

Dipole polarizabilities and hyperpolarizabilities of excited valence states of Be

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We present predictions for the scalar and tensor components of the linear, α , and nonlinear, γ , polarizabilities of the excited valence states of Be, $1s^2 2s 2p^3 P^0$, $1P^0$, $1s^2 2p^2 3P$, and $1s^2 2p^2 1D$. Also reported are results on the previously extensively studied ground state $1s^2 2s^2 1S$. The all-order variational calculations solved state-specific complex eigenvalue matrix equations and accounted for valence electron correlation and field-induced mixing effects. The results demonstrate the importance of valence-Rydberg mixing on these properties, even when the valence states are the lowest of their symmetry. For example, whereas for Be $1s^2 2s 2p^3 P^0$, where such mixing is very small, $\alpha_0 = 39.33$ and $\gamma_0 = 9.49 \times 10^4$ a.u. for $1s^2 2p^2 1D$, which mixes heavily with the $1s^2 2snd$ Rydberg series (especially with $1s^2 2s 3d$), $\alpha_0 = 492.73$ a.u. and $\gamma_0 = 0.48 \times 10^7$ a.u.

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INTRODUCTION

In recent work on the linear, α , and nonlinear, γ , polarizabilities of He doubly excited states [1], it was found that for the $2s^2 1S$ state these properties were of the same order of magnitude as those of the Be $1s^2 2s^2 1S$ ground state. Furthermore, the α and γ of He $2s 2p^3 P^0$ were also of the same magnitude, but, as it was pointed out, there was no *ab initio* theoretical or experimental values for Be $1s^2 2s 2p^3 P^0$ with which to compare.

In fact, although the Be $1s^2 2s^2 1S$ ground state has been the object of many theoretical studies by different methods as regards its polarizability (e.g., [2–8]) and its hyperpolarizability [3,6–8], the *lowest excited valence* bound state of Be, i.e., the metastable $1s^2 2s 2p^3 P^0$, the $1s^2 2s 2p^1 P^0$, the $1s^2 2p^2 3P$, and the $1s^2 2p^2 1D$, have not been examined yet. From the point of view of electronic structure and electron correlation, for a theory to be able to handle the problem of computing α and γ of such excited states, it must be applicable to open shell states with possible heavy valence-Rydberg mixing, as is the case with the $1s^2 2p^2 1D$ state ([9], Table 5).

In this Brief Report we present results on the α and γ of such states, obtained from the application of a state-specific theory of electric properties of polyelectronic ground or excited states (e.g., [1,10,11]), which allow the systematic inclusion of electron correlation and of the effects of field-induced mixing of low- and high-lying excited states and of the continuous spectrum.

The present approach to the calculation of field-induced properties is formulated as a problem of solving variationally to all-orders of complex eigenvalue Schrödinger equation $(H - z_0)\psi = 0$, where $H = H_0 + \sum_i \vec{F} \cdot \vec{r}_i$ and $z_0 = E_0 + \Delta(F) - i\Gamma(F)/2$. H_0 is the free-atom Hamiltonian and \vec{F} represents the external dc field. $\Delta(F)$ and $\Gamma(F)$ are the field-dependent energy shift and width of the state of interest, whose field-free energy is E_0 .

The trial function space is divided into two nonorthonormal multidimensional parts Q and P . The Q space contains state-specific correlated wave functions belonging to the bound spectrum, including the ones that describe the localized part of states in the continuum. The selection of the states that are included in the calculation is based on the electronic structure and on the spectrum of the system under study. Their form is

$$\Psi_0^n = \Phi_0^n + X_{\text{loc}}^n, \quad (1)$$

where Φ_0^n is the zeroth-order multiconfigurational Hartree-Fock (MCHF) wave function and X_{loc}^n represents the remaining localized correlations.

The P space contains \mathcal{L}^2 states that represent the multichannel continuous spectrum. The continuum orbitals are expanded in terms of complex Slater orbitals,

$$\epsilon l(r, \theta) = \sum_n \alpha_n \varphi_{nl}(r, \theta), \quad \varphi_{nl} = r^{n+1} e^{-\beta r} e^{-i\theta}. \quad (2)$$

The nonlinear parameters β and θ are optimized variationally until a stable eigenvalue is obtained of the complex non-Hermitian Hamiltonian,

$$H = \begin{bmatrix} H_{QQ} & H_{QP} \\ H_{PQ} & H_{PP} \end{bmatrix}. \quad (3)$$

The solution corresponds to the root whose overlap with the Ψ_0^n is maximum. From the final complex eigenvalue we obtain the energy shift $\Delta(F)$. For small field strengths, the energy shift of the state (γ, L, M) is expanded as

$$\Delta_{\gamma LM}(F) = -\frac{1}{2!} \alpha_{\gamma LM} F^2 - \frac{1}{4!} \gamma_{\gamma LM} F^4 \dots, \quad (4)$$

where $\alpha_{\gamma LM}$ is the polarizability and $\gamma_{\gamma LM}$ is the hyperpolarizability. These can be expressed as linear combinations of their irreducible parts as

$$\alpha_{LM} = \alpha_0 + \alpha_2 \frac{3M^2 - L(L+1)}{L(2L-1)}, \quad (5)$$

$$\gamma_{LM} = \gamma_0 + \gamma_2 \frac{3M^2 - L(L+1)}{L(2L-1)} + \gamma_4 \frac{35M^4 + \{25 - 30L(L+1)\}M^2 + 3(L-1)L(L+1)(L+2)}{L(2L-1)(2L-2)(2L-3)}, \quad (6)$$

where α_0 and α_2 are the scalar and tensor parts of the dipole polarizability and γ_0 , and γ_2, γ_4 are the scalar and tensor parts of the dipole hyperpolarizability corresponding to tensors of ranks 2 and 4, respectively [12].

DETAILS OF THE CALCULATION

Our calculations accounted for virtual excitations outside a closed $1s^2$ core, since the influence of core excitations to α_k, γ_k is expected to be small. For the ground state of Be, the numerical MCHF function Φ_0 was $0.950(1s^2 2s^2) + 0.312(1s^2 2p^2)$, while X_{loc} was expanded in terms of 14 singly and doubly excited configurations with virtual orbitals up to orbital angular momentum $l=3$ and representing only L -shell correlations. For the first excited state $1s^2 2s 2p \ ^1P^0$ we used the MCHF function $\Phi_0 = 0.972(1s^2 2s 2p) - 0.218(1s^2 2p 3d) + 0.089(1s^2 3s 3p)$, and X_{loc} was expanded in terms of 14 configurations. For $1s^2 2p^2 \ ^1D$, which is the lowest 1D state of Be and has a strong mixing with the Rydberg $1s^2 2s 3d$ state, we used $\Phi_0 = 0.755(1s^2 2p^2) + 0.653(1s^2 2s 3d) + 0.065(1s^2 3p^2) + 0.022(1s^2 3d^2)$, and X_{loc} was expanded in terms of 15 configurations.

In the Q space we also included the Rydberg states $1s^2 2s n l, n=3-6, l=0-(n-1)$, the $1s^2 2p^2 \ ^1S$ state which lies above the first ionization threshold, and the Rydberg states $1s^2 2p n' l', n'=3-6, l'=0-(n-1)$ lying below the second ionization threshold.

The P space included the states $1s^2 2s \epsilon l$ and $1s^2 2p \epsilon l'$, and we used continuum orbitals ϵl and $\epsilon l'$ having $l, l' \leq 5$. The nonlinear parameter β of ϵl was optimal at $\beta=1.5$, while for $\epsilon l', \beta'$ was equal to 1.3.

For the Be $1s^2 2s 2p \ ^3P^0$ state we used the MCHF function $\Phi_0 = 0.994(1s^2 2s 2p) + 0.097(1s^2 2p 3d) - 0.042(1s^2 3s 3p)$, and X_{loc} was expanded in terms of 14 configurations. It is clear that the contribution to the electronic structure of Rydberg configurations

is much smaller here than in the other singlet valence excited states $^1P^0$ and 1D . Finally, for $1s^2 2p^2 \ ^3P$ we used $\Phi_0 = 0.994(1s^2 2p^2) - 0.078(1s^2 3p^2) - 0.082(1s^2 3d^2)$, while X_{loc} was expanded in terms of only 7 configurations, since this electronic structure does not have much electron correlation. The remaining part of the Q of the P spaces had the same form as for singlet states.

RESULTS

We obtained the polarizabilities and hyperpolarizabilities by fitting 30 calculated values of the energy shift to a tenth degree polynomial of even powers of the field strength. The range of the values of the field strength differed from state to state. Specifically, for $1s^2 2s^2 \ ^1S$ $F=0.0 \rightarrow 0.008$ a.u., for $1s^2 2s 2p \ ^1P^0$ $F=0.0 \rightarrow 0.002$ a.u., for $1s^2 2p^2 \ ^1D$ $F=0.0 \rightarrow 0.0014$ a.u., for $1s^2 2s 2p \ ^3P^0$ $F=0.0 \rightarrow 0.004$ a.u., for $1s^2 2p^2 \ ^3P$ ($M=0$) $F=0.0 \rightarrow 0.0030$ a.u. and for $1s^2 2p^2 \ ^3P$ ($M=1$) $F=0.0 \rightarrow 0.0012$ a.u.

By inverting the expressions (5) and (6), we express their irreducible parts in terms of the individual α_{LM} and γ_{LM} . Our results are presented in Table I. There is an obvious M dependence of α_{LM} and γ_{LM} , particularly for the $1s^2 2p^2 \ ^1D$ state. The tensor parts of the $2s 2p$ configuration are much larger for $^1P^0$ than those for $^3P^0$. Also, in the case of $^1P^0$ and 1D , some components have a negative sign.

It is perhaps of interest to the reader to see an example of how α and γ depend on major parts of P and Q . Let us consider the $1s^2 2s 2p \ ^1P^0$ ($M=\pm 1$) level whose $\alpha=81.23$ a.u., and $\gamma=1.04 \times 10^6$ a.u. (Table I). By excluding the continuum above the second ionization threshold we obtain $\alpha=76.78$ a.u. and $\gamma=9.84 \times 10^5$ a.u., while by excluding the continuum above the first ionization threshold and the states that lie within, we obtain $\alpha=75.00$ a.u. and $\gamma=8.06 \times 10^5$ a.u. As regards the

TABLE I. Calculated values of scalar and tensor parts of the polarizabilities and hyperpolarizabilities for the lowest-lying Be valence states by the present state-specific complex eigenvalue approach. All results are in a.u. The numbers in square brackets denote powers of 10.

	$1s^2 2s^2 \ ^1S$	$1s^2 2s 2p \ ^3P^0$	$1s^2 2s 2p \ ^1P^0$	$1s^2 2p^2 \ ^1D$	$1s^2 2p^2 \ ^3P$
α_0	37.62	39.33	128.67	492.73	43.30
α_2		0.47	-47.44	-375.37	2.19
γ_0	3.05[4]	9.49[4]	3.66[6]	0.48[7]	3.75[5]
γ_2		-5.91[4]	-2.62[6]	6.28[7]	1.29[5]
γ_4				-5.61[7]	

TABLE II. Comparison of the polarizability and hyperpolarizability of the Be 1S ground state obtained by different methods. All values are in a.u.

	α	γ
Ref. [2]	36.58±0.81	
Ref. [3]	40.22	3.83[4]
Ref. [4]	37.05	
Ref. [5]	37.9	
Ref. [6]	37.298	3.148[4]
Ref. [7]	37.5312	2.7227[4]
Ref. [8]	37.59	2.93[4]
This work	37.62	3.05[4]

highest Rydberg states of the remaining Q space we found that they have a contribution of 0.2% to polarizability and 4% to hyperpolarizability. In order to demonstrate the level of accuracy of the state-specific calculations, in Table II we compare our results for α and γ of the ground state with other calculations where very large expansions have been used.

CONCLUSION

We have applied a general, electronic structure-based theory of field-induced properties to the calculation of the scalar and tensor components of linear and nonlinear polarizabilities of prototypical excited valence states of Be. The sizes and signs of these quantities depend crucially on the electronic structure and on the symmetry of each state. For example, the α of the metastable $^3P^0$ state, which does not have much correlation beyond the Hartree-Fock function, is very close to that of the 1S ground state where, beyond the near degeneracy mixing $2s^2 \leftrightarrow 2p^2$, which reduces the magnitude of the polarizabilities, the Rydberg state contributions are small. However, the fact that there are correlating Rydberg configurations in the wave functions of the $2s2p^1P^0$ and especially of the $2p^2^1D$ states, which themselves interact via the dipole operator, leads to very high values of α and γ .

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- [1] C. A. Nicolaides and S. I. Themelis, *J. Phys. B* **26**, L387 (1993).
 [2] J. S. Sims and J. R. Rumble, Jr., *Phys. Rev. A* **8**, 2231 (1973).
 [3] N. L. Manakov, V. D. Ovsyannikov, and L. P. Rapoport, *Opt. Spektrosk.* **38**, 115 (1975) [*Opt. Spectrosc. (USSR)* **38**, 206 (1975)].
 [4] D. R. Beck and C. A. Nicolaides, *Chem. Phys. Lett.* **48**, 135 (1977).
 [5] A. Hibbert, M. LeDourneuf, and V. K. Lan, *J. Phys. B* **10**, 1015 (1977).
 [6] A. Thakkar, *Phys. Rev. A* **40**, 1130 (1989).
 [7] H. Koch and R. J. Harrison, *J. Chem. Phys.* **95**, 7479 (1991).
 [8] T. Pluta and H. A. Kurtz, *Chem. Phys. Lett.* **189**, 255 (1992).
 [9] C. A. Nicolaides and D. R. Beck, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and R. R. Beck (Reidel, Dordrecht, 1978), p. 143.
 [10] C. A. Nicolaides, Th. Mercouris, and G. Aspromallis, *J. Opt. Soc. Am. B* **7**, 494 (1990).
 [11] S. I. Themelis and C. A. Nicolaides, *Phys. Rev. A* **46**, R21 (1992).
 [12] V. A. Davydkin and V. D. Ovsyannikov, *J. Phys. B* **19**, 2071 (1986).