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On the computation of molecular electronic affinities*

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Using a multireferent MBPT method (CIPSI) the electronic affinity (EA) of F, CN and HCC is computed. Results show how UMP2 gives unbalanced truncation of the MP series, while ROMP2 has the correct (balanced) behaviour. The good agreement with the experimental EA found for some compounds is accidental and associated to an error compensation. The good agreement with the experimental data found for the ROMP2 and CIPSI EAs is analysed.

Key words: Electron affinity — MBPT-MP2-CIPSI

Introduction

The accurate computation of electronic affinities (EA) of atoms and molecules has proved to be one of the most difficult problems in quantum chemistry [1]. Apart from the use of Koopmans' theorem [2], there are two types of approaches to the problem: one which involves two separate computations on the total energy of the ion and the neutral molecule [3] to give the (vertical or adiabatic) EA, and a second one based on the use of equation-of-motion (EOM) or propagators which computes the (vertical) EA directly [1b; 4]. Even if the second approach seems to be very promising and attractive, as recent computations of Baker et al. [5] have shown, it gives results similar to those obtained with the more conventional techniques based on two computations.

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The main problem behind the accurate computation of EAs is a balanced description of the electronic correlation in both the anion and the neutral system. Due to the importance of the dynamic correlation one normally finds poor estimations of the EAs using the Hartree-Fock (HF) or MCSCF methods where the number of configuration is not very large. However, there have recently been some promising results using the perturbational Møller-Plesset method at various orders (UMPn) [6]. Such computations have shown that UMP2 can obtain accurate molecular EAs (errors lower than 0.2-0.3 eV) with bases sets of moderate to large sizes which include diffuse functions. For atoms, the size of the bases set becomes a critical factor and one needs rather extended bases sets in order to match the experimental EAs [6b].

Such an optimistic view only holds, however, for molecules where the UHF wavefunction presents low spin contamination as OH, NH_2, or O_2. When the spin contamination is not negligible, as in the CN or HCC systems, one finds errors as large as 1 eV between the computed and experimental EAs [5]. A possible cause for such behaviour can be found in the slow convergence rate or even divergence of the MP series in such systems, as was first demonstrated for some systems by Handy and coworkers [7]. Other possible cause is a deficient description of the reference (non-perturbed) wavefunction, that is, the existence of near-degenerate states near to the fundamental one of the anion or neutral molecule. In such a case, the problem will present also a remarkable spin contamination, and can only be adequately described using any of the multireferent methods today available. Finally, there is a last cause of errors associated to the bases set truncation error.

In this work, we have investigated the reason of the reported errors found on the CN and HCC molecules in two ways: using a multireferent perturbational MP method up to order two, and employing a restricted zero order wavefunction apart from the unrestricted. In this way, we can have an insight into the first two causes of errors discussed above.

Methodology

The multireferent method chosen in this work has been CIPSI [8] which basically is a MP2 computation over a multireferent space S formed by all the configurations whose weight in the exact wavefunction is larger than a certain threshold T. Such space is constructed iteratively starting from some set of configurations. Once this space S is known, one can perform a CI computation and obtain the reference wavefunction and energy for the MP2 method. When the MP2 is performed, one obtains the perturbed energy, and the weight of each biexcitation of the reference space in the perturbed wavefunction. If the weight is larger than T this configuration is included in the reference space S. Then, the overall process is repeated until no new configurations are added. Normally the process converges in a small number of iterations.

Using CIPSI one can obtain results for the total energy which include 80%-95% of the total correlation energy for values of T varying between 0.02 and 0.01.

Notice that even if the MP is of order two, the reference space S includes also monoexcitations of some of the configurations (by coupling between the mono- and diexcitations), diexcitations, triexcitations, and so on, and, therefore, the quality of the method is, in general, as good as MP4 or sometimes even better [9]. As previous computations have shown, the main effect of enlarging the space S is to increase the total energy; that is, there is a correction of the overestimation given by a monoreferent MP2. These results are an indication that the quality of the UMP2 EAs is mainly due to a cancellation of errors, as we will see later.

The starting molecular orbitals for CIPSI are never changed and, in principle, have a negligible effect on the final total energy. From the various types available, in the CIPSI computations reported in this work we have chosen the RHF orbitals for closed shell systems, while for open shell systems we have either selected those obtained from the Nesbet-HF ("half electron") method [10], or from a ROHF computation [11]. When the latter choose is done, the reference space S of CIPSI includes all the degenerate configurations with the same weight (their number is indicated in the tables in parentheses). For the other cases, CIPSI is started with only one configuration, the HF one. The results obtained are identified as Nesbet-CIPSI, and ROHF-CIPSI. Furthermore, we have also computed the correlation energy at iteration number zero, equivalent to a ROMP2 computation, which in the ROHF case is multireferent when the highest occupied molecular orbital is degenerate. These results are identified in the tables as Nesbet-MP2 and ROMP2. The difference between the UMP2 and ROMP2 is a measure of the importance of the non-convergence due to the spin contamination of the MP expansion. The difference between the Nesbet-CIPSI and ROHF-CIPSI can be used as an indication of the distance to the FULL-CI results, given that the latter have to be invariant against the starting molecular orbitals.

Finally, we indicate that all the EAs computed in this work are adiabatic, that is, minimum to minimum using the optimum geometries indicated in each case for the anion and the neutral molecule.

Results and discussion

The quality of CIPSI for molecular computations is well described in the bibliography on a variety of problems. However, there are no previous studies on the computation of EAs. Therefore, we have tested the CIPSI EA results against a recent FULL-CI computation of this property for the fluorine atom. The results (given in Table 1 together with those obtained using various methods), do not allow a direct comparison of the energies, because we did not freeze the 1*s* atomic orbital on CIPSI, but show that the EA given by either Nesbet-CIPSI or ROHF-CIPSI differ only by 0.2 eV from the FULL-CI result, a value between those given by the CID and MRCID methods. This is not a surprising result provided that the variational treatment of the S space made by MRDCI is equivalent to an infinite order perturbation, and is an indication of the need to include higher order contribution to the MP expansion in CIPSI. As an indication of the main parameters of the CIPSI computation, the size of the reference space when

Table 1. Total energy (a.u.) and electron affinity (eV) for the fluorine atom computed using the [5*s*4*p*2*d*] basis set given by Bauschlicher [14] with various methods. For the UHF computation the value of $2S+1$ is also given (in braces), while the number of configurations of the reference space is given (in parentheses) for the CIPSI method. All the orbitals are active except the 1*s* when indicated (a)

	E (a.u.)		
Method	F	$F^{(-)}$	EA (eV)
UHF	−99.399755 {0.735}	−99.443696	1.20
UMP2[a]	−99.579075	−99.699525	3.28
UMP2	−99.601354	−99.722027	3.28
UMP3[a]	−99.586827	−99.685888	2.70
Nesbet-HF	−99.391277	−99.443696	2.90
Nesbet-MP2	−99.611244	−99.722026	3.01
Nesbet-CIPSI[b]	−99.608122 (16)	−99.714085 (30)	2.88
Nesbet-CIPSI[c]	−99.607092 (38)	−99.712191 (61)	2.86
Nesbet-CIPSI[d]	−99.607310 (101)	−99.711773 (176)	2.84
ROHF	−99.395825	−99.443696	1.30
ROMP2	−99.610467	−99.722026	3.03
ROHF-CIPSI[b]	−99.608754 (12)	−99.712191 (61)	2.80
ROHF-CIPSI[b]	−99.607664 (86)	−99.711773 (176)	2.83
CID[a]	−99.587105	−99.689101	2.78 [14]
CCSD[a]	−99.591542	−99.698975	2.97 [12]
CCSDT-1[a]	−99.594842	−99.707897	3.08 [12]
MR-CID[a]	−99.592789	−99.703737	3.02 [14]
Full-CI[a]	−99.594877	−99.706690	3.04 [14]
Exp.			3.40 [15]

[a] 1*s* orbital for C is frozen

[b] All the configurations with coefficient larger than 0.020 are included

[c] All the configurations with coefficient larger than 0.015 are included

[d] All the configurations with coefficient larger than 0.010 are included

$T=0.02$ is 86 and 176, for F and $F^{(-)}$ respectively, being the number of effective contribution to the MP2 about 720 000 and 3 000 000 configurations.

Looking at Table 1 results, there appear some other interesting facts. First, when compared with the experimental value, the best result is that given by the UMP2 method (3.28 eV). This value is better than the FULL-CI result and, therefore, has to be artifactual. Using as reference the CIPSI results, which give an EA similar to the FULL-CI method, one finds that a difference between the best CIPSI and UMP2 total energies of +0.0282 and −0.0102 a.u. for F and $F^{(-)}$, with almost no variation when the size of references space S is increased. This means that the MP2 describes in a nonbalanced form the neutral and negative molecules and the error is compensated in part by the bases set truncation error. This explains, first, why the computed UMP2 EA become worse as the bases set becomes better (see [5, 6b, 16]); secondly, the good agreement found between the computed and experimental EA for the first row hydrides using bases sets of moderate size (one expects a similar behaviour for compounds of similar electronic structure), and, finally, the different behaviour found between different

Table 2. Electron affinity (eV) for the CN molecule ($^2\Sigma^+$) computed using various basis set with various methods. For the UHF computation the value of $2S+1$ is also given (in braces), while the number of configurations of the reference space is given (in parentheses) in CIPSI for the largest (anion or neutral) space. All the orbitals are active except the 1s orbital of C and N when indicated (a). The C–N bondlength is 1.186 Å for the neutral molecule, and 1.170 Å for the anion

	Basis		
Method	3-21+G	6-31+G**	6-311+G**
UHF	2.94 {1.28}	2.93 {1.22}	2.97 {1.23}
UMP2[a]	4.68	4.60	4.70
UMP3[a]	4.11	4.32	4.39
Nesbet-HF	3.98	3.88	3.94
Nesbet-MP2	2.67	2.87	2.93
Nesbet-CIPSI[b]	2.78 (3)	3.01 (3)	—
Nesbet-CIPSI[c]	3.11 (104)	3.27 (101)	3.34 (116)
ROHF	3.56	3.44	3.50
ROHF-MP2	3.18	3.36	3.43
ROHF-CIPSI	3.29 (95)	3.45 (108)	3.54 (113)
Exp.			3.82 [17]

[a] 1*s* orbital for C and N is frozen
[b] All the configurations with coefficient larger than 0.02 are included
[c] All the configurations with coefficient larger than 0.01 are included

types of molecules. These results agree with the conclusions obtained by Cole and Barlett for MBPT and CC monoreference methods [12].

When our analysis is extended to the ROMP2 EA, one finds a remarkably good agreement between the ROMP2 EA and the best CIPSI value (Nesbet-MP2 has a similar behaviour because, as expected, in this case the Nesbet wavefunction is similar to the ROHF one). This means that the ROHF is making a balanced description of both systems and, as consequence, is adequate for the study of EAs. Provided that the total energy computed using the ROMP2 and UMP2 methods is the same for the closed shell $F^{(-)}$ system, as expected, one can associate the value of the UMP2 computed EA to the description made by the UMP2 of the correlation energy of the doublet F atom: the difference between the UMP2 and ROMP2 total energy is −0.01 a.u. and can be attributed to a slower convergence of the UMPn series with respect to the ROMPn. Remember that, in any case, the ROMP2 total energy for F and $F^{(-)}$ is, in both cases, lower than the best CIPSI results and the good value for the computed EA is due to a balanced truncation error.

Finally, the last important conclusion from Table 1 is that one has to use very large bases sets to obtain computed EAs which match the experimental values, on the line of the recent work of Almlöf and Taylor [13].

In light of Table 1 results, we have computed the EA for CN and HCC using various bases sets and the UMPn and CIPSI algorithms (Tables 2 and 3). The

Table 3. Electron affinity (eV) for the HCC molecule ($^3\Sigma^+$) computed using various basis set with various methods. For the UHF computation the value of $2S+1$ is also given (in braces) while the number of configurations of the reference space is given (in parentheses) for the CIPSI method for the largest (anion or neutral) space. All the orbitals are active except the 1s orbital of C when indicated (a). The H-C and C-C bondlengths are 1.054 Å and 1.230 Å for the neutral molecule, and, 1.057 and 1.234 Å for the anion

	Basis		
Method	3-21+G	6-31+G**	6-311+G**
UHF	1.54 {1.26}	1.54 {1.22}	1.57 {1.22}
UMP2[a]	3.04	3.28	3.39
UMP3[a]	1.75	3.04	3.14
Nesbet-HF	2.43	2.39	2.43
Nesbet-MP2	2.22	2.40	2.51
Nesbet-CIPSI[b]	2.19 (68)	2.37 (76)	2.49 (83)
Nesbet-CIPSI[c]	2.16 (82)	2.34 (103)	2.43 (101)
ROHF	2.13		2.09
ROHF-MP2	2.30		2.56
ROHF-CIPSI	2.16 (60)		2.51 (69)
Exp.			2.94 [19][d]

[a] 1*s* orbital for C is frozen

[b] All the configurations with coefficient larger than 0.02 are included

[c] All the configurations with coefficient larger than 0.01 are included

[d] Various values of the experimental EA for this compound are found in [18]. Here we are reporting the most recent one

geometry of the neutral molecule and the anion has been optimized at the UHF/4-31G level and also is given in Tables 2 and 3. Results from Tables 2 and 3 show that UMP2 now overestimates the EA for these molecules by almost 1.0 eV, a fact that can be corrected using ROMP2. In such a case we obtain a value which differs by about 0.4 eV from the 6-311+G** bases set, but which becomes better when a multireference space in used. The analysis of such behaviour gives the same result as for F: the doublets are worse described by UMP2 than the singlets, something that does not happen with ROMP2 (using as reference the best CIPSI results) and is the reason for its quality. Furthermore, the computed EA approaches the experimental value as the bases set size increases, in such a way that one can expect that with larger bases sets it will be possible to match the experimental EA value with the desired precision.

In relation to the CIPSI results, the major trends already indicated for F still hold for CN and HCC. In consequence, there is an increase of energy when the size of the reference space S is increased, which has almost no effect on the computed EA. Furthermore, now, because of the different description made by the Nesbet and ROHF methods, one can establish the effect of the starting molecular orbitals on the final CIPSI result: as can be seen in Tables 2 and 3 there are differences of 0.1 and 0.2 eV on the computed EA, a fact that seems to suggest the convenience of using larger sizes of the reference space or increasing the order of the perturbation in order to obtain results nearer to the FULL-CI. This is now the object of further studies including up to fourth order in the MP expansion with promising results. Finally, note that because our ROHF implementation is multireferent in nature, we cannot state definitely whether the real reason for its quality is associated with the absence of spin contamination, the use of more than one reference wavefunction, or both. For CN and HCC, because of the symmetry of their doublet states, at ROHF level includes only one configuration and, in consequence, can be treated as a monoreferent MP method. For these cases, CIPSI gives, for the largest S space, a coefficient of 0.95 for the ROHF configuration. In consequence one can say that previous problems found in the EA computation of these two molecules are associated with the bad description made by the monoreferent UMP2 instead of the need for more than one configuration. The same still holds for fluorine where the doublet state includes three degenerate determinants. In conclusion, ROMP2 seems to be a very promising form of having accurate EAs in a simple form.

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