-1/2}}{(2L_i + 1)(2\ell_k + 1)} \begin{pmatrix} L & \ell_k & L \\ -M & -m_k & M_i \end{pmatrix} \times \frac{P_{\ell_k + L_i}^{M_i}(0) P_{\ell_k}^{m_k}(0) (L_i + L_i - M_i + M)! (\ell_k - m_k)!}{(L + M)!(L - M)!(L_i + M_i)!(L_i - M_i)!(\ell_k + m_k)!(\ell_k - m_k)!}^{1/2}, \]

\[ G_7(L_i, M_i; \ell_k, L, M; Q) = \frac{8\sqrt{\pi^3} Q (\ell_k)^{-1/2}}{(2L_i + 1)(2\ell_k + 1)} \sum_{m_k} \begin{pmatrix} L & \ell_k & L_i \\ -M & m_k & M_i \end{pmatrix} \times \frac{P_{\ell_k + L_i}^{M_i}(0) P_{\ell_k}^{m_k}(0) (L + \ell_k - M + m_k)!(L_i - M_i)!}{(L + M)!(L - M)!(L_i + M_i)!(L_i - M_i)!(\ell_k + m_k)!(\ell_k - m_k)!}^{1/2}, \]

\[(41) \]

\[(42) \]

The detailed derivations are given in the Supplemental Material [74]. From Eqs. (18)–(38), we see that all of these coefficients depend on the atomic states of the three-body system because they include \( a \) and \( b \). In other words, these additive and nonadditive coefficients show a dependence on the configurations of the three-body system. This is clearly a kind of quantum three-body collective effect. In the following subsection, we show that these three-body nonadditive interactions significantly influence the total interaction potentials.
Because of the enhancement through the induction effect, the nonadditive interactions are large enough to be comparable to (or even stronger than) the additive interactions at the same order.

In the present paper, we only consider long-range interaction for the Li($2^2S$)-Li($2^2P$)-Li$^+(1^1S)$ system up to $O(R^{-6})$, since the next terms are $C_7/R^7$, which come from the third-order perturbation theory.

G. Specific results extracted from the general expressions

With the zeroth-order wave functions as shown in Eq. (15), the present work can be easily related to the calculations of long-range interactions for other two-body or three-body systems. For example, if we set $a = 1$, $b = 0$ and remove the terms involving the Li$^+(1^1S)$ ion, the formulae can be used to describe the long-range interactions for the two-body Li($2^2S$)-Li($2^2S$) system; if we set $a = \frac{1}{\sqrt{2}}$, $b = \pm \frac{1}{\sqrt{2}}$ and remove the terms involving the Li$^+(1^1S)$ ion, the formulae can be used to describe the long-range interactions for the two-body Li($2^2S$)-Li($2^2P$) system; if we set $a = 1$, $b = 0$ and remove the terms involving the Li($2^2P$) atom, the formulae can be used to describe the long-range interactions for the two-body Li($2^2S$)-Li$^+(1^1S)$ system; if we set $a = 1$, $b = 0$ and remove the terms involving the Li($2^2S$) atom, the formulae can be used to describe the long-range interactions for the two-body Li($2^2P$)-Li$^+(1^1S)$ system; and if we set $a = 1$, $b = 0$ and $L = 0$, the formulae can be used to describe the long-range interactions for the three-body Li($2^2S$)-Li($2^2S$)-Li$^+(1^1S)$ system. For these long-range additive interaction coefficients, we have arranged the following formulae to show these connections:

\[
C_3^{(12)}(1, M) = C_{3,\text{dip}}^{(P-S)},
\]

\[
C_3^{(23)}(1, M) = |b|^2C_{3,\text{elst}}^{(P-S^+)} ,
\]

\[
C_3^{(31)}(1, M) = |a|^2C_{3,\text{elst}}^{(P-S^+)} ,
\]

\[
C_4^{(23)}(1, M) = |a|^2C_{4,\text{ind}}^{(S-S^+)} + |b|^2C_{4,\text{ind}}^{(P-S^+)}(M),
\]

\[
C_4^{(31)}(1, M) = |a|^2C_{4,\text{ind}}^{(P-S^+)}(M) + |b|^2C_{4,\text{ind}}^{(S-S^+)} ,
\]

\[
C_6^{(12)}(1, M) = C_{6,\text{disp}}^{(P-S)} (M),
\]

\[
C_6^{(23)}(1, M) = |a|^2\left\{ C_{6,\text{ind}}^{(S-S^+)} + C_{6,\text{disp}}^{(S-S^+)} \right\} + |b|^2\left\{ C_{6,\text{ind}}^{(P-S^+)}(M) + C_{6,\text{disp}}^{(P-S^+)}(M) \right\} ,
\]

and

\[
C_6^{(31)}(1, M) = |a|^2\left\{ C_{6,\text{ind}}^{(P-S^+)}(M) + C_{6,\text{disp}}^{(P-S^+)}(M) \right\} + |b|^2\left\{ C_{6,\text{ind}}^{(S-S^+)} + C_{6,\text{disp}}^{(S-S^+)} \right\} ,
\]
where $C^{(P-S)}_{3,dip}$ and $C^{(P-S)}_{6,disp}$, respectively, represent the dipolar and dispersion interaction coefficients for the two-body Li($2^2S$)-Li($2^2P$) system, which have been given in the Ref. \[10\] (also see Eqs. (51) and (52) in the Supplemental Material \[74\]). $C^{(S-S^+)}_{2n,ind}$ and $C^{(S-S^+)}_{2n,disp}$ represent the long-range induction and dispersion coefficients for the Li($2^2S$)-Li($1^1S$) system, which have been given in the Ref. \[12\] (also see Eqs. (48)–(50) in the Supplemental Material \[74\]). For the two-body Li($2^2P$)-Li($1^1S$) system, we provide more detail below in Sec. 111, as no previous numerical results for the coefficients were found in the literature. In short, $C_{3,elst}^{(P-S^+)}$ represents the electrostatic interaction between the charge of the ion and the quadrupole moment of the neutral atom; $C_{2n,ind}^{(P-S^+)}$ and $C_{2n,disp}^{(P-S^+)}$ represent the long-range induction and dispersion coefficients for the Li($2^2P$)-Li($1^1S$) system, where the formulae of these coefficients are given by Eqs. (123)–(126) in subsection II I. Clearly, with these formulae, we can easily relate the long-range additive interactions of the three-body Li($2^2S$)-Li($2^2P$)-Li($1^1S$) system to those of other two-body or three-body systems. On the other hand, the nonadditive interactions of the three-body Li($2^2S$)-Li($2^2P$)-Li($1^1S$) system are induced by the degeneracy and cannot be decomposed in terms of diatomic subsystems. This is in contrast to the nondegenerate Li($2^2S$)-Li($2^2P$)-Li($1^1S$) system \[12\], where the nonadditive interactions start from the third-order energy correction and may still be used to predict contributions to the long-range potentials between the Li($2^2S$) atom and the excited state dimer Li$_2^+$($2^2Σ^+_{g,u}$, $1^2Σ^2_{g,u}$) or between the Li($2^2P$) atom and the ground state dimer Li$_2$($1^2Σ^2_{g,u}$). We note that $C_{4,2,2}^{(12,23)}(1, M)$ [see Eq. (35)] and $C_{2,4,2}^{(31,12)}(1, M)$ [see Eq. (36)] may be very important in the study of the interactions between the cation Li$^+(1^1S)$ and the excited dimer Li$_2^+$($2^2Σ^+_{g,u}$, $1^2Σ^2_{g,u}$).

**H. Orientation-dependence considerations**

In this subsection, we describe the orientation-dependence of the long-range interactions due to the anisotropic charge distribution of the excited Li atom. To illustrate the orientation-dependence, we use the two-body Li($2^2S$)-Li($2^2P$) system as an example. The rotation of the two-body system is illustrated in Fig. 2 where the two-body system is rotated from $z$-axis to $x$-axis (or one of the two atoms is rotated from “p1” to “p3”). In this process, we find that the zeroth-order wave functions of the two-body system $Ψ_{S-P,0}^{(0)}(M)$ and the corresponding long-range interaction coefficients change. Thus we can easily get the following inequality relation

$$C_{n,p_1}^{(S-P)}(M) \neq C_{n,p_2}^{(S-P)}(M) \neq C_{n,p_3}^{(S-P)}(M). \quad (51)$$

In our previous work, we have given the numerical values of the long-range interaction coefficients for the two atoms lying on the $z$-axis (see Table IX in Ref. \[70\]), which would correspond to “p3” in Fig. 2. In the present work, we use the coordinates of Fig. 1 represented as “p1” in Fig. 2 which corresponds to the two atoms lying on the $x$-axis. The comparison of these long-range interaction coefficients is given in Table 1, where the present values were obtained using highly accurate variational wave functions for the Li atom in Hylleraas coordinates with finite nuclear mass effects \[70\]. For these two specific situations (“p1” and “p3”), we also find the following relations

$$C_{n,p_3}^{(S-P)}(M = 0) = C_{n,p_1}^{(S-P)}(M = ±1), \quad (52)$$
FIG. 2. Simple illustration of the rotation of the two-body system from z-axis to x-axis.

TABLE I. The long-range interaction coefficients (in atomic units) of the $\infty\text{Li}(2^2S)\rightarrow\infty\text{Li}(2^2P)$ system for the two atoms lying on the z-axis and the x-axis, respectively, (“p1”) and (“p3”) as shown in Fig. 2. The numbers in parentheses represent the computational uncertainties.

|     | $C_{3,z}^{(S-P)}(M = 0)$ | $C_{3,z}^{(S-P)}(M = \pm 1)$ | $C_{6,z}^{(S-P)}(M = 0)$ | $C_{6,z}^{(S-P)}(M = \pm 1)$ |
|-----|--------------------------|-------------------------------|--------------------------|--------------------------|
| “p1” |                          |                               |                          |                          |
| $\psi_{S-P,z}^{(0)}(\beta=1)$ | 11.000221(2)               | -5.500111(1)                | 2075.40(3)               | 1406.68(3)               |
| $\psi_{S-P,z}^{(0)}(\beta=-1)$ | -11.000221(2)              | 5.500111(1)                 | 2075.40(3)               | 1406.68(3)               |
| “p3” |                          |                               |                          |                          |
| $\psi_{S-P,x}^{(0)}(\beta=1)$ | -5.500111(1)               | 2.750054(1)                 | 1406.68(3)               | 1741.06(5)               |
| $\psi_{S-P,x}^{(0)}(\beta=-1)$ | 5.500111(1)                | -2.750054(1)                | 1406.68(3)               | 1741.06(5)               |

which are obeyed by our numerical values of these coefficients shown in Table I.

In general, the long-range interaction coefficients are given by

$$C_{n,p_i}^{(S-P)}(M) = C_{n,p_i}^{(S-P)}(M, \cos \theta_i),$$

where $p_i$ is the position $i$ of the atom as shown in Fig. 2 and $\theta_i$ is the corresponding polar angle. For the leading coefficients $C_3$, the formulas are simplified as

$$C_{3,p_i}^{(S-P)}(M) = C_{3,p_i}^{(S-P)}(M)P_2(\cos \theta_i),$$

where $P_2(\cos \theta_i)$ is the Legendre polynomial. For the other coefficients $C_n$ with ($n > 3$), the parts containing the polar angle $\theta_i$ would be coupled with the virtual states, which cannot be separated. But we can still utilize the present formulas (calculated at the “p1” orientation) to give the general formulas by changing the Legendre polynomial from $P_{l_l}^{m_l}(0)$ to $P_{l_l}^{m_l}(\cos \theta_i)$. For example, we can use the formula of Eq. (52) in the Supplemental Material [74] to
get the general leading dispersion coefficient $C^{(S-P)}_{6,p_1}(M)$ at orientation $p_1$. Similarly, for other excited Li dimer and trimers, the long-range interactions also contain such orientation dependencies. In the next subsection, we will apply these ideas to derive the long-range potentials for the Li($2^2P$–Li$^+(1^1S)$ system in the “p3” orientation. In Sec. III we will consider the three-body system in detail.

I. The long-range potentials for the Li($2^2P$–Li$^+(1^1S)$ system

In this subsection, we use our results to calculate the long-range potentials of the four states of Li$^+_+$, $1^2\Pi_u$, $1^2\Pi_g$, $2^2\Sigma^+_g$, and $2^2\Sigma^+_u$, correlating to Li($2^2P$–Li$^+(1^1S)$ system. We begin by writing down the long-range potential as calculated in our coordinates, see Fig. 1, with $V^{(P-S^+)}(R; M)$ corresponding to the two-body Li($2^2P$–Li$^+(1^1S)$ system in the orientation “p3” of Fig. 2 which can be written as

$$V^{(P-S^+)}(R; M) = -\frac{C_3(M)}{R^3} - \frac{C_4(M)}{R^4} - \frac{C_6(M)}{R^6} - \cdots,$$

(55)

where $C_3(M)$ represents the electrostatic interaction between the charge of the Li$^+(1^1S)$ ion and the quadrupole moment of the excited Li($2^2P$) atom, $C_4(M)$ represents the leading long-range induction coefficient, which is related to the dipole polarizability of the Li($2^2P$) atom, and the $C_6(M)$ is the sum of long-range induction coefficients $C_{6,\text{ind}}$ and dispersion coefficients $C_{6,\text{disp}}$. The formulae of these coefficients are given by

$$C_3(M) = C_{3,\text{elst}}^{(P-S^+)}(M) = Q(-1)^{1+M} \sqrt{\frac{\pi}{5}} \left( \begin{array}{ccc} 1 & 2 & 1 \\ -M & 0 & M \end{array} \right) \langle n_01\|T_2\|n_01 \rangle,$$

(56)

$$C_4(M) = C_{4,\text{ind}}^{(P-S^+)}(M) = \frac{Q^2}{4\pi} \sum_{n_tL_t} \frac{G_1(L_t, 0; 1, 1; 1, M)\langle n_01\|T_1\|n_tL_t \rangle^2}{E_{n_tL_t} - E_{n_01}^{(0)}},$$

(57)

$$C_6(M) = C_{6,\text{disp}}^{(P-S^+)}(M) + C_{6,\text{ind}}^{(P-S^+)}(M),$$

(58)

where

$$C_{6,\text{disp}}^{(P-S^+)}(M) = \sum_{n_tn_uL_t} \frac{G_1(L_t, 1; 1, 1; 1, M)\langle n_01\|T_1\|n_tL_t \rangle^2 \langle n_01\|T_1\|n_u1 \rangle^2}{(E_{n_tL_t} - E_{n_01}^{(0)}) + (E_{n_u1} - E_{n_01}^{(0)})},$$

(59)

and

$$C_{6,\text{ind}}^{(P-S^+)}(M) = \frac{Q^2}{4\pi} \sum_{n_tn_uL_t} \left\{ \frac{G_1(L_t, 0; 2, 2; 1, M)\langle n_01\|T_2\|n_tL_t \rangle^2}{E_{n_tL_t} - E_{n_01}^{(0)}} \\ + \frac{G_1(L_t, 0; 1, 3; 1, M)\langle n_01\|T_1\|n_tL_t \rangle^*\langle n_01\|T_3\|n_tL_t \rangle}{E_{n_tL_t} - E_{n_01}^{(0)}} \\ + \frac{G_1(L_t, 0; 3, 1; 1, M)\langle n_01\|T_3\|n_tL_t \rangle^*\langle n_01\|T_1\|n_tL_t \rangle}{E_{n_tL_t} - E_{n_01}^{(0)}} \right\},$$

(60)

and the $G_1$ function is defined in Eq. (32).
TABLE II. The long-range interaction coefficients (in atomic units) of the Li(2\(^2\)P)–Li\(^{+}(1\(^2\)S)\) system for the two particles lying on z-axis and x-axis, respectively, “p1” and “p3” as shown in Fig. 2.

Position “p1” corresponds to standard molecular Σ, Π nomenclature where the z-axis joins the atom and the ion. The numbers in parentheses represent the computational uncertainties.

|     | \(C_{3,0}^{(P-S^+)}(M=0)\) | \(C_{4,0}^{(P-S^+)}(M=\pm1)\) | \(C_{4,1}^{(P-S^+)}(M=0)\) | \(C_{4,1}^{(P-S^+)}(M=\pm1)\) | \(C_{6,0}^{(P-S^+)}(M=0)\) | \(C_{6,0}^{(P-S^+)}(M=\pm1)\) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(^\infty\)Li | 10.8199392(2) | 5.409696(1) | 61.8515(2) | 64.2838(2) | 9811.485(6) | -1820.6261(3) |
| \(^7\)Li | 10.8192592(2) | 5.4096296(1) | 61.8385(2) | 64.2911(2) | 9811.274(6) | -1820.7205(2) |
| \(^6\)Li | 10.8191462(2) | 5.4095731(1) | 61.8364(2) | 64.2925(2) | 9811.239(6) | -1820.7362(3) |
|     | \(C_{3,0}^{(P-S^+)}(M=0)\) | \(C_{3,0}^{(P-S^+)}(M=\pm1)\) | \(C_{4,0}^{(P-S^+)}(M=0)\) | \(C_{4,0}^{(P-S^+)}(M=\pm1)\) | \(C_{6,0}^{(P-S^+)}(M=0)\) | \(C_{6,0}^{(P-S^+)}(M=\pm1)\) |
| \(^\infty\)Li | -5.4099696(1) | 2.7049847(1) | 64.2838(2) | 63.0676(3) | -1820.6261(3) | 3995.429(3) |
| \(^7\)Li | -5.4096296(1) | 2.7048148(1) | 64.2911(2) | 63.0648(2) | -1820.7205(2) | 3995.276(3) |
| \(^6\)Li | -5.4095731(1) | 2.7047866(1) | 64.2925(2) | 63.0643(3) | -1820.7362(3) | 3995.251(3) |

The molecular states for \(^2\)Li\(^+\) correlating to Li(2\(^2\)P)–Li\(^+\)(1\(^2\)S) system are the \(^2\)^\(\Sigma^+_g\), \(^2\)^\(\Sigma^+_u\), \(^1\)^\(\Pi_g\) and \(^1\)^\(\Pi_u\) states (we do not consider fine structure). We calculated the long-range interaction coefficients using Eqs. (123)–(126), which include electrostatic, induction, and dispersion energies up to \(O(R^{-6})\); the corresponding numerical values are given in Table II and plotted in Fig. 3. These correspond to position “p3” of the Li(2\(^2\)P) atom as indicated in Fig. 2. Convergence studies of these long-range interaction coefficients \(C_{3,x}^{(P-S^+)}(M)\), \(C_{4,x}^{(P-S^+)}(M)\), and \(C_{6,x}^{(P-S^+)}(M)\) are given in, respectively, Tables III, IV and V. In these tables, \(N_P\) denotes the size of the basis for the \(P\) state of the \(^\infty\)Li atom, and \(N_L\) denotes...
TABLE III. Convergence of the long-range interaction coefficients $C_{3,x}^{(P-S^+)}(M)$ for the $\infty$Li(2$^2$P)-$\infty$Li$^+(1^2S)$ system, where two particles lie on the x-axis (“p3”) as shown in Fig. 2. $N_P$ denotes the size of the basis for the $P$ state of the $\infty$Li(2$^2$P) atom.

| $N_P$ | $C_{3,x}^{(P-S^+)}(M = 0)$ | $C_{3,x}^{(P-S^+)}(M = \pm1)$ |
|-------|---------------------------|-------------------------------|
| 1174  | -5.409965844              | 2.704982922                   |
| 2091  | -5.409968720              | 2.704984360                   |
| 3543  | -5.409969427              | 2.704984713                   |
| 5761  | -5.409969563              | 2.704984781                   |
| Extrapolated | -5.4099696(1) | 2.7049847(1) |

TABLE IV. Convergence of the long-range interaction coefficients $C_{4,x}^{(P-S^+)}(M)$ for the $\infty$Li(2$^2$P)-$\infty$Li$^+(1^2S)$ system, where two particles lie on x-axis (“p3”) as shown in Fig. 2. $N_P$ denotes the size of basis for the $P$ state of the $\infty$Li atom. $N_S$, $N_{(pp)}P$, and $N_D$, respectively, denote the sizes of the bases for the corresponding intermediate states of symmetries $S$, $P$, and $D$, and $(pp)P$ stands for the main configuration of two $p$ electrons coupled to form a total angular momentum of $P$ (since the contribution from the $(pp)P$ configuration is well converged at $N_{(pp)}P = 3413$, we did not increase $N_{(pp)}P$ any further [70]).

| $(N_P, N_S, N_{(pp)}P, N_D)$ | $C_{4,x}^{(P-S^+)}(M = 0)$ | $C_{4,x}^{(P-S^+)}(M = \pm1)$ |
|-----------------------------|---------------------------|-------------------------------|
| (1174,1589,1106,1174)      | 64.282596                 | 63.061604                     |
| (2091,2625,2002,2091)      | 64.283174                 | 63.066184                     |
| (3543,4172,3413,3543)      | 64.283498                 | 63.067033                     |
| (5761,6412,3413,5761)      | 64.283634                 | 63.067338                     |
| Extrapolated               | 64.2838(2)                | 63.0676(3)                    |

TABLE V. Convergence of the long-range interaction coefficients $C_{6,x}^{(P-S^+)}(M)$ for the $\infty$Li(2$^2$P)-$\infty$Li$^+(1^2S)$ system, where two particles lie on the x-axis (“p3”) as shown in Fig. 2. $N_P$ denotes the sizes of basis for the $P$ state of the $\infty$Li atom. $N_S$, $N_{(pp)}P$, and $N_D$, respectively, denote the sizes of the bases for the corresponding intermediate states of symmetries $S$, $P$, and $D$, and $(pp)P$ stands for the main configuration of two $p$ electrons coupled to form a total angular momentum of $P$ (since the contribution from the $(pp)P$ configuration is well converged at $N_{(pp)}P = 3413$, we did not increase $N_{(pp)}P$ any further [70]). $N_S^+$ and $N_P^+$, respectively, denote the sizes of the bases for the ground state and the intermediate states of symmetry $P$ of $\infty$Li$^+$.

| $(N_S^+, N_P^+; N_P, N_S, N_{(pp)}P, N_D)$ | $C_{6,x}^{(P-S^+)}(M = 0)$ | $C_{6,x}^{(P-S^+)}(M = \pm1)$ |
|---------------------------------------------|---------------------------|-------------------------------|
| (504,728,1174,1589,1106,1174)              | -1820.631774              | 3995.37910                   |
| (744,1120,2091,2625,2002,2091)             | -1820.627179              | 3995.40911                   |
| (1050,1632,3543,4172,3413,3543)            | -1820.626701              | 3995.42357                   |
| (1430,2280,5761,6412,3413,5761)            | -1820.626499              | 3995.42669                   |
| Extrapolated                              | -1820.6261(3)             | 3995.429(3)                  |
connect the polarizability components \( \alpha_{zz} \) and \( \alpha_{xx} \). In the present configuration (as shown in Fig. 1), these components can be related to the electric field lying in \( z \) or \( x \) direction, expressed in terms of the principal polarizabilities \( \alpha_1 \) (scalar) and \( \alpha_1^T \) (tensor).

In order to apply the results to the \( \Sigma \) and \( \Pi \) molecular states of standard molecular nomenclature, where the \( z \)-axis joins the atom and ion, we must first apply the considerations of the previous Sec. II H to express our results in terms of position “p1” of Fig. 2. The analysis yields the coefficients, with the numerical values given in Table II. The corresponding general coefficients are defined by

\[
C_3^{(P-S^+)}(M) = C_3^{(P-S^+)}(M) P_2(\cos \theta_i),
\]

\[
C_4^{(P-S^+)}(M = 0) = \frac{1}{2} \alpha_{zz}^{p_1} = \frac{1}{2} [\alpha_1 - 2 \alpha_1^T P_2(\cos \theta_i)],
\]

and

\[
C_4^{(P-S^+)}(M = \pm 1) = \frac{1}{2} \alpha_{xx}^{p_1} = \frac{1}{2} [\alpha_1 + \alpha_1^T P_2(\cos \theta_i)],
\]

where \( \alpha_{zz}^{p_1}, \alpha_{xx}^{p_1} \) are, respectively, the polarizability components, along the \( z \) and \( x \) directions of an applied electric field [75, 76]. \( \alpha_1 \) and \( \alpha_1^T \) are the principal scalar and tensor polarizabilities of Li(2\(^2\)P) atom [70], and \( P_2(\cos \theta_i) \) is the Legendre polynomial. The comparison of the polarizability components \( (\alpha_{zz}^{p_1}, \alpha_{xx}^{p_1}) \) and \( (\alpha_{zz}^{p_3}, \alpha_{xx}^{p_3}) \) is given in Table VI.

In the present configuration (as shown in Fig. 2), these components can be related to the leading induction coefficients \( C_{4,xx}(M) \) (as shown in Table II) by \( \alpha_{zz}^{p_3} = 2C_{4,xx}(M = 0) \) and \( \alpha_{xx}^{p_3} = 2C_{4,xx}(M = \pm 1) \). According to the symmetry of the degenerate system [75, 76], we can connect the polarizability components \( (\alpha_{zz}^{p_3}, \alpha_{xx}^{p_3}) \) with the principal polarizabilities, scalar

| Reference                  | \( \alpha_{zz}^{p_1} = 2C_4^{(P-S^+)}(M = 0) \) | \( \alpha_{xx}^{p_1} = 2C_4^{(P-S^+)}(M = \pm 1) \) |
|----------------------------|-----------------------------------------------|-----------------------------------------------|
| Pipin & Bishop [79] (1993) | 123.634                                       | 128.449                                       |
| Rérat et al. [77] (1997)   | 131                                          | 129                                           |
| Cohen & Themelis [80] (2005)| 122.94                                       | 128.13                                        |
| Johnson et al. [81] (2008) | 123.81                                       | 128.580                                       |
| This work                  | 123.703(4)                                   | 128.5676(4)                                   |

\[
\alpha_{zz}^{p_3} = 2C_4^{(P-S^+)}(M = 0) \quad \alpha_{xx}^{p_3} = 2C_4^{(P-S^+)}(M = \pm 1)
\]

the size of the basis for the corresponding intermediate states of symmetry \( L \). Similarly, \( N_\Sigma \) and \( N_\Pi \) denote respectively the sizes of the bases for the ground state and the intermediate states of symmetry \( P \) of the \( \infty \text{Li}^+ \) ion.
(α₁) and tensor (∇₁), of the Li(2P) atom by α₁ = \(\frac{1}{3}(α_{zz}^2 + 2α_{zz})\) and α₁ = \(\frac{2}{3}(α_{zz}^2 - α_{zz})\). For example, using the present data from Table VI, we find α₁ = 126.9460 and α₁ = 1.6216 in agreement with Ref. [70, Table VIII]. Further details concerning the polarizability components (α₁, α₂) for the two particles lying on the z-axis are given in, for example, Refs. [75–78]. For the coefficient C_6, we can use the formula of Eq. (58) by changing the Legendre polynomial from \(P_{l}^m(0)\) to \(P_{l}^m(\cos θ_i)\) to get the general \(C_{6,p_i}^{(P−S^+)}(M)\) at orientation \(p_i\).

The long-range potential energy functions expressed relative to “p1” follow from Table II. For example, for the 2Σ⁺ states of the \(\infty\)Li₂, we have

\[
V^{(P−S^+)}(R; Σ) = -\frac{10.8199392}{R^3} - \frac{61.8515}{R^4} - \frac{9811.485}{R^6} - \cdots, \tag{64}
\]

and for the 1Π states, we have

\[
V^{(P−S^+)}(R; Π) = \frac{5.4099696}{R^3} - \frac{64.2838}{R^4} + \frac{1820.6261}{R^6} - \cdots. \tag{65}
\]

Similar expressions may be written for \(^6\)Li⁺ and \(^7\)Li⁺ using Table II. To the best of our knowledge, the expressions in Eqs. (64) and (65) are unavailable in the literature.

Magnier et al. [51] calculated the long-range potentials with the inclusion of exchange, electrostatic, induction, and dispersion interactions up to \(O(R^{-8})\); the results were presented graphically. While a direct comparison of long-range coefficients is not possible, we can calculate the exchange energies using the expressions given by Magnier et al. and add that to our long-range potentials to compare with their total potentials for each of the four molecular states. When the exchange energy and the long-range potential energy have opposite signs, a long-range well or barrier results; these singular features provide good quantitative checks between Magnier et al. and the present work. From Magnier et al. [51], Figs. (8)–(10), it is evident that the exchange energies are positive for the 2Σ⁺ and 1Π states and negative for the 2Σ⁺ and 1Π states, while the exchange splitting for the pair of 2Σ⁺ states is larger by a factor of \(R/2\) compared to the pair of 1Π states, where \(R\) is the internuclear distance. Calculations show that the two Σ states and the 1Π state form potential wells, while the 1Π state is purely repulsive [55]. It is evident from the data in Eq. (65) that the net positive long-range potential and positive exchange energy completely account for the repulsive 1Π state. Of the three states with potential wells, the 2Σ⁺ state well exists at the greatest internuclear distance, about 25 \(a_0\), with a depth of only 127 cm⁻¹ according to a recent model potential calculation [55]. With our long-range expansion of Table II evaluated for \(\infty\)Li as in Eq. (64) and using Eq. (8) of Ref. [51], to estimate the contribution of the exchange energy we find a well of depth 119 cm⁻¹ at \(R = 25.8\) \(a_0\) to be compared to the depth 124 cm⁻¹ at 25.7 \(a_0\) obtained by Magnier et al. using a long-range expansion and the exchange energy. We also obtain for the the 1Π state using Eq. (65) a potential barrier of 36 cm⁻¹ at \(R = 23.9\) \(a_0\), compared to 40 cm⁻¹ at 23.4 \(a_0\) found by Magnier et al. The agreement of the well and the barrier positions and energies calculated using Eqs. (64) and (65), with the similar calculations of Magnier et al. is satisfactory. The 2Σ⁺ state is an example of a long-range molecular state [83]. Moreover, we do not attempt

\[\text{By close comparison of Eqs. (2.13) and (3.7) of Ref. [82], we believe that the factor “2” in the denominator of } D \text{ given in Eq. (8) of Ref. [51] should be replaced by “m!” We evaluated the exchange energy splittings with this evident correction included.} \]
to reproduce the wells of the $2^2\Sigma_u^+$ or $1^2\Pi_u$ states, because it is evident from Ref. [54] Figs. 8–9 that these potential wells are fully realized with the inclusion of charge overlap (i.e. in quantum-chemical calculations [54 55]).

Having thus demonstrated that two-body long-range interaction potentials can be extracted from our results, and providing some coefficients that were previously unavailable in the literature [viz. Table II and Eqs. (64) and (65)], we turn back to the three-body system.

III. RESULTS AND DISCUSSIONS

As in Secs. II H–II I, we use highly accurate variational wave functions for lithium atoms and ions in Hylleraas coordinates with finite nuclear mass effects to evaluate the numerical values [70]. We note that in general the zeroth-order wave functions are obtained by using degenerate perturbation theory through Eq. (10) in the Supplemental Material [74] and there are intrinsic geometrical dependencies that complicate the analysis. In particular, the zeroth-order wave functions change with the geometry (interior angles and interatomic separations) of the three-body system. However, when $R_{23} = R_{31} = R$, we have the matrix elements $\Delta_{12} = \Delta_{21}$, see Eq. (10) in the Supplemental Material [74], and the geometrical dependencies don’t appear in the zeroth-order wave functions, simplifying the analysis of the three-body system. Therefore, in this section, we consider the Li($2^2S$)-Li($2^2P$)-Li$^+(1^1S)$ system for the configurations where $R_{23} = R_{31} = R$.

In Sec. III A we introduce the zeroth-order wave functions and in Sec. III B provide the numerical values of these additive coefficients. In Sec. III C, we focus on the two specific arrangements of the three particles, collinear and in an equilateral triangle, providing the nonadditive coefficients.

A. Additive coefficients: Wave functions

With respect to the “p1” orientation as shown in Fig. 2, we calculate the long-range additive potentials for the three-body system lying collinearly on the $z$-axis. According to degenerate perturbation theory, the corresponding zeroth-order wave functions are

$$
\Psi_{1,z}^{(0)} = \frac{1}{\sqrt{2}} \left[ |n_0 1_z; n_0 0; n'_0 0 \rangle + |n_0 0; n_0 1_z; n'_0 0 \rangle \right],
$$

$$
\Psi_{2,z}^{(0)} = \frac{1}{\sqrt{2}} \left[ |n_0 1_z; n_0 0; n'_0 0 \rangle - |n_0 0; n_0 1_z; n'_0 0 \rangle \right],
$$

where the symbol $z$ indicates the three-particles lying on the $z$-axis for the configurations of $R_{23} = R_{31} = R$.

For three particles lying in the $x$-$y$ plane as shown in Fig. 1, the corresponding zeroth-order wave functions are

$$
\Psi_{1,\perp}^{(0)} = \frac{1}{\sqrt{2}} \left[ |n_0 1; n_0 0; n'_0 0 \rangle + |n_0 0; n_0 1; n'_0 0 \rangle \right],
$$

$$
\Psi_{2,\perp}^{(0)} = \frac{1}{\sqrt{2}} \left[ |n_0 1; n_0 0; n'_0 0 \rangle - |n_0 0; n_0 1; n'_0 0 \rangle \right],
$$
TABLE VII. The long-range additive interaction coefficients (in atomic units) of the Li(2^2S)-Li(2^2P)-Li^+(2^1S) system for two different types of the zeroth-order wave functions, where the three particles lie collinearly on the z-axis (similar to the “p1” orientation of the two-body system shown in Fig. [2]). The numbers in parentheses represent the computational uncertainties.

| Coefficients | \( \Psi_{1,z}^{(0)} \) | \( \Psi_{2,z}^{(0)} \) | \( \Psi_{1,z}^{(0)} \) | \( \Psi_{2,z}^{(0)} \) | \( \Psi_{1,z}^{(0)} \) | \( \Psi_{2,z}^{(0)} \) |
|--------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( C_{2,z}^{(12)} (1, M = 0) \) | 11.000221(2) | -11.000221(2) | 11.001853(2) | -11.001853(2) | 11.002125(2) | -11.002125(2) |
| \( C_{2,z}^{(23)} (1, M = 0) \) | 5.409969(6) | 5.409969(6) | 5.409629(6) | 5.409629(6) | 5.409573(1) | 5.409573(1) |
| \( C_{2,z}^{(31)} (1, M = 0) \) | 5.409969(6) | 5.409969(6) | 5.409629(6) | 5.409629(6) | 5.409573(1) | 5.409573(1) |
| \( C_{2,z}^{(23)} (1, M = 0) \) | 71.9539(4) | 71.9539(4) | 71.9594(4) | 71.9594(4) | 71.9604(4) | 71.9604(4) |
| \( C_{2,z}^{(31)} (1, M = 0) \) | 71.9539(4) | 71.9539(4) | 71.9594(4) | 71.9594(4) | 71.9604(4) | 71.9604(4) |
| \( C_{2,z}^{(41)} (1, M = 0) \) | 2075.40(3) | 2075.40(3) | 2076.08(7) | 2076.08(7) | 2076.19(7) | 2076.19(7) |
| \( C_{2,z}^{(63)} (1, M = 0) \) | 5263.218(3) | 5263.218(3) | 5263.151(3) | 5263.151(3) | 5263.140(3) | 5263.140(3) |
| \( C_{2,z}^{(61)} (1, M = 0) \) | 5263.218(3) | 5263.218(3) | 5263.151(3) | 5263.151(3) | 5263.140(3) | 5263.140(3) |

where the symbol \( \perp \) indicates specificity to the the x-y planar configuration with \( R_{23} = R_{31} = R \). Note that Eqs. (68) and (69) include the special case of the three particles lying collinearly on the x-axis, i.e. the orientation “p3”.

B. Additive coefficients: Evaluation

Using the degenerate perturbation theory, we find that different from the ground state Li\(_3^+\) trimer (where there is no analogous quantum three-body effect for these long-range additive coefficients [12]), the atomic states \((a, b)\) and the corresponding additive coefficients are changing with different geometries of the three-body system for the excited Li\(_3^+\) trimer. This phenomenon is absolutely a kind of quantum three-body effect, which is caused by the degeneracy of the excited Li\(_3^+\) trimer. While for the specific geometries with \( R_{23} = R_{31} = R \), we find that the atomic states and the corresponding additive interaction coefficients would remain unchanged due to the symmetry of the three-body system. This feature makes these coefficients be useful in the quantum chemistry studies. In the present paper, we give the calculations of the long-range coefficients for these specific configurations. The additive coefficients \( C_n^{(IJ)} \) [to be in Eqs. (17) and (21)] are calculated for the specific three-body Li(2\(^2\)S)-Li(2\(^2\)P)-Li\(^+\)(1\(^1\)S) system lying on the z-axis or in the x-y plane. The numerical values are shown in Tables VII and VIII where we can also find the orientation dependence (that are demonstrated in Sec. I H for two-body system) of the long-range interaction coefficients for the excited Li\(_3^+\) trimer.
TABLE VIII. The long-range additive interaction coefficients (in atomic units) of the Li(2\textsuperscript{2}S)-Li(2\textsuperscript{2}P)-Li\textsuperscript{+}(2\textsuperscript{1}S) system for two different types of the zeroth-order wave functions, where the three particles lie in the x-y plane with $R_{23} = R_{31} = R$ as shown in Fig. [7]. Note this includes the special case of the three particles collinear on the x-axis. The numbers in parentheses represent the computational uncertainties.

| Coefficients | $\Psi^{(0)}_{1,\perp}$ | $\Psi^{(0)}_{2,\perp}$ | $\Psi^{(0)}_{1,\perp}$ | $\Psi^{(0)}_{2,\perp}$ | $\Psi^{(0)}_{1,\perp}$ | $\Psi^{(0)}_{2,\perp}$ |
|--------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $C_{2}^{(12)}(1, M = 0)$ | $-5.500111(1)$ | $5.500111(1)$ | $-5.500926(1)$ | $5.500926(1)$ | $-5.501062(1)$ | $5.501062(1)$ |
| $C_{2}^{(23)}(1, M = 0)$ | $-2.7049847(1)$ | $-2.7049847(1)$ | $-2.7048148(1)$ | $-2.7048148(1)$ | $-2.7047866(1)$ | $-2.7047866(1)$ |
| $C_{4}^{(31)}(1, M = 0)$ | $73.1701(4)$ | $73.1701(4)$ | $73.1859(4)$ | $73.1859(4)$ | $73.1885(4)$ | $73.1885(4)$ |
| $C_{4}^{(31)}(1, M = 0)$ | $1406.68(3)$ | $1406.68(3)$ | $1407.15(5)$ | $1407.15(5)$ | $1407.20(2)$ | $1407.20(2)$ |
| $C_{4}^{(23)}(1, M = 0)$ | $-552.8371(7)$ | $-552.8371(7)$ | $-552.8460(5)$ | $-552.8460(5)$ | $-552.8472(7)$ | $-552.8472(7)$ |
| $C_{6}^{(31)}(1, M = 0)$ | $-552.8371(7)$ | $-552.8371(7)$ | $-552.8460(5)$ | $-552.8460(5)$ | $-552.8472(7)$ | $-552.8472(7)$ |

For the numerical values of these additive coefficients, we note that the leading long-range interaction coefficient between two neutral atoms $C_{3}^{(12)}(1, M)$ can be positive (attractive) or negative (repulsive) corresponding to the different atomic states related to the symmetry of the system. The leading terms $C_{3}^{(23)}(1, M = \pm 1)$, $C_{3}^{(31)}(1, M = \pm 1)$ (see Table VII) and $C_{3}^{(23)}(1, M = 0)$, $C_{3}^{(31)}(1, M = 0)$ (see Table VIII) are always negative, which represents the repulsive interactions between the charge of the Li\textsuperscript{+}(1\textsuperscript{1}S) ion and the permanent electric quadrupole moments of the Li(2\textsuperscript{2}P) atom generated by its anisotropic charge distribution along the z-axis for $M = \pm 1$ and $M = 0$ states, respectively. The leading terms $C_{3}^{(23)}(1, M = 0)$, $C_{3}^{(31)}(1, M = 0)$ (see Table VII) and $C_{3}^{(23)}(1, M = \pm 1)$, $C_{3}^{(31)}(1, M = \pm 1)$ (see Table VIII) are always positive (attractive), which is caused by induction effect of the Li\textsuperscript{+}(1\textsuperscript{1}S) atom. Similarly, the inductive terms $C_{4}^{(23)}(1, M)$, $C_{4}^{(31)}(1, M)$ (see Table VII) and $C_{4}^{(23)}(1, M)$, $C_{4}^{(31)}(1, M)$ (see Table VIII) are also always positive (attractive). Their numerical values are the linear combinations of the inductive interactions of the Li(2\textsuperscript{2}S)-Li\textsuperscript{+}(1\textsuperscript{1}S) system and the Li(2\textsuperscript{2}P)-Li\textsuperscript{+}(1\textsuperscript{1}S) system [Eqs. (46) and (47)]. The $C_{6}^{(23)}(1, M)$, $C_{6}^{(31)}(1, M)$ (see Table VII) and $C_{6}^{(23)}(1, M)$, $C_{6}^{(31)}(1, M)$ (see Table VIII) are also the linear combinations of inductive and dispersion interactions of the Li(2\textsuperscript{2}S)-Li\textsuperscript{+}(1\textsuperscript{1}S) system and the Li(2\textsuperscript{2}P)-Li\textsuperscript{+}(1\textsuperscript{1}S) system [Eqs. (49) and (50)].
TABLE IX. The long-range nonadditive interaction coefficients (in atomic units) of the Li($^2^2\text{S}$)-Li($^2^2\text{P}$)-Li$^+$($^2^1\text{S}$) system for two different types of the zeroth-order wave functions, where the three particles form an equally-spaced collinear configuration with the ion in the middle lying on the $x$-axis. The numbers in parentheses represent the computational uncertainties.

| Coefficients | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ |
|--------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $C_{12,23}^{(1, 0)}$ | $-936.951(1)$ | $-610.836(1)$ | $-937.136(3)$ | $-1603.176(3)$ | $-937.167(3)$ | $-1603.231(2)$ |
| $C_{23,31}^{(1, 0)}$ | $-936.951(1)$ | $-610.836(3)$ | $-937.136(3)$ | $-1603.176(3)$ | $-937.167(3)$ | $-1603.231(2)$ |
| $C_{31,12}^{(1, 0)}$ | $611.46703(6)$ | $-611.46703(6)$ | $611.6324(1)$ | $-611.6324(1)$ | $611.6600(1)$ | $-611.6600(1)$ |
| $C_{4,2}^{(1, \pm 1)}$ | $2.6490119(5)$ | $-2.6490119(5)$ | $2.649468(1)$ | $-2.649468(1)$ | $2.6497127(6)$ | $-2.6497127(6)$ |
| $C_{5,3}^{(1, \pm 1)}$ | $611.46703(6)$ | $-611.46703(6)$ | $611.6324(1)$ | $-611.6324(1)$ | $611.6600(1)$ | $-611.6600(1)$ |

TABLE X. The long-range nonadditive interaction coefficients (in atomic units) of the Li($^2^2\text{S}$)-Li($^2^2\text{P}$)-Li$^+$($^2^1\text{S}$) system for two different types of the zeroth-order wave functions, where the three particles form an equilateral triangle. The numbers in parentheses represent the computational uncertainties.

| Coefficients | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ | $\Psi_{1,\perp}^{(0)}$ | $\Psi_{2,\perp}^{(0)}$ |
|--------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $C_{12,23}^{(1, 0)}$ | $-936.951(3)$ | $1602.836(3)$ | $-937.136(3)$ | $1603.176(3)$ | $-937.167(3)$ | $1603.231(2)$ |
| $C_{23,31}^{(1, 0)}$ | $-936.951(3)$ | $1602.836(3)$ | $-937.136(3)$ | $1603.176(3)$ | $-937.167(3)$ | $1603.231(2)$ |
| $C_{31,12}^{(1, 0)}$ | $2.6490119(5)$ | $-2.6490119(5)$ | $2.649468(1)$ | $-2.649468(1)$ | $2.6497127(6)$ | $-2.6497127(6)$ |
| $C_{4,2}^{(1, \pm 1)}$ | $611.46703(6)$ | $-611.46703(6)$ | $611.6324(1)$ | $-611.6324(1)$ | $611.6600(1)$ | $-611.6600(1)$ |

C. Nonadditive coefficients: Collinear and equilateral triangle

The nonadditive interaction coefficients of Eq. [33] show a dependence on the interior angles of the three-body system. It is not practical to calculate the nonadditive coefficients for arbitrary cases when $R_{23} = R_{31} = R$. However, for the collinear and the equilateral triangle configuration, which fortunately are probably the most interesting configurations, we can evaluate specific values. In this subsection, these coefficients are given for two geometries: an equally-spaced collinear configuration with the ion in the center ($R_{23} =$
Long-range additive interaction potentials (in atomic units) of the $\infty$Li$(2^2S)$-$\infty$Li$(2^2P)$-$\infty$Li$^+(1^1S)$ system for two types of the zeroth-order wave functions, where three particles lie collinearly on the $z$-axis. For each curve labeled by a wave function, the plotted curve is the sum of $\Delta E^{(1)}$ and $\Delta E^{(2)}$.

$R_{31} = R_1$, see Table IX, and an equilateral triangle configuration ($R_{23} = R_{31} = R_{12} = R$), see Table X. Different from the ground state Li$^+_3$ trimer demonstrated in Ref. [12], the long-range nonadditive interactions of the current excited Li$^+_3$ trimer appear in the second-order correction, not in the third-order correction. This phenomenon is caused by the degeneracy of the three-body system introduced by the presence of the excited Li$(2^2P)$ atom. From Tables IX and X, we can find that most of the nonadditive coefficients are indeed different from each other for these two geometries, even with the same atomic states as shown in Eqs. (68) and (69). This kind of three-body effect is caused by the different interior angles of the two geometries associated with the magnetic quantum number $M$ of the Li$(2^2P)$ atom, which can also be easily figured out from Eqs. (34)–(38). And for the different interior angles of the geometries and for the different magnetic quantum number $M$, these nonadditive terms can be attractive or repulsive.

Due to the induction effect of the Li$^+(1^1S)$ cation, some of these nonadditive coefficients are enhanced. For example, from Table IX, we find that the inductive nonadditive coefficients $|C_{4,2}^{(12,23)}(1, M = 0)| = |C_{2,4}^{(31,12)}(1, M = 0)| = 1873.904(5) \text{ a.u.}$ are much larger than the dispersion nonadditive one $|C_{3,3}^{(23,31)}(1, M = 0)| = 1.0592047(2) \text{ a.u.}$ from Table IX and are even larger than some of the additive dispersion $|C_6^{(12)}(1, M = 0)| = 1406.68(3)$.
FIG. 5. Long-range interaction potentials (in atomic units) of the $^{\infty}\text{Li}(2^2S)^{\infty}\text{Li}(2^2P)^{\infty}\text{Li}^+(1^1S)$ system for two types of the zeroth-order wave functions, where three particles lie collinearly on the $x$-axis. The plotted potentials include all electrostatic, dispersion, and induction type interactions (additive and nonadditive) up to $O(R^{-6})$. For each curve labeled by a wave function, the plotted curve is the sum of $\Delta E^{(1)}$ and $\Delta E^{(2)}$.

a.u. from Table VIII, and additive inductive ones $|C_6^{(23)}(1, M = 0)| = 552.8371(7)$ a.u. from Table VIII at the same order. The competition between the additive attractive and nonadditive repulsive terms of $C_6$ for particular geometries will also be discussed in the following section. These large nonadditive inductive interactions would be indispensable in constructing potential surfaces and be very useful in studies of quantum three-body effect for the excited Li$_3^+$ trimers.

D. Long-range potentials: Results

Evaluating the additive and nonadditive long-range potentials using the coefficients given in Tables VII–X, the potential functions are displayed for two geometries: An equally-spaced collinear configuration with $R_{23} = R_{31} = R$, see Figs. 4 and 5, and an equilateral triangle with sides of length $R$, see Fig. 6. We should indicate that the nonadditive interactions of the present paper are all evaluated for the geometries lying on the $x$-$y$ plane as shown in Fig. 1. Thus for the three particles lying on the $z$-axis, only the additive potentials are shown in Fig. 4 with respect to the two-body $p_1$ situation (see Fig. 2). For the collinear configuration lying on the $x$-$y$ plane, the total additive and nonadditive potentials are displayed in Fig. 5.
FIG. 6. Long-range interaction potentials (in atomic units) of the $^{\infty}\text{Li}(2^2S)^{-\infty}\text{Li}(2^2P)^{-\infty}\text{Li}^+(1^1S)$ system for two types of the zeroth-order wave functions, where three particles form an equilateral triangle on the $x$-$y$ plane. The plotted potentials include all electrostatic, dispersion, and induction type interactions (additive and nonadditive) up to $O(R^{-6})$. For each curve labeled by a wave function, the plotted curve is the sum of $\Delta E^{(1)}$ and $\Delta E^{(2)}$.

The separations between the $M = 0$ and $M = \pm 1$ states are mainly caused by the leading repulsive or attractive electrostatic interaction involving $C_3$ between the ion and the excited atom. In Fig. 6, we display the total long-range potentials (additive and nonadditive) for the geometry of equilateral triangle lying on the $x$-$y$ plane, where a barrier of about $115 \text{ cm}^{-1}$ at internuclear distance of $17 a_0$ is found for the $\Psi_{1,\perp}^{(0)}(1, M = 0)$ state. The barrier results from the interplay of the repulsive leading terms involving $C_3$ and the attractive induction interaction involving $C_4$. For the other states, the long-range potentials are attractive at all internuclear distances. Note that the data presented in this subsection does not include exchange energies, which may contribute at these internuclear distances. We will discuss their contributions in the following subsection.

E. The strong nonadditive potentials and “switch-off” of the additive potentials

As we discussed before, the nonadditive collective effect of the three-body system is caused by its degeneracy, which is introduced by the presence of the excited $\text{Li}(2^2P)$ atom. Meanwhile, the presence of the $\text{Li}^+(1^1S)$ ion introduces the induction effect, which strongly enhances the nonadditive (collective) interaction, as demonstrated in Section III C. In this subsection, we present a graphical comparison of the additive and nonadditive potentials for the equilateral triangle and collinear ($R_{23} = R_{31} = R$) configurations, see Fig. 7.
FIG. 7. Comparison of long-range additive potentials [left side, (A) and (C)] and nonadditive (collective) potentials [right side, (B) and (D)] (in atomic units) of the $^\infty\text{Li}(2^2S)$-$^\infty\text{Li}(2^2P)$-$^\infty\text{Li}^+(1^1S)$ system for two types of the zeroth-order wave functions with $R_{23} = R_{31} = R$: equilateral triangle (A) and (B), equally-spaced collinear configurations (C) and (D). At the labeled points, the two-body additive potentials sum to zero leaving only the net nonadditive collective potentials.

The figure illustrates that the nonadditive potentials are significant and can even be stronger than the net contribution from the additive potentials. For example, for the equilateral triangle configuration, the magnitude of the additive contribution [Fig. 7(A)] becomes less than the nonadditive contribution [Fig. 7(C)] around $R \sim 14 \, a_0$. Indeed, we find that there are specific internuclear distances at which the additive contributions sum to zero leaving only nonadditive contributions. Denoting these special distances by $\bar{R}$, for the equilateral triangle configuration, the additive cancellation occurs at $\bar{R} = 13.58 \, a_0$ for the $\Psi_{1,\Delta}(1, M = 0)$ state with a net energy of 48.42 cm$^{-1}$. For the collinear configuration the additive cancellation occurs at $\bar{R} = 23.68 \, a_0$ for the $\Psi_{1,\Delta}(1, M = 0)$ state with a net energy of 0.25 cm$^{-1}$ and at $\bar{R} = 30.69 \, a_0$ for the $\Psi_{2,\Delta}(1, M = 0)$ state with a net energy of $-0.09 \, \text{cm}^{-1}$.

We now, as promised in the Introduction, Sec. I C, draw a comparison with trapped cold polar molecules. When the additive (two-body) contributions sum to zero at a distance $\bar{R}$, Eq. (16) reduces to

$$\Delta E(\bar{R}) = \Delta E_{\text{non}}^{(2)}(\bar{R}).$$

Comparing Eq. (33) for $\Delta E_{\text{non}}^{(2)}$ with Eq. (2) for the three-body lattice interaction, we observe that they are precisely the same form. Since our results are specific to three-particles, the collinear case is most similar to the case of trapped polar molecules in a linear configuration, such as shown in Fig. 1(A) of Ref. [64]. Our intriguing result deserves further study. In
retrospect, we can understand the appearance of a cancellation analogous to that found for trapped polar molecules: The anisotropy of the present system due to the Li\((2\,^2P)\) atom in the presence of the Li\(^{+}(1\,^1S)\) ion charge is physically similar to the dipole-dipole interaction in the presence of an external electric field in the optical lattice case. To gauge precisely the physical potential energies at the special distances \(\bar{R}\), treatment of the exchange energy contributions, or equivalently quantum-chemical calculations, would be desirable. However, by analogy with the Li\(^{+}(1\,^1S)\)–Li\((2\,^2P)\) results that we presented in Sec. III, we observe that the values of \(\bar{R}\) are probably sufficiently large so that it is likely that only exchange energies will contribute. Nevertheless, the present result suggests an intriguing similarity between the Li\((2\,^2S)\)-Li\((2\,^2P)\)-Li\(^{+}(1\,^1S)\) system and the trapped cold polar molecule scenario.

IV. CONCLUSION

The long-range additive and nonadditive interaction potentials for the Li\((2\,^2S)\)-Li\((2\,^2P)\)-Li\(^{+}(1\,^1S)\) system were calculated by using degenerate perturbation theory. We found that all the first-order and second-order additive and nonadditive interaction coefficients show a dependence on the geometrical configurations of the system. The nonadditive interactions depend on both the atomic states and the interior angles of the configurations. The degeneracy of the system caused by the presence of the Li\((2\,^2P)\) atom leads to the three-body collective effect. The presence of the Li\(^{+}(1\,^1S)\) ion was found to enhance this collective effect, which makes the three-body nonadditive collective interactions of the system even stronger than the two-body additive interactions for some specific configurations of the three-body system. For the two particular configurations with \(R_{23} = R_{31} = R\), the equilateral triangle configuration and the equally-spaced collinear configuration, the interaction coefficients were evaluated with highly accurate wave functions calculated variationally in Hylleraas coordinates. In addition, for the Li\((2\,^2S)\)-Li\((2\,^2P)\)-Li\(^{+}(1\,^1S)\) system, the two-body additive interaction can be “switched off” leaving only three-body nonadditive interactions for particular geometries, which makes this three-body system a prospective platform to study the quantum collective effect. We demonstrated how two-body interaction potentials can be extracted from our results and gave explicit expressions for the long-range potentials of the Li\(^{+}(1\,^1S)\)–Li\((2\,^2P)\) system. The present high-precision results can serve as benchmarks for future quantum-chemical calculations and may be of interest for constructing precise potential energy surfaces. The general formulae for \(A(n_0\,S)\)–\(A(n_0\,L)\)–\(A^{2\,^+}(n''_0\,S)\) are listed in the Supplemental Material.

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Supplemental Material: Long-range additive and nonadditive potentials in a hybrid system: Ground state atom, excited state atom, and ion

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This Supplemental Material provides additional details on the calculations. We introduce elements of the perturbative approach in Secs. IV A–IV C and give specific expressions for Li$^+$(1S)–Li(2S) system in Sec. IV D, for Li(2S)–Li(2P) system in Sec. IV E, for Li(2P)–Li$^+$(1S) system in Sec. IV F and for Li(2S)–Li(2P)–Li$^+$(1S) system in Sec. IV G. In the present work, we take the electrostatic interaction $V_{123}$ between pairs of particles for the $A(n_0S) - A(n_0' L) - A(Q^+)(n''_0S)$ system as a perturbation

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

where $V_{12}$, $V_{23}$ and $V_{31}$ are the two-body mutual electrostatic interactions between atoms 1 and 2 and ion 3. For three well-separated systems, the mutual interaction energy $V_{IJ}$ can be expanded with the same method as used in Refs. [10–12],

$$V_{IJ} = \sum_{l_{IJ} m_{IJ}} T_{l_{I}-m_{I}}(\sigma) T_{l_{J}m_{J}}(\rho) W_{l_{I}l_{J}}^{m_{I}m_{J}}(IJ),$$

where the multipole transition operators are

$$T_{l_{I}-m_{I}}(\sigma) = \sum_{i} Q_{i}^{l_{I}} Y_{l_{I}-m_{I}}(\hat{\sigma}_{i}),$$

$$T_{l_{J}m_{J}}(\rho) = \sum_{j} q_{j}^{l_{J}} Y_{l_{J}m_{J}}(\hat{\rho}_{j}),$$

where $Q_{i}$ and $q_{j}$, respectively, are the charges of the i-th and j-th sub-particles of the atoms I and J. The geometry factor is

$$W_{l_{I}l_{J}}^{m_{I}m_{J}}(IJ) = \frac{4\pi(-1)^{l_{J}}}{R_{l_{I}l_{J}+l_{J}+1}^{l_{I}l_{J}+l_{J}+1}} [(l_{I} + m_{I})(l_{I} - m_{I})(l_{J} + m_{J})(l_{J} - m_{J})]^{1/2} P_{l_{I}+l_{J}}^{m_{I}+m_{J}}(\cos \theta_{IJ}) \times \exp[i(m_{I} - m_{J}) \Phi_{IJ}],$$

where $R_{l_{I}l_{J}} = R_{J} - R_{I}$ is the relative position vector from particle I to particle J, the notation $(l_{I}, l_{J}, \ldots) = (2l_{I} + 1)(2l_{J} + 1)\ldots$, and $P_{l_{I}+l_{J}}^{m_{I}+m_{J}}(\cos \theta_{IJ})$ is the associated Legendre
function with \( \theta_{I,J} \) representing the angle between \( \mathbf{R}_{IJ} \) and the z-axis. If we now choose the z axis to be normal to the plane of the three particles, i.e., \( \theta_{12} = \theta_{23} = \theta_{31} = \pi/2 \), the associated Legendre functions can be simplified as

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

(76)

\( \Phi_{IJ} \) denotes the angle between \( \mathbf{R}_{IJ} \) and the x-axis. It shows the dependence of the mutual dipole-dipole interaction between two atoms on the orientation of the interacting dipoles relative to the line connecting them [14]. The expressions for \( V_{JJ} \) and \( V_{KI} \) are similar to \( V_{IJ} \). For simplicity, in this work, we transform all \( \Phi_{IJ} \) into interior angles \((\alpha, \beta, \gamma)\) of the triangle formed by the three lithium nuclei with the same method as used in Ref. [10].

**A. The zeroth-order wave function**

According to degenerate perturbation theory, the zeroth-order wave function of the unperturbed system \( A(n_0S) - A(n'_0L)_A Q^+(n''_0S) \) can be written as

\[
|\Psi^{(0)}\rangle = a|\phi_1\rangle + b|\phi_2\rangle,
\]

(77)

where the two orthonormalized degenerate eigenvectors of the unperturbed Hamiltonian with the energy eigenvalue \( E_{n_0n'_0n''_0}^{(0)} = E_{n_0S}^{(0)} + E_{n'_0L}^{(0)} + E_{n''_0S}^{(0)} \) can be written as,

\[
|\phi_1\rangle = |n'_0L; n_00; n''_00\rangle,
\]

(78)

\[
|\phi_2\rangle = |n_00; n'_0L; n''_00\rangle.
\]

(79)

The expansion coefficients \( a, b \) are determined by diagonalizing the perturbation in the basis set \( \{\phi_1, \phi_2\} \), which depend on the geometrical configuration formed by the three particles. In the following, we show that all the long-range interaction coefficients would contain \( a, b \) or one of them. This leads to the dependence of these coefficients on the configurations of the three particles. Thus the zeroth-order energy correction is obtained by the perturbation matrix with respect to \( \{\phi_1, \phi_2\} \)

\[
H' = \begin{pmatrix}
\Delta_{11} & \Delta_{12} \\
\Delta_{12}^* & \Delta_{22}
\end{pmatrix},
\]

(80)

where

\[
\Delta_{11} = \langle \phi_1|V_{123}|\phi_1\rangle = \langle \phi_1|V_{12}|\phi_1\rangle + \langle \phi_1|V_{23}|\phi_1\rangle + \langle \phi_1|V_{31}|\phi_1\rangle
\]

\[
= \sum_{l_1} \frac{Q(-1)^{L-M}}{R_{31}^{l_1+1}}(2l_1 + 1)^{\frac{1}{2}}\sum_{l_1} P_{l_1}(0) \begin{pmatrix} L & l_1 & L \\ -M & 0 & M \end{pmatrix} |n'_0L\|T_{l_1}\|n''_0L\rangle,
\]

(81)

\[
\Delta_{12} = \langle \phi_1|V_{123}|\phi_2\rangle = \langle \phi_1|V_{12}|\phi_2\rangle + \langle \phi_1|V_{23}|\phi_2\rangle + \langle \phi_1|V_{31}|\phi_2\rangle
\]

\[
= \frac{4\pi}{R_{12}^{2L+1}}(-1)^{L-M}(2L)!P_{2L}(0)\sum_{l_2} |n_00\|T_{l_2}\|n'_0L\|T_{l_2}\|n''_0L\|^2,
\]

(82)

\[
\Delta_{22} = \langle \phi_2|V_{123}|\phi_2\rangle = \langle \phi_2|V_{12}|\phi_2\rangle + \langle \phi_2|V_{23}|\phi_2\rangle + \langle \phi_2|V_{31}|\phi_2\rangle
\]

\[
= \sum_{l_2} \frac{Q(-1)^{L-M}}{R_{23}^{l_2+1}}(2l_2 + 1)^{\frac{1}{2}}\sum_{l_2} P_{l_2}(0) \begin{pmatrix} L & l_2 & L \\ -M & 0 & M \end{pmatrix} |n'_0L\|T_{l_2}\|n''_0L\rangle.
\]

(83)

We solve this eigenvalue problem to get the eigenvalues and corresponding eigenfunctions.
B. The first-order energy correction

According to perturbation theory, the first-order energy correction is

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

$$= |a|^2 \sum_{t_1} Q(-1)^{L-M} \frac{4\pi}{R_{t1}^{L+1}} \left( \begin{array}{ccc} L & l_1 & L \\ -M & 0 & M \end{array} \right) \langle n_0 L || T_{11} || n_0' L \rangle$$

$$+ |b|^2 \sum_{t_2} Q(-1)^{L-M} \frac{4\pi}{R_{t2}^{L+1}} \left( \begin{array}{ccc} L & l_2 & L \\ -M & 0 & M \end{array} \right) \langle n_0 L || T_{22} || n_0' L \rangle$$

$$+ (a^*b + b*a) \frac{4\pi}{(2L+1)(2L+2)} \sum_{n_0'} \left( \begin{array}{ccc} 0L && n_0' L \end{array} \right) \langle n_0 L || T_{12} || n_0' L \rangle^2 .$$

(84)

C. The second-order energy correction

The second-order energy correction is given by

$$\Delta E^{(2)} = - \sum_{n_0 n_1 n_2 n_3 n_4} \sum_{M_1 M_2 M_3 M_4} \frac{\langle \Psi^{(0)} | V_{123} | n_s L_s; n_t L_t; n_u L_u \rangle^2}{E_{n_s L_s} - E_{n_0 S} - E_{n_0 S} - E_{n_0' L}}$$

$$= V_{12}^{(2)} + V_{23}^{(2)} + V_{31}^{(2)} + V_{123}^{(2)} + V_{231}^{(2)} + V_{312}^{(2)} ,$$

(85)

where \( |n_s L_s; n_t L_t; n_u L_u \rangle \) is an intermediate state of the system with the energy eigenvalue \( E_{n_s L_s} = E_{n_t L_t} = E_{n_u L_u} \). It is noted that the above summations should exclude terms with \( E_{n_s L_s} = E_{n_t L_t} = E_{n_u L_u} = E_{n_0 S} \). The three additive interaction terms, denoted by \( V_{12}^{(2)} \), \( V_{23}^{(2)} \), \( V_{31}^{(2)} \), become, respectively,

$$V_{12}^{(2)} = - |a|^2 \sum_{n_0 n_1 n_2 n_3 n_4} \sum_{M_1 M_2 M_3 M_4} \frac{16\pi^2}{R_{12}^{2L+l_1+l_2+2}} \left( \begin{array}{ccc} L & l_1 & L_s \\ -M & m_1 & M_s \end{array} \right) \left( \begin{array}{ccc} L & l'_{1} & L_s \\ -M & m_1 & M_s \end{array} \right)$$

$$\times \frac{P_{L_t+l_1}^{m_1+m_1}(0)P_{L_t+l_1'}^{m_1+m_1}(0)(L_t + l_1 - M_t + m_1)!(L_t + l_1' - M_t + m_1)!(L_t, L_t)^{-1}(l_1, l_1')^{-1/2}}{E_{n_s L_s} + E_{n_t L_t} - E_{n_0 S} - E_{n_0' L}}$$

\( \times \langle n_0' L || T_{11} || n_s L_s \rangle \langle n_0' L || T_{11} || n_s L_s \rangle \langle n_0 L || T_{12} || n_t L_t \rangle^2$$
\[ -a^*b\sum_{n_m} \sum_{L_lL_{t1}L_{t2}M_{l}M_{l1}m_{l2}} \frac{16\pi^2(-1)^{L_{l}+l_{t2}-M_{l}-m_{l}}}{R_{L_{t1}L_{t2}L_t+L_{t1}l_{t2}+2}} \begin{pmatrix} L & l_{t1} & L_{s} \\ -M & m_{l1} & M_{s} \end{pmatrix} \begin{pmatrix} L & l_{t2} & L_t \\ -M & m_{l2} & M_{t} \end{pmatrix} \\
\times P_{L_{t1}+l_{t1}}^{M_{l}-m_{l1}}(0)P_{L_{t2}+l_{t2}}^{M_{l}-m_{l2}}(0)\langle L_{t1} + l_{t1} - M_{l} - m_{l1} \rangle (L_{s} + l_{t2} - M_{l} - m_{l2} | (L_{s}, L_{t})^{-1} (l_{t1}, l_{t2})^{-1/2} \]
\[ \times \frac{[\langle L_{s} + M_{s} \rangle (L_{t} + M_{t}) | (L_{t} - M_{t})^{-1} (l_{t1} + m_{l1}) (l_{t2} + m_{l2}) (l_{t1} - m_{l1}) (l_{t2} - m_{l2}) |]^{1/2} \}
\times \frac{\langle n_{0}^* L_{L_{s}} n_{0} L_{L_{s}} \rangle \langle n_{0} L_{L_{s}} n_{0} L_{t} \rangle \langle n_{0} L_{L_{s}} T_{L_{t}} n_{0} L_{t} \rangle}{E_{n_{0} L_{s}} + E_{n_{0} L_{t}} - E_{n_{0} L_{s} n_{0} L_{s}} - E_{n_{0} L_{t} n_{0} L_{t}}} \]
\[ -b^*a\sum_{n_m} \sum_{L_lL_{t1}L_{t2}M_{l}M_{l1}m_{l2}} \frac{16\pi^2(-1)^{L_{l}-l_{t2}-M_{l}-m_{l}}}{R_{L_{l1}L_{l2}l_{t1}}^{L_{l}+l_{t1}+l_{t2}+2}} \begin{pmatrix} L & l_{t1} & L_{s} \\ -M & m_{l1} & M_{s} \end{pmatrix} \begin{pmatrix} L & l_{t2} & L_t \\ -M & m_{l2} & M_{t} \end{pmatrix} \\
\times P_{L_{l1}+l_{t1}}^{M_{l}-m_{l1}}(0)P_{L_{l2}+l_{t2}}^{M_{l}-m_{l2}}(0)\langle L_{l1} + l_{t1} - M_{l} - m_{l1} \rangle (L_{s} + l_{t2} - M_{l} - m_{l2} | (L_{l1}, L_{t})^{-1} (l_{t1}, l_{t2})^{-1/2} \]
\[ \times \frac{[\langle L_{s} + M_{s} \rangle (L_{t} + M_{t}) | (L_{t} - M_{t})^{-1} (l_{t1} + m_{l1}) (l_{t2} + m_{l2}) (l_{t1} - m_{l1}) (l_{t2} - m_{l2}) |]^{1/2} \}
\times \frac{\langle n_{0}^* L_{L_{s}} n_{0} L_{L_{s}} \rangle \langle n_{0}^* L_{L_{s}} T_{L_{t}} n_{0} L_{t} \rangle \langle n_{0}^* L_{L_{s}} T_{L_{t}} n_{0} L_{t} \rangle}{E_{n_{0} L_{s}} + E_{n_{0} L_{t}} - E_{n_{0} L_{s} n_{0} L_{s}} - E_{n_{0} L_{t} n_{0} L_{t}}} \]
\[ = -\left\{ |a|^2 \sum_{n_m} \sum_{L_{l1}L_{l2}l_{t1}} \frac{F_{1}(n_{l1}, n_{t1}, L_{l1}, L_{l2}, l_{t1}, l_{t2}; L, M)}{R_{L_{l1}L_{l2}l_{t1}}^{2L_{l1}+2L_{l2}+l_{t1}+l_{t2}+2}} + |b|^2 \sum_{n_m} \sum_{L_{l1}L_{l2}l_{t1}} \frac{F_{1}(n_{l1}, n_{t1}, L_{l1}, L_{l2}, l_{t1}, l_{t2}; L, M)}{R_{L_{l1}L_{l2}l_{t1}}^{2L_{l1}+2L_{l2}+l_{t1}+l_{t2}+2}} \right\} \]
\[ \left\{ \right\} \]
\[ \]
\[
\left. \frac{P_{L_1}^{M_1} (0) P_{L_2}^{M_2} (0)(L_u + l_1 - M_u + m_1)(L_u + l_1' - M_u + m_1)(L_u, L_u)^{-1}(l_1, l_1')^{-1/2}}{(L_u + M_u)! (l_1 + m_1)! (l_1 - m_1)! (l_1' + m_1)! (l_1' - m_1)!} \\
\times \langle n_0 L||T_{l_1}||n_0 L_s||\rangle \langle n_0 L||T_{l_1'}||n_0 L_s||\rangle \langle n_0' 0||T_{L_u}||n_0 L_u||\rangle \right)^2 \] / \left[ E_{n_a L_a} + E_{n_b L_b} - E_{n_0 S} - E_{n_0' L} \right] \\
- \left\{ a^2 \sum_{n_a n_b L_a L_b l_1 l_1'} F_1 (n_a, n_b, L_a, L_b; l_1, l_1', L, M) \right\} + \left\{ b^2 \sum_{n_a n_b L_a L_b l_1 l_1'} F_2 (n_a, n_b, L_a, L_b) \right\}.
\]

The three nonadditive interaction terms, denoted by \(V_{12,23}^{(2)}, V_{23,31}^{(2)}, V_{31,12}^{(2)}\), become respectively,

\[
V_{12,23}^{(2)} = \left\{ a^2 \sum_{n_a L_a M_a l_1} \sum_{l_2} \frac{8\sqrt{\pi^3} Q (-1)^{L_a - M_a - l_a}}{R_{12}^{L_a + l_a + 1} R_{23}^{L_a + 1}} \left( \begin{array}{ccc} L & l_1 & L \\ -M & 0 & M \end{array} \right) \cos (M_l \beta) \right\} \times
\left\{ b^2 \sum_{n_a L_a M_a l_1 l_1'} \times \frac{F_1 (n_a, n_b, L_a, L_b; l_1, l_1', L, M) \times \langle n_0 L||T_{l_1}||n_0' L||\rangle \times \langle n_0 L||T_{L_u}||n_0 L_u||\rangle \rangle \right\}. \]
\[
V_{23,31}^{(2)} = - \sum_{n_u L_u M_u} 16\pi^2 (-1)^{L_u + L_u + M_u - M} \frac{P_{M_u + L}^{M_u}(0)(L_u + L_u - M_u + M)! (L_u, L)^{-1/2}}{(L_u + M_u)! (L_u - M_u)! (L + M)! (L - M)!} \\
\times \left\{ (a^* b) \exp[i(M_u - M)\gamma] + (b^* a) \exp[-i(M_u - M)\gamma] \right\} \\
\times \frac{|\langle n_0' L || T_L || n_0 L \rangle|^2 |\langle n_0' 0 || T_L || n_u L \rangle|^2}{E_{n_u L_u} - E_{n_0 S} + E_{n_0 L} - E_{n_0 S} - E_{n_0' L} + E_{n_0' S}}
\]

\[
\frac{V_{31,12}^{(2)}}{V_{23,31}^{(2)}} = \frac{|b|^2 \sum_{n_u L_u M_u} \sum_{l_2} 8\sqrt{\pi^3} Q(-1)^{L_u - L_u + L_u - M_u} \frac{P_{L_u + l_2}^{M_u}(0)(L_u + l_2 - M_u)!(L_u - l_2)^{-1/2}}{(L_u + M_u)! (l_2)!} \\
\times \langle n_0' L || T_L || n_0' L \rangle^* \langle n_0 || T_L || n_u L \rangle^* |\langle n_0' 0 || T_L || n_u L \rangle^2}{E_{n_u L_u} - E_{n_0 S}}
\]

\[
- \sum_{n_u L_u M_u} \sum_{l_1 m_1} 8\sqrt{\pi^3} Q(-1)^l \frac{P_{l_1 + l_2}^{M_u}(0)(l_1 + L_u - m_1 - M_u)!(L_u - m_1)^{-1/2}}{(l_1 + M_u)! (l_1 - m_1)! (L_u + M_u)! (L_u + M_u)! (L_u + M_u)! (L_u - m_1)! (L - M)! (L + M)! (L + M)! (L + M)! (L + M)!)^{1/2} \\
\times \langle n_0 || T_L || n_0' L \rangle^* \langle n_0' L || T_l || n_s L \rangle^* \langle n_0 || T_L || n_u L \rangle \langle n_0 || T_L || n_u L \rangle}{E_{n_u L_u} - E_{n_0 S}}
\]

\[
- \sum_{n_s L_s M_s} \sum_{l_1' m_1'} 8\sqrt{\pi^3} Q \frac{P_{l_1' + l_1}^{M_u}(0)(l_1 + L - m_1 - M)!(L_u - m_1)^{-1/2}}{(l_1 + M_u)! (l_1 - m_1)! (L_u + M_u)! (L_u + M_u)! (L_u + M_u)! (L_u - m_1)! (L - M)! (L + M)! (L + M)! (L + M)!)^{1/2} \\
\times \langle n_0 || T_L || n_0' L \rangle^* \langle n_0' L || T_l || n_s L \rangle^* \langle n_0 || T_L || n_u L \rangle \langle n_0 || T_L || n_u L \rangle}{E_{n_u L_u} - E_{n_0 S}}
\]
\[
\times \left\{ a^* b \exp[i(m'_1)\alpha] + b^* a \exp[-i(m'_1)\alpha] \right\} \\
\times \left[ \frac{P_{L_s+M}(0)P_{l'_1}^{m'_1}(0)(L_s + L - M_s + M)!}{[(L_s + M_s)!(L_s - M_s)!(L + M)!(L - M)!(l'_1 + m'_1)!(l'_1 - m'_1)]^{1/2}} \right] \\
\times \frac{\langle n_00|T_{L_s}\|n_sL_s\rangle \langle n_00|T_{l'_1}\|n_sL_s\rangle}{E_{n_sL_s} - E_{n'_0L}} \\
= -\left\{ |b|^2 \sum_{n_sL_sM_s} \frac{F_5(n_s, L_s, M_s; l'_2, L, M; Q)\cos(M_s\alpha)}{R_{L_s+1}^{12}R_{l'_2+1}} \right. \\
+ \sum_{n_sL_sM_s} \frac{\{a^* b \exp[i(M_s\alpha)] + b^* a \exp[-i(M_s\alpha)]\} F_7(n_s, L_s, M_s; l'_1, L, M; Q)}{R_{l'_1+1}^{12}R_{L_s+1}} \\
+ \sum_{n_sL_sM_s l'_1 m'_1} \frac{\{a^* b \exp[i(m'_1)\alpha] + b^* a \exp[-i(m'_1)\alpha]\} F_6(n_s, L_s, M_s; l'_1, m'_1, L, M; Q)}{R_{l'_2+1}^{12}R_{L_s+1}} \right\} .
\] (91)

In the above Eqs. (86)-(91), the F_1, F_2, and F_3 functions and the corresponding G_1(L_i; L_j; \ell, \ell_k; L, M), G_2(L_i, L_j, \ell, \ell_k; L, M), and G_3(L_i, L_j) are defined in Ref. [10]. The F_4, F_5, and F_7 functions and the corresponding G_4(L_i, M_i; L, M), G_5(L_i, M_i; \ell, \ell_k; L, M; Q), G_6(L_i, M_i; \ell, \ell_k; M_k; L, M; Q) and G_7(L_i, M_i; \ell, \ell_k; L, M; Q) are defined by

\[
F_1(n_s, n_t, L_s, L_t; l'_1, L, M) = G_1(L_s, L_t, l'_1; L, M) \langle n'_0L\|T_{l'_1}\|n_sL_s\rangle \times \frac{\langle n'_0L\|T_{l'_1}\|n_sL_s\rangle}{E_{n_sL_s} + E_{n_tL_t} - E_{n'_0L}} \\
+ \frac{\langle n_00\|T_{L_s}\|n_sL_s\rangle \langle n_00\|T_{l'_1}\|n_tL_t\rangle}{E_{n_sL_s} + E_{n_tL_t} - E_{n'_0L}} .
\] (92)

\[
F_2(n_s, n_t, L_s, L_t; l'_1, L'_2; L, M) = (-1)^{L_s+L'_2}G_2(L_s, L_t, l'_1, L'_2; L, M) \times \frac{\langle n'_0L\|T_{L_s}\|n_tL_t\rangle \langle n'_0L\|T_{l'_1}\|n_sL_s\rangle}{E_{n_sL_s} + E_{n_tL_t} - E_{n'_0L}} \\
+ \frac{\langle n'_0L\|T_{l'_1}\|n_sL_s\rangle \langle n'_0L\|T_{L_s}\|n_tL_t\rangle}{E_{n_sL_s} + E_{n_tL_t} - E_{n'_0L}} .
\] (93)

\[
F_3(n_s, n_t, L_s, L_t) = G_3(L_s, L_t) \times \frac{\langle n_00\|T_{L_s}\|n_tL_t\rangle \langle n_00\|T_{L_s}\|n_uL_u\rangle}{E_{n_sL_s} + E_{n_uL_u} - E_{n'_0L}} ,
\] (94)

\[
F_4(n_u, L_u, M_u; L, M) = (-1)^{L_u+L+M_u+M}G_4(L_u, M_u; L, M) \times \frac{\langle n'_0L\|T_{L_s}\|n_00\rangle^2}{E_{n_sL_s} - E_{n'_0L}} + \frac{\langle n'_0L\|T_{L_s}\|n'_0L\rangle \langle n'_0L\|T_{L_s}\|n_uL_u\rangle}{E_{n_sL_s} - E_{n'_0L}} ,
\] (95)

\[
F_5(n_t, L_t, M_t; l'_1; L, M; Q) = (-1)^{L_t+L+M_t+M}G_5(L_t, M_t; l'_1; L, M; Q) \times \frac{\langle n'_0L\|T_{l'_1}\|n'_0L\rangle \langle n_00\|T_{L_t}\|n_tL_t\rangle}{E_{n_tL_t} - E_{n_0L}} ,
\] (96)
\[ F_6(n_t, L_t, M_t; l'_2, m'_2; L, M; Q) = G_6(L_t, M_t; l'_2, m'_2; L, M; Q) \]
\[ \times \frac{\langle n_0 \mid T_L \mid n'_0 L \rangle \langle n_0 \mid T_L \mid n_L L_t \rangle^* \langle n'_0 \mid T_L \mid n_L L_t \rangle}{E_{n_L L_t} - E_{n_0 L}} , \]  
\[ F_7(n_t, L_t, M_t; l_2; L, M; Q) = (-1)^2 G_7(L_t, M_t; l_2; L, M; Q) \]
\[ \times \frac{\langle n_0 \mid T_L \mid n'_0 L \rangle^* \langle n'_0 \mid T_L \mid n_L L_t \rangle^* \langle n_0 \mid T_L \mid n_L L_t \rangle}{E_{n_L L_t} - E_{n_0 S}} , \]
\[ G_1(L_i, L_j, \ell_k, \ell_k'; L, M) = \frac{16\pi^2(\ell_k, \ell_k')^{-1/2}}{(2L + 1)^2} \sum_{M_iM_jm_k} \left( \begin{array}{ccc} L & \ell_k & L_i \\ -M & m_k & M_i \end{array} \right) \left( \begin{array}{ccc} L & \ell_k' & L_j \\ -M & m_k & M_i \end{array} \right) \]
\[ \times \frac{(L_j + \ell_k - M_j + m_k)!(L_j + \ell_k' - M_j + m_k)!P_{L_i + \ell_k}(0)P_{L_j + \ell_k'}(0)}{(L_j + M_j)!(L_j - M_j)!!} \]
\[ \frac{[(L_i - M_i)!(L_i + M_i)!(L_i + M_j)!(L_j + M_j)!!]^{1/2}}{(L_i + \ell_k - M_i + m_k)!(L_i + \ell_k' - M_i + m_k')!!} \]
\[ \times \left( L_i + \ell_k - M_i + m_k)!(L_i - M_i)!(L_i + M_j)!(L_j + M_j)!! \right)^{1/2} ; \]
\[ G_2(L_i, L_j, \ell_k, \ell_k'; L, M) = \frac{16\pi^2(\ell_k, \ell_k')^{-1/2}}{(2L + 1)^2(2L_j + 1)} \sum_{M_iM_jm_km_k'} \left( \begin{array}{ccc} L & \ell_k & L_i \\ -M & m_k & M_i \end{array} \right) \left( \begin{array}{ccc} L & \ell_k' & L_j \\ -M & m_k & M_i \end{array} \right) \]
\[ \times \frac{(-1)^{M_i+M_j}P_{L_i + \ell_k}(0)P_{L_j + \ell_k'}(0)}{[(L_i + M_i)!(L_i - M_i)!(L_i + M_j)!(L_j + M_j)!!]^{1/2}} \]
\[ \times \frac{(L_i + \ell_k - M_i + m_k)!(L_i + \ell_k' - M_i + m_k')!!}{[(L_i + m_k)!(L_i - m_k)!(L_i + m_k')!(L_i - m_k')!!]^{1/2}} ; \]
\[ G_3(L_i, L_j) = 16\pi^2(L_i, L_j)^{-1/2} \sum_{M_iM_j} \frac{[P_{L_i + L_j}(0)(L_i + L_j - M_i - M_j)]^2}{(L_i + M_i)!(L_i - M_i)!(L_i + M_j)!(L_j + M_j)!!} ; \]
\[ G_4(L_i, M_i; L, M) = 16\pi^2 \frac{[P_{L_i + L}(0)(L_i + L - M_i + M)](L_i, L, L_i, L)^{-1/2}}{(L_i + M_i)!(L_i - M_i)!(L_i + M)!(L_i + M)!!} ; \]
\[ G_5(L_i, M_i; \ell_k; L, M; Q) = \frac{8\sqrt{\pi}Q P_{L_i + L_i}(0)P^M_{L_i}(0)(\ell_k + L_i - M_i)!}{(2L + 1)^2\sqrt{2\ell_k + 1}(l_i)!(L_i + M_i)!} \left( \begin{array}{ccc} L & \ell_k & L \\ -M & 0 & M \end{array} \right) ; \]
\[ G_6(L_i, M_i; \ell_k, m_k; L, M; Q) = \frac{8\sqrt{\pi}Q(\ell_k)^{-1/2}}{(2L + 1)^2(2L + 1)} \left( \begin{array}{ccc} L & \ell_k & L_i \\ -M & m_k & M_i \end{array} \right) \]
\[ \times \frac{P^M_{L_i + L_i}(0)P^m_{L_i}(0)(L_i + L_i + M_i - M_i)!(\ell_k - m_k)!}{(L_i + M_i)!(L_i - M_i)!(L_i + M_i)!(L_i - M_i)!(\ell_k + m_k)!(\ell_k - m_k)!!} ; \]
\[ G_7(L_i, M_i; \ell_k; L, M; Q) = \frac{8\sqrt{\pi}Q(\ell_k)^{-1/2}}{(2L + 1)^2(2L + 1)} \sum_{m_k} \left( \begin{array}{ccc} L & \ell_k & L_i \\ -M & m_k & M_i \end{array} \right) \]
\[ \times \frac{P^M_{L_i + L_i}(0)P^M_{L_i}(0)(L_i + \ell_k - M_i + m_k)!(L_i - M_i)!(L_i + M_i)!(L_i - M_i)!(\ell_k + m_k)!(\ell_k - m_k)!!} ; \]

where \( n_0 \) and \( n_0'' \), respectively, are the principal quantum numbers for \( A(n_0 S) \) and \( A_{Q\pm}(n_0'' S) \).
For the specific Li(2^2S)-Li(2^2P)-Li^+(1^1S) system, the second-order energy correction is simplified as,

\[ \Delta E^{(2)} = - \sum_{n_2 \geq 2, n_3 \geq 3} \left( \frac{C_{2n_3}^{(12)}(L, M)}{R_{12}^{2n_3}} + \frac{C_{2n_2}^{(23)}(L, M)}{R_{23}^{2n_2}} + \frac{C_{2n_2}^{(31)}(L, M)}{R_{31}^{2n_2}} \right) \\
- \sum_{n_1 \neq n_2, n_1 \geq 1, n_2 \geq 2, n_3 \geq 3} \left( \frac{C_{n_2+1,n_1+1}^{(12,23)}(L, M)}{R_{12}^{n_2+1} R_{23}^{n_1+1}} + \frac{C_{n_1+1,n_2+1}^{(31,12)}(L, M)}{R_{31}^{n_2+1} R_{12}^{n_1+1}} \right) \\
- \sum_{n_3 \geq 3} \left( \frac{C_{n_3,n_3}^{(12,23)}(L, M)}{R_{12}^{n_3} R_{23}^{n_3}} + \frac{C_{n_3,n_3}^{(23,31)}(L, M)}{R_{23}^{n_3} R_{31}^{n_3}} + \frac{C_{n_3,n_3}^{(31,12)}(L, M)}{R_{31}^{n_3} R_{12}^{n_3}} \right), \quad (106) \]

where \( C_{2n_3}^{(12)}(L, M), C_{2n_2}^{(23)}(L, M), C_{2n_2}^{(31)}(L, M), C_{n_3,n_3}^{(12,23)}(L, M), C_{n_1+1,n_2+1}^{(31,12)}(L, M), \) and \( C_{n_1+1,n_2+1}^{(31,12)}(L, M) \) are the additive and nonadditive dispersion coefficients. These coefficients can be expressed as

\[ C_{2n_3}^{(12)}(L, M) = |a|^2 \sum_{n_2,n_4} \sum_{L_1 L_2 l_1 l_2} F_1(n_s, n_s, L_s, L_t; l_1, l_2; L, M) \]
\[ + |b|^2 \sum_{n_2,n_4} \sum_{L_1 L_2 l_1 l_2} F_1(n_s, n_u, L_t; l_2, l_2; L, M) \]
\[ + a^* b \sum_{n_2,n_4} \sum_{L_1 L_2 l_1 l_2} F_3(n_s, n_t, L_s; l_1, l_1; L, M) \]
\[ + b^* a \sum_{n_2,n_4} \sum_{L_1 L_2 l_1 l_2} F_3^*(n_s, n_t, L_s; l_1, l_1; L, M) \], \quad (107) \]

\[ C_{2n_2}^{(23)}(L, M) = |a|^2 \sum_{n_3,n_u} \sum_{L_1 L_u} F_2(n_t, n_u, L_t; L_u) \]
\[ + |b|^2 \sum_{n_3,n_u} \sum_{L_1 L_u} F_1(n_t, n_u, L_t; l_2, l_2; L, M) \], \quad (108) \]

\[ C_{2n_2}^{(31)}(L, M) = |a|^2 \sum_{n_3,n_u} \sum_{L_1 L_u} F_1(n_s, n_u, L_s; l_1, l_1; L, M) \]
\[ + |b|^2 \sum_{n_3,n_u} \sum_{L_1 L_u} F_2(n_s, n_u, L_s; L_u) \], \quad (109) \]

\[ C_{n_2+1,n_1+1}^{(12,23)}(L, M) = \sum_{L_1 L_2} \sum_{l_1, l_2} \mathbb{P}_1(a, b, \beta, Q, L_t, l_2, L_t', l_2, l_1, L, M), \quad (110) \]
\[ C_{n_{1},n_{2}}^{(12,31)}(L, M) = \sum_{\substack{L_{a}l_{1}l_{2} \\ L_{a}+1=n_{1}+1}} \sum_{\substack{L_{a}'l_{1}'l_{2}' \\ L_{a}'+1=n_{1}+1}} \mathbb{P}_{1}(b, a, \alpha, Q, L_{a}, l_{1}, L_{a}', l_{1}', l_{2}, L, M), \] (111)

\[ C_{n_{3},n_{3}}^{(12,23)}(L, M) = \sum_{\substack{L_{a}l_{2}l_{2}' \\ L_{a}+1=n_{3}+1 \ \ L_{a}'+1=n_{3}+1}} \sum_{\substack{L_{a}'l_{2}'l_{2}'' \\ L_{a}'+1=n_{3}+1 \ \ L_{a}''+1=n_{3}+1}} \mathbb{P}_{2}(a, b, \beta, Q, L_{a}, l_{2}, L_{a}', l_{2}', L, M), \] (112)

\[ C_{n_{3},n_{3}}^{(23,31)}(L, M) = \sum_{\substack{L_{a}l_{1}l_{1}' \\ L_{a}+1=n_{3}+1 \ \ L_{a}'+1=n_{3}+1}} \sum_{\substack{L_{a}'l_{1}'l_{1}'' \\ L_{a}'+1=n_{3}+1 \ \ L_{a}''+1=n_{3}+1}} \mathbb{P}_{3}(a, b, \gamma, L_{a}, L, M), \] (113)

\[ C_{n_{3},n_{3}}^{(31,12)}(L, M) = \sum_{\substack{L_{a}l_{1}l_{2} \\ L_{a}+1=n_{3}+1 \ \ L_{a}'+1=n_{3}+1}} \sum_{\substack{L_{a}'l_{1}'l_{2}' \\ L_{a}'+1=n_{3}+1 \ \ L_{a}''+1=n_{3}+1}} \mathbb{P}_{2}(b, a, \alpha, Q, L_{a}, l_{1}, L_{a}', l_{1}', L, M), \] (114)

where the \( \mathbb{P}_{n} \) functions are defined as

\[
\mathbb{P}_{1}(a, b, \beta, Q, L_{t}, l_{2}, L_{t}', l_{2}', l_{1}, L, M) = |a|^{2} \sum_{n_{t}; M_{t}} F_{5}(n_{t}, L_{t}, M_{t} l_{1}; L, M; Q) \cos(M_{t} \beta) \\
+ \sum_{n_{t}'; M_{t}'; m_{2}'} \{a^{*}b \exp[-i(m_{2}')\beta] + \text{c.c.}\} F_{6}(n_{t}', L_{t}', M_{t}'; l_{2}', m_{2}'; L, M; Q) \\
+ \sum_{n_{t}; M_{t}} \{a^{*}b \exp[i(M_{t})\beta] + \text{c.c.}\} F_{7}(n_{t}, L_{t}, M_{t} l_{2}; L, M; Q),
\]

(115)

\[
\mathbb{P}_{2}(a, b, \beta, Q, L_{t}, l_{2}, L_{t}', l_{2}', L, M) = \sum_{n_{t}'; M_{t}'; m_{2}'} \{a^{*}b \exp[-i(m_{2}')\beta] + \text{c.c.}\} F_{6}(n_{t}', L_{t}', M_{t}'; l_{2}', m_{2}'; L, M; Q) \\
+ \sum_{n_{t}; M_{t}} \{a^{*}b \exp[i(M_{t})\beta] + \text{c.c.}\} F_{7}(n_{t}, L_{t}, M_{t} l_{2}; L, M; Q),
\]

(116)

\[
\mathbb{P}_{3}(a, b, \gamma, L_{u}, L, M) = \sum_{n_{u}; M_{u}} \left\{ (a^{*}b) \exp[i(M_{u} - M)\gamma] + \text{c.c.} \right\} F_{4}(n_{u}, L_{u}, M_{u}; L, M),
\]

(117)

and where c.c. indicates the complex conjugate of the preceding term.
D. Long-range interaction coefficients for the Li($2^2S$)-Li$^+(1^1S)$ system

The induction and dispersion coefficients $C_{4,\text{ind}}^{(S-S^+)}$, $C_{6,\text{ind}}^{(S-S^+)}$, and $C_{6,\text{disp}}^{(S-S^+)}$ for the Li($2^2S$)-Li$^+(1^1S)$ system can be written as

$$C_{4,\text{ind}}^{(S-S^+)} = \sum_{n_t n_u} F_2(n_t, n_u, 1, 0),$$  \quad (118)

$$C_{6,\text{ind}}^{(S-S^+)} = \sum_{n_t n_u} F_2(n_t, n_u, 2, 0),$$  \quad (119)

$$C_{6,\text{disp}}^{(S-S^+)} = \sum_{n_t n_u} F_2(n_t, n_u, 1, 1).$$  \quad (120)

E. Long-range interaction coefficients for the Li($2^2S$)-Li($2^2P$) system

The dipolar and dispersion interaction coefficients $C_{3,\text{dip}}^{(S-P)}(M)$ and $C_{6,\text{disp}}^{(S-P)}(M)$ for the Li($2^2S$)-Li($2^2P$) system can be written as

$$C_{3,\text{dip}}^{(S-P)}(M) = (a^* b + b^* a) \frac{4\pi(-1)^{1+M}}{9(1-M)! (1+M)!} |\langle n_00||T_1||n_01 \rangle|^2,$$  \quad (121)

$$C_{6,\text{disp}}^{(S-P)}(M) = \sum_{n_s n_t L_s} F_1(n_s, n_t, L_s, 1; 1, 1; 1, M).$$  \quad (122)

F. Long-range interaction coefficients for the Li($2^2P$)-Li$^+(1^1S)$ system

The electrostatic, dispersion and induction interaction coefficients for the Li($2^2P$)-Li$^+(1^1S)$ system can be written as

$$C_{3,\text{elst}}^{(P-S^+)}(M) = Q(-1)^{1+M} \sqrt{\frac{\pi}{5}} \begin{pmatrix} 1 & 2 & 0 \\ -M & 1 & M \end{pmatrix} \langle n_01||T_2||n_01 \rangle,$$  \quad (123)

$$C_{4,\text{ind}}^{(P-S^+)}(M) = \sum_{n_t n_u L_t} F_1(n_t, n_u, L_t, 0; 1, 1; 1, M),$$  \quad (124)

$$C_{6,\text{disp}}^{(P-S^+)}(M) = \sum_{n_t n_u L_t} F_1(n_t, n_u, L_t, 1; 1, 1; 1, M),$$  \quad (125)

and

$$C_{6,\text{ind}}^{(P-S^+)}(M) = \sum_{n_t n_u L_t} \left\{ F_1(n_t, n_u, L_t, 0; 2, 2; 1, M) + F_1(n_t, n_u, L_t, 0; 1, 3; 1, M) \\
+ F_1(n_t, n_u, L_t, 0; 3, 1; 1, M) \right\},$$  \quad (126)
G. Long-range interaction coefficients for the Li(2\(^2\)S)-Li(2\(^2\)P)-Li\(^+(1^1\)S) system

The additive interaction coefficients for the Li(2\(^2\)S)-Li(2\(^2\)P)-Li\(^+(1^1\)S) system can be written as

\[ C^{(23)}_4(1, M) = |a|^2T_1 + |b|^2T_3(M), \]  
\[ (127) \]

\[ C^{(31)}_4(1, M) = |a|^2T_3(M) + |b|^2T_1, \]  
\[ (128) \]

\[ C^{(12)}_6(1, M) = |a|^2T_4(M) + |b|^2T_4(M), \]  
\[ (129) \]

\[ C^{(23)}_6(1, M) = |a|^2T_2 + |b|^2T_5(M), \]  
\[ (130) \]

\[ C^{(31)}_6(1, M) = |a|^2T_5(M) + |b|^2T_2, \]  
\[ (131) \]

where

\[ T_1 = \sum_{n_t n_u} F_3(n_t, n_u, 1, 0), \]  
\[ (132) \]

\[ T_2 = \sum_{n_t n_u} \left\{ F_3(n_t, n_u, 2, 0) + F_3(n_t, n_u, 1, 1) \right\}, \]  
\[ (133) \]

\[ T_3(M) = \sum_{n_t n_u L_t} F_1(n_t, n_u, L_t, 0; 1, 1; 1, M), \]  
\[ (134) \]

\[ T_4(M) = \sum_{n_s n_t L_s} F_1(n_s, n_t, L_s, 1; 1, 1; 1), \]  
\[ (135) \]

\[ T_5(M) = \sum_{n_t n_u L_t} \left\{ F_1(n_t, n_u, L_t, 1; 1, 1; 1, M) + F_1(n_t, n_u, L_t, 0; 2, 2; 1, M) \right. \]
\[ + F_1(n_t, n_u, L_t, 0; 1, 3; 1, M) + F_1(n_t, n_u, L_t, 0; 3, 1; 1, M) \right\}. \]  
\[ (136) \]

The nonadditive interaction coefficients for the Li(2\(^2\)S)-Li(2\(^2\)P)-Li\(^+(1^1\)S) system are given by

\[ C^{(12,23)}_{4,2}(1, M) = \mathbb{P}_1(a, b, \beta, Q, 1, 2, 2, 1, 2, 1, M), \]  
\[ (137) \]

\[ C^{(31,12)}_{2,4}(1, M) = \mathbb{P}_1(b, a, \alpha, Q, 1, 2, 2, 1, 2, 1, M), \]  
\[ (138) \]

\[ C^{(12,23)}_{3,3}(1, M) = \mathbb{P}_2(a, b, \beta, Q, 2, 1, 1, 2, 1, M), \]  
\[ (139) \]

\[ C^{(23,31)}_{3,3}(1, M) = \mathbb{P}_3(a, b, \gamma, 1, 1, M), \]  
\[ (140) \]

and

\[ C^{(31,12)}_{3,3}(1, M) = \mathbb{P}_2(b, a, \alpha, Q, 2, 1, 1, 2, 1, M). \]  
\[ (141) \]