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Nonrelativistic *ab initio* calculations for 2 ^2S, 2 ^2P, and 3 ^2D lithium isotopes: Applications to polarizabilities and dispersion interactions

Li-Yan Tang,[1,2] Zong-Chao Yan,[3,4] Ting-Yun Shi,[1] and James F. Babb[5]

[1]*State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*
[3]*Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*
[4]*Center for Theoretical Atomic and Molecular Physics, the Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080, China*
[5]*Harvard-Smithsonian Center for Astrophysics, ITAMP, Cambridge, Massachusetts 02138, USA*

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The electric dipole polarizabilities and hyperpolarizabilities for the lithium isotopes ^{6}Li and ^{7}Li in the ground state 2 ^2S and the excited states 2 ^2P and 3 ^2D, as well as the leading resonance and dispersion long-range coefficients for the Li(2 ^2S)-Li(2 ^2S) and Li(2 ^2S)-Li(2 ^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 2 ^2S state is sensitive to the isotopic mass due to a near cancellation between two terms. For the 3 ^2D state polarizability tensor, the calculated components disagree with those measured in the sole experiment and with those calculated semiempirically.

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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 [1], ultracold atom-atom scattering [2,3] and Feshbach resonance analyses [4,5], photoassociation spectroscopy [6,7], atom-molecule scattering [8], and three-atom inelastic collisional loss studies [9]. 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 [10,11].

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 [14] and other calculations [15], semiempirical methods [16], and relativistic approaches [17–19]. 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 2 ^2P and 3 ^2D 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 [12] for the 2 ^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 the 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 [23] in a general form for $n+1$-charged particles. It was applied to generate the Hamiltonian and transition operators for H_2^+ in Ref. [23] and for He in Ref. [22].

We directly follow the expressions given in Eqs. (20)–(26) of Ref. [23], where the particles are labeled by the index $i=0,\dots,n$. We make the replacement $n=3$, identify particle 0 with the nucleus of mass m_0, identify the particles $i=1$, 2, and 3 with the electrons, so that $m_1=m_2=m_3=m$, where m is the electron mass, to obtain the Hamiltonian expressed in the center-of-mass frame describing the internal motion of the Li atom,

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

where $\mathbf{r}_i$ is the position vector of electron i from the nucleus, and $\mu = mm_0/(m+m_0)$ 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^ℓ-pole transition operator is

$$T_\ell = \sum_{i=0}^{3} q_i R_i^\ell Y_{\ell 0}(\hat{\mathbf{R}}_i), \tag{2}$$

where $\mathbf{R}_i$, $i=0,\ldots,3$, 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

$$\mathbf{R}_i = \sum_{j=1}^{3}\epsilon_{ij}\mathbf{r}_j, \tag{3}$$

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_ℓ 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_ℓ with ℓ up to 3 have the following explicit forms:

$$T_1 = \sum_{j=1}^{3}\left(\sum_{i=0}^{3} q_i\epsilon_{ij}\right) r_j Y_{10}(\hat{\mathbf{r}}_j), \tag{4}$$

$$T_2 = \sum_{j=1}^{3}\left(\sum_{i=0}^{3} q_i\epsilon_{ij}^2\right) r_j^2 Y_{20}(\hat{\mathbf{r}}_j) + \sqrt{\frac{15}{2\pi}}\sum_{\{j,k\}}\left(\sum_{i=0}^{3} q_i\epsilon_{ij}\epsilon_{ik}\right) r_j r_k(\hat{\mathbf{r}}_j\otimes\hat{\mathbf{r}}_k)_0^{(2)}, \tag{5}$$

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

$$\begin{aligned} T_3 = {} & \sum_{j=1}^{3}\left(\sum_{i=0}^{3} q_i\epsilon_{ij}^3\right) r_j^3 Y_{30}(\hat{\mathbf{r}}_j) \\ & + 3\sqrt{\frac{35}{8\pi}}\sum_{\substack{j,k=1\\ j\neq k}}^{3}\left(\sum_{i=0}^{3} q_i\epsilon_{ij}^2\epsilon_{ik}\right) r_j^2 r_k((\hat{\mathbf{r}}_j\otimes\hat{\mathbf{r}}_j)^{(2)}\otimes\hat{\mathbf{r}}_k)_0^{(3)} \\ & + 6\sqrt{\frac{35}{8\pi}}\left(\sum_{i=0}^{3} q_i\epsilon_{i1}\epsilon_{i2}\epsilon_{i3}\right) r_1 r_2 r_3((\hat{\mathbf{r}}_1\otimes\hat{\mathbf{r}}_2)^{(2)}\otimes\hat{\mathbf{r}}_3)_0^{(3)}. \end{aligned} \tag{6}$$

For a neutral system, the finite mass effect enters into the transition operator T_ℓ 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

$$\sum_{i=0}^{3} q_i\epsilon_{ij}^3 = q_j - 3q_j\left(\frac{m_j}{M_T}\right) + 3q_j\left(\frac{m_j}{M_T}\right)^2, \tag{7}$$

$$\sum_{i=0}^{3} q_i\epsilon_{ij}^2\epsilon_{ik} = -q_j\left(\frac{m_k}{M_T}\right) + 2q_j\left(\frac{m_j}{M_T}\right)\left(\frac{m_k}{M_T}\right) + q_k\left(\frac{m_j}{M_T}\right)^2, \tag{8}$$

$$\sum_{i=0}^{3} q_i\epsilon_{i1}\epsilon_{i2}\epsilon_{i3} = q_1\left(\frac{m_2}{M_T}\right)\left(\frac{m_3}{M_T}\right) + q_2\left(\frac{m_3}{M_T}\right)\left(\frac{m_1}{M_T}\right) + q_3\left(\frac{m_1}{M_T}\right)\left(\frac{m_2}{M_T}\right). \tag{9}$$

For an atomic system of infinite nuclear mass, all the coefficients are zero except for those of $r_j^\ell Y_{\ell 0}(\hat{\mathbf{r}}_j)$, 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

$$H_0\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = E_0\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3), \tag{10}$$

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

$$\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}e^{-\alpha r_1-\beta r_2-\gamma r_3}\mathcal{Y}_{(\ell_1\ell_2)\ell_{12},\ell_3}^{LM_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)\chi(1,2,3), \tag{11}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the interelectronic separation, $\mathcal{Y}_{(\ell_1\ell_2)\ell_{12},\ell_3}^{LM_L}$ is a vector-coupled product of spherical harmonics to form an eigenstate of the total angular momentum L and component M_L, which can be written in the form

$$\mathcal{Y}_{(\ell_1\ell_2)\ell_{12},\ell_3}^{LM_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3) = \sum_{\text{all } m_i}\langle\ell_1 m_1;\ell_2 m_2|\ell_1\ell_2;\ell_{12}m_{12}\rangle\langle\ell_{12}m_{12};\ell_3 m_3|\ell_{12}\ell_3;LM_L\rangle Y_{\ell_1 m_1}(\hat{\mathbf{r}}_1)Y_{\ell_2 m_2}(\hat{\mathbf{r}}_2)Y_{\ell_3 m_3}(\hat{\mathbf{r}}_3), \tag{12}$$

and $\chi(1,2,3)$ is the three-electron-spin-1/2 function. The variational wave function Ψ_0 is a linear combination of basis functions ϕ antisymmetrized. The procedures followed are similar to those described in Ref. [20]. With some truncations to avoid the potential numerical linear dependence, all terms in Eq. (11) are included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega \ , \tag{13}$$

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

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} Y^*_{\ell_1' m_1'}(\hat{\mathbf{r}}_1) Y^*_{\ell_2' m_2'}(\hat{\mathbf{r}}_2) Y^*_{\ell_3' m_3'}(\hat{\mathbf{r}}_3) Y_{\ell_1 m_1}(\hat{\mathbf{r}}_1) Y_{\ell_2 m_2}(\hat{\mathbf{r}}_2) Y_{\ell_3 m_3}(\hat{\mathbf{r}}_3) \tag{14}$$

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 $\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{z}}$. The initial state is assumed to be a parity eigenstate and is written as $|0\rangle \equiv |n_0 LM\rangle$, 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 $\mathcal{E}$ can be expressed in the form

$$\Delta E = \Delta E_2 + \Delta E_4 \ , \tag{15}$$

where ΔE_2 and ΔE_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 ΔE_2 and ΔE_4 is given in the Appendix. The final expression for ΔE_2 is

$$\Delta E_2 = -\frac{\mathcal{E}^2}{2}[\alpha_1 + \alpha_1^{(T)} g_2(L,M)], \tag{16}$$

where $g_2(L,M)$ is the only M-dependent part, defined in the Appendix by Eq. (A29), and α_1 and $\alpha_1^{(T)}$ are, respectively, the scalar and tensor dipole polarizabilities. The polarizabilities α_1 and $\alpha_1^{(T)}$ can be expressed further in terms of the reduced matrix elements of the dipole transition operator:

$$\alpha_1 = \sum_{L_a} \alpha_1(L_a), \tag{17}$$

$$\alpha_1^{(T)} = \sum_{L_a} W(L,L_a)\alpha_1(L_a), \tag{18}$$

where

$$\alpha_1(L_a) = \frac{8\pi}{9(2L+1)} \sum_n \frac{|\langle n_0 L \| T_1 \| n L_a \rangle|^2}{E_n(L_a) - E_{n_0}(L)}, \tag{19}$$

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

$$W(L,L_a) = (-1)^{L+L_a} \sqrt{\frac{30(2L+1)L(2L-1)}{(2L+3)(L+1)}} \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_a \end{Bmatrix}. \tag{20}$$

In the above, the set of energies and wave functions $\{E_n(L_a), |nL_a M_a\rangle\}$ corresponds 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 $L=0$,

$$\alpha_1 = \alpha_1(P) \ , \tag{21}$$

$$\alpha_1^{(T)} = 0, \tag{22}$$

for $L=1$,

$$\alpha_1 = \alpha_1(S) + \alpha_1(P) + \alpha_1(D), \tag{23}$$

$$\alpha_1^{(T)} = -\alpha_1(S) + \frac{1}{2}\alpha_1(P) - \frac{1}{10}\alpha_1(D), \tag{24}$$

and for $L=2$,

$$\alpha_1 = \alpha_1(P) + \alpha_1(D) + \alpha_1(F), \tag{25}$$

$$\alpha_1^{(T)} = -\alpha_1(P) + \alpha_1(D) - \frac{2}{7}\alpha_1(F). \tag{26}$$

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

$$\Delta E_4 = -\frac{\mathcal{E}^4}{24}[\gamma_0 + \gamma_2 g_2(L,M) + \gamma_4 g_4(L,M)], \tag{27}$$

where $g_4(L,M)$ is given by Eq. (A47) in the Appendix. In Eq. (27), γ_0 is the scalar second hyperpolarizability and γ_2 and γ_4 are the tensor second hyperpolarizabilities, which can be written as

$$\gamma_0 = (-1)^{2L} \frac{128\pi^2}{3} \frac{1}{\sqrt{2L+1}} \sum_{L_a L_b L_c} \mathcal{G}_0(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{28}$$

$$\gamma_2 = (-1)^{2L} \frac{128\pi^2}{3} \sqrt{\frac{L(2L-1)}{(2L+3)(L+1)(2L+1)}} \times \sum_{L_a L_b L_c} \mathcal{G}_2(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{29}$$

$$\gamma_4 = (-1)^{2L}\frac{128\pi^2}{3}\sqrt{\frac{L(2L-1)(L-1)(2L-3)}{(2L+5)(L+2)(2L+3)(L+1)(2L+1)}} \times \sum_{L_aL_bL_c}\mathcal{G}_4(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{30}$$

where $\mathcal{T}(L_a,L_b,L_c)$ and $\mathcal{G}_\Lambda(L,L_a,L_b,L_c)$, respectively, are defined in the Appendix by Eqs. (A44) and (A51). In particular, for the case $L=0$, we only need to consider

$$\gamma_0 = \frac{128\pi^2}{3}\left[\frac{1}{9}\mathcal{T}(1,0,1) + \frac{2}{45}\mathcal{T}(1,2,1)\right]. \tag{31}$$

[Note that the case $L_b=1$ does not enter in Eq. (31). The first 3-j symbol in Eq. (A51) requires $K_1=0$ or 2 and since $L=0$ here, the first 6-j symbol requires $L_b=K_1$; therefore, $L_b=0$ or 2.] For the case $L=1$, we have

$$\begin{aligned}\gamma_0 = \frac{128\pi^2}{3}\Bigg[&\frac{1}{27}\mathcal{T}(0,1,0) + \frac{2}{135}\mathcal{T}(0,1,2) + \frac{1}{54}\mathcal{T}(1,1,1)\\ &- \frac{1}{90}\mathcal{T}(1,1,2) - \frac{1}{90}\mathcal{T}(1,2,1) - \frac{\sqrt{5}}{450}\mathcal{T}(1,2,2)\\ &+ \frac{2}{135}\mathcal{T}(2,1,0) - \frac{1}{90}\mathcal{T}(2,1,1) + \frac{17}{1350}\mathcal{T}(2,1,2)\\ &- \frac{\sqrt{5}}{450}\mathcal{T}(2,2,1) - \frac{1}{450}\mathcal{T}(2,2,2) + \frac{2}{225}\mathcal{T}(2,3,2)\Bigg],\end{aligned} \tag{32}$$

$$\begin{aligned}\gamma_2 = \frac{128\pi^2}{3}\Bigg[&-\frac{1}{27}\mathcal{T}(0,1,0) - \frac{2}{135}\mathcal{T}(0,1,2) + \frac{1}{108}\mathcal{T}(1,1,1)\\ &- \frac{1}{180}\mathcal{T}(1,1,2) - \frac{1}{180}\mathcal{T}(1,2,1) - \frac{\sqrt{5}}{900}\mathcal{T}(1,2,2)\\ &- \frac{2}{135}\mathcal{T}(2,1,0) - \frac{1}{180}\mathcal{T}(2,1,1) - \frac{7}{2700}\mathcal{T}(2,1,2)\\ &- \frac{\sqrt{5}}{900}\mathcal{T}(2,2,1) - \frac{1}{900}\mathcal{T}(2,2,2) - \frac{2}{1575}\mathcal{T}(2,3,2)\Bigg],\end{aligned} \tag{33}$$

and for $L=2$, we have

$$\begin{aligned}\gamma_0 = \frac{128\pi^2}{3}\frac{1}{15750}\{&[140\mathcal{T}(1,0,1) + 119\mathcal{T}(1,2,1)\\ &+ 84\mathcal{T}(1,2,3) + 84\mathcal{T}(3,2,1) + 74\mathcal{T}(3,2,3) + 60\mathcal{T}(3,4,3)]\\ &- [105\mathcal{T}(1,1,1) + 21\sqrt{5}\mathcal{T}(1,1,2) + 21\mathcal{T}(1,2,2)\\ &+ 21\sqrt{5}\mathcal{T}(2,1,1) + 21\mathcal{T}(2,1,2) + 21\mathcal{T}(2,2,1)\\ &- 119\mathcal{T}(2,2,2) + 56\mathcal{T}(2,2,3) + 56\mathcal{T}(2,3,2)\\ &+ 4\sqrt{70}\mathcal{T}(2,3,3) + 56\mathcal{T}(3,2,2) + 4\sqrt{70}\mathcal{T}(3,3,2)\\ &+ 20\mathcal{T}(3,3,3)]\},\end{aligned} \tag{34}$$

$$\begin{aligned}\gamma_2 = \frac{128\pi^2}{3}\frac{1}{154350}\{&-[1960\mathcal{T}(1,0,1) + 1225\mathcal{T}(1,2,1)\\ &+ 840\mathcal{T}(1,2,3) + 840\mathcal{T}(3,2,1) + 380\mathcal{T}(3,2,3)\\ &+ 240\mathcal{T}(3,4,3)] + [735\mathcal{T}(1,1,1) + 147\sqrt{5}\mathcal{T}(1,1,2)\\ &+ 147\mathcal{T}(1,2,2) + 147\sqrt{5}\mathcal{T}(2,1,1) + 147\mathcal{T}(2,1,2)\\ &+ 147\mathcal{T}(2,2,1) + 1519\mathcal{T}(2,2,2) - 448\mathcal{T}(2,2,3)\\ &- 448\mathcal{T}(2,3,2) - 32\sqrt{70}\mathcal{T}(2,3,3) - 448\mathcal{T}(3,2,2)\\ &- 32\sqrt{70}\mathcal{T}(3,3,2) - 160\mathcal{T}(3,3,3)]\},\end{aligned} \tag{35}$$

$$\begin{aligned}\gamma_4 = \frac{128\pi^2}{3}\frac{1}{128625}\Bigg\{&\Bigg[490\mathcal{T}(1,0,1) + 49\mathcal{T}(1,2,1)\\ &+ 14\mathcal{T}(1,2,3) + 14\mathcal{T}(3,2,1) + 4\mathcal{T}(3,2,3) + \frac{5}{3}\mathcal{T}(3,4,3)\Bigg]\\ &+ [245\mathcal{T}(1,1,1) + 49\sqrt{5}\mathcal{T}(1,1,2) + 49\mathcal{T}(1,2,2)\\ &+ 49\sqrt{5}\mathcal{T}(2,1,1) + 49\mathcal{T}(2,1,2) + 49\mathcal{T}(2,2,1)\\ &+ 49\mathcal{T}(2,2,2) + 14\mathcal{T}(2,2,3) + 14\mathcal{T}(2,3,2) + \sqrt{70}\mathcal{T}(2,3,3)\\ &+ 14\mathcal{T}(3,2,2) + \sqrt{70}\mathcal{T}(3,3,2) + 5\mathcal{T}(3,3,3)]\Bigg\}.\end{aligned} \tag{36}$$

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 $\mathcal{T}(1,0,1)$ involves the intermediate states $1s^2np\ ^2P^{\mathrm{o}}$, $1s^2ns\ ^2S^{\mathrm{e}}$, and $1s^2np\ ^2P^{\mathrm{o}}$, which are all natural-parity states; while the term $\mathcal{T}(1,1,1)$ involves the electronic configurations $1s^2np\ ^2P^{\mathrm{o}}$, $1snpn'p\ ^2P^{\mathrm{e}}$, and $1s^2np\ ^2P^{\mathrm{o}}$, where two states are natural-parity states and one unnatural-parity state.

The scalar dipole polarizability defined in Eq. (17) can be generalized to the 2^ℓ-pole polarizability α_ℓ

$$\alpha_\ell = \sum_{L_a}\alpha_\ell(L_a), \tag{37}$$

where

$$\alpha_\ell(L_a) = \frac{8\pi}{(2\ell+1)^2(2L+1)}\sum_n\frac{|\langle n_0L\|T_\ell\|nL_a\rangle|^2}{E_n(L_a) - E_{n_0}(L)}, \tag{38}$$

and T_ℓ is the 2^ℓ-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 the second-order perturbation theory, V_{ab} can be expressed as a series in inverse powers of R,

$$V_{ab} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{39}$$

where

$$C_6 = \frac{3}{\pi} G_{ab}(1,1), \tag{40}$$

$$C_8 = \frac{15}{2\pi} G_{ab}(1,2) + \frac{15}{2\pi} G_{ab}(2,1), \tag{41}$$

and

$$C_{10} = \frac{14}{\pi} G_{ab}(1,3) + \frac{14}{\pi} G_{ab}(3,1) + \frac{35}{\pi} G_{ab}(2,2). \tag{42}$$

Introducing the oscillator strength for the transition $|n_0 L\rangle \rightarrow |nL'\rangle$,

$$\bar{f}_{n0}^{(\ell)} = \frac{8\pi}{(2\ell+1)^2(2L+1)} E_{n0} |\langle n_0 L \| T_\ell \| nL' \rangle|^2, \tag{43}$$

where $E_{n0} = E_n(L') - E_{n_0}(L)$ is the corresponding transition energy, $G_{ab}(\ell_a, \ell_b)$ can be written in the form

$$G_{ab}(\ell_a, \ell_b) = \frac{\pi}{2} \sum_{nn'} \frac{\bar{f}_{n0}^{(\ell_a)} \bar{f}_{n'0}^{(\ell_b)}}{E_{n0}^a E_{n'0}^b (E_{n0}^a + E_{n'0}^b)}, \tag{44}$$

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],

$$\Psi^{(0)} = \frac{1}{\sqrt{2}} [\Psi_a(\boldsymbol{\sigma}) \Psi_b(L_b M_b; \boldsymbol{\rho}) + \beta \Psi_a(\boldsymbol{\rho}) \Psi_b(L_b M_b; \boldsymbol{\sigma})], \tag{45}$$

where $\boldsymbol{\sigma}$ and $\boldsymbol{\rho}$ 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

$$V^{(1)}(L_b M_b; \beta) = -\frac{C_{2L_b+1}^{M_b \beta}}{R^{2L_b+1}}, \tag{46}$$

where

$$C_{2L_b+1}^{M_b \beta} = \beta(-1)^{1+L_b+M_b} \frac{4\pi}{(2L_b+1)^2} \begin{pmatrix} 2L_b \\ L_b + M_b \end{pmatrix} \times |\langle \Psi_a(\boldsymbol{\sigma}) \| T_{L_b}(\boldsymbol{\sigma}) \| \Psi_b(L_b; \boldsymbol{\sigma}) \rangle|^2. \tag{47}$$

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

$$\{\chi_s(L_s M_s; \boldsymbol{\sigma}) \omega_t(L_t M_t; \boldsymbol{\rho})\}, \tag{48}$$

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

$$V^{(2)} = -\frac{C_6^{M_b}}{R^6} - \frac{C_8^{M_b}}{R^8} - \cdots, \tag{49}$$

where

$$C_6^{M_b} = \sum_{st} \frac{\Omega_6^{st}}{E_{st}^{(0)} - E^{(0)}}, \tag{50}$$

$$C_8^{M_b} = \sum_{st} \frac{\Omega_8^{st}}{E_{st}^{(0)} - E^{(0)}}, \tag{51}$$

and the energy for the unperturbed system is $E^{(0)} = E_a^{(0)} + E_b^{(0)}$. Following Ref. [12], one can obtain the following expressions for Ω_6^{st} and Ω_8^{st} that are in agreement with the formulas in Ref. [22]:

$$\Omega_6^{st} = |\langle \Psi_a(\boldsymbol{\sigma}) \| T_1(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle|^2 \sum_{\lambda} G(1,1,1,\lambda,1,M_b) |\langle \Psi_b(1; \boldsymbol{\rho}) \| T_1(\boldsymbol{\rho}) \| \omega_t(\lambda; \boldsymbol{\rho}) \rangle|^2, \tag{52}$$

$$\begin{aligned}
\Omega_8^{st} = {} & 2|\langle \Psi_a(\boldsymbol{\sigma}) \| T_1(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle|^2 \sum_{\lambda} G(1,3,1,\lambda,1,M_b) \langle \Psi_b(1; \boldsymbol{\rho}) \| T_1(\boldsymbol{\rho}) \| \omega_t(\lambda; \boldsymbol{\rho}) \rangle \langle \Psi_b(1; \boldsymbol{\rho}) \| T_3(\boldsymbol{\rho}) \| \omega_t(\lambda; \boldsymbol{\rho}) \rangle \\
& + |\langle \Psi_a(\boldsymbol{\sigma}) \| T_1(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle|^2 \sum_{\lambda} G(2,2,1,\lambda,1,M_b) |\langle \Psi_b(1; \boldsymbol{\rho}) \| T_2(\boldsymbol{\rho}) \| \omega_t(\lambda; \boldsymbol{\rho}) \rangle|^2 \\
& + |\langle \Psi_a(\boldsymbol{\sigma}) \| T_2(\boldsymbol{\sigma}) \| \chi_s(2; \boldsymbol{\sigma}) \rangle|^2 \sum_{\lambda} G(1,1,2,\lambda,1,M_b) |\langle \Psi_b(1; \boldsymbol{\rho}) \| T_1(\boldsymbol{\rho}) \| \omega_t(\lambda; \boldsymbol{\rho}) \rangle|^2 \\
& + G_3(2,2,1,1,1,M_b) \langle \Psi_a(\boldsymbol{\sigma}) \| T_1(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle \langle \Psi_a(\boldsymbol{\rho}) \| T_1(\boldsymbol{\rho}) \| \omega_t(1; \boldsymbol{\rho}) \rangle \\
& \times \langle \Psi_b(1; \boldsymbol{\rho}) \| T_2(\boldsymbol{\rho}) \| \omega_t(1; \boldsymbol{\rho}) \rangle \langle \Psi_b(1; \boldsymbol{\sigma}) \| T_2(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle \\
& + 2G_3(1,2,1,2,1,M_b) \langle \Psi_a(\boldsymbol{\sigma}) \| T_1(\boldsymbol{\sigma}) \| \chi_s(1; \boldsymbol{\sigma}) \rangle \langle \Psi_a(\boldsymbol{\rho}) \| T_2(\boldsymbol{\rho}) \| \omega_t(2; \boldsymbol{\rho}) \rangle
\end{aligned}$$

$$\times \langle \Psi_b(1;\boldsymbol{\rho})\|T_1(\boldsymbol{\rho})\|\omega_t(2;\boldsymbol{\rho})\rangle\langle \Psi_b(1;\boldsymbol{\sigma})\| \, T_2(\boldsymbol{\sigma}))\|\chi_s(1;\boldsymbol{\sigma})\rangle$$
$$+ G_3(1,1,2,2,1,M_b)\langle \Psi_a(\boldsymbol{\sigma})\| \, T_2(\boldsymbol{\sigma}))\|\chi_s(2;\boldsymbol{\sigma})\rangle\langle \Psi_a(\boldsymbol{\rho})\|T_2(\boldsymbol{\rho})\|\omega_t(2;\boldsymbol{\rho})\rangle$$
$$\times \langle \Psi_b(1;\boldsymbol{\rho})\|T_1(\boldsymbol{\rho})\|\omega_t(2;\boldsymbol{\rho})\rangle\langle \Psi_b(1;\boldsymbol{\sigma})\|T_1(\boldsymbol{\sigma})\|\chi_s(2;\boldsymbol{\sigma})\rangle, \tag{53}$$

with

$$G(L,L',L_s,L_t,L_b,M_b) = (-1)^{L+L'}\frac{(4\pi)^2}{(2L_s+1)^2}(L,L')^{-1/2}\sum_{M_sM_t} K_{L_sL}^{-M_s}K_{L_sL'}^{-M_s}\begin{pmatrix} L_b & L & L_t \\ -M_b & M_s & M_t \end{pmatrix}\begin{pmatrix} L_b & L' & L_t \\ -M_b & M_s & M_t \end{pmatrix}, \tag{54}$$

and

$$G_3(L,L',L_s,L_t,L_b,M_b) = (-1)^{L+L_s}\frac{(4\pi)^2}{(2L_s+1)(2L_t+1)}(L,L')^{-1/2}\sum_{M_sM_t} (-1)^{M_s+M_t}K_{L_sL}^{-M_s}K_{L'L_t}^{M_t}\begin{pmatrix} L_b & L & L_t \\ -M_b & M_s & M_t \end{pmatrix}\begin{pmatrix} L_b & L' & L_s \\ -M_b & M_t & M_s \end{pmatrix}. \tag{55}$$

In Eqs. (54) and (55), the coefficient $K_{\ell L}^{\mu}$ is

$$K_{\ell L}^{\mu} = \left[\binom{\ell+L}{\ell+\mu}\binom{\ell+L}{L+\mu}\right]^{1/2}, \tag{56}$$

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

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. II B. In addition, we give some calculated oscillator strengths and sum rules that might be useful.

A. 2 ^2S state: Polarizabilities and hyperpolarizabilities of atoms and dispersion coefficients between two atoms

Table I presents a convergence study for the calculations of the scalar dipole polarizability α_1 of lithium with infinite nuclear mass $^{\infty}$Li in the ground state. In the table, N_0 and N_P, 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 α_1 stays constant as the sizes of the basis sets become infinitely large yields the value 164.112(1). 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 $N_P=1846$, confirming the efficacy of the extrapolation method used in that work. For ^{6}Li and ^{7}Li, a similar convergence pattern exists.

Calculations on the hyperpolarizability γ_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 $\frac{1}{9}\mathcal{T}(1,0,1)$ and $\frac{2}{45}\mathcal{T}(1,2,1)$ in Eq. (31), even though the individual terms are converged to about four significant figures. Table II presents the convergence study for calculations of the hyperpolarizability γ_0 of $^{\infty}$Li in the ground state. At the largest sizes of basis sets in Table II, $\frac{1}{9}\mathcal{T}(1,0,1)=-3463.861$ and $\frac{2}{45}\mathcal{T}(1,2,1)=3471.078$, resulting in a loss of about two significant figures when added.

Table III summarizes the final values of the polarizabilities α_1, α_2, and α_3, γ_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.

TABLE I. Convergence of α_1 for the ground state 2 ^2S of $^{\infty}$Li, in atomic units.

(N_0,N_P)	α_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)	164.11021
(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)	$\mathcal{T}(1,0,1)$	$\mathcal{T}(1,2,1)$	γ_0
(120,120,55,55)	−31221.470	78063.181	177.926
(256,256,138,138)	−31195.797	78088.509	1853.126
(502,502,306,306)	−31177.012	78100.613	2958.636
(918,918,622,622)	−31176.318	78103.456	3044.300
(1589,1589,1174,1174)	−31177.339	78104.691	3019.625
(2625,2625,2091,2091)	−31176.724	78102.359	3004.784
(4172,4172,3543,3543)	−31175.663	78100.447	3018.655
(6412,6412,5761,5761)	−31174.753	78099.257	3038.921
Extrapolated			3060(40)

TABLE III. Values of the polarizabilities α_1, α_2, and α_3, the hyperpolarizability γ_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	α_1	α_2	α_3	γ_0	C_6	C_8	C_{10}
$^\infty$Li	164.112(1)	1423.263(3)	39649.29(2)	3060(40)	1393.42(5)	83429(1)	$73725(2)\times 10^2$
^{7}Li	164.161(1)	1423.415(5)	39653.72(3)	2820(40)	1394.05(5)	83456(5)	$73742(2)\times 10^2$
^{6}Li	164.169(1)	1423.439(4)	39654.46(3)	2780(40)	1394.16(5)	83460(5)	$73745(2)\times 10^2$

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 quad-double (QD) developed by Bailey and co-workers [24], which has 64 decimal digits. The finite nuclear mass effect is most significant for γ_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, α_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 α_1, α_2, and α_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 40 results for α_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 α_2 and α_3 are given in Refs. [12,25]. In Table IV, we collect some theoretical results from between 1996 and the present. The exponentially correlated Gaussian-basis set calculations of Komasa [26] for α_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 α_2; but Ref. [26] does not provide computational uncertainties. Both α_1 and α_2 were calculated using semiempirical 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 semiempirical polarization potential. Of the two semiempirical approaches, the RKR-QDT results are in much better agreement with the present work as the results of Zhang *et al.* for α_3 differ from the present work by the same percentage as do their calculations of α_1 and α_2. Chen and Wang [25] evaluated α_2 and α_3 for the ground states of lithiumlike 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 α_1 generally, the effect is to reduce the nonrelativistic value by a term on the order of $(1/137.037)^2$. Derevianko *et al.* [28] and Porsev and Derevianko [29] calculated α_1, α_2, and α_3, as well as C_6, C_8, and C_{10} for the

TABLE IV. Comparison of the polarizabilities α_1, α_2, and α_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. [17,18,28–30] were calculated using relativistic methods.

Reference	α_1	α_2	α_3	C_6	C_8	C_{10}
Yan *et al.* [12] (1996)	164.111(2)	1423.266(5)	39650.49(8)	1393.39(16)	$8.34258(42)\times 10^4$	$7.3721(1)\times 10^6$
Komasa [26] (2001)	164.11171	1423.282				
Derevianko *et al.* [28] (2001)	164.0(1)			1389(2)		
Porsev and Derevianko [29] (2003)		1424(4)	3.957×10^4		$8.34(4)\times 10^4$	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)	162.48(56)	1421.37(3.51)				
Wansbeek *et al.* [18] (2008)	162.87	1420		1396(6)	8.360×10^4	
Johnson *et al.* [17] (2008)	164.084	1422.73	39624.2			
This work	164.112(1)	1423.263(3)	39649.29(2)	1393.42(5)	$8.3429(1)\times 10^4$	$7.3725(2)\times 10^6$
Molof *et al.* [32] (1974) (experiment)	164.0(3.4)					
Miffre *et al.* [31] (2006) (experiment)	164.2(1.1)					

TABLE V. Values of the hyperpolarizability γ_0 for $^{\infty}$Li in the ground state 2 ^2S, in atomic units.

Reference	γ_0
Pipin and Bishop [37] (1992)	3000
Kassimi and Thakkar [38,39] (1994)	2900(90)
Laughlin [40] (1995)	3930
Jaszunski and Rizzo [41] (1996)	3450
Cohen and Themelis [27] (2005)	3390
Present	3060(40)

ground state of lithium using the relativistic many-body perturbation theory (MBPT). Sahoo [30] calculated the dipole and quadrupole polarizabilities of Li using the relativistic coupled-cluster method. Wansbeek *et al.* [18] 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 the relativistic MPBT. For α_1, the results of Refs. [17,28] obtained using the relativistic MPBT 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 semiempirical calculations of Zhang *et al.* [16] and the relativisitic calculations of Refs. [28,29] 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 α_1 was that of Miffre *et al.* [31] obtained with 0.66% uncertainty using atom interferometry. It is a factor of 3 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 α_1 can be tested stringently. One can see from Table III that the finite nuclear mass correction to α_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 (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 [33–35]. As for the QED effect, Pachucki and Sapirstein [36] 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 cannot 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 γ_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 [37] calculated γ_0 by applying the combined configuration-interaction-Hylleraas method. Their result, with one significant figure, is in good agreement with ours. Kassimi and Thakkar [38,39] used the coupled-cluster approach, where the reported uncertainty of 10% in γ_0 was later readjusted to 3% [39]. Laughlin [40] performed a semiempirical one-electron model potential calculation and found that the final result for γ_0 was highly sensitive to the data used, particularly, the value of α_1. The value from Jaszunski and Rizzo [41] was obtained using a series of multiconfiguration self-consistent-field (SCF) wave functions. Finally, Cohen and Themelis [27] computed γ_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 ^2P state: Polarizabilities and hyperpolarizabilities

Table VI shows the convergence of α_1 and of $\alpha_1^{(T)}$ calculated for $^{\infty}$Li in the 2 ^2P state, where N_S, $N_{(pp')P}$, and N_D are the sizes of bases for the intermediate states of symmetries S,

TABLE VI. Convergence of α_1 and $\alpha_1^{(T)}$ for $^{\infty}$Li in 2 ^2P state, in atomic units.

$(N_0,N_S,N_{(pp')P},N_D)$	$\alpha_1(S)$	$\alpha_1[(pp')P]$	$\alpha_1(D)$	α_1	$\alpha_1^{(T)}$
(55,120,36,55)	−17.181258	0.063053	142.611225	125.493021	2.951662
(138,256,108,138)	−16.258204	0.067825	142.675018	126.484639	2.024615
(306,502,264,306)	−15.950171	0.069135	142.718553	126.837517	1.712883
(622,918,568,622)	−15.871922	0.069501	142.729209	126.926788	1.633752
(1174,1589,1106,1174)	−15.866615	0.069591	142.734228	126.937203	1.627988
(2091,2625,2002,2091)	−15.861376	0.069641	142.735430	126.943695	1.622654
(3543,4172,3413,3543)	−15.860744	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 α_1, $\alpha_1^{(T)}$, α_2, and α_3, and the hyperpolarizabilities γ_0 and γ_2 for $^{\infty}$Li, ^{7}Li, and ^{6}Li in $2\,^2P$ state, in atomic units.

System	α_1	$\alpha_1^{(T)}$	α_2	α_3	γ_0	γ_2
$^{\infty}$Li	126.9458(3)	1.6214(3)	4103.165(5)	321138(4)	$1.00170(9)\times 10^7$	$-6.2234(8)\times 10^6$
^{7}Li	126.9472(5)	1.6351(2)	4102.893(4)	321102(5)	$1.00201(9)\times 10^7$	$-6.2252(8)\times 10^6$
^{6}Li	126.9474(5)	1.6373(3)	4102.848(4)	321096(5)	$1.00206(9)\times 10^7$	$-6.2255(8)\times 10^6$

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 [17,18] are relativistic.

Reference	α_1	$\alpha_1^{(T)}$	γ_0	γ_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)	$1.00170(9)\times 10^7$	$-6.2234(8)\times 10^6$
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	$C_3(M_2=0)$	$C_3(M_2=\pm 1)$	$C_6(M_2=0)$	$C_6(M_2=\pm 1)$	$C_8(M_2=0)$	$C_8(M_2=\pm 1)$
$\beta=-1$						
$^{\infty}$Li	−11.000221(2)	5.500111(1)	2075.40(3)	1406.68(3)	990895(5)	48564.8(5)
^{7}Li	−11.001853(2)	5.500926(1)	2076.08(7)	1407.15(5)	991075(6)	48566.4(2)
^{6}Li	−11.002125(2)	5.501062(1)	2076.19(7)	1407.20(2)	991104(5)	48566.9(4)
$\beta=+1$						
$^{\infty}$Li	11.000221(2)	−5.500111(1)	2075.40(3)	1406.68(3)	274079(2)	103044(2)
^{7}Li	11.001853(2)	−5.500926(1)	2076.08(7)	1407.15(5)	274128(5)	103052(1)
^{6}Li	11.002125(2)	−5.501062(1)	2076.19(7)	1407.20(2)	274137(6)	103053(1)

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	β	$C_3(M_2=0)$	$C_3(M_2=\pm 1)$	$C_6(M_2=0)$	$C_6(M_2=\pm 1)$	$C_8(M_2=0)$	$C_8(M_2=\pm 1)$
Marinescu *et al.* [46] (1995)	−1	−11.01	5.503	2066	1401	9.880×10^5	4.756×10^4
	+1					2.705×10^5	1.021×10^5
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	9.9202×10^5	4.8629×10^4
	+1					2.7431×10^5	1.0316×10^5
This work	−1	−11.000221(2)	5.500111(1)	2075.40(3)	1406.68(3)	$9.90895(5)\times 10^5$	$4.85648(5)\times 10^4$
	+1					$2.74079(2)\times 10^5$	$1.03044(2)\times 10^5$

TABLE XI. Convergence for α_1 and $\alpha_1^{(T)}$ of $^{\infty}$Li in 3 ^2D state, in atomic units.

$(N_0,N_P,N_{(pd)D},N_F)$	$\alpha_1(P)$	$\alpha_1[(pd)D]$	$\alpha_1(F)$	α_1	$\alpha_1^{(T)}$
(138,138,126,132)	−18857.791600	0.059150	1916.643488	−16941.088962	18310.238324
(306,306,322,302)	−16933.479208	0.062827	1916.940725	−15016.475656	16385.844685
(622,622,714,636)	−16850.080546	0.063886	1917.021571	−14932.995089	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	−14928.278040	16297.717843
(3543,3543,4587,4051)	−16845.342790	0.064242	1917.040003	−14928.238545	16297.681317
(5761,5761,4587,6806)	−16845.342870	0.064243	1917.043303	−14928.235324	16297.680455

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 α_1, α_2, and α_3, the tensor dipole polarizability $\alpha_1^{(T)}$, the scalar hyperpolarizability γ_0, and the tensor hyperpolarizability γ_2 for $^{\infty}$Li, ^{7}Li, and ^{6}Li in their 2 ^2P states.

Table VIII is a comparison of the scalar and tensor dipole polarizabilities and hyperpolarizabilities α_1, $\alpha_1^{(T)}$, γ_0, and γ_2 for the 2 ^2P 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 α_1 at the level of 0.05%, was not included in the configuration interaction-Hylleraas calculation of Pipin and Bishop [42]. The relativistic results for α_1 by Wansbeek *et al.* [18] and by Johnson *et al.* [17] are the $(2J+1)$-weighted sums between the $J=1/2$ and $J=3/2$ sublevels. The results of Johnson *et al.* are close to ours. In contrast, the results of Wansbeek *et al.* [18] deviate significantly from ours for example, the value of $\alpha_1^{(T)}$ reported by Wansbeek *et al.* [18] is a factor of 3.6 larger than our calculation.

The uncertainties in the experimental values for α_1 and $\alpha_1^{(T)}$ obtained by Hunter *et al.* [43] and by Windholz *et al.* [44] are too large to reveal finite nuclear mass and relativistic effects. However, the nonrelativistic calculations of Refs. [16,42], 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 [27] *disagree* with the experiment.

For the α_2 and α_3 of the 2 ^2P state, the model potential results of Zhang *et al.* [16] are, respectively, 4104.9 and $3.213\,5\times10^5$, which are slightly larger than our results, given in Table VII.

There are no measurements of γ_0 and γ_2 though our calculated values are in almost perfect agreement with—though substantially more accurate than—the semiempirical results of Cohen and Themelis [27] and the early calculation of Themelis and Nicolaides [45] 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 ^2P) 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 semiempirical model potential of Zhang *et al.* [16]. Our *ab initio* results confirm the more accurate semiempirical 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 α_1 and $\alpha_1^{(T)}$ and for the hyper-

TABLE XII. Convergence for γ_0, γ_2, and γ_4 of $^{\infty}$Li in 3 ^2D state, in atomic units.

$(N_0,N_S,N_P,N_{(pp')P},N_D,N_{(pd)D},N_F,N_{(pf)F},N_G)$	$10^{-12}\ \gamma_0$	$10^{-12}\ \gamma_2$	$10^{-10}\ \gamma_4$
(138, 256, 138, 108, 138, 126, 132, 126, 139)	2.335078929997	−2.435345979367	10.1097221264
(306, 502, 306, 264, 306, 322, 302, 322, 330)	1.673627590440	−1.744707390466	7.1916589358
(622, 918, 622, 568, 622, 714, 636, 714, 720)	1.648569007586	−1.718605330888	7.0875021256
(1174,1589,1174,1106,1174,1428,1248,1428,1458)	1.647221992572	−1.717197712093	7.0814607892
(2091,2625,2091,2002,2091,2640,2307,2640,2769)	1.647149117913	−1.717122212016	7.0812009263
(3543,4172,3543,3413,3543,4587,4051,4587,4975)	1.647145129442	−1.717120442563	7.0814240701

TABLE XIII. Values of the polarizabilities α_1, $\alpha_1^{(T)}$, α_2, and α_3, and the hyperpolarizabilities γ_0, γ_2, and γ_4 for $^{\infty}$Li, ^{7}Li, and ^{6}Li in 3 ^2D state, in atomic units.

System	α_1	$\alpha_1^{(T)}$	α_2	α_3	γ_0	γ_2	γ_4
$^{\infty}$Li	−14928.230(5)	16297.675(5)	158060(10)	$-1.340902(3)\times10^8$	$1.647140(5)\times10^{12}$	$-1.717115(5)\times10^{12}$	$7.0814(2)\times10^{10}$
^{7}Li	−14921.330(4)	16291.094(5)	158070(10)	$-1.339746(5)\times10^8$	$1.644875(5)\times10^{12}$	$-1.714740(5)\times10^{12}$	$7.0700(3)\times10^{10}$
^{6}Li	−14920.180(6)	16290.000(5)	158070(10)	$-1.339554(5)\times10^8$	$1.644500(4)\times10^{12}$	$-1.714345(5)\times10^{12}$	$7.0680(5)\times10^{10}$

polarizabilities γ_0, γ_2, and γ_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 Themelis and Nicolaides [47] using an empirically modeled dipole moment operator and fitting to field-dependent energy shifts. For α_1, the percentage difference between the semiempirical model potential result of Magnier and Aubert-Frécon [48] and ours is about 7%. The values of Ashby and van Wijngaarden [49] obtained using the semiempirical Coulomb approximation method and the values of Zhang *et al.* [16] obtained in the framework of a frozen-core Hamiltonian with a semiempirical 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 α_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 previous results is presented in Table XVI, including the multiconfiguration Hartree Fock of Godefroid *et al.* [15], the semiempirical model potential of Zhang *et al.* [16], and the relativistic many-body approach of Johnson *et al.* [17]. The nonlinear variational parameters in our calculation are optimized only for the lowest-energy eigenstate of the 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 (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 [52] $S(-3)\equiv2\beta_1$, where β_1 is given in terms of the quantities defined in Sec. II, in a manner similar to the definition of α_l in Eqs. (37) and (38), as

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

Reference	$10^{-4}\ \alpha_1$	$10^{-4}\ \alpha_1^{(T)}$	$10^{-5}\ \alpha_2$	$10^{-8}\ \alpha_3$	$10^{-12}\ \gamma_0$	$10^{-12}\ \gamma_2$	$10^{-10}\ \gamma_4$
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					
Ashby and Wijngaarden [49] (2003)	−1.507	1.642					
Zhang *et al.* [16] (2007)	−1.5044	1.6414	1.5786	−1.3548			
Wansbeek *et al.* [18] (2008)	−1.986	2.090					
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)					

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	0.7469563(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)

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

where

$$\beta_1(L_a) = \frac{4\pi}{9(2L+1)} \sum_n \frac{|\langle n_0 L \| T_1 \| n L_a \rangle|^2}{[E_n(L_a) - E_{n_0}(L)]^2}. \tag{58}$$

The results for β_1 are given in Table XVII for $^{\infty}$Li, ^{7}Li, and ^{6}Li in the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states. The result for $^{\infty}$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 12.14404408(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 *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 Li($2\,^2S$)-Li($2\,^2S$) and Li($2\,^2S$)-Li($2\,^2P$) have also been evaluated. Furthermore, the finite nuclear mass effects on these properties have been studied for 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 He [36,55–57].

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 *et al.* [50] and the present results.

TABLE XVII. Values of β_1 of $^{\infty}$Li, ^{7}Li, and ^{6}Li in their $2\,^2S$, $2\,^2P$ and $3\,^2D$ states, in atomic units.

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)

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APPENDIX: STARK EFFECT

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

$$H = H_0 + H' = H_0 - \boldsymbol{\mathcal{E}} \cdot \mathbf{P}, \tag{A1}$$

where H_0 is the unperturbed Hamiltonian and $\mathbf{P}$ is the electric dipole moment of the atom,

$$\mathbf{P} = \sum_i q_i \mathbf{R}_i. \tag{A2}$$

In the above, q_i is the charge of ith 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

$$E = E_0 + \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 + \cdots, \tag{A3}$$

TABLE XVI. Comparison of oscillator strengths of $^{\infty}$Li.

Reference	$2\,^2S$-$2\,^2P$	$2\,^2P$-$3\,^2D$	$3\,^2D$-$4\,^2F$
Yan and Drake [20] (1995)	0.7469572(10)	0.6385705(30)	
Yan *et al.* [51] (1998)	0.7469569396(98)		
Godefroid *et al.* [15] (2001)	0.74690	0.63853	
Zhang *et al.* [16] (2007)	0.7475	0.6388	1.0153
Johnson *et al.* [17] (2008)	0.746944	0.638615	1.015637
This work	0.7469563(5)	0.6385685(5)	1.0153771(5)

$$\Psi = \Psi_0 + \Psi_1 + \Psi_2 \cdots , \tag{A4}$$

where

$$H_0 \Psi_0 = E_0 \Psi_0 \tag{A5}$$

is the zero-order equation, and ΔE_i and Ψ_i are the corresponding ith-order corrections. According to the perturbation theory, the energy corrections can be expressed as

$$\Delta E_1 = \langle \Psi_0 | H' | \Psi_0 \rangle , \tag{A6}$$

$$\Delta E_2 = \langle \Psi_0 | H' | \Psi_1 \rangle , \tag{A7}$$

$$\Delta E_3 = \langle \Psi_1 | H' | \Psi_1 \rangle - \Delta E_1 \langle \Psi_1 | \Psi_1 \rangle , \tag{A8}$$

$$\Delta E_4 = \langle \Psi_1 | H' | \Psi_2 \rangle - \Delta E_2 \langle \Psi_1 | \Psi_1 \rangle - \Delta E_1 \langle \Psi_1 | \Psi_2 \rangle . \tag{A9}$$

If the state of interest Ψ_0 has a fixed parity, as in the case of this work, $\Delta E_1 = 0$ due to the parity selection rule. Ψ_1 and Ψ_2 can be expanded in terms of their spectral representations,

$$|\Psi_1\rangle = \sum_n \frac{\langle n | H' | 0 \rangle}{E_0 - E_n} |n\rangle , \tag{A10}$$

$$|\Psi_2\rangle = \sum_{nk} \frac{\langle n | H' | k \rangle \langle k | H' | 0 \rangle}{(E_0 - E_n)(E_0 - E_k)} |n\rangle , \tag{A11}$$

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,

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

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

1. ΔE_2

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

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

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

$$\begin{aligned} H'|n\rangle\langle n|H' = & \sum_K (-1)^K \sqrt{2K+1} \sum_{q_1 q_2} \begin{pmatrix} 1 & 1 & K \\ q_1 & q_2 & 0 \end{pmatrix} \\ & \times P^{(1)}_{q_1} \lambda_n P^{(1)}_{q_2} [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K)}_0 . \end{aligned} \tag{A15}$$

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

$$\begin{aligned} \Delta E_2 = & \sum_{nK} (-1)^K \sqrt{2K+1} \sum_{q_1 q_2} \begin{pmatrix} 1 & 1 & K \\ q_1 & q_2 & 0 \end{pmatrix} \\ & \times \frac{\langle 0 | P^{(1)}_{q_1} | n \rangle \langle n | P^{(1)}_{q_2} | 0 \rangle}{E_0 - E_n} [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K)}_0 . \end{aligned} \tag{A16}$$

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

$$|0\rangle = |n_0 L M\rangle , \tag{A17}$$

$$|n\rangle = |n L_a M_a\rangle , \tag{A18}$$

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 $P^{(1)}_\mu$, one can recast Eq. (A16) into the following form:

$$\begin{aligned} \Delta E_2 = & \sum_{n L_a K} (-1)^K \sqrt{2K+1} \frac{\langle n_0 L || P^{(1)} || n L_a \rangle \langle n L_a || P^{(1)} || n_0 L \rangle}{E_{n_0}(L) - E_n(L_a)} \\ & \times [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K)}_0 A , \end{aligned} \tag{A19}$$

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

$$\begin{aligned} A = & \sum_{M_a q_1 q_2} (-1)^{L - M + L_a - M_a} \begin{pmatrix} L & 1 & L_a \\ -M & q_1 & M_a \end{pmatrix} \\ & \times \begin{pmatrix} L_a & 1 & L \\ -M_a & q_2 & M \end{pmatrix} \begin{pmatrix} 1 & 1 & K \\ q_1 & q_2 & 0 \end{pmatrix} . \end{aligned} \tag{A20}$$

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

$$A = (-1)^{L-M} \begin{pmatrix} L & L & K \\ -M & M & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ L & L & L_a \end{Bmatrix} , \tag{A21}$$

provided K is an integer, and note that

$$\begin{aligned} [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K)}_0 & = \sqrt{2K+1} \sum_{q_1 q_2} \begin{pmatrix} 1 & 1 & K \\ q_1 & q_2 & 0 \end{pmatrix} \mathcal{E}^{(1)}_{q_1} \mathcal{E}^{(1)}_{q_2} \\ & = \sqrt{2K+1} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \mathcal{E}^2 . \end{aligned} \tag{A22}$$

Therefore, the second-order correction can be written as

$$\Delta E_2 = -\mathcal{E}^2 \sum_{nL_a} \frac{\langle n_0 L \| P^{(1)} \| n L_a \rangle \langle n L_a \| P^{(1)} \| n_0 L \rangle}{E_n(L_a) - E_{n_0}(L)} \sum_K (2K+1) \times (-1)^{L-M} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & L & K \\ -M & M & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ L & L & L_a \end{Bmatrix}. \tag{A23}$$

Since

$$(-1)^{L-M} \begin{pmatrix} L & L & 0 \\ -M & M & 0 \end{pmatrix} = (-1)^{2L} \frac{1}{\sqrt{2L+1}}, \tag{A24}$$

$$(-1)^{L-M} \begin{pmatrix} L & L & 2 \\ -M & M & 0 \end{pmatrix} = (-1)^{2L} \frac{3M^2 - L(L+1)}{\sqrt{(2L+3)(L+1)(2L+1)L(2L-1)}}, \quad L \geq 1, \tag{A25}$$

and also [58]

$$P^{(1)}_\mu = \sqrt{\frac{4\pi}{3}} \sum_i q_i R_i Y_{1\mu}(\hat{\mathbf{R}}_i), \tag{A26}$$

$$\langle n L_a \| P^{(1)} \| n_0 L \rangle = (-1)^{L-L_a} \langle n_0 L \| P^{(1)} \| n L_a \rangle^*, \tag{A27}$$

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

$$\Delta E_2 = -\frac{\mathcal{E}^2}{2} [\alpha_1 + \alpha_1^{(T)} g_2(L,M)]. \tag{A28}$$

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

$$g_2(L,M) = \begin{cases} 0 & \text{if } L = 0, \frac{1}{2} \\ \dfrac{3M^2 - L(L+1)}{L(2L-1)} & \text{otherwise,} \end{cases} \tag{A29}$$

and α_1 and $\alpha_1^{(T)}$ are, respectively, the scalar and tensor dipole polarizabilities,

$$\alpha_1 = \sum_{L_a} \alpha_1(L_a), \tag{A30}$$

$$\alpha_1^{(T)} = \sum_{L_a} W(L,L_a) \alpha_1(L_a), \tag{A31}$$

where

$$\alpha_1(L_a) = \frac{8\pi}{9(2L+1)} \sum_n \frac{|\langle n_0 L \| T_1 \| n L_a \rangle|^2}{E_n(L_a) - E_{n_0}(L)}, \tag{A32}$$

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

$$W(L,L_a) = (-1)^{L+L_a} \sqrt{\frac{30(2L+1)L(2L-1)}{(2L+3)(L+1)}} \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_a \end{Bmatrix}. \tag{A33}$$

2. ΔE_4

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

$$\Delta E_4 = \sum_{kmn} t(k,m,n) \sum_{K_1 K_2} (-1)^{K_1+K_2} (K_1,K_2)^{1/2} \times \sum_{q_1 q_2 q_3 q_4} \begin{pmatrix} 1 & 1 & K_1 \\ q_1 & q_2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & K_2 \\ q_3 & q_4 & 0 \end{pmatrix} \times \langle 0 | P^{(1)}_{q_1} \lambda_m P^{(1)}_{q_2} \lambda_n P^{(1)}_{q_3} \lambda_k P^{(1)}_{q_4} | 0 \rangle \times [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K_1)}_0 [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K_2)}_0, \tag{A34}$$

where the notation $(a,b) = (2a+1)(2b+1)$,

$$t(k,m,n) = \frac{1}{(E_0 - E_m)(E_0 - E_n)(E_0 - E_k)} - \delta(n,0) \frac{1}{(E_0 - E_m)(E_0 - E_k)^2}, \tag{A35}$$

and $\lambda_m = |m\rangle\langle m|$, etc. Writing out the all angular-momentum quantum numbers explicitly

$$|0\rangle = |n_0 L M\rangle, \tag{A36}$$

$$|m\rangle = |m L_a M_a\rangle, \tag{A37}$$

$$|n\rangle = |n L_b M_b\rangle, \tag{A38}$$

$$|k\rangle = |k L_c M_c\rangle, \tag{A39}$$

and applying the Wigner-Eckart theorem, we have

$$\Delta E_4 = \sum_{kmn} \sum_{L_a L_b L_c} t(k,m,n) \sum_{K_1 K_2} (-1)^{K_1+K_2} (K_1,K_2)^{1/2} \times [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K_1)}_0 [\mathcal{E}^{(1)} \otimes \mathcal{E}^{(1)}]^{(K_2)}_0 \langle n_0 L \| P^{(1)} \| m L_a \rangle \times \langle m L_a \| P^{(1)} \| n L_b \rangle \langle n L_b \| P^{(1)} \| k L_c \rangle \langle k L_c \| P^{(1)} \| n_0 L \rangle B, \tag{A40}$$

where B (which contains all the angular coefficients) is

$$B = \sum_{q_1 q_2 q_3 q_4} \sum_{M_a M_b M_c} (-1)^{L-M+L_a-M_a+L_b-M_b+L_c-M_c} \times \begin{pmatrix} 1 & 1 & K_1 \\ q_1 & q_2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & K_2 \\ q_3 & q_4 & 0 \end{pmatrix} \begin{pmatrix} L & 1 & L_a \\ -M & q_1 & M_a \end{pmatrix} \times \begin{pmatrix} L_a & 1 & L_b \\ -M_a & q_2 & M_b \end{pmatrix} \begin{pmatrix} L_b & 1 & L_c \\ -M_b & q_3 & M_c \end{pmatrix} \begin{pmatrix} L_c & 1 & L \\ -M_c & q_4 & M \end{pmatrix}. \tag{A41}$$

Using the graphical method, B can be simplified into

$$B = (-1)^{L-M} \begin{Bmatrix} 1 & 1 & K_1 \\ L & L_b & L_a \end{Bmatrix} \begin{Bmatrix} 1 & 1 & K_2 \\ L & L_b & L_c \end{Bmatrix} \sum_\lambda (2\lambda+1) \times \begin{pmatrix} K_1 & K_2 & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & L & \lambda \\ -M & M & 0 \end{pmatrix} \begin{Bmatrix} K_2 & K_1 & \lambda \\ L & L & L_b \end{Bmatrix}, \tag{A42}$$

provided K_1 and K_2 are integers. From Eqs. (A22), (A26), and (A27), one can further write Eq. (A40) in the form

$$\Delta E_4 = -\mathcal{E}^4\left(\frac{4\pi}{3}\right)^2 \sum_{L_aL_bL_c} \mathcal{T}(L_a,L_b,L_c)\sum_{\lambda}(-1)^{L-M}\begin{pmatrix} L & L & \lambda \\ -M & M & 0 \end{pmatrix} \times \sum_{K_1K_2}(\lambda,K_1,K_2)\begin{pmatrix} 1 & 1 & K_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & K_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} K_1 & K_2 & \lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} 1 & 1 & K_1 \\ L & L_b & L_a \end{Bmatrix}\begin{Bmatrix} 1 & 1 & K_2 \\ L & L_b & L_c \end{Bmatrix}\begin{Bmatrix} K_2 & K_1 & \lambda \\ L & L & L_b \end{Bmatrix}, \tag{A43}$$

where

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

According to the property of $3j$ symbol, the possible values for λ are 0, 2, and 4. Also,

$$(-1)^{L-M}\begin{pmatrix} L & L & 4 \\ -M & M & 0 \end{pmatrix} = \frac{2(-1)^{2L}[3(5M^2-L^2-2L)(5M^2+1-L^2)-10M^2(4M^2-1)]}{\sqrt{(2L+5)(2L+4)(2L+3)(2L+2)(2L+1)(2L)(2L-1)(2L-2)(2L-3)}}, \quad L\geq 2. \tag{A45}$$

Together with Eqs. (A24) and (A25), the fourth-order correction can finally be expressed in the form

$$\Delta E_4 = -\frac{\mathcal{E}^4}{24}[\gamma_0+\gamma_2 g_2(L,M)+\gamma_4 g_4(L,M)], \tag{A46}$$

where $g_2(L,M)$ is defined in Eq. (A29), and $g_4(L,M)$ is given by

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

In Eq. (A46), γ_0 is the scalar hyperpolarizability, and γ_2 and γ_4 are the tensor hyperpolarizabilities, which can be written as

$$\gamma_0 = (-1)^{2L}\frac{128\pi^2}{3}\frac{1}{\sqrt{2L+1}}\sum_{L_aL_bL_c}\mathcal{G}_0(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{A48}$$

$$\gamma_2 = (-1)^{2L}\frac{128\pi^2}{3}\sqrt{\frac{L(2L-1)}{(2L+3)(L+1)(2L+1)}}\sum_{L_aL_bL_c}\mathcal{G}_2(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{A49}$$

$$\gamma_4 = (-1)^{2L}\frac{128\pi^2}{3}\sqrt{\frac{L(2L-1)(L-1)(2L-3)}{(2L+5)(L+2)(2L+3)(L+1)(2L+1)}}\sum_{L_aL_bL_c}\mathcal{G}_4(L,L_a,L_b,L_c)\mathcal{T}(L_a,L_b,L_c), \tag{A50}$$

where

$$\mathcal{G}_\Lambda(L,L_a,L_b,L_c) = \sum_{K_1K_2}(\Lambda,K_1,K_2)\begin{pmatrix} 1 & 1 & K_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & K_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} K_1 & K_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} 1 & 1 & K_1 \\ L & L_b & L_a \end{Bmatrix}\begin{Bmatrix} 1 & 1 & K_2 \\ L & L_b & L_c \end{Bmatrix}\begin{Bmatrix} K_2 & K_1 & \Lambda \\ L & L & L_b \end{Bmatrix}. \tag{A51}$$

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