Ab Initio Calculation of the Polarizability for the Ground State $X^1\Sigma^+$ and the First Low-Lying Excited States $a^3\Sigma^+$ and $A^1\Sigma^+$ of LiH and NaH

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The dipole polarizabilities of the ground $X^1\Sigma^+$ and the lowest-lying $A^1\Sigma^+$ singlet states of LiH and NaH have been investigated at the ab initio level by using the time-dependent gauge invariant method (TDGI). For the ground-state dipole polarizability of LiH and NaH, and the triplet $a^3\Sigma^+$ excited state of LiH, an alternative method, namely, the coupled cluster with single, double, and a perturbative treatment of the connected triple excitations (CCSD(T)), has been computed for comparison. We found that the long in-plane component α_{zz} of the excited $A^1\Sigma^+$ state of NaH exhibits an unusual calculated negative value, due to the large negative contribution of the $X^1\Sigma^+$ state. At the TDGI level, the convergence of the calculated electric properties with respect to the number of the spectroscopic states has been carefully investigated. The dipole polarizability components as a function of the diatomic distances up to dissociation have also been computed. The results obtained are particularly relevant to the understanding of the variation of the polarizability for small and large internuclear distances. The properties computed in this work are in very good agreement with the experimental and theoretical data available in the literature. With regard to the $a^3\Sigma^+$ and $A^1\Sigma^+$ excited states, most of the calculated electric properties are new for LiH and NaH.

I. Introduction

One of the interests in studying electronic properties of atoms and molecules is the importance of these quantities in different models of interacting systems.[1−5] In contrast to ground state electric properties, which in most cases can be obtained with high accuracy both by experiment and theory, experimentally determined excited state properties are less commonly available and generally of lower accuracy. In fact, most of them arise from the study of molecular spectra in solutions, and their evaluation heavily depends on the assumed model of solvent−solute interactions.[6−10] Recent progress in laser Stark spectroscopy[11−13] has made possible the determination of ground to excited state property differences in some cases, but such measurements still seem difficult to perform routinely. This situation justifies even more the need for accurate theoretical results. Moreover, because excited-state electric properties of atoms or molecules may be quite different from those in their ground state, interactions involving electronically excited atoms or molecules may also be considerably different from those in the ground electronic state. Thus, knowledge of the electric properties for atomic or molecular excited states should be as important as they are for atoms and molecules in their ground electronic state.

In previous papers,[14−17] we have shown that the time-dependent gauge invariant (TDGI) approach is an efficient and reliable method for calculating ground and excited states polarizabilities of atoms and the ground state of molecules. More recently,[18−21] it is shown that this method is also suitable for an accurate prediction of the polarizability of the low-lying excited states of Li_2, Na_2, NaLi, and K_2. In this work, we propose reliable values of the polarizabilities of the ground $X^1\Sigma^+$ and low-lying $A^1\Sigma^+$ and $a^3\Sigma^+$ excited states of LiH and NaH. With regard to the excited states, for the sake of comparison, the polarizability of the lowest triplet $a^3\Sigma^+$ state has also been calculated through the CCSD(T) method implemented in the Gaussian 98 package.[22] Then, in the case of LiH, the polarizability components of this lowest but dissociative $a^3\Sigma^+$ excited state have been computed for five different internuclear distances at both TDGI and CCSD(T) methods. Finaly, the dependence of the polarizability on internuclear separation has been investigated, in more detail for the associative $X^1\Sigma^+$ and $A^1\Sigma^+$ states.

The pseudo-potential approach including core-valence correlation has been used. Because it is possible for these systems, containing a small number of valence electrons, to fully treat the valence shell, very accurate oscillator strengths and transition energies needed for the calculation of the polarizability can be achieved at a small computational cost. On the other hand, we have shown in an earlier previous paper[23] devoted to the ground and excited states polarizabilities of Na and K atoms and to the evaluations of the van der Waals coefficients for the interacting pairs Na−Na, K−K, and Na−K that the use of pseudopotentials including core-valence correlation yields oscillator strengths in very satisfactory agreement with previous all-electron results and experiments but generally slightly overestimated. Thus, a correction of oscillator strengths has been taken into account in this work through the use of modified transition operator as proposed by Hameed et al.[24,25]

In section II, we briefly present our computational method. The numerical results including values for the transition energies, oscillator strengths, and electric dipole polarizabilities are presented, discussed, and compared with earlier theoretical and experimental results in section III. Unless stated, atomic units are used throughout this paper.

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TABLE 1: First Oscillator Strengths (f_{ik}) and Vertical Transition Energies (ΔE_{ik}) Needed in the Calculations of the TDGI (Pseudopotential) Dipole Polarizabilities of the Ground ($X^1\Sigma^+$) and Excited ($A^1\Sigma^+$) States of LiH, at Their Respective Calculated Equilibrium Geometry of 1.604 and 2.559 Å[a]

transitions	ΔE_{ik}	f_{ik}	transitions	ΔE_{ik}	f_{ik}
$X^1\Sigma^+ \rightarrow A^1\Sigma^+$	0.129880, 0.120794[b] 0.1325,[c] 0.1314[d] 0.1319,[e] 0.1295[f]	0.246	$X^1\Sigma^+ \rightarrow (1)^1\Pi$	0.167375, 0.159036[b] 0.1697,[c] 0.1696[d] 0.1718,[e] 0.1671,[f] 0.200549[g]	0.620
$X^1\Sigma^+ \rightarrow 3^1\Sigma^+$	0.214765, 0.222894[g]	0.066	$X^1\Sigma^+ \rightarrow (2)^1\Pi$	0.235162, 0.262888[g]	0.006
$X^1\Sigma^+ \rightarrow 4^1\Sigma^+$	0.228296	0.010	$X^1\Sigma^+ \rightarrow (3)^1\Pi$	0.237585	0.122
$X^1\Sigma^+ \rightarrow 5^1\Sigma^+$	0.235258	0.122	$X^1\Sigma^+ \rightarrow (4)^1\Pi$	0.263958	0.001
$A^1\Sigma^+ \rightarrow X^1\Sigma^+$	−0.077167	−0.537	$A^1\Sigma^+ \rightarrow (1)^1\Pi$	0.038316	0.204
$A^1\Sigma^+ \rightarrow 3^1\Sigma^+$	0.091837	0.225	$A^1\Sigma^+ \rightarrow (2)^1\Pi$	0.108110	0.013
$A^1\Sigma^+ \rightarrow 4^1\Sigma^+$	0.096602	0.853	$A^1\Sigma^+ \rightarrow (3)^1\Pi$	0.110597	0.280
$A^1\Sigma^+ \rightarrow 5^1\Sigma^+$	0.108206	0.100	$A^1\Sigma^+ \rightarrow (4)^1\Pi$	0.136912	0.004

[a] All quantities are given in a.u. [b] Reference 39: Experimental value. [c] Reference 14: All electron calculation, at experimental equilibrium bond distance of 1.5955 Å. [d] Reference 41: Multireference coupled cluster calculations. [e] Reference 42: MCSCF calculations. [f] Reference 43: MCTDHF calculations. [g] Reference 44: Algebraic approach.

II. Method and Computational Details

In this work, we use the TDGI method, which is a variation-perturbation method with an original expression of the first-order wave function $|1\rangle$, including a first degree polynomial function,[26] and taking into account correlation effects as described in detail elsewhere.[14,15] In short the construction of the first-order wave function $|1\rangle$, which needs in addition to the polynomial function $g(r)$, the use of a combination of true spectral states ψ_n and a quasi-spectral series ϕ_m, is given by

$$|1\rangle = g(r)|\psi_0\rangle + \sum_{n\neq 0}^{N} b_n|\psi_n\rangle + \sum_{m\neq 0}^{M} C_m|\phi_m\rangle$$

The expansion coefficients are obtained variationally. The polarizability α is then related to the second-order perturbation energy.

We have shown that the use of such a function ensures "gauge invariance" simulates part of the continuum contribution and partly corrects the restricted number of states in the construction of the first-order wave function, giving rise to a consistent method which is suitable for the calculation of the ground as well as excited states dipole polarizabilities of atoms and molecules. In fact, for nondegenerate molecular excited states considered in this study, the general formalism underlying the concept and calculations of electric properties remains virtually the same as that for the ground electronic state.

Electron correlation effects on the electric properties have been taken into account by means of the multireference second-order many-body perturbation theory through the configuration interaction selected by the iterative process (CIPSI) algorithm.[27] Single and double excitations relative to the multireference were included to separately build the first excited states of each symmetry. Static dipole polarizabilities have been computed by including in the first-order wave function the 21 low-lying spectroscopic states of each symmetry and taking into account the quasi-spectral series and the first degree polynomial function. Thus, the convergence of the calculated properties with respect to the number of spectroscopic states can be investigated, as well as the evaluation of the contribution of each spectroscopic state to the dipole polarizability components. This will therefore support the accuracy of the converged values. Except for the dissociative $a^3\Sigma^+$ state of LiH, the final polarizability values have been performed at optimized nuclear geometries.

Pseudo-potential calculations with core polarization potential (CPP) of Poteau and Spiegelmann[28] and that of Durand-Barthelat,[29] for Li and Na, respectively, have been used. The core polarization potential operator is defined as in Meyer's initial formulation[30]

$$V_{\mathrm{CPP}} = -\frac{1}{2}\sum_i \alpha_i \vec{f}_i \cdot \vec{f}_i$$

where $\vec{f}_i$ is the electric field at core i, with a core polarizability α_i. We followed the extension of Meyer's approach proposed by Foucrault et al.,[31] with an l-dependent cutoff function $F_l(r_{ij}, \rho_i^l)$ (r_{ij} being the distance between the core i and an electron j, ρ_i^l the l-dependent cutoff radius) suitable for the study of excited configurations. For the present two-valence electron systems, the excited states are full configuration interaction (CI) functions. The cutoff parameters were fitted on the first transition energies of Li and Na. Each value of the cutoff radius is obtained independently by fitting the first ^2S, ^2P, and ^2D energy levels to experimental data.[32] The resulting values are $\rho(2s) = 1.434a_0$, $\rho(2p) = 0.979a_0$, and $\rho(3d) = 0.600a_0$ and $\rho(3s) = 1.436a_0$, $\rho(3p) = 1.100a_0$, and $\rho(3d) = 0.640a_0$, for Li and Na atoms, respectively. The Gaussian-type orbital (GTO) basis sets for Li and Na built from Jeung's original basis sets[33,34] are taken from ref 28 and 35. These basis sets including more diffuse functions consist of contracted [7s,5p,3d,1f] and [7s,5p,5d,2f], for Li and Na, respectively. Because of the fitting process, the most diffuse exponents have been slightly modified.

As mentioned earlier, a correction of the oscillator strengths has been taken into account as proposed by Hameed et al.[24,25] In fact, a modified transition operator defined as

$$\mu_i = -r_i + \sum_i \alpha_c f_c(i)$$

gives an effective valence electron expression for the oscillator strengths

$$f_{0k} = 2\langle\psi_0|\sum_i^N \mu_i|\psi_k\rangle \Delta E_{0k}$$

ψ_0 and ψ_k are valence electron wave functions, N is the number of valence electrons, and ΔE_{0k} is the transition energies between the two states. This correction slightly decreases the oscillator strengths, making them consistent with experiment and all-electron calculations.

CCSD(T) all electron calculations have been carried out by using the basis set of contracted Gaussian functions developed for the purpose of accurate high-level-correlated calculations of electric properties by Sadlej and Urban.[36] The s-, p-, and d-type Gaussian-type functions (GTFs) consist of (10s6p4d)

TABLE 2: First Oscillator Strengths (f_{ik}) and Vertical Transition Energies (ΔE_{ik}) Needed in the Calculations of the TDGI (Pseudopotential) Dipole Polarizabilities of the Ground ($X^1\Sigma^+$) and Excited ($A^1\Sigma^+$) States of NaH, at Their Respective Calculated Equilibrium Geometry of 1.913 and 3.213 Å[a]

transitions	ΔE_{ik}	f_{ik}	transitions	ΔE_{ik}	f_{ik}
$X^1\Sigma^+ \rightarrow A^1\Sigma^+$	0.115700, 0.103522[b]	0.621	$X^1\Sigma^+ \rightarrow (1)^1\Pi$	0.150858	0.684
$X^1\Sigma^+ \rightarrow 3^1\Sigma^+$	0.185067	0.062	$X^1\Sigma^+ \rightarrow (2)^1\Pi$	0.202959	0.095
$X^1\Sigma^+ \rightarrow 4^1\Sigma^+$	0.195251	0.094	$X^1\Sigma^+ \rightarrow (3)^1\Pi$	0.208535	0.071
$X^1\Sigma^+ \rightarrow 5^1\Sigma^+$	0.202904	0.023	$X^1\Sigma^+ \rightarrow (4)^1\Pi$	0.227164	0.001
$A^1\Sigma^+ \rightarrow X^1\Sigma^+$	−0.055916	−0.945	$A^1\Sigma^+ \rightarrow (1)^1\Pi$	0.042911	0.239
$A^1\Sigma^+ \rightarrow 3^1\Sigma^+$	0.076583	1.466	$A^1\Sigma^+ \rightarrow (2)^1\Pi$	0.096576	0.378
$A^1\Sigma^+ \rightarrow 4^1\Sigma^+$	0.083028	0.009	$A^1\Sigma^+ \rightarrow (3)^1\Pi$	0.101336	0.0001
$A^1\Sigma^+ \rightarrow 5^1\Sigma^+$	0.096227	0.149	$A^1\Sigma^+ \rightarrow (4)^1\Pi$	0.120324	0.006

[a] All quantities are given in a.u. [b] Reference 40: Experimental value.

TABLE 3: Dipole Polarizabilities (a.u.) of the $a^3\Sigma^+$ State of LiH, Calculated by Using the TDGI (Pseudopotentiel) and the CCSD(T) (All Electron) Methods

R(Å)	α_{xx}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
1.005	270.05,[a] 269.24[b] (<1%)	71.24,[a] 73.04[b] (2.5%)	203.78,[a] 203.84[b]	−198.81,[a] −196.2[b]
1.604	261.12,[a] 266.54[b] (2%)	79.42,[a] 81.74[b] (3%)	200.55,[a] 204.94[b]	−181.70,[a] −184.8[b]
2.328	207.00,[a] 212.78[b] (3%)	107.00,[a] 110.84[b] (3.5%)	173.67,[a] 178.80[b]	−100.00,[a] −101.9[b]
3.704	170.49,[a] 173.65[b] (2%)	151.27,[a] 154.73[b] (2%)	164.08,[a] 167.34[b]	−19.22,[a] −18.9[b]
6.350	168.14,[a] 172.36[b] (2.5%)	170.00,[a] 173.00[b] (2%)	168.76,[a] 172.57[b]	1.86,[a] 0.64[b]

[a] TDGI: pseudopotential calculations. [b] CCSD(T): all-electron calculations.

TABLE 4: Contributions of the Low-Lying Spectroscopic States to the Parallel (α_{zz}) and Perpendicular (α_{xx}) Dipole Polarizability Components, of the Ground $X^1\Sigma^+$ and Excited $A^1\Sigma^+$ States, at Their Calculated Equilibrium Geometry

LiH

state	cont[a]	$\alpha_{zz}(X^1\Sigma)$[b]	state	cont[a]	$\alpha_{xx}(X^1\Sigma)$[b]
$A^1\Sigma^+$	14.58	(54%)	$(1)^1\Pi$	22.13	(74%)
$3^1\Sigma^+$	1.43	(5.3%)	$(2)^1\Pi$	0.11	(0.4%)
$4^1\Sigma^+$	0.19	(0.7%)	$(3)^1\Pi$	2.16	(7.2%)
$5^1\Sigma^+$	2.20	(8%)	$(4)^1\Pi$	0.01	(0.04%)

state	cont[a]	$\alpha_{zz}(A^1\Sigma)$[b]	state	cont[a]	$\alpha_{xx}(A^1\Sigma)$[b]
$X^1\Sigma^+$	−90.2	(−156.6%)	$(1)^1\Pi$	139	(78.4%)
$3^1\Sigma^+$	26.68	(46.3%)	$(2)^1\Pi$	1.11	(0.63%)
$4^1\Sigma^+$	91.40	(159%)	$(3)^1\Pi$	22.89	(12.9%)
$5^1\Sigma^+$	8.54	(14.8)	$(4)^1\Pi$	0.21	(0.12%)

NaH

state	cont[a]	$\alpha_{zz}(X^1\Sigma)$[b]	state	cont[a]	$\alpha_{xx}(X^1\Sigma)$[b]
$A^1\Sigma^+$	46.41	(80%)	$(1)^1\Pi$	30.06	(73%)
$3^1\Sigma^+$	1.81	(3.1%)	$(2)^1\Pi$	2.31	(5.5%)
$4^1\Sigma^+$	2.47	(4.3%)	$(3)^1\Pi$	1.63	(3.9%)
$5^1\Sigma^+$	0.56	(1.0%)	$(4)^1\Pi$	0.02	(0.04%)

state	cont[a]	$\alpha_{zz}(A^1\Sigma)$[b]	state	cont[a]	$\alpha_{xx}(A^1\Sigma)$[b]
$X^1\Sigma^+$	−302.2	(−188.9%)	$(1)^1\Pi$	129.8	(68%)
$3^1\Sigma^+$	250.0	(156.3%)	$(2)^1\Pi$	40.5	(21.3%)
$4^1\Sigma^+$	1.31	(8.2%)	$(3)^1\Pi$	0.01	(0.005%)
$5^1\Sigma^+$	16.09	(100.5%)	$(4)^1\Pi$	0.41	(0.2%)

[a] Contributions to dipole polarizability components. [b] Percentage with respect to total polarizability component (Table 4), calculated with twenty spectroscopic states and taking into account the polynomial and quasi-spectral series contributions.

contracted to [5s,3p,2d] and (13s10p4d) contracted to [7s,5p,-2d], for Li and Na, respectively. The contracted-Gaussian-type functions set of hydrogen[37] consists of (10s6p).

III. Results and Discussion

A good description, with a correct ordering, of the close-lying excited states are crucial for a good estimate of the excited-state polarizability. The calculated vertical excitation energies for the ground $X^1\Sigma^+$ and excited $A^1\Sigma^+$ states of LiH and NaH are given in Tables 1 and 2. Good agreement is found with experiment[39,40] and theoretical data.[14,41−44] The computed vertical excitation energies for the first low-lying transitions are within 5−7% of the experimental values. One could anticipate the large energy gaps in the case of the ground state to work as a stabilizing factor leading to a rapid convergence of the polarizability components, whereas for the $A^1\Sigma^+$ excited state, the energy gaps are significantly smaller and errors in excitation energies might strongly affect the accuracy of the polarizability components. The calculated equilibrium distance of 1.604 Å, found for the $X^1\Sigma^+$ ground state is in perfect agreement (1%) with the value of 1.594 914 Å, measured by Yamada et Hirota.[45] This provides a reliable criterion of the quality of the wave functions used.

The polarizability components of the $a^3\Sigma^+$ state of LiH, as a function of internuclear separation, computed at both TDGI and CCSD(T) methods, are collected in Table 3. The agreement between the two methods is excellent, and all of the TDGI polarizability components (α_{zz},α_{xx}) compare very well within a deviation less than 3.5%, with the CCSD(T) values.

Contrary to the polarizabilty of the ground state which involves only positive contributions of the close-lying excited states of appropriate symmetry, in the case of excited states, there may also be negative contributions to a polarizability component, which may even lead to an overall negative value of the component. By using the excited states linear response (LR) method, Jonsson et al.[38] have found for the 2^1A_1 excited state of formaldehyde a mean polarizability value of $\alpha = -117$ au, due to the large polarizability $\alpha_{xx} = -621$ au component, with $\alpha_{zz} = 58.7$ au and $\alpha_{yy} = 212$ au.

In this study, LiH and NaH having both at equilibrium geometry, for the $\alpha_{zz}(A^1\Sigma^+)$ component a large negative polarizability contribution (see Table 4) of the $X^1\Sigma^+$ state to $\alpha_{xx}(A^1\Sigma^+)$, however, exhibit two different situations. In the case of LiH, this negative contribution value of −90.2 au, is entirely compensated by the positive contributions of the above close-lying excited states, giving rise to a positive converged value of $\alpha_{zz} = 57.69$ au. In contrast, for NaH, because this large negative contribution value (−302.2 au) is not compensated by the positive contributions of the states above the $A^1\Sigma^+$ state, the total converged value is found to be negative: $\alpha_{zz} = -16.0$ au. Thus, the final sign of the total polarizability component of an excited state depends on the balance between positive and negative contributions of the states above and below the state of interest.

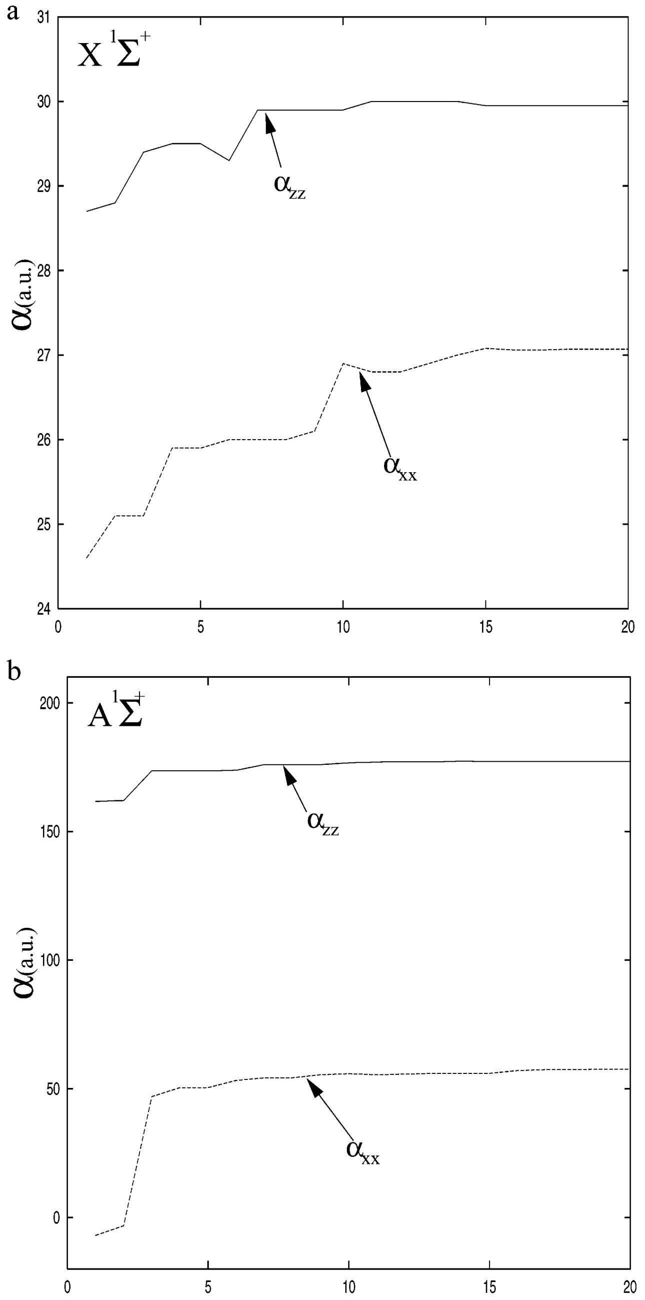

Figure 1. Convergence of dipole polarizability components of LiH with respect to the number of spectroscopic states, calculated at the TDGI level.

As noted earlier, the convergence of the polarizabilty versus the number of spectroscopic states has been studied (see Figure 1 for LiH). A glance at this figure shows that, for each component, convergence is practically reached with fifteen spectroscopic states. Moreover, it is also clear that the main contributors to the total polarizability components are the first five low-lying spectroscopic states. We have collected in Table 4 the contributions of the close-lying spectroscopic states to the polarizability components of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of LiH and NaH. In Table 5 are listed our final dipole moment and polarizability values, together with a selection of literature data. Excellent agreement with the best available data[14,44,46,47−55] is found for the ground $X^1\Sigma^+$ state. The agreement between the dipole polarizability of LiH and NaH, calculated by using the TDGI method with a pseudo-potential approach including core-valence correlation and the coupled cluster all-electron calculations with single, double, and a perturbative treatment of the connected triple excitations (CCSD(T)), is excellent for the two systems.

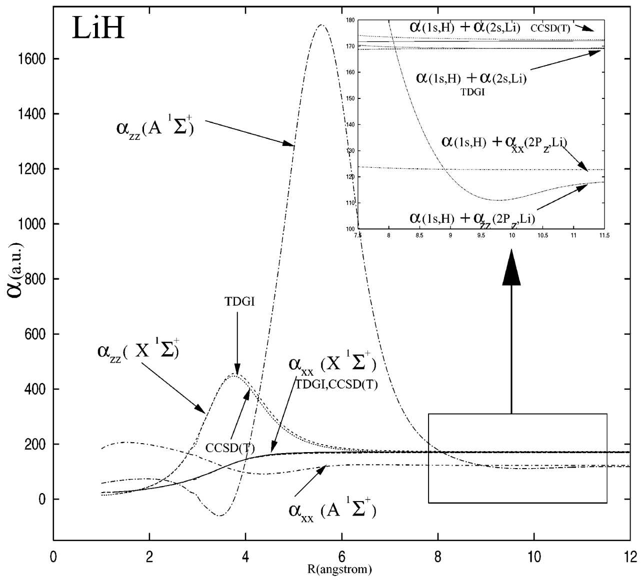

Figure 2. Dipole polarizability components of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of LiH as a function of interatomic distance, calculated with the TDGI and CCSD(T) methods.

To the best of our knowledge, the excited $A^1\Sigma^+$ state dipole polarizabilities of LiH have been previously calculated only by Jonsson et al.[56] By using the cubic response calculations, when considering the $A^1\Sigma^+$ state as a reference state, they have found for the parallel component the value of 138.4 au, at the ruby laser frequency ($\omega = 0.0656$ au). This value has to be compared with the TDGI value of 149.0 au, when the large negative contribution of the $X^1\Sigma^+$ state has not been taken into account. As expected, the α_{zz} and α_{xx} polarizability components of the $A^1\Sigma^+$ state are quite different compared to that of the ground state. At optimized equilibrium geometries of 2.559 and 3.213 Å, for LiH and NaH, respectively, the TDGI converged values for the parallel (α_{zz}) and perpendicular (α_{xx}) components are $\alpha_{zz} = 57.69$ and $\alpha_{xx} = 177.27$ au, for LiH, and $\alpha_{zz} = -16.0$ and $\alpha_{xx} = 190.6$ au, for NaH.

We have computed the polarizability components (α_{zz},α_{xx}), the polarizability anisotropy ($\Delta\alpha$), and the mean polarizability ($\bar{\alpha}$) as a function of internuclear separation. Their variations with respect to the internuclear distances for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states, for LiH and NaH, are presented in Figures 2−4. For the ground state, at small interatomic separation, the α_{zz} curves have a maximum corresponding to $R \simeq 2 \times R_{eq}$. This maximum, due to dipole−induced dipole effects, corresponds to an optimal combination of a large bond length with still sufficient overlap to produce efficient charge transfer. Such behavior has also been found for the ground state of Li_2, Na_2, and K_2 dimers from the calculations of Müller and Meyer,[57] for H_2 from the calculations of Kolos and Wolniewicz[58] and for the ground state of LiH and H_2 from the calculation of Hyams et al.[59] The α_{zz} component of the excited $A^1\Sigma^+$ state also presents a maximum at $R \simeq 2 \times R_{eq}$ but exhibits a minimum value which correlates practically with the maximum of the α_{zz} of the ground $X^1\Sigma^+$ state, at the same internuclear distance. Obviously, this is not surprising because, for this component, the negative contribution of the polarizability of the $X^1\Sigma^+$ state to the polarizability of $A^1\Sigma^+$ has its largest value at this maximum.

At large interatomic distances, the polarizability components α_{zz} and α_{xx} of the $X^1\Sigma^+$ state of LiH and NaH tend to the sum

TABLE 5: Atomic (H, Li) Dipole Polarizabilities and Molecular ((LiH, NaH) $X^1\Sigma^+$,$A^1\Sigma^+$) Static Dipole Polarizabilities (a.u.), at Their Corresponding Equilibrium Geometry (equil) and Dissociation (diss) [Comparison with a Selection of Literature Values].

system	states	α_{zz}	α_{xx}	$\bar{\alpha}$		
H	1^2S	4.487, 4.487^{a}	4.487, 4.487^{a}	4.487, 4.487^{a}		
Li	2^2S	165, 168^{a}	165, 168^{a}	165, 168^{a}	164,^{b} 164.5^{c}	164.0 ± 3.4^{d}
	2^2P	109	118	115		
Na	3^2S	163, 166^{a}	163, 166^{a}	163, 166^{a}	165.06^{e}	162.7 ± 0.8^{f}
	3^2P	532	270	357		

system	states	μ	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$
LiH	$X^1\Sigma^+$-equil	−2.284	27.04	29.96	28.99	−2.92
		−2.307,^{g} −2.309^{a}	26.61,^{g} 26.68^{a}	29.62,^{g} 29.66^{a}	28.61,^{g} 28.67^{a}	−3.01,^{g} −2.98^{a}
		−2.3133,^{h} −2.310^{i}	26.08,^{h} 26.92^{i}	29.75,^{h} 29.84^{i}	28.53,^{h} 28.87^{i}	−3.67,^{h} −2.93^{i}
		−2.294,^{j} −2.294^{k}	26.15,^{j} 25.79^{k}	29.70,^{e} 29.57^{k}	28.52,^{e} 28.31^{k}	−3.55,^{e} −3.78^{k}
		−2.311^{m}	26.3,^{l} 26.36^{m}	29.3,^{l} 29.76^{m}	28.3,^{l} 28.63^{m}	−3.0,^{l} −3.4^{m}
	$X^1\Sigma^+$-diss.	0.0006	169.10	169.20	169.20	−0.10
	$A^1\Sigma^+$-equil	1.185	57.69	177.27	137.41	−119.58
	$A^1\Sigma^+$-diss.	−0.0011	112.73	122.98	119.56	−10.25
NaH	$X^1\Sigma^+$-equil	−2.629	58.01	41.37	46.92	16.64
		−2.519,^{g} −2.624^{a}	54.6,^{g} 58.3^{a}	40.1,^{g} 39.6^{a}	44.9,^{g} 45.8^{a}	14.5,^{g} 18.7^{a}
		−2.514,^{i} −2.52^{n}	58.24,^{i} 56.53^{n}	39.51,^{i} 39.97^{n}	45.75,^{i} 45.49^{n}	18.73,^{i} 16.56^{n}
		−2.518 ± 0.275^{o}				
	$X^1\Sigma^+$-diss.	0.0015	187.70	184.00	185.20	3.70
	$A^1\Sigma^+$-equil	−0.342	−16.01	190.60	121.73	−206.60
	$A^1\Sigma^+$-diss.	0.0002	536.50	293.70	374.70	242.80

[a] This work: CCSD(T) all electron calculation. [b] Reference 60: CCSD(T) calculation. [c] Reference 61: CCSD(T) calculation. [d] Reference 62: CCSD(T) calculation. [e] Reference 63: Experimental value. [f] Reference 64: Experimental value. [g] This work: CCSD(T), computations performed by correlating two electrons. [h] Reference 14: TDGI all electron calculation. [i] Reference 49: CCSD(T). [j] Reference 50: Full-CI calculations. [k] Reference 51: CCSD(T) calculations. [l] Reference 52: CASSCF calculations. [m] Reference 53: MCSCF calculations. [n] Reference 46: QCISD(T) calculations. [o] Reference 47: Experimental value.

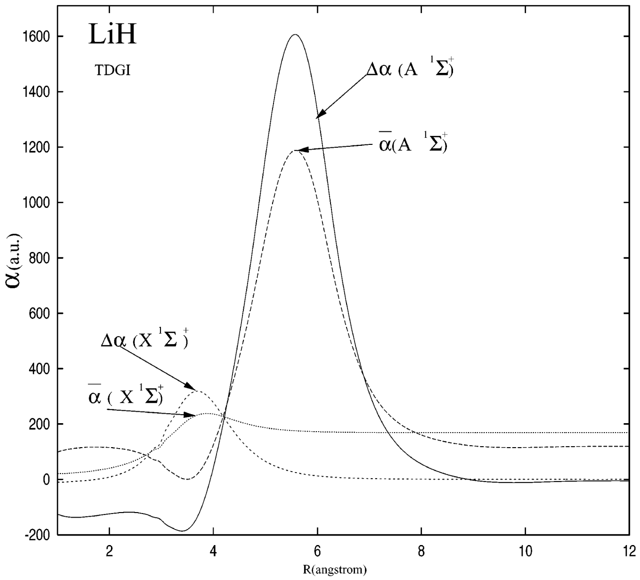

Figure 3. Isotropic ($\bar{\alpha}$) and anisotropic ($\Delta\alpha$) dipole polarizabilities of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of LiH as a function of interatomic distance, calculated with the TDGI method.

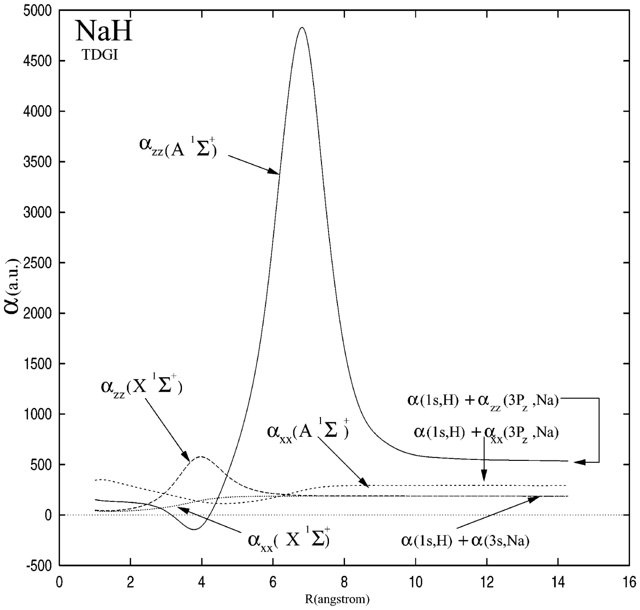

Figure 4. Dipole polarizability components of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of NaH as a function of interatomic distance, calculated with the TDGI method.

of the isotropic dipole polarizabilities of the corresponding atoms in their ground (^2S) state, namely, $\alpha(1^2S,\mathrm{H}) + \alpha(2^2S,\mathrm{Li}) = 169.1$ au and $\alpha(1^2S,\mathrm{H}) + \alpha(3^2S,\mathrm{Na}) = 187.7$ au (not totally dissociated). The anisotropy $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ falls to zero (see Figure 3), the isolated alkali-metal atom and hydrogen being isotropically polarizable (S states) in their ground state. In the case of the $A^1\Sigma^+$ state which involves the alkali-metal atom in its excited (^2P) state, with anisotropic polarizability, the α_{zz} and α_{xx} components tend at large interatomic distances to two different values converging to $\alpha(1^2S,\mathrm{H}) + \alpha_{zz}(2^2P_z,\mathrm{Li}) = 115.33$ au, $\alpha(1^2S,\mathrm{H}) + \alpha_{zz}(3^2P_z,\mathrm{Na}) = 536.5$ au and $\alpha(1^2S,\mathrm{H}) + \alpha_{xx}(2^2P_z,\mathrm{Li}) = 122.8$ au, $\alpha(1^2S,\mathrm{H}) + \alpha_{xx}(3^2P_z,\mathrm{Na}) = 293.7$ au (not totally dissociated). The ground and excited states polarizabilities for the corresponding atoms calculated with the basis sets extracted from molecular basis set are collected in Table 5.

IV. Conclusion

One of the main purposes of the present work was to calculate the polarizability for the $A^1\Sigma^+$ excited states of LiH and NaH.

We have first shown that the TDGI method with a pseudopotential approach including core-valence correlation yields polarizability values of the $X^1\Sigma^+$ state in very good agreement with the best values obtained from high-correlated methods.

Second, we have investigated the excited-state properties with a carreful check of convergence in order to provide reliable values for the $A^1\Sigma^+$ excited state of LiH and NaH. As expected, for a given excited state, the vicinity of other electronic states of appropriate symmetry is one of the main factors leading to a considerable increase of the polarizabilities, and even to negative values. The polarizabilities increase by a factor of 2−6 upon excitation. The largest change is found for the perpendicular component of NaH

Third, the polarizability changes with internuclear distance have been calculated. We found that this change is more pronounced for the long in-plane component of the ground and excited-state polarizabilities, which display a strong dependence on internuclear distance.

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References and Notes

(1) Wang, H.; Stwalley, W. C. *J. Chem. Phys.* **1998**, *108*, 5767.
(2) Jing-Yuan, Z. *Inst. Phys. Conf. Ser.* **1986**, *84*, Sect. 5.
(3) Marinescu, M.; Sadeghpour, H. R.; Dalgarno, A. *Phys. Rev. A* **1994**, *49*, 982.
(4) Rolston, S.; Phillips, W. D. *Proc. IEEE79* **1991**, 943.
(5) Lett, P. D.; Jessen, P. S.; Phillips, W. D.; Rolston, S. L.; Westbrook, C. I.; Gould, P. L. *Phys. Rev. Lett.* **1991**, *67*, 2139.
(6) Morales, R. G. E. *J. Phys. Chem.* **1982**, *86*, 2550.
(7) Ghoneim, N.; Suppan, P. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 2079.
(8) Chongwain, P. T.; Iweibo, I. *Spectrochim. Acta A* **1991**, *47*, 713.
(9) Iwebo, I.; Chongwain, P. T.; Obi-Egbedi, N. O.; Lesi, A. F. *Spectrochim. Acta A* **1991**, *47*, 705.
(10) Sinha, H. K.; Thomson, P. C. P.; Yates, K. *Can. J. Chem.* **1990**, *68*, 1507.
(11) Heitz, S.; Weidauer, D.; Hese, A. *Chem. Phys. Lett.* **1991**, *176*, 55.
(12) Heitz, S.; Weidauer, D.; Hese, A. *J. Chem. Phys.* **1991**, *95*, 7952.
(13) Heitz, S.; Weidauer, D.; Rosenow, B.; Hese, A. *J. Chem. Phys.* **1992**, *96*, 976.
(14) Rérat, M.; Mérawa, M.; Pouchan, C. *Phys. Rev. A* **1992**, *45*, 6263.
(15) Rérat, M.; Mérawa, M.; Pouchan, C. *Phys. Rev. A* **1992**, *46*, 5471.
(16) Mérawa, M.; Bégué, D.; Rérat, M.; Pouchan, C. *Chem. Phys. Lett.* **2001,** *334*, 403.
(17) Mérawa, M.; Tendero, C.; Rérat, M. *Chem. Phys. Lett.* **2001**, *343*, 397.
(18) Mérawa, M.; Rérat, M. *Eur. Phys. J. D* **2001**, *17*, 329.
(19) Rérat, M.; Bussery-Honvault, B. *Mol. Phys.* **2003**, *101*, 373.
(20) Mérawa, M.; Bégué, D.; Dargelos, A. *Chem. Phys. Lett.* **2003**, *372*, 529.
(21) Mérawa, M.; Rérat, M.; Bussery-Honvault, B. *J. Mol. Struct.* (*THEOCHEM*) **2003**, *633*, 137.
(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.
(23) Rérat, M.; Mérawa, M.; Honvault-Bussery, B. *J. Chem. Phys.* **1998**, *109*, 7246.
(24) Hameed, S.; Herzenberg, A.; James, M. G. *J. Phys. B* **1968**, *1*, 822.
(25) Hameed, S. *J. Phys. B* **1972**, *5*, 746.
(26) Rérat, M. *Int. J. Quantum Chem.* **1989**, *36*, 169.
(27) Huron, B.; Rancurel, P.; Malrieu, J. P. *J. Chem. Phys.* **1973**, *58*, 5745. Evangelisti, S.; Daudey, J. P.; Malrieu, J. P. *Chem. Phys.* **1983**, *75*, 91.
(28) Poteau, R.; Spiegelmann, F. *J. Mol. Spectrosc.* **1995**, *171*, 299.
(29) Durand, Ph.; Barthelat, J. C. *Theo. Chim. Acta* **1975**, *38*, 283.
(30) Müller, W.; Flesch, J.; Meyer, W. *J. Chem. Phys.* **1984**, *80*, 3297.
(31) Foucrault, M.; Millié, Ph.; Daudey, J. P. *J. Chem. Phys.* **1992**, *96*, 1257.
(32) Wiese, W. L.; Smith, M. W.; Miles, B. M. *Atomic Transition Probabilities* (NSRDS−NBS); U.S. Government Printing Office: Washington, DC, 1969; Vol. 2.
(33) Jeung, G. H. *J. Phys. B, At. Mol. Phys.* **1983**, *16*, 699.
(34) Jeung, G. H. *J. Phys. A* **1987**, *35*, 26.
(35) Magnier, S.; Millié, Ph.; Dulieu, O.; Masnou-Seeuws, F. *J. Chem. Phys.* **1993**, *98*, 7113.
(36) Sadlej, A. J.; Urban, M. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 147.
(37) Sadlej, A. J. *Collec. Czech. Chem. Commun.* **1988**, *53*, 1995.
(38) Johnsson, D.; Norman, P.; Ågren, H. *Chem. Phys.* **1997**, *224*, 201.
(39) Stwalley, W. C.; Zemke, W. T. *J. Phys. Chem. Ref. Data* **1993**, *22*, 87.
(40) Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structures IV, constants of diatomic molecules; Van Nostrand: New York, 1979.
(41) Ben-Shlomo, S.; Kaldor, U. *J. Chem. Phys.* **1988**, *89*, 956.
(42) Docken, K. K.; Hinze, J. *J. Chem. Phys.* **1972**, *57*, 4936.
(43) Sasagane, K.; Mori, K.; Ichihara, A.; Itoh, R. *J. Chem. Phys.* **1990**, *92*, 3619.
(44) Frank, A.; Lemus, R.; Lachello, F. *J. Chem. Phys.* **1989**, *91*, 29.
(45) Yamada, C.; Hirota, E. *J. Chem. Phys.* **1988**, *88*, 6702.
(46) Costa, M. F.; Fonseca, T. L.; Amaral, O. A. V.; Castro, M. A. *Phys. Lett. A* **1999**, *263*, 186.
(47) Dagdigian, P. J. *J. Chem. Phys.* **1979**, *71*, 2328.
(48) Lee, B. K.; Stout, J. M.; Dykstra, C. E. *J. Mol. Struct.* **1997**, *400*, 57.
(49) Avramopoulos, A.; Papadopoulos, M. G. *Mol. Phys.* **2002**, *100*, 821.
(50) Bendazzoli, G. L.; Magnasco, V.; Figari, G.; Rui, M. *Chem. Phys. Lett.* **2000**, *330*, 146.
(51) Tunega, D.; Noga, J. *Theor. Chem. Acc.* **1998**, *100*, 72.
(52) Karlström, G.; Roos, B. O.; Sadlej, A. J. *Chem. Phys. Lett.* **1982**, *86*, 374.
(53) Bishop, D. M.; Lam, B. *J. Chem. Phys.* **1985**, *83*, 6307.
(54) Kobus, J.; Moncrieff, D.; Wilson, S. *J. Phys. B: At. Mol. Opt. Phys.* **2001**, *34*, 5127.
(55) Diercksen, G. H. F.; Sadlej, A. J. *Chem. Phys.* **1991**, *158*, 9.
(56) Jonsson, D.; Norman, P.; Ågren, H. *J. Chem. Phys.* **1996**, *105*, 6401.
(57) Müller, W.; Meyer, W. *J. Chem. Phys.* **1986**, *85*, 953.
(58) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1967**, *46*, 1426.
(59) Hyams, P. A.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1994**, *100*, 4417.
(60) Kassimi, N. E.; Thakkar, A. J. *Phys. Rev. A* **1994**, *50*, 2948.
(61) Maroulis, G.; Thakkar, A. J. *J. Phys. B At. Mol. Phys.* **1989**, *22*, 2439.
(62) Maroulis, G. *Chem. Phys. Lett.* **2001**, *334*, 207.
(63) Molof, R. W.; Schwartz, H. L.; Miller, T. M.; Bederson, B. *Phys. Rev. A* **1974**, *10*, 1131.
(64) Ekstrom, C. R.; Schmiedmayer, J.; Chapman, M. S.; Hammond, T. D.; Pritchard, D. E. *Phys. Rev. A* **1995**, *51*, 3883.