Approximate ab initio calculations of polarizabilities via the excitation scheme

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Abstract

The excitation scheme is explored as an alternative to the more usual coupled Hartree–Fock and similar analytical derivative calculations of polarizabilities and other molecular properties. The scheme can be implemented more easily and requires only a small fraction of the computer time and memory needed for conventional calculations. The accuracy of the two approaches is fully comparable for calculations done with incomplete basis sets. This is documented on computations of polarizabilities and magnetic susceptibilities of water, pyridine and pyrimidine molecules performed at the HF and DFT (B3LYP) levels.

1. Introduction

Molecular property tensors [1] (dipole moment, polarizability, magnetic susceptibility, optical activity tensor, etc.) determine the behaviour of molecules under the influence of an external electromagnetic field and thus became the natural target of ab initio quantum chemical calculations. Computational techniques, which are used most frequently, include the numerical differentiation of total energy according to the intensity of applied fields [2] and the analytical derivative technique (AD) elaborated, for example, by Pople et al. [3] or Amos [4]. The numerical differentiation is easier to implement and requires a relatively small increase of occupied computer memory if compared to a single energy calculation, yet its disadvantage is a long computational time and limited accuracy dependent on the differentiation step. The AD techniques thus became the primary choice since they are more accurate and lead to the solution of a single set of self consistent equations, which can be solved by an iterative scheme. These AD techniques are implemented in the Gaussian [5] and CADPAC [6] program packages, for instance. Nevertheless, consideration of the external field still leads to a substantial increase of computer time and occupied memory if compared to the uncoupled problem. This obstacle is encountered especially in complex calculations, like in simulations of Raman spectra, where also the coordinate dependence of the tensors is to be determined. In many cases, particularly for some DFT calculations, even the dependence of the effective Hamiltonian (DFT functional) on the magnetic field is not known. Thus the purpose of this

study is to find an alternative computational approach which would, preferably, lessen the demands on the computer power.

2. Theory

Under the influence of an external electric (E) or magnetic (B) field the molecular Hamiltonian operator H_0 changes to

$$H = H_0 - \boldsymbol{\mu} \cdot \mathbf{E} - \boldsymbol{m} \cdot \boldsymbol{B} - (1/2)\boldsymbol{B} \cdot \chi^{(d)} \cdot \boldsymbol{B},$$
(1)

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are the electric and magnetic dipole moment operators, respectively, and $\chi^{(d)}$ is the diamagnetic susceptibility. From Eq. (1) can be derived the commutator relation

$$\boldsymbol{\mu} = [H, \partial/\partial E],$$
(2a)

$$\boldsymbol{m} = [H, \partial/\partial B] + \chi^{(d)} \cdot \boldsymbol{B}.$$
(2b)

These commutator relations can be conveniently used for practical calculations of integrals between molecular states $|j\rangle$ and $|n\rangle$ (with energies W_j and W_n):

$$\langle j| \boldsymbol{\mu}|n\rangle = \langle j|[H, \partial/\partial E]|n\rangle = W_{jn}\langle j|\partial n/\partial E\rangle|_{E=0},$$
(3a)

$$\langle j|\boldsymbol{m}|n\rangle = \langle j|[H, \partial/\partial B] + \chi^{(d)} \cdot \boldsymbol{B}|n\rangle$$
$$= W_{jn}\langle j|\partial n/\partial B\rangle|_{B=0}$$

$$(W_{jn} = W_j - W_n).$$
(3b)

In the case of the electric polarizability, for example, these equations can be used as follows. The polarizability is defined as the second derivative of the total energy, W,

$$\alpha_{\alpha\beta} = -\partial^2 W/(\partial E_\alpha \partial E_\beta) = \partial \mu_\alpha/\partial E_\beta.$$
(4)

The derivative is supposed to be estimated at the limit of the zero electric field. Since the molecular dipole moment $\mu_\alpha = \langle n| \mu_\alpha|n\rangle$, where $|n\rangle$ is the molecular ground state,

$$\alpha_{\alpha\beta} = (\partial/\partial E_\beta)\langle n| \mu_\alpha|n\rangle = 2\langle n| \mu_\alpha|\partial n/\partial E_\beta\rangle.$$
(5)

Then the unit operator $\mathbf{1} = \sum_j |j\rangle\langle j|$ (sum runs over all molecular quantum states $|j\rangle$) can be inserted into Eq. (5) and

$$\alpha_{\alpha\beta} = 2\sum_j\langle n| \mu_\alpha|j\rangle\langle j|\partial n/\partial E_\beta\rangle.$$
(6)

The matrix element $\langle j|\partial n/\partial E_\beta\rangle$ can finally be expressed using Eq. (3a) so that

$$\alpha_{\alpha\beta} = 2\sum_j W_{jn}^{-1}\langle n| \mu_\alpha|j\rangle\langle j| \mu_\beta|n\rangle.$$
(7)

Thus Eq. (5) and Eq. (7) are two equivalent ways (for exact wavefunctions) by which the polarizability can be calculated. For practical purposes, however, Eq. (5) has been preferred, since it includes the derivative of the ground-state electronic wavefunction only. For simplicity, we will refer to this approach as the AD procedure, because its implementation is based on the analytical derivative of the wavefunction according to the field. Here we want to show that the calculation based on Eq. (7) (referred to as the excitation scheme (EXC) here since it presumes the knowledge of excited electronic states) leads faster to results of the same quality as the AD computation in many cases, particularly if the calculation is implemented at the HF or a hybrid HF-DFT level with an incomplete basis set. For model calculations, the water molecule and the pyridine and pyrimidine molecules were chosen and, in addition to the polarizability, the paramagnetic susceptibilies ($\chi^{(p)}$) were calculated similarly, using the AD and EXC schemes:

$$(\text{AD}) \quad \chi_{\alpha\beta}^{(p)} = 2\langle n|m_\alpha|\partial n/\partial B_\beta\rangle.$$
(8)

$$(\text{EXC}) \quad \chi_{\alpha\beta}^{(p)} = 2\sum_j W_{jn}^{-1}\langle n|m_\alpha|j\rangle\langle j|m_\beta|n\rangle.$$
(9)

3. Implementation

The Gaussian 94 program [5] was used for the AD calculations. All calculations are done for geometries optimized by an energy minimization. For the EXC calculations a program written in house was used. By the program the Gaussian output was read, and the required molecular orbital matrix elements and the Coulomb and exchange integrals recalculated. This rather inefficient procedure was chosen to achieve a greater flexibility for the modelling, although in principle as little as one single-point energy calculation suffices for the EXC calculation: in our implementation the excited states were modelled by single excited spin adapted Slater determinants [7], $|j\rangle =$

$|\Psi_{K \to J}\rangle$. Thus the energies in Eq. (7) or Eq. (9) could be evaluated as

$$W_{jn} = \varepsilon_J - \varepsilon_K - J_{JK} + 2K_{JK},\qquad(10)$$

where ε_J and ε_K are the HF energies of the unoccupied and occupied molecular orbitals, J_{JK} and K_{JK} are the Coulomb and exchange integrals, respectively. For the DFT calculations the so called Becke3LYP (B3LYP) functional [8,9] was chosen, since it belongs to the group of the latest and most successful hybrid HF-DFT methods, used widely in ab initio explorations of organic molecules. The same energy expression was used for the DFT calculation and the molecular orbitals (K, J) were replaced by the Kohn–Sham orbitals [10] calculated by the Gaussian program. We wish to stress that the Fock energies were recalculated for each Kohn–Sham orbital as

$$\varepsilon_I = \langle I|F|I\rangle = H_I + \Sigma_{L,\text{occ}}(2J_{IL} - K_{IL}),$$

where H_I is the core Hamiltonian (see Ref. [10]), i.e.

they are not identical with the Kohn–Sham energies given in the Gaussian output. The other approach lead to erroneous results. The working expression for the electric dipolar polarizability, for example, thus becomes

$$\alpha_{\alpha\beta} = 4\Sigma_{K,\text{occ}}\Sigma_{J,\text{unocc}}(\varepsilon_J - \varepsilon_K - J_{JK} + 2K_{JK})^{-1}$$
$$\times \langle K|\mu_\alpha|J\rangle\langle J|\mu_\beta|K\rangle,\qquad(11)$$

where the sums run over occupied and unoccupied molecular orbitals.

4. Results and discussion

The water molecule was chosen as a model system, on witch the basis set dependence could be tested easily. In Table 1 the polarizability components and paramagnetic susceptibilities calculated at different levels are given. In the 'real world' molecular properties are modelled regularly using medium

Table 1
Ab initio calculations of the water polarizability and magnetic susceptibility

Number of bf	13		19		25		
Basis	6-31G		6-31G*		6-31G**		
Level	HF	B3LYP	HF	B3LYP	HF	B3LYP	LSDA
α_{xx} A/E	1.41/1.44	1.45/1.39	2.78/3.17	2.83/3.08	2.93/3.35	2.99/3.29	3.02/3.30
α_{yy} A/E	6.34/7.29	7.50/8.68	6.68/7.76	7.40/8.97	6.77/7.94	7.51/9.17	7.60/9.39
α_{zz} A/E	3.84/4.09	4.71/5.05	4.81/5.54	5.43/6.30	4.90/5.70	5.56/6.52	5.68/6.62
$\|\alpha\|$A/E	3.90/4.27	4.55/5.04	4.76/5.49	5.22/6.12	4.87/5.66	5.35/6.33	5.43/6.44
$\|\chi^{(p)}\|$ A/E	0.194/0.174	0.278/0.234	0.207/0.191	0.267/0.230	0.254/0.233	0.324/0.287	0.319/0.281
W	−75.9854	−76.3861	−76.0107	−76.4090	−76.0236	−76.4197	−76.0505
μ	0.983	0.944	0.865	0.825	0.845	0.804	0.824

Number of bf	31		67		105		EXP
Basis	6-31 + +G**		6-31 + +G(3d,pd)		AUG-cc-pVTZ		
Level	HF	B3LYP	HF	B3LYP	HF	B3LYP	
α_{xx} A/E	5.27/5.63	6.68/6.53	7.49/8.40	9.02/9.61	7.71/8.19	9.56/9.87	
α_{yy} A/E	7.28/8.21	8.16/9.64	8.56/10.1	9.68/11.9	8.89/9.92	10.3/12.2	
α_{zz} A/E	5.72/6.09	6.78/7.29	7.90/9.17	9.21/10.8	8.20/9.16	9.83/11.2	
$\|\alpha\|$A/E	6.09/6.64	7.21/7.82	7.98/9.23	9.30/10.8	8.27/9.09	9.90/11.1	9.785 [a]
$\|\chi^{(p)}\|$ A/E	0.254/0.233	0.308/0.287	0.280/0.252	0.325/0.287	0.291/0.251	0.336/0.293	0.316 [b]
W	−76.0313	−76.4341	−76.0402	−76.4432	−76.0617	−76.4673	
μ	0.876	0.861	0.768	0.737	0.759	0.724	0.729 [a]

Symbols (all properties given in atomic units): α_{xx}: x-component of the polarizability, $\|\alpha\| = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, $\chi^{(p)}$: the paramagnetic susceptibility, W: molecular energy, μ: dipole moment. Conversion to SI units: α [$C^2 m^2 J^{-1}$] = $1.6488 \times 10^{-41}\alpha$ [au], μ[C m] = $8.4784 \times 10^{-30} \mu$ [au], W [J] = $4.3598 \times 10^{-18} W$ [au], χ [$C^2 m^2 kg^{-1}$ = J T^{-2}] = $7.889 \times 10^{-29} \chi$ [au]. The water molecule is placed in the yz plane, z is the molecular axis. A/E the analytical derivative and excitation calculations.
[a] Ref. [11]. [b] Ref. [12].

basis sets, to achieve the best compromise between accuracy and computer cost. From this perspective the 6-31G** basis set can be thought of as a medium case. Calculations done with more sophisticated bases are rarely the first choice for big organic molecules, as far as the accuracy of the results is sufficient for simulations of molecular spectra, for example [13]. It is apparent from Table 1, that the 6-31G** basis is not sufficient for the determination of the magnitude of the polarizability, since all the calculations underestimate the mean value ($\| \alpha \|$) by about 40%. Also the ratio of the x, y and z components (in reality about 1:1:1, if the B3LYP/AUG-cc-pVTZ calculation is taken as a reference) is calculated rather incorrectly as 1:2:2. Such a result can still be usable if one is interested in the relative values of polarizabilities for different molecules or in a coordinate dependence of the tensor. Within a given basis set, the DFT approximation lead to results consistently better than the HF calculation. A less advanced LSDA [10] DFT approach was also tested using the 6-31G** basis; the results do not deviate substantially from those obtained with the B3LYP functional. More significantly, with respect to the aim of this study, the excitation calculation gives results consistently better than the AD calculations. This has an important implication for practical modelling, since the EXC scheme is much faster than the AD calculations. For example, the B3LYP/6-31G** Gaussian 94 calculation of the water polarizability takes 7 minutes on an IBM/RS-6000 workstation. A single-point energy calculation takes 50 seconds under the same conditions. The computer demands of the single point and EXC calculations are almost the same (!), because the calculation of the one-electron integrals (needed additionally for polarizability calculation, see Eq. (11)) takes a negligible time if compared to the time of the full SCF cycle, limited by the two-electron integral evaluation and by the numerical integrations required for the DFT functionals. However, as pointed out above, a lower efficiency was achieved in the present implementation of the excitation scheme (about 3 min of the total CPU time for this case).

Fig. 1 shows the overall dependence of the mean polarizability on the basis size and computational level. Clearly, the primary limitation comes from the basis set used while the EXC calculation gives simi-
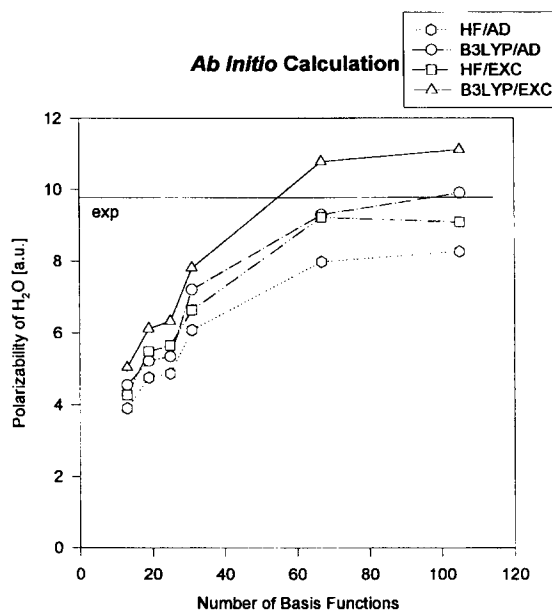

Fig. 1. The dependence of polarizability on basis set size.

lar results as the AD technique if used with the same basis. The HF/EXC calculation converges faster to an infinite basis set limit than the HF/AD calculation. For the DFT calculation the EXC results are closer to the experiment for the first four basis sets, the EXC limit value for an infinite basis (if such a limit exists) seems to be higher than the limit for the AD calculation. Earlier observations suggest that the BLYP/AD calculations slightly overestimate the water polarizability for large bases [14] and this error is probably bigger for the EXC approach. Thus part of the success of the DFT computations in small basis sets can be attributed to a cancellation of errors.

Although the EXC paramagnetic susceptibility is consistently by about 10% lower than the AD value (see Table 1), this difference is comparable with the influence of the basis set size. For example, the magnitude of $\chi^{(p)}$ calculated with the 6-31 + +G** basis set is about 80 (74) % of the experimental value for the AD (EXC) procedure. If the basis set is approximately doubled, 89 and 80% of the target value ($\chi^{(p)} = 0.316$) is achieved by the AD and EXC calculation, respectively. Thus both approaches can be used for the susceptibility evaluation, the AD

scheme being slightly more accurate while the EXC computation is much faster.

A schoolbook example of the demands of polarizabilities, susceptibilities, dipole moments and energies on the size of basis set is shown in Table 1. The increase in the number of basis functions from 13 to 105, which increases the real CPU time approximately 400 times, leads to a 0.1% decrease in the total energy, 22% change in the dipole moment (first energy derivative) while the polarizability and susceptibility (second energy derivatives) increases by about 110% and 60%, respectively.

Finally, as a more 'practical' example the pyridine and pyrimidine molecules were chosen for the calculation of the same properties as calculated for the water molecule. These molecules with large polarizabilities which are relatively easy to measure can be conveniently used as benchmarks for calculational studies [15]. The results summarized in Table 2 generally correspond to the trend observed for the water calculation. Given a basis set size the DFT results are better than the HF results. The EXC values of the polarizability results are more realistic than those obtained by the AD calculations, but in many cases the experimental value lies between the AD and EXC results. An infinite basis set limit for

the B3LYP/EXC calculation is probably higher than the experimental value, nevertheless the results are still superior to the AD calculation for the 6-31G** basis set.

For the paramagnetic susceptibilities the experimental data is not available. Unlike the case for water, the EXC calculations yield usually bigger susceptibilities than the AD computations. Also, their values seems to be less sensitive on the basis set size in terms of relative changes.

Further improvement of the excitation scheme calculation is straightforward for the HF level of computations, where configuration interaction, multiple excitations or many body perturbation theory can be used for more realistic models of the molecular wavefunctions and energies.

Various modifications of the EXC method (known as the sum over states (SOS) approach in perturbation theory) are proposed for DFT calculations of NMR tensors in Ref. [18]. DFT, at least in its present form, is not a self-consistent variational theory and thus does not offer a universal treatment of excited states. Hence we prefer modelling based on the singly-excited state space based on the Kohn–Sham determinant. Although such a single-determinant approach may seem too crude for a post-HF calcula-

Table 2
Ab initio calculations of pyridine and pyrimidine polarizabilities and magnetic susceptibilities

Basis	4-31G		6-31G**		EXP
Level	HF	B3LYP	HF	B3LYP	
Pyridine					
α_{xx} A/E	63.1/87.6	66.7/114.9	65.2/90.8	68.9/90.9	80.2 [a]
α_{yy} A/E	16.5/20.2	17.1/32.7	20.9/29.8	24.1/28.8	39.0 [a]
α_{zz} A/E	57.2/81.2	60.0/92.6	59.9/84.5	62.6/86.1	73.2 [a]
$\|\alpha\|$ A/E	40.6/63.0	48.0/80.0	48.6/68.4	50.8/68.6	64.1 [a]
$\|\chi^{(P)}\|$ A/E	23.1/25.3	32.1/30.3	32.5/34.6	33.6/35.2	
W	− 246.3306	− 247.8814	− 246.7067	− 248.2926	
μ	1.030	0.967	0.909	0.859	0.872 [b]
Pyrimidine					
α_{xx} A/E	16.4/28.1	17.2/20.5	20.3/29.2	20.7/28.0	38.7 [c]
α_{yy} A/E	52.0/102.1	54.7/83.9	54.3/79.2	56.9/85.4	67.7 [c]
α_{zz} A/E	56.0/88.6	59.9/81.0	57.6/80.0	61.7/84.7	71.8 [c]
$\|\alpha\|$ A/E	41.5/72.9	44.0/61.8	44.1/62.8	46.4/66.0	60.6 [c]
$\|\chi^{(P)}\|$ A/E	23.1/29.2	31.4/24.2	31.3/33.4	32.5/33.6	
W	− 262.2862	− 263.9543	− 262.7003	− 264.32948	
μ	1.085	1.015	0.909	0.900	0.919 [b]

Symbols and units same as in Table 1.
[a] Refs. [15,16]. [b] Ref. [11]. [c] Refs. [15,17].

tion, it is actually much more appropriate for DFT theory than for the HF approximation: the Kohn–Sham Slater ground state determinant already includes the correlation energy. The DFT functional is supposed to provide the true ground state wavefunction. Moreover, only single excitations (states $|j\rangle$, see Eq. (6) and Eq. (7)) contribute to the polarizabilities, because the dipole moment is a one-electron operator [7]. Under such circumstances the HF-like energies given in Eq. (10) represent realistic estimates of the true excitation energies since the biggest Coulombic and kinetic part, determining about 90% of the energy, is calculated exactly and even the biggest part of the correlation energy (HF exchange terms) is included. Generally, however, the advantages of the excitation scheme presented above could stimulate further progress in the DFT description of excited states.

5. Conclusions

The excitation scheme can be used as a faster alternative to analytical derivative calculations of molecular electromagnetic properties. If calculations are done in incomplete, medium-sized basis sets, the accuracy of the two approaches is fully comparable not only for the HF calculations, but also for the hybrid DFT/HF Hamiltonian. For the DFT modelling more appropriate descriptions of the space of excited molecular states should lead to a further increase in the accuracy of the results.

Acknowledgements

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