Response to "Comment on 'Fe2: As simple as a Herculean labour. Neutral (Fe2), cationic (Fe2+), and anionic (Fe2−) species'" [J. Chem. Phys. 144, 027101 (2016)]

Apostolos Kalemos

Response to "Comment on 'Fe₂: As simple as a *Herculean* labour. Neutral (Fe₂), cationic (Fe₂⁺), and anionic (Fe₂⁻) species'" [J. Chem. Phys. 144, 027101 (2016)]

Apostolos Kalemos[a)]

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Greece

In the Introduction section of our recent work on the iron dimer,[1] we criticized some aspects of the work by Hoyer *et al.*[2] Our critique appears in their Comment[3] and will not be duplicated here. We shall presently reiterate our arguments in a more eloquent way establishing *urbi et orbi* the undisputable validity of our initial commentary.

In Section III B of Ref. 2 we read statements like "...*which shows that our calculations predict a* $^9\Sigma_g^-$ *ground state for Fe₂*.", "*Our calculated ground state potential energy curve in Figure 1 exhibits a barrier to dissociation because the ground adiabatic state has an avoided crossing. This is due to a crossing of two diabatic potentials;* ...", and "*The presence of a barrier raises an important issue concerning the experimental dissociation energy of the Fe dimer.*" In Figure 1 of Ref. 2 we read "*Adiabatic ground state of Fe₂...*" and we see a potential curve with a barrier to dissociation to the supposed adiabatic channel Fe(^{5}D) + Fe(^{5}D) due to the avoided crossing between two curves of $^9\Sigma_g^-$ symmetry displayed in Fig. 2.[2] From their Fig. 1, it is also evident that the adiabatic dissociation energy is 0.77 eV as clearly stated in their Table IV.[2] In their Comment, Hoyer *et al.*[3] state that the ground state displayed in Fig. 1 of Ref. 2 is indeed the adiabatic ground state of Fe₂ but not the $^9\Sigma_g^-$ state, the latter being the ground state around the equilibrium structure, in complete disagreement with the shape of the potential curve in Fig. 1 and its constituent parts (of $^9\Sigma_g^-$ symmetry) displayed in Fig. 2. Certainly, a ground state is not a collection of the lowest energy points disregarding the symmetry properties of the associate wavefunctions and definitely not an adiabatic one. There is a "labeling error" in Fig. 2 (Ref. 2), corrected in their Comment,[3] but this error does affect the discussion in Section III B of Ref. 2. Provided that they displayed in their original Fig. 1 a properly dissociating ground state (and definitely of $^9\Sigma_g^-$ symmetry at all points of the internuclear distance), the reported binding energy (see Table IV of Ref. 2) would not be 0.77 eV but 0.77 + ΔE(^{5}F ← ^{5}D) = 0.77 + 0.79 = 1.56 eV, the barrier to

dissociation would not exist and certainly it could not "*raise an important issue concerning the experimental dissociation energy of the Fe dimer.*"[2] Moreover, the term "adiabatic"[4] means that the symmetry properties of the state are conserved at all points of the configuration space and does not merely "*mean electronic states that diagonalize the fixed-nuclei electronic Hamiltonian at some level of approximation.*"[3]

In point #2 of their Comment they say that "...*our paper does not state that there is an avoided crossing in the Λ−S scheme.*" However, in their paper[2] they state exactly the opposite "...*the ground adiabatic state has an avoided crossing. This is due to a crossing of two diabatic potentials;* ...." The rest of the discussion on the spin orbit couplings is irrelevant, at some points incorrect[5] and therefore meaningless.

Finally, in point #4 of the Comment they criticize the quality of our numerical results presented in Ref. 1, but they deliberately ignored our discussion on the reasons behind that and on how these results could have been better.

The error made in Ref. 2 is more than a "labeling" typo and we strongly believe that this is not mitigated by their present Comment.

[1]A. Kalemos, J. Chem. Phys. **142**, 244304 (2015).
[2]C. E. Hoyer, G. L. Manni, D. G. Truhlar, and L. Gagliardi, J. Chem. Phys. **141**, 204309 (2014).
[3]C. E. Hoyer, G. L. Manni, D. G. Truhlar, and L. Gagliardi, J. Chem. Phys. **144**, 027101 (2016).
[4](a) E. Merzbacher, *Quantum Mechanics*, 3rd ed. (John Wiley & Sons, Inc., 1998); (b) A. Messiah, *Quantum Mechanics* (North Holland, 1961).
[5]We read "*A widely used approximation in treating non adiabatic dynamics is to treat the adiabatic states in the absence of spin–orbit coupling (SOC) as diabatic states for the full Hamiltonian including spin–orbit coupling.*[4,5]" In such cases the "diabatic" states that should be considered in a nonadiabatic treatment are the "adiabatic" ones in the Λ−S scheme plus the diagonal spin–orbit coupling see e.g., H. Lefebvre-Brion and R. W. Field, in *The Spectra and Dynamics of Diatomic Molecules* (Elsevier, 2004). So, the statement "*For Fe₂, the full-problem ground state has contributions from three such diabatic states, resulting in two avoided crossings, each due to two states, when spin-orbit coupling is included.*" is not of any practical value for either an adiabatic or a nonadiabatic consideration.

[a)]kalemos@chem.uoa.gr