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Research Article

The Magnetism Studies on the Radicals Generated by OH Attacking DNA Bases

Angyang Yu*
Liaoning University of Petrol and Chemical Engineering, China

***Corresponding author:** Angyang Yu, Liaoning University of Petrol and Chemical Engineering, China

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Abstract

Because the strong ionization radiation could result in the production of OH radicals, which attack and damage the DNA bases. It is possible to lead to the occurrence of disease if not repaired in time. Therefore, it is very important to investigate the spin polarization or magnetic properties of products generated by OH radical attacking DNA bases, which help understand radiation damage to DNA. By means of ab initio calculations, this work delves into the magnetic properties of DNA radicals produced in the addition and dehydrogenation reactions. GGA calculation shows that spin polarization exists in all the radicals, with 1μB total net magnetic moment for each free radical. The undamaged bases are free of magnetism, whereas the DNA bases attacked by OH radicals have magnetic properties.

Keywords: Cytosine; Thymine; First-principles; Magnetic properties

Introduction

In recent years, great efforts have been devoted to the study of radiation effects on DNA. There are many reasons for the interests in this area, for instance, radiation therapy can lead to disorder of DNA. Additionally, more and more people are exposed to ultraviolet radiation with the depletion of ozone layer, which draws great attention about radiation effects on DNA. The disorder of DNA caused by radiation damage includes changes in the base and sugar, as well as the rupture of chains. Ionizing radiation can cause direct or indirect damage to DNA. The energy is absorbed directly by DNA for direct damage, generating dehydrogenation radical and other products. The indirect damage comes from the attack on DNA by the free radicals, which are formed by the radiation in the environment of DNA [1,2]. These free radicals, in which OH radical is the most important one, are mainly produced from water [3-5]. OH radical could react with DNA bases, generating hydroxyl radicals. There are many experimental and theoretical investigations concerning the damage mechanism of DNA bases, as well as the possible products from the addition and dehydrogenation reactions between OH radical and DNA bases [6-16].

Previous experiments have proved that OH can add into the cytosine's double bond [17-19]. Theoretical calculations also confirm that the OH could add into cytosine at particular sites. In addition, the hydrogen abstraction reaction may happen in one of the C-H bonds of cytosine [20]. It is the same case for thymine [21-25]. However, up until now, there are no systematical theoretical and experimental reports about the electronic and magnetic properties of the reaction products, which are generated by the OH radical's attack on DNA bases. Using ab initio calculation, this paper delves into the magnetism of DNA radicals produced in the addition and dehydrogenation reactions.

Calculation Details

The calculations in the present work adopt two procedures: GAUSS03 [26] and VASP [27,28] program. The GAUSS program is used to simulate the addition process of OH radical and optimize the structure of dehydrogenation radical. By means of WB97XD computational level and 6-31G** basis set, Figure 1 presents the optimized structures of cytosine and thymine, as well as the numbering scheme. According to the analysis of literatures, we use the C6 site of cytosine and thymine as the attack position of OH radical in the addition reaction. The initial position of OH is perpendicular to the plane of each base, and the distance between O in OH radical and the target position is set to be 1.45A. For the dehydrogenation reaction, we calculated the magnetic properties of H9 deleted cytosine radical and H11 removed thymine. All the optimized radicals are further computed to confirm the magnetism. For the first-principles calculations, the augmented plane wave method is used, and the GGA-PBE approximation is used to describe the exchange correlation energy. The cutoff energy of plane wave is set at 450eV, where the integration of Brillouin zone makes use of the 4x4x4 gamma-centered K point grid.

Calculation Results

Figure 1b and 2b presents the optimized structure of hydroxyl radicals. As can be seen from the graph, the distances between O in OH and the target atom are 1.434 and 1.427 for cytosine and thymine, respectively, which are shorter than the initial distance 1.45A. Thus, it can be concluded that there is the covalent bond formed between the O atom and the target C atom. Figure 2 (1a and 2a) also shows the total DOS of the undamaged cytosine and thymine. It is evident that the spin-up DOS and spin-down DOS are completely symmetric, which indicates that the investigated system is free of magnetism. The total net magnetic moment of the system is computed to be 0μB. Overall, cytosine and thymine show no magnetism when in the absence of an attack.

Figure 2 (1b and 2b) shows the total density of states of hydroxyl radicals. It can be seen that the total DOS splits in the neighborhood of Femi level, which indicates the magnetism of the investigated system.

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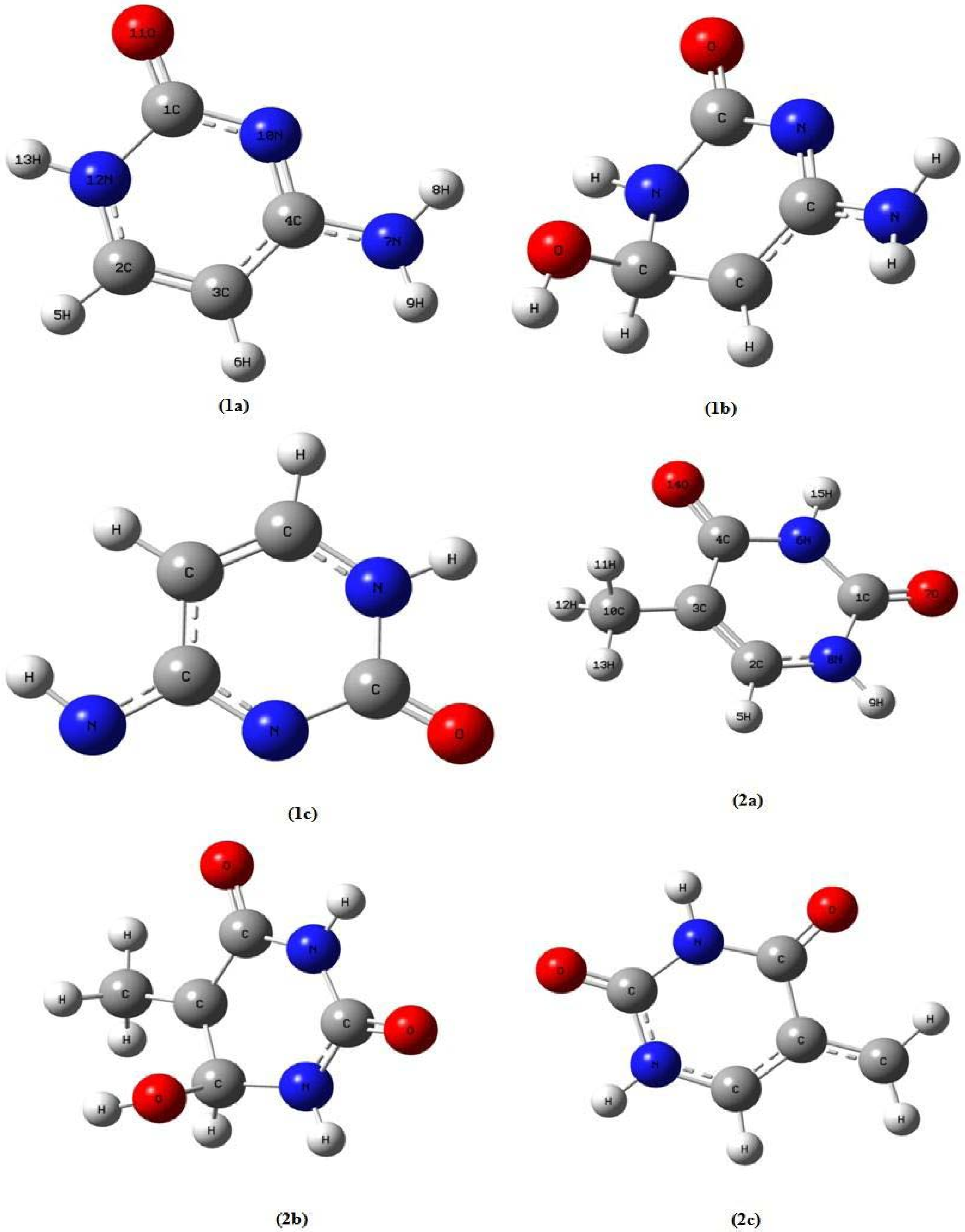
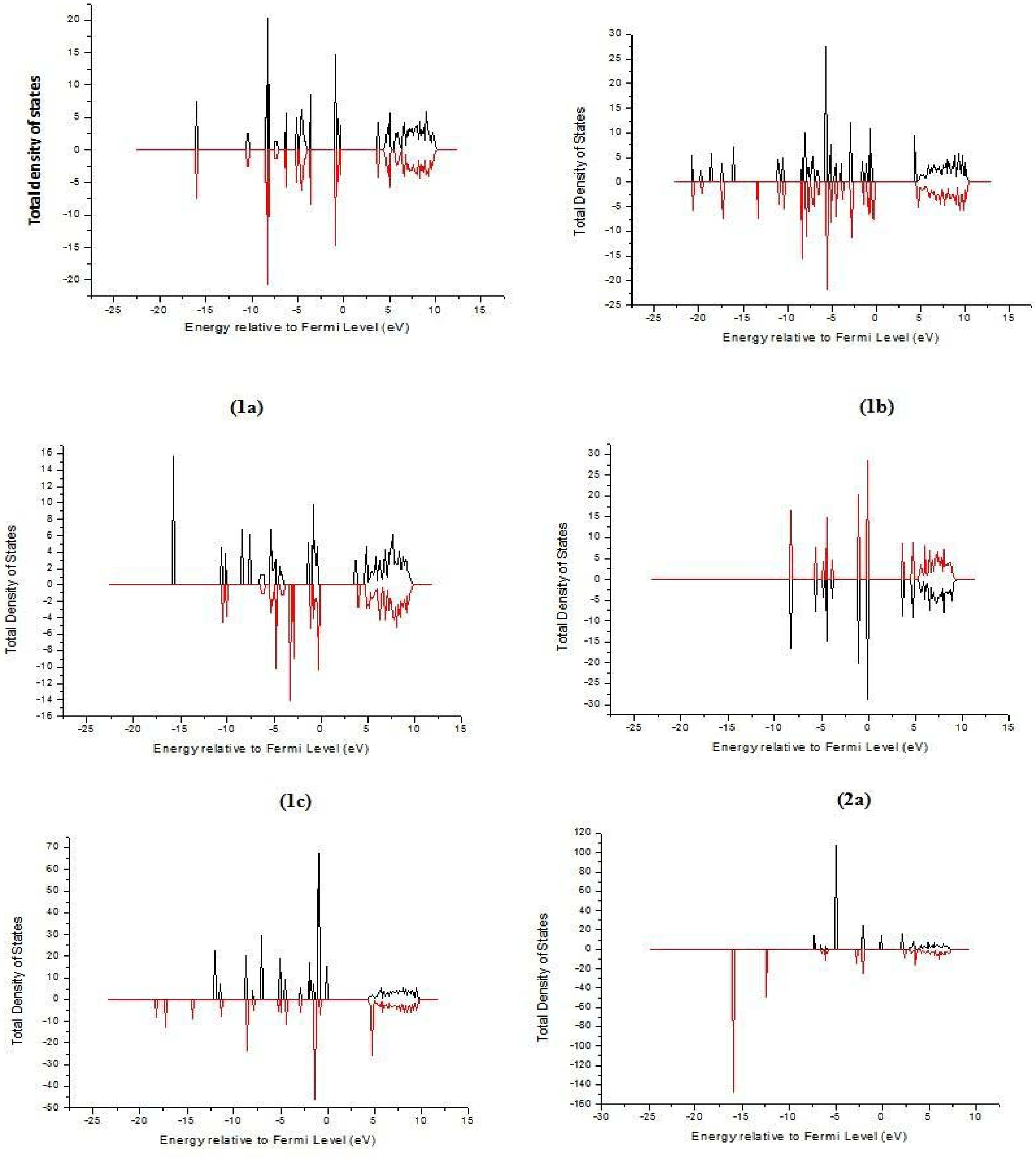


Figure 1: Structures of cytosine (1a) and thymine (2a), the hydroxyl radicals (1b and 2b) as well as the dehydrogenation radicals (1c and 2c).

Actually, the total magnetism moment of the system is calculated to be 1.0μB. Figure 1(1c and 2c) presents the optimized structures of dehydrogenation radicals. It could be found from Figure 2 that the total density of states for the dehydrogenation radicals (1c and 2c) show magnetism because the spin down and spin up density of states are not symmetric, which is consistent with the results of magnetic



(1a)

(1b)

(1c)

(2a)

(2b)

(2c)

Figure 2: The density of states for cytosine (1a) and thymine (2a), the hydroxyl radicals (1b and 2b) as well as the dehydrogenation radicals (1c and 2c), with the black line denoting spin up and the red line standing for spin down.

moments 1.0μB. Generally speaking, the concentration of OH formed by ionizing radiation is relatively low. Therefore, the addition or dehydrogenation reactions between OH radical and DNA bases can only produce paramagnetic properties in the investigated system.

Conclusion

Since the strong ionization radiation could result in the damage to DNA bases caused by the attack of OH radical. It is possible to induce disease if not repaired in time. Therefore, the investigation of the reaction (OH+DNA bases) products' spin polarization or magnetic properties is very important for understanding radiation damage to DNA. The magnetic properties of hydroxyl radical and dehydrogenation DNA base radicals were calculated in detail by GGA method. Spin polarization occurs in all the free radicals, with the total net magnetic moment of 1μB. The undamaged bases have no magnetism, whereas the DNA bases attacked by OH radical show magnetic properties.

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