On the dipole moment of the ground state $X^3\Delta$ of iron carbide, FeC

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In the light of experimental results on the dipole moment of the FeC $X^3\Delta$ state, we have re-examined our recent theoretical numbers of this property, by increasing our basis set size and calculating also the dipole moment by the finite field method. Our best result is 1.94 D as compared to the experimental value of 2.36 D, signifying that care should be exercised in obtaining one-electron properties even from highly correlated wave functions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1545680]

Despite the clear progress of theoretical and/or computational chemistry in the last 30 years[1] and the claims that we are entering the era of quantum biology, there are still some simple and well defined molecular properties that certain times defy our calculational prowess, even for small systems such as the diatomics MX, where M=first row transition metal atom and X a main group element. What we have in mind is the dipole moment vector $\boldsymbol{\mu}$ of a neutral MX species.

The dipole moment is defined either as an expectation value

$$\boldsymbol{\mu} = \langle \Phi | \hat{\boldsymbol{\mu}} | \Phi \rangle, \tag{1}$$

where Φ is a normalized exact ($=\psi$) or approximate wave function, and $\hat{\boldsymbol{\mu}}$ is the usual dipole operator, or as the gradient of the total electronic energy E of the system at hand with respect to an (external) electric field $\mathcal{E}$, i.e.,

$$\boldsymbol{\mu} = \nabla_\mathcal{E} E,$$

where $\nabla_\mathcal{E} = (\partial/\partial\mathcal{E}_x, \partial/\partial\mathcal{E}_y, \partial/\partial\mathcal{E}_z)$.

In practice, and for a diatomic say molecule whose internuclear axis defines the z direction,

$$\mu_z = \lim_{\delta\mathcal{E}_z \to 0} \frac{\delta E}{\delta\mathcal{E}_z}, \tag{2}$$

where δE the energy difference of the system calculated before and after the application of an electric field ($\delta\mathcal{E}_z$) along the z axis.

Although definitions (1) and (2) [finite field method (FF)] are equivalent to the limit, that is when $\Phi = \psi$ and $E = E_{\text{exact}}$ within the method applied, in most other cases results can differ appreciably. This is because Eq. (1) is a functional of the wave function Φ, where in Eq. (2) the wave function is indirectly involved through the energy E. However, and as a result of the variational theorem,[2] if

$$\Phi = \psi + \epsilon \mathcal{X}$$

and assuming that

$$E = E_{\text{exact}} + \epsilon E^{(1)} + \epsilon^2 E^{(2)},$$

then

$$E = \langle \Phi | \hat{\mathcal{H}} | \Phi \rangle = E_{\text{exact}} + \epsilon^2 E^{(2)},$$

a nice property of the energy but which does not hold for other properties. Therefore, for the calculation of the dipole moment, formula (2) is to be recommended in general.

Although all the above are well recognized, it never occurred to the present authors that the expectation value relationship (1), and for certain molecular systems, could lead to completely erroneous values of the dipole moment even for highly correlated wave functions (*vide infra*). This is exactly what motivated the present report.

Recently we have published *ab initio* results on the iron monocarbide FeC (Ref. 3) using CASSCF+single+double replacements (CASSCF+1+2=MRCI) methods coupled with the ANO-$[7s6p4d3f]$ and cc-pVTZ-$[4s3p2d1f]$ basis sets for the Fe (Ref. 4) and C [Ref. 5(a)] atoms, respectively. For the ground state only ($X^3\Delta$) the basis set was extended to $[7s6p4d3f2g/_{\text{Fe}}5s4p3d2f1g/_{\text{C}}]$. The zeroth order space (CASSCF) was composed of 10 "valence" orbitals and 12 active electrons; calculations including the semicore electrons of Fe $(3s^23p^6)$ at the MRCI level have been referred to as C-MRCI. In that work,[3] in addition to the ground $X^3\Delta$ state, we also reported results on 40 excited states (see also Ref. 6).

Results of the above work for the $X^3\Delta$ state are reproduced in the first two entries of Table I, namely, total energies (E), bond distances (r_e), dissociation energies (D_e), harmonic frequencies (ω_e), and dipole moments ($\langle\mu\rangle$) in different methods, including the coupled cluster singles and doubles with perturbative triples approach, CCSD(T). It should be mentioned that in the CCSD(T) method CASSCF orbitals were employed due to the impossibility of obtaining single reference orbital functions.

Most of the numbers of Ref. 3 were in fair agreement with the totality of existing experimental findings when the paper was submitted for publication. For instance, for the $X^3\Delta$ state at the C-MRCI level (see second entry of Table I) we obtain $r_e = 1.581$ Å, $D_e = 86.7$ kcal/mol, $\omega_e = 877$ cm^{-1} as compared to, perhaps the best experimental results, $r_e = 1.5889$ Å,[10] $D_e = 91.2 \pm 7$ kcal/mol,[14,15] $\omega_e = 867$ cm^{-1}.[10] So it came as surprise to us when Steimle and Virgo[11] obtained by optical Stark spectroscopy and for the first time, the experimental permanent dipole moment of the $X^3\Delta_3$

TABLE I. Absolute energies E (hartree), bond lengths r_e (Å), binding energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), dipole moments μ (Debye), at CASSCF, MRCI,[a] MRCI+Q,[b] and CCSD(T) level of the ground state $X\,^3\Delta$ of the FeC molecule. Experimental and other theoretical results are also included.

Methods	$-E^c$	r_e	D_e	ω_e	$\langle\mu\rangle$	$\mu_{FF}=\delta E/\delta\mathcal{E}$
		ANO-Bauschlicher-g+cc-pVTZ: $\rightarrow[7s6p4d3f]_{Fe}/[4s3p2d1f]/_C$				
CASSCF	0.233 82	1.640	53.7(53.7[p])	622.7	1.48	1.48
MRCI	0.528 03	1.605	79.6(78.7[p])	810.1	1.34	1.90
MRCI+Q	0.554 0	1.609	80.4(79.5[p])			2.01
CCSD(T)	0.551 68	1.583	76.1	892		2.09
C-MRCI[d]	0.813 66	1.596	81.3	834	1.28	1.88
C-MRCI+Q[d]	0.870 7	1.598	84.2			2.04
C-CCSD(T)[d]	0.881 08	1.569	76.7	958		2.17
		ANO-Bauschlicher+cc-pVQZ: $\rightarrow[7s6p4d3f2g]_{Fe}/[5s4p3d2f1g]/_C$				
CASSCF	0.236 38	1.635	54.2(54.2[p])	631.4	1.49	1.49
MRCI	0.549 54	1.593	83.5(83.1[p])	840.8	1.34	1.90
MRCI+Q	0.577 1	1.596	84.7(84.2[p])			2.01
CCSD(T)	0.576 75	1.572	80.8	908		2.14
C-MRCI[d]	0.881 41	1.581	86.7	877	1.25	1.87
C-MRCI+Q[d]	0.945 0	1.582	90.5			2.04
C-CCSD(T)[d]	0.959 42	1.558	83.1	977		2.19
		ANO-Bauschlicher+aug-cc-pVQZ: $\rightarrow[7s6p4d3f2g]_{Fe}/[6s5p4d3f2g]/_C$				
CASSCF	0.236 56	1.636	53.6	632.5	1.49	1.49
MRCI	0.550 69	1.593	83.8	841.5	1.34	1.95
MRCI+Q	0.578 4	1.596	85.2			2.08
		ANO-Bauschlicher+h+aug-cc-pVQZ: $\rightarrow[7s6p4d3f2g1h]_{Fe}/[6s5p4d3f2g]/_C$				
CASSCF	0.236 59	1.636	53.6	632.9	1.49	1.49
MRCI	0.552 61	1.592	84.4	845.9	1.33	1.94
MRCI+Q	0.580 4	1.595	85.8			2.08
C-MRCI[d]	0.889 27	1.578	89.5	880	1.23	1.88
C-MRCI+Q[d]	0.953 6	1.579	93.8			2.07
		Previous work				
MP4/SCF[e]		1.92	95.5			
DFT/LDA[e]		1.54	143.2			
DFT/NL[e]		1.57	107.0			
DFT/LDA[f]		1.565	155.6			
MRCI[g]		1.589	66.4	848	1.855	
MRCI+rel[g,h]		1.585	64.3	859		
MRCI[i]	0.5512	1.5922			1.30	1.93
MRCI+Q[i]	0.5789	1.5931	83.1	866.0		2.07
MRCI+Q+rel[i,h,j]		1.5907	82.4	871.5		
MRCI+Q+rel[i,h,k]	9.5029	1.5912	81.4	868.8		2.24
ACPF[i]	0.5783	1.5959				2.06
ACPF+rel[i,h,k]	9.3698	1.5944	83.0			2.22
Expt[j]		1.596[n]	91.2±7[q,r]	862.9±6.2[t]		
Expt[j]		1.596 21[o]	81.7±4.6[s]	~804[u]		
Expt[k]		1.591[n]		866.6±8.2[t]		
Expt[k]		1.592 39[o]				
Expt[l,j]		1.588 845 6		867.32		
Expt[l,j]		1.588 941 4		866.919		
Expt[m]						2.36(3)

[a]Internally contracted MRCI.
[b]+Q refers to the multireference Davidson correction.
[c]$-1300+E$.
[d]Core $3s^2 3p^6$ of the Fe atom included at the MRCI level.
[e]Reference 7, no specification of the state.
[f]Reference 8, it is only reported that the ground state is a triplet.
[g]Reference 9, MRCI/$[8s6p3d1f/_{Fe}4s3p1d/_C]$.
[h]Scalar relativistic corrections included.
[i]Reference 6, MRCI+Q/$[8s7p5d3f2g/_{Fe}$ aug-cc-pVQZ/$_C]$.
[j]$X\,^3\Delta_3$.
[k]$X\,^3\Delta_2$.

[l]Reference 10.
[m]Reference 11.
[n]Reference 12, r_0.
[o]Reference 13, r_0.
[p]D_e values corrected for BSSE.
[q]Reference 14.
[r]The D_e value has been extracted using the $D_0(FeC^+)$ value of Ref. 15.
[s]The D_e value has been extracted using the $D_0(FeC^+)$ value of Ref. 16.
[t]Reference 17.
[u]Reference 12, $\Delta G_{1/2}$ value.

state of FeC, $\mu=2.36(3)$ D, almost twice as large of our best value,[3] $\langle\mu\rangle=1.25$ D (Table I).

We decided to re-examine our calculations on the dipole moment of the $X\,^3\Delta$ state of FeC by increasing the basis set size, and using also the finite field method for obtaining the dipole moment (μ_{FF}) which has not been used in Ref. 3. Our basis set on C is now the aug-cc-pVQZ=$[6s5p4d3f2g]$,[5(b)]

while an h angular momentum Gaussian function ($\alpha=0.8$) was added to the previously employed basis set of Fe, therefore our largest one-electron expansion includes 175 spherical Gaussians. All our results at the CASSCF, MRCI, MRCI (+Q), C-MRCI, C-MRCI(+Q) (Q=the Davidson correction) and CCSD(T) were performed by the MOLPRO package.[18] We do not report CCSD(T) results using this

larger basis due to severe convergence problems even using CASSCF orbitals. Our largest C-MRCI expansion contains 2.97×10^9 configuration functions, reduced to 32×10^6 using the internal contraction technique. Table I lists our new results (third and fourth entries) as well as previous theoretical and pertinent experimental numbers.

It is interesting to follow the results of Table I: as the basis set increases the r_e, D_e, and ω_e values improve monotonically as compared to the experiment, in both MRCI and C-MRCI level. Our best C-MRCI r_e, D_e, and ω_e values (fourth entry) are in almost complete harmony with corresponding experimental findings. However, this is not the case with the dipole moment. Observe first that the expectation ($\langle\mu\rangle$) and finite field (μ_{FF}) dipole moment values are the same 1.48–1.49 D, at the CASSCF level, because the CASSCF wave function is exact within the chosen space. At the MRCI level $\langle\mu\rangle$ (=1.34 D) is basis set independent, while at the C-MRCI level decreases slightly as the basis set increases (1.28, 1.25, 1.23 D) drifting away from the experimental value[11] [=2.36(3) D], due to increased size-nonextensivity errors.

A dramatic improvement is observed using the finite field method: the μ_{FF} value increases by approximately 0.6 D as compared to the $\langle\mu\rangle$ value in both MRCI and C-MRCI levels of theory, while it seems to be independent of the basis set size, at least within these particular series of basis sets. Our best MRCI value is 1.94 D, still about 0.4 D smaller than the experimental value. Previous theoretical work (see last entry of Table I) confirms our findings indicating also that scalar relativistic effects do not play a significant role in these systems.[6,9] The $\langle\mu\rangle$=1.855 D at the MRCI level of Shim and Gingerich[9] is rather fortuitous, perhaps due to small basis sets and limited CI. Now notice the relatively good μ_{FF} values obtained at the C-CCSD(T) and MRCI(+Q) level, 2.17, 2.19, and 2.08 D, respectively (Table I), notwithstanding the problems of the CCSD(T) approach (single reference method for a multireference problem like the present one+symmetry problems).

Finally we would like to add that we have also encountered the same behavior of $\langle\mu\rangle$ versus μ_{FF} in the systems titanium methylidyne (TiCH),[19] and the diatomics titanium and vanadium fluoride (TiF, VF).[20] Employing large basis sets and MRCI methods the following dipole moment values are obtained for the ground states:

$$\text{TiCH } (\tilde{X}^2\Sigma^+): \langle\mu\rangle = 1.96, \quad \mu_{FF} = 2.51 \text{ D},$$

$$\text{TiF } (X^4\Phi): \langle\mu\rangle = 2.54, \quad \mu_{FF} = 2.85 \text{ D},$$

$$\text{VF } (X^5\Pi): \langle\mu\rangle = 2.31, \quad \mu_{FF} = 2.77 \text{ D}.$$

Unfortunately there are no experimental μ values for the above systems, so a clear assessment is not possible at this moment.

The conclusions of the present report are, first, that the finite field method for the calculation of dipole moments is to be preferred in general, and second, seemingly adequate wave functions otherwise, can fail badly for certain, for instance, one-electron properties.

[1] See, for instance, H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules. A Survey of Rigorous Quantum Mechanical Results* (Addison–Wesley, Massachusetts, 1972), and the book of abstracts of the 6th WATOC conference, 4–9 August, Lugano, Switzerland, 2002.

[2] See, for instance, J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley, Massachusetts, 1961).

[3] D. Tzeli and A. Mavridis, J. Chem. Phys. **116**, 4901 (2002).

[4] C. W. Bauschlicher, Jr., Theor. Chim. Acta **92**, 183 (1995).

[5] (a) T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989); (b) R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[6] S. S. Itono, T. Taketsugu, T. Hirano, and U. Nagashima, J. Chem. Phys. **115**, 11213 (2001).

[7] B. K. Nash, B. K. Rao, and P. Jena, J. Phys. Chem. **105**, 11020 (1996).

[8] R. M. Sosa, P. Gardiol, and G. Beltrame, Int. J. Quantum Chem. **65**, 919 (1997).

[9] I. Shim and K. A. Gingerich, Eur. Phys. J. D **7**, 163 (1999).

[10] M. Fujitake, A. Toba, M. Mori, F. Miyazawa, N. Ohashi, K. Aiuchi, and K. Shibuya, J. Mol. Spectrosc. **208**, 253 (2001).

[11] T. C. Steimle and W. L. Virgo, J. Chem. Phys. **117**, 1511 (2002).

[12] W. J. Balfour, J. Cao, C. V. V. Prasad, and C. X. W. Qian, J. Chem. Phys. **103**, 4046 (1995).

[13] M. D. Allen, T. C. Pesch, and L. M. Ziurys, Astrophys. J. Lett. **472**, L57 (1996).

[14] D. J. Brugh and M. D. Morse, J. Chem. Phys. **107**, 9772 (1997).

[15] R. L. Hettich and B. S. Freiser, J. Am. Chem. Soc. **108**, 2537 (1986).

[16] C. Angeli, G. Berthier, C. Rolando, M. Sablier, C. Alcaraz, and O. Dutuit, J. Phys. Chem. A **101**, 7907 (1997).

[17] K. Aiuchi, K. Tsuji, and K. Shibuya, Chem. Phys. Lett. **309**, 229 (1999).

[18] MOLPRO 2000 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions by R. D. Amos, A. Bernhardsson, A. Berning *et al.*

[19] A. Kalemos, T. H. Dunning, Jr., J. F. Harrison, and A. Mavridis (unpublished).

[20] Unpublished results of this laboratory.