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Theoretical study on pure organomagnetic conductors with model clusters

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Abstract

Ab initio MO and hybrid-DFT calculations have been carried out by using model clusters; **a** $[(NH_3)_2]_n^{+n}$ for pure organic conductors and **b** $[H_2NO{-}(NH_3)_2]_n^{+n}$ for pure organomagnetic conductors. The results have shown that these models are reliable for investigation of intrinsic electronic states of magnetic/conductive organic compounds in detail by quantum chemical methods.

Keywords: Ab inito MO calculation; Hybrid-DFT; Organomagnetic conductors; Electronic structure; Effective exchange integral

1. Introduction

For a decade, our group has proposed organic and organomagnetic conductors as possible analogues of the copper oxides [1,2]. Recently organic conductors with low dimensional electronic sheets have attracted a great deal of attention. Among such trends, phenomena involving π-donor molecules coupled with localized spins have interested many researchers of material science. Organomagnetic conductors have been discovered or synthesized successfully by several groups so far. For example, Coronado et al. reported compounds that show ferromagnetic and metallic conductance [3]. Uji et al. presented an organic conductor that exhibits magnetic-field-induced superconductivity [4].

A pure organomagnetic conductor is a conductive and magnetic compound that consists of only nonmetals, although the compounds mentioned above [3,4] contain metallic elements. Attempts to synthesize pure organomagnetic conductors have occurred in the fields of organic chemistry and so on. The latest one is a compound that is based on the phenalenyl structure produced by Itkis et al. [5].

In this work, we have introduced simplified model clusters of a pure organic/organomagnetic conductor, which were improved from our previous study [6]. Several special electronic states in ab initio MO and hybrid-DFT methods, spin density-controlled solutions (SDSs) and charge density-controlled solutions (CDSs), explained in Section 3.1, have been constructed by using the model clusters. Then we have clarified electronic structures and magnetic interactions for the model clusters with the SDS or CDS as well as their relative stabilities. Moreover, the effective exchange integral of the Heisenberg model has been employed in order to investigate the magnetic interaction.

2. Model clusters

2.1. Cluster a: a model for pure organic conductors

Cluster **a**: $[(NH_3)_2]_n^{+n}$ (here, $n = 4$) has been designed simply for pure organic conductors, which consists of planar ammonia molecules as shown in Fig. 1(1). The structure of the ammonia molecules was optimized by UB3LYP/6-31G* within a planar; bond length N–H is 1.029 Å and bond angle N–H–N is 120.0°. The geometry of the planar ammonia is a regular triangle. The lone pair on this molecule distributes perpendicularly above its plane. This planar ammonia is regarded

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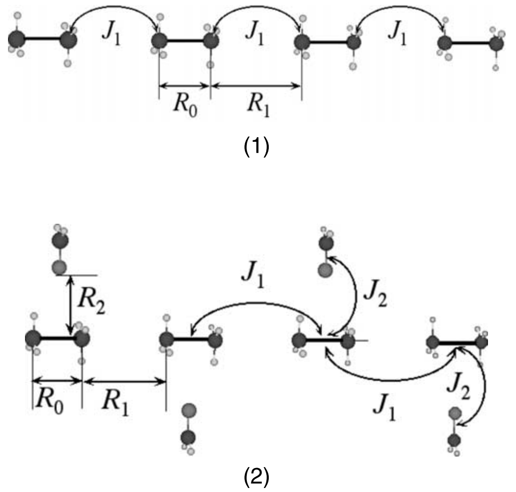

Fig. 1. (1) Cluster **a** ($n = 4$); R_0 is the intra-dimeric distance, R_1 is the inter-dimeric distance and J_1 is the effective exchange integral between dimers. (2) Cluster **b** ($n = 4$); R_2 is the distance between the nitroxide radical and the donor and J_2 is corresponded to R_2.

as the organic π-donor molecule, since such a typical organic conductor as BETS is a planar molecule and its π-electrons spread over the molecular planes.

Cluster **a** has +1 charge per two molecules since these molecules are virtually put between counter anion (radical) layers, expected to make the partially-filled band. Therefore, the model has an unpaired electron (a spin) by two planar ammonia molecules. Intermolecular distances are R_0 and R_1, which enable these molecules to make pairs alternatively, as depicted in Fig. 1(1). From the results of our former studies for $n = 2$, [6,7] these molecules tended to form dimeric pairs and the most stable intermolecular distances are as $(R_0, R_1) = (2.5, 3.5)$ Å, which is relevant to Peierls instability. Hence, in the present work, we have also adopted these values of intermolecular distances for cluster **a**.

2.2. *Cluster **b**; a model for pure organomagnetic conductors*

Cluster **b**: $[H_2NO{-}(NH_3)_2]_n^{+n}$ (here, $n = 4$) is a model for pure organomagnetic conductors, which has nitroxide radical ($H_2NO^{\bullet}$) layers in addition to the π-donor layers of cluster **a** as in Fig. 1(2). The nitroxide radical was optimized within a planar structure. Bond lengths N–O and N–H are 1.267 and 1.025 Å, respectively, and bond angle O–N–H is 121.0°. The planar nitroxide radical forms an isosceles triangle. Fig. 1(2) illustrates that the O atoms in the nitroxide radicals are put oriented towards the ammonia layer (cluster **a**) in the distance of $R_2 = 3.3$ Å. A parameter set $(R_0, R_1, R_2) = (2.3, 4.0, 3.3)$ defined here has reproduced antiferromagnetic interaction between spins in the nitroxide radical when **b** is calculated by UB3LYP/6-31G* [7]. Then R_2 was changed to 5.5 Å as a next step. Cluster **b** has one spin at a site of the nitroxide; one spin per a dimeric pair of the ammonia as like in **a**.

3. Theoretical calculation; ab initio MO methods

3.1. *The spin/charge density-controlled solutions*

The SDS and the CDS defined for ab initio MO solutions of these models have been displayed in Figs. 2 and 3. Relative stabilities of these solutions have been investigated in terms of their energies and the validity of the models has been examined.

The SDS has been divided into four kinds: ${}^{i}S_{-}^{AF}$, ${}^{i}S_{+}^{AF}$, ${}^{i}S_{-}^{F}$ and ${}^{i}S_{+}^{F}$. The superscript i ($i = \mathbf{a}, \mathbf{b}$) indicate the names of the model clusters. The AF (antiferromagnetic) and F (ferromagnetic) represent magnetic interaction in the middle two dimeric pairs of molecules; the subscripts − and + specify respectively antiferromagnetic and ferromagnetic interaction in the two dimeric pair of molecules at the both ends (see Figs. 2 and 3). The four positive charges distribute all over the atoms in the cluster evenly.

The CDS can involve four patterns: ${}^{i}C^{\alpha}$, ${}^{i}C_1^{\beta}$ ${}^{i}C_2^{\beta}$ and ${}^{i}C^{\gamma}$. The superscripts on the right shoulder show charge alignment in the middle four molecules (see Fig. 2)). In α, the four positive charges gather to the middle four sites, (1)(1)(1)(1). In β, the middle four sites have a charge arrangement (0)(0)(1)(1) and, in addition, the labels 1 and 2 distinguish the charge density distribution in the two sites on the ends. The positive charges aligned alternatively in γ, (0)(1)(0)(1), where (•) means charge density of a dimeric pair of the molecules. In this study,

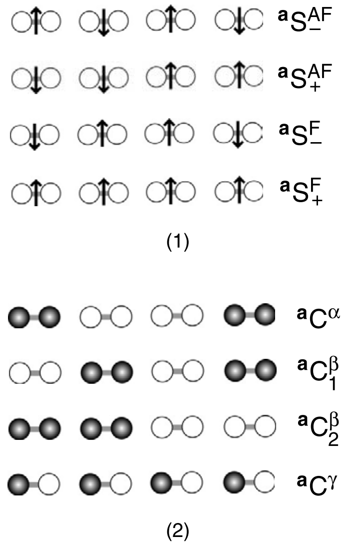

Fig. 2. (1) Diagrams for the SDSs of **a**; a circle represents the planar ammonia and an arrow means 1 spin density site ideally. (2) The CDSs of **a**; a blank circle represents formally +1 charges on the molecule and a solid one represents a neutral molecule.

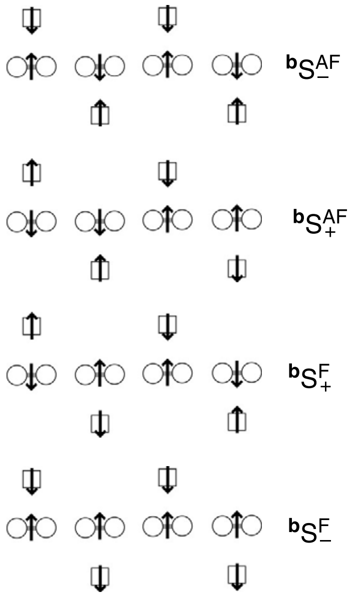

Fig. 3. Diagrams for the SDSs of **b**; a square is the nitroxide radical.

the CDS in the singlet state have been determined by quantum chemical calculations.

3.2. *Ab initio MO calculations*

Since most of calculations here have dealt with the broken-symmetry solutions, it is inevitable that the solutions involve contamination by states of higher spin multiplicity. Therefore, a symmetry-adapted method, complete active space-configuration interaction (CASCI), has been employed to compensate the spin contamination in our works. The CASCI calculation also can evaluate energies for excited states within its active spaces. Among the CAS methods, we have used conventionally the UNO-CASCI (CASCI using natural orbitals based on UHF). The CDSs was obtained only by UNO-CASCI, implying they are excited states.

In order to estimate magnetic interactions among spins quantitatively, the effective exchange integral, J, of the Heisenberg model have been applied. That is defined as

$$H = \sum_{\langle ij \rangle} (-2J_{ij}) \mathbf{s}_i \cdot \mathbf{s}_j \tag{1}$$

where $\mathbf{s}_i$ is a spin vector on the ith spin site and $\langle ij \rangle$ means the nearest pair of spins. The summation is taken for all of the nearest pair in the cluster models. Here, an organic radical is regarded as a spin site. In this definition, a negative J shows antiferromagnetic interaction, while a positive J ferromagnetic. When the unrestricted or the spin-polarized wave functions are employed to evaluate an eigenvalue for the Hamiltonian, the $\mathbf{s}$ is reduced to be only its z-component s, as like the Ising model. Then, for instance, J_1 in **a** have been calculated as follows; the Heisenberg spin Hamiltonian is approximately given by

$$H \approx -2J_1(s_1 s_2 + s_2 s_3 + s_3 s_4) \tag{2}$$

then each expectation value of Eq. (1) is written by using corresponding Js,

$$E({}^{a}S_{-}^{AF}) = -2J_1\left(-\frac{1}{2} \times \frac{1}{2}\right) \times 3 = \frac{3}{2}J_1,$$

$$E({}^{a}S_{+}^{F}) = -2J_1\left(\frac{1}{2} \times \frac{1}{2}\right) \times 3 = -\frac{3}{2}J_1$$

From the difference in energy, we derive

$$J_1 = \{E({}^{a}S_{-}^{AF}) - E({}^{a}S_{+}^{F})\}/3 \tag{3}$$

where $E(X)$ ($X = {}^{a}S_{-}^{AF}$, ${}^{a}S_{+}^{F}$) represent an energy of solution X calculated by UNO-CASCI and UB3LYP. The above procedure has also been applied for the symmetry-breaking solution by UB3LYP, despite of spin-contamination, since the spin contamination is negligibly small for DFT methods. No other corrections such as the AP procedure have been carried out to these Js [8], because it may not change the J values qualitatively.

4. Results and discussion

4.1. *Cluster **a***

Fig. 4(1) depicts spin density distribution on the spin sites, the N atoms in the π-donor dimer, of each SDS of **a**. Although spin density gathers to the both end slightly more than the middle, this is negligible enough to regard these solutions meaningful. All of the ab initio solutions were successfully derived by UNO-CASCI [6, 6].

Shown in Table 1 is the result of calculations for SDS and CDS of **a**. The most stable solution by UNO-CASCI was ${}^{a}S_{-}^{AF}$, in which all spins are arranged in an *anti*-parallel fashion to each other. The other solutions become less stable in the order of $E^{a}(S_{+}^{AF})$, $E({}^{a}S_{+}^{F})$, $E({}^{a}S_{-}^{AF})$. It is found that, upon a condition (R_0, R_1) = (2.5, 3.5) Å, spins on the π-dimers in **a** are inclined to interact each other with antiferromagnetic coupling. Tendency that ‘AF’ solutions are more stable than ‘F’ in the SDS has been found from Table 1. The intermolecular exchange integral J_1 was obtained as -106 cm^{-1}. This negative J_1 should make ‘−’ solutions always more stable than ‘+’, but ${}^{a}S_{+}^{F}$ is less stable than ${}^{a}S_{-}^{F}$ merely. This is partially because of the edge effect. Therefore, we had better take the mean values for ‘+’ and ‘−’ solutions to evaluate the interaction more precisely. However, even if do so, ‘AF’ solutions are still more stable than ‘F’ by 237 cm^{-1}, which is alike that most existing organic conductors show.

As also depicted on Table 1, ${}^{a}C^{\alpha}$, the most stable CDS, is as 10^5 figures unstable as ${}^{a}S_{-}^{F}$, the least stable

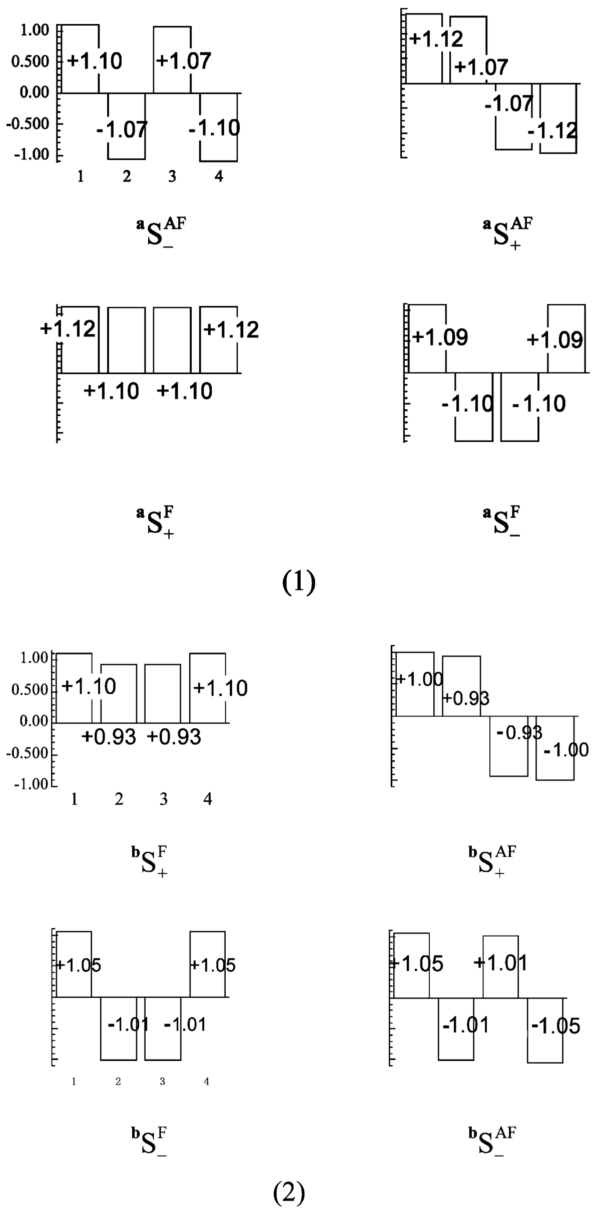

Fig. 4. Bar charts for spin densities on the N atoms in the dimers in each SDS of (1) **a** and (2) **b** calculated by UB3LYP/6-31G*. The horizontal axis represents the ammonia dimers layer.

SDS. This order is almost the same as the result for $n = 2$ [6]. The other energy gaps among the CDSs are also incredibly large, showing that these states are much unstable in **a** on the condition. The necessity of the long-range interaction to stabilize the CDS still remains as well, even if the size of the cluster is doubled. It is found that the smaller parts the positive charges disperse to, the less stable cluster **a** turns.

Considering above with the fact that **a** undergoes Peierls distortion, **a** would be a model for diamagnetic insulators.

Table 1
Energy gaps, ΔE, among the SDS and CDS calculated by UNO-CASCI [6, 6], as well as J_1 for **a** by UB3LYP/6-31G* unit: cm^{-1}. This list reads as $^{a}S_{-}^{AF}$ is more stable than $^{a}S_{+}^{AF}$ by 200.3 cm^{-1}, and so on.

(1)		(2)	
Code	ΔE	Code	ΔE ($\times 10^3$)
$^{a}S_{-}^{AF}$		$^{a}C^{\alpha}$	
	+200.3		+805.1
$^{a}S_{+}^{AF}$		$^{a}C_{1}^{\beta}$	
	+117.1		+179.2
$^{a}S_{+}^{F}$		$^{a}C_{2}^{\beta}$	
	+39.13		+412.7
$^{a}S_{-}^{F}$		$^{a}C^{\gamma}$	

$J_1 = -105.8$, $E(^{a}C^{\alpha}) - E(^{a}S_{-}^{F}) = 180.6$

4.2. Cluster b

The results for **b** show us how the order of the SDS stability varies when the π-donors in cluster **a** are perturbed by spins on the organic radicals. Fig. 4(2) displays spin density distribution in SDS on cluster **b**. Since all the values are close to 1, these solutions also reliable to discuss. Comparison to the SDS on **a**, spin densities on the N-atoms decreased by a few percents except for $^{b}S_{-}^{AF}$. This shows that, in this model, magnetic perturbation from spins on the organic radicals declines spin-polarization on the π-donor molecules.

As shown in Table 2, the most stable solution is $^{b}S_{+}^{F}$, in which all spins on the π-donor molecules undergo ferromagnetic interaction. Next comes $^{b}S_{+}^{AF}$ with energy gap 76.80 cm^{-1}. By somewhat a large gap $^{b}S_{-}^{F}$ is less stable than $^{b}S_{+}^{AF}$ and $^{b}S_{-}^{AF}$ is the least stable of the four. When UB3LYP/6-31G* is employed to evaluate the SDSs for cluster **b**, the inclination of the stability is found that '+' solution is more stable than '−'. In order to compare the 'AF' and the 'F' solutions, the mean values were taken for + and −. Getting the average of the energy level at $R_2 = 3.3$ Å, it is found that the 'F' solution is more stable than the 'AF' by 49.17 cm^{-1} under the perturbation of spins on organic radicals. The

Table 2
Energy gaps, ΔE, among the SDS, as well as Js for **b** calculated by UB3LYP/6-31G* unit: cm^{-1}.

Code	ΔE ($R_3 = 3.3$ Å)	ΔE ($R_3 = 5.0$ Å)
$^{b}S_{+}^{F}$		
	+78.60	+219.5
$^{b}S_{+}^{AF}$		
	+903.0	+1346
$^{b}S_{-}^{F}$		
	+19.73	+141.8
$^{b}S_{-}^{AF}$		
J_1	332.5	569.1
J_2	−440.3	−2581

CDS on **b** was not investigated, since it was hard to implement UNO-CASCI [6, 6] in our computational system.

Magnetic interaction between π-donors J_1 was evaluated 332.5 cm^{-1}, while J_2 was -440.3 cm^{-1}. These are not ridiculous values in organic compounds. Variation of R_2 from 3.3 to 5.0 Å increased J values keeping their signs.

This results implies that **b** would be a model for pure organomagnetic insulators. The difference from **a** is that ferromagnetic interaction is dominant in the π-dimer layer of **b**.

4.3. Remarks

In general, pure organomagnetic conductors can be illustrated schematically as Fig. 5. The code D means π-donor molecules and the code A represents counter anions of D. D and A ($R^\bullet$) have been NH_3 and $H_2NO^\bullet$, respectively, in our works so far [6,7]. If A is modified to be anion radicals denoted as $^\bullet R\text{–}A^-$, the model may describe more realistic compounds. (BEDT-TTF)-(F_1TCNQ), for instance, is an existing pure ogranomagnetic conductor [9]. This would be the case in which D is BEDT-TTF and A is F_1TCNQ in our model. $(\text{BETS})_2$-(X_2TCNQ) (X = Br, Cl) is a pure organic (super)conductor [9] and would be mentioned as the case in which D is BETS and A is (X_2TCNQ). Modification of $R^\bullet$ into $^\bullet R\text{–}A^-$ and investigation by using the model with $^\bullet R\text{–}A^-$ has been carried out for our next step.

5. Conclusion

As a step to construct a model for pure organic/organomagnetic conductors, model clusters **a** and **b** have been introduced. Investigation of **a** has shown that antiferromagnetic interaction is dominant among the π-donor molecules in **a** for the SDSs and all the CDSs are unstable. From the results of **b**, we have obtained that magnetic perturbation can affect the interaction of spins on the π-donors to turn it ferromagnetic from antiferromagnetic and slightly reduce spin densities on the π-donor molecules. Considering data of existing organomagnetic conductors, **a** and **b** would be modes for pure organo-diamagnetic compounds though we need to take thermodynamical limit for exact discussions. Moreover, since these models showed Peierls dimerization, they are insulators. These results are supported by the fact that typical organic compounds are diamangetic insulator. The next step is to find model molecules that stabilize CDSs to a meaningful value.

With these model clusters, investigation of intrinsic electronic structures of organic/organomagnetic conductors can be performed in quantum chemical methodology. If the long-range-order interaction is needed, these clusters should also be formed a loop, as presented our previous study [7].

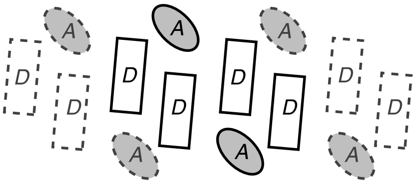

Fig. 5. A schematic illustration of the crystal structure along an axis of a pure organomagetic conductor. The solid lines represent the crystallographic unit. D denotes the π-donor and A displays counter anion of D. In the present work, D and A are the planar ammonia, NH_3, and the planar nitroxide radical, $H_2NO^\bullet$, respectively. For example, D = BEDT-TTF, BETS, TMTSF and $A = X^-$, $X_n\text{TCNQ}^-$, PX_6^- can be mentioned as pure organomagnetic conductors synthesized so far successfully.

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References

[1] K. Yamaguchi, Int. J. Quant. Chem. 37 (1990) 447.
[2] K. Yamaguchi, M. Okumura, T. Fueho, K. Nakasuji, Synth. Metals 41–43 (1991) 3631.
[3] E. Coronado, J.R. Galán-Mascarós, C.J. Gómes-García, V. Laukhin, Nature 408 (2000) 447.
[4] S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumito, A. Kobayashi, H. Tanaka, H. Kobayashi, Nature 410 (2001) 908.
[5] M.E. Itkis, X. Chi, A.W. Cordes, R.C. Haddon, Science 296 (2002) 1443.
[6] T. Taniguchi, S. Nakano, T. Kawakami, K. Yamaguchi, Mol. Cryst. Liq. Cryst. 379 (2002) 483.
[7] T. Taniguchi, S. Nakano, T. Kawakami, K. Yamaguchi, Synth. Metals 137 (2003) 63.
[8] T. Kawakami, Thesis of Doctor, 1999.
[9] T. Kohdo, S. Kagoshima, T. Hasegawa, Solid State Phys. 35 (2000) 63 (in Japanese).
[10] GAUSSIAN-98, Revision A.6, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.