COMMENTS

Comment on “Excited States of DNA Base Pairs Using Long-Range Corrected Time-Dependent Density Functional Theory”

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The recent work of Jensen and Govind[1] reports on the transition energies in DNA monomer and AT and GC base pairs using time dependent density functional theory (TD-DFT) but incorrectly assigns the HOMO in the AT base pair to thymine. In their work, a comparison between long-range corrected (LC) functionals (BNL, CAM-B3LYP, and LC-PBE0) with the B3LYP functional has been made with emphasis on the issue of excitation induced charge transfer states in the AT and GC base pairs. In their report these authors point out the inadequacy of the B3LYP functional in predicting the transition energies for charge transfer states. On this point the authors are clearly correct as the energies of such transitions are well-known to be underestimated by TD-DFT, especially with the B3LYP functional. Treatments for this particular problem are well-known in the literature and have been reported in several works of Dreuw and Head-Gordon.[2]

In their work,[1] the authors report the location of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) on an AT base pair using B3LYP and CAM-B3LYP methods. This point is the main concern of this comment. The authors report that the CAM-B3LYP method shows the HOMO, in the AT base pair, is localized on T rather than on A and state that this assignment is correct.[1] This is emphasized in the table of content (TOC) graphic of this paper as well.

The HOMO, in fact, should be located on adenine not on thymine in the AT base pair. This is well established by a number of theoretical and experimental reports:

1. For the AT base pair it is well established the HOMO is on adenine by a number of theoretical reports including simple HF and more recent DFT calculations that employ the B3LYP functional which has a history of correctly predicting ground state properties.[3] To make this point clearer, we have performed a new calculation using the MP2/cc-pVTZ method and it clearly shows the localization of the HOMO in the AT base pair on A (see Figure 1. The calculation was performed using the BP86 optimized geometries of AT base pair as used in the calculation by Jensen and Govind.[1] As expected the HOMO is on adenine.
2. The experimental gas phase vertical ionization energies (IE) of the bases A and T are 8.44 eV for A and 9.14 eV for T.[4a,b] These results are supported by the theoretical calculations at various levels of theories.[4c−e] These IEs are strong evidence that the position of the HOMO will be on A in the AT base pair.
3. It is well-known that A undergoes one electron oxidation more easily than T. This is reflected in the oxidation potentials for A (ca. −1.4 V) and T (ca. −1.6 eV) measured by different experimental techniques, e.g., cyclic voltametry,[5a] pulse radiolysis,[5b] and fluorescence[5c] in monomers.
4. Electron spin resonance (ESR) spectroscopic data show that in γ-irradiated double stranded poly(dA):poly(dT), the hole (cation radical site) is localized on A and the electron (anion radical site) is localized on T.[6] This means that after hole transfer processes have taken place the hole is most stable on A which is consistent with the HOMO localized on A.

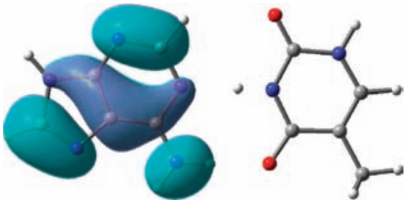

Figure 1. MP2/cc-pvtz calculated highest occupied molecular orbital (HOMO). The geometry was optimized using the BP86 functional, for details see ref 1. Gaussian 03 and GaussView were use for the calculation.[7,8]

The lower transition energy of the thymine $\pi-\pi^*$ transition (local excitation) relative to that of the $\pi-\pi^*$ A to T transition (charge transfer excitation) (see Table 3 and Figure 1 of ref 1) is incorrectly associated with the position of the HOMO in AT pair. The HOMO contributes only partially to the overall transition energy. The transition energy from A to T has the additional energy of electron hole separation that makes the local excitation on T lower in energy.

If a functional does not predict the proper HOMO for the AT base pair, its applicability to these systems is suspect. The B3LYP method is well tested for ground state systems as well as for local excitations, as evident from Tables 2 and 3 of ref 1. It does, however, underpredict the charge transfer transition energies and this must be taken into account.

References and Notes

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