

Spin Contamination in Hartree–Fock and Density Functional Theory Wavefunctions in Modeling of Adsorption on Graphite

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We have examined the effect of spin contamination in single determinant wave function at the Hartree–Fock and density functional theory in studying adsorption on graphite. Particularly, we examined NO adsorption on a single-layer graphene where some carbon atoms were left unsaturated to simulate the active sites in char. Upon comparison with the results from the restricted open-shell Hartree–Fock (ROHF) method, we found that UHF has a large spin contamination. Consequently, this yields large errors in the Hartree–Fock ground-state wave function, energy-level splitting, and adsorption energy. Interestingly, the spin contamination using unrestricted density functional theory was small, and the energetic information was almost unaffected.

I. Introduction

The heterogeneous reactions at the gas–carbon interface are of particular importance to coal chemistry, such as those in coal gasification and combustion. Previous experimental studies have identified oxygen complexes formed on the carbonaceous surface after reaction with oxider gases.^{1–5} However, its mechanism has not been well understood. Several theoretical studies based on both semiempirical molecular orbital (MO) theories^{6–9} and ab initio MO theories¹⁰ have studied oxygen complexes on carbonaceous surface. These studies assumed the active sites to be those carbons on the side of the graphene layer, as suggested from analyzing X-ray diffraction data¹¹. It is known that the carbonaceous surface involved in the process of gasification and combustion has a turbostratic character where the graphene layers can have random orientations. However, for practical purposes, the models of carbonaceous surface used in these theoretical studies consist of only a single graphene layer, in which some carbons on the boundaries were left unsaturated in order to simulate the active sites.^{12,13,6,10}

Due to the unsaturated carbon sites, these graphene models have high spin electronic states. It is known that unrestricted single-determinant wave function such as Unrestricted Hartree–Fock (UHF) theory would have a large spin contamination in modeling aryl and benzyl radicals^{14,15}. One can expect that such a spin contamination would affect the calculated geometry as well as energetic information of the adsorption processes on unsaturated graphenes. However, the effects of the spin contamination for modeling adsorption on carbonaceous surfaces to date have not been examined. As these molecular modeling techniques become increasingly used in studying these processes, it is important to gain knowledge regarding the reliability of the theoretical methods being used. For this purpose, in the present study, we examined the spin contamination in unre-

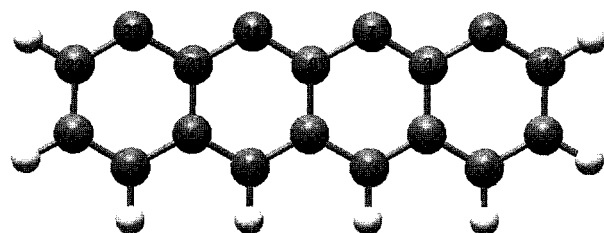


Figure 1. Single graphene layer used as a model of char.

stricted wave functions at both the HF level and the nonlocal density functional theory (DFT) by comparing the results to those obtained from restricted open-shell calculations. We have selected the adsorption of NO to illustrate the effects of the spin contamination because of its importance in coal gasification and because of the availability of experimental and theoretical data for comparison.

II. Computational Details

Much like previous theoretical studies,¹² the carbonaceous surface is modeled by a single graphene layer, as shown in Figure 1, in which the edge atoms on the upper side are unsaturated in order to simulate the free active sites, whereas others are terminated with hydrogen atoms. The geometries of the graphene layer and its NO adsorption complexes have been fully optimized at the HF and B3LYP DFT level, where B3LYP stands for Becke's 3-parameter nonlocal exchange functional¹⁶ with the nonlocal correlation functional of Lee, Yang, and Parr¹⁷. Both unrestricted and restricted open-shell wave functions were used with the 6-31G(d) basis set. To determine the ground state of the graphene layer, different electronic states were calculated at the HF level. All of the calculations were done using the Gaussian98 package¹⁸.

III. Results and Discussion

First, we discuss the magnitude of the spin contaminations in both the UHF and UB3LYP wave functions for the graphene

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TABLE 1: Calculated Relative Energy Levels (kcal/mol), $\langle S^2 \rangle$ Values, the Difference $\langle S^2 \rangle - S(S+1)$, of the Graphite Model at Different Electronic States.

| state | ΔE | $\langle S^2 \rangle$ | $\langle S^2 \rangle - S(S+1)$ |
|---------|------------|------------------------|--------------------------------|
| | | UHF | |
| quintet | 0 | 8.8 (6.2) ^a | 2.8 (0.2) |
| triplet | 15.2 | 5.6 | 3.6 |
| singlet | 60.9 | 2.2 | 1.2 |
| septet | 73.0 | 13.0 | 1.0 |
| | | ROHF | |
| quintet | 0 | 6 | 0 |
| triplet | 125.2 | 2 | 0 |

^a Values in the parentheses are from UB3LYP calculations.

molecule. This is illustrated by the deviation of the average $\langle S^2 \rangle$ values from its eigenvalues $S(S+1)$ as listed in Table 1 for several electronic states. The ground state is a quintet state for the molecular graphene system as shown in Figure 1. Table 1 also lists the energies for several excited states using the ground-state optimized geometry at a specified level of theory. Our results indicate that there is a large spin contamination in the UHF wave functions for the first three electronic states. This is also reflected in the vertical excitation energy from the ground-state to the first triplet excited state. UHF yields the value of only 15.2 kcal/mol, as compared to 125.2 kcal/mol from the ROHF calculations. It is interesting to note that the spin contamination is rather small in the B3LYP wave function. The same conclusion was found for aryl compounds using the BLYP method.¹⁴ This spin contamination can be further shown in the total spin density plotted in Figure 2. Both unrestricted and restricted open-shell B3LYP total spin densities are similar to each other, and they are similar to the restricted open-shell HF level. The UHF total spin density is noticeably different, particularly in the active-site region, i.e., unsaturated carbons.

The fully optimized geometrical parameters of the graphene system at different levels of theory are shown in Table 2. Although the experimental values¹⁹ corresponds to the crystal structure, the geometrical parameters obtained from the isolate molecular system using DFT and ab initio MO levels of theory are in very good agreement with the bond lengths determined experimentally. The largest deviation, only 0.02 Å, was obtained for the ROHF C–C bond length. There is no substantial

TABLE 2: Optimized Geometrical Parameters Using Different Levels of Theory of Graphene Molecule Shown in Figure 1 in the Ground State^a

| parameter | ROHF | ROB3LYP | UHF | UB3LYP | exp ^b |
|-----------|-------------------|---------|--------|--------|------------------|
| C–C | av 1.40 | 1.41 | 1.41 | 1.41 | 1.42 |
| | σ_n 0.08 | 0.03 | 0.02 | 0.04 | |
| C–H | av 1.08 | 1.09 | 1.08 | 1.09 | 1.07 |
| | σ_n 0.0006 | 0.0007 | 0.0007 | 0.0006 | |
| <C–C–C | av 120.80 | 120.00 | 120.82 | 120.33 | 120 |
| | σ_n 3.18 | 3.0 | 3.17 | 3.46 | |
| <C–C–H | av 119.80 | 120.00 | 119.71 | 119.51 | 120 |
| | σ_n 1.30 | 1.12 | 0.97 | 1.20 | |

^a σ_n Standard Deviation. av: Average. Bond Length (Å). Bond Angle (°) ^b Ref. Error! Bookmark not defined.

TABLE 3: Calculated Adsorption Geometry (Bond Lengths are in Å) and Binding Energy, D_e , (kcal/mol) for NO Adsorption on a Char Model.

| method | D_e | C11–N | C7–O | $\langle S^2 \rangle - S(S+1)$ |
|---------|----------------------------|-------------------|-------------------|--------------------------------|
| ROHF | 90.1 | 1.29 | 1.33 | 0.0 |
| UHF | 44.1 | 1.33 | 1.35 | 1.78 |
| UB3LYP | 126.1 | 1.33 | 1.35 | 0.03 |
| ROB3LYP | 135.2 | 1.32 | 1.35 | 0.0 |
| exp | (–71 to –120) ^a | 1.35 ^b | 1.36 ^b | |

^a Heat of adsorption from ref 20 ^b From ref 19

difference between the results obtained from unrestricted and restricted open-shell wave functions.

The effects of the spin contamination on the adsorption geometry and binding energy of NO on a char model are shown in Table 3. We examined two possible adsorption directions, one from the side of the unsaturated carbons and the other from the top of the graphene basal plane, as shown in Figure 3. The later adsorption direction was suggested from a theoretical study for O₂ adsorption on a single graphene layer at the CNDO/2 semiempirical level of theory.⁷ In the present study, in all unrestricted and restricted open-shell cases, we found that the NO molecule prefers to adsorb only from the side. In this case, both B3LYP and HF methods predict the adsorption complex to have a planar structure. The most important geometrical parameters are shown in Table 3. The expected S^2 values indicates that the UHF wave function has a much larger spin contamination compared to the UB3LYP case, much like the

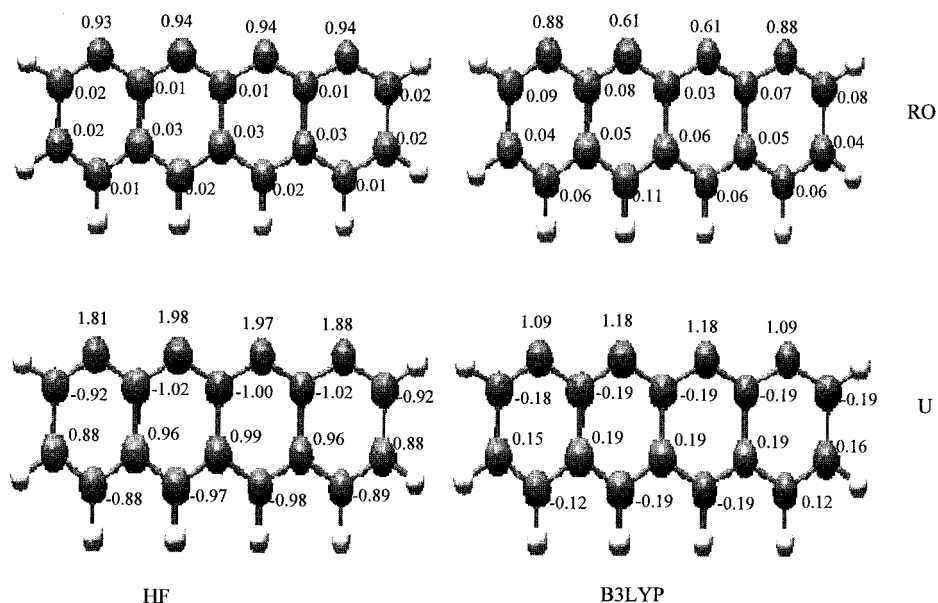


Figure 2. Total spin density on a single graphene layer obtained with restricted-open wave function (top) and unrestricted (bottom) at Hartree–Fock (left) and B3LYP functional (right) levels.

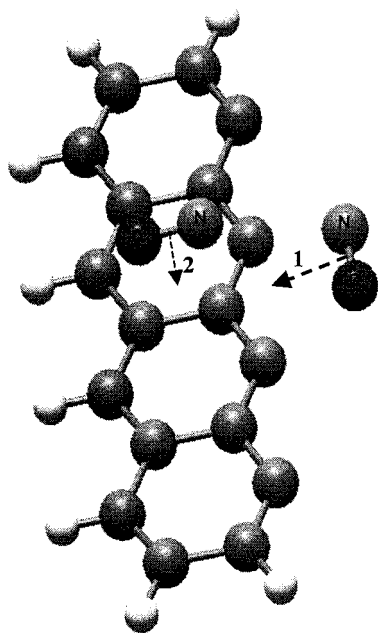


Figure 3. Two positions of NO adsorption on graphite system: (1) Side NO adsorption, (2) Basal NO adsorption.

graphene case above. Consequently, there is nearly a factor of 2 difference in the UHF and ROHF binding energies, particularly 44.1 and 90.1 kcal/mol from UHF and ROHF, respectively. In addition, the adsorption bond distances, namely C11–N and C7–O, where C11 and C7 are the two nearest adsorption sites, are somewhat shorter in the ROHF as compared to the UHF case by at most 0.04 Å. Because the spin contamination is quite small in the DFT calculations, we found that the adsorption geometry is similar in both unrestricted and restricted open-shell cases. The ROB3LYP binding energy of 135.2 kcal/mol is about 9 kcal/mol larger than that of the UB3LYP result. Adding the zero-point energy correction calculated at the UB3LYP level, both predict the heat of adsorption in the range of –113 to –122 kcal/mol for UB3LYP and ROB3LYP, respectively, which can be compared with the experimental estimate of –71 to –120 kcal/mol at low coverage²⁰.

IV. Conclusion

We have examined the effects of spin contamination in the unrestricted single determinant wave function at the HF and B3LYP levels of theory in calculating geometry and binding energy of adsorption on carbonaceous surfaces. We have used a single graphene layer with unsaturated carbon atoms to model the active sites. Due to the nature of the active sites, we found that there is a significantly large spin contamination in the UHF wave function. This leads to an error of 46 kcal/mol in the NO binding energy, 51% of the ROHF binding energy. It is known that such a spin contamination would be more severe in the transition state region. Thus, care should be taken in using UHF-

based methods in modeling reaction mechanisms on carbonaceous surfaces. The B3LYP method has a much smaller spin contamination. Consequently, there are smaller differences in both adsorption geometry and binding energy between the unrestricted and restricted open-shell wave function. Due to the computational efficiency of the unrestricted open-shell methods compared to the restricted open-shell ones, we suggested nonlocal DFT methods should be used in modeling adsorption processes or reactions on carbonaceous surfaces.

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