

Effects of Spin Contamination on the Stability and Spin Density of Wavefunction of Graphene: Comparison between First Principle and Density Functional Methods

(Kesan Pemumusan Spin Terhadap Kestabilan dan Ketumpatan Spin bagi Fungsi Gelombang Grafen pelumusan: Perbandingan antara Kaedah Prinsip Pertama dan Kaedah Kefungsian Ketumpatan)

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ABSTRACT

The effects of spin contamination on the stability and the spin densities of a model of graphene in the Hartree-Fock wavefunction (HF), Møller-Plesset perturbation theory (second order, MP2 and fourth order, MP4) and density functional theory (B3LYP and PBEPBE) are reported. It was found that the Hartree-Fock and MP2 wavefunctions of graphene suffer from the contamination from higher spin states and spin projection method failed to project out the spin contaminants. The spin density from HF was overestimated, while for MP2 it has the wrong trend. B3LYP and PBEPBE wavefunctions however have negligible contamination for higher spin states. Comparison with reported results showed that the spin densities at the center of the molecule from the pure functionals of PBEPBE were underestimated. Based on the comparison made, it was concluded that among the methods considered, the suitable one for use in the calculations of pristine graphene was B3LYP.

Keywords: Density functional theory; grapheme; Hartree-Fock; Møller-Plesset perturbation theory; spin contamination

ABSTRAK

Kesan pelumusan spin ke atas kestabilan dan ketumpatan spin di dalam fungsi gelombang Hartree-Fock (HF), teori gangguan Møller-Plesset (tertib kedua, MP2 dan tertib keempat, MP4) dan teori fungsi ketumpatan (B3LYP dan PBEPBE) bagi model grafen dilaporkan. Didapati bahawa fungsi gelombang HF dan MP2 bagi grafen mengalami pelumusan daripada keadaan spin lebih tinggi dan kaedah projeksi gagal mengeluarkan pelumusan putaran. Nilai ketumpatan spin daripada HF adalah terlebih anggar, manakala untuk MP2 ia mempunyai corak yang salah. B3LYP dan PBEPBE mempunyai pelumusan spin yang boleh diabaikan. Perbandingan dengan keputusan yang telah dilaporkan menunjukkan bahawa ketumpatan spin pada bahagian tengah molekul daripada kefungsi tulen PBEPBE adalah terkurang anggar. Berdasarkan perbandingan yang dilakukan, disimpulkan bahawa antara kaedah-kaedah yang dipertimbangkan, B3LYP merupakan kaedah yang sesuai untuk pengiraan melibatkan grafen tulen.

Kata kunci: Grafen; Hartree-Fock; pencemaran putaran; teori gangguan Møller-Plesset; teori fungsi ketumpatan

INTRODUCTION

Spin contamination is a long standing problem in open-shell calculations. It is a phenomenon where a certain spin state is mixed with higher spin states. The admixtures render the spin of the original state impure. Spin contamination occurs in open-shell calculations because the wavefunctions from such calculations are not eigenvectors of the total spin operator. But not all open-shell calculations will encounter severe spin contamination. For example, open-shell calculations utilising full configuration interaction (full CI) and density functional theory (DFT) with exact functionals are spin contamination-free (Wittbrodt & Schlegel 1996). Because performing full CI is a computationally tedious task, and the exact functionals in DFT have not yet been found, open-shell calculations must be contended with the existence of spin contamination. Spin contamination

will degrade the quality of the potential energy surface (Cremaschi et al. 1976; Schlegel 1986; Wittbrodt & Schlegel 1996) and spin densities (Amos & Snyder 1964; Claxton & McWilliams 1970; Snyder & Amos 1965) of small molecules. If the underlying unrestricted Hartree-Fock wavefunction is spin contaminated, the calculations of Møller-Plesset series will have the problem of slow convergence (Handy et al. 1985).

Spin contamination has been studied in a few types of systems (Andrews et al. 1991; Baker et al. 1993; Burnham 1969; Chen & Schlegel 1994; Chuang et al. 1999; Donzelli et al. 1996; Li & Paldus 2000), including systems involving graphene/graphite (Montoya et al. 2000; Plakhutin et al. 2005). Graphene is a material that has been prepared experimentally in 2004 (Geim 2009; Geim & Novoselov 2007; Novoselov et al. 2004; Novoselov

et al. 2005). In computing the properties of graphene utilising molecular orbitals cluster method, graphene may be represented by a carbon cluster that might have zigzag and armchair edges or both. These edges might be terminated by hydrogen atoms or other adatoms to saturate the dangling bonds. Specifically, the ground state for monohydrogenated zigzag-edged finite graphene nanodots and graphene nanoribbons (GNRs) is predicted to show antiferromagnetism (AFM) (Son et al. 2006a, 2006b). To account for this magnetic property, calculations with open-shell singlet calculations are necessary in order to show the spin polarization at the zigzag edges.

In the HF calculations, the value of the calculated spin eigenvalue (S^2) is an indicator of the quality of the calculated wavefunction (Nandi et al. 1996). The use of S^2 as an indicator is also applicable to the post-SCF methods (Chen & Schlegel 1994). For DFT, the use of S^2 in judging the quality of the calculated wavefunction is still in debate (Grafenstein et al. 2002; Menon & Radom 2008), and there exists ambiguity in determining the corresponding value for DFT (Cohen et al. 2007). The general arguments are based on the premise that the value of S^2 has no physical significance to the wavefunction from DFT, therefore the values of S^2 that deviates from the correct spin states is not a necessary indicator that the underlying wavefunction is spin contaminated (Grafenstein et al. 2002). The degree of spin contamination in hybrid functionals of density functional theories was found to increase with the increasing portion of Hartree-Fock exchange (Menon & Radom 2008). Thus, it is interesting to gauge the suitability of B3LYP in calculating the properties of graphene, subjected to the issue of spin contamination, as this hybrid functional has become the benchmark in calculating the electronic properties of materials.

One of the suggested methods to overcome spin contamination is the spin projection method (Löwdin 1955). Using this method, the spin eigenfunction of next higher spin will be projected out. Application of this method may not always produce the desired results. After annihilation of the first spin contamination ($S+1$), S^2 may increase (Davidson & Clark 2005; Plakhutin et al. 2005). In this case, the major contribution is arriving from the few higher spin multiplets (Plakhutin et al. 2005). Spin projected methods may not necessarily yield satisfactory results as they are shown to give incorrect curves for bond dissociation (Wittbrodt & Schlegel 1996). Restricted-open method provides another way to perform open-shell calculations without the problem of spin contamination. Although this method gives the correct value of S^2 , the arrangement of electrons in this method is incorrect in that it cannot show spin polarization for configuration of open-shell singlet. Thus results from this kind of calculations should be treated with caution. In the present work, the focus was on the open-shell calculations in the graphene system. The relevant methodologies are presented in the next section.

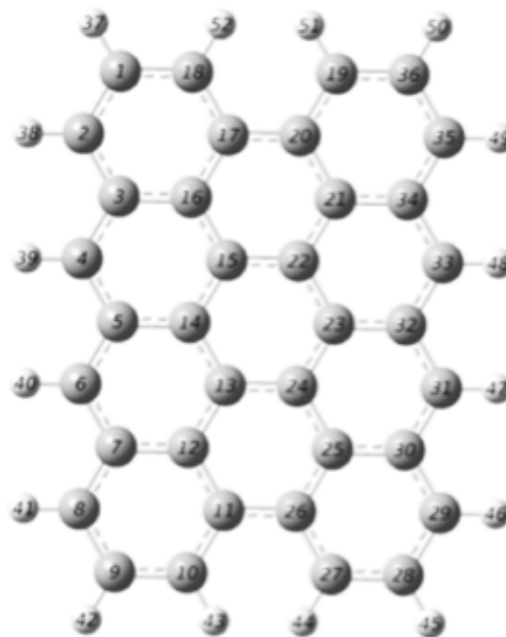


FIGURE 1. Model cluster of graphene used in this study. The large spheres (grey) are carbon atoms (numbers 1 to 36), and the small spheres (white) are hydrogen atoms (numbers 37 to 52)

METHOD

In this investigation, six methods ranging from pure wavefunction-based (Hartree-Fock (HF), Restricted Open-shell Hartree-Fock (ROHF)), post-SCF (second- and forth-order Møller-Plesset perturbation theory (MP2 and MP4)), density functional theory in the forms of pure (exchange-correlation functionals of Perdew Becke Ernzerhof (PBE) and hybrid functionals (Becke's three parameter hybrid functional using the Lee-Yang-Parr correlation functional (B3LYP, 20 % HF exchange (Menon & Radom 2008))) were chosen. The 6-31G(d) basis set was utilized in all the calculations. A model of $C_{36}H_{16}$ was chosen in this investigation. This carbon cluster, as shown in Figure 1, is among the smallest graphene nanodots that exhibit AFM (Hod et al. 2008; Jiang et al. 2007). The properties of this model have been reported before (Dias 2008; Hod et al. 2008; Jiang et al. 2007; Peralta-Inga et al. 2001). Thus comparison can be made between the results obtained here and those available in the literature. Modeling characteristics of AFM requires open-shell singlet calculations, which were prone to spin contamination from higher spin states. The selection of $C_{36}H_{16}$ has also been made based on the computational resources for post-SCF calculations especially MP4.

For the methods of HF, ROHF, MP2, B3LYP, and PBE, the geometry of the graphene model was initially optimized at singlet closed shell state. The optimized geometry was then used for subsequent single point calculations with multiplicities of 3, 5, 7, and 9 in order to find the correct spin for the ground state. This

approach (Gao et al. 2008; Menon & Radom 2008) is justified because the geometries of the closed-shell and open shell calculations are very close (Gao et al. 2008). Tests of this approach was performed using the method of B3LYP on cluster $C_{36}H_{16}$. It was found that the most stable state is the open-shell singlet, and the difference of spin eigenvalues for triplet and above between the optimized geometry and non-optimized geometry did not show any significant deviation. Only in the open shell singlet state significant deviations of spin eigenvalues occurred. Thus in this report, the geometry and electronic structure for open shell singlet were optimized at the open shell spin state. For MP4, because of the large requirement for the computational resources, only single point calculations were performed using the optimized geometry from RHF/6-31G*. Solutions from the open shell singlet state, the so-called broken symmetry solution, were also examined in all the methods in order to model the AFM state. All calculations were carried out using Gaussian 03 program (Frisch et al. 2004).

Another issue concerning the open-shell calculation is the use of spin projected densities. For MP4, the spin projected energy is more accurate than the unprojected UMP4 energies (Schlegel 1988). This is different in the case of DFT (B3LYP), where there are two contradicting views (Cramer et al. 1995; Wittbrodt & Schlegel 1996). While Wittbrodt et al. pointed out that spin projection could degrade the quality of the wavefunction of DFT and advocates against its usage for certain area (Wittbrodt & Schlegel 1996), Cramer et al. found that the spin annihilation in DFT improves the quality of the quantities predicted with calculations using DFT (Cramer et al. 1995). In this investigation, spin projected densities were used for all the methods except for the pure DFT in performing the population analysis.

The stability of the cluster is examined by comparing the energies of the multiplets. The net spin S of a molecule is given by the formula:

$$S = \frac{1}{2}(N_{\alpha} - N_{\beta}), \quad (1)$$

where N_{α} and N_{β} are the number of spin up and spin down electrons, respectively. The spin eigenvalue for the specific state is $S(S+1)$. The deviations from the specific eigenvalue is considered as spin contaminated. The validation (1) in this investigation is performed in quantum mechanical way by comparing the energies of the multiplets. The spin clusters are found in graphene by measuring the Hall effect (Shrivastava 2011).

RESULTS AND DISCUSSION

The calculated energies and the corresponding spin eigenvalues are shown in Tables 1 and 2. Based on (1), singlet should be the ground state because the number of spin up and spin down electrons are the same in this molecule. In Table 1, except for the methods of ROHF and MP2, the calculated energies of all other methods showed the open-shell singlet (BS) as the ground state. For ROHF, the closed-shell singlet and open-shell singlet are the same because in this method, the spin up and spin down orbitals are constrained to be the same. As for the MP2, the ground state is a closed-shell singlet, which contradicts with results from Hod et al. (Hod et al. 2008) and Jiang et al. (Jiang et al. 2007). Thus ROHF and MP2 are incapable of producing the correct results. For ROHF, the deficiency lies on its formalism as it cannot model electrons that are even in separate α and β orbitals. In Table 2, it can be seen that before annihilation of the spin contaminant, the spin eigenvalues are relatively closer together for all methods at all multiplicities, where correct spin eigenvalues are in the column of ROHF. The DFT values are slightly lower. This agrees with results of Montoya et al. (2000) for the graphene system. After the annihilation of the first spin contaminant, the results indicate a wider variation for the spin eigenvalues. For B3LYP and PBEPBE, the S^2 of BS after annihilation (0.62 and 0.077, respectively), is the most serious contamination of the states studied using DFT. The spin contamination is more severe in the HF and MP2 wavefunctions, especially from BS to quintet. For example, in triplet state, the values of 7.54 for MP2 and 6.47 for HF deviates significantly from the theoretical value of 2.00, indicating that those wavefunctions were severely

TABLE 1. The energy calculated by different methods with respect to HF singlet energy

Spin state	Energy (eV), relative to HF singlet				
	HF	ROHF	MP2	B3LYP	PBEPBE
Singlet	0.0000	0.0000	-124.7218	-242.3480	-196.0714
BS	-3.7550	0.0000	-117.5826	-242.4999	-196.0924
Triplet	-1.2491	0.5941	-120.5257	-242.2899	-195.9216
Quintet	1.3398	3.9714	-118.3453	-239.7583	-193.5751
Septet	6.5018	8.2000	-114.9148	-235.9472	-190.0748
Nonet	12.4602	14.2315	-106.2033	-231.3882	-186.0889

TABLE 2. Calculated spin eigenvalues for different spin states for HF, B3LYP, ROHF and MP2

Spin state	S^2					S^2 after annihilation				
	HF	ROHF	MP2	B3LYP	PBEPBE	HF	ROHF	MP2	B3LYP	PBEPBE
BS	4.760	0.000	5.084	0.881	0.588	18.141	0.000	19.065	0.617	0.077
Triplet	3.856	2.000	4.060	2.057	2.020	6.469	2.000	7.535	2.002	2.000
Quintet	7.594	6.000	7.713	6.090	6.034	7.719	6.000	8.043	6.003	6.001
Septet	12.897	12.000	13.026	12.051	12.022	12.295	12.000	12.402	12.001	12.000
Nonet	20.547	20.000	22.446	20.029	20.030	20.075	20.000	22.301	20.000	20.000

contaminated with higher spin states. It must be pointed out that the base wavefunction for the MP calculations is the HF wavefunction. These showed that MP2 calculation is not able to annihilate the spin contaminant in the HF wavefunction and resulted in the wrong conclusion in the energy. The agreement of the stability from the HF calculations may be fortuitous due to the high spin contaminations in the wavefunctions.

The results of the spin density for the open-shell singlet calculations are given in Table 3 and Figure 2. As can be seen from Table 3, the signs of the spin densities

for the atoms in the graphene model for HF, MP4, B3LYP, PBEPBE are the same. This shows that these methods produced the same trend of spin densities for the graphene model. Discrepancies occurred in MP2 method, as the signs of the spin densities for the atoms in the center region (C11 to C26) are different from the other methods. Figure 2 is shown to facilitate the visualization of the spin densities based on the values in Table 3. The same surface isovalue is used (0.002 au) across all the methods. This is to enable direct comparison for the spin densities between the different methods. In Figure 2(b), the center region of

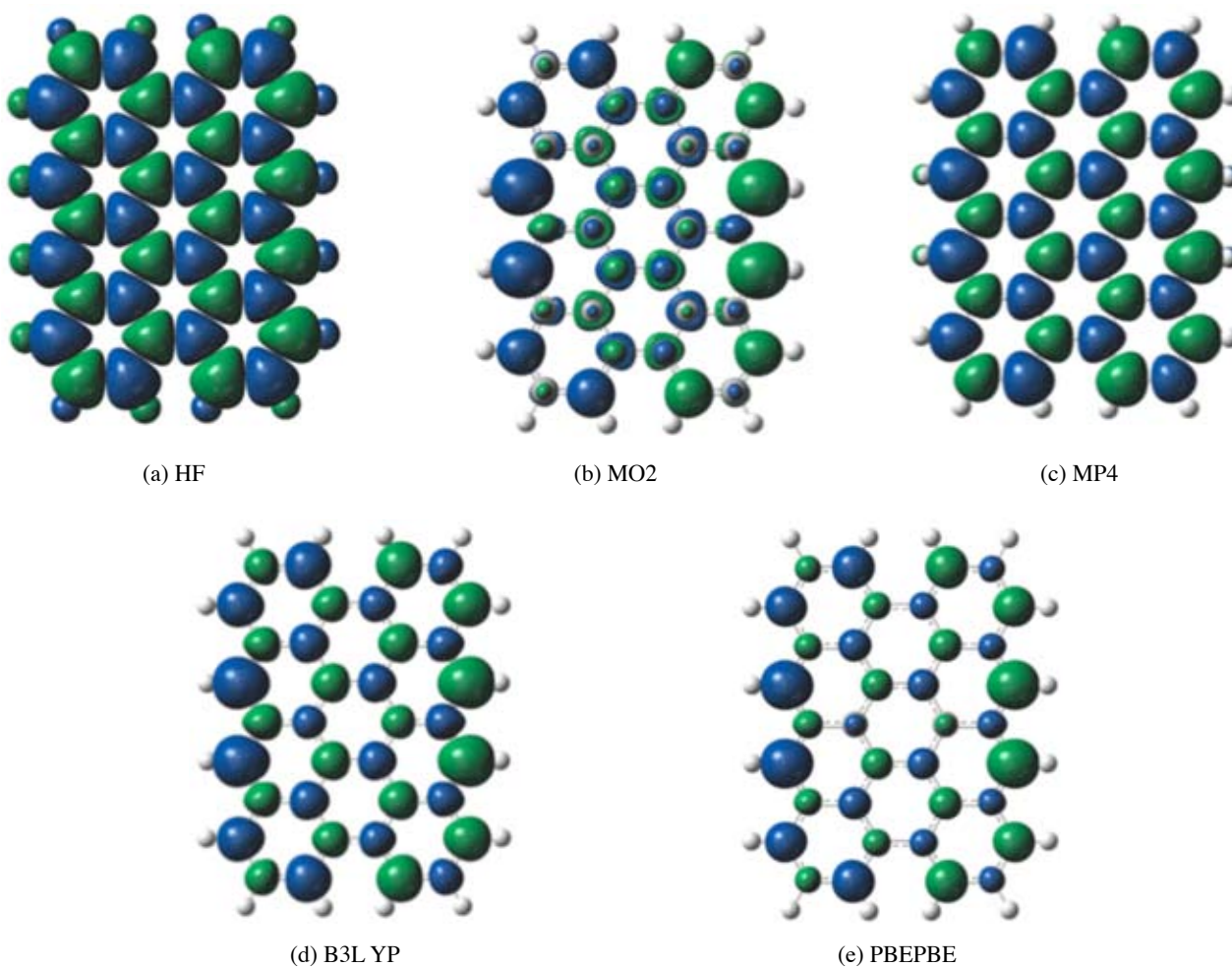


FIGURE 2. The pictorial representation of the values of spin densities shown in Table 3. The blue is for the spin up density, while the green is for the spin down density. The surface isovalue used is 0.002 au

TABLE 3. Spin densities obtained by the methods considered in this study. The values are given in atomic unit. The label of the atoms are the same as in Figure 1. The spin densities of the hydrogens are not shown

	Spin densities				
	HF	MP2	MP4	B3LYP	PBEPBE
C1	-0.8262	-0.0103	-0.2547	-0.1102	-0.0560
C2	0.8838	0.1215	0.2903	0.1911	0.1208
C3	-0.9039	-0.0071	-0.3103	-0.1375	-0.0703
C4	0.9781	0.3846	0.4527	0.3874	0.2596
C5	-0.9350	-0.0876	-0.3470	-0.1662	-0.0824
C6	0.9781	0.3846	0.4527	0.3874	0.2596
C7	-0.9039	-0.0071	-0.3103	-0.1375	-0.0703
C8	0.8838	0.1215	0.2903	0.1911	0.1208
C9	-0.8262	-0.0103	-0.2547	-0.1102	-0.0560
C10	0.9000	0.1414	0.3628	0.2082	0.1376
C11	-0.9621	0.0158	-0.3282	-0.1240	-0.0634
C12	0.9905	-0.0665	0.3301	0.1435	0.0806
C13	-1.0418	0.0320	-0.3871	-0.1460	-0.0790
C14	1.0296	-0.0435	0.3331	0.1073	0.0436
C15	-1.0418	0.0320	-0.3871	-0.1460	-0.0790
C16	0.9905	-0.0665	0.3301	0.1435	0.0806
C17	-0.9621	0.0158	-0.3282	-0.1240	-0.0634
C18	0.9000	0.1414	0.3628	0.2082	0.1376
C19	-0.9000	-0.1414	-0.3628	-0.2082	-0.1376
C20	0.9621	-0.0158	0.3282	0.1240	0.0634
C21	-0.9905	0.0665	-0.3301	-0.1435	-0.0806
C22	1.0418	-0.0320	0.3871	0.1460	0.0790
C23	-1.0296	0.0435	-0.3331	-0.1073	-0.0436
C24	1.0418	-0.0320	0.3871	0.1460	0.0790
C25	-0.9905	0.0665	-0.3301	-0.1435	-0.0806
C26	0.9621	-0.0158	0.3282	0.1240	0.0634
C27	-0.9000	-0.1414	-0.3628	-0.2082	-0.1376
C28	0.8262	0.0103	0.2547	0.1102	0.0560
C29	-0.8838	-0.1215	-0.2903	-0.1911	-0.1208
C30	0.9039	0.0071	0.3103	0.1375	0.0703
C31	-0.9781	-0.3846	-0.4527	-0.3874	-0.2596
C32	0.9350	0.0876	0.3470	0.1662	0.0824
C33	-0.9781	-0.3846	-0.4527	-0.3874	-0.2596
C34	0.9039	0.0071	0.3103	0.1375	0.0703
C35	-0.8838	-0.1215	-0.2903	-0.1911	-0.1208
C36	0.8262	0.0103	0.2547	0.1102	0.0560

MP2 method consists of spin-up and spin-down lobes. Based on the results of Mulliken population analysis in Table 3, the values are for the lobes that are in the plane of the molecule. Thus this figure shows that there are residue spins that are perpendicular to the planar surface of the molecule. For PBEPBE, although the trend of the size of the

lobes is the same with MP4 and B3LYP, the spin densities at the central region are small as compared to MP4 or B3LYP.

The spin densities are the largest with the HF method. This is apparent when comparing Figure 2(b), (c), (d) with (a). From the literature, the spin densities of the protruding

TABLE 4. S^2 , projected HF and approximate MPn energies after annihilation of unwanted spin states. PUHF, PMP2, PMP3 are the energy after the unwanted spin states have been projected out

spin annihilated	S^2	S^2 (annihilated)	PUHF	PMP2	PMP3
S+1	14.8618	13.72126	-1372.63308	-1376.79947	-1376.94476
S+1, s+2	19.6207	15.61091	-1372.55655	-1376.72701	-1376.87974
S+1 to s+3	36.3148	38.37997	-1372.26870	-1376.44174	-1376.59912
S+1 to s+4	35.4214	19.54227	-1372.31150	-1376.48568	-1376.64508
S+1 to s+5	112.346	19.54227	-1371.03587	–	–
S+1 to s+6	28.7676	19.54227	-1372.46172	–	–

carbon atoms at the zigzag edge range from 0.17 to 0.47 au, depending on the position (sites from the armchair edge) and the level of theory (Dias 2008; Hod et al. 2008; Kudin 2008). The values reported here for MP4 and B3LYP (C2, C4, C6, C8 in Table 3) agree with those values in the literature while for PBEPBE, the spin densities at the edges and at the central region are lower than the one reported in literature. At the surface isovalue of 0.002, the spin densities are visible for the hydrogen atoms for Figure 2(a). For HF, the spin density for the carbon atoms range from 0.8 to 1.0. This is larger by almost 50% than the value reported in the literature. In Figure 2 (a), even the hydrogen can be seen to contribute to the spin density.

Based on the values of S^2 in Table 2, it was found that after annihilation of the first spin contaminant, there was increment in some of the values of S^2 . The reason for this increase is that the contaminants are of higher spin states than the one that is projected out (Plakhutin et al. 2005). It is of interest to figure out which spin states constitute the largest percentage to the spin contamination. This is the motivation in performing the MP4 calculation. Different from the calculations at HF, MP2, B3LYP, and PBEPBE, where annihilation of the spin contaminant is just for the next higher states (for example, annihilation of quartet for a wavefunction that was performed as doublet), spin annihilations at the MP4 level are carried out to a few higher states. With the annihilation of the higher spin contaminants, the resultant wavefunction will represent better the system that is being studied. Thus the energy from the calculation will be more close to the correct spin state. Results from the MP4 calculations are given in Table 4. It was found that the main contributor to the contaminant is not in the region of S+1 to S+6, as the value of S^2 is still high at 19.5. Thus the agreement of the spin densities between MP4 and B3LYP may be fortuitous, based on the value of S^2 which indicates that the wavefunction is severely contaminated. Another explanation for the correctness in the trend and values of spin densities for MP4 may be due to the irrelevance of the S^2 in predicting the quality of the MP4 wavefunction. Further works are needed in this area in order to elucidate the use of MP4 in calculating the properties of system involving graphene.

Even though the wavefunction at this level of theory may be reliable in calculating the spin properties of graphene, it is not a practical method to be used in

calculating the large graphene in terms of computing time and memory. While the trend of spin densities from PBEPBE agrees with B3LYP and MP4, the values were underestimated at the edge and the central region of the graphene system. The mixture of HF exchange in the functional, B3LYP, although introduces some spin contamination into the wavefunction, seems to be necessary in order to get the acceptable distribution of the spin density. Thus the most efficient method, in terms of performance and cost, is B3LYP. This method has been utilized by others in performing calculations involving graphene (Liu et al. 2007; Sendt & Haynes 2005, 2007; Xu & Li 2005). The conclusion that B3LYP is a better choice among the methods considered here also agrees with the conclusion made by Davidson and Clark in their investigation of diradicals, that for large molecules, DFT (B3LYP) is still better method to use in modeling broken symmetry calculations (Davidson & Clark 2005).

CONCLUSION

It was found that spin contamination plays an important role in determining the quality of the HF and MP2 wavefunctions. The high percentage of spin contamination renders the stability incorrect and the spin density unacceptable in these two methods. Spin projection of a few contaminants through the calculation of MP4 indicated that the contaminant states were higher than S+6. Pure density functional theory in the form of PBEPBE, although comparatively free from spin contamination, is found to underestimate the spin densities at the edge and the central region of the graphene model. The spin density distribution of the MP4 wavefunction is unexpectedly similar to the one from B3LYP, considering the wavefunction is severely contaminated from the higher spin states. It was found that B3LYP is the most efficient method to use in performing calculations involving graphene.

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