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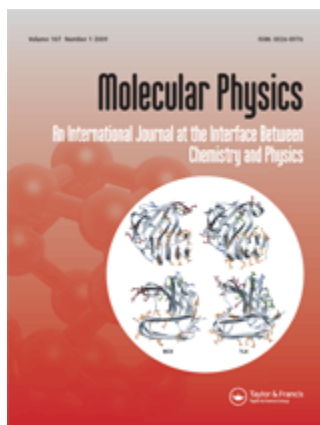
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## RESEARCH ARTICLE

A Multireference Perturbation Theory Study on the Fe<sub>2</sub> molecule:  
in quest of the ground state

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The  $^9\Sigma_g^-$  and  $^7\Delta_u$  states of the iron dimer, which according to a long-standing debate are the most probable candidates for the assignment of the ground state, have been investigated within the frame of multireference perturbation theory (PC-NEVPT2 and SC-NEVPT3) up to the third order in the energy. At short internuclear distances the  $^7\Delta_u$  state originates from the interaction of a ground-state  $^5D$  Fe atom with an excited-state  $^5F$ , whereas at large distances it results from the Van der Waals interaction of two  $^5D$  atoms. At all levels of calculation the  $^9\Sigma_g^-$  term appears to have lower energy than the short-range  $^7\Delta_u$  state and can thus be assigned as the ground state of the iron dimer. The spectroscopic constants of the  $^9\Sigma_g^-$  state ( $R_e=2.164 \text{ \AA}$ ,  $\omega_e=302.6 \text{ cm}^{-1}$  at the SC-NEVPT3 level of approximation) are in good accordance with the other high level *ab initio* calculation published thus far. The  $^9\Sigma_g^-$  and  $^7\Delta_u$  states of the iron dimer, which according to a long-standing debate are the most probable candidates for the assignment of the ground state, have been investigated within the frame of multireference perturbation theory (PC-NEVPT2 and SC-NEVPT3) up to the third order in the energy. At short internuclear distances the  $^7\Delta_u$  state originates from the interaction of a ground-state  $^5D$  Fe atom with an excited-state  $^5F$ , whereas at large distances it results from the Van der Waals interaction of two  $^5D$  atoms. At all levels of calculation the  $^9\Sigma_g^-$  term appears to have lower energy than the short-range  $^7\Delta_u$  state and can thus be assigned as the ground state of the iron dimer. The spectroscopic constants of the  $^9\Sigma_g^-$  state ( $R_e=2.164 \text{ \AA}$ ,  $\omega_e=302.6 \text{ cm}^{-1}$  at the SC-NEVPT3 level of approximation) are in good accordance with the other high level *ab initio* calculations published thus far.

**Keywords:** iron dimer (Fe<sub>2</sub>); multireference perturbation theory; NEVPT; transition metal dimers

## 1. Introduction

The accurate description of the electronic structure of the dimers of the transition metals constitutes one of the most difficult tasks for nowadays' quantum chemical methods. The reasons for this situation are essentially due to the concomitance of various factors: a) a zero order description of the electronic states is often essentially multireference; b) the outermost *s* and *d* electrons in the atoms necessitate different requirements of dynamical correlation energy, with the size of the outer *s* orbital significantly larger, especially in the first-row transition metals, than that of the *d* orbitals; c) many molecular electronic states of different total spin and of different  $L_z$  angular momentum often lie in a tiny energy interval; d) in many cases the ground state of the atom has an electronic configuration with two electrons in the highest occupied *s* orbital, so that the molecular states correlating to the ground states of the atoms are essentially dissociative (with only at most a shallow van der Waals minimum); e) the molecular states correlating to the atomic states with

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1 only one electron in the highest occupied  $s$  orbital are usually bound; f) the  $s \rightarrow d$   
2 excitation energy in the atom is often sufficiently low to justify the formation of the  
3 dimer bond as due to either atom (or even both) in an excited state; g) relativistic  
4 effects, especially for the transition metal rows other than the first, are significant.

5 In the iron dimer all the factors above mentioned, with the only possible excep-  
6 tion of the relativistic effects, are relevant and come into play, making  $\text{Fe}_2$  one of  
7 the most difficult transition dimers to deal with from the theoretical viewpoint.  
8 Experimentally, the information on the iron dimer is not abundant; in particular,  
9 the determination of the dissociation energy ( $D_0$ ) is subjected to uncertainties. Lin  
10 and Kant[1] with a second-law method estimate  $D_0 = 0.82 \pm 0.30$  eV, a value which  
11 is confirmed by Shim and Gingerich[2] who, on the basis of a third-law method,  
12 give  $D_0 = 0.78 \pm 0.17$  eV. Arguably, these values for  $D_0$  refer to the dissociation to  
13 the atoms in their ground state ( $^5D$ ). Moskovits and DiLella[3, 4], analysing reso-  
14 nance Raman spectra of  $\text{Fe}_2$  in noble gas matrices, obtained a value of  $\omega_e = 300.26$   
15  $\text{cm}^{-1}$  and  $\omega_e x_e = 1.45 \text{ cm}^{-1}$  from which, fitting with a Morse oscillator, a value of  
16  $D_e = 1.9$  eV could be obtained; however, using a LeRoy-Bernstein analysis[5], the  
17 same authors[4] obtain a value of  $D_e = 1.20$  eV. In a later work Haslett *et al.*[6]  
18 yield values in the range 1.25–1.75 eV for  $D_e$  and, more recently, Lian *et al.*[7]  
19 give a value of  $D_e = 1.14$  eV using collision-induced dissociation. The determina-  
20 tion of the equilibrium distance and of the frequency for  $\text{Fe}_2$  is subjected to much  
21 less uncertainty. Montano[8] and Purdum *et al.*[9] in EXAFS (Extended X-rays  
22 Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure)  
23 experiments found  $R_e = 1.87 \pm 0.13$  Å in argon matrix and  $R_e = 2.02 \pm 0.02$  Å in neon  
24 matrix. Concerning the determination of the equilibrium vibration frequency, be-  
25 sides the values already quoted from Moskovits and DiLella[3, 4], the photoelec-  
26 tron spectra experiments carried out on  $\text{Fe}_2^-$  by Leopold and Lineberger[10] yield  
27 a value of  $\omega_e = 300 \pm 15 \text{ cm}^{-1}$ . In a later work, Leopold *et al.*[11] provided a sim-  
28 ple and convincing explanation of the features of the experimental photoelectron  
29 spectra, advocating a nonet ground state ( $^9\Sigma_g^-$ ) originating from the interaction of  
30 an atom in the  $^5D$  ( $3d^6 4s^2$ ) ground state with another in the excited  $^5F$  ( $3d^7 4s^1$ )  
31 state.

32 The computational work on the iron dimer has been largely committed to DFT  
33 (Density Functional Theory) studies, most of which [12–21] agree in designating  
34  $^7\Delta_u$  as the ground state with more or less reasonable values for the equilibrium  
35 distance but with too large values for  $\omega_e$ . A noticeable exception in the DFT studies  
36 is provided by Irigoras *et al.*[22] and by Kulik *et al.*[23], where the  $^9\Sigma_g^-$  term turns  
37 out to be the ground state, with reasonable values of  $R_e$  and  $\omega_e$ . Irigoras *et al.*[22]  
38 use one of the most commonly adopted functionals (B3LYP) whereas Kulik *et al.*  
39 make use of the GGA (Generalised-Gradient Approximation) augmented by a  
40 Hubbard “U” term[24].

41 *Ab initio* work dedicated to  $\text{Fe}_2$  is not abundant: Shim and Gingerich[2] per-  
42 formed a limited CI (Configuration Interaction) study based on HF (Hartree-Fock)  
43 orbitals on the interaction of two  $^5F$  atoms and found a  $^7\Delta_u$  ground state with  $R_e$   
44 and  $\omega_e$  in large deviation from experiment. Tomonari and Tatewaki[25] and Noro *et al.*[26]  
45 introduced a certain amount of dynamical correlation in their multireference  
46 CI calculations and also found a  $^7\Delta_u$  ground state. A breakthrough in the  $\text{Fe}_2$  *ab*  
47 *initio* work is provided by Hübner and Sauer[27] who perform internally contracted  
48 multireference CI calculations (IC-MRCI) starting from a CASSCF wavefunction.  
49 They find  $^9\Sigma_g^-$  as the ground state (with  $R_e = 2.19$  Å and  $\omega_e = 303 \text{ cm}^{-1}$ ) and es-  
50 tablish that  $^7\Delta_u$  is higher in energy by 0.69–0.70 eV, with  $R_e$  and  $\omega_e$  varying  
51 considerably if a size consistency correction is brought to the IC-MRCI calcula-  
52 tion. Almost at the same time, Bauschlicher and Ricca[28] published a work, again  
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1 based on IC–MRCI calculations, where the results of Ref.[27] are confirmed, yield-  
2 ing a  ${}^9\Sigma_g^-$  ground state ( $R_e=2.19 \text{ \AA}$ ,  $\omega_e=301 \text{ cm}^{-1}$ ) with the  ${}^7\Delta_u$  state being higher  
3 in energy by 0.72–0.75 eV. Yet, Bauschlicher and Ricca advocate the opinion that,  
4 in order to reconcile theory and experiment, the  ${}^7\Delta_u$  state should be expected to be  
5 the true ground state, thus explaining the absence of ESR spectra[29], while  ${}^9\Sigma_g^-$   
6 would be the only possible state accessible in the photodetachment experiment[10].  
7 This supposition is seemingly confirmed by Casula *et al.*[30] who perform quan-  
8 tum Montecarlo (QMC) calculations based on the resonant valence bond (RVB)  
9 wavefunction. Actually the QMC calculations of Ref.[30] yield a  ${}^9\Sigma_g^-$  ground state  
10 with  ${}^7\Delta_u$  higher by 0.64 eV but the authors envisage to bring a correction, based  
11 on the asymptotic values of the energies, which upsets the energy ordering of the  
12 molecular terms.  
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15 As can be noticed from the cursory exposition reported above, the question of  
16 the attribution of the ground state for the iron dimer is not yet fully solved. Also,  
17 apart from the early works[2, 25, 26] and from Hübner and Sauer’s results[27], most  
18 theoretical works are confined to the determination of the equilibrium distance and  
19 of the harmonic frequency but are reluctant to produce the potential energy curve  
20 (PEC) for a wide range of internuclear distances. In the present work we shall  
21 investigate the lowest  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states of  $\text{Fe}_2$  making use of the  $n$ -electron  
22 valence state perturbation theory[31–33] up to the second (NEVPT2) and third  
23 order (NEVPT3)[34] in the energy. So far, only Ref.[28] has made use of multiref-  
24 erence perturbation theory (MRPT), yielding rather disappointing results. In the  
25 following sections we shall present the computational details of our approach (sec-  
26 tion 2), the results for the atomic calculations (section 3), those for the molecular  
27 calculations (section 4) and some conclusive remarks (section 5).  
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## 32 2. Computational details

33  
34 The calculations reported in this paper make use of the NEVPT2 form of MRPT  
35 developed in our laboratory[31–34]. The results for the iron dimer have been ob-  
36 tained with the “partially contracted” variant of the second order perturbation  
37 theory (PC–NEVPT2) and with the “strongly contracted” third order approach  
38 (SC–NEVPT3). We recall that the partially contracted approach makes use of the  
39 full dimensionality of the internally contracted first-order interacting space (IC–  
40 FOIS) whereas the strongly contracted variant only uses a subspace thereof. In a  
41 recent paper dedicated to the study of the scandium dimer[35], it has been shown  
42 that the third order strongly contracted approach yields results that are hardly dis-  
43 tinguishable from the computationally heavier third order partially contracted one.  
44 It is worth remembering that the NEVPT theory is endowed with two properties  
45 that make it particularly appealing for the study of the transition metal dimers: It  
46 is exempt from the intruder state problem, which afflicts most multireference PT’s  
47 and it is fully size–consistent, provided the underlying CASSCF wavefunction is  
48 itself size–consistent.  
49

50  
51 The atomic basis adopted in this work is the ANO–RCC (Atomic natural Orbitals  
52 Relativistic Correlation Consistent) set developed by Roos and coworkers[36] and  
53 consists of  $21s15p10d6f4g2h$  primitive gaussians contracted to  $10s9p8d6f4g2h$ .  
54 Scalar relativistic effects have been accounted for by use of the Douglas–Kroll–Hess  
55 Hamiltonian[37]. The calculations have been carried out with the 2009.1 release of  
56 the MOLPRO[38] program, which contains an implementation of the NEVPT2  
57 code. The NEVPT3 calculations have been performed with a stand-alone program  
58 interfaced with the MOLPRO package. The zero order wavefunctions to be next  
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submitted to the perturbation treatment have been built with a CASSCF procedure with the active space consisting of the molecular orbitals stemming from the  $4s$  and  $3d$  atomic orbitals (CASSCF 16/12 with 16 active electrons distributed over 12 molecular orbitals). For the degenerate states studied in this paper ( ${}^7\Delta_u$ ) the CASSCF calculations have been performed by averaging over the two degenerate components. To make sure that the calculated states have the desired value of  $L_z$  (the component of the total electronic angular momentum on the internuclear axis), a feature of the MOLPRO program has been exploited (the LQUANT parameter) and the mean value of the bielectronic  $\hat{L}_z^2$  operator has been evaluated after the CASSCF. The perturbation calculations have been done by leaving the  $1s$ ,  $2s$  and  $2p$  electrons uncorrelated. In this work we have drawn on the experience gained in our previous studies on the transition metal dimers for the group VI elements[34, 39] ( $\text{Cr}_2$ ,  $\text{Mo}_2$ ,  $\text{W}_2$  and  $\text{CrMo}$ ), for  $\text{Mn}_2$ [40] and for  $\text{Sc}_2$ [35].

### 3. Atomic calculations

Experimentally[41] the energy separation between the  ${}^5D$  ( $3d^64s^2$ ) ground state of the Fe atom and the first excited state  ${}^5F$  ( $3d^74s^1$ ) is rather small, amounting to 0.87 eV (difference between  $J$ -averaged values). The next excited states of Fe are located at 1.49 eV ( ${}^3F$  ( $3d^74s^1$ )) and 2.14 eV ( ${}^5P$  ( $3d^74s^1$ )). In this section we report the results of the calculations done on the  ${}^5D$  and  ${}^5F$  states. Starting from a CASSCF wavefunction obtained by utilising the  $4s$  and the five  $3d$  orbitals as active space, NEVPT calculations have been carried out at the second (PC-NEVPT2) and at the third order (SC-NEVPT3). In all cases, the CASSCF calculations have been performed by averaging over all the  $L_z$  components. Firstly, calculations have been conducted using orbitals optimised for the  ${}^5D$  and  ${}^5F$  states separately. Secondly, another set of computations has been performed with orbitals obtained with an averaged CASSCF over the  ${}^5D$  and  ${}^5F$  states altogether. This latter choice was dictated by the consideration that for the molecular states of  $\text{Fe}_2$  dissociating to the  ${}^5D + {}^5F$  limit, the CASSCF calculation actually involves an average over a subset of the  ${}^5D$  and  ${}^5F$  atomic components. The results are summarised in Table 1 where it can be remarked that, for the  ${}^5D$  term with single-state orbitals, the third order contribution to the energy is small, indicating that the zero order CASSCF description is adequate for this state and that the perturbation series appears to be converging. On the other hand, the  ${}^5F$  state, with one electron promoted from  $4s$  to  $3d$ , exhibits a second order correction much larger than the corresponding one for  ${}^5D$ , followed by a large positive third order contribution. The CASSCF description of  ${}^5F$  appears to be poor, with too large an amount of correlation energy at the second order and with a vast oscillation at the third order. The poor description of the  ${}^5F$  state at the CASSCF level lies at the root of the difficulties encountered in the  $\text{Fe}_2$  calculations. Table 1 also shows the results obtained with a common set of orbitals originating from the averaged CASSCF calculation. As can be seen from Table 1, the perturbation results suffer from a large oscillation for both atomic states when going from second to third order. We can therefore anticipate that: a) the molecular states of  $\text{Fe}_2$  dissociating to the  ${}^5D + {}^5D$  limit will benefit, at the CASSCF level, by a much better description than those tending to the  ${}^5D + {}^5F$  limit, b) at the second order of NEVPT the dissociation limits will be even upset, with  ${}^5D + {}^5D$  lying above  ${}^5D + {}^5F$  (-2543.948554 hartrees for  ${}^5D + {}^5D$ , twice the NEVPT2 energy with state specific orbitals; -2543.976573 hartrees for  ${}^5D + {}^5F$ , the sum of the two NEVPT2 energies with averaged CASSCF orbitals), c) at the third order of NEVPT the correct ordering will be restored but the energy

1 difference between the two limits will be numerically incorrect by roughly 1 eV.

2 All these difficulties would be much alleviated by the introduction of a second set  
3 of  $d$  orbitals in the Fe atom. Actually, calculations carried out with 11 active orbitals  
4 ( $4s$ ,  $3d$  and  $4d$ ) considerably improve on the CASSCF wavefunction and yield  
5 very small third order contributions to both atomic states; the resulting excitation  
6 energy from  ${}^5D$  to  ${}^5F$  amounts to 0.80 eV (CASSCF), 0.63 eV (PC-NEVPT2) and  
7 0.82 eV (SC-NEVPT3). Unfortunately, molecular calculations at the CASSCF level  
8 with an active space of 22 orbitals are still unfeasible nowadays.  
9

#### 10 4. The ${}^9\Sigma_g^-$ and ${}^7\Delta_u$ states of the $\text{Fe}_2$ molecule

11 In this section we report our calculations on the electronic states of the iron dimer,  
12 focussing our attention on the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  terms only, since it appears to be  
13 ascertained from all the works published to date that the ground state of  $\text{Fe}_2$  has  
14 to be attributed to either of such states. From Wigner and Witmer's rules[42], the  
15  ${}^9\Sigma_g^-$  terms may not dissociate to the  ${}^5D + {}^5D$  limit (nor to the  ${}^5F + {}^5F$  one);  
16 there are three  ${}^9\Sigma_g^-$  states dissociating to the  ${}^5D + {}^5F$  limit. On the other hand,  
17 for the  ${}^7\Delta_u$  terms, the situation is as follows: There are two, four and three states  
18 dissociating to  ${}^5D + {}^5D$ ,  ${}^5D + {}^5F$  and  ${}^5F + {}^5F$ , respectively. In order for the  
19  ${}^9\Sigma_g^-$  state (or the  ${}^7\Delta_u$  state with  ${}^5D + {}^5F$  character) to be the ground state, a  
20 necessary condition is that the dissociation energy with respect to the  ${}^5D + {}^5F$   
21 limit must be higher than the atomic excitation energy from  ${}^5D$  to  ${}^5F$ .  
22

23 The results of our calculations are collected in Figure 1. The left side of  
24 the figure reports the PEC's of the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states without any fur-  
25 ther correction, whereas in the right side the curves of the  ${}^7\Delta_u$  state disso-  
26 ciating to the  ${}^5D + {}^5D$  atomic limit are shifted by a constant amount such  
27 as to guarantee the experimental energy difference of 0.87 eV between the  
28 asymptotic limits. The upper (a, a'), middle (b, b') and lower part (c, c') of  
29 the figure relate to the CASSCF, PC-NEVPT2 and SC-NEVPT3 calculations,  
30 respectively. The CASSCF results for the  ${}^9\Sigma_g^-$  state are continuous all over  
31 the range of internuclear distances and show a well defined physical charac-  
32 ter originating from the interaction of a  ${}^5D$  with a  ${}^5F$  iron atom. At the dis-  
33 tance of 4.10 a.u., close to the minimum, the occupation pattern for the active  
34 orbitals is given by  $\sigma^{2.97}(4s)\sigma^{3.00}(d_{z^2})\delta^{2.03}(d_{x^2-y^2})\delta^{2.03}(d_{xy})\pi^{2.99}(d_{zx})\pi^{2.99}(d_{zy})$ ,  
35 where we have summed over the  $g$  and  $u$  components of the various sym-  
36 metries. The  ${}^7\Delta_u$  state, on the contrary, suffers from a marked discontinu-  
37 ity in the vicinity of  $R=4.20$  a.u., where the character of the state suddenly  
38 passes from  ${}^5D + {}^5F$  to  ${}^5D + {}^5D$ . At  $R=4.20$  a.u. the occupation pattern  
39 is  $\sigma^{2.97}(4s)\sigma^{2.06}(d_{z^2})\delta^{2.02}(d_{x^2-y^2})\delta^{3.00}(d_{xy})\pi^{2.98}(d_{zx})\pi^{2.98}(d_{zy})$  whereas at  $R=4.30$   
40 a.u. we obtain  $\sigma^{3.90}(4s)\sigma^{2.10}(d_{z^2})\delta^{2.00}(d_{x^2-y^2})\delta^{2.00}(d_{xy})\pi^{3.00}(d_{zx})\pi^{3.00}(d_{zy})$ . Usu-  
41 ally, when an abrupt change of physical character takes place in the CASSCF  
42 description of the PEC of a molecule, it is sufficient to carry out an appropriate  
43 average over a few electronic states to resolve the discontinuity. In the case of the  
44  ${}^7\Delta_u$  state of  $\text{Fe}_2$ , however, the difference in physical nature between the short-  
45 range (s.r.)  ${}^5D + {}^5F$  and the long-range (l.r.)  ${}^5D + {}^5D$  states, is so pronounced  
46 that no average of states could be revealed to be effective in attenuating the dis-  
47 continuity. In the light of the considerations exposed in the description of the  ${}^5D$   
48 and  ${}^5F$  states of the iron atom, it is apparent that the l.r. branch of the  ${}^7\Delta_u$  state  
49 is described much better, at the CASSCF level, than the s.r. branch. In order to  
50 make the curves comparable, we have empirically raised all the points of the l.r.  
51  ${}^7\Delta_u$  PEC by a constant value so as to obtain the correct asymptotic difference  
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of 0.87 eV between the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states. Passing now to examine the second order results for the PEC's, we observe that PC-NEVPT2 brings a vast negative correction to the states with  ${}^5D + {}^5F$  character ( ${}^9\Sigma_g^-$  and s.r.  ${}^7\Delta_u$ ), leading to a wrong location of the asymptotic states. By empirically lowering the l.r.  ${}^7\Delta_u$  PEC, we obtain the situation depicted in the right side of Figure 1. Finally, the third order results, with a positive third order contribution to the energy of both  ${}^9\Sigma_g^-$  and s.r.  ${}^7\Delta_u$ , restore the correct ordering of the asymptotic atomic limits but yield too large a value for the asymptotic energy difference.

The s.r. branch of  ${}^7\Delta_u$  symmetry describes a state which shares the same physical nature as  ${}^9\Sigma_g^-$ , namely the interaction of a  ${}^5D$  ( $3d^64s^2$ ) with a  ${}^5F$  ( $3d^74s^1$ ) atom; arguably, it can be considered as a quasi-diabatic state tending asymptotically to the  ${}^5D + {}^5F$  atomic limit. The correlation requirements of such a state are similar to those of  ${}^9\Sigma_g^-$  and Figure 1 shows that its energy is higher than  ${}^9\Sigma_g^-$  in the zone of the minimum. The energy difference between the minima of the s.r.  ${}^7\Delta_u$  and  ${}^9\Sigma_g^-$  states (assuming  $R=4.20$  a.u. as the minimum for the s.r.  ${}^7\Delta_u$ ) amounts to 0.62 for CASSCF, 0.66 eV for PC-NEVPT2 and 0.57 eV for SC-NEVPT3, suggesting that states with the same physical nature are dealt with in a balanced way. On the other hand, the l.r. branch of  ${}^7\Delta_u$  symmetry describes a state originating from the van der Waals interaction of two  ${}^5D$  atoms, yielding a shallow minimum at large distance (PC-NEVPT2 predicts  $R_e=3.66$  Å,  $D_e=0.076$  eV,  $\omega_e=37.8$  cm $^{-1}$  whereas SC-NEVPT3 gives  $R_e=3.81$  Å,  $D_e=0.052$  eV,  $\omega_e=33.4$  cm $^{-1}$ ). The spectroscopic constants for the  ${}^9\Sigma_g^-$  state are reported in Table 2 where a good accordance can be noted with the values obtained by the other *ab initio* calculations. The dissociation energy for the  ${}^9\Sigma_g^-$  state, calculated with respect to the  ${}^5D + {}^5F$  limit, is probably overestimated by PC-NEVPT2 (2.35 eV) and underestimated by SC-NEVPT3 (1.26 eV), a situation which we have met also in our preceding studies on the transition metal dimers.

## 5. Conclusive remarks

In this article the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states of the iron dimer have been analysed within the formalism of the NEVPT theory up to the third order in energy. In all of our calculations, namely CASSCF, PC-NEVPT2 and SC-NEVPT3, the  ${}^7\Delta_u$  state, albeit showing a discontinuity the origin of which has been discussed in section 4, exhibits a  ${}^5D + {}^5F$  character in the zone of the minimum where it has higher energy than the  ${}^9\Sigma_g^-$  state. Our results are in accordance with the accurate MR-CI calculations of Hübner and Sauer[27] and of Bauschlicher and Ricca[28]. Among the high level *ab initio* calculation published so far, it is only the work of Casula *et al.*[30] which assigns the ground state to  ${}^7\Delta_u$ . Anyway such an assignment is obtained thanks to a correction which is brought to the QMC calculations of Ref[30]. The correction is based on the atomic limit of the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states which Casula *et al.*[30] assume to be  ${}^5D + {}^5F$  and  ${}^5D + {}^5D$ , respectively. However the  ${}^7\Delta_u$  state in the zone of the minimum has  ${}^5D + {}^5F$  character and the pertinent correction to be brought should be related to the  ${}^5D + {}^5F$  limit. Therefore, in our opinion, also the work of Ref[30] bears out that  ${}^9\Sigma_g^-$  is the ground state for the iron dimer. Actually, the energy difference between the  ${}^7\Delta_u$  and  ${}^9\Sigma_g^-$  states reported in Ref[30] without correction (0.64 eV) is very similar to the one reported in the present work (0.57 eV in the SC-NEVPT3 calculation).

In conclusion, the accurate description of the electronic states of the Fe $_2$  molecule stands out as a most difficult task and the present work can be considered as only partially satisfactory. The origin of the difficulties lies in the defective description



1 of the  ${}^5F$  atomic state of Fe, for which the usage of an active space restricted to  
2 the valence shell orbitals  $4s$  and  $3d$  reveals itself as not entirely adequate. The use  
3 of a larger active space, possibly doubling the  $d$  orbitals in each centre, is likely to  
4 resolve both the discontinuity of the  ${}^7\Delta_u$  PEC and the unbalanced description of  
5 the states dissociating to the  ${}^5D + {}^5D$  and  ${}^5D + {}^5F$  atomic limits; unfortunately  
6 such a strategy is not yet viable nowadays. On the one hand the comparison of the  
7 absolute energies of the molecular states with  ${}^5D + {}^5F$  character with those of  ${}^5D$   
8 +  ${}^5D$  is defective because of the too different requirements of correlation energy of  
9 those states. On the other hand, the two states with  ${}^5D + {}^5F$  character ( ${}^9\Sigma_g^-$  and  
10 short-range  ${}^7\Delta_u$ ) are well comparable with one another and the present study has  
11 shown that  ${}^9\Sigma_g^-$ , at all levels of approximation, always shows a lower energy than  
12  ${}^7\Delta_u$ .  
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15 The perplexities raised by Bauschlicher and Ricca[28] about the reconciliation  
16 of the theoretical results with experiment still remain unanswered.  
17

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## References

- [1] S. Lin and A. Kant, *J. Phys. Chem.* **73**, 2450 (1969).
- [2] I. Shim and K.A. Gingerich, *J. Chem. Phys.* **77**, 2490 (1982).
- [3] M. Moskovits and D.P. DiLella, in *Metal Bonding and Interactions in High Temperature Systems*, edited by J. L. Gole and W. C. Stwalley, ACS Symposium Series 179 (American Chemical Society, Washington, DC, 1982), p. 153.
- [4] M. Moskovits and D.P. DiLella, *J. Chem. Phys.* **73**, 4917 (1980).
- [5] R.J. LeRoy and R.B. Bernstein, *J. Chem. Phys.* **52**, 3869 (1970).
- [6] T.L. Haslett, M. Moskovits and A.L. Weitzman, *J. Mol. Spectry* **135**, 259 (1989).
- [7] L. Lian, C.X. Su and P.B. Armentrout, *J. Chem. Phys.* **97**, 4072 (1992).
- [8] P.A. Montano, *Solid State Commun.* **35**, 53 (1980).
- [9] H. Purdum, P.A. Montano, G.K. Shenoy and T. Morrison, *Phys. Rev. B: Condens. Matter* **25**, 4412 (1982).
- [10] D.G. Leopold and W.C. Lineberger, *J. Chem. Phys.* **85**, 51 (1986).
- [11] D.G. Leopold, J. Almlof and W.C. Lineberger, *J. Chem. Phys.* **88**, 3780 (1988).
- [12] H.M. Nagarathua, P.A. Montano and V.M. Naik, *J. Am. Chem. Soc.* **105**, 2938 (1983).
- [13] E.A. Rohlffing, D.M. Cox, A. Kaldor and K.H. Johnson, *J. Chem. Phys.* **81**, 3846 (1984).
- [14] J. Harris and R.O. Jones, *J. Chem. Phys.* **70**, 830 (1979).
- [15] D. Guenzburger and E. Saitovitch, *Phys. Rev. B: Condens. Matter* **24**, 2368 (1981).
- [16] S. Dhar and N.R. Kestner, *Phys. Rev. A* **38**, 1111 (1988).
- [17] J.L. Chen, C.S. Wang, K.A. Jackson and M.R. Pederson, *Phys. Rev. B: Condens. Matter* **44**, 6558 (1991).
- [18] M. Castro and D.R. Salahub, *Phys. Rev. B: Condens. Matter* **49**, 11842 (1994).
- [19] P. Ballone and R.O. Jones, *Chem. Phys. Letters* **233**, 632 (1995).
- [20] S. Yanagisawa, T. Tsuneda and K. Hirao, *J. Chem. Phys.* **112**, 545 (2000).
- [21] C.J. Barden, J. Rienstra-Kiracofe and H.F. Schaefer III, *J. Chem. Phys.* **113**, 690 (2000).
- [22] A. Irigoras, M. Michelini, E. Sicilia, N. Russo, J.M. Mercero and J.M. Ugalde, *Chem. Phys. Letters* **376**, 690 (2003).
- [23] H.J. Kulik, M. Cococcioni, D.A. Scherlis and N. Marzari, *Phys. Rev. Letters* **97** (10), 103001 (2006).
- [24] V.I. Anisimov, J. Zaanen and O.K. Andersen, *Phys. Rev. B: Condens. Matter* **44**, 943 (1991).
- [25] M. Tomonari and H. Takewaki, *J. Chem. Phys.* **88**, 1828 (1988).
- [26] T. Noro, C. Ballard, M.H. Palmer and H. Takewaki, *J. Chem. Phys.* **100**, 452 (1994).
- [27] O. Hübner and J. Sauer, *Chem. Phys. Letters* **358**, 442 (2002).
- [28] C.W. Bauschlicher Jr. and A. Ricca, *Mol. Phys.* **101**, 93 (2003).
- [29] C.A. Baumann, R.J. Van Zee and W. Weltner, *J. Phys. Chem.* **88**, 1815 (1984).
- [30] M. Casula, M. Marchi, S. Azadi and S. Sorella, *Chem. Phys. Letters* **477**, 255 (2009).
- [31] C. Angeli, R. Cimraglia, S. Evangelisti, T. Leininger and J.P. Malrieu, *J. Chem. Phys.* **114**, 10252 (2001).
- [32] C. Angeli, R. Cimraglia and J. Malrieu, *J. Chem. Phys.* **117**, 9138 (2002).
- [33] C. Angeli, M. Pastore and R. Cimraglia, *Theor. Chem. Accounts* **117**, 743 (2007).
- [34] C. Angeli, B. Bories, A. Cavallini and R. Cimraglia, *J. Chem. Phys.* **124**, 054108 (2006).
- [35] C. Camacho, H. Witek and R. Cimraglia, *J. Chem. Phys.* **132**, 244306 (2010).
- [36] B.O. Roos, R. Lindh, P.m. Malmqvist, V. Veryazov and P. Widmark, *J. Phys. Chem. A* **109**, 6575 (2005).
- [37] B.A. Hess, *Phys. Rev. A* **33**, 3742 (1986).
- [38] MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, Version 2009.1, R. Lindh, F. R. Manby, M. Schütz *et al.*
- [39] C. Angeli, A. Cavallini and R. Cimraglia, *J. Chem. Phys.* **127**, 074306 (2007).
- [40] C. Angeli, A. Cavallini and R. Cimraglia, *J. Chem. Phys.* **128**, 244317 (2008).
- [41] Y. Ralchenko, A.E. Kramida, J. Reader and NIST ASD Team. NIST Atomic Spectra Database (version 3.1.4) available online at <http://physics.nist.gov/asd3>.
- [42] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics. Non-relativistic theory* (Pergamon Press, Oxford, 1977).

Table 1. Results of the atomic calculations. In parentheses are reported the values referring to the averaged CASSCF orbitals (see main text). Absolute energy values are in hartrees, excitation energies in eV.

State	CASSCF	$E_{corr}(PC2)$	$E_{corr}(SC3)$
$^5D$	-1271.326224 (-1271.284081)	-0.648053 (-0.721572)	-0.645590 (-0.666792)
$^5F$	-1271.250518 (-1271.230863)	-0.706643 (-0.740057)	-0.676990 (-0.698389)
$\Delta E^a$	2.060 (1.448)	0.466 (0.945)	1.206 (0.588)

<sup>a</sup>Experimental value[41] ( $J$ -averaged) is 0.87 eV.

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Table 2. Spectroscopic constants for the  ${}^9\Sigma_g^-$  state. Equilibrium distances  $R_e$  in Å, equilibrium vibration frequencies  $\omega_e$  and anharmonicity constants  $\omega_e x_e$  in  $\text{cm}^{-1}$ , dissociation energies  $D_e$  in eV. Dissociation energies are given with respect to the  ${}^5D + {}^5F$  limit. Experimental results refer to the (unspecified) ground state.

Method	$R_e$	$\omega_e$	$\omega_e x_e$	$D_e$
CASSCF <sup>a</sup>	2.229	234.7	2.92	0.24
PC-NEVPT2 <sup>a</sup>	2.189	322.0	0.78	2.35
SC-NEVPT3 <sup>a</sup>	2.164	302.6	2.86	1.26
IC-MRCI+Q <sup>b</sup>	2.190	301	-	-
IC-MRCI+Q <sup>c</sup>	2.187	302.8	-	-
QMC-RVB <sup>d</sup>	2.166	301±15	-	-
Experimental	1.87±0.13 <sup>e</sup>	300.26 <sup>g</sup>	1.45 <sup>g</sup>	-
	2.02±0.02 <sup>f</sup>	300±15 <sup>h</sup>	-	-

<sup>a</sup>This work

<sup>b</sup>Ref[28]

<sup>c</sup>Ref[27]

<sup>d</sup>Ref[30]

<sup>e</sup>Ref[8](from data in argon matrix)

<sup>f</sup>Ref[9](from data in neon matrix)

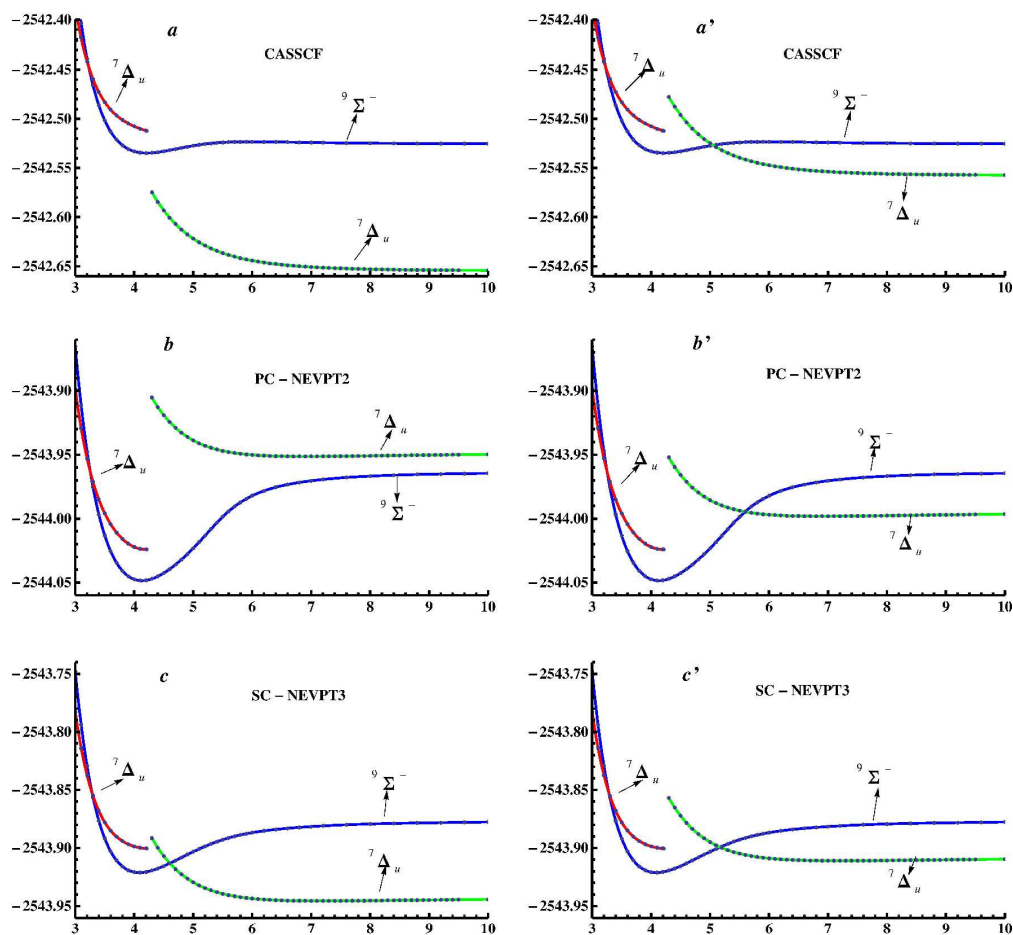
<sup>g</sup>Ref[4]

<sup>h</sup>Ref[10]

1 Figure caption.  
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4 Figure 1. The potential energy curves for the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states. Energies and distances are in atomic  
5 units. Parts a, b and c reports the calculation results uncorrected while in parts a', b' and c' constant  
6 shifts have been brought to the long range  ${}^7\Delta_u$  curves (see main text)  
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The potential energy curves for the  ${}^9\Sigma_g^-$  and  ${}^7\Delta_u$  states. Energies and distances are in atomic units. Parts a, b and c reports the calculation results uncorrected while in parts a', b' and c' constant shifts have been brought to the long range  ${}^7\Delta_u$  curves (see main text).

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