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Accurate variational calculations of energies of the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states and the dipole, quadrupole, and dipole-quadrupole polarizabilities and hyperpolarizability of the lithium atom

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The combined configuration-interaction–Hylleraas method has been used to calculate the energies for the ground $2\,^2S$ and the excited $2\,^2P$ and $3\,^2D$ states of the lithium atom. The energies obtained, $-7.478\,060\,1$ a.u. for the $2\,^2S$ state, $-7.410\,155\,4$ a.u. and $-7.335\,523\,1$ a.u. for the $2\,^2P$ and $3\,^2D$ states, respectively, are the lowest nonrelativistic variational upper bounds found so far. Ionization potentials, lifetimes, dipole oscillator strengths and their sums, dynamic dipole, quadrupole and dipole-quadrupole polarizabilities, and the static second hyperpolarizability are also reported and compared with experimental and other theoretical results.

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I. INTRODUCTION

During the past few years a number of articles have been published by King *et al.* [1–5] on the energy and properties of the ground $2\,^2S$ state of the lithium atom. The work was carried out within the framework of the Hylleraas method. A good deal of effort has been devoted to extensive many-body-perturbation-theory (MBPT) [6–8] and multiconfiguration Hartree-Fock (MCHF) [9] calculations of the energies, including relativistic and quantum-electrodynamic effects for the ^2S and ^2P states of the lithium atom and for its isoelectronic ions.

In this paper we present the results of accurate calculations of the energy levels of the lowest $2\,^2S$, $2\,^2P$, and $3\,^2D$ states together with the ionization potentials, lifetimes, dipole oscillator strengths and their sums, dynamic dipole (α), quadrupole (C), and dipole-quadrupole (B) polarizabilities, and the static second hyperpolarizability (γ). We employ the combined configuration-interaction (CI)–Hylleraas method [10], which was successfully used for evaluating energies of the ground and excited states for the helium atom [11] and for the lithium isoelectronic sequence [12–15].

The aim of this paper is twofold. The first is to probe the possibility of further improvement of nonrelativistic upper bounds to the energies of the ground $2\,^2S$ state and excited $2\,^2P$, and $3\,^2D$ states, using large, explicitly electron-correlated expansions of the variational wave functions with carefully optimized nonlinear parameters.

A comparison of our variational energies, $-7.478\,060\,1$, $-7.410\,155\,4$, and $-7.335\,523\,1$ a.u. for the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states, respectively, with the literature estimates of their nonrelativistic limits [13,16,17], $-7.478\,062\,4$, $-7.410\,157\,8$, and $-7.335\,523\,5$ a.u., shows that our values lie approximately 0.5, 0.53, and 0.088 cm^{-1} above the nonrelativistic limits. Although the differences between our variational energies and the nonrelativistic limits do not approach those attainable for the helium atom [18], they indicate a significant improvement, especially for the $2\,^2P$ and $3\,^2D$ states, over previous results [5,14,15].

The second goal of this paper is to generate wave functions capable of giving accurate dipole and quadrupole moments that can be used for precise calculations of the dynamic and static properties.

Accurate calculation of polarizabilities and hyperpolarizabilities for atoms and molecules is difficult and requires elaborate wave functions capable of giving converged values of these properties. The most challenging task, however, is the calculation of the hyperpolarizability. In our previous articles we have reported dynamic values of γ for the helium atom [19] and for the hydrogen molecule [20], for which we were able to achieve excellent agreement with experiment [21]. For the lithium atom, the simplest of open-shell atoms, there is a large discrepancy between the various theoretical estimates of γ. Earlier theoretical values of the static hyperpolarizability range from -778×10^3 to $746\times10^3 e^4a_0^4E_h^{-3}$ (Maroulis and Bishop [22] and references therein). Until the recent work of Maroulis and Thakkar [23] there were no calculations of γ for the lithium atom which took into account electron correlation, and even the sign of γ was uncertain. Their static value of γ, $4350e^4a_0^4E_h^{-3}$, obtained using fourth-order Møller-Plesset perturbation theory, although not converged, has the same sign and order of magnitude as our own result. Experimental determination of γ for the lithium atom is feasible, at least for the Kerr effect [24], but to our knowledge has not been done.

The value of the static hyperpolarizability γ obtained in this work is $3\times10^3 e^4a_0^4E_h^{-3}$. Its reliability and an attempt to calculate dynamic values of γ pertaining to various nonlinear optical processes are discussed later. The static values of α ($1.641\times10^2 e^2a_0^2E_h^{-1}$), C ($1.423\times10^3 e^2a_0^4E_h^{-1}$), and B ($-5.43\times10^4 e^3a_0^4E_h^{-2}$) are converged to the number of significant figures quoted.

Atomic units are used throughout this paper and their SI equivalents are the following:

$$E_h \cong 4.359\,75\times 10^{-18}\ \mathrm{J}\ ,$$

$$\alpha = e^2 a_0^2 E_h^{-1} \cong 1.648\,78\times 10^{-41}\ \mathrm{C^2\,m^2\,J^{-1}}\ ,$$

$$C = e^2 a_0^4 E_h^{-1} \cong 4.617\,05\times 10^{-62}\ \mathrm{C^2\,m^4\,J^{-1}}\ ,$$

$$B = e^3 a_0^4 E_h^{-2} \cong 1.696\,73\times 10^{-63}\ \mathrm{C^3\,m^4\,J^{-2}}\ ,$$

$$\gamma = e^4 a_0^4 E_h^{-3} \cong 6.235\,38\times 10^{-65}\ \mathrm{C^4\,m^4\,J^{-3}}\ .$$

II. THEORY

A. Wave functions

In the CI Hylleraas method the variational wave function is

$$\Psi = \sum_R C_R \chi_R\ , \tag{1}$$

where the abbreviated symbol $\{\chi_R\} = \chi^{(v)}_{K,ij,g}$ denotes the set of spin and angular momentum projected correlated configurations

$$\chi^{(v)}_{K,ij,g} = \hat{O}_A \hat{O}_{L,M_L} \hat{O}_S (F_K r_{ij}^{v} \Theta_g)\ . \tag{2}$$

$\hat{O}_A$ is the N-particle antisymmetrizer, $\hat{O}_{L,M_L}$ and $\hat{O}_S$ are idempotent projection operators [25] for a state of total quantum numbers $L, M_L, S, M_S = S$; LS coupling is assumed. Θ_K is a primitive spin function being a product of one-electron α and β functions, and r_{ij}^{v} denotes a nonnegative power of the interelectronic distance r_{ij} ($ij = 12, 13, 23$)—one correlation factor per term. A primitive spatial function is constructed from a set of one-electron orbitals $\{\phi_{Ki}\}$ corresponding to a given configuration K as a Hartree-type product

$$F_K = \phi_{K_1}(r_1)\phi_{K_2}(r_2)\cdots\phi_{K_N}(r_N)\ , \tag{3}$$

where some of the orbitals may appear twice. We have used Slater-type orbitals (STO's) for the one-electron functions ϕ:

$$\phi(r) = r^{n-1}\exp(-\alpha r) Y_{l,m}(\Theta,\phi)\ , \tag{4}$$

$Y_{l,m}$ being normalized spherical harmonics in the Dirac phase convention. For three-electron doublet states there exist two independent primitive spin functions Θ_g: $\Theta_1 = \alpha\alpha\beta$ and $\Theta_2 = \alpha\beta\alpha$.

B. Properties

The underlying theory employed for calculation of dynamic dipole, quadrupole, and dipole-quadrupole polarizabilities as well as static hyperpolarizability is the same as that used in our previous papers [19,20] and is based on the perturbation expressions [26]

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \hbar^{-1} \sum_P \sum_{m(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)}\ , \tag{5}$$

$$C_{\alpha\beta,\gamma\delta}(-\omega_\sigma;\omega_1) = \hbar^{-1} \sum_P \sum_{m(\neq g)} \frac{\langle g|\Theta_{\alpha\beta}|m\rangle\langle m|\Theta_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)}\ , \tag{6}$$

$$B_{\alpha\beta,\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-2} \sum_P \sum_{m,n(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\Theta_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)}\ , \tag{7}$$

$$\begin{aligned}\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3} \sum_P \Bigg[&\sum_{m,n,p(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1-\omega_2)(\omega_{pg}-\omega_1)} \\ &- \sum_{m,n(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1)(\omega_{ng}+\omega_2)} \Bigg]\ ,\end{aligned} \tag{8}$$

where, in all equations, ω_σ is the sum of the frequencies following the semicolon. In Eqs. (5) and (6) $\sum_P$ is the sum of permutations of the pairs $(-\omega_\sigma/\mu_\alpha)$, (ω_1/μ_β), and $(-\omega_\sigma/\Theta_{\alpha\beta})$, $(\omega_1/\Theta_{\gamma\delta})$, respectively, where μ_α is the α component of the electric dipole moment operator, $\Theta_{\alpha\beta}$ is the $\alpha\beta$ component of the electric quadrupole moment operator, $|m\rangle$ is an excited-state wave function, $|g\rangle$ is the ground-state wave function, and ω_{mg} is the transition frequency between the two. $\sum_P$ in Eq. (7) implies the summation over the permutations of the pairs $(-\omega_\sigma/\mu_\alpha)$, (ω_1/μ_β), and $(\omega_2/\Theta_{\gamma\delta})$. Further on we will consider only the case when $\omega_1 = \omega$, $\omega_2 = 0$, and the single (zz) and (zz,zz) components of α and C, B.

The sum over P in Eq. (8) runs over the 24 terms generated by permuting the frequencies with their associated spatial subscripts. Although Eq. (8) is general and, depending on the choice of frequencies $\omega_1, \omega_2, \omega_3$, can be used to calculate the γ related to various nonlinear optical processes such as the Kerr effect or electric-field-induced second-harmonic generation, we calculated only the static ($\omega_1 = \omega_2 = \omega_3 = 0$) $zzzz$ component ($\gamma_{zzzz} = \gamma$).

For the lithium atom the ground state is $2\,^2S$, so that the intermediate states in the expression for α must be of ^2P symmetry; for C they must be of ^2D symmetry, for B both ^2P and ^2D symmetries must be included, and for γ the summations run over ^2S, ^2P, and ^2D states. Finally, to calculate the absorption oscillator strengths for dipole transitions between lower (i) and upper (k) states we used the formula

$$f_{ik}=\tfrac{2}{3}g_i^{-1}(E_k-E_i)S_{ik}\ , \tag{9}$$

where $g_i=(2L_i+1)(2S_i+1)$ and the line strength S_{ik} for $\Delta L=1$, $\Delta M_L=0$ reads [27]

$$S_{ik}(SL_i,SL_i+1)=\frac{(2S+1)(2L_i+1)(L_i+1)(2L_i+3)}{(L_i+1)^2-M_{L_i}^2}\times|\langle L_i,S,M_{L_i},M_S|\mu|L_i+1,S,M_{L_i},M_S\rangle|^2\ . \tag{10}$$

In our case $S=M_S=\frac{1}{2}$, $M_L=0$.

The mean lifetime τ_{ki} of the upper level is

$$\tau_{ki}=1\Big/\sum_i A_{ki}\ , \tag{11}$$

where the Einstein spontaneous transition probability (in $\sec^{-1}$) is given by

$$A_{ki}=\frac{2.026\times10^{18}}{\lambda^3 g_k}S_{ik}\ , \tag{12}$$

and λ is the wavelength in angstroms.

III. COMPUTATIONAL PROCEDURE

The basic problems in atomic calculations involving explicitly electron-correlated wave functions are the proper choice of correlated configurations and the optimization of the nonlinear parameters appearing in the STO's. Instead of making an "intelligent" choice of the correlated configurations, usually guided by trial and error, we have built up our wave functions, for each state considered, from several groups of Hartree-type products. For the ground $2\,^2S$ state we included $(n_1sn_2s)n_3s'$, $(n_1pn_2p)n_3s''$, $(n_1dn_2d)n_3s'''$, and $(n_1fn_2f)n_3s''''$ types of Hartree products. For the $2\,^2P$ state we considered $(n_1sn_2s)n_3p$, $(n_1p'n_2p')n_3p''$, and $(n_1s'n_2p''')n_3d$ Hartree-type products and the $3\,^2D$ wave function was constructed from $(n_1sn_2s)n_3d$, $(n_1pn_2p)n_3s'$ and $(n_1p'n_2p')n_3d'$ Hartree-type products. The choice of the correlated configurations within each type of Hartree product was governed by the index ω

$$\omega=n_1+n_2+n_3+\nu\ , \tag{13}$$

where ν is the power of r_{ij}.

In Table I we give an example of the $(n_1sn_2s)n_3s'r_{ij}^{\nu}$ configurations for $\omega=5$, in the same order as they were generated by the program. Our final wave function for the ground 2^2S state included 750 ($\omega=10$) configurations of $(n_1sn_2s)n_3s'$ type, 462 ($\omega=11$) configurations of $(n_1pn_2p)n_3s''$ type, 266 ($\omega=12$) configurations of $(n_1dn_2d)n_3s'''$ type, and 140 ($\omega=13$) configurations of $(n_1fn_2f)n_3s''''$ type, giving, finally, a 1618-configuration expansion.

The $2\,^2P$ wave function was constructed from 750 ($\omega=11$) configurations of $(n_1sn_2s)n_3p$ type, 462 ($\omega=12$) configurations of $(n_1p'n_2p')n_3p''$ type, and 242 ($\omega=10$) configurations of $(n_1s'n_2p''')n_3d$ type—altogether 1454 correlated configurations.

TABLE I. An example of the wave function for the $2\,^2S$ state for $\omega=5$. An asterisk indicates the configuration for which both spin functions $\alpha\beta\alpha$ and $\alpha\alpha\beta$ are included. The total number of correlated configurations is 25.

Hartree-type product F_K	Correlation factor r_{ij}^{ν}
$1s1s1s'$	r_{12}^0
$1s1s1s'$	r_{12}^1
$1s1s2s'$	r_{12}^0
$(1s2s1s')^*$	r_{12}^0
$1s1s1s'$	r_{12}^2
$1s1s2s'$	r_{12}^1
$(1s2s1s')^*$	r_{12}^1
$1s1s3s'$	r_{12}^0
$(1s2s2s')^*$	r_{12}^0
$(1s3s1s')^*$	r_{12}^0
$2s2s1s'$	r_{12}^0
$(1s1s1s')^*$	r_{13}^1
$(1s1s1s')^*$	r_{13}^2
$(1s1s2s')^*$	r_{13}^1
$(1s2s1s')^*$	r_{13}^1
$(1s2s1s')^*$	r_{23}^1

The $3\,^2D$ wave function included 1478 correlated configurations consisting of 750 ($\omega=12$) configurations of $(n_1sn_2s)n_3d$ type, 462 ($\omega=11$) configurations of $(n_1pn_2p)n_3s'$ type, and 266 ($\omega=12$) configurations of $(n_1p'n_2p')n_3d'$ type.

The optimization of the orbital exponents for each state considered in this work was carried out for smaller expansions: 882 (462+140+140+140) configurations for the $2\,^2S$ state, 524 (266+140+118) configurations for the $2\,^2P$ state, and 546(266+140+140) configurations for the $3\,^2D$ state. The values of the optimal nonlinear parameters are given in Table II.

To verify the completeness of the expansions for the wave functions of ^2S, ^2P, and ^2D symmetries, we checked the following relations, which hold exactly only for complete expansions:

$$\langle 2\,^2S|z^4|2\,^2S\rangle=\sum_n[\langle 2\,^2S|z^2|n\,^2S\rangle\langle n\,^2S|z^2|2\,^2S\rangle+\langle 2\,^2S|z^2|n\,^2D\rangle\langle n\,^2D|z^2|2\,^2S\rangle]\ , \tag{14}$$

$$\langle 2\,^2S|z^4|2\,^2S\rangle=\sum_n\sum_m\sum_p[\langle 2\,^2S|z|n\,^2P\rangle\langle n\,^2P|z|m\,^2S\rangle\times\langle m\,^2S|z|p\,^2P\rangle\langle p\,^2P|z|2\,^2S\rangle+\langle 2\,^2S|z|n\,^2P\rangle\langle n\,^2P|z|m\,^2D\rangle\times\langle m\,^2D|z|p\,^2P\rangle\langle p\,^2P|z|2\,^2S\rangle]\ , \tag{15}$$

where $z=z_1+z_2+z_3$. It was found that the above relations were satisfied to three significant figures.

Finally, before deciding which types of correlated configurations should be included in the basis set expan-

TABLE II. Optimal nonlinear parameters for the $2\,^2S$, $2\,^2P$, and $3\,^2D$ wave functions.

State	α_s	$\alpha_{s'}$	$\alpha_{s''}$	$\alpha_{s'''}$	$\alpha_{s''''}$	α_p	$\alpha_{p'}$	$\alpha_{p''}$	$\alpha_{p'''}$	α_d	$\alpha_{d'}$	α_f
$2\,^2S$	3.2200	0.7224	1.8516	0.8395	0.7165	2.5716				3.6471		4.2384
$2\,^2P$	2.8285	3.5069				0.7938	2.2881	1.1449	2.6297	2.0363		
$3\,^2D$	3.3009	2.6509				2.0075	2.6984			0.4023	0.4244	

sions for $2\,^2S$, $2\,^2P$, and $3\,^2D$ states, we also considered $(n_1 g n_2 g) n_3 s'''''(^2S)$, $(n_1 d' n_2 d') n_3 p''''(^2P)$, and $(n_1 d'' n_2 d'') n_3 s''(^2D)$ types of configuration, but their contributions to the energies were at least an order of magnitude smaller than those coming from the configurations already chosen.

IV. RESULTS AND DISCUSSION

A. Energies

The results of our calculations for the energies of the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states are presented in Table III. In the same table, we give the nonrelativistic estimates of the exact energies, the Hartree-Fock values, and the values of the scale factor $-\langle V\rangle/2\langle T\rangle$, where $\langle V\rangle$ and $\langle T\rangle$ stand for potential and kinetic energy. We also show the percentage (Δ) of the correlation energy and the lower bound (S_-) to the overlap of the exact wave function with its variational approximation. S_- was calculated using Weinberger's formula [28]. It should be noted that although the closeness of S_- to 1.0 represents a sensitive criterion of the overall accuracy of the variational wave function, the true accuracy of the wave function for each of the states considered is higher than that suggested by the value of S_-. This is related to the fact that S_- calculated from Weinberger's formula depends on the ability of the wave function to precisely described the excited states of a given symmetry, and even if we were able to include an infinite number of them, S_- would not be equal to unity because the formula does not take into account the contribution from the continuum. In view of the above it is not totally unexpected that S_- for the $3\,^2D$ state is much better than for the $2\,^2S$ or $2\,^2P$ states. This can be explained by the fact that, coincidentally, the wave functions of ^2D symmetry describe very well some of the excited states. For example, the energy of the $4\,^2D$ state is $-7.311\,187$ a.u. in comparison with its nonrelativistic estimate of $-7.311\,189$ a.u.

At this point we would like to focus our attention on the recent estimate of the nonrelativistic energy of the ground $2\,^2S$ state by Jitrik and Bunge [17]. Their result $E_{\text{nr}} = -7.478\,0624$ a.u. based on CI calculations with an empirical estimation of various sources of truncation error is much closer to our nonrelativistic variational energy for the ground state $E = -7.478\,060\,1$ a.u. than any of the older [13,29,30] estimates of E_{nr}. We feel, however, that it would be desirable to have relativistic, quantum electrodynamics, and mass polarization corrections recalculated using more accurate wave functions than in previous calculations. Until then any conclusions concerning closeness of E_{nr} to the true energy should be delayed.

In Table IV we compare our variational nonrelativistic energies for $2\,^2S$, $2\,^2P$, and $3\,^2D$ states with some other previously published results. For the ground $2\,^2S$ state our energy is slightly better than the extensive Hylleraas-type values of King and Bergsbaken [3,5]. The very good result of King and Bergsbaken [5], obtained with only the 296-term expansion, was possible due to a great number of nonlinear parameters and an elaborate

TABLE III. Calculated energies for the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states (in a.u.) compared with estimates of the exact nonrelativistic energies, together with criteria of their accuracy.

State	$-E$	$-E_{\text{nr}}$	$-E_{\text{HF}}$	Scale factor	S_- [a]	Δ [b]
$2\,^2S$	7.478 060 1	7.478 062 4 [c] 7.478 07 [d] 7.478 069 [e] 7.478 068 2 [f]	7.432 74 [g]	1.000 000 1	0.999 950	99.995
$2\,^2P$	7.410 155 4	7.410 157 8 [f] 7.410 16 [h]	7.365 07 [g]	1.000 000 4	0.999 973	99.995
$3\,^2D$	7.335 523 1	7.335 523 4 [i]	7.292 00 [g]	1.000 000 2	0.999 990	99.999

[a] $S_- \equiv$ the lower bound to the overlap with the exact wave function; see Ref. [28].

[b] $\Delta = [(E - E_{\text{HF}})/(E_{\text{nr}} - E_{\text{HF}})] \times 100$ is the percentage contribution to the correlation energy.

[c] Reference [17].

[d] Reference [29].

[e] Reference [30].

[f] Reference [13].

[g] Reference [31].

[h] Reference [32].

[i] Reference [16].

TABLE IV. Comparison of the upper bounds to the nonrelativistic energies of the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states of Li in atomic units.

Type of wave function		$-E$		
		$2\,^2S$	$2\,^2P$	$3\,^2D$
Larsson[a]	100-term Hylleraas	7.478 025		
Ahlenius and Larsson[b]	97-term Hylleraas		7.410 078	
Sims and Hagstrom[c]	150-term ($2\,^2S$) 120-term ($2\,^2P$) CI-Hylleraas	7.478 023	7.410 053	
Muszyńskam Papierowska, and Woźnicki[d]	139-term ($2\,^2S$) 120-term ($2\,^2P$) CI-Hylleraas	7.478 044	7.410 097	
Ho[e]	92-term Hylleraas	7.478 031		
Pipin and Woźnicki[f]	170-term CI-Hylleraas	7.478 044	7.410 106	
Pipin[g]				7.335 468
King and Shoup[h]	352-term Hylleraas	7.478 058		
King[i]	602-term Hylleraas	7.478 059		
King and Bergsbaken[j]	296-term Hylleraas	7.478 059 5		
Present work		7.478 060 1	7.410 155 4	7.335 523 1

[a] Reference [30].
[b] Reference [32].
[c] Reference [15].
[d] Reference [12].
[e] Reference [33].
[f] Reference [14].
[g] Reference [16].
[h] Reference [1].
[i] Reference [3].
[j] Reference [5].

process of optimization, whereas in the present work only eight optimal nonlinear parameters were used to describe the K- and L-shell electrons. For the $2\,^2P$ and especially the $3\,^2D$ state there are no previously published results which approach our accuracy.

In Table V a comparison of the theoretical and experimental ionization energies is given. Our values were obtained by subtracting the nonrelativistic energies of the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states from the nonrelativistic energy ($-7.279\,913\,4$ a.u.) of the ground state of the lithium ion as reported by Freund, Huxtable, and Morgan [34]. The MBPT result of Lindgren [6] for $2\,^2S$ ionization energy includes a relativistic correction of 0.000 016 a.u. (3.5 cm^{-1}). The results of Johnson, Blundell, and Sapirstein [7(a)] include relativistic and mass polarization and/or reduced mass corrections. If we add Lindgren's relativistic correction and quantum-electrodynamic correction [35] (-2.1 cm^{-1}) to our nonrelativistic $2s$-$2p$ transition energy we obtain 14 903.86 cm^{-1} ($R_M = 109\,728.63$), which is in perfect agreement with the empirical value [36–38] of 14 903.88 cm^{-1}. For the $2p$-$3d$ transition the experimental value is 16 379.20 cm^{-1} and our nonrelativistic result is 16 378.60 cm^{-1}.

B. Properties

In Table VI a comparison of the experimental and theoretical values of the absorption oscillator strengths and the lifetimes is given. For the sake of completeness the values of dipole and quadrupole moments are also included in this table. As can be seen there is good agreement between our and other theoretical f values with the exception of Lindgård and Nielsen's results [43] obtained using the Coulomb approximation.

TABLE V. Ionization energies for $2\,^2S$, $2\,^2P$, and $3\,^2D$ states, in atomic units. The data refer to the centers of gravity of the states.

	$2\,^2S$	$2\,^2P$	$3\,^2D$
Lindgren[a]	0.198 154(3)	0.130 221(3)	0.055 60
Johnson, Idress, and Sapirstein[b]	0.197 97	0.130 01	0.055 60
Johnson, Blundell and Sapirstein[c]	0.198 076	0.130 147	
Present work	0.198 147	0.130 242	0.055 610
Experimental[d]	0.198 158	0.130 245	0.055 610

[a] Reference [6].
[b] Reference [7(b)].
[c] Reference [7(a)].
[d] References [36–38].

TABLE VI. Comparison of theoretical and experimental oscillator strengths, lifetimes and transition moments for $2\,^2S$, $2\,^2P$, and $3\,^2D$ states.

	Transition moments							
	Dipole		Quadrupole		Oscillator strengths		Lifetimes (nsec)	
	$2\,^2S$-$2\,^2P$	$2\,^2P$-$3\,^2D$	$2\,^2S$-$3\,^2D$	$2\,^2P$-$2\,^2P$	$2\,^2S$-$2\,^2P$	$2\,^2P$-$3\,^2D$	$2\,^2P$	$3\,^2D$
Experiment								
Heldt and Leuchs[a]					0.726±0.03	0.643±0.03	27.9±1.0	14.5±0.7
Azencot and Goutte[b]								14.8±1.9
Schulze-Hagenest *et al.*[c]								14.60±0.13
Gaupp, Kuske, and Andrä[d]					0.7416±0.0012		27.29±0.04	
Theory								
Lindgård and Nielsen[e]					0.7412	0.6354	27.32	14.66
Froese Fischer[f]					0.7480			
Sims, Hagstrom and Rumble[g]					0.7476			
Pipin and Woźnicki[h]							27.1	
Johnson, Idrees, and Sapirstein[i]					0.7495			
Heavens[j]							27.2	14.5
Present results	2.3452	2.2652	8.6706	10.820	0.7470	0.6382	27.12	14.60

[a] Resonance fluorescence technique, Ref. [39].
[b] Atomic ionoluminescence technique, Ref. [40].
[c] Fast beam technique, Ref. [41].
[d] Fast beam technique, Ref. [42].
[e] Coulomb approximation, Ref. [43].
[f] MCHF method, Ref. [44].
[g] CI Hylleraas, Ref. [45].
[h] CI Hylleraas, Ref. [14].
[i] MBPT, Ref. [7(b)].
[j] Coulomb approximation, Ref. [46].

Table VII contains a comparison of the dipole oscillator strength sums

$$S_{-k}=2\sum_{m\,(\neq g)}\langle g|\mu|m\rangle^2/(\hbar\omega_{mg})^k \qquad (16)$$

with the semiempirical values of Zeiss *et al.* [47] and Kouba and Meath [48].

Table VIII presents some theoretical and experimental values of the static dipole, quadrupole, dipole-quadrupole polarizabilities and hyperpolarizability. To get values of these properties we used Eqs.(5)–(8) in which the summation over the true states was replaced by the summation over the lowest states and pseudostates of ^2S, ^2P, and ^2D symmetry. This is the same as in checking the closure relations, Eqs. (14) and (15), and in calculating the dipole oscillator strength sums, Eq. (16). Had we determined the true states, it would be necessary to include the continuum contributions to each of the properties considered.

Our value of the dipole polarizability is in excellent agreement with the experimental value of Molof *et al.* [49] and other theoretical results. The value of the quadrupole polarizability agrees within 0.3% with the results of Reinsch and Meyer [53], and Maroulis and Thakkar [23]. The pseudopotential result of Meader and Kutzelnigg [52] is an underestimate. Our dipole-quadrupole polarizability agrees within ~1% with the fourth-order Møller-Plesset perturbation value of Maroulis and Thakkar [23].

In Table VIII we have included only two other theoretical values of γ. The result of Maroulis and Bishop [22] illustrates the difficulty of obtaining reliable values of the hyperpolarizability using a method which does not take into account electron correlation. As we already mentioned Maroulis and Thakker's [23] result is the only one obtained to date by a method accounting for electron correlation and although it is far from being converged, it has the same sign and order of magnitude as our value of γ.

Our analysis of the convergence of α, C, and B, and γ

TABLE VII. Dipole oscillator strength sums for the ground $2\,^2S$ state of the lithium atom.

Reference	S_0	S_{-1}	S_{-2}	S_{-3}	S_{-4}	S_{-5}
Zeiss *et al.*[a]	3.000	12.14	163.6	2385	35 040	
Kouba and Meath[b]		12.09±0.14	163.3±0.3	2383±2	35 011	
Present work	2.999	12.13	164.1	2394	35 170	517 600

[a] Reference [47].
[b] Reference [48].

TABLE VIII. Comparison of theoretical and experimental values of the static dipole, quadrupole, dipole-quadrupole polarizabilities and hyperpolarizability for the ground $2\,^2S$ state. Atomic units are used.

Method	α	C	B	γ
EH gradient balance technique, experimental[a]	164.0±3.4			
PNO-CEPA[b]	164.5			
CI[c]	164±2			
Pseudopotential[d]	164.3	1383		
PNO-CEPA[e]		1428.0		
CI Hylleraas[f]	163.8			
CI Hylleraas[g]	163.8			
CI Hylleraas[h]	163.9			
CRHF, CUHF[i]			−58 210	
SCF[j]			−58 880	−86 400
Fourth-order MP[k]	164.8	1428.0	−54 926	4350
This work	1.641×10^2	1.423×10^3	-5.43×10^4	3×10^3

[a] Molof *et al.*, Ref. [49]. Electric-magnetic field-gradient balance techniques.

[b] Werner and Meyer, Ref. [50]. Pseduo-natural-orbital coupled-electron-pair approximation.

[c] Pouchan and Bishop, Ref. [51].

[d] Meader and Kutzelnigg, Ref. [52].

[e] Reinsch and Meyer, Ref. [53].

[f] Sims, Hagstrom, and Rumble, Ref. [54].

[g] Muszyńska *et al.*, Ref. [13].

[h] Pipin and Woźnicki, Ref. [14].

[i] Bhattacharya and Mukherjee, Ref. [55]. Coupled-restricted-Hartree-Fock and coupled-unrestricted-Hartree-Fock approximation.

[j] Maroulis and Bishop, Ref. [22]. Self-consistent-field approximation.

[k] Maroulis and Thakkar, Ref. [23]. Møller-Plesset approximation.

values, performed with somewhat different basis set expansions for ^2S, ^2P, and ^2D states, indicated that the values of α, C, and B are converged to the number of significant figures given. The value of γ, however, has only one significant figure (3×10^3 a.u.). In view of the accuracy of our variational wave functions we consider the static value of γ to be converged within a few percent.

We made an effort to calculate dynamic values of γ pertaining to different nonlinear processes: the Kerr effect, electric-field-induced second-harmonic generation, etc. A simple analysis of the Eq.(8) shows that the final value of γ comes from

$$\langle 2\,^2S|\mu_\alpha|^2P\rangle\langle ^2P|\mu_\delta|^2S\rangle\langle ^2S|\mu_\gamma|^2P\rangle\langle ^2P|\mu_\beta|2\,^2S\rangle$$

and

$$\langle 2\,^2S|\mu_\alpha|^2P\rangle\langle ^2P|\mu_\delta|^2D\rangle\langle ^2D|\mu_\gamma|^2\rangle\langle ^2P|\mu_\beta|2\,^2S\rangle$$

types of transitions (divided by appropriate energetic denominators), which are added, and also from a second group of terms

$$\langle 2\,^2S|\mu_\alpha|^2P\rangle\langle ^2P|\mu_\delta|2\,^2S\rangle\langle 2\,^2S|\mu_\gamma|^2P\rangle\langle ^2P|\mu_\beta|2\,^2S\rangle$$

which are subtracted. The orders of magnitude of these terms are 10^6 so one needs four significant figures in each of the terms to get just one significant figure in γ. To be definitive about the frequency dependence of γ we would have to get converged values of these terms to at least five significant figures. That, however, was not achieved in spite of the fact that accurate energies and wave functions were obtained.

TABLE IX. Values of the dynamic dipole α, quadrupole C, and dipole-quadrupole B polarizabilities for the ground $2\,^2S$ state of the lithium atom, in atomic units. Numbers in square brackets are powers of ten.

$\hbar\omega$ (a.u.)	$\alpha(\omega)$[a]	$C(\omega)$[b]	$B(\omega)$[c]
0.000	1.641[2]	1.423[3]	−5.43[4]
0.005	1.650[2]	1.425[3]	−5.48[4]
0.010	1.677[2]	1.430[3]	−5.64[4]
0.015	1.724[2]	1.438[3]	−5.94[4]
0.020	1.795[2]	1.449[3]	−6.39[4]
0.025	1.896[2]	1.464[3]	−7.06[4]
0.030	2.034[2]	1.482[2]	−8.06[4]
0.035	2.228[2]	1.505[3]	−9.57[4]
0.040	2.503[2]	1.532[3]	−1.20[5]
0.045	2.910[2]	1.564[3]	−1.61[5]
0.050	3.561[2]	1.601[3]	−2.39[5]

[a] $\alpha(\omega)=\alpha_{zz}(-\omega;\omega)$.

[b] $C(\omega)=C_{zz,zz}(-\omega;\omega)$.

[c] $B(\omega)=B_{zz,zz}(-\omega;\omega,0)$.

To complete the results we give in Table IX values of dynamic dipole, quadrupole, and dipole-quadrupole polarizabilities for frequencies below the $2s$-$2p$ transition frequency.

V. CONCLUSIONS

We have presented the lowest nonrelativistic upper bounds to the energies of the $2\,^2S$, $2\,^2P$, and $3\,^2D$ states of the lithium atom. This does not, however, preclude the possibility of additional, though small, improvements to the nonrelativistic calculations. It seems to us that further refinements of the nonrelativistic energies may be accomplished by employing more nonlinear parameters in the wave functions [5] or by using exponentially correlated wave functions. Exponentially correlated wave functions proved to be rapidly convergent for the helium atom [56] and the recent work of From and Hill [57] makes feasible their application to the lithium atom.

The values of the dipole, quadrupole, and dipole-quadrupole polarizabilities may serve as a reference for less accurate calculations. Having rather limited computer resources, we were not able to calculate the dynamic hyperpolarizability, though our static γ is the most reliable estimate to date.

After completion of this work, we learned of a Hylleraas calculation by D. K. McKenzie and G. W. F. Drake. Their energy for the $2\,^2S$ ground state of the lithium atom is $-7.478\,060\,312$ a.u. [58].

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