

Ab initio calculation of excited state dipole polarizability – Application to the first $1,3\Sigma_{g,u}^+$ states of Li_2

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Abstract. Firstly, imaginary frequency-dependent dipole polarizabilities of Li in its $2S$ ground state and the first $2P$ excited state are calculated from a time-dependent gauge-invariant method using effective core pseudo-potentials and the multi-configuration one-electron wave function. C_6 dispersion coefficients of the $2s + 2s$ and $2s + 2p$ dissociations are deduced and also compared with all-electron values. Then, static polarizabilities of Li_2 in its ground and first excited $1,3\Sigma_{g,u}^+$ states are obtained at interatomic distance corresponding to the energy minimum of each state.

PACS. 31.15.Ar Ab initio calculations – 31.50.Df Potential energy surfaces for excited electronic states – 33.15.Kr Electric and magnetic moments (and derivatives), polarizability, and magnetic susceptibility

1 Introduction

Dynamic polarizabilities of atoms and molecules in their ground state are important parameters to evaluate accurately their interaction at long distance and to plot the lowest potential energies of their dissociation. Effectively, the van der Waals dispersion coefficient C_6 which is the main term playing a part in the attractive potential between two neutral systems can be obtained from the imaginary frequency-dependent dipole polarizability of each system through the Casimir-Polder relation [1]. For the collision involving excited states of one or both interacting electronic systems, this latter relation is no longer available. However, the van der Waals dispersion coefficient C_6 may also be obtained by fitting the imaginary frequency dependence of the polarizability of each atom or molecule in its ground or excited state [2].

Moreover for molecules like *s*-tetrazine, the polarizability anisotropy of the ground state is significantly different [3] from the first excited state, showing that the approach of molecules in physisorption for example could be different when the molecules are in their ground or excited states.

These two examples show the importance of experimental and theoretical investigations of the excited state electric properties. However, in contrast with the numerous ground state data available in the literature, the excited state electric property values are scarce and generally of low accuracy. Nevertheless, the progress in experiment and *ab initio* calculation of wave functions for excited states (see [4, 5] for example) should allow us to reach these properties more accurately.

In this work, first we calculate the dynamic polarizability of the lithium atom in its $2s$ and $2p$ states with the time-dependent gauge-invariant (TDGI) method [6]. Effective core pseudo-potentials [7] are used and valence one-electron wave functions are developed over interacting electronic configurations. We compare the new polarizability values to previous all-electron values [2] as well as the deduced C_6 values. Then we calculate the static polarizability of the two-valence electron diatomic Li_2 system in its singlet and triplet (1) $1,3\Sigma_{g,u}^+$ ($2s + 2s$), (2) $1,3\Sigma_{g,u}^+$ ($2s + 2p$) and (1) $1,3\Sigma_{u,g}^+$ ($2s + 2p$) states, in their respective equilibrium geometry.

2 Methodological details

The effective core potential technique with core polarization potentials (CPP) of Poteau and Spiegelmann [7] has been used. The same Gaussian function basis set was used for both the one and two valence electron systems Li and Li_2 , in order to describe the all-electron spectrum of both systems with the same accuracy, and to obtain the first excited potential surfaces of Li_2 more easily. However the *l*-dependent cutoff radii of the pseudo-potentials have been slightly changed for the *s* and *p* functions (1.428 and 0.987 instead of 1.434 and 0.979 respectively) as well as the exponent values of *d*-Gaussian orbitals (0.2, 0.04, 0.012 and 0.008574) of the atomic orbital basis set, in order to obtain comparable transition energy and moment values involving four S, three P and two D states of Li found experimentally [8]. If the new data describes one state more in each symmetry, this does not modify significantly the first transition energy and oscillator strength values. Moreover, the contribution of the third P($4p$) state in the polarizability

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Table 1. Low-lying transition energies (a.u.), oscillator strengths and transition probabilities^a of Li atom calculated with corrected (C) dipole moment due to core polarization effect (see the text), and without correction (NC).

Transition	ΔE	$\Delta E(\text{Exp.})^b$	$f_{ik}(C)$	$f_{ik}(NC)$	$f_{ik}(\text{Exp.})^b$	$A_{ki}^*(C)$	$A_{ki}^*(NC)$	$A_{ki}^*(\text{Exp.})$
$1s^2 2s(^2S) \rightarrow 1s^2 2p(^2P^0)$	0.067912	0.067911	0.752	0.759	0.753	3.713	3.748	3.720
$1s^2 2s(^2S) \rightarrow 1s^2 3p(^2P^0)$	0.140906	0.140914	0.004	0.005	0.0055	0.085	0.106	0.117
$1s^2 2s(^2S) \rightarrow 1s^2 4p(^2P^0)$	0.184709	0.166177	0.022	0.021	0.0048	0.800	0.767	0.142
$1s^2 3s(^2S) \rightarrow 1s^2 2p(^2P^0)$	-0.056066	-0.056056	-0.331	-0.329				
$1s^2 3s(^2S) \rightarrow 1s^2 3p(^2P^0)$	0.016928	0.016947	1.212	1.213	1.23	0.372	0.372	0.377
$1s^2 3s(^2S) \rightarrow 1s^2 4p(^2P^0)$	0.060731	0.042210	0.011	0.011	0.0002	0.043	0.043	0.0004
$1s^2 2p(^2P^0) \rightarrow 1s^2 2s(^2S)$	-0.067912	-0.067911	-0.251	-0.253				
$1s^2 2p(^2P^0) \rightarrow 1s^2 3s(^2S)$	0.056066	0.056056	0.110	0.110	0.115	3.332	3.332	3.49
$1s^2 2p(^2P^0) \rightarrow 1s^2 4s(^2S)$	0.099270	0.091625	0.024	0.024	0.0125	2.279	2.279	1.01
$1s^2 2p(^2P^0) \rightarrow 1s^2 3d(^2D)$	0.074871	0.074633	0.643	0.644	0.667	6.947	6.958	7.16
$1s^2 2p(^2P^0) \rightarrow 1s^2 4d(^2D)$	0.103713	0.098967	0.198	0.199	0.122	4.106	4.127	2.30

^a $A_{ki}^* = A_{ki} \times 10^7 \text{s}^{-1}$, ^b experimental results: reference [8].

Table 2. Spectroscopic constants for the singlet and triplet (1) $^{1,3}\Sigma_{g,u}^+ 2s + 2s$ states and the (2) $^{1,3}\Sigma_{g,u}^+$ and (1) $^{1,3}\Sigma_{u,g}^+ 2s + 2p$ states.

States	$R_e(\text{\AA})$		$D_e(\text{cm}^{-1})$		$\omega_e(\text{cm}^{-1})$		$T_e(\text{cm}^{-1})$		Dissociations
	this work	others	this work	others	this work	others	this work	others	
(1) $^1\Sigma_g^+(X)$	2.659	2.673 ^a	8523	8516.9 ^a	369	351.39 ^a	0	0	$2s + 2s$
(1) $^3\Sigma_u^+$	4.166	4.127 ^e	317	336 ^e	69	67.53 ^e	8206	8181 ^e	$2s + 2s$
(2) $^1\Sigma_g^+$	3.673	3.651 ^b	3166	3318.86 ^b	134	128.67 ^b	20261	20101 ^b	$2s + 2p$
(2) $^3\Sigma_u^+$	3.175		-5437		218				$2s + 2p$
(1) $^1\Sigma_u^+$	3.099	3.108 ^d	9475	9352.50 ^d	266	257.47 ^d	13953	14068 ^d	$2s + 2p$
(1) $^3\Sigma_g^+$	3.064	3.068 ^c	7149	7091.50 ^c	261	251.50 ^c	16279	16329 ^c	$2s + 2p$

^areference [13], ^breference [14], ^creference [15], ^dreference [16], ^ereference [17].

of the ground $S(2s)$ state of the Li atom is very small because of the weak oscillator strength $2s \rightarrow 4p$ (see Tab. 1). However, good description of the $4s$ and $4d$ states can be important in the determination of the polarizability of the $2p$ state.

The wave functions corresponding to the ground and first excited states ($\Psi_n^{(0)}$) of the atomic and diatomic Li have been obtained by the configuration interaction CIPSI algorithm [9,10]. The low-lying transition energies and oscillator strengths are given in Table 1 for Li, and a rather good comparison can be made with experimental values of Wiese *et al.* [8] (except for results concerning the $4p$ state). Concerning the calculation of transition moments, we must emphasize that the core polarization effect has been also considered. We use the modified transition operator proposed by Hameed *et al.* [11] and given in reference [12]: $\mu = -r + \sum_c \alpha_c f_c$ where α_c and f_c are the polarizability of the core and the electric field acting on the core due to the valence electrons, respectively. In fact,

this correction has a small effect for this light electronic system.

With regards to Li_2 , spectroscopic data have been calculated and reported in Table 2, and are in good agreement with experimental results [13–17]. We notice that the lowest triplet state (1) $^3\Sigma_u^+$ is practically unbound and has a small dissociation D_e energy, while the following one (2) $^3\Sigma_u^+$ is dissociative ($D_e < 0$) but owns a local minimum at relatively short interatomic distance due to cross-over states. These low-lying states are plotted in Figure 1. More details of the Li_2 spectrum can be found in reference [7]. Calculated transition energies and oscillator strengths at the geometry corresponding to the energy minimum of the studied ground or excited states are given in Tables 3 and 4. While only one large oscillator strength corresponding to the $2s \rightarrow 2p$ atomic transition appears for the $2s + 2s$ molecular states (Tab. 3), the allowed transitions from the $2s + 2p$ molecular states are spread over different transition energies with positive and negative oscillator strengths (Tab. 4).

Table 3. Calculated transition energies (ΔE) and oscillator strengths (f_{ik}) for the first lowest energy singlet $(1) \ ^1\Sigma_g^+$ and triplet $(1) \ ^3\Sigma_u^+ 2s + 2s$ states of Li_2 (a.u.).

Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(1) \ ^1\Sigma_g^+ \rightarrow (1) \ ^1\Sigma_u^+$	0.067489	1.354	$(1) \ ^1\Sigma_g^+ \rightarrow (1) \ ^1\Pi_u$	0.096357	1.422
$(1) \ ^1\Sigma_g^+ \rightarrow (2) \ ^1\Sigma_u^+$	0.140648	0.009	$(1) \ ^1\Sigma_g^+ \rightarrow (2) \ ^1\Pi_u$	0.143046	0.074
$(1) \ ^1\Sigma_g^+ \rightarrow (3) \ ^1\Sigma_u^+$	0.160582	0.005	$(1) \ ^1\Sigma_g^+ \rightarrow (3) \ ^1\Pi_u$	0.161426	0.005
$(1) \ ^1\Sigma_g^+ \rightarrow (4) \ ^1\Sigma_u^+$	0.165289	0.004	$(1) \ ^1\Sigma_g^+ \rightarrow (4) \ ^1\Pi_u$	0.166080	0.015
$(1) \ ^1\Sigma_g^+ \rightarrow (5) \ ^1\Sigma_u^+$	0.184684	0.022	$(1) \ ^1\Sigma_g^+ \rightarrow (5) \ ^1\Pi_u$	0.185096	0.004
Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(1) \ ^3\Sigma_u^+ \rightarrow (1) \ ^3\Sigma_g^+$	0.045982	1.457	$(1) \ ^3\Sigma_u^+ \rightarrow (1) \ ^3\Pi_g$	0.076133	1.349
$(1) \ ^3\Sigma_u^+ \rightarrow (2) \ ^3\Sigma_g^+$	0.098560	0.024	$(1) \ ^3\Sigma_u^+ \rightarrow (2) \ ^3\Pi_g$	0.099926	0.154
$(1) \ ^3\Sigma_u^+ \rightarrow (3) \ ^3\Sigma_g^+$	0.116064	0.021	$(1) \ ^3\Sigma_u^+ \rightarrow (3) \ ^3\Pi_g$	0.124172	0.002
$(1) \ ^3\Sigma_u^+ \rightarrow (4) \ ^3\Sigma_g^+$	0.134210	0.003	$(1) \ ^3\Sigma_u^+ \rightarrow (4) \ ^3\Pi_g$	0.142479	0.005
$(1) \ ^3\Sigma_u^+ \rightarrow (5) \ ^3\Sigma_g^+$	0.139645	0.012	$(1) \ ^3\Sigma_u^+ \rightarrow (5) \ ^3\Pi_g$	0.148757	0.001

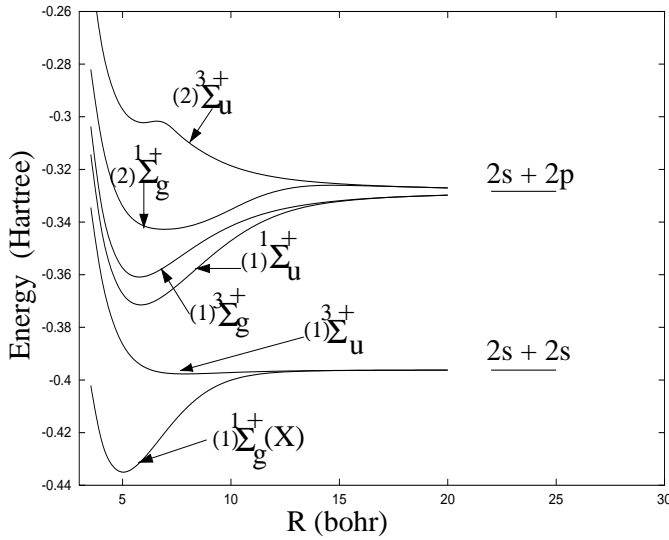
Table 4. Calculated transition energies (ΔE) and oscillator strengths (f_{ik}) for the first singlet and triplet $(2) \ ^{1,3}\Sigma_{g,u}^+$ and $(1) \ ^{1,3}\Sigma_{u,g}^+ 2s + 2p$ excited states of Li_2 (a.u.).

Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(2) \ ^1\Sigma_g^+ \rightarrow (1) \ ^1\Sigma_u^+$	-0.025235	-0.099	$(2) \ ^1\Sigma_g^+ \rightarrow (1) \ ^1\Pi_u$	0.007207	0.001
$(2) \ ^1\Sigma_g^+ \rightarrow (2) \ ^1\Sigma_u^+$	0.048179	0.409	$(2) \ ^1\Sigma_g^+ \rightarrow (2) \ ^1\Pi_u$	0.049992	0.125
$(2) \ ^1\Sigma_g^+ \rightarrow (3) \ ^1\Sigma_u^+$	0.062875	0.832	$(2) \ ^1\Sigma_g^+ \rightarrow (3) \ ^1\Pi_u$	0.066202	0.085
$(2) \ ^1\Sigma_g^+ \rightarrow (4) \ ^1\Sigma_u^+$	0.072226	0.156	$(2) \ ^1\Sigma_g^+ \rightarrow (4) \ ^1\Pi_u$	0.069299	0.524
$(2) \ ^1\Sigma_g^+ \rightarrow (5) \ ^1\Sigma_u^+$	0.080769	0.179	$(2) \ ^1\Sigma_g^+ \rightarrow (5) \ ^1\Pi_u$	0.090672	0.361
Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(2) \ ^3\Sigma_u^+ \rightarrow (1) \ ^3\Sigma_g^+$	-0.058287	-1.343	$(2) \ ^3\Sigma_u^+ \rightarrow (1) \ ^3\Pi_g$	-0.017456	-0.158
$(2) \ ^3\Sigma_u^+ \rightarrow (2) \ ^3\Sigma_g^+$	-0.008180	-0.086	$(2) \ ^3\Sigma_u^+ \rightarrow (2) \ ^3\Pi_g$	0.008287	0.033
$(2) \ ^3\Sigma_u^+ \rightarrow (3) \ ^3\Sigma_g^+$	0.009033	1.742	$(2) \ ^3\Sigma_u^+ \rightarrow (3) \ ^3\Pi_g$	0.019624	0.902
$(2) \ ^3\Sigma_u^+ \rightarrow (4) \ ^3\Sigma_g^+$	0.027074	0.106	$(2) \ ^3\Sigma_u^+ \rightarrow (4) \ ^3\Pi_g$	0.037907	0.064
$(2) \ ^3\Sigma_u^+ \rightarrow (5) \ ^3\Sigma_g^+$	0.031916	0.025	$(2) \ ^3\Sigma_u^+ \rightarrow (5) \ ^3\Pi_g$	0.044785	0.001
Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(1) \ ^1\Sigma_u^+ \rightarrow (1) \ ^1\Sigma_g^+$	-0.059000	-1.433	$(1) \ ^1\Sigma_u^+ \rightarrow (1) \ ^1\Pi_g$	0.040654	0.102
$(1) \ ^1\Sigma_u^+ \rightarrow (2) \ ^1\Sigma_g^+$	0.030771	0.424	$(1) \ ^1\Sigma_u^+ \rightarrow (2) \ ^1\Pi_g$	0.081781	0.486
$(1) \ ^1\Sigma_u^+ \rightarrow (3) \ ^1\Sigma_g^+$	0.061377	0.372	$(1) \ ^1\Sigma_u^+ \rightarrow (3) \ ^1\Pi_g$	0.098591	0.484
$(1) \ ^1\Sigma_u^+ \rightarrow (4) \ ^1\Sigma_g^+$	0.075423	1.336	$(1) \ ^1\Sigma_u^+ \rightarrow (4) \ ^1\Pi_g$	0.112549	0.190
$(1) \ ^1\Sigma_u^+ \rightarrow (5) \ ^1\Sigma_g^+$	0.089274	0.522	$(1) \ ^1\Sigma_u^+ \rightarrow (5) \ ^1\Pi_g$	0.114757	0.213
Transition	ΔE	f_{ik}	Transition	ΔE	f_{ik}
$(1) \ ^3\Sigma_g^+ \rightarrow (1) \ ^3\Sigma_u^+$	-0.033135	-1.145	$(1) \ ^3\Sigma_g^+ \rightarrow (1) \ ^3\Pi_u$	-0.017816	-0.048
$(1) \ ^3\Sigma_g^+ \rightarrow (2) \ ^3\Sigma_u^+$	0.058729	1.252	$(1) \ ^3\Sigma_g^+ \rightarrow (2) \ ^3\Pi_u$	0.061089	0.391
$(1) \ ^3\Sigma_g^+ \rightarrow (3) \ ^3\Sigma_u^+$	0.072402	0.159	$(1) \ ^3\Sigma_g^+ \rightarrow (3) \ ^3\Pi_u$	0.081951	0.022
$(1) \ ^3\Sigma_g^+ \rightarrow (4) \ ^3\Sigma_u^+$	0.081496	0.463	$(1) \ ^3\Sigma_g^+ \rightarrow (4) \ ^3\Pi_u$	0.091694	0.594
$(1) \ ^3\Sigma_g^+ \rightarrow (5) \ ^3\Sigma_u^+$	0.086190	0.109	$(1) \ ^3\Sigma_g^+ \rightarrow (5) \ ^3\Pi_u$	0.095237	0.004

Table 5. Ground and excited states dipole polarizabilities of Li atom (a.u.). Pseudo-potential TDGI calculations with corrected (C) and non corrected (NC) dipole moments.

	$\alpha_0(2^2S)$	$\alpha_0(3^2S)$	$\alpha_0(2^2P)$	$\alpha_2(2^2P)$	
(C)	165	4131	125	2.3	
(NC)	166	4134	125	2.9	
Other results	165 ^a , 164.0±3.4 ^b 165 ^c , 164.1 ^d	4020 ^a , 4130 ^c	130 ^a , 126 ^c	-0.9 ^a , 2.3 ^c	
	$\alpha_{01}(2^2S)$	$\alpha_{01}(3^2S)$	$\alpha_{10}(2^2P)$	$\alpha_{11}(2^2P)$	$\alpha_{12}(2^2P)$
(C)	-494	-12391	148	0	-1271
(NC)	-498	-12403	153	0	-1274
Other results	-494 ^a	-12100 ^a	119 ^a	2.7 ^a	-1280 ^a

^aTDGI all-electron calculations reference [2], ^breference [18], ^creference [19], ^dreference [20].

**Fig. 1.** Potential curves for the low-lying $1,3\Sigma_{g,u}^+$ states of Li_2 .

Once the low-energy discrete spectrum is obtained, a method developed in our team is used in order to calculate angular frequency-dependent dipole polarizabilities $\alpha(\omega)$ of a system in its ground or excited state $\Psi_n^{(0)}$ [6]. This consists of a variational determination of a first order perturbation wave function $\Psi_n^{(1)}$ obtained by the projection of the first-order perturbation Schrödinger equation:

$$(H^{(0)} - E_n^{(0)} \pm \hbar\omega)|\Psi_n^{(1)}\rangle = -(H^{(1)} - E_n^{(1)})|\Psi_n^{(0)}\rangle$$

on the basis set over which $\Psi_n^{(1)}$ is developed, where the perturbation $H^{(1)}$ is time-dependent and $E_n^{(1)}$ is defined as: $\langle\Psi_n^{(0)}|H^{(1)}|\Psi_n^{(0)}\rangle$.

The dynamic polarizability for imaginary angular frequency is calculated as follows:

$$\alpha(i\omega) = 2\langle\Psi_n^{(0)}|H^{(1)}|\Psi_n^{(1)}(i\omega)\rangle.$$

In this work where only one-valence or two-valence electron systems are studied, $\Psi_n^{(1)}$ is mainly developed on some N spectroscopic states $\Psi_{n' \neq n}^{(0)}$ energetically closed to the studied $\Psi_n^{(0)}$ state and the method corresponds to the sum over states (SOS) second-order perturbation energy, converging relatively rapidly in these cases ($N < 10$). However, particularly for Li_2 , Slater determinants ϕ_m can be added as pseudo-states ($M < 100$), and their coefficients are variationally obtained at the same time as the spectroscopic states, the corresponding $H^{(0)}$ matrix being no longer diagonal for this basis set. Another possibility is to introduce directly the ϕ_m Slater determinants in the CIPSI algorithm from a dipole moment perturbation criterion in addition to the energy one, and use the SOS formula with more spectroscopic states ($\simeq N + M$).

Once $\alpha(i\omega)$ of $\text{Li}(2s)$ and $\text{Li}(2p)$ are calculated for different values of ω , a fit of “pseudo-spectrum” transition energies \tilde{E}_i and oscillator strengths \tilde{f}_i as parameters of a finite SOS continuous function $\sum_i \tilde{f}_i / (\tilde{E}_i^2 + \omega^2)$ is carried out over the obtained $\alpha(i\omega)$ values. This leads to C_6 dispersion coefficients related by the following sums (see Ref. [2]):

$$\sum_{i,j} \frac{\tilde{f}_i \tilde{f}_j}{\tilde{E}_i \tilde{E}_j (\tilde{E}_i + \tilde{E}_j)}.$$

For $\text{Li}(2s)+\text{Li}(2p)$ dissociation, the dipole-dipole Hamiltonian interaction appears at the first order of perturbation and leads to the C_3 term depending of the transition moment $\langle 2s|\mathbf{r}|2p\rangle$.

3 Polarizability results

In Table 5, the static polarizability values of Li in its $2s$, $3s$ and $2p$ states are reported and compared to other results [2, 18–20]. Firstly, we notice that the core polarization effect taken into account in the dipole moment calculation acts very slightly upon the polarizability results of $\text{Li}(2s)$ and $\text{Li}(3s)$. However, the use of effective core potentials

Table 6. Van der Waals C_3 and C_6 coefficients of Li_2 for the $2^2\text{S}+2^2\text{S}$ and $2^2\text{S}+2^2\text{P}$ dissociations. Calculations with corrected (C) and non corrected (NC) dipole moments.

Li-Li		C_3			C_6		
		(C)	(NC)	other results	(C)	(NC)	other results
$2s-2s$	$1,3\Sigma_{g,u}^+$				1424	1448	1410^a [1390–1480] ^b
$2s-2p$	$1,3\Sigma_{g,u}^+$	11.08	11.16	11.0^a [(11.0)–(11.5)] ^c	1974	2019	2410^a [1927–2066] ^c
	$1,3\Sigma_{u,g}^+$	–11.08	–11.16	-11.0^a [(–11.0)–(–11.5)] ^c	1974	2019	2410^a [1927–2066] ^c
	$1,3\Pi_{g,u}$	–5.54	–5.58	-5.50^a [(–5.5)–(–5.8)] ^c	1312	1328	1530^a [1301–1750] ^c
	$1,3\Pi_{u,g}$	5.54	5.58	5.50^a [(5.5)–(5.8)] ^c	1312	1328	1530^a [1301–1750] ^c

^aTDGI all-electron calculations reference [2], ^breferences [21–27], ^creferences [21–23,28].

Table 7. Dipole polarizabilities of the singlet and triplet (1) $1,3\Sigma_{g,u}^+$ $2s+2s$ states, and the (2) $1,3\Sigma_{g,u}^+$ and (1) $1,3\Sigma_{u,g}^+$ $2s+2p$ states of Li_2 (a.u.), at their corresponding equilibrium geometry (Equ.) and dissociation (Diss.).

States	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$	
(1) $1\Sigma_g^+(X)$	Equ.	303	160	208	143
	Other results	310^a [296–311] ^b	169^a [140–169] ^b	216^a [212–216] ^b	141^a [132–141] ^b
	Exp.			229 ± 20^c	
	Diss.	330	330	330	0
(1) $3\Sigma_u^+$	Equ.	698	252	401	446
	Diss.	330	330	330	0
(2) $1\Sigma_g^+$	Equ.	307	274	285	33
	Diss.	285	292	290	–7
(2) $3\Sigma_u^+$	Equ.	2.00×10^4	2.42×10^3	8.27×10^3	1.75×10^4
	Diss.	285	292	290	–7
(1) $1\Sigma_u^+$	Equ.	462	224	303	238
	Diss.	285	292	290	–7
(1) $3\Sigma_g^+$	Equ.	–511	69	–124	–580
	Diss.	285	292	290	–7 ^b

^aTDGI all-electron calculations: [29], ^bother theoretical results: [30–33], ^cexperimental result: [34].

implies that Li is described by a one-electron wave function and then leads to $\alpha_{11} = 0$ for $\text{Li}(2p)$, which is not exactly true with all-electron calculations [2]. This is probably the reason why the sign of $\alpha_2(2^2\text{P})$ changes. In the same way when the all electron and effective core potential calculations are compared, a relative difference of 10–20% is found for C_6 coefficients of the $2s+2p$ dissociations (see Tab. 6). Nevertheless in the $2s+2p$ dissociation case, the C_3 term prevails in the potential surfaces so that the error on C_6 has a smaller impact on the behaviour of $2s+2p$ dissociation with interatomic distance. Moreover, a rela-

tively good agreement with other results is obtained for C_3 and C_6 [21–28].

The $(1,3)\Sigma_{g,u}^+$ ground and first excited states dissociating into $2s+2s$ and $2s+2p_z$ (z is the molecular axis) have been plotted in Figure 1, with the corresponding polarizability values of Li_2 given in Table 7. These latter values are reported for the calculated equilibrium (R_e) geometries and compared to the values of each dissociated Li+Li molecular state.

At dissociation, the polarizability of each $\Sigma_{g/u}^+$ state is equal to the sum of the polarizabilities of the lithium atom in its $2s$ or/and $2p_z$ state, so that the polarizability of the dissociated (1) $(1,3)\Sigma_{g,u}^+$ ($2s + 2s$) states is equal to $\bar{\alpha} = \alpha_{zz} = \alpha_{xx} = 2\alpha(2s)$, and the components α_{zz} and α_{xx} of the polarizability of both (2) $(1,3)\Sigma_{g,u}^+$ and (1) $(1,3)\Sigma_{u,g}^+$ states are equal to $\alpha_0(2s) + \alpha_{zz}(2p_z)$ and $\alpha_0(2s) + \alpha_{xx}(2p_z)$ respectively. According to the values reported in Table 5 for the components of the polarizability of Li in the $2s$ and $2p$ states, we should find: $\alpha_{zz} = \alpha_{xx} = 2 \times 165 = 330$ a.u. for both singlet and triplet (1) $(1,3)\Sigma_{g,u}^+$ states, and $\alpha_{zz} = 165 + 120 = 285$ a.u. and $\alpha_{xx} = 165 + 127 = 292$ a.u. for the others, since $\alpha_{zz}(P_z) = -\alpha_{10}/3 - 2\alpha_{12}/15$ and $\alpha_{xx}(P_z) = -\alpha_{11}/6 - \alpha_{12}/10$ [2]. It is not completely verified at the interatomic distance $R = 45$ a.u. for which calculations have been done, but not reported, particularly for the predissociation $2s + 2p$ and also for the anisotropy $\Delta\alpha$ which is not exactly equal to zero for $2s + 2s$, showing that the dissociation Li+Li is not yet complete for this interatomic distance. For the singlet and triplet $2s + 2p$ excited states, $\Delta\alpha (= \alpha_{zz}(2p_z) - \alpha_{xx}(2p_z))$ should be equal to $-3\alpha_2 = -7$ a.u., which is nearly verified at $R = 45$ a.u. The small differences with the expected values (less than 1% for α_{zz} and α_{xx} components have been found in this work) could also be due to basis set superposition errors or size consistency problem.

At the equilibrium geometry of the ground “ $2s + 2s$ ” (1) $^1\Sigma_g^+$ state of Li_2 (dissociating into $2s + 2s$), we notice that the parallel component α_{zz} (303 a.u.) is slightly smaller than the polarizability of the two isolated Li atoms (330 a.u.) while the perpendicular α_{xx} one (160 a.u.) decreases much more rapidly with the bond length. This is due to the fact that the first vertical transition energy corresponding to (1) $^1\Sigma_g^+ \rightarrow (1) ^1\Sigma_u^+$ (“ $2s + 2s$ ” \rightarrow “ $2s + 2p_z$ ”) and required for α_{zz} calculation remains practically unchanged while the one corresponding to (1) $^1\Sigma_g^+ \rightarrow (1) ^1\Pi_u$ (“ $2s + 2s$ ” \rightarrow “ $2s + 2p_x$ ”) for α_{xx} increases. These transitions contribute strongly to the polarizability components with oscillator strengths practically twice as large as the $2s \rightarrow 2p$ oscillator strength of one Li atom (see Tab. 3). Our ground state polarizability values are in good agreement with other theoretical and experimental results [29–34].

To our knowledge, neither experimental nor theoretical results are given for excited states of Li_2 in the literature. In the case of the triplet state (1) $^3\Sigma_u^+$, the first transition energy “ $2s + 2s$ ” \rightarrow “ $2s + 2p_z$ ” is much smaller than the singlet one (0.045982 instead of 0.067489 a.u., see Tab. 3). This is because the first triplet state is practically unbound ($D_e = 317 \text{ cm}^{-1}$, see Fig. 1 and Tab. 2). That is not the case for the excited state ((1) $^3\Sigma_g^+$) which contributes strongly to its polarizability. Then the component α_{zz} of the lowest energy triplet “ $2s + 2s$ ” state is more than twice as large as that of the ground state ($\alpha_{zz} = 698$ a.u. to be compared to 303 a.u. for the ground state). This effect is less for the perpendicular component, and the anisotropy becomes larger ($\Delta\alpha = 446$ a.u., see Tab. 7).

For singlet and triplet “ $2s + 2p$ ” excited states, the results obtained in Table 7 are more difficult to discuss because it is no longer a two-level transition problem. Several states dissociating into $2s + 2s$, $2p + 2p$ and $2s + 3d$, contribute to the polarizability of these (2) $^{1,3}\Sigma_{g,u}^+$ and (1) $^{1,3}\Sigma_{u,g}^+$ excited states. Moreover, the contributions have not the same sign because the transition energies and oscillator strengths can be negative (see Tab. 4). In the triplet (1) $^3\Sigma_g^+$ state case, the unique negative contribution for α_{zz} even prevails because the corresponding energy transition is negative and small while the absolute value of the oscillator strength is large. Then α_{zz} is negative while the perpendicular component α_{xx} is nearly equal to zero. For this latter component, positive and negative contributions annihilate. This leads finally to a negative value of the mean polarizability $\bar{\alpha}$ for the triplet (1) $^3\Sigma_g^+$ excited state and the anisotropy is large and negative. As for the (2) $^3\Sigma_u^+$ excited state, large polarizability components are obtained owing to spectroscopic states very close in energy which contribute strongly to the electric field perturbation of this state. The difference of their electric behaviour in comparison with the equivalent singlet states is due to the different symmetry allowed transitions. Moreover, the variation of transition energies and oscillator strengths between spectroscopic states can be important with the interatomic distance. For example, the transition energy and oscillator strength corresponding to (1) $^1\Sigma_u^+ \rightarrow (2) ^1\Sigma_g^+$ are equal to 0.0308 a.u. and 0.424 respectively at the equilibrium geometry of (1) $^1\Sigma_u^+$ ($R_e = 3.099 \text{ \AA}$), compared to -0.0252 a.u. and -0.099 at the equilibrium geometry of (2) $^1\Sigma_g^+$ ($R_e = 3.673 \text{ \AA}$). Note this is not opposite as it would be with the same R_e value (see Tab. 4).

4 Conclusion

In this work, first we have shown that the use of the one electron wave function with core polarization potentials yields relatively good values of the polarizability of Li. However, a slight difference is found for the polarizability of the excited $2p$ state of Li compared to the all-electron one where the $2p \rightarrow np$ transitions for example can contribute to its value.

Nevertheless, these core polarization potentials allow us to rapidly obtain accurate spectroscopic data of Li_2 and the equilibrium geometry of several singlet and triplet $^{1,3}\Sigma_{g,u}^+$ states. To our knowledge, the polarizability values obtained for the excited states of Li_2 are new. These are very sensitive to the accurate description of the Li_2 spectrum, and should be of the same accuracy as those of the Li atom found using the same computational conditions for the lowest energy molecular states.

This study shows important variation of anisotropy of Li_2 when the dimer is excited. Moreover, the sign of components and mean value of α can even change. In this case adsorption on material surface of such excited state molecule must be very different.

Finally, the study of the variation of dynamic dipole polarizability of excited state systems *versus* the electric

field frequency should lead in a future work to the determination of van der Waals C_6 dispersion coefficients between dissociating aggregates.

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