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Calculation of dynamic polarizabilities with a multideterminental ket including a dipole-moment factor: Extrapolation method and application to Li_2, LiH, and CO

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An alternative method is proposed for the calculation of dynamic polarizability: one that combines the usual development over the excited states with additional terms obtained by multiplying the zeroth-order wave function with a dipole-moment factor (i.e., a polynomial of first degree in the electronic coordinates). The zeroth-order wave function includes correlation effects accounted for by a configuration-interaction perturbation subspace iterative method. The dipole-moment factor makes extrapolation possible if the number of states is limited. Applications are presented for Li_2, LiH, and CO. The obtained values are in excellent agreement with the experimental ones. The analysis of the calculations shows that the extrapolation is not necessary for Li_2 and LiH, the first excited states of which are of valence character, contributing strongly to the polarizability. In the case of the parallel component of the polarizability of CO, extrapolation is necessary because the first excited state of valence character appears in the seventh ${}^1\Sigma^+$ state. In addition, we have calculated transition energies and moments for the few low-lying excited states of ${}^1\Sigma^+$ and ${}^1\Pi$ symmetry for each molecule.

I. INTRODUCTION

Since the advent of laser technology, there has been much interest in both the measurement and calculation of optical polarizabilities, which, in the limit of zero frequency, are the well-known static electric polarizabilities. Accurate experimental data are, however, rather scarce, and often theoretical polarizabilities are considered to provide the sole available or the more reliable information about the system. Most of these calculations are limited within the static dipole polarizability approach. This paper is concerned with the accurate calculation of the isotropic and anisotropic components of the dynamic dipole polarizability $\alpha(\omega)$ of Li_2, LiH, and CO for a wide range of frequencies ω. These components are of considerable interest because from them one can derive the transition frequencies, refractive index, and Verdet constants of a system, as well as information about its Rayleigh and Raman scattering.

The calculation of static polarizabilities is now well documented. Among the most commonly adopted methods one may quote the uncoupled and coupled perturbed Hartree-Fock approximation (UCHF and CPHF);[1-3] the CPHF is now almost routinely used (for instance see Ref. 4). The finite-field method[5] has also been widely employed at the self-consistent-field (SCF) level[6] and within the configuration-interaction method.[7-9] In the CPHF the molecular orbitals in the presence of the external field are obtained by perturbation ($\varphi_i=\varphi_i^{(0)}+\varphi_i^{(1)}$), while in the finite-field approach they are the variational solution of the Hartree-Fock equations, including the external field Hamiltonian. In the latter case, the polarizability is derived from the second derivative of the energy in the presence of the external field. In the limit of small fields and good numerical differential techniques, both methods become equivalent.[10] To circumvent the difficulties of large basis sets, the use of electric-field-dependent atomic orbitals has been suggested, after an idea originating in the early 1930s.[11,12] Two approaches have been proposed: either the origin of the atomic orbitals of Gaussian form is shifted by an amount proportional to the field,[13] or the orbitals are multiplied by an exponential factor as in the gauge-invariant atomic orbitals (GIAO) theory for magnetic properties.[14]

The practical calculation of dynamical polarizabilities is not yet a routine work, owing to the increased number of difficulties to be overcome. Indeed, besides the original problems raised by the calculation of static polarizabilities already mentioned, one must deal with the good description of the excited states. The frequency dependence of molecular polarizability has been examined in essentially two ways: the self-consistent-field configuration interaction (SCF-CI) method[15,16] and the polarization propagator method [the random-phase approximation (RPA) or the more elaborate second-order polarization propagator approximation (SOPPA)].[17] Some recent developments have shown that one can avoid the summation over states by inverting the CI or RPA matrix.[18-20] These last methods were derived in the spirit of the variation-perturbation method,[21,22] later used by Karplus and Kolker for the time-dependent interaction.[23]

We propose here a mixed method, introducing a dipole-moment factor in the SCF-CI method, combining thus the advantages of Karplus and Hameka-Iwata's methods; this time-dependent ket method was initiated by one of us (M.R.) in a previous paper.[24] The method is presented in Sec. II. In Sec. III we give a description of the computational procedures, because accurate determination of polarizabilities requires both carefully designed basis sets and correlated wave functions. In Sec. IV we present and discuss the results of our calculations on three systems for which static polarizabilities have been calculated previously as $Li_2(^1\Sigma_g^+)$ (Refs. 25–28), $LiH(^1\Sigma^+)$,[25,29–34] and $CO(^1\Sigma^+)$.[17,35,36] A number of reasons have guided us in choosing these molecules for our exploratory studies: (i) they have recently been the object of experimental and/or theoretical treatments, and electric and spectroscopic data available are often known; (ii) the molecules have different properties offering a probative test for our method—different symmetry properties and important ranges of static polarizability and anisotropy; (iii) in the case of Li_2 and LiH, all our results concerning the dynamic polarizability are new.

In summary, our aims for this work on the calculations of the dynamic polarizabilities $\alpha(\omega)$ of Li_2, LiH, and CO are twofold: (i) using a relatively large atomic orbital basis and taking into account the correlation effects, to test the time-dependent ket method; (ii) to properly evaluate the influence and the usefulness of the polynomial factor and the electronic correlation effects on the wave functions leading to the best static $\alpha(0)$ and dynamic $\alpha(\omega)$ polarizabilities.

Throughout, atomic units will be used: $a_0=1$ bohr$\simeq 5.291\,77\times10^{-11}$ m; $E_H=1$ hartree $\simeq 4.359\,75\times10^{-18}$ J. The dipole moment is equal to $ea_0\simeq 8.478\,36\times10^{-30}$ C m, and the dipole polarizability is equal to $e^2a_0^2E_H^{-1}\simeq 1.648\,78\times10^{-41}$ $C^2m^2J^{-1}$.

II. THEORY

A. Method

We consider an atom or molecule characterized by the time-independent Hamiltonian H_0 (eigenstates $\{|n\rangle, E_n\}$), subject to the time-dependent perturbation $H_1(t)$:

$$\begin{aligned} H_1(t) &= -q\sum_{\pm}\sum_{j}\mathcal{E}^{\pm}(\mathbf{r})\cdot\mathbf{r}_j e^{\pm i\omega t} \\ &= \mathcal{E}_0 V(\mathbf{r})(e^{i\omega t}+e^{-i\omega t}) \;. \end{aligned} \tag{1}$$

Equation (1) holds for a monochromatic radiation (pulsation ω) in the electric dipole approximation $[\mathcal{E}^{+}(r)=\mathcal{E}^{-}(r)=\mathcal{E}_0(0)]$, and in the gauge where the electromagnetic field appears through its electric part of modulus $\mathcal{E}_0$ and not through its vector potential $\mathcal{A}$.

For the system initially in its unperturbed ground state, i.e.,

$$|\psi_0(t)\rangle = e^{-iE_0t/\hbar}|0\rangle \;, \tag{2}$$

one usually introduces a dynamical first-order polarizability tensor $\alpha(\omega)$ as follows:

$$\begin{aligned} \alpha(\omega) &= -\sum_n\left[\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0-E_n-\hbar\omega}+\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0-E_n+\hbar\omega}\right] \\ &= -\sum_n\left[\frac{\langle 0|\mu|n\rangle\langle n|\mu|0\rangle}{E_0-E_n-\hbar\omega}+\frac{\langle 0|\mu|n\rangle\langle n|\mu|0\rangle}{E_0-E_n+\hbar\omega}\right] . \end{aligned} \tag{3}$$

Expressions (3), where μ is the electric dipole operator,[37,38] converge to the static polarizability $\alpha(0)$ as ω tends to zero:

$$\alpha(0) = -2\sum_n\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0-E_n} \;. \tag{4}$$

Putting

$$\epsilon''(\omega) = \sum_n\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0-E_n-\hbar\omega} \;, \tag{5}$$

one has[16]

$$\alpha(\omega) = -\epsilon''(\omega)-\epsilon''(-\omega) \tag{6}$$

and

$$\epsilon''(\omega) = \langle 0|V|\Phi_1^+\rangle \;, \tag{7}$$

where

$$|\Phi_1^+\rangle = \sum_{n\,(\neq 0)}|n\rangle\frac{\langle n|V|0\rangle}{E_0-E_n-\hbar\omega} \;. \tag{8}$$

The ket $|\Phi_1^+\rangle$ (together with its counterpart $|\Phi_1^-\rangle$) was introduced by Karplus and Kolker[23] in their variation-perturbation treatment, where the perturbed ground state $|\psi_0^{\mathcal{E}}(t)\rangle$ is first expanded in powers of $\mathcal{E}_0$:

$$|\psi_0^{\mathcal{E}}(t)\rangle = \sum_m\mathcal{E}_0^m|\Phi_m(t)\rangle \;, \tag{9}$$

with

$$\left[H_0-i\hbar\frac{d}{dt}\right]|\Phi_m(t)\rangle = -V(e^{i\omega t}+e^{-i\omega t})|\Phi_{m-1}(t)\rangle \;. \tag{10}$$

In the steady state (after damping out of the initial transient phenomena), the simple harmonic dependence of the perturbation allows us to write down directly

$$|\Phi_1(t)\rangle = (|\Phi_1^+(\mathbf{r})\rangle e^{i\omega t}+|\Phi_1^-(\mathbf{r})\rangle e^{-i\omega t})e^{-iE_0t/\hbar} \;, \tag{11}$$

where $|\Phi_1^{\mp}\rangle$ satisfy Eq. (12),[16,38]

$$(H_0-E_0\pm\hbar\omega)|\Phi_1^{\mp}\rangle = (\langle 0|V|0\rangle - V)|0\rangle \;, \tag{12}$$

and also Eq. (13),[23]

$$(H_0-E_0\pm\hbar\omega)|\Phi_1^{\mp}\rangle = -V|0\rangle \;, \tag{13}$$

provided

$$\langle 0|V|0\rangle = 0, \text{ i.e., } \langle 0|\mu|0\rangle = 0 \;. \tag{14}$$

For reasons that will appear later, we assume that condition (13) is fulfilled, i.e., the r origin is taken at the center of electronic charge. It ensures continuity between the dynamic and static polarizabilities $\alpha(\omega)$ and $\alpha(0)$ when ω tends to zero.

Determination of the first-order kets $|\Phi_1^+\rangle$ and $|\Phi_1^-\rangle$ plays a central role in the actual calculation of polarizabilities $\alpha(\omega)$. For a few systems, this can be done by direct resolution of Eq. (13).[23] In the general case, however, a variational procedure is recommended, involving the functionals

$$L^{\pm}=\langle \Phi_1^{\pm}|H_0-E_0\pm\hbar\omega|\Phi_1^{+}\rangle+2\langle 0|V|\Phi_1^{\pm}\rangle \ . \tag{15}$$

Obtaining accurate values generally involves use of extended atomic-orbital (AO) basis sets. Some authors, however, find relatively good results with a small basis set, for static polarizabilities, when using electric-field-variant atomic orbitals (EFVAO),[13,14,39] eventually followed by the introduction of some correlation.[40] As in the GIAO method used for magnetic properties,[41] unfortunately, this implies evaluation of additional two-electron integrals. Kirkwood[42] and later Karplus[23] write $|\Phi_1^{\pm}\rangle$ as a product of $|0\rangle$ by a linear combination of the electronic coordinates; but, as already observed in a similar formulation for magnetic effects,[22,43] the method fails when orbitals with higher quantum number are present because it does not account for the existence of nodal surfaces in the zeroth-order wave function.[44]

In the same spirit as in Ref. 44, we adopt here for the construction of $|\Phi_1^{\pm}\rangle$ (in the case where the electric field lies in the x direction) a "mixed" procedure:

$$|\Phi_1^{\pm}\rangle=g^{x\pm}(\mathbf{r})|0\rangle+\sum_{\pm,n\,(\neq 0)} c_n^{x\pm}|n\rangle \ , \tag{16}$$

where

$$g^{x\pm}(\mathbf{r})=\sum_u a_u^{x\pm}u \quad (u=x,y,z) \ . \tag{17}$$

Introduction of (16) into (12) and (13) is equivalent to projecting these equations onto a basis $\{x|0\rangle,y|0\rangle,z|0\rangle,|1\rangle,\dots,|n\rangle\}$ and gives for an $\mathcal{E}_x$ perturbation the following set of linear nonhomogeneous equations:

$$M_0^{\pm}\begin{bmatrix} a_x^{x\pm}\\ a_y^{x\pm}\\ a_z^{x\pm}\\ \vdots\\ c_p^{x\pm}\\ \vdots \end{bmatrix}=\begin{bmatrix} q\langle x^2\rangle\\ q\langle xy\rangle\\ q\langle xz\rangle\\ \vdots\\ q\langle p|x|0\rangle\\ \vdots \end{bmatrix} , \tag{18}$$

where (n_e is the number of electrons)

$$M_0^{\pm}=\begin{bmatrix} \frac{\hbar^2}{2m}n_e\pm\hbar\omega\langle x^2\rangle & \pm\hbar\omega\langle xy\rangle & \pm\hbar\omega\langle xz\rangle & \cdots & \frac{\hbar^2}{m}\langle 0|\nabla_x|n\rangle\pm\hbar\omega x_n\\ \pm\hbar\omega\langle yx\rangle & \frac{\hbar^2}{2m}n_e\pm\hbar\omega\langle y^2\rangle & \pm\hbar\omega\langle yz\rangle & \cdots & \frac{\hbar^2}{m}\langle 0|\nabla_y|n\rangle\pm\hbar\omega y_n\\ \pm\hbar\omega\langle zx\rangle & \pm\hbar\omega\langle zy\rangle & \frac{\hbar^2}{2m}n_e\pm\hbar\omega\langle z^2\rangle & \cdots & \frac{\hbar^2}{m}\langle 0|\nabla_z|n\rangle\pm\hbar\omega z_n\\ \cdots & \cdots & \cdots & & \cdots\\ \frac{\hbar^2}{m}\langle 0|\nabla_x|p\rangle\pm\hbar\omega x_p & \frac{\hbar^2}{m}\langle 0|\nabla_y|p\rangle\pm\hbar\omega y_p & \frac{\hbar^2}{m}\langle 0|\nabla_z|p\rangle\pm\hbar\omega z_p & \cdots & \langle p|H_0-E_0\pm\hbar\omega|n\rangle\\ \cdots & \cdots & \cdots & & \cdots \end{bmatrix} , \tag{19}$$

and, symbolically,

$$\langle uv\rangle=\left\langle 0\left|\left[\sum_{i=1}^{n_e}u_i\right]\left[\sum_{j=1}^{n_e}v_j\right]\right|0\right\rangle \quad (u \text{ or } v=x,y,z) \ , \tag{20}$$

$$x_p=\left\langle 0\left|\left[\sum_{i=1}^{n_e}x_i\right]\right|p\right\rangle \ . \tag{21}$$

After solving this system, and using the notation introduced in Eq. (18), we get for component α_{xv} of the polarizability tensor (3) (in a.u.):

$$\alpha_{xv}=\sum_{\pm,w} a_w^{x\pm}\langle vw\rangle+\sum_{\pm,n} c_n^{x\pm}\langle 0|v|n\rangle \tag{22}$$

with $w=x,y,z$.

1. Remark

Exactly as for the magnetic case,[44] formulation (16) combines a purely polynomial method ($g^{\pm}\neq 0$, $C_n^{\pm}=0$) with the SCF-CI procedure ($g^{\pm}=0$, $c_n^{\pm}\neq 0$) related to the second-order polarization propagator.[17,45,46] Electronic correlation is easily introduced (see applications below) by simple extension of the set of $|n\rangle$-kets; however, contrary to the magnetic case [where the intrinsic purely imaginary character of the perturbation H_1 and of the first-order ket$|\Phi_1\rangle$ automatically ensures fulfillment of the normalization condition ($\langle 0|\Phi_1\rangle+\langle\Phi_1|0\rangle=0$), the purely real character of H_1 and $|\Phi_1^{\pm}\rangle$ in the electric case imposes to move the origin to the center of electronic charge ($\langle 0|u|0\rangle=0$, $u=x,y,z$) at each step of a configuration-interaction calculation. This is not a difficult task for computation, since this concerns the whole electronic wave function: it doesn't involve previous calculation of additional two-electron integrals.

B. Role of the dipole-moment factor $g(r)$

1. Gauge invariance

It has been shown[24,47] that, when changing the gauge from $\mathcal{E}\cdot\mathbf{r}$ (used here) to $\mathcal{A}\cdot\mathbf{p}$, only the coefficients of function $g(\mathbf{r})$ change; the contribution of the kets $|n\rangle$ remains unchanged. The variation Δg corresponds exactly to the function $\chi(\mathbf{r})$ appearing in the unitary operator $\exp[i(q/h)\chi(\mathbf{r})]$ of the gauge transformation.[37] The polynomial $g(\mathbf{r})$ thus ensures gauge invariance.

2. Limited summation and extrapolation procedure

In Appendix A it is shown that, in the limit of a complete basis set of exact kets $|n\rangle$, the coefficients a_u of $g(\mathbf{r})$ are undetermined. If a limited number of states N is used, then $a_u(N)\simeq(E_N-E_0\pm\hbar\omega)^{-1}$ and tends to $a_u(\infty)=0$ as N becomes infinite.

In the same spirit, one can show that increasing N leads to an increase of the calculated value α together with a decrease of $a_u(N)$. Thus the variation rate $\Delta\alpha/\Delta a$ is negative (this also holds for the corresponding curvature) if we add states in increasing energy order, and tends to zero as N becomes infinite.

As a practical consequence, it is possible to extrapolate a final value for α from the results obtained with a finite number of discrete states. Since the continuum is not taken into account in our calculations, we have to restrict the summation to the discrete states lying below the first ionization potential.

Formula (B5) of the appendix shows that the polarizability may be written as

$$\alpha_N-\alpha_N^{(0)}=a_N^2 f(N) .$$

This suggests the use of an extrapolation formula of the form

$$\alpha_N-\alpha_N^{(0)}=ca_N^p , \tag{23}$$

where α_N and $\alpha_N^{(0)}$ are the polarizabilities calculated with N states, with and without the "polynomial" contribution.

The value of the exponent p is determined by a least-square fit, and then the extrapolated polarizability is obtained by a linear regression in which the computed values of α are written as

$$\alpha_N=\alpha_\infty+ba_N^p \tag{24}$$

In the case of the dynamic polarizabilities ($\hbar\omega\neq0$), this extrapolation is done separately for the cases $+\hbar\omega$ and $-\hbar\omega$.

We must stress the fact that the above extrapolation rests upon the hypothesis of exact or very accurate eigenstates $|n\rangle$. In practical calculations it is seldom the case, except for small systems like Li_2 or LiH. The case of carbon monoxide studied below has shown that the extrapolation procedure is still relevant for larger systems. The function $g(\mathbf{r})$ partly compensates the weakness of the AO basis set.

III. COMPUTATIONAL DETAILS

All the calculations reported in the present work have been carried out at the *ab initio* CI level.

The choice of the atomic basis set is crucial for the calculation of the spectroscopic and electric properties. Indeed, if the calculation of energy and static dipole polarizability $\alpha(0)$ may be considered as a test for the choice of Gaussian atomic basis sets and for the performance of various CI methods, it is an even more severe test when concerning the calculation of the dynamic polarizability $\alpha(\omega)$. In this case such calculation requires to describe as well as possible (i) not only the $X\,^1\Sigma^+$ ground state, in order to reproduce the static polarizability at zero frequency, but also (ii) the excited states ($^1\Sigma^+$ and $^1\Pi$), in order to give the different discontinuities corresponding to the resonance energies of these states correctly.

In this study, Li_2, LiH, and CO are ideal systems of increasing difficulty upon which to test our computational method.

We first carried out a series of checks on our computational techniques by calculating electronic transition moments and dipole polarizability of Li_2. This molecule was chosen since there is a large body of theoretical information concerning the determination of spectroscopic and electric properties available with different basis sets.[25–28,48–57] In the treatment of Li_2 two different Gaussian-type orbital (GTO) or contracted GTO (CGTO) basis sets of increasing size and flexibility have been used. Their detailed description as well as the reasons of their choice are given in previous papers,[26,48] where they are referred to as basis 1 for the $[10s5p/5s5p]$ GTO-CGTO basis 3 for the $[10s5p2d/5s5p2d]$ GTO-CGTO, built from basis 1 augmented by two d orbitals with exponents equal to 0.05 and 0.017.

As second example, we have selected lithium hydride (LiH) because it is a two-valence-electron, singly bonded molecule; features identified for LiH should be representative of what might be found in many chemical species. For the same reason, LiH has been the subject of numerous investigations in order to obtain spectroscopic and electric properties from different methods and at different levels of calculations,[29–34,58–64] and the evaluation of the polarizability tensor of LiH has been considered as a challenge for theoreticians. Comparison of our results with previous accurate calculations[29–34] should provide a reliable test for our method. The basis set used for LiH consists in the $[10s5p3d/5s5p3d]$ GTO-CGTO set for Li (basis 3 described before with an additional d orbital exponent equal to 0.2) and a $(10s6p)$ basis for H built from the $[8s6p]$ set of Huzinaga[65] and Lazzeretti *et al.*[66] augmented by two additional diffuse s orbitals ($\alpha_s=0.03$ and 0.01). This basis set has been found to give reasonable values for energies, dipole moment, and polarizabilities of the LiH molecule.

The study of CO molecule is certainly a severe test for the performance of our method. Recently Kello *et al.*[67] have presented an interesting analysis of the performance of high-level correlated methods (many-body perturbations theory and coupled cluster methods) through the geometry dependence of the energy, dipole moment, and the parallel component of the static dipole polarizability of this molecule. In our study, CO was chosen, too, in the determination of the dynamic polarizabilities on the basis of its specific difficulties. The main reason leading to treat CO in the calculations of electric properties consists in the possible difference between the two atoms as regards intramolecular charge transfers, especially for the electrons assigned to carbon and oxygen orbitals. Such a difference induces a displacement of electrons along the CO bond. However, the dipole moment, anomalously weak, 0.1222 D (corresponding to polarity C^-O^+) at the equilibrium geometry,[68] is consistent with the description of a triple bond and a lone pair of electrons on each atom. It is well known that all electron calculations including configuration interaction must be done in order to take into account these particularities.[69] The last difficulty in the CO molecule is the presence of avoided crossings between the covalent and a series of ionic potential-energy curves, and it is not easy to construct wave functions which give reliable descriptions of valence-Rydberg interactions in the bonding region, as pointed out by Cooper and Kirby.[70] In order to solve the particular difficulties of CO we have used a large basis set, which may account for internal correlation effects and the possible Rydberg character of excited states. The basis set used for CO consists in 64 CGTO's built from the contracted $(5s,3p)$ basis sets given by Dunning and Hay.[71] To give more flexibility, this basis set is decontracted in $(6s,4p)$ and augmented by one s and one p diffuse orbital and two d shells on each nucleus to correctly describe the Rydberg states and to ensure the polarization and angular correlation of the valence shell, respectively. The additional orbital exponents of the Rydberg orbitals are equal to 0.02 and 0.03 for s and p functions on carbon and oxygen, respectively. The exponents of the d functions are chosen in the same way as those used by Meyer and Rosmus[72] in their calculation of the dipole moment. For C and O, the basis set used is denoted as $(10s6p2d/7s5p2d)$ GTO-CGTO.

To investigate the effects of electron correlation on the spectroscopic states and dynamic polarizability, a series of configuration-interaction studies was undertaken using canonical molecular orbitals [linear combination of atomic orbitals and molecular orbitals (LCAO-MO)] for Li_2 and LiH and hybridized atomic orbitals (HAO) for CO. Indeed, to take account of the nondynamic correlation energy (i.e., the correlation within a shell of valence occupied and virtual molecular orbitals), it is convenient to start with a set of molecular orbitals different from the usual canonical one resulting from the SCF ground state. The HAO proposed by Malrieu *et al.*[73] for this purpose are obtained by diagonalizing the block matrices corresponding to the AO's centered on each atom in the ground-state Hartree-Fock density matrix. In the case of CO, the Hartree-Fock determinant is

$$(\text{core MO's})(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4 .$$

Since the three σ occupied MO's are orbital mixtures describing both the lone pairs and the σ C—O bond, it is worthwhile to isolate the lone pairs which contribute poorly to the nondynamical correlation. The HAO procedure transforms the σ canonical MO's into two lone pairs O(2s) and C(2s), and the O($2p_z$)—C($2p_z$) bond MO. The CO-HAO determinant becomes

$$(\text{core MO's})(3\sigma_0)^2(4\sigma_c)^2(5\sigma_{\text{CO}})^2(1\pi_{\text{CO}})^4 .$$

In this way, the HAO procedure provides a partition of the virtual MO's into valence antibonding MO's (σ^*,π^*), node-rich MO's localized on each atom, and Rydberg-type diffuse MO's.

Correlation effects have been taken into account through the configuration interaction with perturbatively selected interactions (CIPSI) procedure[74,75] that treats the external correlation by a multireference second-order perturbation treatment from a variational subspace S built up in an iterative way. Preliminary calculations of energies have been made by the standard CIPSI algorithm[74] on small S subspaces of ≈ 400 determinants. Perturbation treatments involving larger subspaces (6000 up to 8000 for the Li_2 and LiH (LCAO-MO procedure) and about 1000 for CO (HAO procedure) have been achieved using the diagrammatic version of CIPSI.[75]

IV. RESULTS AND DISCUSSION

As we can see in Eq. (22), the calculation of the polarizability requires a sum over all the states $|n\rangle$ of the system.

All low-lying states of the molecules connected to the ground state by dipole-allowed transitions are of particular importance in calculating the polarizability. The ground state being of $^1\Sigma^+$ symmetry ($^1\Sigma_g^+$ for Li_2), we have been concerned by the calculation of the $^1\Pi$ states ($^1\Pi_u$ for Li_2) for the determination of the perpendicular component of the dipole polarizability and the $^1\Sigma^+$ state ($^1\Sigma_u^+$ for Li_2) for the parallel one. The number of low-lying states essential for a correct evaluation of the polarizabilities increases drastically from Li_2 to LiH and CO.

A. Li_2

Calculations were carried out with the two basis sets described above. The three first low-lying states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry have been calculated and their energies were computed at the experimental equilibrium geometry of the ground state $^1\Sigma_g^+$ (5.051 a.u.).

Our results are displayed in Table I and are compared with previously published values obtained at the same (or close) geometry. Except for the third transition of each symmetry, the transition moment appears slightly sensitive to the basis set used, and all the calculated values of the vertical energies are in the range of 0.1 eV. Our calculated electronic transition moments are in remarkable agreement with those reported in the literature by different authors[49,51,57] for $1\,^1\Sigma_g^+ \rightarrow 1\,^1\Pi_u$ and $1\,^1\Sigma_g^+ \rightarrow 1\,^1\Sigma_u^+$ transitions. The energies calculated with

TABLE I. Energies of the low-lying excited singlet states ($^1\Sigma_u^+$, $^1\Pi_u$) of Li_2 and transition moments calculated at 5.051 a.u. with basis 1 and 3.

	Energies (hartree)			Transition moments (a.u.)		
Excited states	1	3	Previous[a] works	1	3	Previous works
$1\,^1\Sigma_u^+$	0.065 383	0.067 198	0.068 481	3.32	3.24	3.1615[b] 3.16[c]
$2\,^1\Sigma_u^+$	0.137 749	0.139 178	0.141 282	0.22	0.26	0.20[b]
$3\,^1\Sigma_u^+$	0.169 417	0.165 578	0.164 467	0.03	0.21	
$1\,^1\Pi_u$	0.100 032	0.095 433	0.095 302	2.73	2.80	2.7489[b] 2.75[d]
$2\,^1\Pi_u$	0.142 475	0.141 909		0.67	0.59	0.3596[b]
$3\,^1\Pi_u$	0.171 584	0.167 155		0.04	0.23	

[a] From Ref. 56 (at 5 a.u.).

[b] From Ref. 57.

[c] From Ref. 49.

[d] From Ref. 51.

basis 3 compare well with the values of Schmidt-Mink *et al.*,[56] who used slightly larger basis sets, and are also in excellent agreement with the experimental data.[76–78] The values of the two components of the polarizability calculated with basis 3 are listed in Table II for Li_2. The influence of the polynomial and the contribution of each state show the essential role of the first $1\,^1\Sigma_u^+$ and $1\,^1\Pi_u$ states, the weak participation of $2\,^1\Pi_u$ state for the perpendicular component, and the negligible contribution of the others states. The static components calculated with the polynomial (318 and 174 a.u.) and without the polynomial (314 and 170 a.u.) differ by about 1–2 % and are in very good agreement with our previous correlated values obtained via LCAO-MO-CI (306 and 169 a.u.) and approximate natural orbital (324 and 173 a.u.) in a similar basis set.[26] Comparisons with the recent calculations of Müller and Meyer[27] and Maroulis[28] show a very good agreement with the α_{xx} values of Maroulis obtained at single-double-triple-quadrupole fourth-order Møller-Plesset perturbation theory [SDTQ-MPPT(4)] level while the valence configuration-interaction plus core-polarization potentials [CI(v)+CPP] results of Müller yields a perpendicular component 3–5 % smaller than our results. Presumably, the reason for this discrepancy lies either in the absence of a small exponent on the d functions or on the use of a core polarization potential in the study of Ref. 27. When the axial component is concerned, our α_{zz} value is higher by about 5% than the respective correlated values obtained by Maroulis[28] or Muller and Meyer.[27] Our overestimated value is partly

TABLE II. Static polarizabilities components (a.u.) calculated for Li_2 at 5.051 a.u. and comparison with other calculations.

	Without polynomial[a]		With polynomial	
Basis set	α_{zz}	α_{xx}	α_{zz}	α_{xx}
1	338	161	344	163
3	314	170	318	174
	Other calculations			
Basis set	α_{zz}	α_{xx}		
1	324[b]	173[b]		
3	306[b]	169[b]		
$6s2p1d+(2s3p$ bond orbital)	316[c]	169.4[c]		
CI(v)+CPP:$12s7p2d1f$	298.7[d]	164.2[d]		
CI(v)+CPP:$12s7p2d$	301.8[d]	163.9[d]		
CI(v):$12s7p2d$	305.4[d]	166.8[d]		
MPPT(4):$5s5p1d$	300[e]	171[e]		
SDTQ:$6s6p1d1f$	292[e]	170[e]		

[a] The contribution of the three states are, respectively (337;1;0); (149;12;0) for basis 1 and (312;1;1); (164;5,1) for basis 3.

[b] From Ref. 26.

[c] From Ref. 25.

[d] From Ref. 27.

[e] From Ref. 28.

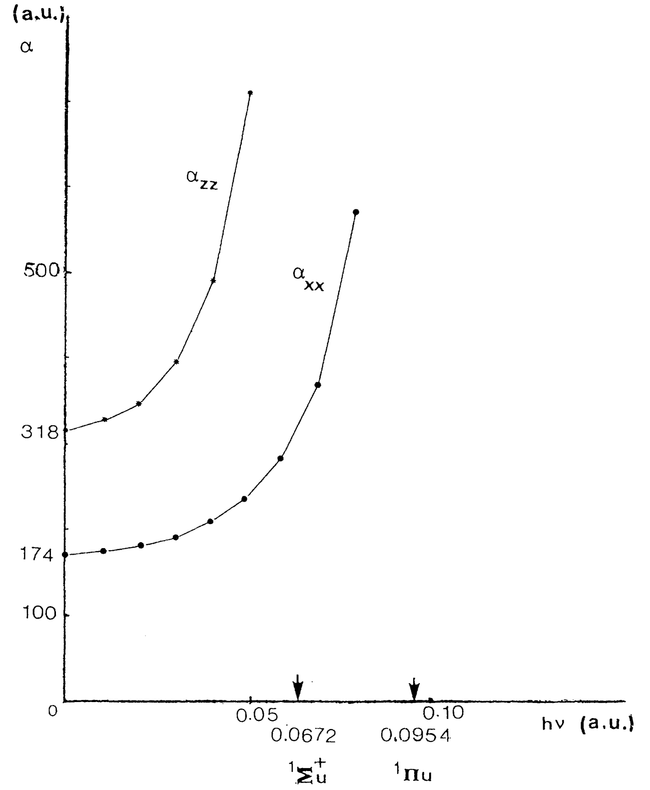

FIG. 1. Dynamic polarizability components of Li_2 calculated at 5.051 a.u. with basis 3.

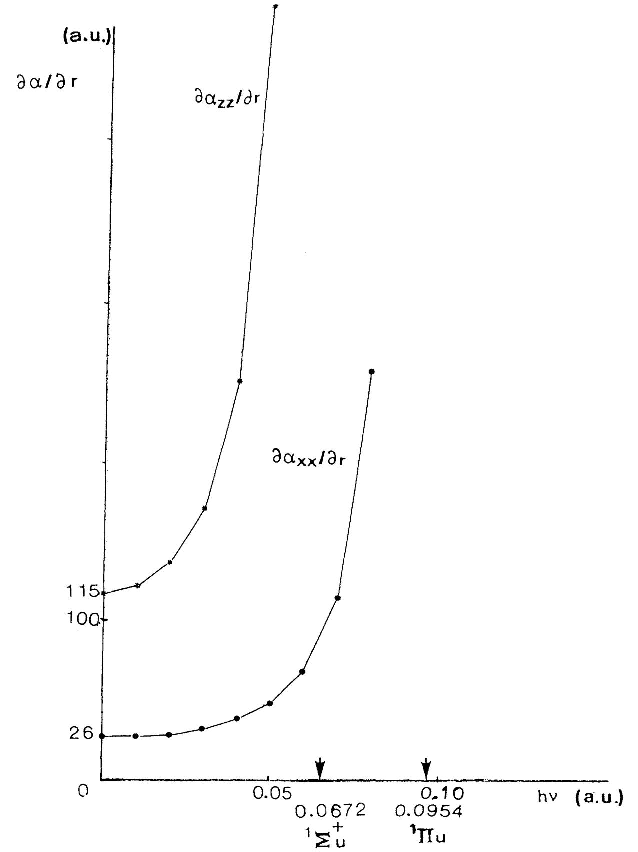

FIG. 2. Dynamic polarizability derivative components of Li_2 calculated at 5.051 a.u. with basis 3.

TABLE III. Energies and electronic transition moments of the low-lying $^1\Sigma^+$ and $^1\Pi$ states calculated for LiH at 3.015 a.u.

Transitions	Energies (hartree)		Transition moment (a.u.)	
	This work	Previous work	This work	Previous work
$X^1\Sigma^+ \rightarrow A\ ^1\Sigma^+$	0.131 402	0.1314[a] 0.1319[b] 0.1354[c]	0.939	0.9599[b] 0.9376[c]
$2\ ^1\Sigma^+$	0.215 756		0.386	
$3\ ^1\Sigma^+$	0.229 146		0.157	
$4\ ^1\Sigma^+$	0.237 234		0.513	
$5\ ^1\Sigma^+$	0.256 819		0.254	
$6\ ^1\Sigma^+$	0.267 065		0.014	
$7\ ^1\Sigma^+$	0.273 853		0.458	
$8\ ^1\Sigma^+$	0.281 096		0.189	
$9\ ^1\Sigma^+$	0.319 637		0.606	
$X^1\Sigma^+ \rightarrow B\ ^1\Pi$	0.168 641	0.1696[a] 0.1682[b] 0.1718[c]	1.344	1.9223[b] 1.3117[c]
$2\ ^1\Pi$	0.236 525		0.021	
$3\ ^1\Pi$	0.236 530		0.580	
$4\ ^1\Pi$	0.275 719		0.038	
$5\ ^1\Pi$	0.297 572		0.488	
$6\ ^1\Pi$	0.320 979		0.443	
$7\ ^1\Pi$	0.376 446		0.023	

[a] From Ref. 64.
[b] From Ref. 58.
[c] From Ref. 60.

due to an absence of f functions, which increases the magnitude of the correlation correction. For Li_2 it is not necessary to carry out an extrapolation procedure to obtain improved values of the static polarizabilities; the difference

$$(\langle 0|u_i u_j|0\rangle - \sum_{n=1,3} \langle 0|u|n\rangle^2)(E_3-E_0)^{-1}$$

(Ref. 79) is weak compared to the values of α calculated from the three first states taken into consideration.

The frequency-dependent polarizabilities of Li_2 are displayed in Fig. 1. The first resonance occurs at the lowest excitation energy of ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ symmetry i.e., at 0.067 198 and 0.095 433 a.u., respectively. Our results also show that the polarizability derivatives increase more rapidly for the axial component than for the perpendicular one, with increasing frequency of the exciting radiation (Fig. 2).

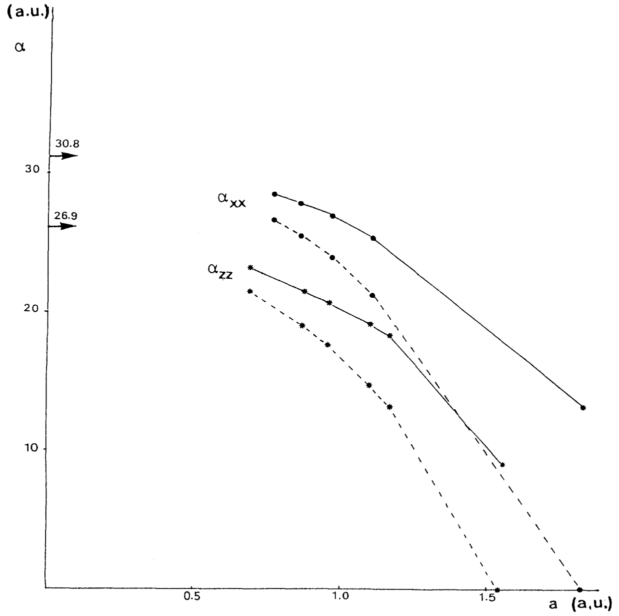

FIG. 3. LiH: static polarizability components versus polynomial factor. Extrapolated values are obtained from the following equations: $\alpha_{xx}-\alpha_{xx}^{(0)}=3.323a^{2.309}$, $\alpha_{zz}-\alpha_{zz}^{(0)}=3.387a^{2.317}$. (Dashed lines, without dipole-moment factor; solid lines, with dipole-moment factor.)

B. LiH

For a correct evaluation of the static polarizabilities, the number of low-lying states studied in the extrapolation procedure are 9 and 7 for α_{zz} and α_{xx} components, respectively. In all cases, however, the contribution of the first excited states of each symmetry is preponderant.

Energies and electronic transition moments calculated from $X\,{}^1\Sigma^+$ to ${}^1\Sigma^+$ and ${}^1\Pi$ states of LiH at equilibrium distance ($3.015a_0$) are displayed in Table III. Comparisons with previous theoretical works[58,60,64] show for both symmetry species an excellent agreement for the first vertical energy transition $X\,{}^1\Sigma^+ \rightarrow A\,{}^1\Sigma^+$ and $X\,{}^1\Sigma^+ \rightarrow B\,{}^1\Pi$.

Our calculated electronic transition moments for $X\,{}^1\Sigma^+ \rightarrow A\,{}^1\Sigma^+$ (0.939 a.u.) and $X\,{}^1\Sigma^+ \rightarrow B\,{}^1\Pi$ (1.344 a.u.) also are in excellent agreement with those reported by Partridge and Langhoff[60] at 3 a.u. (0.9376; 1.3117) and recently corroborated by Vojtik *et al.*[63]

With many spectroscopic states involved in the calculations of the polarizabilities, we have obtained the final values of the components by means of the extrapolation technique described in Sec. II. This procedure gives an upper limit of the polarizabilities components. Figure 3 shows the contribution of the different states as well as the influence of the polynomial function. The only experimental result available for any polarizability of LiH is the anisotropy $\Delta\alpha=\alpha_{zz}-\alpha_{xx}=1.7\pm4.0$ a.u. by Klemperer *et al.* cited in Ref. 80. All calculations carried out so far emphasize the importance of the correlation effects, which increase the SCF results and confirm that the α_{xx} electronic value is greater than the α_{zz} one. Our extrapolated values displayed in Table IV are compared with those derived from the CI calculations of Gready *et al.*,[25] the multiconfigurational self-consistent-field (MCSCF) calculations of Bishop and Lam,[31] the highly accurate finite-field-perturbation theory with complete active space (FPTCAS) SCF results of Karlstrom *et al.*[29] and Roos and Sadlej[30] known to take into account the majority of important correlation effects and also with the diffusion quantum Monte Carlo (DQMC) method of Vrbik *et al.*[34] The present calculated energy (−8.043 588 a.u.), slightly inferior to the recent accurate

TABLE IV. Total energy, dipole moment, and polarizabilities of LiH in a.u. for a bond length of 3.015 a.u.

				Others		
	This work	DQMC[a]	CI($D+S$)[b]	MCSCF[c]	CAS-SCF[d]	CAS-SCF[e]
E	−8.043 588	−8.0670		−8.020 369	−8.046 990	−8.020 638
μ_z	2.322	2.27		2.3107	2.308	2.320
α_{zz}	26.9	24.6	34.2	26.4	26.3	26.3
α_{xx}	30.8	30.9	34.4	29.8	29.3	29.9
$\Delta\alpha_{xx}(T)$[g]	0.4[f]					
$\Delta\alpha_{zz}(T)$[g]	1.6[f]					
$\Delta\alpha_{zz}(E)$[g]	2.9[f]					

[a] From Ref. 34.
[b] From Ref. 25.
[c] From Ref. 31.
[d] From Ref. 29.
[e] From Ref. 30.
[f] From Ref. 81.
[g] See text.

DQMC result of Ref. 34, compares favorably to the largest CAS-SCF energy of Ref. 29 and is better than the MCSCF value[31] and the CAS-SCF result.[30] In the same way, our dipole-moment value, equal to 2.322 a.u., agrees very well with those derived from CAS-SCF calculations carried out with different active subspaces.[29,30] This confirms the correctness of our choice of the correlated wave function. Since our basis set has more diffuse functions in the H region than the basis used by Karlstrom *et al.*,[29] the ionic character of LiH is more pronounced, giving an increased value to the dipole moment and to the polarizability components.

Our predicted accurate values of the electronic static polarizability components ($\alpha_{zz}^{e}=26.9$, $\alpha_{xx}^{e}=30.8$), which are approximately 2% above the convergent MCSCF and CAS-SCF values previously published, give a similar negative electronic anisotropy. Moreover, it should be emphasized that our α_{xx} value, found to be 30.8 a.u., is in perfect agreement with the recent DQMC value (30.9 a.u.).[34]

The rovibrational contributions evaluated by taking into account temperature $\Delta\alpha(T)$ and electric-field dependence[81] $\Delta\alpha(E)$ have been found to be quite important. Indeed, the vibronic parallel component correction (4.5 a.u.) greater than that of the perpendicular one (0.4 a.u.) leads to a change in the sign of the static anisotropy, in agreement with the positive experimental data of Klemperer. If now we consider the dynamic polarizability of LiH, our calculations show that the parallel component increases more rapidly than the perpendicular one with increasing frequency of the exciting radiation. Figure 4 illustrates the variation of the electronic anisotropy versus the frequencies showing a change of the dynamic polarizability anisotropy sign at ≈4950 Å.

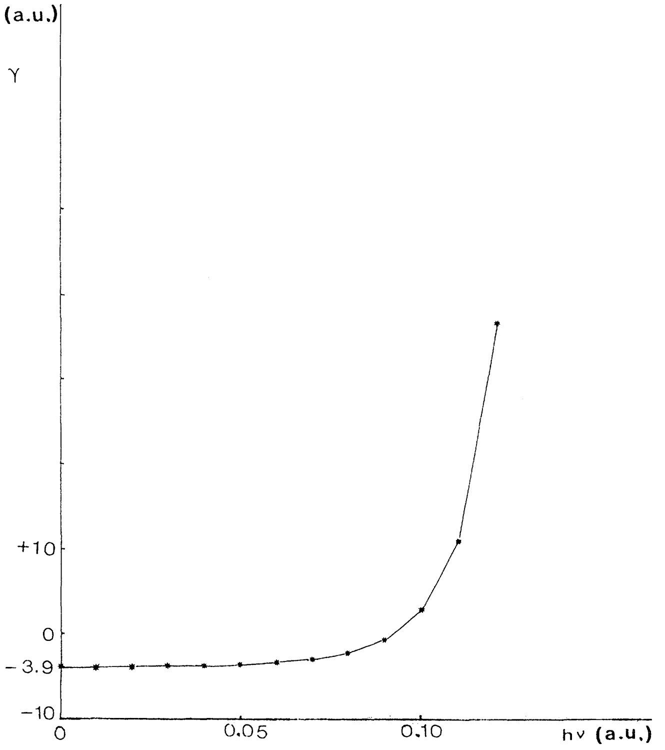

FIG. 4. Plot of dynamic anisotropy $\gamma(\omega)$ for LiH.

C. CO

The calculations have been done at the internuclear distance of $2.135a_0$, which corresponds to the minimum of the ground-state energy calculated by us at the CI level (experimental value $2.132a_0$). Energies are listed in Table V for the states of interest. For some of them, we can compare our results with those of Cooper and Kirby[70] and those of Nielsen *et al.*[82] Our values an in quite good agreement with the experimental ones,[68] as well as those calculated in Ref. 70.

We give also their electronic configuration, the net atomic charge, and the dipole moment between each excited state and the ground state (Table VI). The dipole transition moment is an important observable, since it determines the contribution of each excited state to the polarizability. For the first two excited states of each symmetry, we can compare our results (in atomic units) with those obtained by Kirby and Cooper,[83] respectively: 0.086 and 0.654 for the $X\,{}^1\Sigma^+\rightarrow 2\,{}^1\Sigma^+$ and $X\,{}^1\Sigma^+\rightarrow 3\,{}^1\Sigma^+$; 0.899 and 0.435 for the $X\,{}^1\Sigma^+\rightarrow 1\,{}^1\Pi$ and $X\,{}^1\Sigma^+\rightarrow 2\,{}^1\Pi$. The first perpendicular and second parallel transitions are of the same magnitude in both calculations, but the discrepancy is important for the first parallel and second perpendicular ones. On the other hand, our value for the first parallel transition (0.302 a.u.) is close to that deduced from the oscillator strength calculated by Nielsen *et al.*[82]–0.328 a.u. Comparisons with experiment can be done through the measurements of oscillator strength and radiative lifetime. Kirby and Cooper[83] have calculated these quantities for the relevant transitions. For the fourth positive system $X\,{}^1\Sigma^+\rightarrow A\,{}^1\Pi$, which is the best studied of the electronic transitions in CO, the experimental data are in good agreement with their calculations and so with our result. For the other

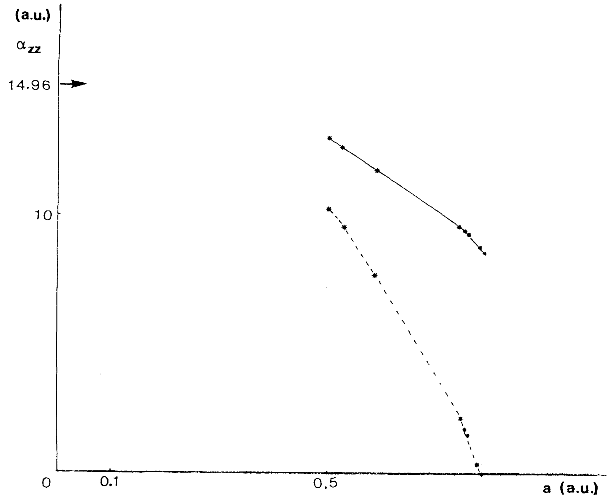

FIG. 5. Static polarizability versus polynomial factor for CO. Extrapolated value is obtained from the following equation: $\alpha_{zz}-\alpha_{zz}^{(0)}=15.94a^{2.538}$. (Dashed lines, without dipole-moment factor; solid lines, with dipole-moment factor.)

TABLE V. Energies (hartree) of the low-lying excited singlet states $(1^{\Sigma^+}, {}^1\Pi)$ of CO calculated at 2.135 a.u.

States	This work	Nielsen *et al.*[a]	Other work Cooper and Kirby[b]	Experimental values[c]
$2\,{}^1\Sigma^+$ (*B-D′* states)	0.384 898	0.4028	0.386 82	0.396 15
$3\,{}^1\Sigma^+$ (*C-C′* states)	0.405 567	0.4241	0.405 22	0.418 80
$4\,{}^1\Sigma^+$ (*F* state)	0.463 972	0.4711		0.4547
$5\,{}^1\Sigma^+$	0.480 940	0.4968		0.462 05
$6\,{}^1\Sigma^+$	0.506 798			
$7\,{}^1\Sigma^+$	0.521 806			
$8\,{}^1\Sigma^+$	0.589 122			
$9\,{}^1\Sigma^+$	0.588 675			
$1\,{}^1\Pi$ (*A* state)	0.304 281	0.3135	0.324 47	0.2965
$2\,{}^1\Pi$ (*E* state)	0.415 545	0.4281	0.414 33	0.4232
$3\,{}^1\Pi$ (*L* state)	0.471 111	0.4843	0.492 41	0.470 45

[a] From Ref. 82.
[b] From Ref. 70.
[c] From Ref. 68.

transitions, comparisons are complicated by the large discrepancies among the experimental measurements, apparent even in the most recent studies, as we can see in the diversity of values quoted in Ref. 83. At the present time there seems to be agreement only for the first excited state $A\ {}^1\Pi$, which has an important dipole-moment transition with the ground state (confirmed by the experimental data) and contributes greatly to the polarizability.

In Fig. 5 we have plotted the calculated values obtained for both components of the polarizability of CO. In the studied energy range (0 to 0.4 hartree) each component exhibits a discontinuity. The corresponding energy ω_d is in very good agreement with the experimental value for the first excited state of each symmetry, as it is seen in Table VII. Such results confirm the quality of the electronic calculations.

Moreover, for each excited state involved in the calculations, we have determined its contribution to the static polarizability α_{xx} for the ${}^1\Pi$ states and α_{zz} for the ${}^1\Sigma^+$ states (see Table VI). It is easy to see how the contribution of each state is a compromise between the magnitude of its transition dipole moment and its proximity with the ground state.

Another point of interest is that such partial calculations allow a better understanding of the contribution of each state in terms of its electronic configuration.

TABLE VI. Low-lying singlet states (${}^1\Sigma^+$ and ${}^1\Pi$) of CO: electronic configuration, net atomic charge of C, transition moment, and contribution to the static polarizability (α_{zz} for the ${}^1\Sigma^+$ states and α_{xx} for the ${}^1\Pi$).

States	Predominant electronic configuration[a]	Rydberg character[b]	Net atomic charge of C	Transition moment	Contribution to the static polarizability
$1\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^4\pi_{CO}^4$		−0.39		
$2\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\sigma_{CO}^{*1}$	3*s*(O)+3*s*(C)	−0.37	0.302	0.476
$3\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\sigma_{CO}^{*1}$	$3p_z$(C)	−0.29	0.450	0.998
$4\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\sigma_{CO}^{*1}$	$3p_z$(O)	1.22	0.227	0.222
$5\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\sigma_{CO}^{*1}$	3*s*(O)+3*s*(C)	1.78	0.011	0.0005
$6\,{}^1\Sigma^+$	$\sigma_O^2\sigma_C^2\sigma_{CO}^2\pi_{CO}^3\pi_{CO}^{*1}$	3*p*(C)	−0.35	0.336	0.447
$7\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^4\pi_{CO}^3\pi_{CO}^{*1}$		0.67	1.202	5.537
$8\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\sigma_{CO}^{*1}$		−0.18	0.757	1.945
$9\,{}^1\Sigma^+$	$\sigma_O^2\sigma_{CO}^4\pi_{CO}^3\pi_{CO}^{*1}$	3*p*(O)	0.71	0.458	0.713
$1\,{}^1\Pi$	$\sigma_O^2\sigma_{CO}^3\pi_{CO}^4\pi_{CO}^{*1}$		+0.15	0.777	3.975
$2\,{}^1\Pi$	$\sigma_O^2\sigma_{CO}^2\sigma_O^1\pi_{CO}^4(3p_c)^1$	3*p*(C)	+0.23	0.202	0.196
$3\,{}^1\Pi$	$\sigma_O^2\sigma_{CO}^2\sigma_O^1\pi_{CO}^{*1}$	3*p*(O)	+1.02	0.143	0.087

[a] Without the core.
[b] Valence character when nothing specified.

TABLE VII. Polarizability of CO: comparison with experimental results. All values are in a.u.

	This work	Experimental
$\alpha_{xx}(\omega=0)$	11.22 11.25[a]	12.15[d]
Discontinuity energy	0.304	0.296[e]
$\alpha_{zz}(\omega=0)$	13.39 14.96[b] 15.66[c]	15.72[d]
Discontinuity energy	0.385	0.396[e]

[a] With vibronic correction (temperature dependence); see Ref. 81.

[b] With extrapolation versus the number of $^1\Sigma^+$ states involved (see text).

[c] With extrapolation and vibronic correction (temperature and electric-field dependence, this last correction has been evaluated at 0.70; see Ref. 81).

[d] From Ref. 84.

[e] From Ref. 68.

(i) If the excited state is a valence state, without Rydberg character, its contribution to the polarizability may be important and sometimes essential. This is the case of the first $^1\Pi$ state.

(ii) If the excited state presents an important Rydberg character, its contribution is very weak and is thus negligible. For example, this is the case for all the $^1\Sigma^+$ states but the 7 and 8 ones.

To summarize, the contribution to the polarizability decreases with the Rydberg character of the excited state. Such explanations illustrate the difficulty of calculating the polarizability of the CO molecule and the wide range of published values, especially for the parallel component, whereas the calculation of the perpendicular component is easier.

The first $^1\Pi$ state, the $A\,^1\Pi$ state, is a valence state whose dipole-moment $X\,^1\Sigma^+ \rightarrow A\,^1\Pi$ may be reflected by the relevant one-electron matrix element $\langle 5\sigma|r|2\pi\rangle$. So in the calculation of the α_{xx} component, the first $^1\Pi$ state already gives the magnitude of the polarizability. The contribution of the polynomial function is of the same magnitude. It is reduced, progressively but not drastically, by the contribution of higher excited states having mostly Rydberg character. It is not necessary to include these states in the calculations; the first $^1\Pi$ state is sufficient to give an accurate lower bound of the perpendicular component.

On the other hand, let us consider the contribution of the $^1\Sigma^+$ states. As noted by Kirby and Cooper,[83] the first excited state ($2\,^1\Sigma^+$) presents two wells spectroscopically observed, $B\,^1\Sigma^+$ and $D'\,^1\Sigma^+$. While $D'\,^1\Sigma^+$ is a valence state ($3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi$), the $B\,^1\Sigma^+$ state has mostly Rydberg character ($3\sigma^2 4\sigma^2 5\sigma 1\pi^4 7\sigma$). Our calculations at the equilibrium geometry of the ground state, $R_e = 2.135$ a.u., describe the inner well $B\,^1\Sigma^+$. The predominant electronic configuration is in good agreement with that of Ref. 83; it presents a great Rydberg character through the "*s*" diffuse orbital of the carbon atom and, for a third of it, on the "*s*" diffuse orbital of oxygen.

The same situation holds for the $3\,^1\Sigma^+$ state, which also presents two wells, $C\,^1\Sigma^+$ (Rydberg state) and $C'\,^1\Sigma^+$ (valence state: $3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi^2$). We describe the inner well $C\,^1\Sigma^+$, which has mostly C($3p\sigma$) Rydberg character, in total agreement with Ref. 83. The three following states also have Rydberg character: O($3p\sigma$) for $4\,^1\Sigma^+$; O($3s\sigma$) and some C($3s\sigma$) for $5\,^1\Sigma^+$; and C($3p\pi$) for $6\,^1\Sigma^+$. Except for the $3\,^1\Sigma^+$ state, whose contribution is about 1 a.u., all other $^1\Sigma^+$ states do not contribute significantly to the value of α_{zz}. In order to augment the contribution to the $^1\Sigma^+$ states significantly we must introduce the 7 and 8 $^1\Sigma^+$ ones, which are the only valence states at the equilibrium geometry among the low-lying excited $^1\Sigma^+$ states. The contribution of the polynomial function is thus essential in the calculation of the parallel component of the polarizability.

Since many states are involved in these calculations, we can improve the calculation of α_{zz} by the method developed in Sec. II, which is based on the extrapolation with the number N of excited states. Figure 6 represents such an extrapolation at zero frequency from the first eight excited $^1\Sigma^+$ states. After extrapolation, the parallel component increases from 13.39 ($N=8$) to 14.96 ($N \rightarrow \infty$).

Table VII takes into account this correction. If, in addition, we take into account the rovibronic correction, temperature and electric field dependence, as developed in Ref. 81, the parallel component is now in very good agreement with the experimental value.

Moreover, in Table VIII, we give some results of polarizability computations corresponding to the energy values for which comparison can be done with other calculations, TDHF and SOPPA,[17] or experimental results.[84,85] Our values have been calculated as indicated before; α_{xx} from the first $^1\Pi$ states, α_{zz} by extrapolation with the number of $^1\Sigma^+$ states. The extrapolation is similar to the zero-frequency case, except that we must extrapolate separately for $+\hbar\omega$ and $-\hbar\omega$. Our results for $\alpha=(2\alpha_{xx}+\alpha_{zz})/3$ are in quite good agreement, until $\lambda \geq 3511$ Å, with those from SOPPA calculations. The

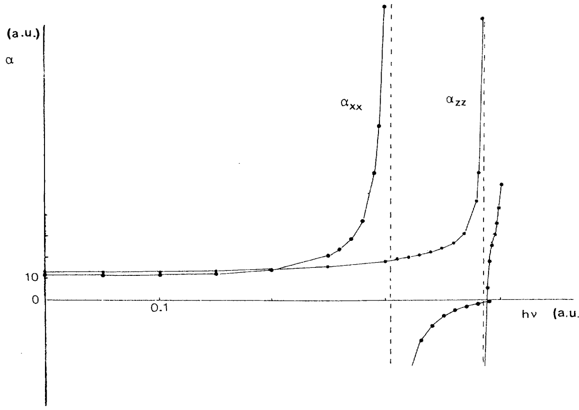

FIG. 6. Dynamic polarizability components of CO calculated at 2.135 a.u.

TABLE VIII. Some dynamic polarizabilities, in a.u., for CO: comparison with experiments and other calculations.

						Other calculations[d]					
		This work[a]				TDHF		SOPPA		Experiment	
λ (Å)	E (hartree)	α_{xx}	α_{zz}	α[b]	γ[c]	α	γ	α	γ	α[e]	γ[f]
∞	0.0000	11.22	14.96	12.47	+3.74	11.56	+2.94	12.45	+4.45	13.08	+3.57
6328	0.0720	11.52	15.32	12.79	+3.80	11.76	+2.93	12.69	+4.52	13.35	+3.59
5145	0.0886	11.68	15.45	12.94	+3.77	11.87	+2.92	12.82	+4.55	13.49	
4880	0.0934	11.74	15.51	13.00	+3.77	11.91	+2.92	12.86	+4.56	13.54	
4579	0.0995	11.81	15.58	13.07	+3.77	11.96	+2.91	12.92	+4.57	13.60	
4358	0.1045	11.88	15.64	13.13	+3.76	12.00	+2.91	12.97	+4.58	13.66	
3638	0.1252	12.22	15.92	13.45	+3.70	12.21	+2.88	13.22	+4.64	13.93	
3511	0.1297	12.31	15.98	13.53	+3.67	12.27	+2.88	13.29	+4.65	14.00	
2000	0.2278	17.38	17.30	17.35	−0.03	14.49	+2.07	15.95	+4.57	16.39	

[a] Our calculated values are given without rovibronic corrections. For the parallel component, we have extrapolated with the number of excited states involved in the calculations, as in the text.

[b] $\alpha=(2\alpha_{xx}+\alpha_{zz})/3$.

[c] $\gamma=\alpha_{zz}-\alpha_{xx}$.

[d] From Ref. 17.

[e] From international critical tables (Ref. 85 quoted in Ref. 17).

[f] From Ref. 84.

difference with the experimental values is ≈0.5 a.u., which is the order of magnitude of the rovibronic correction as shown for zero frequency.[81] For λ=2000 Å ($E=0.2278$ hartree) our α value is greater by 1 unit than the experimental one. In fact, the α_{xx} component is beginning to increase very quickly, as shown in Fig. 5, and its determination is very sensitive to the wavelength. Our γ parameter, which characterizes the anisotropy of the polarizability, is a little larger than the experimental value. It is intermediate between the TDHF and SOPPA results; the values obtained by these methods for λ=2000 Å are inaccurate, since these calculations do not show the quick increase of the α_{xx} component sufficiently as the energy approaches the value of the first $^1\Pi$ state.

V. CONCLUSION

We have presented calculations of the static and dynamic polarizabilities of Li_2, LiH, and CO. The method used is the conventional SCF-CI method of Hameka and Iwata, based on the variational-perturbation techniques, in which the first-order wave function includes two parts: (i) the traditional one, developed over the excited states, and (ii) additional terms obtained by multiplicating the zeroth-order function by a polynomial of first order in the electronic coordinates. This dipole-moment factor makes an extrapolation procedure possible in critical cases.

Applications to Li_2, LiH, and CO have shown the reliability of the method: Li_2 and LiH are ideal molecules, for which the hypervirial theorem may be verified quite easily, so that the method may be checked (see Appendix A). On the other hand, CO presents a critical case, where extrapolation is necessary. Indeed, the low-lying $^1\Sigma^+$ states are of Rydberg character, thus giving small contributions to the polarizabilities; one must use up to at least eight states since the valence states strongly contributing to α appear only at the seventh and eight $^1\Sigma^+$ states. On the contrary, the perpendicular component may be more easily computed, since the first $^1\Pi$ state is of valence character and extrapolation is not necessary.

In every case, our results agree very well with experimental ones, if available.

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APPENDIX A: LIMIT OF THE POLYNOMIAL

In order to simplify the formulas, the calculations presented in Appendices A and B are done with condition $\langle 0|x|0\rangle=0$ satisfied. However, the conclusions remain valid without fulfilling it.

Let us consider the peculiar case of the α_{xx} component at zero frequency. In the principal axis of the polarizability tensor, the single nonzero component of $g^{(x)}(\mathbf{r})$ is $a_x^x=a$. Then Eq. (18) reduces to

$$\begin{aligned} a\frac{n_e}{2}+c_nP_n&=\langle x^2\rangle \;, \\ aP_n+c_n\omega_n&=x_n \;, \end{aligned} \tag{A1}$$

with

$$P_n=\left\langle 0\left|\sum_{i=1}^{n_e}\frac{\partial}{\partial x_i}\right|n\right\rangle \;, \tag{A2}$$

$$x_n=\langle 0|\sum_{i=1}^{n_e}x_i|n\rangle \;, \tag{A3}$$

$$\omega_n=E_n-E_0 \;. \tag{A4}$$

In the case of exact eigenstates $|n\rangle$, the hypervirial theorem holds, and thus

$$x_n\omega_n = P_n \ . \tag{A5}$$

The solution of Eq. (A1) is straightforward; we get

$$c_n = \frac{x_n - aP_n}{\omega_n} \ , \tag{A6}$$

$$a = \frac{\langle x^2\rangle - \sum_n^{\infty} \frac{x_nP_n}{\omega_n}}{\frac{n_e}{2} - \sum_n^{\infty} \frac{P_n^2}{\omega_n}} = \frac{\langle x^2\rangle - \sum_n^{\infty} x_n^2}{\frac{n_e}{2} - \sum_n^{\infty} \omega_n x_n^2} \ . \tag{A7}$$

In actual calculations we must limit the number of states N in the summation. Let a_N be the corresponding coefficient. By introducing the decomposition of the identity operator

$$1 = \sum_{n=0}^{\infty} |n\rangle\langle n| \ , \tag{A8}$$

we can write a_N as

$$a_N = \frac{\sum_{n=N+1}^{\infty} x_n^2}{\sum_{n=N+1}^{\infty} \omega_n x_n^2} \ . \tag{A9}$$

Since ω_n is the energy of the transition from the ground state, it is positive, and so a_N. Moreover, the ω_n appearing in the denominator of a_N are all greater than ω_N, so that we have

$$\sum_{n=N+1}^{\infty} \omega_n x_n^2 > \omega_N \sum_{n=N+1}^{\infty} x_n^2 \ , \tag{A10}$$

and an upper bound to a_N,

$$0 < a_N < \frac{1}{\omega_N} \ . \tag{A11}$$

So, as N tends to infinity, a_N tends to zero. Besides,

$$a_{N+1} - a_N = \frac{\sum_{n=N+2}^{\infty} x_n^2}{\sum_{n=N+2}^{\infty} \omega_n x_n^2} - \frac{x_{N+1}^2 + \sum_{n=N+2}^{\infty} x_n^2}{\omega_{N+1}x_{N+1}^2 + \sum_{n=N+2}^{\infty} \omega_n x_n^2} \ , \tag{A12}$$

or

$$a_{N+1} - a_N = \frac{x_{N+1}^2\left(\omega_{N+1}\sum_{n=N+2}^{\infty} x_n^2 - \sum_{n=N+2}^{\infty} \omega_n x_n^2\right)}{\left[x_{N+1}^2\omega_{N+1} + \sum_{n=N+2}^{\infty} \omega_n x_n^2\right]\sum_{n=N+2}^{\infty} \omega_n x_n^2} \ . \tag{A13}$$

Because of (A10) we have

$$a_{N+1} < a_N \ . \tag{A14}$$

APPENDIX B: VARIATION OF THE α_N VERSUS a_N

When limiting the summation to N states, Eq. (22) becomes, for α_{xx},

$$\alpha_N = a_N\langle x^2\rangle + \sum_{n=1}^{N} c_n x_n \ . \tag{B1}$$

With (A6),

$$\alpha_N = a_N\langle x^2\rangle + \sum_{n=1}^{N} \frac{x_n^2}{\omega_n} - a_N \sum_{n=1}^{N} \frac{x_nP_n}{\omega_n} \ , \tag{B2}$$

$$\alpha_N = a_N\left[\langle x^2\rangle - \sum_{n=1}^{N} x_n^2\right] + \sum_{n=1}^{N} \frac{x_n^2}{\omega_n} \ . \tag{B3}$$

In Eq. (B3), α_N is the polarizability computed with the formula including the effect of the polynomial $g(\mathbf{r})$, and the last term, which we denote $\alpha_N^{(0)}$, is the usual polarizability calculated by the "sum-over-states" method. We may rewrite Eq. (B3) as

$$\alpha_N - \alpha_N^{(0)} = a_N^2\left[\frac{n_e}{2} - \sum_{n=1}^{N} \omega_n x_n^2\right] \tag{B4}$$

with the help of Eq. (A7).

One can read that equation as

$$\alpha_N - \alpha_N^{(0)} = a_N^2 f(N) \ . \tag{B5}$$

With the condition of Eq. (14), Eq. (B3) leads to

$$\alpha_{N+1} - \alpha_N = (a_{N+1} - a_N)\sum_{n=N+1}^{\infty} x_n^2 - \left[a_{N+1} - \frac{1}{\omega_{N+1}}\right]x_{N+1}^2 \ . \tag{B6}$$

With the help of Eq. (A9),

$$a_{N+1} - \frac{1}{\omega_{N+1}} = \frac{\omega_{N+1}\sum_{n=N+2}^{\infty} x_n^2 - \sum_{n=N+2}^{\infty} \omega_n x_n^2}{\omega_{N+1}\sum_{n=N+2}^{\infty} \omega_n x_n^2} \ , \tag{B7}$$

so that with Eq. (A13) we have

$$\begin{aligned} \frac{a_{N+1} - \frac{1}{\omega_{N+1}}}{a_{N+1} - a_N} &= \frac{\omega_{N+1}x_{N+1}^2 + \sum_{n=N+2}^{\infty} \omega_n x_n^2}{\omega_{N+1}x_{N+1}^2} \\ &= \frac{\sum_{n=N+1}^{\infty} \omega_n x_n^2}{\omega_{N+1}x_{N+1}^2} > \frac{\sum_{n=N+1}^{\infty} x_n^2}{x_{N+1}^2} \ , \\ \frac{\alpha_{N+1} - \alpha_N}{a_{N+1} - a_N} &= \sum_{n=N+1}^{\infty} x_n^2 - \frac{1}{\omega_{N+1}}\sum_{n=N+1}^{\infty} \omega_n x_n^2 < 0 \ . \end{aligned} \tag{B8}$$

As a consequence, α_N is a decreasing function of a_N.

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