

Dynamic dipole and quadrupole polarizabilities for the ground 2^1S and the low-lying 3^1S and 3^3S states of Be

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Static and dynamic dipole $\alpha(\omega)$ and quadrupole $\alpha_2(\omega)$ polarizabilities for the 2^1S ground state, and the low-lying S states: 3^1S and 3^3S of Be are calculated using our time-dependent gauge invariant method. The results obtained for the dipole polarizability are compared with previous accurate theoretical data. The quadrupole dynamic polarizabilities proposed here are new, to our knowledge. In all cases dynamic components are calculated for dipole and quadrupole polarizability up to the first two resonances. [S1050-2947(98)05004-5]

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I. INTRODUCTION

There is a great interest in the determination of the electrical properties of atoms in their ground and excited states [1–11], because these properties are involved in many physical and chemical processes such as electro-optical phenomena [12] and intermolecular interactions [13]. Accurate experimental data are, however, rather scarce, and often theoretical polarizabilities are considered to provide the sole available or the most reliable information about the system, particularly for a description of the excited states [10,11,14,15].

Atoms in their ground states are the most easy to handle for these investigations. However, in the last few years there has been increasing interest in the study of excited states, accessible as a result of the development of techniques for stepwise level excitation with the help of tunable lasers. The study of the structure of these levels and their response to external electromagnetic fields give important information on the elementary properties of atoms, and on the applicability of theoretical methods in the corresponding calculations [16–20]. For example, there have recently been several atomic interference experiments culminating in the demonstration of atom interferometers that are now beginning to be used as experimental tools in the field of atomic physics. It is therefore of great interest to have at our disposal flexible theoretical methods capable of accounting quantitatively for these properties in order to interpret them correctly. To illustrate this phenomenon, the long-range potential for scattering processes between atoms in their ground and excited states may be strongly affected or even dominated by the induction interaction which depends directly on the atomic polarizabilities [2,10,11,21].

The purpose of this paper is to present theoretical calculations of the dynamic (at real frequencies) dipole $\alpha(\omega)$ and quadrupole $\alpha_2(\omega)$ polarizabilities for the 2^1S ground state and for the two first S low-lying states 3^1S and 3^3S of Be using our time dependent gauge-invariant (TDGI) method [20,22–25]. To our knowledge, no experimental result is available for electrical properties of the ground and low-lying states of Be. In opposition to the amount of theoretical works about the $1s^2 2s^2$ ground state for the spectrum [26–29], and for the $\alpha(\omega)$ properties [15,30–37], very little is

known about the two first excited S states [36]. In the case of small systems like the Be atom, it is possible to correlate all electrons employing rather large active spaces, and thus to include a substantial part of the dynamical correlation energy as well. For these reasons, the 2^1S state is extensively studied, and the corresponding TDGI values will be compared with the previously mentioned works. For the two 3^1S and 3^3S states, the comparison is only possible with the MCT-DHF (multi-configuration time-dependent Hartree-Fock) values obtained by Graham and Yeager [36]. Static and dynamic $\alpha_2(\omega)$ ($3^1S, 3^3S$ states), values calculated here are new, to our knowledge.

Some methodological and computational details are given in Sec. II. Results are presented and discussed in Sec. III. Atomic units are used throughout the paper.

II. METHODOLOGICAL AND COMPUTATIONAL DETAILS

The static and dynamic dipole and quadrupole polarizabilities $\alpha(\omega)$ and $\alpha_2(\omega)$ were computed according to the TDGI method, which used a first-order wave function combining a polynomial function and both true spectral states and quasispectral series as described in Ref. [24],

$$|1\rangle = g(\vec{r})|\Psi_0\rangle + \sum_{n \neq 0}^N b_n |\Psi_n\rangle + \sum_{m \neq 0}^M c_m |\phi_m\rangle, \quad (2.1)$$

where $g(\vec{r}) = \sum_u a_u^\nu u$ (with $u, \nu = x, y, z$) is a polynomial function of the electronic coordinates when the electric field lies in the ν direction, Ψ_n are the true spectral states, ϕ_m is a quasispectral series, and a_u^ν, b_n , and c_m are expansion coefficients obtained variationally. The use of the first degree polynomial function $g(\vec{r})$ presents several advantages because it ensures the “gauge invariance,” it compensates for the limited size of the molecular basis set, it simulates part of the continuum contribution, and it partly corrects the results due to the unavoidably restricted number of states in the construction of the first-order wave function $|1\rangle$ [38]. In this way, the TDGI method appears as an improvement of the sum over states method for the configuration interaction expansion of limited size, rather than considering the orbital relaxation effect. If good static values of polarizabilities may

TABLE I. Basis set for beryllium.

Basis	GTF	Description
$12s, 4p, 3d, 1f$	46	$s(4700.24, 704.83, 160.43, 45.4253, 14.7983, 5.35124, 2.154\ 20$ $0.933\ 637, 0.187\ 914, 0.074\ 648\ 3, 0.032\ 650\ 5, 0.014\ 281\ 0)$ $+p(0.5472, 0.1824, 0.0608, 0.0203)$ $+d(0.1569, 0.0523, 0.017\ 43)$ $+f(0.0523)$

be found from a quasispectral series Φ_n , including a part of the continuum [38], accurate dynamic values near the resonances required knowledge of the true spectral states Ψ_n . Reliable static and dynamic values could therefore be obtained when the quasispectral series Φ_n is added to the low-lying spectroscopic states Ψ_n , but the calculated values depend on the quality of this choice. Our method, successfully applied for systems like He (1^1S , 2^1S , and 2^3S) [25], Li (2^2S and 2^2P) [39] and B (2^1P_0) [40], is now used to calculate the $\alpha(\omega)$ and the $\alpha_2(\omega)$ properties for the three first S states of Be. To obtain accurate values of dynamic polariz-

abilities with the TDGI formalism, it is necessary to describe accurately the energy and wave functions corresponding to the lower states of the spectrum, i.e., the ground 2^1S and excited 3^1S , 3^3S , 2^1P , and 2^3P states, as well as the dipole-transition moments [39,40]. The wave functions used for the description of these previous states are calculated using a second-order many-body perturbation theory through the configuration interaction by perturbation selected by an iterative process (CIPSI) algorithm [41,42] including single and double excitations relative to the multireference. Each state is obtained separately, from a supermatrix containing

TABLE II. Comparison between calculated and experimental transition energies (ΔE), oscillator strengths (f_{ik}), and transition probability (A_{ki}) involving 2^1S , 2^1P , 3^1S , 3^3S , and 2^3P states of Be. Experimental values [26] are in parentheses.

Transition	ΔE (a.u.)	f_{ik}		A_{ki}^* ($10^8\ s^{-1}$)
		length	velocity	
$2^1S \rightarrow 2^1P$	0.196 09 0.194 01 ^a	1.398 (1.341 \pm 0.050) ^b	1.364	5.63 (5.47)
$2s^2 \rightarrow 2s2p$	0.194 94 ^c (0.193 94)	1.376 ^d 1.385 ^e (1.34)	1.378 ^d 1.331 ^e	5.66 ^f
$3^1S \rightarrow 2^1P$	-0.053 12 -0.055 12 ^a	0.131 (0.130)	0.125	0.12 (0.13)
$2s3s \rightarrow 2s2p$	-0.054 18 ^c (-0.055 19)	0.119 ^d 0.128 ^e	0.117 ^d 0.123 ^e	0.11 ^f
$3^3S \rightarrow 2^3P$	-0.136 67 (-0.137 15)	0.0263 (0.034)	0.0256	0.47 (0.62)
$2s3s \rightarrow 2s2p$	-0.136 48 ^a			0.50 ^f
$2^1S \rightarrow 3^1D$	0.260 88 (0.257 12)			
$2s^2 \rightarrow 2p^2$	0.259 17 ^c			
$2^1S \rightarrow 3^1D$	0.295 48 (0.293 55)			
$2s^2 \rightarrow 2s3d$				
$3^1S \rightarrow 3^1D$	0.045 27 (0.044 43)			
$2s3s \rightarrow 2s3d$				
$3^3S \rightarrow 3^3D$	0.048 71 (0.045 43)			
$2s3s \rightarrow 2s3d$				
$3^3S \rightarrow 3^3P$	0.035 51 (0.030 57)	1.095		0.12 (0.119) ^f
$2s3s \rightarrow 2s3p$				
$3^1S \rightarrow 3^1P$	0.026 91 (0.025 10)	1.098		0.05 (0.068) ^f
$2s3s \rightarrow 2s3p$				
$3^3S \rightarrow 3^3P$	0.036 18 (0.034 70)			
$2s3s \rightarrow 2p^2$				

^aReference [27].

^bReference [46] (expt).

^cReference [28] (CCSDT).

^dReference [28] (SOC).

^eReference [45] (CI).

^fReference [33].

TABLE III. Energetic position and dipole polarizability of the first three S states: 2^1S , 3^1S , and 3^3S states of Be.

States	$\Delta E(\bar{X} \rightarrow exc.)$		α_0	
	our work	other works	our work	other works
3^1S	0.249 220	(0.249 126) ^a 0.249 13 ^c 0.249 12 ^d	1257.7	(~ 1400) ^b
3^3S	0.236 823	(0.237 302) ^a 0.237 30 ^c	1191.84	(~ 1200) ^b
2^1S	0.0	(0.0) ^a	37.62	37.62 ^e 37.54 ^f 36.9 ^g 37.59 ^h 37.53 ⁱ 37.45 ^j 37.84 ^k 37.64 ^b 37.49 ^l 37.73 \pm 0.05 ^m

^aReference [26].

^bReference [36].

^cReference [27].

^dReference [28].

^eReference [15].

^fReference [30].

^gReference [31].

^hReference [32].

ⁱReference [33].

^jReference [34].

^kReference [35].

^lReference [37].

^mReference [47].

about 20 000 determinants chosen from an iterative procedure, with the Davidson diagonalization method [43]. The basis set used consists of (12s4p3d1f) Gaussian-type functions (GTF's) and is specific for polarizability calculations [44] (Table I). The tight polarization functions were chosen roughly to minimize the energy of the free atom, and the diffuse ones roughly to maximize the mean dipole polarizability $\bar{\alpha}$ at the self-consistent-field level. Moreover, an f -GTF is needed to obtain a reliable value of the quadrupole polarizability. The transition energies ΔE_{ik} obtained in all cases can be considered as multireference double-configuration interaction results.

As an additional test of the accuracy and completeness of the wave functions, we have computed the absorption oscillator strengths f_{ik} for the dipole transitions between lower (i) S states and upper (k) P states as well as the Einstein spontaneous-transition probability A_{ki} related to the total intensity I_{ki} of a line of frequency ν_{ik} by

$$I_{ki} = \frac{1}{4\pi} A_{ki} h \nu_{ik} N_k, \quad (2.2)$$

where h is Planck's constant and N_k the the population of k state. A_{ki} may therefore be obtained from the measurement of I_{ki} or from the knowledge of the conversion factor between the f_{ik} quantity, as reproduced from Ref. [26]:

$$A_{ki} = \frac{6.670 \times 10^{15}}{4\lambda^2} \frac{g_i}{g_k} f_{ik}. \quad (2.3)$$

This transition probability is in units s^{-1} , and the f value is dimensionless. The wavelength λ is given in \AA , and g_i and g_k are statistical weights of the lower and upper states, respectively.

Finally the dipole oscillator sum rules $S(-2)$, $S(-4)$, $S(-6)$, and $S(-8)$, which are the leading contributions to the Cauchy expansion of the dynamic polarizability, have been calculated at the TDGI level from a polynomial fit to

this expansion. Indeed, it is well known that the frequency-dependent polarizability $\alpha(\omega)$ may be written in the form of an infinite sum following

$$\alpha_{\gamma\delta}(\omega) = \sum_{k=0}^{\infty} S_{\gamma\delta}(-2k-2) \omega^{2k}, \quad (2.4)$$

where $\gamma\delta$ indicates the component directions.

The $S(-2)$ sum rule can be identified as the static polarizability $\alpha(0)$, while the higher sum rules $S(-4)$, $S(-6)$, \dots express the quadratic, quartic, \dots dependences

TABLE IV. Dynamic dipole polarizability of the 2^1S , 3^1S , and 3^3S states of Be obtained with the first transition energy values calculated here. All results are in a.u.

$\hbar\omega$	$\bar{\alpha}(2^1S)$	$\hbar\omega$	$\bar{\alpha}(3^1S)$	$\hbar\omega$	$\bar{\alpha}(3^3S)$
0	37.6	0	1257.7	0	1191.8
0.0125	37.8	0.0025	1263.7	0.0025	1199.1
0.0250	38.2	0.0050	1282.1	0.0050	1222.1
0.0375	39.0	0.0075	1314.3	0.0075	1262.6
0.0500	40.1	0.0100	1362.9	0.0100	1324.0
0.0625	41.7	0.0125	1432.4	0.0125	1412.5
0.0750	43.7	0.0150	1530.1	0.0150	1538.2
0.0875	46.5	0.0175	1668.6	0.0175	1719.3
0.1000	50.2	0.0200	1870.5	0.0200	1990.1
0.1125	55.1	0.0225	2181.0	0.0225	2423.8
0.1250	62.0	0.0250	2703.5	0.0250	3206.5
0.1375	72.1	0.0350	-8014.4	0.0275	4993.6
0.1500	87.8	0.0375	-3725.1	0.0295	9704.0
0.1625	115.6	0.0400	-2459.7	0.0375	-2796.8
0.1750	176.5	0.0425	-1888.4	0.0400	-1902.4
0.1875	413.9	0.0450	-1608.6	0.0425	-1417.1
0.2000	-141.8	0.0475	-1525.1	0.0450	-1113.7
0.2125	73.9	0.0500	-1721.1	0.0475	-906.7
0.2250	116.2	0.0525	-3383.1	0.0500	-756.9
0.2375	150.1	0.0550	2308.5	0.0525	-643.7

TABLE V. Values of the $S(-2)$, $S(-4)$, $S(-6)$, and $S(-8)$ dipole oscillator sum rules in the length and velocity representation at the TDGI level. (a.u.).

State	$S(-2)$				$S(-4)$	$S(-6)$	$S(-8)$		
	Our work	Other works			Our work	Our work	Our work		
2^1S	length	37.62	44.098 ^a	45.605 ^b	37.216 ^c	52.444 ^d	945.95	16 086.5	1 538 514.5
	velocity	37.59						945.90	16 089.6

^aReference [48] (Hartree-Fock level).

^bReference [48] (random-phase approximation level).

^cReference [48] (CCSOPPA level).

^dReference [49].

upon the frequency of the perturbing field. Calculated in the length and in the velocity representation comparison of the sum rule, results provide a good test of the quality of the wave function.

III. RESULTS AND DISCUSSION

The results of our calculated transition energies and oscillator strengths are presented in Table II, and are compared with previous experimental and theoretical works [27–29,45]. Very good agreement between our transition energies values and the experimental ones [46] is observed for the first singlet $S \rightarrow P$ transitions. The dipole oscillator strengths were calculated for all possible electric dipole transitions between the S and P states treated here. The length and velocity oscillator strengths are given by the usual two forms

$$f_{ik} = \frac{2}{3g_i} \Delta E_{i \rightarrow k} |\langle \Psi_i | r | \Psi_k \rangle|^2 \quad (\text{length}), \quad (3.1)$$

$$f_{ik} = \frac{2}{3g_i} \frac{1}{\Delta E_{i \rightarrow k}} |\langle \Psi_i | \nabla | \Psi_k \rangle|^2 \quad (\text{velocity}), \quad (3.2)$$

where $\Delta E_{i \rightarrow k}$ represent the transition energy between the i and k states. The agreement between length and velocity oscillator strengths is remarkably good, emphasizing the good quality of the ground- and excited-state descriptions. Our length value (1.398) for the $2^1S \rightarrow 2^1P$ transition agree within 1% and 2% with the results of Moccia and Spizzo [45] (1.385) and the more recent SOC (superposition of configurations) value obtained by Weiss [28] (1.376). A similar agreement is worth noting for the $3^1S \rightarrow 3^1P$ transition (0.131). In all cases for these singlet transitions the oscillator strengths proposed here are close to the experimental values quoted in Ref. [26] and proposed by Martinson, Gaupp, and Curtis [46] from the lifetimes given by beam-foil spectroscopy studies without corrections for branching and cascade effects. For the triplet $3^3S \rightarrow 2^3P$ transition, very little is known about the oscillator strength. Our length (0.0263) and velocity (0.0256) values are in quite good agreement with the experimental result (0.03400 given in Ref. [26]). Our values give a transition probability A_{ki} 25% lower than the experimental determination. It should be noted that our transition energy ($-0.136\ 67$ a.u.) compares very well with those proposed by Baskin and Stoner ($-0.13\ 715$ a.u.) [27], and with the experimental data given in Ref. [26] ($-0.136\ 48$

a.u.). This fair agreement between our calculated transition energy and oscillator strengths with the most recent and accurate calculations is needed to obtain accurate values of dynamic dipole and quadrupole polarizabilities for the ground (2^1S) and excited states (3^1S , 3^3S) of Be.

For the ground state (2^1S) a selection of recent theoretical predictions expected to give accurate dipole polarizability values is displayed in Table III. The correlated results range, respectively, between 36.90 and 37.73 a.u. For this system in which the correlation to α has been found to be large, our 2^1S ground-state static polarizability value (37.62 a.u.) shows a very good agreement with the more recent and reliable calculations. Indeed, the TDGI value is identical to those obtained by Themelis and Nicolaides [15] from the applica-

TABLE VI. Dynamic quadrupole polarizability of the 2^1S , 3^1S , and 3^3S states of Be obtained with the first transition energy values calculated here. All results are in a.u. $C_{zz,zz}$ is defined [50] as $C_{zz,zz}(\omega) = \sum_{m \neq g} 2\hbar | \langle g | \theta_{zz} | m \rangle |^2 / 3\omega_{mg} = \frac{1}{3} \alpha_2$.

$\hbar \omega$	$C_{zz,zz}(2^1S)$	$\hbar \omega$	$C_{zz,zz}(3^1S)$	$C_{zz,zz}(3^3S)$
0	95.2	0	13 724.9	14 855.9
0.015	95.4	0.0027	13 765.1	14 902.3
0.030	96.2	0.0054	13 887.4	15 043.4
0.045	97.6	0.0081	14 096.4	15 284.8
0.060	99.5	0.0111	14 440.4	15 682.9
0.075	102.2	0.0138	14 864.9	16 175.9
0.090	105.7	0.0165	15 418.1	16 820.9
0.105	110.2	0.0192	16 127.8	17 653.0
0.120	116.0	0.0219	17 034.4	18 723.7
0.135	123.4	0.0246	18 197.6	20 110.4
0.150	133.2	0.0276	19 903.3	22 172.1
0.165	146.4	0.0303	21 974.0	24 722.4
0.180	164.9	0.0330	24 818.4	28 316.6
0.195	192.2	0.0357	28 915.8	33 695.2
0.210	236.9	0.0384	35 254.7	42 537.5
0.225	322.4	0.0411	46 251.3	59 641.7
0.240	555.3	0.0441	74 151.3	117 212.4
0.255	4037.9	0.0468	-1 798 406.1	2 851 673.1
0.270	-577.0	0.0495	-337 067.6	-114 827.8
0.285	-187.5	0.0522	-82 441.0	-52 934.0
0.290	-58.8	0.0552	-43 277.5	-31 176.0
0.292	102.5	0.0582	-28 582.1	-20 612.0
0.300	-206.4	0.0612	-20 896.6	-13 932.9
0.315	-100.5	0.0642	-16 177.3	-8613.6

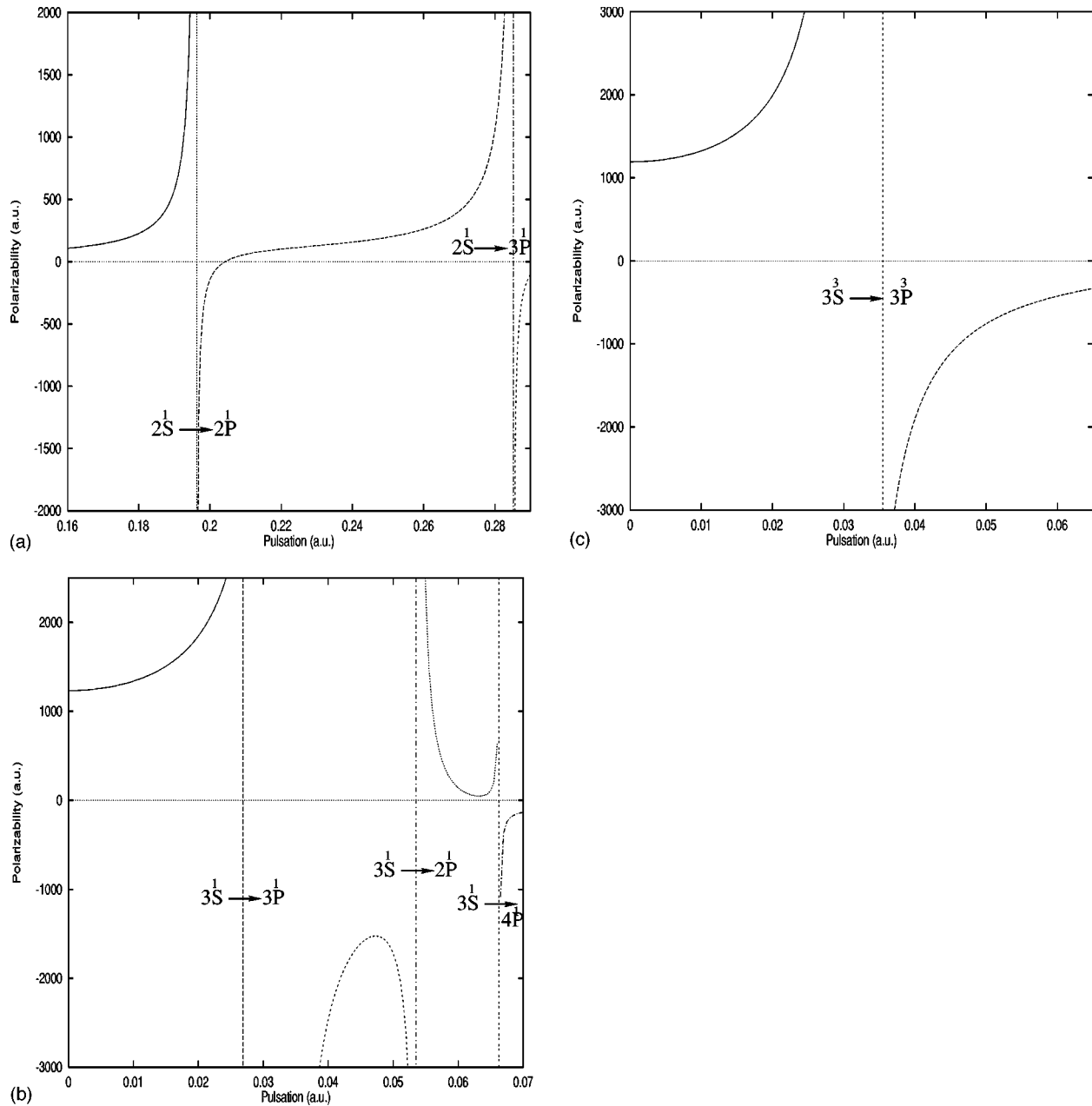


FIG. 1. Dynamic TDGI mean polarizability $\bar{\alpha}(\omega)$ (a.u.) of the 2^1S (a), 3^1S (b), and 3^3S (c) states of Be up to the first two resonances. The vertical broken lines are at calculated excitation energies.

tion of a state-specific theory which allows, as our method, a systematic inclusion of electron correlation, and takes into account the field-induced effects mixing of low- and high-lying excited states and of the continuous spectrum. An indicator of the reliability of our 2^1S dipole polarizability is also given by the fact that the TDGI result is included in the range 37.53–37.73 a.u., respectively, obtained by Koch and Harrison [33] from a full configuration interaction (FCI) calculations and by Tunega, Noga, and Klopper [47] from a coupled-cluster method (CCR12) developed with a high-quality basis set (18s13p10d9f8g). To our knowledge, the dynamic values of the ground state are only quoted by Koch and Harrison [33] in the range 0.0–0.2405 a.u. from their FCI response calculations. The behavior of the ground-state MCTDHF frequency-dependent polarizability is also available up to the first resonance in the study of Graham and

Yeager [29]. Figure 1 and Table IV illustrate the behavior of the TDGI $\alpha(\omega)$ values, and show the continuous variation with the frequency until the two first resonances ($\hbar\omega = E_{2^1P} - E_{2^1S}$ and $\hbar\omega = E_{3^1P} - E_{2^1S}$). A fair agreement is observed between the TDGI and the MCTDHF plots, this latter being known to be a very good method for determining a linear-response property. Because of the accuracy of the low-lying excitation energies, the excellent value of $X^1S \rightarrow ^1P_0$ oscillator strength and the good zero-order sum rule, we expect the TDGI dynamic polarizabilities to be among the most reliable in the limit $\omega \rightarrow 0$ (0–0.03 a.u.). The excellent agreement between our dynamic values and those obtained at the FCI level by Koch and Harrison [33] should be noted: our static dipole polarizability value and derivative $d\alpha(\omega)/d\omega$ value appear, respectively, 0.2% higher and 8% lower than the FCI ones. The good static and dynamic results

obtained for the ground state show how the initial description of spectroscopic states which contribute in the evaluation of the polarizability is important. In order to gauge the performance of our calculations, for the ground state we have calculated the sum rules using the excitations energies and transition moments. The $S(-2)$, $S(-4)$, $S(-6)$, and $S(-8)$ sum rules are given in the length and velocity formulation in Table V. It should be noted the excellent agreement between the two different representations. Comparison with other theoretical works [48,49] shows, for $S(-2)$, a great similitude between our TDGI (37.62 a.u.) and the coupled-cluster single and double polarization propagator approximation (CCSDPPA) (37.216 a.u.) results given by Oddershede and Sabin [48].

For the next S states, (3^1S and 3^3S), static and dynamic results also are given in Table IV and Fig. 1, respectively. Very few references are available for comparison. Graham and Yeager [36] illustrate the behavior of the frequency-dependent polarizabilities of the 3^1S and 3^3S states, and our dynamic plots are very similar. The static α values proposed here are 1257.2 and 1191.8 a.u. for the singlet and triplet states, respectively. It can be favorably compared with the approximate values (1400 and 1200 a.u.) deduced from the figure given by Graham and Yeager [36].

The difficulty of calculating accurate electron-correlation values is generally more important in the case of the quadrupole polarizability α_2 defined as in Table VI, in accordance with the formulation given by Orr and Ward [50]. Indeed, it is necessary to obtain very good wave functions of the first 1D and 3D states, at least able to generate good transition energies and accurate dipole and quadrupole mo-

ments which can be used for precise calculations of the dynamic and static properties. As in the case of the dipole polarizability, many theoretical works propose a quadrupole polarizability ($\alpha_2 = 3C_{zz,zz}$) estimation of the ground state of Be. The best accurate values given in the literature range in the interval 276–299 a.u. Our α_2 value 285.6 a.u. compares favorably with the fourth-order Moller Plesset results of Maroulis and Thakkar (292.0 a.u.) [34], and with the single and double configuration interaction (SDCI) values obtained by Dierksen and Sadlej [51] with three optimized basis sets ($279.8 \leq \alpha_2 \leq 280.4$ a.u.). Our α_2 TDGI value differs about 3% from the second-order variational result obtained in Ref. [52] (276.1 a.u.) and 4% from the coupled-cluster [CCD+ST(CCD)] result given by Thakkar (298.8 a.u.) [53]. Generally, very little is known about the quadrupole polarizability of the excited states. We are not aware of any references in the literature, and the two values proposed here are 13 724.9 and 14 855.9 a.u. for the 3^1S and 3^3S states, respectively. Dynamic values up to the two first corresponding resonances ($\hbar\omega = E_{1D(2s3d)} \rightarrow 1S(2s3s)$) and ($\hbar\omega = E_{3D(2s3d)} \rightarrow 3S(2s3s)$) are also displayed in Table VI in the range 0–0.0642 a.u.

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