Non-relativistic ab initio calculations for $^2S$, $^2P$ and $^3D$ lithium isotopes: Applications to polarizabilities and dispersion interactions

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The electric dipole polarizabilities and hyperpolarizabilities for the lithium isotopes $^6$Li and $^7$Li in the ground state $^2S$ and the excited states $^2P$ and $^3D$, as well as the leading resonance and dispersion long-range coefficients for the Li($^2S$)–Li($^2S$) and Li($^2S$)–Li($^2P$) systems, are calculated nonrelativistically using variational wave functions in Hylleraas basis sets. Comparisons are made with published results, where available. We find that the value of the second hyperpolarizability of the $^2S$ state is sensitive to the isotopic mass due to a near cancellation between two terms. For the $^3D$ state polarizability tensor the calculated components disagree with those measured in the sole experiment and with those calculated semi-empirically.

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I. INTRODUCTION

The energies, transition probabilities, and polarizabilities of the lithium atom and its isotopes and their mutual long-range interaction coefficients have been extensively studied, and many calculational approaches have been developed and tested against each other and against available experimental results. Nevertheless—as we shall show—there is still a need for calculations of increasingly high-precision to serve as benchmarks, to predict atomic and interatomic coefficients, and to help understand discrepancies between various results. Calculations at the level reflecting the mass of lithium isotopes may be applied to a diverse set of recent areas of interest in, for example, astrophysics, ultracold atom-atom scattering and Feshbach resonance analyses, photoassociation spectroscopy, atom-molecule scattering and three-atom inelastic collisional loss studies. Measurements and calculations on excited states and their properties are also at the frontier, though discrepancies between theory and experiment remain even for the lowest fine structure levels.

It has been demonstrated that ab initio wave functions obtained variationally using Hylleraas-type basis functions are capable of yielding highly accurate results for Li properties, cf. 12, 13. In turn, those results have proven useful in gauging the effectiveness of Gaussian-type basis functions and other calculations, semi-empirical methods, and relativistic approaches. The purpose of the present work is to apply and extend methods developed over a series of previous papers (e.g., 12, 20, 21) to the excited $^2P$ and $^3D$ states of the lithium isotopes thereby providing a consistent and highly accurate ab initio treatment of the polarizabilities and their related quantities using the nonrelativistic Schrödinger equation. We also refine the previous results for the $^2S$ ground state by improving the accuracy and by the inclusion of the isotope mass. For the excited states of the isotopes we provide calculations of static polarizabilities and static second hyperpolarizabilities and we investigate the excited state resonance and dispersion long-range interaction potential energy coefficients.

II. THEORY

In this section, the Hamiltonian and basis sets will be exhibited along with expressions for the electric multipole transition operators, polarizabilities, second hyperpolarizabilities, and dispersion coefficients. The formulation extends and unifies those given previously for Li [12, 20, 21], for He [22], and for H$_2$ [23]; we include the isotopic mass and we treat the response of the atom to an applied electric field.
A. Hamiltonian

The transformation from the laboratory frame to the center of mass frame that we will use for describing the Li atom was given by Zhang and Yan [22] in a general form for \( n + 1 \) charged particles. It was applied to generate the Hamiltonian and transition operators for \( H_x^2 \) in Ref. [23] and for He in Ref. [22].

We directly follow the expressions given in Eqs. (20)–(26) of Ref. [23], which may be written in the form

\[
H_0 = -\frac{1}{2\mu} \sum_{i=1}^{3} \nabla_i^2 - \frac{1}{m_0} \sum_{i>j \geq 1} \nabla_i \cdot \nabla_j + q_0 \sum_{i=1}^{3} \frac{q_i}{r_i} + \sum_{i>j \geq 1} \frac{q_i q_j}{r_{ij}} ,
\]

(1)

where \( r_i \) is the position vector of electron \( i \) from the nucleus, and \( \mu = m m_0 / (m + m_0) \) is the reduced mass. In this subsection \( j \) stands for a summation index (in subsequent parts of the paper it will be an angular momentum quantum number), and \( q_j, j = 0, \ldots, 3 \) are the charges of the respective particles.

The 2\( \ell \)-pole transition operator is

\[
T_{\ell} = \sum_{i=0}^{3} q_i R_i^\ell Y_{\ell 0}(\hat{\mathbf{r}}_i) ,
\]

(2)

where \( R_i, i = 0, \ldots, 3 \), as shown in Eq. (27) of Ref. [23]. It can be transformed into the center of mass frame by applying Eqs. (23) and (24) of Ref. [23], which may be written in the form

\[
R_{\ell} = \sum_{j=1}^{3} \epsilon_{ij} r_j ,
\]

(3)

with \( \epsilon_{ij} = \delta_{ij} - m_j / M_T, i = 0, 1, 2, 3 \), \( j = 1, 2, 3 \), and \( M_T = m_0 + 3m \). The general formula for \( T_{\ell} \) expressed in the center of mass frame is given in Eq. (30) of Ref. [23].

For a four-particle system, it can be shown that the transition operators \( T_{\ell} \) with \( \ell \) up to 3 have the following explicit forms:

\[
T_1 = \sum_{j=1}^{3} \left( \sum_{i=0}^{3} q_i \epsilon_{ij} \right) r_j Y_{10}(\hat{\mathbf{r}}_j) ,
\]

(4)

\[
T_2 = \sum_{j=1}^{3} \left( \sum_{i=0}^{3} q_i \epsilon_{ij}^2 \right) r^2 j Y_{20}(\hat{\mathbf{r}}_j) + \sqrt{\frac{15}{2\pi}} \sum_{j,k=1}^{3} \sum_{j \neq k}^{3} q_i \epsilon_{ij} \epsilon_{ik} \left( \sum_{i=0}^{3} q_i \epsilon_{ik} \right) r_j r_k (\hat{\mathbf{r}}_j \otimes \hat{\mathbf{r}}_k)^{(2)} ,
\]

(5)

with \( \{ j, k \} = (1, 2), (2, 3), \) and \( (3, 1) \), and

\[
T_3 = \sum_{j=1}^{3} \left( \sum_{i=0}^{3} q_i \epsilon_{ij}^3 \right) r^3 j Y_{30}(\hat{\mathbf{r}}_j) + \sqrt{\frac{35}{8\pi}} \sum_{j,k=1}^{3} \sum_{j \neq k}^{3} q_i \epsilon_{ij} \epsilon_{ik} \left( \sum_{i=0}^{3} q_i \epsilon_{ik} \right) r^2 j r^2 k (\hat{\mathbf{r}}_j \otimes \hat{\mathbf{r}}_k)^{(2)} \otimes \hat{\mathbf{r}}_k^{(3)}
\]

\[+ 6\sqrt{\frac{35}{8\pi}} \sum_{i=0}^{3} q_i \epsilon_{i1} \epsilon_{i2} \epsilon_{i3} r_1 r_2 r_3 (\hat{\mathbf{r}}_1 \otimes \hat{\mathbf{r}}_2)^{(2)} \otimes \hat{\mathbf{r}}_3^{(3)} .
\]

(6)

For a neutral system, the finite mass effect enters into the transition operator \( T_{\ell} \) as a polynomial of degree \( \ell - 1 \) in \( m_j / M_T \). For Li, the three coefficients appearing in the sets of parentheses in Eq. (6) for the transition operator \( T_3 \), for example, can be written as

\[
\sum_{i=0}^{3} q_i \epsilon_{ij}^3 = q_j - 3q_j \left( \frac{m_j}{M_T} \right)^2 + 3q_j \left( \frac{m_j}{M_T} \right)^2 ,
\]

(7)

\[
\sum_{i=0}^{3} q_i \epsilon_{ij}^2 \epsilon_{ik} = -q_j \left( \frac{m_k}{M_T} \right) + 2q_j \left( \frac{m_j}{M_T} \right) \left( \frac{m_k}{M_T} \right) + q_k \left( \frac{m_j}{M_T} \right)^2 ,
\]

(8)

\[
\sum_{i=0}^{3} q_i \epsilon_{i1} \epsilon_{i2} \epsilon_{i3} = q_i \left( \frac{m_2}{M_T} \right) \left( \frac{m_3}{M_T} \right) + q_2 \left( \frac{m_2}{M_T} \right) \left( \frac{m_3}{M_T} \right) + q_3 \left( \frac{m_1}{M_T} \right) \left( \frac{m_2}{M_T} \right) .
\]

(9)
For an atomic system of infinite nuclear mass, all the coefficients are zero except for those of \( r_j^3 Y_{00}(\hat{r}_j) \), which are equal to \( q_j \), as expected. We now let \( m = 1 \) to utilize atomic units for the remainder of the paper.

### B. Variational basis sets

The wave functions are obtained by solving variationally the energy eigenvalue equation for lithium

\[
H_0 \Psi_0 (r_1, r_2, r_3) = E_0 \Psi_0 (r_1, r_2, r_3),
\]

with \( H_0 \) given by Eq. (1), in terms of the explicitly correlated basis functions in Hylleraas coordinates,

\[
\phi(r_1, r_2, r_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-a r_1 - \beta r_2 - \gamma r_3} \Psi_{L, M}(\hat{r}_1, \hat{r}_2, \hat{r}_3) \chi(1, 2, 3),
\]

where \( r_{ij} = |r_i - r_j| \) is the inter-electronic separation, \( \Psi_{LM} \) is a vector-coupled product of spherical harmonics to form an eigenstate of total angular momentum \( L \) and component \( M_L \), which can be written in the form

\[
\Psi_{LM} \equiv (\ell_1, \ell_2, \ell_3) = \sum_{m_1} \langle \ell_1 m_1; \ell_2 m_2; \ell_3 m_3 \rangle \times \langle \ell_1 m_1; \ell_2 m_2; \ell_3 m_3 \rangle \rho(\hat{r}_1, \hat{r}_2, \hat{r}_3),
\]

and \( \chi(1, 2, 3) \) is the three-electron spin 1/2 function. The variational wave function \( \Psi_0 \) is a linear combination of basis functions \( \phi \), anti-symmetrized. The procedures followed are similar to those described in Ref. [20]. With some truncations to avoid potential numerical linear dependence, all terms in Eq. (11) are included such that

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

where \( \Omega \) is an integer, and the convergence for the energy eigenvalue is studied by increasing \( \Omega \) progressively. The basic type of integral that appears in this work is of the form

\[
\int d\hat{r}_1 d\hat{r}_2 d\hat{r}_3 \rho^{*}_{\ell_1, m_1}(\hat{r}_1) \rho^{*}_{\ell_2, m_2}(\hat{r}_2) \rho^{*}_{\ell_3, m_3}(\hat{r}_3) Y_{\ell_1, m_1}^{*}(\hat{r}_1) Y_{\ell_2, m_2}^{*}(\hat{r}_2) Y_{\ell_3, m_3}^{*}(\hat{r}_3)
\]

and computational details for this integral can be found in Ref. [21].

### C. Stark effect and polarizabilities

The polarizability of an atom can be considered as a measure of the response of the charge cloud to an external electric field, which can be illustrated by the Stark effect. Consider a lithium atom in a weak external electric field \( \mathbf{E} = E \hat{z} \). The initial state is assumed to be a parity eigenstate and is written as \( |0\rangle \equiv |n_0LM\rangle \), where \( n_0 \) is the principal quantum number and \( L \) and \( M \) are the usual angular momentum quantum numbers. According to the perturbation theory, the energy shift due to \( \mathbf{E} \) can be expressed in the form

\[
\Delta E = \Delta E_2 + \Delta E_4,
\]

where \( \Delta E_2 \) and \( \Delta E_4 \) are, respectively, from the second- and fourth-order corrections, whereas the first- and third-order corrections are zero because of the parity selection rule. The detailed derivation for \( \Delta E_2 \) and \( \Delta E_4 \) is given in the Appendix. The final expression for \( \Delta E_2 \) is

\[
\Delta E_2 = -\frac{E^2}{2} \left[ \alpha_1 + \alpha_1^{(T)} g_2(L, M) \right],
\]

where \( g_2(L, M) \) is the only \( M \)-dependent part, defined in the Appendix by Eq. (A29), and \( \alpha_1 \) and \( \alpha_1^{(T)} \) are, respectively, the scalar and tensor dipole polarizabilities. The polarizabilities \( \alpha_1 \) and \( \alpha_1^{(T)} \) can be expressed further in terms of the reduced matrix elements of the dipole transition operator:

\[
\alpha_1 = \sum_{L_a} \alpha_1(L_a),
\]

\[
\alpha_1^{(T)} = \sum_{L_a} W(L, L_a) \alpha_1(L_a),
\]
where
\[ \alpha_1(L_a) = \frac{8\pi}{9(2L+1)} \sum_n \frac{|\langle n_0L|T_1|nL_a \rangle|^2}{E_n(L_a) - E_{n_0}(L)}, \] (19)

with \( T_1 = \sum_{i=0}^3 q_i R_i Y_{10}(\hat{R}_i) \), Eq. (2), and

\[ W(L, L_a) = (-1)^{L+L_a} \sqrt{\frac{30(2L+1)L(2L-1)}{(2L+3)(L+1)}} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L & L & L_a \end{array} \right\}. \] (20)

In the above, the set of energies and wave functions \( \{ E_n(L_a), |nL_aM_a \rangle \} \) correspond to an intermediate energy spectrum allowed by the dipole selection rule, which can be obtained by diagonalizing the Hamiltonian in a Hylleraas basis set of given symmetry \( L_a \). In particular, for the case of \( L = 0 \),
\[ \alpha_1 = \alpha_1(P), \] (21)
\[ \alpha_1^{(T)} = 0; \] (22)
for \( L = 1 \),
\[ \alpha_1 = \alpha_1(S) + \alpha_1(P) + \alpha_1(D), \] (23)
\[ \alpha_1^{(T)} = -\alpha_1(S) + \frac{1}{2} \alpha_1(P) - \frac{1}{10} \alpha_1(D); \] (24)
and for \( L = 2 \),
\[ \alpha_1 = \alpha_1(P) + \alpha_1(D) + \alpha_1(F), \] (25)
\[ \alpha_1^{(T)} = -\alpha_1(P) + \alpha_1(D) - \frac{2}{7} \alpha_1(F). \] (26)

In Eqs. (23) and (24), \( \alpha_1(P) \) is the contribution from the even-parity configuration \((pp')P\). In Eqs. (25) and (26), \( \alpha_1(D) \) is from the odd-parity configuration \((pd)D\).

The fourth-order energy shift can be written in the form
\[ \Delta E_4 = -\frac{\varepsilon^4}{24} \left[ \gamma_0 + \gamma_2 g_2(L, M) + \gamma_4 g_4(L, M) \right]. \] (27)

where \( g_4(L, M) \) is given by Eq. (A37) in the Appendix. In Eq. (27), \( \gamma_0 \) is the scalar second hyperpolarizability, and \( \gamma_2 \) and \( \gamma_4 \) are the tensor second hyperpolarizabilities, which can be written as
\[ \gamma_0 = (-1)^{2L} \frac{128\pi^2}{3} \frac{1}{\sqrt{2L+1}} \sum_{L_aL_bL_c} G_0(L_a, L_b, L_c) T(L_a, L_b, L_c), \] (28)
\[ \gamma_2 = (-1)^{2L} \frac{128\pi^2}{3} \sqrt{\frac{L(2L-1)}{(2L+3)(L+1)(2L+1)}} \sum_{L_aL_bL_c} G_2(L_a, L_b, L_c) T(L_a, L_b, L_c), \] (29)
\[ \gamma_4 = (-1)^{2L} \frac{128\pi^2}{3} \sqrt{\frac{L(2L-1)(L-1)(2L-3)}{(2L+5)(L+2)(2L+3)(L+1)(2L+1)}} \sum_{L_aL_bL_c} G_4(L_a, L_b, L_c) T(L_a, L_b, L_c), \] (30)

where \( T(L_a, L_b, L_c) \) and \( G_4(L_a, L_b, L_c) \), respectively, are defined in the Appendix by Eqs. (A44) and (A51). In particular, for the case \( L = 0 \) we only need to consider
\[ \gamma_0 = \frac{128\pi^2}{3} \left[ \frac{1}{9} T(1, 0, 1) + \frac{2}{45} T(1, 2, 1) \right]. \] (31)
where brackets involve the intermediate states of unnatural parities, which make subordinate contributions. For example,

\[\begin{align*}
\gamma_0 &= \frac{128\pi^2}{3} \left[ \frac{1}{27} T(0,1,0) + \frac{2}{135} T(0,1,2) + \frac{1}{54} T(1,1,1) - \frac{1}{90} T(1,1,2) - \frac{1}{90} T(1,2,1) \\
&\quad - \frac{\sqrt{5}}{450} T(1,2,2) + \frac{2}{135} T(2,1,0) - \frac{1}{90} T(2,1,1) + \frac{17}{1350} T(2,1,2) - \frac{\sqrt{5}}{450} T(2,2,1) \\
&\quad - \frac{1}{450} T(2,2,2) + \frac{2}{225} T(2,3,2) \right], \\
\gamma_2 &= \frac{128\pi^2}{3} \left[ \frac{1}{27} T(0,1,0) - \frac{2}{135} T(0,1,2) + \frac{1}{108} T(1,1,1) - \frac{1}{180} T(1,1,2) - \frac{1}{180} T(1,2,1) \\
&\quad - \frac{\sqrt{5}}{900} T(1,2,2) - \frac{2}{135} T(2,1,0) - \frac{1}{180} T(2,1,1) - \frac{7}{2700} T(2,1,2) - \frac{\sqrt{5}}{900} T(2,2,1) \\
&\quad - \frac{1}{900} T(2,2,2) - \frac{2}{1575} T(2,3,2) \right],
\end{align*}\]

and for \(L = 2\), we have

\[\begin{align*}
\gamma_0 &= \frac{128\pi^2}{3} \cdot \frac{1}{15750} \left[ 140 T(1,0,1) + 119 T(1,2,1) + 84 T(1,2,3) + 84 T(3,2,1) + 74 T(3,2,3) + 60 T(3,4,3) \\
&\quad - 105 T(1,1,1) + 21\sqrt{5} T(1,1,2) + 21 T(1,2,2) + 21\sqrt{5} T(2,1,1) + 21 T(2,1,2) + 21 T(2,2,1) - 119 T(2,2,2) \\
&\quad + 56 T(2,2,3) + 56 T(3,2,2) + 4\sqrt{70} T(3,2,3) + 56 T(3,2,2) + 4\sqrt{70} T(3,3,2) + 20 T(3,3,3) \right], \\
\gamma_2 &= \frac{128\pi^2}{3} \cdot \frac{1}{154350} \left[ - 1960 T(1,0,1) + 1225 T(1,2,1) + 840 T(1,2,3) + 840 T(3,2,1) + 380 T(3,2,3) + 240 T(3,4,3) \\
&\quad + 735 T(1,1,1) + 147\sqrt{5} T(1,1,2) + 147 T(1,2,2) + 147\sqrt{5} T(2,1,1) + 147 T(2,1,2) + 147 T(2,2,1) + 1519 T(2,2,2) \\
&\quad - 448 T(2,2,3) - 448 T(2,3,2) - 32\sqrt{70} T(2,3,3) - 448 T(3,2,2) - 32\sqrt{70} T(3,3,2) - 160 T(3,3,3) \right], \\
\gamma_4 &= \frac{128\pi^2}{3} \cdot \frac{1}{128625} \left[ 490 T(1,0,1) + 49 T(1,2,1) + 14 T(1,2,3) + 14 T(3,2,1) + 4 T(3,2,3) + \frac{5}{3} T(3,4,3) \\
&\quad + 245 T(1,1,1) + 49\sqrt{5} T(1,1,2) + 49 T(1,2,2) + 49\sqrt{5} T(2,1,1) + 49 T(2,1,2) + 49 T(2,2,1) + 49 T(2,2,2) \\
&\quad + 14 T(2,2,3) + 14 T(2,3,2) + \sqrt{70} T(2,3,3) + 14 T(3,2,2) + \sqrt{70} T(3,3,2) + 5 T(3,3,3) \right].
\end{align*}\]

In each of Eqs. (34)-(36), the terms in the first set of square brackets only involve the intermediate states of natural parities, which make the dominant contributions to the hyperpolarizabilities, while the terms in the second set of square brackets involve the intermediate states of unnatural parities, which make subordinate contributions. For example, the term \(T(1,0,1)\) involves the intermediate states \(1s^2np^2p^o, 1s^2ns^2p^e\), and \(1s^2np^2p^o\), which are all natural-parity states, while the term \(T(1,1,1)\) involves the electronic configurations \(1s^2np^2p^o, 1snp^1p^2p^o\), and \(1s^2np^2p^o\), where two states are natural-parity states and one unnatural-parity.

The scalar dipole polarizability defined in Eq. (17) can be generalized to the \(2\ell\)-pole polarizability \(\alpha_\ell\)

\[\alpha_\ell = \sum_{L_\alpha} \alpha_\ell(L_\alpha),\]  

where

\[\alpha_\ell(L_\alpha) = \frac{8\pi}{(2\ell + 1)^2(2L + 1)} \sum_n \frac{|\langle n_0 L_\alpha | T_\ell | n L_\alpha \rangle|^2}{E_n(L_\alpha) - E_{n_0}(L)},\]

and \(T_\ell\) is the \(2\ell\)-pole transition operator given by Eq. (2).
D. Coefficients for long-range interactions between two atoms

First, let us consider the simplest case where both a and b are Li atoms in their ground states \[12\]. At large separations \( R \), using second-order perturbation theory, \( V_{ab} \) can be expressed as a series in inverse powers of \( R \),

\[
V_{ab} = - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots ,
\]

where

\[
C_6 = \frac{3}{\pi} G_{ab}(1, 1) ,
\]

\[
C_8 = \frac{15}{2\pi} G_{ab}(1, 2) + \frac{15}{2\pi} G_{ab}(2, 1) ,
\]

and

\[
C_{10} = \frac{14}{\pi} G_{ab}(1, 3) + \frac{14}{\pi} G_{ab}(3, 1) + \frac{35}{\pi} G_{ab}(2, 2) .
\]

Introducing the oscillator strength for the transition \( |n_0L\rangle \rightarrow |nL'\rangle \)

\[
\tilde{f}_{n0}^{(t)} = \frac{8\pi}{(2\ell + 1)^2(2L + 1)} E_{n0} |\langle n_0L\|T_{\ell}\|nL'\rangle|^2 ,
\]

where \( E_{n0} = E_n(L') - E_{n0}(L) \) is the corresponding transition energy, \( G_{ab}(\ell_a, \ell_b) \) can be written in the form

\[
G_{ab}(\ell_a, \ell_b) = \frac{\pi}{2} \sum_{n'n} \frac{\tilde{f}_{n0}^{(\ell_a)} \tilde{f}_{n'0}^{(\ell_b)}}{E_{n0}^a P_{n'0}^b (E_{n0}^a + E_{n'0}^b)} ,
\]

where throughout \( a \) and \( b \), respectively, denote atom a and atom b.

Next, we consider two like lithium atoms a and b, where atom a is in the ground state and atom b in an excited state with orbital angular momentum \( L_b \) and associated magnetic quantum number \( M_b \). The zeroth order wave function for the combined system ab can be written in the form \[12\]:

\[
\Psi^{(0)} = \frac{1}{\sqrt{2}} [\Psi_a(\sigma)\Psi_b(L_bM_b; \rho) + \beta \Psi_a(\rho)\Psi_b(L_bM_b; \sigma)] ,
\]

where \( \sigma \) and \( \rho \) represent, respectively, the set of all of the internal coordinates for atom a and atom b, and \( \beta = \pm 1 \) describes the symmetry of the system due to the exchange of two atoms. According to the perturbation theory, the first-order interaction energy is given by

\[
V^{(1)}(L_bM_b; \beta) = - \frac{C_{2L_b+1}^M_b \beta}{R^{2L_b+1}} ,
\]

where

\[
C_{2L_b+1}^M_b \beta = \beta (-1)^{1+L_b+M_b} \frac{4\pi}{(2L_b + 1)^2} \left( \frac{2L_b}{L_b + M_b} \right) |\langle \Psi_a(\sigma)\|T_{L_b}(\sigma)\|\Psi_b(L_b; \sigma)\rangle|^2 .
\]

One can see from Eq. \[46\] that, for the Li(S)-Li(P) system, the interaction energy is proportional to \( R^{-3} \). To get the next order energy, let the complete set for the intermediate states of the system be

\[
\{ \chi_s(L_sM_s; \sigma)\omega_t(L_tM_t; \rho) \} ,
\]

with the energy eigenvalue \( E_{st}^{(0)} = E_s^{(0)} + E_t^{(0)} \). According to the second-order perturbation theory, the second-order energy is

\[
V^{(2)} = - \frac{C_6^{M_b}}{R^6} - \frac{C_8^{M_b}}{R^8} - \cdots ,
\]
where

\[ C_{6}^{M_{b}} = \sum_{st} \frac{\Omega_{6}^{st}}{E_{st}^{(0)} - E^{(0)}} , \]  
\[ C_{8}^{M_{b}} = \sum_{st} \frac{\Omega_{8}^{st}}{E_{st}^{(0)} - E^{(0)}} , \]

and the energy for the unperturbed system is \( E^{(0)} = E_{a}^{(0)} + E_{b}^{(0)} \). Following [12], one can obtain the following expressions for \( \Omega_{6}^{st} \) and \( \Omega_{8}^{st} \) that are in agreement with the formulas in Ref. [22]:

\[ \Omega_{6}^{st} = |\langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle|^{2} \sum_{\lambda} G(1,1,1,\lambda,1,M_{b}) \langle \Psi_{b}(1;\rho)\|T_{1}(\rho)\|\omega_{t}(\lambda;\rho)\rangle|^{2} , \]

\[ \Omega_{8}^{st} = \frac{2}{3} |\langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle|^{2} \sum_{\lambda} G(1,3,1,\lambda,1,M_{b}) \langle \Psi_{b}(1;\rho)\|T_{2}(\rho)\|\omega_{t}(\lambda;\rho)\rangle|^{2} \]

\[ + G_{3}(2,1,1,1,M_{b}) \langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle \langle \Psi_{b}(1;\rho)\|T_{2}(\rho)\|\omega_{t}(\lambda;\rho)\rangle \]

\[ \times \langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle \langle \Psi_{b}(1;\rho)\|T_{2}(\rho)\|\omega_{t}(\lambda;\rho)\rangle \]

\[ + 2 G_{3}(1,2,2,1,M_{b}) \langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle \langle \Psi_{b}(1;\rho)\|T_{2}(\rho)\|\omega_{t}(\lambda;\rho)\rangle \]

\[ + G_{3}(1,2,1,1,M_{b}) \langle \Psi_{a}(\sigma)\|T_{2}(\sigma)\|\chi_{s}(2;\sigma)\rangle \langle \Psi_{b}(1;\rho)\|T_{1}(\rho)\|\omega_{t}(\lambda;\rho)\rangle \]

\[ \times \langle \Psi_{a}(\sigma)\|T_{1}(\sigma)\|\chi_{s}(1;\sigma)\rangle \langle \Psi_{b}(1;\rho)\|T_{2}(\rho)\|\omega_{t}(\lambda;\rho)\rangle \]  

with

\[ G(L, L', L_{a}, L_{t}, L_{b}, M_{b}) = (-1)^{L+L'} \frac{(4\pi)^{2}}{(2L+1)^{2}} (L, L')^{-1/2} \sum_{M_{s}M_{t}} K_{L,L}^{-M_{s}} K_{L,L'}^{-M_{t}} \left( \begin{array}{ccc} L_{b} & L & L_{t} \\ -M_{b} & M_{s} & M_{t} \end{array} \right) \left( \begin{array}{ccc} L_{b} & L' & L_{t} \\ -M_{b} & M_{s} & M_{t} \end{array} \right) , \]

\[ G_{3}(L, L', L_{a}, L_{t}, L_{b}, M_{b}) = (-1)^{L+L_{a}} \frac{(4\pi)^{2}}{(2L_{a}+1)(2L'+1)} (L, L')^{-1/2} \sum_{M_{s}M_{t}} (-1)^{M_{s}+M_{t}} K_{L,L}^{-M_{s}} K_{L,L'}^{M_{t}} \left( \begin{array}{ccc} L_{b} & L & L_{t} \\ -M_{b} & M_{s} & M_{t} \end{array} \right) \left( \begin{array}{ccc} L_{b} & L' & L_{t} \\ -M_{b} & M_{s} & M_{t} \end{array} \right) \]

In Eqs. (54) and (55), the coefficient \( K_{L,L}^{M_{s}} \) is

\[ K_{L,L}^{M_{s}} = \left[ \left( \begin{array}{ccc} L + L' & L + L' \\ L + M & L + M \end{array} \right) \right]^{1/2} , \]

and \((L, L, \ldots) = (2L+1)(2L+1)\ldots\).

### III. RESULTS AND DISCUSSIONS

In this section, we present the results of the calculations of the static electric dipole, quadrupole, and octupole polarizabilities, the second hyperpolarizabilities, and the resonance and dispersion long-range coefficients for the pairs of atoms using the wave functions obtained as described in Sec. [113]. In addition, we give some calculated oscillator strengths and sum rules that might be useful.
A. $^{2}\Sigma$ state: Polarizabilities and hyperpolarizabilities of atoms and dispersion coefficients between two atoms

Table III presents a convergence study for the calculations of the scalar dipole polarizability $\alpha_1$ of lithium with infinite nuclear mass, $^{\infty}$Li, in the ground state. In the table, $N_0$ and $N_F$, respectively, are the sizes of the basis sets for the ground state and for the intermediate states of symmetry $P$. The extrapolation, obtained by assuming that the ratio between two successive differences in $\alpha_1$ stays constant as the sizes of the basis sets become infinitely large, yields the value $164.111(2)$. This is in perfect agreement with the value $164.111(2)$ of Ref. [12], based on calculations up to much smaller values $N_0 = 919$ and $N_F = 1846$, confirming the efficacy of the extrapolation method used in that work. For $^6$Li and $^8$Li, a similar convergence pattern exists.

Calculations on the hyperpolarizability $\gamma_0$, on the other hand, require much larger basis set sizes to achieve accuracies even approaching that achieved for the polarizabilities. In our approach, there is a partial cancellation of significant figures between the sum of the two terms $\frac{1}{2} T(1,0,1)$ and $\frac{1}{2} T(1,2,1)$ in Eq. (31), even though the individual terms are converged to about 4 significant figures. Table III presents the convergence study for calculations of the hyperpolarizability $\gamma_0$ of $^{\infty}$Li in the ground state. At the largest sizes of basis sets in Table III, $\frac{1}{5} T(1,0,1) = -3463.861$ and $\frac{1}{5} T(1,2,1) = 3471.078$, resulting in a loss of about two significant figures when added.

Table III summarizes the final values of the polarizabilities $\alpha_1$, $\alpha_2$, and $\alpha_3$, and the dispersion coefficients $C_6$, $C_8$, and $C_{10}$ for $^{\infty}$Li, $^7$Li, and $^8$Li in their ground states $^{2}\Sigma$. The dispersion coefficients were calculated similarly to those calculated in Ref. [12], but with the treatment of finite nuclear mass. In order to maintain numerical stability, especially in diagonalizing the Hamiltonian for large basis sets, all the calculations were performed using the multiple precision arithmetic QD developed by Bailey et al. [24], which has 64 decimal digits. The finite nuclear mass effect is most significant for $\gamma_0$, as shown in Table III. Fitting the results, we find, roughly, that $\gamma_0 \sim 3060[1 - 1000(1/m_0)]$, where $m_0$ is the nuclear mass and where the coefficient of $1/m_0$ is about 1000 times larger than it is for, say, $\alpha_1$. The effect is numerically significant since, as discussed above, our convergence studies show that at least two digits of the hyperpolarizabilities are accurate. It would be interesting to explore this effect for other systems.

In Table IV we compare our results to some of those from the literature for the polarizabilities $\alpha_1$, $\alpha_2$, and $\alpha_3$ and for the dispersion coefficients $C_6$, $C_8$, and $C_{10}$ of ground state Li atoms. As most of the previously published works have been devoted to $^{\infty}$Li, we list our infinite nuclear mass calculations in Table IV. The most accurate Hylleraas-type calculation prior to the present work is that of Ref. [12], which was obtained using a basis size up to 1846 using methods similar to the present work, extrapolated as discussed previously. An extensive tabulation of over forty results for $\alpha_1$ covering much of the published work from 1959 to 1996 can be found in the review article by King [13] and another tabulation is given in Ref. [12]. Tabulations including $\alpha_2$ and $\alpha_3$ are given in Refs. [12] and [23]. In Table IV we tabulate some theoretical results from between 1996 and the present. The exponentially correlated Gaussian-basis set calculations of Komasa [26] for $\alpha_1$ are in excellent agreement with the present work and they were carried out with a much smaller basis size. There is a slight discrepancy, however, for $\alpha_2$, but Ref. [26] does not provide computational uncertainties. Both $\alpha_1$ and $\alpha_2$ were calculated using semi-empirical model potential-based methods by Cohen and Themelis [27] and by Zhang et al. [16]. Cohen and Themelis [27] used a method dubbed Rydberg-Klein-Rees quantum defect theory (RKR-QDT), which utilized experimental energy levels and it contained some adjustable parameters fixed using the experimentally determined $2p$ state lifetime. The results of Zhang et al. [16] were obtained in the framework of a frozen core Hamiltonian with a semi-empirical polarization potential. Of the two semi-empirical approaches, the RKR-QDT results are in much better agreement with the present work; the results of Zhang et al. for $\alpha_3$ vary from the present work by the same percentage as do their calculations of $\alpha_1$ and $\alpha_2$. Chen and Wang [25] evaluated $\alpha_2$ and $\alpha_3$ for the ground states of lithium-like ions using the full core plus correlation method. The present values lie just outside the lower limit of Chen and Wang’s error bars, but Ref. [25] does not reveal how the uncertainties were obtained.

We can also compare our results to recent relativistic calculations. For $\alpha_1$ generally the effect is to reduce the non-relativistic value by a term of order $(1/137.037)^2$. Derevianko et al. [28] and Porsev and Derevianko [29] calculated $\alpha_1$, $\alpha_2$, and $\alpha_3$, as well as $C_6$, $C_8$, and $C_{10}$ for the ground state of lithium using relativistic many-body perturbation theory (MBPT). Sahoo et al. [18, 30] performed ab initio relativistic coupled-cluster calculations on the dipole and quadrupole polarizabilities, and the dispersion coefficients $C_6$ and $C_8$ of Li. Very recently, Johnson et al. [17] also calculated the polarizabilities of $^7$Li by applying relativistic MPPT. For $\alpha_1$, the results of Refs. [28] and [17] obtained using relativistic MPPT are smaller than our results by the expected factor. The results of Refs. [18, 30] are significantly lower, perhaps due to neglected higher-order effects [18], see Table IV.

For $C_6$, compared to the previous value [12], the uncertainty in the present result has been reduced by a factor of 3. The semi-empirical calculations of Zhang et al. [16] and the relativistic calculations of Refs. [28] and [29] are in good agreement with the present results, though Zhang et al. slightly overestimate the coefficients, as shown in Table IV.

The most precise measurement of $\alpha_1$ was that of Miffre et al. [31] obtained with 0.66% uncertainty using atomic interferometry. It is a factor of three more precise than the earlier measurement of Molof et al. [32]. These values are
included in Table IV.

Currently, however, the experimental accuracy has not reached the stage where finite nuclear mass and relativistic effects in \( \alpha_1 \) can be tested stringently. One can see from Table III that the finite nuclear mass correction to \( \alpha_1 \) for \(^7\)Li is 0.049 a.u., of which 0.038 a.u. comes simply from the mass scaling of the Bohr radius. The remaining part 0.011 a.u. is due to the mass polarization terms \((-1/m_0) \nabla_i \cdot \nabla_j\) in the Hamiltonian Eq. (1), where \( m_0 \) is the mass of the \(^7\)Li nucleus. Furthermore, although the relativistic effect has not been evaluated rigorously, it can be, however, estimated to be \(-0.06\) a.u. based on a relativistic coupled-cluster approach. As for the QED effect, Pachucki and Sapirstein performed a relativistic and QED calculation on the dipole polarizability of helium and found that the QED correction is about a factor of 2.5 smaller than the relativistic correction and is opposite in sign. If we take this reduction factor for the case of lithium, the QED correction is thus estimated to be 0.02 a.u. Hence, the finite nuclear mass, relativistic, and QED corrections cancel out almost entirely, just as in the case of helium. However, a definitive conclusion regarding this cancellation can not be drawn until the calculation of Pachucki and Sapirstein can be extended to the case of Li.

As discussed above, we have found that the hyperpolarizability is extraordinarily sensitive to the finite nuclear mass. In Table V we compare our calculated value of \( \gamma_0 \) with some of the published results, all for \(^\infty\)Li. A more comprehensive table of earlier work is given in Ref. [13]. Pipin and Bishop calculated \( \gamma_0 \) by applying the combined configuration-interaction-Hylleraas method. Their result, with one significant figure, is in good agreement with ours. Kassimi and Thakkar used the coupled-cluster approach, where the reported uncertainty of 10\% in \( \gamma_0 \) was later re-adjusted to 3\%. Laughlin performed a semi-empirical one-electron model potential calculation and found that the final result for \( \gamma_0 \) was highly sensitive to the data used, particularly the value of \( \alpha_1 \). The value from Jaszuński and Rizzo was obtained using a series of multi-configuration SCF wave functions. Finally, Cohen and Themelis computed \( \gamma_0 \) using RKR-QDT. Comparing to our result, the level of accuracy they achieved is about 10\%. The RKR-QDT calculation was sensitive to the potential adopted, as discussed in Ref. [27]. The present methodology has the advantage that no adjustment is required. Once the convergence pattern is established, the extrapolated value should be reliable.

### B. \(^2\)P state: Polarizabilities and hyperpolarizabilities

Table VI shows the convergence of \( \alpha_1 \) and of \( \alpha_1^{(T)} \) calculated for \(^\infty\)Li in the \(^2\)P state, where \( N_S, N_{(pp')}P, \) and \( N_D \) are the sizes of bases for the intermediate states of symmetries \( S, P, \) and \( D \) respectively, 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.

Table VII summarizes the final values of the scalar polarizabilities \( \alpha_1, \alpha_2, \) and \( \alpha_3 \), the tensor dipole polarizability \( \alpha_1^{(T)} \), the scalar hyperpolarizability \( \gamma_0 \), and the tensor hyperpolarizability \( \gamma_2 \) for \(^\infty\)Li, \(^7\)Li, and \(^9\)Li in their \(^2\)P states.

Table VIII is a comparison of the scalar and tensor dipole polarizabilities and hyperpolarizabilities \( \alpha_1, \alpha_1^{(T)}, \gamma_0, \) and \( \gamma_2 \) for the \(^2\)P state of \(^\infty\)Li. In general, our calculations provide significantly more accurate results, particularly, for \( \alpha_1^{(T)} \). A more extensive tabulation of previous results is given in Ref. [27].

It should be mentioned that the intermediate configuration of symmetry \( (pp')P \), which contributes to \( \alpha_1 \) at the level of 0.05\%, was not included in the CI-Hylleraas calculation of Pipin and Bishop. The relativistic results for \( \alpha_1 \) by Wansbeck et al. and by Johnson et al. are the \((2J+1)\)-weighted sums between the \( J = 1/2 \) and \( J = 3/2 \) sub-levels. The results of Johnson et al. are close to ours. In contrast, the results of Wansbeck et al. deviate significantly from ours; for example, the value of \( \alpha_1^{(T)} \) reported by Wansbeck et al. is a factor of 3.6 larger than our calculation.

The uncertainties in the experimental values for \( \alpha_1 \) and \( \alpha_1^{(T)} \) obtained by Hunter et al. and by Windholz et al. are too large to reveal finite nuclear mass and relativistic effects. However, the nonrelativistic calculations of Refs. 42, 43, and the present work, as well as the relativistic calculations of Ref. 17, agree with the experiment of Windholz et al., though in contrast, as was also observed by Johnson et al., the values obtained using RKR-QDT by Cohen and Themelis disagree with the experiment.

For the \( \alpha_2 \) and \( \alpha_3 \) of the \(^2\)P state, the model potential results of Zhang et al. are, respectively, 4104.9 and 3.2135 \times 10^6, which are slightly larger than our results, given in Table VII.

There are no measurements of \( \gamma_0 \) and \( \gamma_2 \) though our calculated values are in almost perfect agreement with, though substantially more accurate than, the semi-empirical results of Cohen and Themelis and the early calculation of Themelis and Nicolaides, obtained by fitting electric-field induced energy shifts calculated using Hartree-Fock wave functions.
C. Long-range interactions between a $2^2S$ atom and a $2^2P$ atom

Table IX lists the final values of $C_3$, $C_6$, and $C_8$ for the system $2^2S - 2^2P$ between two like-atoms $\infty$Li, $^7$Li, and $^6$Li with all possible symmetries.

Table X contains comparisons for $C_3$, $C_6$, and $C_8$ for the system $\infty$Li($2^2S$) - $\infty$Li($2^3P$) with some published results, including the Hylleraas-type calculations of Yan et al. [12], the model potential approach of Marinescu and Dalgarno [46], and the semi-empirical model potential of Zhang et al. [16]. Our ab initio results confirm the more accurate semi-empirical results of Zhang et al. [16], though their results are systematically slightly larger in magnitude than ours. It is also evident that the present results have substantially improved the precision of $C_8$.

D. $3^2D$ state: Polarizabilities and hyperpolarizabilities

Tables XI and XII respectively, list convergence studies for the dipole polarizabilities $\alpha_1$ and $\alpha_1^{(T)}$ and for the hyperpolarizabilities $\gamma_0$, $\gamma_2$, and $\gamma_4$ of $\infty$Li in $3^2D$.

Table XIII is the summary of all the values for the polarizabilities and the hyperpolarizabilities of $\infty$Li, $^7$Li, and $^6$Li in their $3^2D$ states.

Table XIV presents comparisons of our calculated scalar and tensor dipole polarizabilities of $\infty$Li with the existing theoretical and experimental values for the $3^2D$ state. The relative signs and magnitudes (though of limited accuracy) were correctly predicted by Thelemis and Nicolaides [17] using an empirically modeled dipole moment operator and fitting to field-dependent energy shifts. For $\alpha_1$, the percentage difference between the semi-empirical model potential result of Magnier and Aubert-Frécon [18] and ours is about 7%. The values of Ashby and van Wijngaarden [49], obtained using the semi-empirical Coulomb approximation method and the values of Zhang et al. [16] obtained in the framework of a frozen core Hamiltonian with a semi-empirical model potential, are very close to each other, but they differ from our results at the levels of, respectively, 0.9% and 0.8%. The experimental results of Ashby et al. [50] and the relativistic calculations of Wansbeek et al. [18] are expressed in the LSJ coupling scheme, which may be converted into the LS coupling by averaging over the fine structure using a $(2J+1)$-weighted sum [16]. One can see that our result for $\alpha_1$ disagrees with the experiment at the level of 1%. Similarly, for $\alpha_1^{(T)}$, the discrepancy is at the level of 0.5%. It should be pointed out that, at this level of accuracy, the finite nuclear mass and relativistic effects do not account for the discrepancy. The present calculation and that of Wansbeek et al. [18] are ab initio. Their results, which may suffer from an incomplete treatment of correlation effects, differ drastically from our own.

E. Some oscillator strengths and sum rules

As by-products in calculating the dipole polarizabilities, we have obtained the oscillator strengths of $\infty$Li, $^7$Li, and $^6$Li for the transitions of $2^2S - 2^2P$, $2^2P - 3^2D$, and $3^2D - 4^2F$, listed in Table XV. For the case of $\infty$Li, a comparison with some published results is presented in Table XVI including the multiconfiguration Hartree-Fock of Godefroid et al. [15], the semi-empirical model potential of Zhang et al. [16], and the relativistic many-body approach of Johnson [17]. The nonlinear variational parameters in our calculation are optimized only for the lowest energy eigenstate of given symmetry and thus individual oscillator strengths for excited state transitions may not necessarily be of better accuracy than other dedicated calculations. Nevertheless, the present calculations have slightly improved the previous values [20] for the $2^2S - 2^2P$ and $2^2P - 3^2D$ transitions, which were obtained variationally using smaller Hylleraas basis sets up to about 3500 terms. The most accurate results for the $2^2S - 2^2P$ oscillator strength was obtained by Yan et al. [51] using variational trial functions that contained the core and valence electron wave functions in the zeroth order. [Note that for $^7$Li and $^6$Li, the present definition for the oscillator strength Eq. 43 differs from the one adopted in Refs. 20, 51 by a factor of $1 + (3/m_0)$, where $m_0$ is the nuclear mass.]

Finally, we have calculated the oscillator strength sum rule $\sum L \equiv 2\beta_1$, where $\beta_1$ is given in terms of the quantities defined in Sec. 11 in a manner similar to the definition of $\alpha_1$ in Eqs. (37) and (38), as

$$\beta_1 = \sum_{L_a} \beta_1(L_a), \quad (57)$$

where

$$\beta_1(L_a) = \frac{4\pi}{9(2L+1)} \sum_n \frac{|\langle n_0L||T_1||nL_a\rangle|^2}{|E_n(L_a) - E_{n_0}(L)|^2}. \quad (58)$$
The results for $\beta_1$ are given in Table XVII for $^8\text{Li}$, $^7\text{Li}$, and $^6\text{Li}$ in the $2^2S$, $2^2P$, and $3^2D$ states. The result for $^7\text{Li}$ in the $2^2S$ state is in agreement with the value $\beta_1 = 1197$ given by Pipin and Bishop [37].

Another sum rule $S(-1)$ can be related to the interaction potential between an atom and a perfectly conducting wall, see Ref. [53]. A highly accurate value obtained [53] using matrix elements from Ref. [54] is $12.14400408(24)$ and the present work does not give an improvement. The value from Bishop and Pipin [37] is $12.13$.

IV. CONCLUSIONS

In this paper, the nonrelativistic polarizabilities and hyperpolarizabilities have been calculated \textit{ab initio} in a unified manner for the $2^2S$, $2^2P$, and $3^2D$ states of lithium using fully-correlated Hylleraas basis sets. The dispersion coefficients for $\text{Li}(2^2S)$–$\text{Li}(2^2S)$ and $\text{Li}(2^2S)$–$\text{Li}(2^2P)$ have also been evaluated. Furthermore, the finite nuclear mass effects on these properties have been studied for $\text{Li}$ laying the foundation for future work such as investigating relativistic and QED effects on the polarizabilities, especially on the dipole polarizability of the ground state of lithium, using the approach of Pachucki and Sapirstein [36], following the progress on $\text{He}$ [36, 54, 57].

Our results can also be used as a benchmark for other methods that may be developed in future research. For the dipole polarizabilities of lithium in $3^2D$ state, an improved measurement would be important in resolving the existing discrepancy between the experimental values of Ashby \textit{et al.} [50] and the present results.

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TABLE I: Convergence of $\alpha_1$ for the ground state $2^2S$ of $\infty$Li, in atomic units.

| $(N_0, N_P)$ | $\alpha_1$          |
|--------------|----------------------|
| (120,55)     | 163.92934            |
| (256,138)    | 164.03473            |
| (502,306)    | 164.06958            |
| (918,622)    | 164.09123            |
| (1589,1174)  | 164.10058            |
| (2625,2091)  | 164.10695            |
| (4172,3543)  | 164.11023            |
| (6412,5761)  | 164.11154            |
| Extrapolated | 164.112(1)           |

TABLE II: Convergence for the hyperpolarizability of $\infty$Li in the ground state $2^2S$, in atomic units.

| $(N_0,N_S,N_P,N_D)$ | $\gamma_0$ |
|---------------------|-------------|
| (120,120,55,55)    | -3121.470   |
| (256,256,138,138)  | -3119.797   |
| (502,502,306,306)  | -3117.012   |
| (918,918,622,622)  | -3116.318   |
| (1589,1589,1174,1174) | -3117.339 |
| (2625,2625,2091,2091) | -3117.724 |
| (4172,4172,3543,3543) | -3117.563 |
| (6412,6412,5761,5761) | -3117.753 |
| Extrapolated       | 3060(40)    |
TABLE III: Values of the polarizabilities $\alpha_1$, $\alpha_2$, and $\alpha_3$, the hyperpolarizability $\gamma_0$, and the dispersion coefficients $C_6$, $C_8$, and $C_{10}$ for $\infty$Li, $^7$Li, and $^6$Li in their ground states $2^2S$, in atomic units.

| System | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\gamma_0$ | $C_6$ | $C_8$ | $C_{10}$ |
|--------|------------|------------|------------|------------|-------|-------|---------|
| $\infty$Li | 164.112(1) | 1423.263(3) | 39649.29(2) | 83429(1) | 73725(2)×10^2 |
| $^7$Li | 164.161(1) | 1423.415(5) | 39653.72(3) | 83456(5) | 73742(2)×10^2 |
| $^6$Li | 164.169(1) | 1423.439(4) | 39654.46(3) | 83460(5) | 73745(2)×10^2 |

TABLE IV: Comparison of the polarizabilities $\alpha_1$, $\alpha_2$, and $\alpha_3$, and the dispersion coefficients $C_6$, $C_8$, and $C_{10}$ for the ground state $2^2S$ of $\infty$Li, in atomic units. The results from Refs. [28], [29], [30], [18], and [17] were calculated using relativistic methods.

| Reference | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $C_6$ | $C_8$ | $C_{10}$ |
|-----------|------------|------------|------------|-------|-------|---------|
| Yan et al. [12] (1996) | 164.111(2) | 1423.266(5) | 39650.49(8) | 8.34258(42)×10^4 | 7.3721(1)×10^6 |
| Komasa [26] (2001) | 164.11171 | 1423.282 | | | |
| Derevianko et al. [28] (2001) | 164.0(1) | 1389(2) | | | |
| Derevianko et al. [29] (2003) | 1424(4) | 3.957×10^4 | 8.34(4)×10^4 | 7.35×10^6 |
| Chen and Wang [25] (2004) | 1423.48(17) | 39650.96(94) |
| Cohen and Themelis [27] (2005) | 164.14 | 1423.3 | | |
| Zhang et al. [16] (2007) | 164.21 | 1424.4 | 39680 | 1394.6 | 8.3515×10^4 | 7.3811×10^6 |
| Sahoo [30] (2007) | 164.112(1) | 1423.263(3) | 39649.29(2) | 83429(1) | 73725(2)×10^2 |
| Molof et al. [32] (experiment) (1974) | 164.21 | 1424.4 | 39680 | 1394.6 | 8.3515×10^4 | 7.3811×10^6 |
| Miffre et al. [31] (experiment) (2006) | 164.0(3.4) | | | | |

TABLE V: Values of the hyperpolarizability $\gamma_0$ for $\infty$Li in the ground state $2^2S$, in atomic units.

| Reference | $\gamma_0$ |
|-----------|------------|
| Pipin and Bishop [37] (1992) | 3000 |
| Kassini and Thakkar [38, 39] (1994) | 2900(90) |
| Laughlin [40] (1995) | 3930 |
| Jaszuński and Rizzo [41] (1996) | 3450 |
| Cohen and Themelis [27] (2005) | 3390 |
| Present | 3060(40) |

TABLE VI: Convergence of $\alpha_1$ and $\alpha_1^{(T)}$ for $\infty$Li in $2^2P$ state, in atomic units.

| $(N_0,N_2,N_{pp}),(N_D)$ | $\alpha_1(S)$ | $\alpha_1((pp')P)$ | $\alpha_1(D)$ | $\alpha_1$ | $\alpha_1^{(T)}$ |
|---------------------------|--------------|-------------------|-------------|----------|----------|
| (55,120,36,55) | -17.18258 | 0.063063 | 142.61225 | 128.499201 | 2.951062 |
| (138,256,108,138) | -16.258204 | 0.067825 | 142.675018 | 126.484639 | 2.024615 |
| (306,502,264,306) | -15.950171 | 0.069135 | 142.718553 | 128.837517 | 1.712883 |
| (622,918,568,622) | -15.871922 | 0.069501 | 142.729209 | 126.926788 | 1.633752 |
| (1174,1589,1106,1174) | -15.86615 | 0.069591 | 142.734228 | 126.937203 | 1.627988 |
| (2091,2625,2002,2091) | -15.86176 | 0.069641 | 142.735430 | 126.943695 | 1.622654 |
| (3543,4172,3413,3543) | -15.860741 | 0.069646 | 142.736141 | 126.945043 | 1.621953 |
| (5761,6412,3413,5761) | -15.860549 | 0.069648 | 142.736441 | 126.945540 | 1.621729 |
| Extrapolated | | | | | 126.9458(3) | 1.6214(3) |
TABLE VII: Values of the polarizabilities $\alpha_1$, $\alpha_1^{(T)}$, $\alpha_2$, and $\alpha_3$, and the hyperpolarizabilities $\gamma_0$ and $\gamma_2$ for $^{\infty}$Li, $^7$Li, and $^6$Li in $2^2P$ state, in atomic units.

| System | $\alpha_1$ | $\alpha_1^{(T)}$ | $\alpha_2$ | $\alpha_3$ | $\gamma_0$ | $\gamma_2$ |
|--------|------------|-----------------|------------|------------|------------|------------|
| $^{\infty}$Li | 126.9458(3) | 1.6214(3) | 4103.165(5) | 321138(4) | 1.00170(9)×$10^7$ | -6.2234(8)×$10^6$ |
| $^7$Li | 126.9472(5) | 1.6351(2) | 4102.893(4) | 321102(5) | 1.00201(9)×$10^7$ | -6.2252(8)×$10^6$ |
| $^6$Li | 126.9474(5) | 1.6373(3) | 4102.848(4) | 321096(5) | 1.00206(9)×$10^7$ | -6.2255(8)×$10^6$ |

TABLE VIII: Comparison of the scalar and tensor dipole polarizabilities and hyperpolarizabilities for $^{\infty}$Li in $2^2P$ state, in atomic units. The results from [18] and [17] are relativistic.

| Reference | $\alpha_1$ | $\alpha_1^{(T)}$ | $\gamma_0$ | $\gamma_2$ |
|-----------|------------|-----------------|------------|------------|
| Themelis and Nicolaides [45] (1992) | 135.7 | 0.13 | 1.10×$10^7$ | -6.970×$10^6$ |
| Pipin and Bishop [42] (1993) | 126.844 | 1.605 |
| Cohen and Themelis [27] (2005) | 126.4 | 1.73 | 1.002×$10^7$ | -6.21×$10^6$ |
| Zhang et al. [16] (2007) | 126.95 | 1.6627 |
| Wansbeek et al. [18] (2008) | 125.20 | 5.95 |
| Johnson et al. [17] (2008) | 126.990 | 1.59 |
| This work | 126.9458(3) | 1.6214(3) | 1.00170(9)×$10^7$ | -6.2234(8)×$10^6$ |
| Hunter et al. [43] (1991) (experiment) | 126.8(3.4) |
| Windholz et al. [44] (1992) (experiment) | 126.87(36) | 1.64(4) |

TABLE IX: Values of $C_3$, $C_6$, and $C_8$ for $2^2S$–$2^2P$ of $^{\infty}$Li, $^7$Li, and $^6$Li, in atomic units.

| System | $C_3(M_2 = 0)$ | $C_5(M_2 = 0)$ | $C_6(M_2 = 0)$ | $C_8(M_2 = 0)$ |
|--------|----------------|----------------|----------------|----------------|
| $^{\infty}$Li | $\beta = -1$ | $\beta = +1$ |
| $^7$Li | $-11.000221(2)$ | $5.500111(1)$ | $2075.40(3)$ | $1406.68(3)$ | $990895(5)$ | $48564.8(5)$ |
| $^6$Li | $-11.0002125(2)$ | $5.500162(1)$ | $2076.19(7)$ | $1407.20(2)$ | $991104(5)$ | $48566.9(4)$ |

TABLE X: Comparison of $C_3$, $C_6$, and $C_8$ for the system $^{\infty}$Li($2^2S$)–$^{\infty}$Li($2^2P$), in atomic units.

| Reference | $\beta$ | $C_3(M_2 = 0)$ | $C_5(M_2 = \pm 1)$ | $C_6(M_2 = 0)$ | $C_8(M_2 = \pm 1)$ |
|-----------|--------|----------------|-----------------|----------------|----------------|
| Marinescu et al. [46] (1995) | $-1$ | $-11.01$ | $5.503$ | $2066$ | $1401$ | $9.880 \times 10^9$ | $4.756 \times 10^9$ |
| Yan et al. [12] (1996) | $-1$ | $-11.000226(15)$ | $5.5001133(74)$ | $2075.05(5)$ | $1406.08(5)$ |
| Zhang et al. [16] (2007) | $-1$ | $-11.008$ | $5.5041$ | $2076.3$ | $1407.4$ | $9.920 \times 10^5$ | $4.8629 \times 10^4$ |
| This work | $-1$ | $-11.000221(2)$ | $5.500111(1)$ | $2075.40(3)$ | $1406.68(3)$ | $9.90895(5) \times 10^5$ | $4.85648(5) \times 10^4$ |

TABLE XI: Convergence for $\alpha_1$ and $\alpha_1^{(T)}$ of $^{\infty}$Li in $3^2D$ state, in atomic units.
TABLE XII: Convergence for $\gamma_0$, $\gamma_2$, and $\gamma_4$ of $^\infty$Li in $3s^2D$ state, in atomic units.

| $(N_0, N_F, N_{(pd)}, N_{pD})$ | $\alpha_1(P)$ | $\alpha_1((pd)D)$ | $\alpha_1(F)$ | $\alpha_1$($^T_2$) |
|-------------------------------|---------------|--------------------|--------------|----------------|
| (138, 138, 126, 132)         | $-18857.791600$ | 0.059150           | 1916.643488  | $-16941.088962$ | $18310.238324$ |
| (306, 306, 322, 302)         | $-19633.479208$ | 0.062827           | 1916.940725  | $-15016.475656$ | $16385.844685$ |
| (622, 622, 714, 636)         | $-16850.080545$ | 0.063886           | 1917.021571  | $-14932.965089$ | $16302.423983$ |
| (1174, 1174, 1428, 1248)     | $-16845.626886$ | 0.064157           | 1917.026639  | $-14928.536090$ | $16297.969146$ |
| (2091, 2091, 2640, 2307)     | $-16845.378158$ | 0.064226           | 1917.035892  | $-14928.978040$ | $16297.718434$ |
| (3543, 3543, 4587, 4051)     | $-16845.342790$ | 0.064242           | 1917.040003  | $-14928.235545$ | $16297.681317$ |
| (5761, 5761, 4587, 6806)     | $-16845.342870$ | 0.064243           | 1917.043303  | $-14928.235324$ | $16297.680455$ |

TABLE XIII: Values of the polarizabilities $\alpha_1$, $\alpha_1(T)$, $\alpha_2$, and $\alpha_3$, and the hyperpolarizabilities $\gamma_0$, $\gamma_2$, and $\gamma_4$ for $^\infty$Li, $^7$Li, and $^6$Li in $3s^2D$ state, in atomic units.

| System | $\alpha_1$ | $\alpha_1(T)$ | $\alpha_2$ | $\alpha_3$ | $\gamma_0$ | $\gamma_2$ | $\gamma_4$ |
|--------|------------|----------------|------------|------------|-------------|-------------|-------------|
| $^\infty$Li | $-14928.230(5)$ | 16297.675(5) | 158060(10) | $-1.340902(3) \times 10^0$ | $1.647140(5) \times 10^{-12}$ | $-1.717115(5) \times 10^{10}$ | 7.0814(2) $\times 10^{10}$ |
| $^7$Li  | $-14921.330(4)$ | 16291.094(5) | 158070(10) | $-1.339746(5) \times 10^0$ | $1.644875(5) \times 10^{-12}$ | $-1.714740(5) \times 10^{12}$ | 7.0700(3) $\times 10^{10}$ |
| $^6$Li  | $-14920.180(6)$ | 16290.000(5) | 158070(10) | $-1.339554(5) \times 10^0$ | $1.644500(4) \times 10^{-12}$ | $-1.714345(5) \times 10^{12}$ | 7.0680(5) $\times 10^{10}$ |

TABLE XIV: Comparison of the scalar and tensor polarizabilities and hyperpolarizabilities for $^\infty$Li in $3s^2D$ state, in atomic units. The results from [18] are relativistic.

| Reference           | $10^{-4} \alpha_1$ | $10^{-3} \alpha_1(T)$ | $10^{-5} \alpha_2$ | $10^{-8} \alpha_3$ | $10^{-12} \gamma_0$ | $10^{-12} \gamma_2$ | $10^{-10} \gamma_4$ |
|---------------------|---------------------|------------------------|--------------------|---------------------|---------------------|---------------------|---------------------|
| Themelis and Nicolaides [47] (1995) | -2.0468 | 2.1944 | 4.56 | -3.97 | 19.5 |
| Magnier and Aubert-Frécon [48] (2002) | -1.3950 | 1.5324 | 2.000 | 1.643(6) | 1.643(6) | 1.5786 | -1.3548 |
| Ashby and Wijnegaarden [49] (2003) | -1.507 | 1.642 | 1.6414 | 1.6414 | 1.6414 | 1.6414 | 1.6414 | 1.6414 |
| Zhang et al. [16] (2007) | -1.5044 | 1.6414 | 1.5786 | -3.97 | 19.5 |
| Wansbeek et al. [18] (2008) | -1.986 | 2.000 | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) |
| This work | -1.4928230(5) | 1.6297675(5) | 1.58060(10) | $-1.340902(3)$ | $1.647140(5)$ | $-1.717115(5)$ | 7.0814(2) |
| Ashby et al. [50] (2003) (experiment) | -1.513(4) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) | 1.643(6) |

TABLE XV: Values of oscillator strengths of $^\infty$Li, $^7$Li, and $^6$Li.

| System | $2^2S-2^2P$ | $2^2P-3^2D$ | $3^2D-4^2F$ |
|--------|------------|------------|------------|
| $^\infty$Li | 0.7469653(5) | 0.6385685(5) | 1.0153771(5) |
| $^7$Li  | 0.7469614(4) | 0.6385835(5) | 1.0154562(5) |
| $^6$Li  | 0.7469623(4) | 0.6385858(4) | 1.0154695(5) |

TABLE XVI: Comparison of oscillator strengths of $^\infty$Li.
| System | $\beta_1(2^2S)$ | $\beta_1(2^2P)$ | $\beta_1(3^2D)$ |
|--------|----------------|----------------|----------------|
| $^\infty$Li | 1196.9696(2) | 1614.68(2) | 5202428(1) |
| $^7$Li | 1197.4886(2) | 1614.99(2) | 5197637(1) |
| $^6$Li | 1197.5750(2) | 1615.04(2) | 5196841(1) |

**APPENDIX A: STARK EFFECT**

The Hamiltonian for an atom in a uniform electric field $E = E \hat{z}$ is given by

$$H = H_0 + H' = H_0 - E \cdot P,$$

where $H_0$ is the unperturbed Hamiltonian and $P$ is the electric dipole moment of the atom:

$$P = \sum_i q_i \mathbf{R}_i.$$

In the above, $q_i$ is the charge of $i$th particle, $\mathbf{R}_i$ is its position vector relative to a laboratory frame, and the summation is over all charged particles inside the atom, including the nucleus. Under the perturbation $H'$, the energy eigenvalue and eigenfunction of $H$ can be written in the form

$$E = E_0 + \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 + \cdots,$$

$$\Psi = \Psi_0 + \Psi_1 + \Psi_2 + \cdots,$$

where

$$H_0 \Psi_0 = E_0 \Psi_0$$

is the zero-order equation, and $\Delta E_i$ and $\Psi_i$ are the corresponding $i$th-order corrections. According to the perturbation theory, the energy corrections can be expressed as

$$\Delta E_1 = \langle \Psi_0 | H' | \Psi_0 \rangle,$$

$$\Delta E_2 = \langle \Psi_0 | H' | \Psi_1 \rangle,$$

$$\Delta E_3 = \langle \Psi_1 | H' | \Psi_1 \rangle - \Delta E_1 \langle \Psi_1 | \Psi_1 \rangle,$$

$$\Delta E_4 = \langle \Psi_1 | H' | \Psi_2 \rangle - \Delta E_2 \langle \Psi_1 | \Psi_1 \rangle - \Delta E_1 \langle \Psi_1 | \Psi_2 \rangle.$$

If the state of interest $\Psi_0$ has a fixed parity, as in the case of this work, $\Delta E_1 = 0$ due to the parity selection rule. $\Psi_1$ and $\Psi_2$ can be expanded in terms of their spectral representations:

$$| \Psi_1 \rangle = \sum_n \frac{\langle n | H' | 0 \rangle}{E_0 - E_n} | n \rangle,$$

$$| \Psi_2 \rangle = \sum_{nk} \frac{\langle n | H' | k \rangle \langle k | H' | 0 \rangle}{(E_0 - E_n)(E_0 - E_k)} | n \rangle.$$
where $|0\rangle \equiv |\Psi_0\rangle$ and $\{E_n, |n\rangle\}$ is a complete set of $H_0$, including the continuum. Inserting Eq. (A10) into Eq. (A8) yields $\Delta E_3 = 0$, also due to the parity consideration. Thus,

$$\Delta E_2 = \sum_n \frac{\langle 0|H'|n\rangle \langle n|H'|0\rangle}{E_0 - E_n}, \quad (A12)$$

$$\Delta E_4 = \sum_{kmn} \left[ \frac{1}{(E_0 - E_m)(E_0 - E_n)(E_0 - E_k)} - \delta(n,0) \frac{1}{(E_0 - E_m)(E_0 - E_k)^2} \right] \times \langle 0|H'|m\rangle \langle m|H'|n\rangle \langle n|H'|k\rangle \langle k|H'|0\rangle. \quad (A13)$$

1. $\Delta E_2$

Let us first consider the operator $H'|n\rangle \langle n|H'$ in Eq. (A12). Using spherical tensor operator technique, we have the following decomposition

$$H'|n\rangle \langle n|H' = \sum_{Kq} (-1)^{K+q}[P^{(1)} \otimes \lambda_n P^{(1)}]_{q}^{(K)}[\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]_{-q}^{(K)}, \quad (A14)$$

where $\lambda \equiv |n\rangle |n\rangle$. Since $\mathcal{E}$ is along the $z$-axis, only the $q = 0$ component survives in the above equation. Thus,

$$H'|n\rangle \langle n|H' = \sum_K (-1)^K \sqrt{2K + 1} \sum_{q_1 q_2} \left( \begin{array}{ccc} 1 & 1 & K \\ q_1 & q_2 & 0 \end{array} \right) P_{q_1}^{(1)} \lambda_n P_{q_2}^{(1)} \mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)} \mid_{0}^{(K)}. \quad (A15)$$

After substituting the Eq (A15) into Eq (A12), one has

$$\Delta E_2 = \sum_{nK} (-1)^K \sqrt{2K + 1} \sum_{q_1 q_2} \left( \begin{array}{ccc} 1 & 1 & K \\ q_1 & q_2 & 0 \end{array} \right) \frac{\langle 0|P_{q_1}^{(1)}|n\rangle \langle n|P_{q_2}^{(1)}|0\rangle}{E_0 - E_n} \mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)} \mid_{0}^{(K)} \times \langle 0|H'|n\rangle \langle n|H'|0\rangle, \quad (A16)$$

To be specific, let us write out explicitly the angular momentum quantum numbers in the initial and intermediate states:

$$|0\rangle = |n_0LM\rangle, \quad (A17)$$

$$|n\rangle = |nLaMa\rangle, \quad (A18)$$

where $n_0$ and $n$ are the corresponding principal quantum numbers. Then, the summation over $n$ in Eq (A16) actually means the summation over $\{n, L_a, M_a\}$. By applying the Wigner-Eckart theorem for the irreducible tensor operator $P^{(1)}_L$, one can recast Eq (A16) into the following form

$$\Delta E_2 = \sum_{nLaK} (-1)^K \sqrt{2K + 1} \frac{\langle n_0L||P^{(1)}||nLa\rangle \langle nLa||P^{(1)}||n_0L\rangle}{E_{n_0}(L) - E_n(L_a)} \mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)} \mid_{0}^{(K)} A, \quad (A19)$$

where $E_{n_0}(L)$ and $E_n(L_a)$ stand for $E_0$ and $E_n$ respectively in Eq. (A16), and

$$A = \sum_{M_a q_1 q_2} (-1)^{L - M + L_a - M_a} \left( \begin{array}{ccc} L & 1 & L \\ -M & q_1 & M_a \end{array} \right) \left( \begin{array}{ccc} L_a & 1 & L \\ -M_a & q_2 & M \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K \\ q_1 & q_2 & 0 \end{array} \right). \quad (A20)$$

The quantity $A$ can be simplified by using the standard graphical method of dealing with angular momentum [58],

$$A = (-1)^{L-M} \left( \begin{array}{ccc} L & L & K \\ -M & M & 0 \end{array} \right) \left\{ \begin{array}{ccc} 1 & 1 & K \\ L & L & L_a \end{array} \right\}, \quad (A21)$$

provided $K$ is an integer, and note that

$$[\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]_{0}^{(K)} = \sqrt{2K + 1} \sum_{q_1 q_2} \left( \begin{array}{ccc} 1 & 1 & K \\ q_1 & q_2 & 0 \end{array} \right) \mathcal{E}_{q_1}^{(1)} \mathcal{E}_{q_2}^{(1)} = \sqrt{2K + 1} \left( \begin{array}{ccc} 1 & 1 & K \\ 0 & 0 & 0 \end{array} \right) \mathcal{E}^2. \quad (A22)$$
Therefore, the second-order correction can finally be written

\[ \Delta E_2 = -\varepsilon^2 \sum_{nL_a} \frac{\langle n_0 L \| P^{(1)} \| nL_a \rangle \langle nL_a \| P^{(1)} \| n_0 L \rangle}{E_n(L_a) - E_{n_0}(L)} \times \sum_K (2K + 1)(-1)^{L-M} \left( \begin{array}{ccc} 1 & 1 & K \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L & L & K \\ -M & M & 0 \end{array} \right) \left\{ \begin{array}{ccc} 1 & 1 & K \\ L & L & L_a \end{array} \right\} . \]

(A23)

Since

\[ (-1)^{L-M} \left( \begin{array}{ccc} L & L & 0 \\ -M & M & 0 \end{array} \right) = (-1)^{2L} \frac{1}{\sqrt{2L+1}} , \]

\[ (-1)^{L-M} \left( \begin{array}{ccc} L & L & 2 \\ -M & M & 0 \end{array} \right) = (-1)^{2L} \frac{3M^2 - L(L+1)}{(2L+3)(L+1)(2L+1)(2L-1)} , \]

(L ≥ 1 , )

and also 58

\[ P^{(1)}_{\mu} = \sqrt{\frac{4\pi}{3}} \sum_i q_i R_i Y_{1\mu}(\hat{R}_i) , \]

(A26)

\[ \langle nL_a \| P^{(1)} \| n_0 L \rangle = (-1)^{L-L_a} \langle n_0 L \| P^{(1)} \| nL_a \rangle^* , \]

(A27)

the second-order energy correction can finally be expressed in the form

\[ \Delta E_2 = -\varepsilon^2 \left( \alpha_1 + \alpha_1^{(T)} g_2(L, M) \right) . \]

(A28)

In the above, \( g_2(L, M) \) is the only \( M \)-dependent part:

\[ g_2(L, M) = \begin{cases} 0 , & \text{if } L = 0 , \frac{1}{2} \\ \frac{3M^2 - L(L+1)}{L(2L-1)} , & \text{otherwise} \end{cases} \]

(A29)

and \( \alpha_1 \) and \( \alpha_1^{(T)} \) are, respectively, the scalar and tensor dipole polarizabilities

\[ \alpha_1 = \sum_{L_a} \alpha_1(L_a) , \]

(A30)

\[ \alpha_1^{(T)} = \sum_{L_a} W(L, L_a) \alpha_1(L_a) , \]

(A31)

where

\[ \alpha_1(L_a) = \frac{8\pi}{9(2L+1)} \sum_n \frac{| \langle n_0 L \| T_1 \| nL_a \rangle |^2}{E_n(L_a) - E_{n_0}(L)} , \]

(A32)

with \( T_1 = \sum q_i R_i Y_{10}(\hat{R}_i) \), and

\[ W(L, L_a) = (-1)^{L+L_a} \sqrt{\frac{30(2L+1)L(2L-1)}{(2L+3)(L+1)}} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L & L & L_a \end{array} \right\} . \]

(A33)

2. \( \Delta E_4 \)

According to Eq. [A15], the fourth-order energy correction of Eq. [A13] can be written as

\[ \Delta E_4 = \sum_{k,m,n} t(k,m,n) \sum_{K_1,K_2} (-1)^{K_1+K_2} (K_1, K_2)^{1/2} \sum_{q_1,q_2,q_3} \left( \begin{array}{ccc} 1 & 1 & K_1 \\ q_1 & q_2 & 0 \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K_2 \\ q_3 & q_4 & 0 \end{array} \right) \times \langle 0 \| P^{(1)}_{q_1} P^{(1)}_{q_2} \langle nL_a \| P^{(1)}_{q_3} P^{(1)}_{q_4} \| 0 \rangle |E^{(1)} \otimes E^{(1)} \rangle_{K_1} |E^{(1)} \otimes E^{(1)} \rangle_{K_2} , \]

\[ \times \left( \langle 0 \| P^{(1)}_{q_1} P^{(1)}_{q_2} \langle nL_a \| P^{(1)}_{q_3} P^{(1)}_{q_4} \| 0 \rangle |E^{(1)} \otimes E^{(1)} \rangle_{K_1} |E^{(1)} \otimes E^{(1)} \rangle_{K_2} , \right. \]
where the notation \((a,b) = (2a+1)(2b+1)\),

\[
t(k, m, n) = \frac{1}{(E_0 - E_m)(E_0 - E_n)(E_0 - E_k)} - \frac{1}{(E_0 - E_m)(E_0 - E_k)^2},
\]

and \(\lambda_m = |m\rangle\langle m|, \text{ etc.}\). Writing out the all angular momentum quantum numbers explicitly

\[
|0\rangle = |n_0LM\rangle, \quad (A36)
\]
\[
|m\rangle = |mL_aM_a\rangle, \quad (A37)
\]
\[
|n\rangle = |nL_bM_b\rangle, \quad (A38)
\]
\[
|k\rangle = |kL_cM_c\rangle, \quad (A39)
\]

and applying the Wigner-Eckart theorem, we have

\[
\Delta E_4 = \sum_{k,m,n} \sum_{L_aL_bL_c} t(k, m, n) \sum_{K_1K_2} (-1)^{K_1+K_2}(K_1, K_2)^{1/2}[\mathcal{E}(1) \otimes \mathcal{E}(1)]_0^{(K_1)}[\mathcal{E}(1) \otimes \mathcal{E}(1)]_0^{(K_2)}
\]
\[
\times \langle n_0L\|P(1\|mL_a\rangle \langle mL_a\|P(1\|nL_b\rangle \langle nL_b\|P(1\|kL_c\rangle \langle kL_c\|P(1\|n_0L) \rangle B, \quad (A40)
\]

where \(B\) (which contains all the angular coefficients) is

\[
B = \sum_{q_1q_2q_3q_4} \sum_{M_aM_bM_c} (-1)^{L-M+L_a-M_a+L_b-M_b+L_c-M_c} \left( \begin{array}{ccc} 1 & 1 & K_1 \\ q_1 & q_2 & 0 \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K_2 \\ q_3 & q_4 & 0 \end{array} \right) \left( \begin{array}{ccc} L & 1 & L_a \\ -M & q_1 & M_a \end{array} \right) \times \left( \begin{array}{ccc} L_a & 1 & L_b \\ -M_a & q_2 & M_b \end{array} \right) \left( \begin{array}{ccc} L_b & 1 & L_c \\ -M_b & q_3 & M_c \end{array} \right) \left( \begin{array}{ccc} L_c & 1 & L \\ -M_c & q_4 & M \end{array} \right), \quad (A41)
\]

Using the graphical method, \(B\) can be simplified into

\[
B = (-1)^{L-M} \left( \begin{array}{ccc} 1 & 1 & K_1 \\ L & L_b & L_a \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K_2 \\ L & L_c & L_b \end{array} \right) \sum_\lambda (2\lambda + 1) \left( \begin{array}{ccc} K_1 & K_2 & \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L & 1 & K_1 \\ -M & M & 0 \end{array} \right) \left( \begin{array}{ccc} K_2 & K_1 & \lambda \\ L & L_b & L_b \end{array} \right), \quad (A42)
\]

provided \(K_1\) and \(K_2\) are integers. From Eqs. (A22), (A20), and (A27), one can further write Eq. (A40) in the form

\[
\Delta E_4 = -\mathcal{E}^4 \left( \frac{4\pi}{3} \right)^2 \sum_{L_aL_bL_c} T(L_a, L_b, L_c) \sum_\lambda (-1)^{L-M} \left( \begin{array}{ccc} L & L & \lambda \\ -M & M & 0 \end{array} \right) \sum_{K_1K_2} (\lambda, K_1, K_2) \left( \begin{array}{ccc} 1 & 1 & K_1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K_2 \\ 0 & 0 & 0 \end{array} \right), \quad (A43)
\]

where

\[
T(L_a, L_b, L_c) = \sum_{k,m} \frac{\langle n_0L\|T_1\|mL_a\rangle \langle mL_a\|T_1\|nL_b\rangle \langle nL_b\|T_1\|kL_c\rangle \langle kL_c\|T_1\|n_0L \rangle}{[E_k(L_c) - E_{n_0}(L)][E_m(L_a) - E_{n_0}(L)][E_n(L_b) - E_{n_0}(L)]} - \delta(L_b, L) (-1)^{2L-L_a-L_c} \sum_m \frac{|\langle n_0L\|T_1\|mL_a\rangle|^2}{[E_m(L_a) - E_{n_0}(L)]} \sum_k \frac{|\langle n_0L\|T_1\|kL_c\rangle|^2}{[E_k(L_c) - E_{n_0}(L)]^2}. \quad (A44)
\]

According to the property of 3j symbol, the possible values for \(\lambda\) are 0, 2, and 4. Also,

\[
(-1)^{L-M} \left( \begin{array}{ccc} L & L & 4 \\ -M & M & 0 \end{array} \right) = -\frac{2(-1)^L[3(5M^2 - L^2 - 2L)(5M^2 + 1 - L^2) - 10M^2(4M^2 - 1)]}{\sqrt{(2L + 5)(2L + 4)(2L + 3)(2L + 2)(2L + 1)(2L)(2L - 1)(2L - 2)(2L - 3)}} \quad L \geq 2. \quad (A45)
\]

Together with Eqs. (A23) and (A22), the fourth-order correction can finally be expressed in the form

\[
\Delta E_4 = -\frac{\mathcal{E}^4}{24} (\gamma_0 + \gamma_2 g_2(L, M)) + \gamma_4 g_4(L, M)), \quad (A46)
\]
where $g_2(L, M)$ is defined in Eq. (A29), and $g_4(L, M)$ is given by

$$
g_4(L, M) = \begin{cases} 
0, & \text{if } L \leq \frac{3}{2}, \\
\frac{3(5M^2 - L^2) - 2L(5M^2 + 1 - L^2) - 10M^2(4M^2 - 1)}{L(2L - 1)(2L - 2)(2L - 3)}, & \text{otherwise}
\end{cases} \quad (A47)
$$

In Eq. (A46), $\gamma_0$ is the scalar hyperpolarizability, and $\gamma_2$ and $\gamma_4$ are the tensor hyperpolarizabilities, which can be written as

$$
\gamma_0 = (-1)^{2L} \frac{128\pi^2}{3} \frac{1}{\sqrt{2L + 1}} \sum_{L_a L_b L_c} G_0(L, L_a, L_b, L_c) T(L_a, L_b, L_c), \quad (A48)
$$

$$
\gamma_2 = (-1)^{2L} \frac{128\pi^2}{3} \sqrt{\frac{L(2L - 1)}{(2L + 3)(L + 1)(2L + 1)}} \sum_{L_a L_b L_c} G_2(L, L_a, L_b, L_c) T(L_a, L_b, L_c), \quad (A49)
$$

$$
\gamma_4 = (-1)^{2L} \frac{128\pi^2}{3} \sqrt{\frac{L(2L - 1)(L - 1)(2L - 3)}{(2L + 5)(L + 2)(2L + 3)(L + 1)(2L + 1)}} \sum_{L_a L_b L_c} G_4(L, L_a, L_b, L_c) T(L_a, L_b, L_c), \quad (A50)
$$

where

$$
G_{\Lambda}(L, L_a, L_b, L_c) = \sum_{K_1, K_2} (A, K_1, K_2) \begin{pmatrix} 1 & 1 & K_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & K_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & K_1 \\ L & L & L_a \end{pmatrix} \begin{pmatrix} 1 & 1 & K_2 \\ L & L_b & L_c \end{pmatrix}. \quad (A51)
$$