PHYSICAL REVIEW A VOLUME 45, NUMBER 9 1 MAY 1992

Performance of a gauge-invariant method on calculated dynamic polarizabilities

Michel Rérat, Mohammadou Mérawa, and Claude Pouchan
Laboratoire de Chimie Structurale, Université de Pau, 64000 Pau, France

(Received 3 September 1991)

In the calculation of the dynamic polarizability including electronic correlation and ensuring gauge invariance, contributions of spectroscopic states and quasispectral series are analyzed. An improvement of our original electric-field variant ket approach is proposed and illustrated by application to H and LiH systems.

PACS number(s): 31.20.Di, 03.65.−w, 35.10.Di, 35.20.My

I. INTRODUCTION

In preceding papers [1,2] a method based on the use of a time-dependent gauge operator was developed for the calculation of dynamic polarizability. Accurate results were obtained provided that the limited size of the molecular-basis-set effects and the influence of the continuum states were partly simulated through a polynomial gauge factor, which moreover ensured the gauge invariance. A part of these effects is explicitly taken into account in the extrapolation procedure, which leads, as was pointed out [2], actually to the upper limit of the static polarizability α from the knowledge of a finite number of discrete states. Rapid convergence of the expansion in terms of discrete states is generally assumed with a small number of them except if the first spectroscopic states have a Rydberg character.

In this paper we consider in the context of the electric-field variant ket approach an improvement of our preliminary method, which not only reduces and simplifies the calculations, but also corrects some drawbacks, namely those due to the accuracy of the extrapolation procedure that is difficult to estimate precisely.

The purpose of this article is to present this approach briefly summarized in Sec. II and illustrated by application to the H atom and LiH molecule in Sec. III with the aim of showing the reliability of the proposed method by comparing our results with previous theoretical data [3–15].

II. THEORY

The static polarizability can be obtained from a variational method:

$$\alpha = -2\langle 0|H_1 - E_1|1\rangle$$

with

$$(H_0 - E_0)|1\rangle = -(H_1 - E_1)|0\rangle \tag{1}$$

and where $|0\rangle$ is the wave function of the unperturbed system, E_0 the corresponding energy, H_1 the first-order perturbation Hamiltonian, $E_1 = \langle 0|H_1|0\rangle$ and $|1\rangle$ the corresponding first-order energy and wave function, respectively. When $|1\rangle$ is described as a sum over the "true" spectroscopic kets $|\psi_n\rangle$ such as $H_0|\psi_n\rangle = E_n|\psi_n\rangle$, the usual expression of the static polarizability is given by

$$\alpha = 2\sum_{n>0} \frac{\langle \psi_0|H_1|\psi_n\rangle^2}{E_n - E_0}\ , \tag{2}$$

where

$$H_1 = -q\epsilon\cdot\mathbf{r}\ .$$

In order to obtain accurate values of polarizability, this sum not only must be infinite over the true spectral states but also extended into continuum. We have shown elsewhere [2] that the use of a polynomial function $\hat{g}(\mathbf{r})$ in the expression of the first-order wave function $|1\rangle$ such as

$$|1\rangle = \hat{g}(\mathbf{r})|\psi_0\rangle + \sum_{n>0}^{N} C_n|\psi_n\rangle \tag{3}$$

allows us to reach an extrapolate value of α for the ground state ψ_0 from a finite number N (usually less than 10) of low-lying true spectral states. In this case the first-degree polynomial function $g(\mathbf{r})$ presents several main advantages.

(i) It ensures the gauge invariance.
(ii) It compensates for the limited size of the molecular basis set.
(iii) It corrects the results due to the unavoidably restricted number N of states used in the calculations.
(iv) It simulates a part of the continuum contribution.
(v) It allows the use of the extrapolation procedure.

The two latter points will be discussed in Sec. III for the H atom.

The calculation of a finite number N of true spectral states ψ_n, however, can be expensive, and often accurate values of static polarizability may be found from a quasispectral series ϕ_m including a part of the continuum contribution [16,17]. Unfortunately if the first low-lying symmetry states connected to the ground state by allowed dipole transition are not the true spectral states ψ_n, then the value of dynamic polarizability near the first resonance is poor.

Consequently we can now present a scheme of our time-dependent gauge method, which combines both true spectral states ψ_n necessary near the resonance and quasispectral states ϕ_m.

The first-order wave function $|1\rangle$ is constructed according to a mixed procedure analogous to that reported [2] and leading to

$$|1\rangle=\hat{g}(\mathbf{r})|\psi_0\rangle+\sum_{n>0}^{N} c_n|\psi_n\rangle+\sum_{m}^{M} c_m|\phi_m\rangle\ , \tag{4}$$

where $\hat{g}(\mathbf{r})$ is a first-degree polynomial function of the electronic coordinate

$$\hat{g}^{v}(\mathbf{r})=\sum_{u} a_u^v u \quad \text{with } u,v=x,y,z$$

when the electric field lies in the v direction, ψ_n is the true spectral state built from Slater determinants

$$\psi_n=\sum_m C_m^n \phi'_m\ ,$$

and ϕ_m is a quasispectral series determined by Slater determinants selected using the following threshold:

$$s=\left|\frac{q\langle\psi_0|v|\phi_m\rangle}{H_{mm}-E_0}\right| \tag{5}$$

with $H_{mm}=\langle m|H_0|m\rangle$.

It should be emphasized that some of the ϕ_m determinants of the quasispectral series can be identical to ϕ'_m used in the spectral states. The ϕ_m and ϕ'_m sets of Slater determinants thus are not necessarily orthogonal, and this leads to additional terms in the following variational treatment (see (9)).

The computation of the dynamic polarizability then requires the calculations of a_u^v, c_n^v, and c_m^v factors, which, for an ϵ_v perturbation, leads to the following system of linear equations:

$$M_0^{\pm}U_1^{v\pm}=V_1^{v\pm}\ , \tag{6}$$

where

$$U_1^{v\pm}=\begin{bmatrix} a_u^{v\pm} \\ c_n^{v\pm} \\ c_m^{v\pm} \end{bmatrix} \tag{7}$$

is the solution we are trying to find for the frequency-dependent system $(\pm\nu)$, and

$$V_1^{v\pm}=q\begin{bmatrix} \langle uv\rangle-\langle u\rangle\langle v\rangle \\ \langle\psi_0|v|\psi_n\rangle-\langle\psi_0|\psi_n\rangle\langle v\rangle \\ \langle\psi_0|v|\phi_m\rangle-\langle\psi_0|\phi_m\rangle\langle v\rangle \end{bmatrix} \tag{8}$$

with

$$\langle v\rangle=\left\langle\psi_0\left|\sum_{i=1}^{n_e} v_i\right|\psi_0\right\rangle$$

and

$$\langle uv\rangle=\left\langle\psi_0\left|\left[\sum_{i=1}^{n_e} u_i\right]\left[\sum_{j=1}^{n_e} v_j\right]\right|\psi_0\right\rangle .$$

n_e is the number of electrons. When the origin of the molecular system studied is set at the center of electronic charge, then $\langle v\rangle=0$, the right-hand side of the linear nonhomogeneous system is notably simplified, and $M_0^{\pm}$ will be written (in a.u.)

$$\begin{bmatrix} \frac{ne}{2}\delta_{uv}\pm h\nu\langle uv\rangle & \langle\psi_0|\nabla_u|\psi_n\rangle\pm h\nu\langle\psi_0|u|\psi_n\rangle & \langle\psi_0|\nabla_u|\phi_m\rangle\pm h\nu\langle\psi_0|u|\phi_m\rangle \\ & (E_n-E_0\pm h\nu)\delta_{nn'} & (E_n-E_0\pm h\nu)C_m^n \\ & & H_{mm'}+(-E_0\pm h\nu)\delta_{mm'} \end{bmatrix}\ , \tag{9}$$

where C_m^n can be replaced by the more general expression $\langle\Psi_n|\phi_m\rangle$.

$M_0^{\pm}$ thus defined is valid only for exact ψ_0 and ψ_n wave functions; this remains relevant when the approximate functions used verify the hypervirial theorem within a reasonable range (i.e., $\langle\psi_0|\nabla_u|\psi_n\rangle/(E_n-E_0)\simeq\langle\psi_0|u|\psi_n\rangle$) (see Ref. [2]).

With respect to our previous scheme [2] the contribution of the quasispectral series is now taken into account by means of the last column in $M_0^{\pm}$. The coupling factors $(E_n-E_0\pm h\nu)C_m^n$ between the true spectral states ψ_n and the quasispectral series ϕ_m can be zero if the Slater determinants are different in the description of the spectroscopic states and quasispectroscopic series. Except for the use of the extrapolation procedure the main advantages of the gauge factor remain.

As a general rule, the dynamic polarizability components are then given in atomic units by

$$\begin{aligned}\alpha_{uv}^{(\nu)}=q&\sum_{\pm,w} a_w^{v\pm}(\langle wu\rangle-\langle w\rangle\langle u\rangle)\\ &+q\sum_{\pm,n} c_n^{v\pm}(\langle\psi_0|u|\psi_n\rangle-\langle\psi_0|\psi_n\rangle\langle u\rangle)\\ &+q\sum_{\pm,m} c_m^{v\pm}(\langle\psi_0|u|\phi_m\rangle-\langle\psi_0|\phi_m\rangle\langle u\rangle)\ .\end{aligned}$$

(Once more, it should be emphasized that a simplification occurs when the origin is fixed at the electronic centroid, $\langle v\rangle=0$.)

III. RESULTS AND DISCUSSION OF RESULTS

Hydrogen atom

In order to demonstrate the efficiency of our polynomial factor in the calculation of the polarizability, a first calculation was carried out for the ground state of the hydrogen atom for which exact wave functions are known.

If the sum-over-states formula is used taking into account only the true spectral states $\psi_0, \ldots, \psi_n$, the discrete series converges on a α_1^d value defined by

$$\alpha_l^d(N) = C_l \sum_{n=l+1}^{N\to\infty} A_{nl} \, .$$

The α_l^d dipole polarizability ($l=1$) reduces to the well-known value (3.663 257 89) given by Tanner and Thakkar [5]. An exact value of the polarizability α_l can be obtained by adding to α_l^d the continuum contribution α_l^c. For the dipole polarizability of the hydrogen atom the continuum contribution is then found to be 0.8367 a.u., i.e., about 18.6% of the total electronic polarizability (4.500 a.u.) [3].

We have reported in Table I for the hydrogen atom, taking into account only the true spectral states ψ_n, the value of the static polarizability with $[\alpha_G^d(N)]$ and without $[\alpha^d(N)]$ the gauge factor against the number N of states. This table shows the large contribution of the gauge factor to the dipole polarizability of hydrogen and illustrates the fact that a large part of the continuum contribution can be simulated through the polynomial function. Indeed, the convergence of such series $\alpha^d(N)$ and $\alpha_G^d(N)$ leads to discrete values of 3.6632 and 4.4018 a.u. corresponding, respectively, to 81.4% and 97.8% of the exact value. In other respects it should be noted that convergence is most rapid in the gauge series where the first state gives a predominant contribution (4.3168 a.u.) even though the polynomial gauge value alone is found to be 4 a.u. As pointed out by Kutzelnigg [6] an exact value should be obtained from the more complex polynomial function,

$$g^x(\mathbf{r}) = ax + bxr \, ,$$

the exact solution of (1) leading in this case to $a=1$, $b=\frac{1}{2}$.

The final upper limit of the static polarizability obtained from the knowledge of a finite number N of discrete states can be calculated from an extrapolation technique [2]. This procedure consists in the use of an extrapolation formula of the form

$$\alpha_G^d(N) - \alpha^d(N) = \xi[a(N)]^{\zeta} \, .$$

TABLE I. Partial sums of discrete series for static polarizabilities of hydrogen. The extrapolated final value $\alpha(N\to\infty)=4.503$ a.u. is obtained from the following equations: $\alpha_G^d(N)-\alpha^d(N)=0.264\,956[a(N)]^{3.87285}$, $\alpha_G^d(N)/\mathrm{p} \ =\alpha(N\to\infty) -0.036\,411[a(N)]^{3.87285}$.

N	$\alpha^d(N)$	$\alpha_G^d(N)$	$a(N)$
0	0.000 000	4.000 000	2.000 000 0
1	2.959 621	4.316 847	1.524 729 5
10	3.639 246	4.398 945	1.312 575 9
100	3.662 954	4.401 826	1.303 178 6
200	3.663 181	4.401 853	1.303 087 9
300	3.663 224	4.401 858	1.303 070 9
400	3.663 238	4.401 860	1.303 062 1
500	3.663 245	4.401 861	1.303 062 1

The value of the exponent ζ is determined by a least-squares fit, and then the extrapolated polarizability is obtained by a linear regression in which the computed values of $\alpha_G^d(N)$ are written as

$$\alpha_G^d(N) = \alpha(N\to\infty) + \eta[a(N)]^{\zeta} \, .$$

In the case of hydrogen, the final $\alpha(N\to\infty)$ value is found to be 4.503 a.u., i.e., 0.07% above the exact static value of α.

To summarize, when exact wave functions are used as in the hydrogen case, our results show the precise role and the rigorous contribution of the polynomial part in the calculation of the discrete value of polarizability and the efficiency of the extrapolation procedure to obtain an accurate value of the static dipole polarizability.

LiH molecule

Electrical properties of LiH have been theoretically investigated by several methods and at different levels of calculations. Since an exact wave function is not available for this molecule, a true discrete value of the polarizability obtained from a sum over states generally speaking is not directly accessible. On the other hand, in a finite basis set the spectroscopic states ψ_n can be obtained like the quasispectral series ϕ_m, allowing us to test our time-dependent gauge method.

For LiH, the calculations have been carried out at the *ab initio* configuration interaction (CI) level using the experimental internuclear distance 3.015 a.u. Our basis set [2] consists in the segmented contractions scheme $(5s5p3d/10s6p)$ for both Li and H, leading to reasonable values for the energy and the dipole moment. Correlation effects have been taken into account by means of the multireference, second-order many-body perturbation theory through the configuration interaction with perturbatively selected interactions (CIPSI) algorithm [18,19]. Single and double excitations relative to the multireference were included. At correlated level our ground-state-energy ($-8.043\,588$ a.u.) and dipole-moment (2.313 a.u.) values compare very well with those obtained from finite field perturbation theory with complete active space (FPTCAS-SCF) and diffusion quantum Monte Carlo (DQMC) methods by Karlstrom, Roos, and Sadlej [8] and Vrbik, Legare, and Rothstein [14], respectively.

Static polarizability components of LiH have been calculated according to our gauge method using the following hypothesis:

(i) the low-lying spectroscopic states ψ_n only, followed by an extrapolation procedure [2] as for hydrogen;

(ii) the same low-lying spectroscopic states ψ_n, enlarged by a quasispectral series ϕ_m;

(iii) the first spectroscopic state ψ_1 and the quasispectral series ϕ_m.

In the latter two cases the value of the threshold (5)

TABLE II. Static polarizability components ($\alpha_{\|},\alpha_{\perp}$) of LiH calculated in a.u.

Hypothesis[a]	ψ_n	s[b]	$a_{\|}$[c]	$\alpha_{\|}$
(iii)	$N=1$	0.001	0.96	25.83
(ii)	$N=9$	0.01	0.71	26.08
(ii)	$N=9$	0.001	0.60	26.25
(i)	$N=\infty$	$\gg 1$	0	26.9

Hypothesis[a]	ψ_n	s[b]	$a_{\perp}$[c]	$\alpha_{\perp}$
(iii)	$N=1$	0.001	0.97	29.70
(ii)	$N=7$	0.01	0.88	29.75
(ii)	$N=7$	0.001	0.82	29.90
(i)	$N=\infty$	$\gg 1$	0	30.8

[a] See text.

[b] See Eq. (5).

[c] Parallel ($a_{\|}$) and perpendicular ($a_{\perp}$) gauge coefficients.

used to construct the quasispectral series is fixed at 0.01 and 0.001, respectively, leading to spaces including 200 to 1000 determinants ϕ_m.

As in Ref. [2], the low-lying spectroscopic states ψ_n are obtained by diagonalizing a matrix ($\simeq 10\,000$ determinants ϕ'_m) that includes the most important second-order perturbational contributions of the multireference zero-order wave functions. These wave functions spanned over a subspace including the most significant determinants (about 200) are built up iteratively from the total set of canonical orbitals. For the two polarizability components, the results are depicted in Table. II. The overall agreement between the static values obtained using these different assumptions is very good, and the discrepancies appear to be not greater than 4% for both calculated polarizability components. The main cause of this difference is likely due to the overestimation arising from the extrapolation procedure. Improved and comparable results are obtained when the quasispectral series ϕ_m is added to the low-lying spectroscopic states ψ_n. Calculations carried out with several spectroscopic states (seven for $^1\Pi$ and nine for $^1\Sigma^+$) lead to the more reliable values. These values depend on the quality of the quasispectral series ϕ_m selected from a fixed threshold. The significantly better results obtained then are 26.25 and 29.90 a.u. respectively, for the parallel and perpendicular components, in perfect agreement with the complete active space self-consistent field (CAS-SCF) results of Roos and Sadlej [10]. When only the first spectroscopic state is taken into account, with the same quasispectral series ϕ_m, the value of the two components decreases by about 1%. This latter approximation, which requires less time than the former, gives, however, close results.

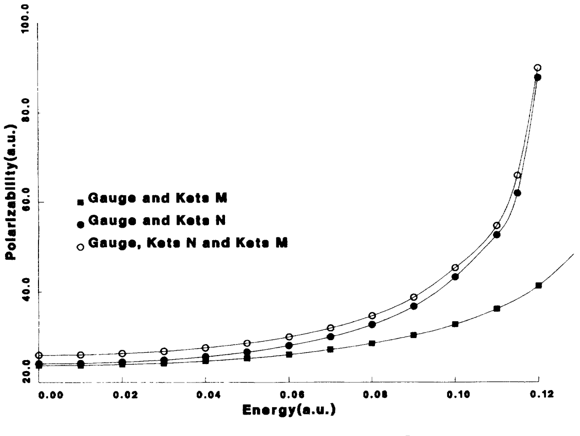

FIG. 1. Plot of $\alpha_{\perp}$ against $h\nu$ (a.u.) (● gauge and kets N without extrapolation procedure).

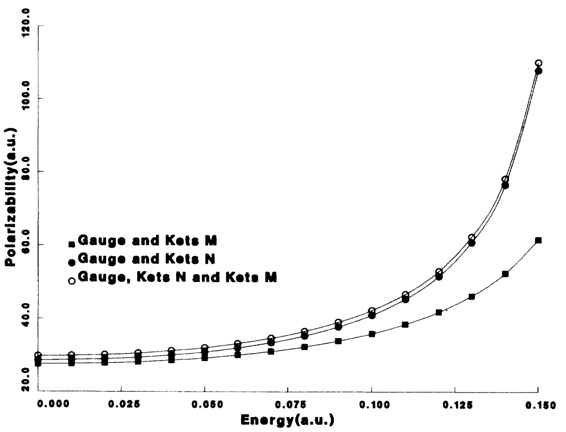

FIG. 2. Plot of $\alpha_{\|}$ against $h\nu$ (a.u.) (● gauge and kets N without extrapolation procedure).

The decreasing gauge coefficients ($a_{\|},a_{\perp}$) should also be noted in Table II when the size of the quasispectral series increases (or when the threshold s decreases), showing their complementary role.

The static anisotropy is slightly dependent on the kind of approximation used, this electronic value is within the range -3.65 to -3.90 a.u., in perfect agreement with multiconfigurational self-consistent field (MCSCF) [11] and CAS-SCF [10] calculations. A particular emphasis must be placed on the important role of the rovibrational contributions [20]. These contributions amounting to 4.5 and 0.4 a.u., respectively, the parallel and the perpendicular component lead to a positive sign of the anisotropy in agreement with the experimental data.

TABLE III. Dynamic polarizability components and anisotropy calculated with $s=0.01$ and $N=7$ or 9 (values in a.u.).

$h\nu$	$\alpha_{\|}$	$\alpha_{\perp}$	γ
0.00	26.08	29.75	-3.67
0.01	26.17	29.83	-3.66
0.02	26.45	30.09	-3.64
0.03	26.93	30.52	-3.59
0.04	27.65	31.16	-3.51
0.05	28.67	32.02	-3.35
0.06	30.07	33.16	-3.09
0.07	32.00	34.63	-2.63
0.08	34.75	36.52	-1.77
0.09	38.84	38.98	-0.14
0.10	45.44	42.24	$+3.20$
0.11	57.85	46.66	$+11.19$
0.12	89.86	52.92	$+36.94$

Contributions of the polynomial factor, spectroscopic states ψ_n, and quasispectral series ϕ_m are analyzed in the calculations of the dynamic components. Figures 1 and 2 illustrate the behavior of the dynamic polarizabilities in a wide range of frequencies until the first resonance energy.

In the vicinity of zero frequency the performance of all hypotheses studied, including gauge factor and spectroscopic states ψ_n, gauge factor and quasispectral series ϕ_m, and gauge factor and ψ_n plus ϕ_m, is found to be reasonably good. The frequency dependence then is rapidly and considerably affected by the accurate description of the first spectroscopic states ψ_n. Quasispectral series ϕ_m give poor quality of the polarizability components near the resonance.

The most satisfactory results are those obtained through the high-level approach. Accurate calculated values of dynamic polarizabilities and electronic anisotropy are given in Table. III. The main conclusion that emerges from the data is the rapid increase of the parallel component leading to a change in the dynamic anisotropy sign when $h\nu \simeq 0.09$ a.u. Similar behavior is reported by Sasagane *et al.* [15] in a multiconfigurational time-dependent Hartree-Fock (MCTDHF) approach, but their values are not accurate owing to the small size of the basis set used.

ACKNOWLEDGMENTS

The calculations were carried out on the Vax of the Centre Informatique Universitaire de Pau et des Pays de l'Adour (CIUPPA) and on the IBM-3090/600-VF of the Centre National Universitaire Sud de Calcul (CNUSC). We thank the scientific council of the CNUSC and the Conseil Régional d'Aquitaine for their financial support in this project. The Laboratoire de Chimie Structurale is "Unité associée au CNRS No. 474."

[1] M. Rérat, Int. J. Quantum Chem. **36**, 169 (1989).
[2] M. Rérat, C. Pouchan, M. Tadjeddine, J. P. Flament, H. P. Gervais, and G. Berthier, Phys. Rev. A **43**, 5832 (1991).
[3] A. Dalgarno, Adv. Phys. **11**, 281 (1962).
[4] W. Kutzelnigg and F. Maeder, Chem. Phys. **35**, 397 (1978).
[5] A. C. Tanner and A. J. Thakkar, Int. J. Quantum Chem. **24**, 345 (1983).
[6] W. Kutzelnigg, J. Mol. Struct. **202**, 11 (1989).
[7] J. E. Gready, G. B. Backsay, and N. S. Hush, Chem. Phys. **23**, 9 (1977).
[8] G. Karlstrom, B. O. Roos, and A. J. Sadlej, Chem. Phys. Lett. **86**, 374 (1982).
[9] P. Lazzeretti, E. Rossi, and R. Zanasi, J. Phys. B **15**, 521 (1982).
[10] B. O. Roos and A. J. Sadlej, J. Chem. Phys. **76**, 5444 (1982).
[11] D. M. Bishop and B. Lam, Chem. Phys. Lett. **120**, 69 (1985).
[12] D. J. Malik and C. E. Dykstra, J. Chem. Phys. **83**, 6307 (1985).
[13] G. Maroulis and D. M. Bishop, Theor. Chim. Acta **69**, 161 (1986).
[14] J. Vrbik, D. A. Legare, and S. M. Rothstein, J. Chem. Phys. **92**, 1221 (1990).
[15] K. Sasagane, K. Mori, A. Ichihara, and R. Itoh, J. Chem. Phys. **92**, 3619 (1990).
[16] D. M. Bishop and B. Lam, J. Phys. B **21**, 383 (1988).
[17] D. M. Bishop and M. Rérat, J. Chem. Phys. **91**, 5489 (1989).
[18] B. Huron, P. Rancurel, and J. P. Malrieu, J. Chem. Phys. **58**, 5745 (1973).
[19] E. Evangelisti, J. P. Daudey, and J. P. Malrieu, Chem. Phys. **75**, 91 (1983).
[20] M. Tadjeddine, J. P. Flament, N. El Bakali Kassimi, H. P. Gervais, G. Berthier, M. Rérat, and C. Pouchan, J. Chim. Phys. **87**, 989 (1990).