

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244132832>

A comparison between DFT and other ab initio schemes on the activation energy in the automerization of cyclobutadiene

ARTICLE *in* CHEMICAL PHYSICS LETTERS · FEBRUARY 2000

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(99)01399-8

CITATIONS

20

READS

7

3 AUTHORS, INCLUDING:



Angel J Pérez-Jiménez

University of Alicante

71 PUBLICATIONS 1,274 CITATIONS

SEE PROFILE

A comparison between DFT and other ab initio schemes on the activation energy in the automerization of cyclobutadiene

J.C. Sancho-García^{*}, A.J. Pérez-Jiménez, F. Moscardó

Departamento de Química Física, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

Received 2 November 1999; in final form 7 December 1999

Abstract

The influence of the multireference character in the transition state for the automerization reaction of cyclobutadiene is considered. We have analyzed two forms of taking into account this effect: either by the use of two-body density functionals or traditional density functional theory (DFT) correlation functionals conveniently modified. Comparison has also been made with conventional density functional theory Kohn–Sham (DFT–KS) [15] approaches. It is shown that only when the aforementioned multideterminantal character is included in the computational scheme is the activation energy in accord with accurate benchmark calculations. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Being an antiaromatic system, the chemistry of cyclobutadiene has been of great interest for both experimental [1] and theoretical chemists [2–4]. It has been clearly shown that the detailed understanding of the structure and spectroscopy of cyclobutadiene needs a close collaboration between theory and experiment. Cyclobutadiene is an extremely unstable molecule, and due to this fact experimental data on this system have been difficult to obtain. In recent years controversy has surrounded the exact structure and mechanism of automerization of this molecule [5,6], and the experimental difficulties make theory an attractive alternative for studying these systems. In the absence of reliable experimental data it is necessary to carry out high-level ab initio calculations

in order to achieve a proper description of its chemical properties. For example, quantitative interpretation of the kinetics of automerization, or of the splitting of the ground vibrational state, requires knowledge of an accurate value for the automerization barrier.

The automerization of cyclobutadiene, interconversion of two rectangular structures of D_{2h} symmetry through a square transition state of D_{4h} symmetry, seems to be one of the most clear cases where inclusion of nondynamic correlation effects is vital because of the degeneracy in the square structure. In spite of the instability expected by the Hückel $4n + 2$ rule, it has been well established that the ground state of cyclobutadiene is a singlet with rectangular equilibrium structure. For this structure a single-reference approach is adequate for an accurate treatment since it may be treated as a well-behaved closed-shell molecule. On the other hand, the degeneracy of π orbitals at square geometries makes the single-reference approaches unsuitable. In this sys-

^{*} Corresponding author. Fax: +34-65903537; e-mail: juancar@fisic1.ua.es

tem the highest occupied molecular orbital is a pair of degenerate π (e_g) orbitals housed with two electrons. This two-determinantal character calls for using a multiconfigurational wavefunction to describe the ground state singlet, or a methodology able to include both the nondynamic and dynamic effects in order to take into account this nature. Nowadays the most prominent methods capable of describing both effects are not routinely implemented. Several accurate calculations on these systems have been reported in the literature [2–4], using a multi-reference extension of the successful and well-known coupled-cluster (CC) methods [7–10], which can be used as a benchmark. In spite of the results reached, a more economic method, without losing efficacy, is desired, including a balanced treatment of both dynamic and nondynamic correlation effects.

The aim of the present work is to analyze the results obtained using such a method and to compare them with those obtained by a traditional DFT approach. A brief description of the methodology employed is presented in Section 2, as well as the technical details of the calculations. The results are summarized and discussed in Section 3 and the main conclusions are drawn in Section 4.

2. Methodology

In the present study two types of calculations are performed. The first set comprises traditional DFT–KS calculations with some of the most widely used functionals for exchange and correlation; namely the non-local correlation functionals of Lee–Yang–Parr [16], Perdew [17], and Perdew–Wang [18], combined with the exchange functional of Becke [19]. The calculations are labeled BLYP, BP86 and BPW91 respectively. Finally, the B3LYP hybrid method [20] has also been considered. A second type of calculations has been fulfilled in which the energy is evaluated in two stages. First of all, a zero-order energy is obtained by both unrestricted Hartree–Fock (UHF) and multiconfigurational calculations of the generalized-valence-bond type with perfect-pairing (GVB) [11]. In the next step the correlation energy is calculated by a correlation energy functional, so that the total energy may be written as:

$$E = E_0 + E_c[\rho^0, (\rho_2^0)], \quad (1)$$

where E_0 is the UHF or GVB energy, and $E_c[\rho^0, (\rho_2^0)]$ is the remaining correlation energy, being ρ^0 the UHF or GVB density while ρ_2^0 represents the two-body density. The notation $E_c[\rho^0, (\rho_2^0)]$ has been introduced to distinguish between correlation density functionals which only depend on ρ^0 ($E_c[\rho^0]$) from two-body density functionals which also depends on ρ_2^0 ($E_c[\rho^0, (\rho_2^0)]$). While conventional DFT functionals may fail to describe the square structure, due to the degeneracy exhibited, a more elaborated methodology is necessary in order to represent properly the two-determinantal character of this molecule. The situation can be greatly improved with the use of two-body density functionals developed in our group [12]. Since they depend not only on ρ^0 but also in ρ_2^0 they are not restricted to a one-determinant wavefunction as a reference and, consequently, they can give accurate results for the energetical magnitude studied here. These functionals have provided very good results in previous applications [13,14], solving satisfactorily problems where a improved wavefunction, better than HF, is needed. Two of these functionals, denoted as MPJ1 and MPJ5, are used along this work. For their detailed expression see Ref. [12].

On the other hand Ref. [21] presents an approximate way of incorporating the $\rho_2^0(\mathbf{r})$ dependence in the density functionals for the correlation energy, by means of the relations

$$\rho'_\alpha(\mathbf{r}) + \rho'_\beta(\mathbf{r}) = \rho^0(\mathbf{r}) \quad (2)$$

$$\rho'_\alpha(\mathbf{r})\rho'_\beta(\mathbf{r}) = \rho_2^0(\mathbf{r}) \quad (3)$$

where, now, $\rho^0(\mathbf{r})$ and $\rho_2^0(\mathbf{r})$ correspond to a multi-determinantal wavefunction, being $\rho'_\alpha(\mathbf{r})$ and $\rho'_\beta(\mathbf{r})$ the new spin densities to use in a density functional. This transformation allows us to extend the applicability of density functionals to a wavefunction other than HF, correcting the deficiencies of the energy functionals characteristic of DFT. For testing the validity of this approximation we have selected the Vosko–Wilk–Nusair [22], Perdew [17] and Becke [23] correlation energy functionals. The corresponding calculations have been denoted VWN(mod)^{GVB}, P86(mod)^{GVB} and Becke(mod)^{GVB}.

All the calculations have been performed using the correlation-consistent basis set cc-pVXZ (X = D, T) developed by Dunning and co-workers [24].

Table 1

Energies (in au) of the rectangular and square structures of cyclobutadiene and the automerization barrier (in kcal/mol). Basis set employed: cc-pVDZ

Method	Rectangular ^a	Square ^b	ΔE
HF	– 153.651 959	– 153.603 943	30.2
LYP(UHF)	– 154.561 086	– 154.513 786	29.7
P86(UHF)	– 154.635 792	– 154.589 152	29.3
PW91(UHF)	– 154.618 233	– 154.571 589	29.3
MPJ1(UHF)	– 154.755 865	– 154.708 068	30.0
MPJ5(UHF)	– 154.773 336	– 154.725 651	30.0
BLYP	– 154.612 647	– 154.572 158	25.4
BP86	– 154.684 344	– 154.644 517	25.0
BPW91	– 154.668 636	– 154.628 863	25.0
B3LYP	– 154.685 188	– 154.644 855	25.3
GVB	– 153.663 783	– 153.646 349	11.0
MPJ1(GVB)	– 154.763 949	– 154.743 561	12.8
MPJ5(GVB)	– 154.781 101	– 154.760 556	12.9
VWN(mod) ^{GVB}	– 154.579 960	– 154.560 053	12.5
P86(mod) ^{GVB}	– 154.645 579	– 154.627 848	11.1
Becke(mod) ^{GVB}	– 154.597 901	– 154.578 974	11.9
Reference			6.4

^a The geometry assumed (in bohr): 1.495 907, 1.289 171 for carbon and 2.957 930, 2.754 310 for hydrogen.

^b The geometry assumed (in bohr): 1.377 714 for carbon and 2.834 307 for hydrogen.

These are examples of hierarchical sequences of one-electron basis sets, providing a systematic convergence towards the basis set limit [25,26], and it is demonstrated that an improvement is obtained increasing the level of hierarchy in the series [28]. The effect of the basis set has been investigated carrying out three sets of calculations at all levels of theory included in this work: (1) one set with all the electrons correlated in the cc-pVDZ basis set; (2) one set with all the electrons correlated in the cc-pVTZ basis; and (3) one set extrapolating the correlation energy to the basis set limit, following the scheme proposed in Ref. [25], to minimize the effect of the basis set in the magnitude of the barrier. For an excellent review of other extrapolation formulas a recent study is recommended [27]. The molecular geometries used are those specified in Ref. [4], which have also been detailed in the footnotes of Table 1. When a monodeterminantal wavefunction was considered the square structure was slightly distorted from the D_{4h} symmetry to invoke the ‘rectangular’ D_{2h} molecular orbitals (for details, see Refs. [29] and [30]). To determine the effect of the geometry relaxation on the computed energy quantities we also

perform, with the cc-pVDZ basis set, the geometry optimizations of both structures at MPJ1,5 (GVB) level (which means to use a GVB wavefunction in conjunction with a two-body density functional in Eq. (1)), and at all DFT levels: BLYP, BP86, BPW91 and B3LYP. The geometrical parameters are shown in Table 3, as well as the optimized energy and the respective automerization energies. In all the cases the exterior angle between the C–H and the longer

Table 2

Energies (in au) of the rectangular and square structures, at reference geometries, using a UHF and a GVB wavefunction respectively, and automerization barrier (in kcal/mol). Basis set employed: cc-pVDZ

Method	Rectangular	Square	ΔE
MPJ1	– 154.755 865	– 154.743 561	7.7
MPJ5	– 154.773 336	– 154.760 556	8.0
VWN(mod)	– 154.570 669	– 154.560 053	6.7
P86(mod)	– 154.635 792	– 154.627 848	5.0
Becke(mod)	– 154.589 996	– 154.578 974	6.9
Reference			6.4

Table 3

The cc-pVDZ optimized geometries (bond lengths in Å), energies (in au) and automerization barrier (in kcal/mol)

Method	Rect.				Square			ΔE
	$R_{C=C}$	R_{C--C}	R_{C--H}	energy	R_{C--C}	R_{C--H}	energy	
HF	1.5686	1.3230	1.0795	–153.657 062	1.4314	1.0778	–153.607 172	33.4
GVB	1.5806	1.3446	1.0797	–153.666 667	1.4336	1.0796	–153.648 792	11.2
BLYP	1.5961	1.3493	1.0976	–154.613 263	1.4605	1.0956	–154.572 216	25.8
BP86	1.5884	1.3489	1.0992	–154.684 918	1.4560	1.0972	–154.644 666	25.3
BPW91	1.5855	1.3472	1.0972	–154.669 270	1.4533	1.0952	–154.628 996	25.3
B3LYP	1.5812	1.3389	1.0904	–154.686 647	1.4453	1.0888	–154.645 370	25.9
MPJ1(GVB)	1.5808	1.3366	1.0692	–154.770 514	1.4192	1.0671	–154.750 121	12.8
MPJ5(GVB)	1.5800	1.3359	1.0679	–154.788 518	1.4167	1.0648	–154.768 140	12.8
Reference	1.5832	1.3644	1.0953		1.4581	1.0901		

C–C bonds, in the rectangular molecule, was 134.9° so that it is not included in the table.

The suite of programs used for the calculations includes the GAUSSIAN 98 package [31] for DFT calculations, and a modified version of GAMESS [32] developed in our group which allows us to handle correlation functionals combined with a multiconfigurational wavefunction. The correlation energy was evaluated by numerical integration in both cases [33].

3. Results and discussion

In Table 1 we report the results obtained using the methodologies considered in the previous section when the cc-pVDZ basis set is employed. The geometry used for both the D_{2h} and D_{4h} states is that detailed in the table. The last one was obtained by an accurate multireference CC approach [34]. A comparison of the multireference geometries with the data obtained with single-reference methods was analyzed in Ref. [4]. The reference values for the activation energy have been taken from Ref. [4]. From the results exposed in the table it is clear the decisive importance of considering the multideterminantal character of the transition state. In this sense, the value for the barrier is overestimated by a factor of 4–5 for both DFT (entries BLYP, BP86, BPW91 and B3LYP) and the monodeterminantal calculations using Eq. (1) (entries labeled UHF). However, the use of Becke exchange seems to slightly improve them. Once the aforementioned multideterminantal character is considered in the calculations, either by

the two-body density functionals MPJ1 and MPJ5 or by the approximation given by Eqs. (2) and (3), the activation energy is lowered considerably, giving much more realistic values. In particular, the approximate form of introducing the multideterminantal character on density functionals given by Eqs. (2) and (3) seems to work quite well. An important fact is that, while the transition state description needs, at least, two determinants to take into account the degeneracy of the system, the rectangular ground state can be described fairly well by just one configuration. In this sense we have performed a second set of calculations in which the energy of the D_{2h} ground state is obtained from Eq. (1) using a UHF wavefunction as a reference, adding the correlation energy functionals MPJ1, MPJ5, VWN, P86 and Becke. The energy of the transition state has been calculated adding the MPJ1 and MPJ5 two-body density functionals and the VWN, P86 and Becke correlation density functionals with the corrections in Eqs. (2) and (3) to a GVB reference wavefunction. The results are summarized in Table 2, from which it can be seen the overall improvement in the activation energy caused by the non-overstabilization of the ground state implicit in the GVB plus dynamic correlation calculations¹.

In Table 3 we show the results obtained when a geometry optimization is done, both on the ground

¹ The lack of continuity implied by the use of different SCF calculations for each of the two stationary points precludes this approach in a scan of the potential energy surface.

and transition states, using the traditional DFT schemes and the MPJ1,5 (GVB) approaches. The results point out two interesting facts: first, that the activation energy has a low geometry dependence in the precision range studied here, and validates the approach used in obtaining the results of Tables 1 and 2. Therefore, in the following calculations the reference geometries, those of Ref. [4], will be used. Secondly, that the DFT C–C and C–H distances are in very good agreement with the reference values [4]. The situation is less favorable for the MPJ1, MPJ5 (GVB) cases: the C–H distance is always underestimated, as occurs also with the C–C distance of the square structure. In any case, the activation energy provided by the DFT calculations still is much higher than the more accurate values reached by the MPJ1, MPJ5 (GVB) calculations.

In order to fix the basis set dependence on the results, we have performed the same calculations as before with the cc-pVTZ basis set, reporting the corresponding activation energies in Tables 4 and 5. The increase in the barrier closely follows that found in the reference calculations, which is in order of 0.6 kcal/mol with respect to the cc-pVDZ results. Apart from this overall effect the tendencies and facts

Table 4

Energies (in au) of the rectangular and square structures, at reference geometries, of cyclobutadiene and the automerization barrier (in kcal/mol). Basis set employed: cc-pVTZ

Method	Rectangular	Square	ΔE
HF	–153.690103	–153.642695	29.8
LYP(UHF)	–154.599474	–154.552650	29.4
P86(UHF)	–154.670787	–154.624439	29.1
PW91(UHF)	–154.652781	–154.606327	29.2
MPJ1(UHF)	–154.793825	–154.746441	29.8
MPJ5(UHF)	–154.811005	–154.763689	29.7
BLYP	–154.663880	–154.627859	22.6
BP86	–154.728120	–154.687951	25.2
BPW91	–154.711204	–154.671041	25.2
B3LYP	–154.731499	–154.691253	25.3
GVB	–153.701509	–153.683186	11.5
MPJ1(GVB)	–154.801623	–154.780408	13.3
MPJ5(GVB)	–154.818513	–154.797149	13.4
VWN(mod) ^{GVB}	–154.617692	–154.596902	13.1
P86(mod) ^{GVB}	–154.680318	–154.661672	11.7
Becke(mod) ^{GVB}	–154.633654	–154.613960	12.3
Reference			7.0

Table 5

Energies (in au) of the rectangular and square structures, at reference geometries, using a UHF and a GVB wavefunction respectively, and automerization barrier (in kcal/mol). Basis set employed: cc-pVTZ

Method	Rectangular	Square	ΔE
MPJ1	–154.793825	–154.780408	8.4
MPJ5	–154.811005	–154.797149	8.7
VWN(mod)	–154.608732	–154.596902	7.4
P86(mod)	–154.670787	–154.661672	5.7
Becke(mod)	–154.626026	–154.613960	7.6
Reference			7.0

discussed so far for the cc-pVDZ basis set are maintained when the basis set is changed. Hence, extension of the basis set seems to be more important than optimizing the geometry with the new basis set. Thus, applying the extrapolation procedure of Ref. [25], to account for the basis set limit, we have obtained the values listed in Table 6. We are fully aware of the limitations of such an extrapolation scheme since the cc-pVDZ and cc-pVTZ basis set are not totally saturated, and the respective error in the extrapolation may be large, but the extrapolation procedure used has the advantage of requiring only two calculated correlation energies and it has been demonstrated that, applying the simple formula (7) of Ref. [25], the error in the correlation energy obtained with the highest basis set level, cc-pVTZ in our case, is reduced by about one order of magnitude. The extrapolated correlation energy has been added to the UHF/cc-pVTZ and GVB/cc-pVTZ rectangular and square energy, respectively, in order

Table 6

Correlation energies, extrapolated to the basis set limit, of the rectangular and square structures, at reference geometries, and automerization barrier (in kcal/mol) corrected by the extrapolated correlation energies

Method	Rectangular	Square	ΔE
MPJ1	–1.103644	–1.097226	8.4
MPJ5	–1.120702	–1.113860	8.6
VWN(mod)	–0.918595	–0.913721	7.4
P86(mod)	–0.979358	–0.977217	5.7
Becke(mod)	–0.935033	–0.929994	7.5
Reference			7.4

to compute the final values of the automerization barrier. The cc-pVTZ basis set, in the light of these new data, seems to be sufficiently accurate and useful for the methodologies employed here. The results obtained are in extremely good agreement with accurate reference calculations; particularly those obtained using the VWN and Becke correlation energy functionals, together with the approximate way of incorporating the ρ_2 dependence through Eqs. (2) and (3).

4. Conclusions

In the present work we have analyzed the influence of the multideterminantal character of the wavefunction typical of the D_{4h} transition state in the automerization reaction of cyclobutadiene. It has been shown that traditional DFT schemes, as well as calculations that do not account for this multideterminantal character, provide energy barriers that are too high in comparison with accurate multiconfigurational coupled-cluster calculations. Using the last as a benchmark, it has been demonstrated that much less cost-demanding calculations, based on a two-step energy evaluation with inclusion of the ρ_2 dependence, are able to provide activation energies in agreement with the results derived from more sophisticated computational schemes. In particular, the approximate way of introducing the ρ_2 dependence on traditional correlation density functionals has proved to be a valuable tool for improving the results. Encouraged by these results, we are now interested in applying the same strategy to other systems with a similar multideterminantal character.

Acknowledgements

This work has been supported by the DGICYT of Spain under project PB97-0122. One of us (J.C.S.G.) wishes to acknowledge the friendly hospitality and advice of Professor Petr Čársky and the help of Professor Jiří Pittner during a stay at the J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic.

References

- [1] B. Arnold, J. Michl, in: M. Platz (Ed.), *Kinetics and Spectroscopy of Carbenes and Biradicals*, Plenum, New York, 1989.
- [2] P. Čársky, R.J. Barlett, G. Fitzgerald, J. Noga, V. Spirko, *J. Chem. Phys.* 89 (1988) 3008.
- [3] A. Balková, R.J. Barlett, *J. Chem. Phys.* 101 (1994) 8972.
- [4] J.C. Sancho-García, J. Pittner, P. Čársky, I. Hubač (1999), submitted.
- [5] V.I. Minkin, M.N. Glukhovtsev, B.Ya. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley, New York, 1994.
- [6] P. Čársky, J. Michl, *Theor. Chim. Acta* 84 (1992) 125.
- [7] J. Paldus, in: S. Wilson, G.H.F. Diercksen (Eds.), *Methods in Computational Molecular Physics*, NATO Adv. Stud. Inst. Ser., Plenum, New York, 1992.
- [8] R.J. Barlett (Ed.), *Recent Advances in Coupled-Cluster Methods. Recent Advances in Computational Chemistry*, vol. 3, World Scientific, Singapore, 1997.
- [9] D. Mukherjee, S. Pal, *Adv. Quantum Chem.* 20 (1989) 292.
- [10] J. Mášik, I. Hubač, *Adv. Quantum Chem.* 31 (1998) 75.
- [11] F.W. Bobrowicz, W.A. Goddard III, in: H.F. Schaefer III (Ed.), *Methods of Electronic Structure Theory*, Plenum, New York, 1977.
- [12] F. Moscardó, A.J. Pérez-Jiménez, *Int. J. Quantum Chem.* 61 (1997) 313.
- [13] F. Moscardó, F. Munoz-Fraile, A.J. Pérez-Jiménez, J.M. Pérez-Jordá, E. San-Fabián, *J. Phys. Chem.* 102 (1998) 10900.
- [14] F. Moscardó, A.J. Pérez-Jiménez, *J. Mol. Struct. (Theochem)* 426 (1998) 47.
- [15] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [16] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [17] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822.
- [18] J.P. Perdew, in: P. Ziesche, H. Eschrig (Eds.), *Electronic Structure of Solids '91*, Akademie Verlag, Berlin, 1991.
- [19] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [20] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [21] F. Moscardó, E. San-Fabián, *Phys. Rev. A* 44 (1991) 1549.
- [22] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [23] A.D. Becke, *J. Chem. Phys.* 88 (1988) 1053.
- [24] T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [25] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, *Chem. Phys. Lett.* 286 (1998) 243.
- [26] T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.* 106 (1997) 9639.
- [27] J.M.L. Martin, G. de Oliveira, *J. Chem. Phys.* 111 (1999) 1843.
- [28] A.K. Wilson, T.H. Dunning, *J. Chem. Phys.* 106 (1997) 8718.
- [29] W.T. Borden, E.R. Davidson, D. Feller, *J. Am. Chem. Soc.* 103 (1981) 5725.
- [30] K. Nakamura, Y. Osamura, S. Iwata, *Chem. Phys.* 136 (1989) 67.
- [31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Mont-

- gomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98 (Revision A.6), Gaussian, Inc., Pittsburgh, PA, 1998.
- [32] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery Jr., *J. Comput. Chem.* 14 (1993) 1347.
- [33] J.M. Pérez-Jordá, A.D. Becke, E. San-Fabián, *J. Chem. Phys.* 100 (1994) 6520.
- [34] A. Balková, R.J. Barlett, *Chem. Phys. Lett.* 193 (1992) 364, and references therein.