20 June 2002

ELSEVIER

Chemical Physics Letters 359 (2002) 343–348

CHEMICAL
PHYSICS
LETTERS

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Molecular electric quadrupole moments calculated with matrix dressed SDCI

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Received 8 February 2002; in final form 1 May 2002

Abstract

We have calculated the molecular electric quadrupole moment (MEQM) for the set of molecules N_2, C_2H_2, CO, CO_2, CS_2, HF, and BH. We have used SR-SDCI and $(SC)^2$-SR-SDCI methods and we have compared our results with high-level theoretical ones, including FCI values for HF and BH, and with experimental values. The calculated MEQM provides a test of the effect that the energy converged $(SC)^2$ dressing method brings to the SDCI wavefunctions. The results suggest that the $(SC)^2$-SR-SDCI method can be a cost-effective and quite accurate method for the calculation of post-SCF effects on electric quadrupole moments. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The molecular electric quadrupole moment (MEQM) is a property of special importance for non-polar molecules, where it is the first non-zero electric moment. It determines, in these systems, the Coulomb interaction between the molecule and other molecules, or, in a more general way, with non-uniform external electric fields.

The MEQM can be determined directly from electric-field-gradient-induced birefringence (EFGB) [1,2] measurements. The EFGB is the anisotropy of the refraction index observed when plane-polarized light passes through a medium in a direction that is perpendicular to an applied external field gradient. Two effects originate the EFGB. The first one is the partial orientation in the molecules due to the interaction of the electric field gradient with the MEQM. The second one is related to changes in the effective polarizability induced by the field gradient. The first effect is temperature dependent and can be expressed in terms of the MEQM and the molecular electric-dipole polarizability. The second effect is independent of the temperature and is determined by higher order polarizabilities. The two effects can be separated by measuring at different temperatures.

However, the experimental procedure faces some difficulties and it cannot be applied to all systems. Hence, it is very common to perform measurements at a single temperature and to obtain therefore the MEQM by neglecting the

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PII: S0009-2614(02)00722-4

contribution of the second effect, which is of higher order and can be assumed to be less important. In the few cases when theoretical estimations of this hyperpolarizability term are available, they are used to get the experimental MEQM [3,4].

It is well known that the theoretical determination of the MEQM is difficult because the calculated values are very sensitive to the theory approach level [5]. It is then important to establish the accuracy of each theoretical approach for the calculation of this property. A convenient way to do this is to compare simultaneously to theoretical calculations of increasing accuracy and to experimental data as well. To compare to FCI results is convenient because they are exact for the basis set, even if the basis sets are small and physically poor.

In this study, we present an ab initio investigation of the MEQM for a series of small molecules. The set of molecules for which high-level calculations (noteworthy based in first-order CC energy derivatives [6]) and accurate experimental values are available is very reduced, so that the number of systems that can be studied as test calculations cannot be large. Our goal is to assess the adequacy of the size-consistent self-consistent single reference configuration interaction method, $(SC)^2$-SR-SDCI, for the calculation of this property. A number of works have shown the noticeable improvement that the $(SC)^2$ matrix dressing procedure provides to the SDCI energy eigenvalues. In this work, we try to test the effect on the quality of the SDCI wavefunction brought about by the dressing method by means of the evaluation of an electric molecular property.

2. Definitions and computational details

The traceless quadrupole moment as defined by Buckingham [1,7,8] is calculated as

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i Q_i(3r_{i\alpha}r_{i\beta} - \delta_{\alpha\beta}r_i^2), \tag{1}$$

where the summation runs over all the particles (nuclei and electrons) with charge Q_i and position vectors r_i. The Greek indices denote the Cartesian coordinates x, y and z. In the case of linear molecules the quadrupole moment tensor is diagonal and $\Theta \equiv \Theta_{zz} = -2\Theta_{yy} = -2\Theta_{xx}$. Only one component requires to be calculated but, in order to test the program code,the expectation value of each component has been independently calculated from the one-electron integrals and the first-order density matrix of either the SDCI or $(SC)^2$-SDCI ground states.

The geometries as well as the basis sets have been taken from the reference calculations. All molecules have been calculated with the aug-cc-pVTZ basis set [9–11]. This basis set is well known for its physical flexibility and consequently it is of common usage. Data from the literature for this basis set in the different reference systems are easily available. Other basis sets have been used when required, as it is indicated in the text. The diffuse functions are relevant due to the quadratic dependence of the MEQM operator on the electron position coordinates.

A recent benchmark study of the MEQM of HF and BH [12] using FCI and other size-consistent correlation methods such as MP2 and some CC approaches has shown that the quality of the results can be ordered, in decreasing order of accuracy, as CCSDT, CCSD(T), and, far apart, MP2 and CCSD. Hence, it seems convenient to use CCSDT or CCSD(T) values as benchmark references when FCI results are not available.

The size-consistent self-consistent CI, or simply $(SC)^2$, approach is a method for correcting the improper scaling of the truncated CI method with the number of correlated electrons (size-extensivity error). The method is formulated as a matrix dressing procedure [13] where the CI matrix is modified by a diagonal shifting Δ_{ii} added to the SDCI matrix. The Δ_{ii} shifts depend on the coefficients c_j of diexcited determinants that satisfy some conditions in respect to ϕ_i. Hence, an iterative self-consistent convergence is required.

The theoretical foundations of the $(SC)^2$ method, its implementation for excited states and other technical details have been thoroughly discussed elsewhere [14,15]. Let us mention here that other than simply correct at higher orders the lack of size-extensivity of the CI calculation by means of the cancellation of non-linked diagrams, the $(SC)^2$ method introduces some renormalization effects in both the wavefunction and the energy value. In particular, infinite summations of some series of exclusion principle violating (EPV) diagrams are taken into account. It has been verified [13] that $(SC)^2$-SDCI energies closely follow the CCSD dissociation curve for a single-bond breaking. However, the present work provides the first test that directly implies the effects on the wavefunction of the $(SC)^2$ dressing by looking at the effect on a molecular property. In principle, one could expect to have MEQM close to (perhaps a bit poorer than) the corresponding CCSD ones. However, as the results in the next section show, this is not always the case.

All the calculations have been performed with the PROP [16] code that has been added to the CASDI [17] programs chain. The SCF wavefunction and one-electron integrals have been calculated with the MOLCAS programs system [18]. In all calculations the quadrupole moment is relative to the centre of mass. The vibrational averaging has not been taken into account, so that care has been taken to always comparing to reference calculations that did not include it.

Atomic units are used throughout this Letter. The next conversion factors have been used: Length, 1 $a_0 = 0.529177249$ Å $= 0.529177249 \times 10^{-10}$ m, dipole moment, 1 $ea_0 = 2.541804$ Debye $= 8.478358 \times 10^{-30}$ C m, quadrupole moment, 1 ea_0^2 $= 1.345033$ Debye Å $= 4.486554 \times 10^{-40}$ C m^2.

3. Results and discussion

3.1. The quadrupole moment of N_2, acetylene and carbon monoxide

Table 1 presents the results for three cases where the $(SC)^2$ quadrupole moments lie close to the respective CCSD ones. The reference theoretical results for the same basis set are also reported, as well as the experimental values, and the best available theoretical estimates using CC wavefunctions along with the largest basis sets.

N_2 has been calculated at the experimental equilibrium geometry ($R_{N-N} = 2.07432a_0$) [19]. The calculation conditions for C_2H_2 and CO molecules are those of the reference calculations [20–22]. Hence, the experimental equilibrium geometries have been taken, $R_{C-C} = 2.27351a_0$, $R_{C-H} = 2.00719a_0$, and $R_{C-O} = 2.1322a_0$. According to the reference calculations [22], the core electrons of CO have been kept frozen during the post-SCF steps.

The systems reported in Table 1 are triply bonded molecules, and the effects of correlation upon the single reference Hartree–Fock determinant are expected to be large. SDCI and MP2 must be clearly insufficient approaches and this is the case for C_2H_2 and CO, but the SDCI result is surprisingly good for N_2, where it lies close to the mean experimental values. In the three cases, the

Table 1
Molecular electric quadrupole moment of N_2, C_2H_2 and CO (atomic units)

Method	N_2	Reference	C_2H_2	Reference	CO	Reference
SCF			5.4631	[21]	−1.5457	[22]
SR-SDCI	−1.0638	PROP[a]	5.1127	PROP[a]	−1.5244	PROP[a]
$(SC)^2$-SR-CI	−1.1191	PROP[a]	4.9165	PROP[a]	−1.4888	PROP[a]
MP2			4.8424	[21]	−1.5093	[22]
CCSD	−1.1205	[20]	4.9086	[21]	−1.4764	[22]
CCSD(T)			4.8464	[21]	−1.4807	[22]
Best theor.	−1.1280	[20][b]	4.8587	[21][c]	−1.4626	[22][c]
Exp.	−1.09 ± 0.07	[19][d]	4.55 ± 0.2	[20][d]	−1.44 ± 0.3	[23][d]
	−1.05 ± 0.06	[19][d]	4.57 ± 0.1	[20][d]	−1.4 ± 0.1	[23][d]
			4.66	[20][d]	−1.5 ± 0.7	[23][d]

[a] This work.

[b] CCSD; t-aug-cc-pVTZ.

[c] CCSD(T); t-aug-cc-pVQZ.

[d] And references therein.

$(SC)^2$-SR-SDCI values are closer to the best CC values than the SDCI values but farther than the CCSD ones. This does not necessarily imply that the $(SC)^2$-SR-SDCI values are worse than the CCSD ones if compared to the experimental values.

3.2. The quadrupole moment of carbon dioxide and carbon disulphide

The equilibrium distance for CO_2 is $R_{C–O} = 2.19169a_0$ [8] and for CS_2 is $R_{C–S} = 2.93391a_0$ [8]. The results for both linear systems at these geometries are reported in Table 2.

Understanding the $(SC)^2$-SR-SDCI values for the MEQM of CO_2 and CS_2, as compared to the CCSD ones, is less simple than it was suggested by the values discussed in Table 1. For CO_2 the CCSD absolute value falls in the higher limit of the experimental error interval. The SDCI absolute value is too high and the MP2 value, too small. However, the $(SC)^2$-SR-SDCI value is in good agreement with the best available theoretical estimate and well in accord to the experimental value. Note that in both systems, CO_2 and CS_2, the correction due to the $(SC)^2$ dressing improves the values of the SDCI starting point. One can wonder why the $(SC)^2$-SR-SDCI calculation with aug-cc-pVTZ basis set provides the best theoretical result for the MEQM of CS_2 as compared to the experiment. This is surely the result of a fortuitously well placed SDCI starting value plus the $(SC)^2$ correction performing a correct job, as it does in the other systems studied yet. Note that the value of CCSD(T) with the same basis set are even worse than the SCF values, and very large basis sets are required to get higher MEQM values from CC wavefunctions. This fact had been noted by Coriani et al. [8] who have found difficult to give estimates of the accuracy and precision of their CCSD(T) results for this molecule. It may be noted that the present $(SC)^2$ values for the MEQM are the only theoretical values that enter into the range of error of two the three independent reported measurements.

3.3. The quadrupole moment of HF and BH

These two small systems give to us the possibility of evaluating the dressing effects on the MEQM values by comparing to the FCI results of Halkier et al. [12]. The calculations have been performed at the same geometry ($R_{H–F} = 1.7329a_0$ and $R_{B–H} = 2.3289a_0$) and the same basis set (aug-cc-pVDZ). The 1s(B) and 1s(F) electrons have been removed from the correlation treatment. The results for Θ_{zz} are reported in Table 3.

As it is expected, the dressed CI results show smaller deviation from the exact ones than the conventional SDCI results. However, the accuracy

Table 2
Molecular electric quadrupole moment of CO_2 and CS_2 (atomic units)

Method	CO_2	Reference	CS_2	Reference
SCF	−3.82061	[8]	2.30587	[8]
SR-SDCI	−3.457023	PROP[a]	2.422081	PROP[a]
$(SC)^2$-SR-SDCI	−3.142467	PROP[a]	2.487968	PROP[a]
MP2	−3.09018	[8]	2.29274	[8]
CCSD	−3.30098	[8]	2.32272	[8]
CCSD(T)	−3.19229	[8]	2.26536	[8]
Best theor.	−3.16886	[8][b]	2.33847	[8][c]
Exp.	−3.19 ± 0.13	[8][d]	2.56 ± 0.11	[8][d]
	−3.18 ± 0.14	[8][d]	2.67 ± 0.13	[8][d]
			3.12 ± 0.67	[8][d]

[a] This work.

[b] CCSD(T); t-aug-cc-pVQZ.

[c] CCSD(T); d-aug-cc-pV5Z.

[d] And references therein.

Table 3
Calculated MEQM for the HF and BH molecules with the aug-cc-pVDZ basis set

	Θ_{zz}(HF)	Θ_{zz}(BH)
SCF[a]	0.03867	−0.29458
MP2[a]	0.02399	−0.18476
MP3[a]	0.00914	−0.12543
MP4[a]	0.00258	−0.08610
CCSD[a]	0.00598	−0.01974
CCSD(T)[a]	0.00062	−0.00574
CCSDT[a]	0.00020	−0.00263
SR-SDCI[b]	0.00418	−0.01745
$(SC)^2$-SR- SDCI[b]	0.00271	−0.01354
FCI[a]	1.69586	−2.40371

FCI results and deviations from FCI results (e.g., $\Theta_{\mathrm{model}}-\Theta_{\mathrm{FCI}}$) (atomic units).

[a] Results obtained from [12].

[b] This work.

relative to FCI of the SR-SDCI values is unexpected, the deviations being smaller than for the CCSD values, and once again, this contributes to improve the quality of the $(SC)^2$-SR-SDCI values.

4. Summary and conclusions

The main goal of the present work is to provide, for the first time and by means of a molecular electronic property, a quantitative evaluation of the improvement that the $(SC)^2$ dressing method brings to the SDCI wavefunctions. The results, still limited in their number, points to the reliability of the $(SC)^2$-SR-SDCI method using the aug-cc-pVTZ basis set and experimental equilibrium geometries for the calculation of MEQM. The values of Θ are comparable to the CCSD ones in some cases, but this cannot be assumed as guaranteed. The results are in other cases closer to the best CCSD(T) ones and in good agreement with the experimental values. A number of factors that have been put aside can help to understand these facts. It is important to note that expectation values can be only reliable, if compared to energy derivative results, provided that the wavefunction is accurate enough. It is clear then that the $(SC)^2$-SR-SDCI are better than the SDCI ones, but both of them can be consistently improved going towards a MR-SDCI description. Other aspects to keep in mind are the use of experimental equilibrium geometries instead of the $(SC)^2$-SR-SDCI ones, the absence of rovibrational corrections, and the limited extent of the diffuses manifold in the basis set. The quality of the SDCI results seems also to play a relevant role in the success of the $(SC)^2$-SR-SDCI results. The influence of the basis set in the MEQM calculations using the $(SC)^2$ approach as well as the use of MR-SDCI wavefunctions as starting point for the dressing will be the matter of a future work.

Acknowledgements

Financial support from the projects BQU2001-2935-C02-01 of Spanish DGI and DGEUI (Generalitat Valenciana Projects INF00-15 and INF01-051) is acknowledged. J.M.J.H. acknowledges the Spanish MEC for a FPU grant.

References

[1] A.D. Buckingham, J. Chem. Phys. 30 (1959) 1580.

[2] J.N. Watson, I.E. Craven, G.L.D. Ritchie, Chem. Phys. Lett. 274 (1997) 1.

[3] R.I. Keir, D.W. Lamb, G.L.D. Ritchie, J.N. Watson, Chem. Phys. Lett. 279 (1997) 22.

[4] C. Graham, D.A. Imrie, R.E. Raab, Mol. Phys. 93 (1998) 49.

[5] R. Glaser, Z. Wu, M. Lewis, J. Mol. Struct. 556 (2000) 131.

[6] A. Halkier, H. Koch, O. Christiansen, P. Jorgensen, T. Helgaker, J. Chem. Phys. 107 (1997) 849.

[7] A.D. Buckingham, Adv. Chem. Phys. 12 (1967) 107.

[8] S. Coriani, A. Halkier, A. Rizzo, K. Ruud, Chem. Phys. Lett. 326 (2000) 269.

[9] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.

[10] R.A. Kendall, T.H. Dunning, R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.

[11] D.E. Woon, T.H. Dunning, J. Chem. Phys. 100 (1994) 2975.

[12] A. Halkier, H. Larsen, J. Olsen, P. Jorgensen, J. Gauss, J. Chem. Phys. 110 (1999) 734.

[13] J.P. Daudey, J.L. Heully, J.P. Malrieu, J. Chem. Phys. 99 (1993) 1240.

[14] J.L. Heully, J.P. Malrieu, I. Nebot-Gil, J. Sánchez-Marín, Chem. Phys. Lett. 256 (1996) 589.

[15] J. Sánchez-Marín, I. Nebot-Gil, J.P. Malrieu, J.L. Heully, D. Maynau, Theor. Chim. Acta 95 (1997) 215.

[16] J.M. Junquera-Hernández, J. Sánchez-Marín, D. Maynau, PROP, University of Valencia (Spain) and University of Toulouse (France), 2000.

[17] D. Maynau, N. Ben Amor, J.V. Pitarch-Ruíz, CASDI, University of Toulouse (France), 1999.
[18] K. Andersson, et al., MOLCAS, Version MOLCAS 4, 4th edn., University of Lund, Sweden, 1997.
[19] D.B. Lawson, J.F. Harrison, J. Phys. Chem. A 101 (1997) 4781.
[20] S. Coriani, C. Hättig, P. Jorgensen, A. Rizzo, K. Ruud, J. Chem. Phys. 109 (1998) 7176.
[21] A. Halkier, S. Coriani, Chem. Phys. Lett. 303 (1999) 408.
[22] A. Rizzo, S. Coriani, A. Halkier, C. Hättig, J. Chem. Phys. 113 (2000) 3077.
[23] G. Maroulis, Chem. Phys. Lett. 334 (2001) 214.