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Ab initio determination of polarizabilities and van der Waals coefficients of Li atoms using the relativistic coupled-cluster method

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We report on a technique to determine the van der Waals coefficients of lithium (Li) atoms based on relativistic coupled-cluster theory. These quantities are determined using the imaginary parts of the scalar dipole and quadrupole polarizabilities, which are evaluated using an approach that we have proposed earlier [B. K. Sahoo, Chem. Phys. Lett. **448**, 144 (2007)]. Our procedure is fully *ab initio*, and avoids the sum-over-the-states approach. We present the dipole and quadrupole polarizabilities of many of the low-lying excited states of Li. Also, the off-diagonal dipole and quadrupole polarizabilites between some of the low-lying states of Li have been calculated.

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I. INTRODUCTION

The scattering between ultracold atoms is dominated by the long-range van der Waals interaction. Lithium (Li) is an interesting candidate for ultracold atomic experiments since it possesses both fermionic (^{6}Li) and bosonic (^{7}Li) isotopes. These isotopes are used in the study of boson-boson [1,2], boson-fermion [3], and fermion-fermion mixtures [2,4].

For the theoretical description of such systems, a knowledge of the interatomic potential is necessary. At a large nuclear separation R, the s-wave scattering interatomic potential is accurately represented by the sum of two independent contributions, the exchange potential and the electrostatic potential [5]. The former is related to the ionization energies and scattering lengths and will not be discussed hereafter. The electrostatic potential $V(R)$ is given by Ref. [6] as

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} + \cdots, \tag{1.1}$$

where C_6 and C_8 are known as dispersion or van der Waals coefficients. For large R, $V(R)$ is dominated by $-C_6/R^6$ and $-C_8/R^8$, where the higher-order terms are sufficiently weak to be neglected. Both coefficients can be evaluated from the knowledge of the imaginary parts of the dynamic dipole and quadrupole polarizabilities [7,8]. Several groups have evaluated these quantities because they are required for the simulation, prediction, and interpretation of experiments on cold-atom collisions, photoassociation, and fluorescence spectroscopy [9,10].

Since the classic work of Dalgarno and Lewis [11], different procedures have been followed to determine polarizabilities. An often-used method is the sum-over-intermediate-states approach, which employs dipole-quadrupole matrix elements and excitation energies of important states [12–14]. This method, however, is limited in its accuracy because of the exclusion of the high-lying states for computational reasons. Coupled-cluster based linear response theory [15,16] is a promising method to study both static and dynamic polarizabilities, which does not involve summing over intermediate states. However, relativistic extensions of this theory to calculate atomic polarizabilities have not been attempted so far. In this work, we present a novel approach, different from linear response theory, to determine the static and dynamic polarizabilities for atoms within the framework of the relativistic coupled-cluster (RCC) method. The imaginary parts of the dynamic polarizabilities are used to calculate the van der Waals coefficients for Li atoms. This method has recently been employed to determine static polarizabilities in closed-shell and one-valence open-shell systems [17–19].

In this paper we also present the static dipole and quadrupole polarizabilities for many of the excited states of Li. These could be useful in the calculation of the dispersion coefficients and the determining of Stark shifts. So far, only a few studies have been carried out on the polarizabilities of the Li excited states [20–25]. Most of these studies, however, use nonrelativistic theories, and we will compare those results to our relativistic calculations to assess the relevance of relativistic effects. We also present the scalar polarizabilities among two different states, which are of interest for several types of studies [26].

The outline of the rest of the paper is as follows. We start by presenting the theory for polarizabilities and van der Waals coefficients in Sec. II. Next, we discuss our method of calculation in Sec. III and in Sec. IV we present and discuss our results.

II. THEORY

In this section we give the definitions of the static and dynamic polarizabilities and the van der Waals coefficients.

A. Polarizability

The static dipole polarizability $\alpha_1(J_v, m_{J_v})$ of a valence (v) state $|\Psi_v\rangle$ of a single valence system is given by [27,28]

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$$\begin{aligned}\alpha_1(J_v,m_{J_v}) &= \sum_{I\neq v}\frac{\langle\Psi_v|D|\Psi_I\rangle\langle\Psi_I|D|\Psi_v\rangle}{E_I-E_v}\\ &= \alpha_1^0(J_v) + \frac{3m_{J_v}^2 - J_v(J_v+1)}{J_v(2J_v-1)}\alpha_1^2(J_v),\end{aligned} \tag{2.1}$$

where the scalar polarizability $\alpha_1^0(J_v)$ is given by

$$\alpha_1^0(J_v) = \frac{2}{3(2J_v+1)}\sum_{I\neq v}\frac{|\langle J_I\|D\|J_v\rangle|^2}{E_I-E_v} \tag{2.2}$$

and the tensor polarizability $\alpha_1^2(J_v)$ by

$$\begin{aligned}\alpha_1^2(J_v) &= 2\left[\frac{10J_v(2J_v-1)}{3(J_v+1)(2J_v+1)(2J_v+3)}\right]^{1/2}\\ &\quad\times\sum_{I\neq v}(-)^{J_v-J_I}\begin{Bmatrix} J_v & 1 & J_I\\ 1 & J_v & 2\end{Bmatrix}\frac{|\langle J_v\|D\|J_I\rangle|^2}{E_v-E_I}.\end{aligned} \tag{2.3}$$

Here D is the dipole operator and J_v and m_{J_v} are the angular momentum quantum numbers of $|\Psi_v\rangle$. $|\Psi_I\rangle$ represents allowed intermediate states with respect to $|\Psi_v\rangle$ with E_I and E_v their respective energies. Similarly, the scalar quadrupole polarizability of the valence state $|\Psi_v\rangle$ is given by

$$\alpha_2^0(J_v) = \sum_{I\neq v}\frac{|\langle\Psi_v|Q|\Psi_I\rangle|^2}{E_I-E_v} = \frac{2}{5(2J_v+1)}\sum_{J_I\neq J_v}\frac{|\langle J_v\|Q\|J_I\rangle|^2}{E_I-E_v}, \tag{2.4}$$

where Q is the quadrupole operator.

Extending these definitions, the scalar polarizability between two (possibly different) states $|\Psi_f\rangle$ and $|\Psi_i\rangle$ is given by [29]

$$\alpha_k^0(J_i,J_f) = -\sum_{I\neq i,f}\left[\frac{1}{E_f-E_I}+\frac{1}{E_i-E_I}\right]\times\langle\Psi_f|O^{(k)}|\Psi_I\rangle\langle\Psi_I|O^{(k)}|\Psi_i\rangle,$$

where $O^{(k)}$ represents the dipole operator D for $k=1$ and the quadrupole operator Q for $k=2$, respectively. As a special case the scalar polarizabilities of a state can be recovered by setting $i=f$ in the above equation. Apart from the static polarizability, a dynamic polarizability can also be defined. The imaginary part of the dynamic polarizability between two states is given by

$$\alpha_k^0(i\omega) = -\sum_{I\neq i,f}\left[\frac{E_f-E_I}{(E_f-E_I)^2+\omega^2}+\frac{E_i-E_I}{(E_i-E_I)^2+\omega^2}\right]\times\langle\Psi_f|O^{(k)}|\Psi_I\rangle\langle\Psi_I|O^{(k)}|\Psi_i\rangle, \tag{2.5}$$

where ω is the frequency of the external electromagnetic field. From these definitions it follows that the determination of the polarizabilities requires the evaluation of transition matrix elements and the excitation energies, hence a powerful many-body approach is necessary to evaluate the above quantities to high accuracy.

B. Van der Waals coefficients

The general expression for the van der Waals coefficients between two different atoms a and b in terms of their dynamic polarizabilities is given by [7]

$$C_{2n}^{ab} = \frac{(2n-2)!}{2\pi}\sum_{l=1}^{n-2}\frac{1}{(2l)!\,(2l')!}\int_0^\infty \alpha_l^a(i\omega)\alpha_{l'}^b(i\omega)d\omega, \tag{2.6}$$

where $l'\equiv n-l-1$ and $\alpha_l^a(i\omega)$ and $\alpha_{l'}^b(i\omega)$ are the 2^l-pole polarizability of atom a and $2^{l'}$-pole polarizability of atom b, respectively. In this article, we evaluate the C_6 and C_8 coefficients for the s-wave ground state of the Li atom using the simple formulas

$$C_6 = \frac{3}{\pi}\int_0^\infty d\omega[\alpha_1(i\omega)]^2, \tag{2.7}$$

$$C_8 = \frac{15}{\pi}\int_0^\infty d\omega[\alpha_1(i\omega)\alpha_2(i\omega)], \tag{2.8}$$

obtained from Eq. (2.6). The long-range part of the interaction between three ground-state atoms is not exactly equal to the interaction energies taken in pairs. There is an extra term which comes from the third-order perturbation. This correction to the van der Waals potential can be given as $V(R)\propto -v/R^3$, where [6]

$$v = \frac{3}{\pi}\int_0^\infty d\omega[\alpha_1(i\omega)]^3, \tag{2.9}$$

is called the triple-dipole constant. We have also determined this quantity v for the Li atom and present the result here.

III. METHOD OF CALCULATION

The aim of this work is to evaluate Eq. (2.5) for both static ($\omega=0$) and dynamic (finite ω) polarizabilities, while avoiding the sum-over-intermediate-states approach and at the same time treating electron-correlation effects rigorously. Coupled-cluster (CC) theory is one of the most powerful methods to incorporate the electron-correlation effects to all orders in the atomic wave functions. We employ here a relativistic CC theory that can determine the atomic wave functions accurately.

Using Eq. (2.5), we write for the dynamic polarizability between states $|\Psi_f\rangle$ and $|\Psi_i\rangle$

$$\alpha_k(i\omega) = \langle\Psi_f|O^{(k)}|\Psi_i'\rangle + \langle\Psi_f'|O^{(k)}|\Psi_i\rangle. \tag{3.1}$$

Comparing Eq. (2.5) and Eq. (3.1), we can express $|\Psi_v'\rangle$, where $v=i,f$, as

$$\begin{aligned}|\Psi'_v\rangle &= \sum_{I\neq v}\frac{E_I-E_v}{(E_I-E_v)^2+\omega^2}|\Psi_I\rangle\langle\Psi_I|O^{(k)}|\Psi_v\rangle\\ &= \frac{H_I-E_v}{(H_I-E_v)^2+\omega^2}\sum_{I\neq v}|\Psi_I\rangle\langle\Psi_I|O^{(k)}|\Psi_v\rangle\\ &= \frac{H-E_v}{H-E_v+i\omega}\left[|\Psi_v\rangle\langle\Psi_v| + \sum_{I\neq v}|\Psi_I\rangle\langle\Psi_I|\right]O^{(k)}|\Psi_v\rangle\\ &= \frac{H-E_v}{H-E_v+i\omega}O^{(k)}|\Psi_v\rangle\\ &= \left[\frac{1}{H-E_v-i\omega}\right]\left[\frac{H-E_v}{H-E_v+i\omega}O^{(k)}\right]|\Psi_v\rangle, \qquad (3.2)\end{aligned}$$

where H is the Dirac-Coulomb Hamiltonian. If we define next an effective Hamiltonian

$$H_{\text{eff}} = H - i\omega$$

and an effective dipole or quadrupole operator

$$O^{(k)}_{\text{eff}} = \frac{H-E_v}{H-E_v+i\omega}O^{(k)}$$

we can find $|\Psi'_v\rangle$ as the solution of

$$(H_{\text{eff}}-E_v)|\Psi'_v\rangle = O^{(k)}_{\text{eff}}|\Psi_v\rangle, \qquad (3.3)$$

where $|\Psi'_v\rangle$ is the perturbed wave function.

A. Determination of the dc wave functions

To carry out our calculations, we will use CC cluster theory. As this has been described in detail in many other papers, we will limit ourselves to a short overview. In CC theory, the atomic wave function $|\Psi_v\rangle$ due to the real part of the effective Hamiltonian of a single valence (v) open-shell system can be expressed as [30–32]

$$|\Psi_v\rangle = e^T\{1+S_v\}|\Phi_v\rangle, \qquad (3.4)$$

where we define the reference state $|\Phi_v\rangle = a_v^\dagger|\Phi_0\rangle$, with $|\Phi_0\rangle$ the closed-shell Dirac-Fock (DF) state, which is taken as the Fermi vacuum. T and S_v are the CC excitation operators for core to virtual electrons, and valence-core to virtual electrons, respectively. The curly bracket in the above expression represents the normal-ordered form. In our calculation, we consider all possible single (S) and double (D) excitations, as well as the most important triple (T) excitations, an approximation known as the CCSD(T) method [33]. To determine the amplitudes of the CC excitation operators we use

$$\begin{aligned}\langle\Phi^L|H_c|\Phi_0\rangle &= \Delta E_0 \quad \delta_{L,0},\\ \langle\Phi_v^K|H_cS_v|\Phi_v\rangle &= -\langle\Phi_v^K|H_c|\Phi_v\rangle\\ &\quad + \langle\Phi_v^K|S_v|\Phi_v\rangle\langle\Phi_v|H_c\{1+S_v\}|\Phi_v\rangle\delta_{K,0}\\ &= -\langle\Phi_v^K|H_c|\Phi_v\rangle + \langle\Phi_v^K|S_v|\Phi_v\rangle\Delta E_v\delta_{K,0}, \qquad (3.5)\end{aligned}$$

where we have defined $H_c \equiv \{H_N e^T\}_c$. The superscript $L(=1,2)$ represents the singly or doubly excited states from the closed-shell reference (DF) wave function and ΔE_0 is the correlation energy for the closed-shell system. Further, ΔE_v is the electron affinity energy of the valence electron v, $K(=1,2)$ denotes the singly or doubly excited states from the single valence reference state, and the subscripts N and c represent the normal-ordered form and connected terms, respectively. Equations (3.5) are nonlinear, and they are solved self-consistently by using a Jacobi iterative procedure. With the amplitudes of the CC excitation operators known, the zeroth-order wave functions can be calculated by using Eq. (3.4).

B. Determination of the perturbed wave functions

The next step is to determine the perturbed wave functions. We write the wave function of a state with valence electron v in the presence of a perturbed source as

$$|\tilde{\Psi}_v\rangle = |\Psi_v\rangle + |\Psi'_v\rangle, \qquad (3.6)$$

where $|\Psi_v\rangle$ is the wave function of the system due to the Dirac-Coulomb Hamiltonian and $|\Psi'_v\rangle$ is the correction to $|\Psi_v\rangle$ as explained above. In the spirit of the CC approach, we take the ansatz

$$|\tilde{\Psi}_v\rangle = e^{\tilde{T}}\{1+\tilde{S}_v\}|\Phi_v\rangle, \qquad (3.7)$$

where $\tilde{T}$ and $\tilde{S}_v$ are defined as

$$\tilde{T} = T + T', \qquad (3.8)$$

$$\tilde{S}_v = S_v + S'_v. \qquad (3.9)$$

Here T' and S'_v are the corrections to the T and S_v operators in the presence of the operator $O^{(k)}_{\text{eff}}$, respectively.

Substituting Eqs. (3.9) and (3.8) in Eq. (3.7), we find

$$|\tilde{\Psi}_v\rangle = e^T[1+S_v+T'\{1+S_v\}+S'_v]|\Phi_v\rangle, \qquad (3.10)$$

where only the terms linear in T' and S'_v exist, since Eq. (3.3) contains just one $O^{(k)}_{\text{eff}}$ operator. By comparing Eqs. (3.4), (3.6), and (3.10), we get

$$|\Psi'_v\rangle = e^T[T'\{1+S_v\}+S'_v]|\Phi_v\rangle. \qquad (3.11)$$

We evaluate these perturbed CC operator amplitudes using the following equations [see Eqs. (3.5)]:

$$\langle\Phi^L|\frac{[H_c^2+\omega^2]}{H_c}T'|\Phi_0\rangle = \langle\Phi^L|\{O^{(k)}e^T\}_c|\Phi_0\rangle$$

and

$$\begin{aligned}\langle\Phi_v^K|\frac{[(H_c-\Delta E_v)^2+\omega^2]}{H_c-\Delta E_v}S'_v|\Phi_v\rangle &= -\langle\Phi_v^K|\frac{[(H_c-\Delta E_v)^2+\omega^2]}{H_c-\Delta E_v}T'\{1+S_v\}|\Phi_v\rangle\\ &\quad + \langle\Phi_v^K|\{O^{(k)}e^T\}_c|\Phi_v\rangle, \qquad (3.12)\end{aligned}$$

where the meaning of L and K was explained above. The perturbed wave functions are determined using Eq. (3.11) after obtaining the perturbed CC amplitudes.

TABLE I. The static dipole polarizability α_1 of many low-lying levels in Li [a.u.].

Level	Experiments		Other theoretical works		This work	
	Scalar	Tensor	Scalar	Tensor	Scalar	Tensor
$2s\ ^2S_{1/2}$	164(3.4)[a] 164.2(1.1)[b]		162.3[e], 164[f] 164.084[j]		162.87	
$3s\ ^2S_{1/2}$			4136[c], 3832[d] 4133[e], 4098[f]		4107	
$4s\ ^2S_{1/2}$			3.526×10^{4} [e] 35040[f]		3.449×10^{4}	
$2p\ ^2P_{1/2}$	126.9(6)[g], 127(3.4)[i] 126.980[j]		117.8[e]		129.41	
$3p\ ^2P_{1/2}$			2.835×10^{4} [e]		2.938×10^{4}	
$4p\ ^2P_{1/2}$			2.734×10^{5} [e]		2.635×10^{5}	
$2p\ ^2P_{3/2}$	127.2(7)[g] 126.995[j]	1.64(4)[g] 1.59[j]	117.8[e]	3.874[e]	123.09	5.95
$3p\ ^2P_{3/2}$			2.835×10^{4} [e]	−2173 [e]	2.929×10^{4}	−2078
$4p\ ^2P_{3/2}$			2.735×10^{5} [e]	-2.074×10^{4} [e]	2.634×10^{5}	-1.473×10^{4}
$3d\ ^2D_{3/2}$	−15130(40) [h]	$1.643(6)\times10^{4}$ [h]	-1.504×10^{4} [e]	1.147×10^{4} [e]	-1.953×10^{4}	1.412×10^{4}
$4d\ ^2D_{3/2}$			3.093×10^{6} [e]	-5.355×10^{5} [e]	3.834×10^{6}	-6.650×10^{5}
$3d\ ^2D_{5/2}$	−15130(40) [h]		-1.504×10^{4} [e]	1.645×10^{4} [e]	-2.008×10^{4}	2.139×10^{4}
$4d\ ^2D_{5/2}$			3.103×10^{6} [e]	-7.678×10^{5} [e]	3.843×10^{6}	-9.496×10^{5}

[a] Molof *et al.* (1974) [37].
[b] Miffre *et al.* (2006) [38].
[c] Themelis *et al.* (1995) [21].
[d] Mérawa *et al.* (1998) [22].
[e] Ashby *et al.* (2003) [39].
[f] Magnier *et al.* (2002) [24].
[g] Windholz *et al.* (1992) [40] (^{6}Li values).
[h] Ashby *et al.* (2003) [41].
[i] Hunter *et al.* (1991) [42].
[j] Johnson *et al.* (2008) [43].

C. Evaluation of α using the RCC approach

The expression for the polarizabilities using our CC approach can now be obtained by substituting Eqs. (3.4) and (3.11) in Eq. (3.1). In this way we get (we also normalize the wave functions)

$$\begin{aligned}\alpha_k(i\omega) &= \frac{\langle\Psi_f|O^{(k)}|\Psi_i'\rangle + \langle\Psi_f'|O^{(k)}|\Psi_i\rangle}{\sqrt{\langle\Psi_f|\Psi_f\rangle\langle\Psi_i|\Psi_i\rangle}}\\ &= \frac{1}{\sqrt{N_iN_f}}(\langle\Phi_f|\{1+S_f^\dagger\}O^{(k)}[T'\{1+S_i\}+S_i']|\Phi_i\rangle\\ &\quad + \langle\Phi_f|[S_f'^\dagger + \{1+S_f^\dagger\}T'^\dagger]\overline{O^{(k)}}\{1+S_i\}|\Phi_i\rangle),\end{aligned} \tag{3.13}$$

where

$$N_v = \langle\Phi_v|\{1+S_v^\dagger\}\mathcal{N}_0\{1+S_v\}|\Phi_v\rangle,$$

with $v=i,f$, and we have defined $\overline{O^{(k)}}=e^{T^\dagger}O^{(k)}e^{T}$ and $\mathcal{N}_0=e^{T^\dagger}e^{T}$.

We first evaluate, by using the generalized Wick's theorem, the intermediate terms $\overline{O^{(k)}}$ and $\mathcal{N}_0$ in the above expressions as effective one-body, two-body, and so on, terms. Next we sandwich the open-shell valence-core electron excitation operators to evaluate the exact expression.

D. Generation of DF reference states

We have used partly numerical and partly analytical orbitals to generate the complete basis sets. The numerical orbitals were obtained using GRASP [34], and the analytical orbitals were obtained using Gaussian-type orbitals (GTO's) [35].

TABLE II. The static quadrupole polarizability α_2^0 of many important states in Li [a.u.].

Level	Other theoretical works	This work
$2s\ ^2S_{1/2}$	1423[a], 1424[b], 1430[c], 1423.266(5)[d] 1403[e], 1393[f], 1424(4)[g], 1424.4[h]	1420
$3s\ ^2S_{1/2}$	3.5642×10^{5} [h]	3.475×10^{5}
$4s\ ^2S_{1/2}$	1.1587×10^{7} [h]	1.113×10^{7}
$2p\ ^2P_{1/2}$		7.804×10^{4}
$3p\ ^2P_{1/2}$		1.033×10^{7}
$4p\ ^2P_{1/2}$		3.301×10^{9}

[a] Spelsberg *et al.* (1993) [12].
[b] Marinescu *et al.* (1994) [44].
[c] Mérawa *et al.* (1994) [45].
[d] Yan *et al.* (1996) [6].
[e] Patil and Tang (1997) [46].
[f] Patil and Tang (1999) [47].
[g] Snow *et al.* (2005) [48].
[h] Zhang *et al.* (2007) [23].

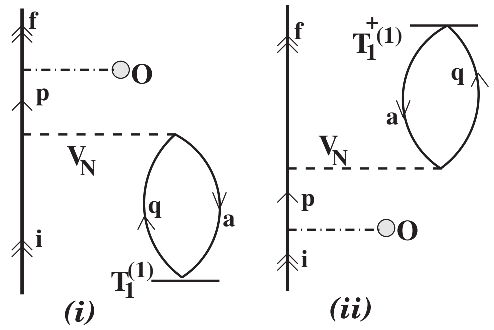

FIG. 1. Extra correlation diagrams which appear in the calculation of the polarizabilities using our novel approach. These diagrams do not appear when the CC wave functions are used in the sum-over-the-states method.

In total, we have taken up to the $30s$, $30p$, $25d$, $25f$, and $20g$ orbitals to calculate the DF wave function. Out of these, we have generated the first 4, 3, 2, 2, and 2 orbitals from the s, p, d, f, and g symmetries, respectively, using GRASP. The remaining continuum orbitals were obtained analytically from GTO's, using as parameters α=0.00525 and β=2.73. After this, the final orbitals were orthogonalized using Schmidt's procedure [36].

IV. RESULTS AND DISCUSSIONS

Tables I and II show our values of the static dipole and quadrupole polarizabilities of several important low-lying states of Li. In these tables, we have also listed other theoretical results and, where available, the most recent experimental results. For the ground state a number of theoretical dipole polarizability results are available, for the excited states, however, few calculations have been carried out. Moreover, all other theoretical results, except two [25,43], are based on nonrelativistic theory. Some of these calculations are also performed using molecular codes, which do not take atomic symmetries into account [24]. Of the two available relativistic calculations on the excited states, the first [25] is carried out using a rather approximate method to include the correlation effects due to the Coulomb interaction. The second [43] is based on a linearized CC method and the sum-over-the-states approach. Our calculation uses a relativistic approach which considers correlation effects to all orders in the form of CC amplitudes.

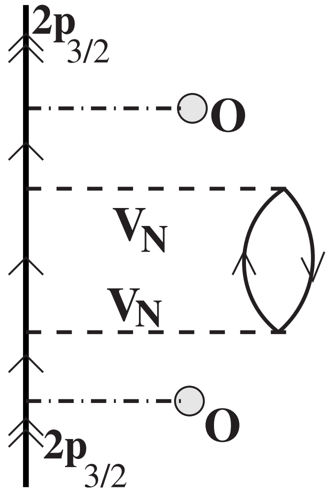

FIG. 2. The correlation diagram that causes a large discrepancy between the calculated and the experimental results of the tensor polarizability of the ${}^2P_{3/2}$ state.

TABLE III. The off-diagonal scalar polarizability in Li [a.u.].

	Dirac-Fock	CCSD(T)
	Dipole	
$2s$-$3s$	−27.18	−20.41
$2s$-$4s$	−202.9	−164.2
$3s$-$4s$	−105.8	6.292
	Quadrupole	
$2s$-$3s$	2.495×10^4	2.219×10^4
$2s$-$4s$	1.245×10^5	1.134×10^5
$3s$-$4s$	9.281×10^5	6.647×10^5

Table II shows the result for the static quadrupole polarizabilities. No experimental data is available for comparison, and the available theoretical results for the $2s$ ${}^2S_{1/2}$ level are not very consistent.

Although our method is theoretically superior to the previously employed methods to determine both dipole and quadrupole polarizabilities, it seems that some of the earlier results are in better agreement with the experimental results

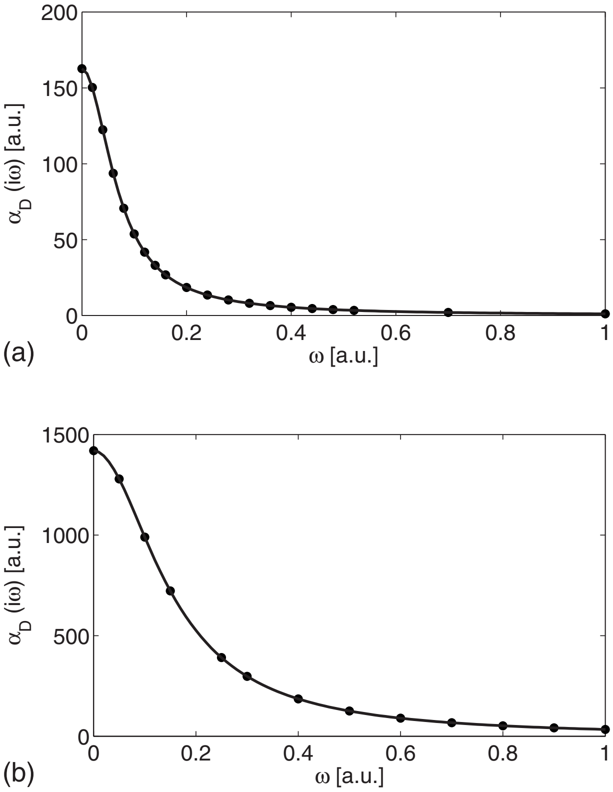

FIG. 3. The imaginary parts of the dipole (i) and quadrupole (ii) polarizabilities of the ground state of Li as a function of the angular frequency ω.

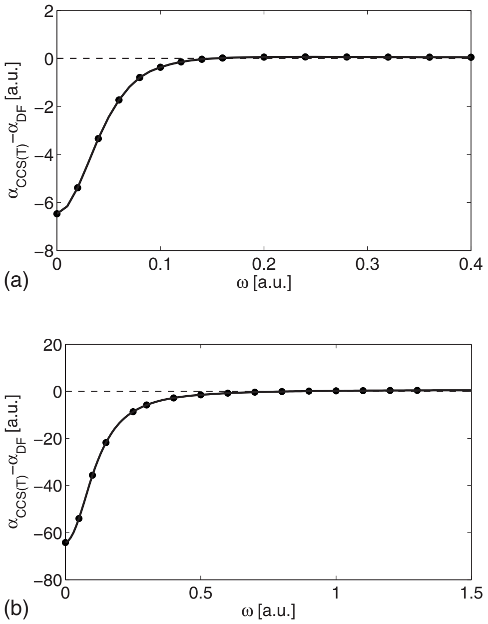

FIG. 4. The difference between the DF and CCSD(t) results for the imaginary parts of the dipole (i) and quadrupole, (ii) polarizabilities of the ground state of Li as a function of the angular frequency ω.

than ours. This may be due to the fact that experimental energies are used in some of these calculations in contrast to our method which is fully *ab initio*. This means that in our calculation there may be strong cancellations with neglected higher-order excitations in the correlation effects. Note that in our approach we implicitly take into account certain correlation effects that cannot be accounted for in the usual sum-over-states approach that is used in many of the earlier calculations, including the RCC method employed in Ref. [43]. These diagrams, which are shown diagrammatically in Fig. 1, are part of the random-phase approximation.

As Table I shows, our value for the tensor polarizability of the $2p\ ^2P_{3/2}$ level is larger than the experimental result. We found that this large value is due to the unusual behavior of the correlation effects produced by the diagram shown in Fig. 2. Leaving out this diagram yields a value for the tensor polarizability of the $2p\ ^2P_{3/2}$ level of ~1.6, which agrees nicely with the experiment. For the completeness of the theory this effect cannot be left out. We expect that this effect will cancel with the neglected higher-order excitations.

TABLE IV. C_6 and C_8 values for the ground states of Li-Li [a.u.].

	$C_6(\times 10^3)$	$C_8(\times 10^5)$
This work		
Dirac-Fock	1.473	0.8891
CCSD(T)	1.396(6)	0.8360
Other theoretical works		
Marinescu *et al.* (1994) [44]	1.388	0.8324
Spelsberg *et al.* (1996) [12]		
Yan *et al.* (1996) [6]	1.39322	0.834258(42)
Patil and Tang (1999) [47]	1.360	0.8100
Porsev and Derevianko (2003) [49]	-	0.834(4)
Mitroy and Bromley (2003) [14]	1.3946	0.83515

TABLE V. The triple-dipole constant υ for Li-Li-Li [a.u.].

	$\upsilon(\times 10^4)$
This work	
Dirac-Fock	18.576
CCSD(T)	16.934
Other theoretical works	
Yan *et al.* (1996) [6]	17.0595(6)
Mitroy and Bromley (2003) [14]	17.087

In Table III, we present scalar dipole and quadrupole polarizabilities among different s states of Li which are also important in the determination of the van der Waals coefficients of the excited states for ultracold atom experiments. Our method can also be employed to determine these quantities in heavy alkali atoms such as Cs and Fr that are important candidates for the study of atomic parity nonconservation [26]. To our knowledge, no other results are available to compare with these results. As the table shows, the scalar dipole polarizability between the ground state and the first excited states in Li is of opposite sign to the other alkali atoms [26].

The main goal of this work is to illustrate how to evaluate the van der Waals coefficients using the present method. Figure 3 shows the imaginary parts of the dipole and quadrupole polarizabilities of the ground state of Li as functions of angular frequency ω. As the figures show, these quantities fall off exponentially for higher values of ω. To illustrate the effect of electron correlation as a function of frequency, we have plotted the difference between the CCSD(T) and the DF results in Fig. 4. This figure suggests that the correlation effects vanish for higher frequencies. Using the imaginary parts of the dipole and quadrupole polarizabilities in Eqs. (2.7)–(2.9), we evaluated the C_6, C_8, and υ coefficients, respectively, using a numerical integration method.

In Table IV we present our C_6 and C_8 coefficients and compare them with the other available results. Although our value for the static polarizability of the ground state of Li is slightly smaller than the results presented by others, our C_6 and C_8 values are in good agreement with the other results. We present the coefficient υ of the third-order correction to the long-range potential in Table V, which matches well with the other available semiempirical results.

V. CONCLUSION

We have employed an approach to determine both ground and excited states polarizabilities by treating the electron-correlation effects and wave functions due to external operators in the spirit of the RCC ansatz. This approach was used to determine the imaginary parts of the polarizabilities which we used to evaluate the van der Waals coefficients for Li atoms. By using this novel technique, we were able to consider the electron-correlation effects rigorously through the RCC theory.

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