Accurate multireference calculations of the electron affinity of NO, BO and O_2

P. Stampfuß, W. Wenzel [*]

Forschungszentrum Karlsruhe GmbH, Institut fur Nanotechnologie, Postfach 3640, D 76021 Karlsruhe, Germany

Abstract

We report a systematic investigation of the adiabatic electron affinities (EA) of BO, NO and O_2 using a specifically adapted massively parallel version of the configuration selective configuration interaction method (MR CI) which permits the explicit treatment of the most important triple and quadruple excitations (TQ). We find the EA(BO) = 2.52 eV, EA(NO) = 0.015 eV and EA(O_2) = 0.39 eV in good agreement with experimental results. We elucidate the physical mechanism that is responsible for the failure of standard MRCI to quantitatively describe the EA of oxygen containing molecules.

1. Introduction

The determination of accurate data for bond dissociation energies as well as for electron affinities and ionization potentials is important for the interpretation of many chemical phenomena. While much progress has been made in the accurate computation of dissociation energies [1,2], the treatment of weakly bound anions has remained a challenge for theoretical chemistry. In particular, oxides have proven problematic [3,4], calling for high-level methods in large basis sets to obtain quantitative agreement with experiment.

Recent theoretical work [5] suggested a revision of the experimental value of the EA of BO to 2.52 eV at the CCSD(T) level of theory with a large aug-cc-pVQZ basis set. This result was experimentally verified [6] and is now supported by a number of additional calculations [4]. Notably, Davidson corrected MRCI+Q and MR-ACPF calculations [7] were reported to miss the experimental value by more than 0.3 eV even using d-aug-pV5Z basis sets. Similarly, NO is a very difficult system, as the anion is bound only very weakly (0.026 eV) [8] by the presence of differential zero-point motion effects. Accurate QCISD (T)/CCSD(T) calculations in aug-cc-pVDZ and aug-cc-pVTZ quantitatively reproduce this result [5,7]. The calculation of the electron affinity of the oxygen molecule (0.42 eV) [8] has also posed significant theoretical challenges [3]. At the level of a CAS-SCF description the adiabatic electron affinity of the oxygen molecule is predicted with the wrong sign even in the basis set limit. A careful

---

[*] Corresponding author.

E mail address: wolfgang.wenzel@int.fzk.de (W. Wenzel).

study concluded that strong differential dynamical correlation effects responsible for this discrepancy [3], but even valence MRCI-SD calculations barely reach the correct sign for the electron affinity using augmented-quadruple-zeta quality basis sets. A semiquantitative agreement between experiment and theory was reached, when the multireference generalization of the Davidson correction [9] was applied to estimate the effect of higher excitations.

These results indicate that an interplay of strong dynamical as well as non-dynamical correlation effects is involved in the attachment of an additional electron to oxygen. The perturbative addition of triples in CCSD(T) appears to incorporate a balanced account of these effects and yields quantitatively correct results (that are typically absent using CCSD alone), while straightforward applications of MRCI typically fare worse. Both the relevance of non-valence excitations [3] as well as the existence of particularly large size-consistency errors [7] have been blamed for this behavior. In the following we report a systematic investigation of the EA of small oxides using a specifically adapted version of the configuration-selective MRCI method (MRD-CI) [10,11] that includes the selective addition of triple and quadruple excitations (TQ). For both NO and BO we find excellent quantitative agreement between our calculation and the best available experimental and theoretical data. For O_2 we estimate the adiabatic EA at 0.39 eV, still at variance with the best experimental result (0.45 eV).

2. Method

Since the number of higher-than-doubly excited configuration rises very quickly with the system size, FCI as well as CI-SDTQ calculations are prohibitively expensive for all but the smallest systems. In the present investigation we have therefore used a configuration-selecting version of MRCI [10,12,13] to treat higher-than-double excitations of the reference set. Configuration-selecting CI presently provides a particularly effective, maybe the only viable, compromise between computational efficiency and accuracy for this investigation. In configuration-selective versions of the MRCI method (MRD-CI) only the most important configurations of the interacting space of a given set of primary configurations are chosen for the variational wavefunction, while the energy contributions of the remaining configurations are estimated on the basis of second-order Rayleigh Schrödinger perturbation theory [14,15]. A configuration is selected for the variational wavefunction if its perturbative energy contribution or coefficient is above a given threshold λ and the total energy (the sum of the variational and the perturbative contributions) is extrapolated to the limit $\lambda \to 0$.

It is important to recognize that there is a double hierarchy in the importance of the many body configurations of the full Hilbert space. The importance of a particular configuration is primarily governed by its overall excitation level, i.e., the number of non-active-space orbitals. In addition, the type of occupied orbitals can be used as a secondary classification criterion. It conforms to chemical intuition that e.g., quadruple excitations comprising only (3s) type orbitals are more important than those comprising combinations of d- or f-orbitals [16]. In very large basis sets the most important TQ excitations may be as important as single- and double (SD) excitations into orbitals with very high principle or angular momentum quantum number (see Fig. 1). The latter are required to account for dynamical correlation effects at the level of SD excitations [17]. TQ excitations into such orbitals, however, contribute little to the overall wavefunction.

In this scenario configuration-selecting CI becomes an ideal tool to explore Hilbert spaces that can no longer be treated with conventional CI methods. MRD-CI automatically selects only the most important configurations of the TQ space and treats configurations of all excitations levels on an equal basis. We have therefore adapted our massively parallel implementation of MRD-CI [11,18] to selectively include TQ excitations into the Hilbert space, by defining an additional orbital subspace that incorporates orbitals that may be included in TQ excited configurations.

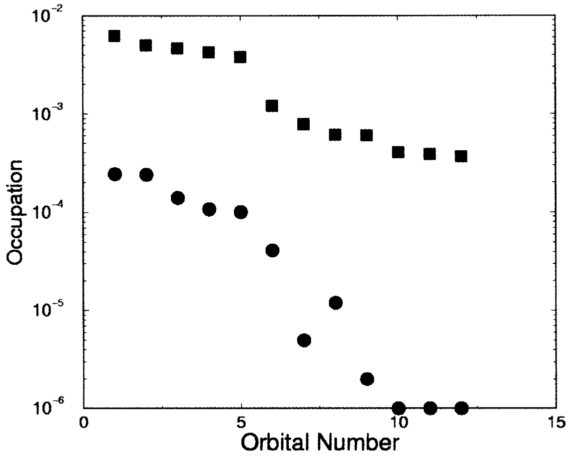

Fig. 1. Total contributions of individual orbitals (of a_g symmetry) to the diagonal matrix elements of the single particle density matrix that arise from single and double excitations of the reference configurations (squares) or triple and quadruple excitations (circles). The data were obtained in a CI SDTQ calculation for O_2 in a cc pVDZ basis at the experimental geometry.

3. Computational details

Previous calculations [7,21] have established that augmented-triple-zeta quality basis sets are sufficient to obtain quantitatively correct results for all the oxides considered here. All calculations reported here used approximate natural orbitals, obtained in Brillouin Wigner multireference perturbation theory [22], from aug-cc-pVTZ basis sets [23,24]. For O_2 additional calculations in aug-cc-pVQZ basis sets were performed to check for convergence. The MRD-CI calculations, performed in C_{2h} and D_{2h} symmetry for NO, BO and O_2, respectively, used (2s2p) active spaces with reference selection, where indicated. The 1s electrons were not correlated unless otherwise noted. Energies labeled as MRCI were obtained by extrapolating the energies of configuration-selective calculations against the unselected fraction of the Hilbert space. Energies labeled by MRCI+Dav. include the multireference version of the a posteriori Davidson correction [9,25]. To validate these results we undertook additional MR-ACPF [26] calculations. For O_2 we used additionally the method of diagonal dressings $(SC)^2$ [27] to account implicitly for the effect of higher excitations. In the calculations labeled TQ configurations with single- and double-excitations into the next higher principal quantum number (3s3p) were included in the valence space and double excitations of these configurations into the remaining non-valence orbitals were permitted. These calculations serve to systematically increase the explicitly considered Hilbert space towards the full CI limit. Their computational cost, however, rises steeply with the number of orbitals that are included in the TQ segment. The Hilbert space in a typical TQ calculation for O_2^-, e.g., has over 2100 references, resulting in more than 6×10^7 configurations, of which about 1.2×10^7 were selected in the variational subspace. When running on 64 nodes of the IBM-SP/SMP of the HLRZ Karlsruhe, the calculation converges in 3.5 h (comprising of five MR-BWPT calculations for the iterative natural orbital generation and the subsequent MRD-CI calculation, four-index transforms, etc.). A similar calculation for BO^- ($N_{\mathrm{ref}} = 5048$, $N_{\mathrm{conf}} = 2.2 \times 10^8$, $N_{\mathrm{sel}} = 7.4 \times 10^6$) requires about 7.2 h on eight nodes of a massively parallel PC cluster (1.8 GHZ dual Ad-Ion with SCI), demonstrating the performance of our code on this relatively inexpensive hardware platform.

4. Results

Spurred by theoretical work [5], the electron affinity of BO was experimentally re-examined from the 315 nm photoelectron spectrum of BO^- to be 2.508 ± 0.008 eV [8]. This value was confirmed in further CCSD(T) calculations using very large basis sets [7], but deviations were reported for MRCI, MRCI+Dav. and MR-ACPF calculations even with d-aug-cc-pV5Z basis sets, which obtained a valued of EA(BO) = 2.18 eV. To address this discrepancy we have determined the equilibrium bond distance, harmonic frequencies and dissociation energies of BO and its anion with MR-ACPF calculations in a aug-cc-pVTZ basis set. We note that such a basis set was sufficient to determine the EA of BO to within 0.03 eV with CCSD(T) [7]. The results, summarized in Table 1, demonstrate excellent agreement for bond distance and frequencies in comparison with experiment. The dissociation energies for the triple bonds in

Table 1
Spectroscopic constants of BO, NO and O_2 and their anions computed with (2s2p) CAS MR ACPF in an aug cc pVTZ basis in comparison with experiment (taken from [20] unless otherwise indicated)

	r_0 (Å)			ω (cm ^{1})			D_e (kcal/mol)		
	Calc.	Exp.		Calc.	Exp.		Calc.	Exp.	
BO	1.215	1.205	[19]	1868	1875	[6]	188.4	194.9	[19]
BO	1.249	1.236	[6]	1709	1655	[6]	214.92	218.8	[19]
NO	1.158	1.151		1875	1904		146.2	152.4	
NO	1.277	1.271		1347	1285		117.1	118.5	
O_2	1.215	1.208		1583	1580		117.5	120.1	
O_2	1.364	1.341		1103	1089		93.2	95.9	

BO and BO^- are about 6 kcal/mol in error, which is consistent with the errors of CCSD(T) calculations in similar quality basis sets [7]. Table 2 demonstrates that at the level of SD-MRCI the EA of BO is about 0.2 eV in error, in accordance with earlier studies. However, extensivity corrections by either Davidson's method or MR-ACPF correct these errors, reproducing the experimental value of 2.52 eV. The physical source of the error becomes apparent when explicitly considering TQ excitations in the variational calculations, which results in $\mathrm{EA(BO)} = 2.47$ eV. Extensivity corrections of this result again reproduce the experimental result. On the basis of these calculations we can conclude that the major source of error for the EA of BO in traditional MRCI stems from the omission of TQ excitations into the (3s3p) type orbitals. The inclusion of core-correlation leads to a negative correction of −0.1 and −0.08 eV for the MRD-CI and MR-ACPF calculations, respectively. This is somewhat surprising because the number of core-valence excitations increases when one electron is added. Thus one would expect the effect to be larger for the anion, resulting in a positive correction to the EA. However, the orbitals change what may lead to a decreasing correlation-energy of the valence-electrons and finally a negative effect to the EA. Adding the core-valence correction to the MRD-CI(TQ)+Dav. and MR-ACPF(TQ) calculations leads to values for the EA of 2.42 and 2.47 eV, respectively.

NO^- is the one of the most weakly bound diatomic anions ($\mathrm{EA} = 0.026$ eV) [8], the computation of its EA is therefore a significant challenge for theoretical chemistry. A recent, highly accurate CCSD(T) study [21] using a aug-cc-pVTZ basis set reproduced the experimental value to within 0.01 eV when differential zero-point corrections (ZPC)

Table 2
Total energies (a.u.) of BO and BO and adiabatic electronic electron affinities (EA) (eV) computed with MRD CI, MRD CI with Davidson correction (+Dav.) or configuration selecting MR ACPF without and with the explicit inclusion of TQ excitations at the geometries of Table 1

	Neutral	Anion	EA
MRCI	99.86700	99.95173	2.31
MRCI+Dav.	99.87600	99.96807	2.51
MR ACPF	99.87477	99.96740	2.52
MRCI (CV)	99.89686	99.97816	2.21
MRCI+Dav. (CV)	99.90709	99.99559	2.40
MR ACPF (CV)	99.90662	99.99633	2.44
MRCI(TQ)	99.87270	99.96351	2.47
MRCI(TQ)+Dav.	99.87484	99.96755	2.52
MR ACPF(TQ)	99.87568	99.96984	2.55

The energies indicated with (CV) are computed with inclusion of core valence excitations.

were taken into account. MR-ACPF using the same basis set and an (2s2p)-electron complete active space reproduced the bond-distances of NO and NO$^-$ to within 0.01 Å in comparison to the experiment and prior calculations. The frequencies for NO and its anion are estimated at 1875 and 1347 cm^{-1}, the latter falls well in the available experimental data (1285 1370 cm^{-1}). Straightforward MRCI calculations of the EA give an error of almost 0.5 eV (see Table 3). Incorporating the Davidson correction reduces this error to about 0.12 eV while the approximate, but self-consistent treatment of higher excitations in MR-ACPF reduces it further to within 0.01 eV. The source of possible difficulty of these approximations becomes obvious when one considers that the absolute value of the extensivity correction is about 0.5 eV, more than an order of magnitude larger than the desired effect. Including TQ excitations in the Hilbert space leads to a better approximation of the ‘ideal’ underlying FCI calculation and reduces the error to about 0.1 eV at the level of MRD-CI(TQ). When one applies extensivity corrections to this calculation, values of EA(NO) = 0.034 eV and EA(NO) = 0.018 eV are obtained with MRD-CI(TQ)+Dav. and MR-ACPF(TQ), respectively, which bracket the experimental result. The MR-ACPF(TQ) energies were obtained at bond-distances of $r_0 = 1.1587$ Å for NO and $r_0 = 1.2746$ Å for NO$^-$ which were determined from a MR-ACPF(TQ) potential energy surface (PES). The energies calculated at this bond-distances differ only by less than 0.002 eV from the bond-distances given in Table 1. Given these small energy differences we abstained from calculating a complete MR-ACPF(TQ) PES for BO and O_2 and used the MR-ACPF geometries instead. Again the inclusion of core-valence excitations leads to a negative correction to the EA for the MRD-CI calculation (−0.06 eV) but to a positive effect for the MR-ACPF calculation (+0.018 eV). Applying these corrections to the MRD-CI(TQ)+Dav. and the MR-ACPF(TQ) results one obtains EA(NO) = −0.0263 eV and EA(NO) = +0.0354 eV for MRCI(TQ)+Dav. and MR-ACPF(TQ), respectively.

Finally we have applied the same strategy to the computation of the EA of O_2. Again (see Table 1) equilibrium bond-distances and harmonic frequencies are in excellent agreement with experiment. In agreement with earlier studies [3] we find that (2s2p) valence MRCI calculations yield the wrong sign of the EA(MRCI) = −0.10/−0.09 eV in aug-cc-pVTZ/aug-cc-pVQZ basis sets, respectively. Approximate extensivity corrections (see Table 4) manage to qualitatively correct this error, but fail to reach quantitative agreement with experiment. Comparison of calculations with aug-cc-pVTZ and aug-cc-pVQZ basis sets demonstrate that this is not a basis set effect. With the explicit inclusion of TQ excitations in the Hilbert space the EA(O_2) drops dramatically and yield values of 0.38, 0.36 and 0.36 eV with MRD-CI (TQ), MRD-CI(TQ)+Dav. and MR-ACPF(TQ), respectively. In the case of MR-ACPF the ZPC of 0.03 eV nearly cancels with the effect of the core-valence

Table 3
Total energies (a.u.) of NO and NO and adiabatic electron affinities (EA) (both electronic and with the inclusion of ZPC in electronvolt) computed with MRD CI, MRD CI with Davidson correction (+Dav.) and configuration selecting MR ACPF without and with the explicit inclusion of TQ excitations at the geometries of Table 1

	Neutral	Anion	EA (el)	EA (+ZPC)
MRCI	129.70995	129.69293	0.4631	0.4286
MRCI+Dav.	129.72981	129.72511	0.1278	0.0933
MR ACPF	129.72984	129.72886	0.0266	0.0079
MRCI (CV)	129.73674	129.71758	0.5215	0.4870
MRCI+Dav. (CV)	129.75813	129.75122	0.1881	0.1536
MR ACPF (CV)	129.75863	129.75888	+0.0067	0.0254
MRCI(TQ)	129.72416	129.71965	0.1222	0.0877
MRCI(TQ)+Dav.	129.73071	129.73069	0.0005	0.0340
MR ACPF(TQ)	129.73029	129.72965	0.0174	0.0179

The energies indicated with (CV) are computed with inclusion of core valence excitations.

Table 4
Total energies (a.u.) of O_2 and O_2 and electronic adiabatic electron affinities (EA) (eV) computed with MRD CI, MRD CI with Davidson correction (+Dav.), configuration selecting MR ACPF and MRCI with diagonal dressings (MRCI+$(SC)^2$) without and with the explicit inclusion of TQ excitations at the geometries of Table 1

		Neutral	Anion	EA
MRCI	aug cc pVTZ	150.11644	150.11270	0.10
MRCI+Dav.	aug cc pVTZ	150.14254	150.14855	0.16
MR ACPF	aug cc pVTZ	150.14230	150.15174	0.26
MRCI+$(SC)^2$	aug cc pVTZ	150.12958	150.13805	0.23
MRCI (CV)	aug cc pVTZ	150.14254	150.13721	0.14
MRCI+Dav. (CV)	aug cc pVTZ	150.17024	150.17474	0.12
MR ACPF (CV)	aug cc pVTZ	150.17184	150.18066	0.24
MRCI	aug cc pVQZ	150.15153	150.14805	0.09
MRCI+Dav.	aug cc pVQZ	150.17938	150.18591	0.18
MR ACPF	aug cc pVQZ	150.17924	150.18931	0.27
MRCI(TQ)	aug cc pVTZ	150.13579	150.14992	0.38
MRCI(TQ)+Dav.	aug cc pVTZ	150.14475	150.15818	0.36
MR ACPF(TQ)	aug cc pVTZ	150.14441	150.15762	0.36

The energies indicated with (CV) are computed with inclusion of core valence excitations.

excitations of −0.02 eV, resulting in a final value of the EA of 0.037 eV. With inclusion of the ZPC- and CV-corrections we a final value of 0.035 eV for the MRD-CI(TQ)+Dav. calculation in comparison to an experimental value of 0.452 ± 0.007 eV obtained in negative ion photoelectron spectroscopy [8].

5. Summary and Conclusion

We have performed accurate calculations of the electron affinities of BO, NO and O_2 using a specifically adapted version of the configuration-selecting MRCI method that includes an important subset of triple and quadruple excitations of the valence shell. Using this approach we have obtained excellent agreement of the EA of BO and NO while for O_2 a discrepancy of about 0.06 eV remains between our calculations and the experimental result. These results correct the longstanding difficulty of the MRCI method to quantitatively describe the electronic structure of anions containing oxygen and elucidate the mechanism for this failure. In oxygen containing molecules, triple and quadruple excitations into non-valence orbitals contribute substantially to differential effects in the electronic structure (see Fig. 1). As a result, straightforward MRCI fails to account quantitatively for the EA of these molecules even in the basis set limit. The explicit consideration of these excitations, which is automatically included in perturbative triples correction of CCSD(T), is required to obtain qualitatively correct results. The computational strategy employed here, which selectively treats only the most important TQ excitations, offers a viable and affordable compromise to account for these effects.

Acknowledgements

We are grateful for many stimulating discussions with M.M. Steiner, J. Wilkins and K.G. Wilson and I. Shavitt. Part of this work was supported by DFG Grant KEI-164/11-2 and We 1863/10-1. The calculations were performed at the HLRZ Karlsruhe and the von Neumann Institute for Computing.

References

[1] H. J. Werner, P. Rosmus, in: R.J. Bartlett (Ed.), Comparison of Ab Initio Quantum Chemistry with Experiment, Reidel, Dordrecht, 1985.

[2] L.A. Curiss, R. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.

[3] R. Gonzáles Luque, M. Merchán, M.P. Fulscher, B.O. Roos, Chem. Phys. Lett. 204 (1993) 323.

[4] B.S. Jursic, Theochem. 467 (1999) 1.

[5] J.C. Rienstra, H.F. Schaefer III, J. Chem. Phys. 106 (1997) 4472.

[6] P.G. Wentholt, J.B. Kim, K. L. Jones, W.C. Lineberger, J. Phys. Chem. A 101 (1997) 4472.

[7] A. Papakondylis, A. Mavridis, Chem. Phys. Lett. 341 (2001) 382.

[8] M.J. Travers, D.C. Cowles, G.B. Ellison, Chem. Phys. Lett. 164 (1989) 449.

[9] W. Butscher, S. Shih, R.J. Buenker, S.D. Peyerimhoff, Chem. Phys. Lett. 52 (1977) 457.

[10] R.J. Buenker, S.D. Peyerimhoff, Theor. Chim. Acta 35 (1974) 33.

[11] P. Stampfuß, H. Keiter, W. Wenzel, J. Comput. Chem. 20 (1999) 1559.

[12] R.J. Bunker, S. Peyerimhoff, TCA 12 (1968) 183.

[13] R.J. Buenker, S.D. Peyerimhoff, Theor. Chim. Acta 39 (1975) 217.

[14] Z. Gershgorn, I. Shavitt, Int. J. Quantum Chem. 2 (1968) 751.

[15] B. Huron, J.P. Malrieu, P. Rancurel, J. Chem. Phys. 58 (1973) 5745.

[16] M.M. Steiner, W. Wenzel, J.W. Wilkins, K.G. Wilson, Chem. Phys. Lett. 231 (1994) 263.

[17] M.M. Steiner, W. Wenzel, Int. J. Quantum Chem. 70 (1998) 147.

[18] P. Stampfuß, W. Wenzel, J. Mol. Struct. 506 (2000) 99.

[19] M. Tanimoto, S. Saito, E. Hirota, J. Chem. Phys. 84 (1986) 1210.

[20] K.P. Huber, G. Herzberg, Constants of Diatomic Mole cules, Van Nostrand, New York, 1979.

[21] M.C. McCarthy, J.W.R. Allington, K.S. Griffith, Chem. Phys. Lett. 289 (1998) 156.

[22] W. Wenzel, M.M. Steiner, J. Chem. Phys. 108 (1998) 4714.

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

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

[25] S.R. Langhoff, E.R. Davidson, Int. J. Quantum Chem. 8 (1974) 61.

[26] R. Gdanitz, R. Ahlrichs, Chem. Phys. Lett. 143 (1988) 413.

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