Two Typical Examples of Scaling Ionic Partition Scheme for Estimating Correlation Energy of A_2 Type Molecules

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Based on the calculation results of pair correlation energy contributions of the various electron pairs in Na_2 and H_2NNH_2 systems and the application of the scaling ionic partition scheme for symmetrical A_2 type systems, the total correlation energies of Na_2 and H_2NNH_2 have been reproduced by using this simple scheme. The two results show that the absolute deviations are within an acceptable range of error, however, in this way, more than 90% of computational work can be saved. The most attractive result in present paper is that, in these two molecules the coefficients c_1 and c_2 in the estimation equation can be obtained by the proportion of correlation energy of A^- to that of A^+ singlet system. Therefore, it is believed that the proposed ionic partition scheme for symmetrical A_2 molecules would be very useful to estimate the correlation energies of large symmetrical molecules.

Keywords   pair correlation energy contribution, A_2 type molecule, ionic partition scheme

Introduction

The accurate energy data of molecular system are the base to study its chemical and physical properties in various research fields such as chemical materials, biochemistry, atmospheric and environmental chemistry. Therefore, the calculation of the electron correlation energy plays a very important role in quantum chemistry, and has been always the most active research field in modern theoretical chemistry.[1] In last decades, several classical methods to compute the electron correlation energies of atoms and molecules accurately have been built up. However, the application of these classical methods is strictly limited by the large disk demand, slow convergence, or divergence and by the huge computational demand for large molecules. In recent years, Kristyan[2,3] has developed a method called RECEP (rapid estimation of correlation energy from partial charges). However, this approach is impossible to treat the molecular systems in which the partial charges of atoms are zero, such as homonuclear diatomic A_2 molecule, and RECEP method considers it as $E_{corr}(A_2) = 2E_{corr}(A)$, which is obviously incorrect in treating this kind of molecules. In our previous work, based on the intrapair and interpair correlation energy analysis model[4-9] and our computation experience, a simple scheme called "Separating Large System into Smaller Ones" was proposed to estimate the correlation energy for strong ionic compounds.[10-15] By using this scheme, not only can we get the total correlation energy for large ionic compound with much less computational work, but also it can reach chemical accuracy. In addition, in order to solve the problem of large covalent molecules, the simple scheme is applied to A_2 type molecules such as F_2, O_2^{2-} and CH_3CH_3 system by partitioning A_2 into A^- and A^+ singlet ionic units and it is found that this procedure yields the optimal estimation results for A_2 type molecules.[16] However, in this previous study, the c_1 and c_2 parameters in the estimation equations should be *a priori* known. In the present study, the study of two typical A_2 type molecules, *i.e.*, Na_2 and H_2NNH_2 systems is extended to assess the reliability of the ionic partition scheme on more symmetrical A_2 molecules. Furthermore, the most important point in this paper is to look for the relationship of the coefficients in the estimation equation with the relative values of the correlation energies of A^- and A^+ ionic terms so as to estimate the correlation energies of large A_2 type molecules very rapidly and effectively. It should be pointed out that although the 6-311++G(d) basis set used in the calculation is not large enough to include all kinds of correlation in the system, it is sufficient because of our focus on searching the relative regularities in A_2 type molecules.

Computation method

The method used in the calculation of intrapair and interpair correlation energies has been outlined in Ref. 4.

On the basis of the intrapair and interpair correlation energies, the pair electron correlation energy contribution of one electron pair to a system is defined as the sum of the intrapair correlation energy plus half of the sum of interpair correlation energies between this electron pair and the other electron pair in the system.[16]

All geometry structures of the systems studied in this paper were optimized by Gaussian-98 program[17] at HF/6-311++G(d) level. In the calculation of intrapair and interpair correlation energies of Na^+, Na^-, Na, Na_2, NH_2^+, NH_2, NH_2^-, H_2NNH_2, systems, MP2-OPT2 method[18,19] with 6-311++G(d) split-valence polarization basis set was used for these systems. All calculations of the intrapair and interpair electron correlation energies were performed using the MELD[20] suite of electron code developed by Davidson *et al*. The pair correlation energy contribution values were calculated by our local program.

Results and discussion

Pair correlation energy contributions in Na_2 and the comparison with those in (Na^-+Na^+) and $(Na+Na)$ systems

According to the general chemical sense, in estimating the correlation energy of A_2 type molecule, two partition schemes should be examined, *i.e.*, the ionic partition scheme, $A_2 \rightarrow (A^-+A^+)$, and the diradical partition scheme, $A_2 \rightarrow (A^{\cdot}+A^{\cdot})$. Comparing the number of electron pairs in (A^-+A^+) and $(A^{\cdot}+A^{\cdot})$ partition schemes, one can see that A_2 molecule has the same number of electron pairs as the hypothetical (A^-+A^+) system, however, there is two unpaired electrons in the $(A^{\cdot}+A^{\cdot})$ system. Since the correlation energy is very sensitive to spin pairing effects and the opposite spin electrons have different correlation energy from the parallel spin electrons, therefore, it is more reasonable to approximate the total correlation energy of A_2 by using the ionic partitioning scheme than that by using the diradical partitioning scheme.

In Table 1, the results of pair correlation contribu-

tions in Na_2, Na^+, Na and Na^- systems using the same method with 6-311++G(d) basis set are given. As it can be seen in Table 1, the pair correlation energy contributions of $1a_g^2$, $1b_{1u}^2$ in Na_2 and $1s^2$ in Na^+, Na and Na^- are -13.725, -13.725, -13.755, -13.765, and -13.720 mh respectively, and those of $2a_g^2$ and $2b_{1u}^2$ in Na_2 and $2s^2$ in Na^+, Na and Na^- are -19.66, -19.665, -21.275, -20.965, and -20.740 mh respectively. All these values change little in the above systems, which indicates the correlation energies of inner core electrons are of some transferability in Na^+, Na, Na^- and Na_2 systems. The six electron pairs in $3a_g^2$, $1b_{3u}^2$, $1b_{2u}^2$, $3b_{1u}^2$, $1b_{2g}^2$ and $1b_{3g}^2$ molecular orbitals in Na_2 are composed of 2p atomic orbitals in Na atom, the correlation contributions of these electron pairs are between -34.02—34.14 mh, these values are more close to the correlation contributions of $2p^2$ pair in Na^+ and Na^- which are -34.62 and -34.66 mh respectively than to those of $2p^2$ pair in Na which are -35.35 mh. In Na_2 system, the correlation contribution of bonding electron pair $4a_g^2$ is only -26.595 mh which shows that the chemical bond in Na_2 system is very weak. This resulted from the little overlapping of the electron cloud between two $3s_{Na}$ orbitals.

Comparing the calculation results of the correlation energies of Na_2, (Na^-+Na^+) and $(Na+Na)$ systems which are -297.74, -300.95, and -284.34 mh respectively, it is obvious to see that the relationship between the total correlation energy of Na_2 molecule and the sum of the correlation energies of the terms in two partition schemes (Na^-+Na^+) and $(Na+Na)$ is as follows,

$$|E_{corr}(Na^-+Na^+)| > |E_{corr}(Na_2)| > |E_{corr}(Na+Na)| \quad (1)$$

From the above analysis, it is shown that the electron correlation pattern in Na_2 molecule is more close to (Na^-+Na^+) system than to that in $(Na+Na)$ system. Thus, it is confirmed that the more reasonable scheme to approximate the total correlation energy of Na_2 is the ionic partition scheme (Na^-+Na^+).

Table 1 Pair correlation contributions and total correlation energies of Na_2, Na^+, Na and Na^- systems ($-$mh)

	Na_2		Na^+	Na	Na^-
$E_{corr}[1a_g(1s_{Na})]$	13.725	$E_{corr}(1s^2)$	13.755	13.765	13.72
$E_{corr}[2a_g(2s_{Na})]$	19.66	$E_{corr}(2s^2)$	21.275	20.965	20.74
$E_{corr}[3a_g(2p_{zNa})]$	34.02	$E_{corr}(2p_x^2)$	34.62	35.35	34.66
$E_{corr}[4a_g(3s_{Na})]$	26.595	$E_{corr}(2p_y^2)$	34.62	35.35	34.66
$E_{corr}[1b_{3u}(2p_{xNa})]$	34.055	$E_{corr}(2p_z^2)$	34.62	35.35	34.66
$E_{corr}[1b_{2u}(2p_{yNa})]$	34.055	$E_{corr}(3s^{1,2})$	—	1.37	23.64
$E_{corr}[1b_{1u}(1s_{Na})]$	13.725	—	—	—	—
$E_{corr}[2b_{1u}(2s_{Na})]$	19.66	—	—	—	—
$E_{corr}[3b_{1u}(2p_{zNa})]$	34.14	—	—	—	—
$E_{corr}[1b_{2g}(2p_{xNa})]$	34.08	—	—	—	—
$E_{corr}[1b_{3g}(2p_{yNa})]$	34.08	—	—	—	—
$E_{corr}(total)$	297.74	—	138.89	142.17	162.06

Ionic partition scheme

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Pair correlation contributions in H_2NNH_2 and the comparison with those in ($NH_2^- + NH_2^+$) and ($NH_2^. + NH_2^.$) systems

Table 2 gives the results of pair correlation contributions in H_2NNH_2, NH_2^+, $NH_2^.$ and NH_2^- systems of MP2-OPT2 method with 6-311++G(d) basis set. As it is seen in Table 2, the two pair correlation contributions of $1s_N^2$ in H_2NNH_2 molecule are -17.74, -17.755 mh, and the pair correlation contributions of $1s_N^2$ in NH_2^-, NH_2^+, and $NH_2^.$ are -17.365, -17.46 and -16.79 mh respectively. This indicates that the inner core pair correlation contribution of $1s_N^2$ of N atom may change little in these systems which shows the transferable property in the above NH-containing systems. The $2s_N^2$ pair correlation contributions in H_2NNH_2 molecule are -41.955 and -46.31 mh, and the corresponding values of $2s_N^2$ pair correlation contributions in NH_2^-, NH_2^+ and $NH_2^.$ systems are -43.645, -45.45 and -47.31 mh respectively. All these $2s_N^2$ pair correlation contributions in H_2NNH_2, NH_2^-, NH_2^+ and $NH_2^.$ are within -41.955—-47.31 mh. The $2p_N$-$1s_H$ bonding pair correlation contributions in NH_2^-, NH_2^+, $NH_2^.$ and H_2NNH_2 systems are within -48.89—-64.485 mh. The pair correlation contribution of the lone electron pair in NH_2^- is -61.62 mh. The only one N—N bonding electron pair correlation contribution in H_2NNH_2 is -73.50 mh which is the largest value among those of all electron pairs in the above NH-containing systems, indicating the strong covalent bonding between two N atoms in H_2NNH_2 molecule. From the above analysis, it is shown that the pair correlation contributions of inner shell electron pairs have somewhat transferable property in these NH-containing systems. In addition, the further comparison of the correlation energies in H_2NNH_2, ($NH_2^+ + NH_2^-$) and ($NH_2^. + NH_2^.$) systems, which are -441.89, -407.30 and -391.32 mh respectively, shows that the following relationship is correct for the above systems, *i.e.*,

$$|E_{corr}(H_2NNH_2)| > |E_{corr}(NH_2^- + NH_2^+)| >$$

$$E_{corr}(NH_2^. + NH_2^.)| \qquad (2)$$

Combining the above relationship in H_2NNH_2, ($NH_2^- + NH_2^+$) and ($NH_2^. + NH_2^.$) systems and the analysis of intrapair and interpair correlation results in Table 2. One can see that the electron correlation patterns in H_2NNH_2 molecule is more close to a hypothetical ($NH_2^- + NH_2^+$) system than to ($NH_2^. + NH_2^.$) system. Thus, it is again confirmed that ionic partition scheme is the more suitable way to reproduce the total correlation energy of symmetrical A_2 system.

Simple scaling approach for symmetrical A_2 type molecules by the ionic partition scheme ($A^- + A^+$)

On the basis of the above analysis, a simple approach would provide the total correlation energy for symmetrical A_2 molecules by the logical ionic partition scheme. Therefore, in the specific conditions, the formula to estimate the correlation energy of A_2 molecular system can be expressed in the following equation, *i.e.*,

$$E_{corr}(A_2) = c_1 E_{corr}(A^-) + c_2 E_{corr}(A^+) \qquad (3)$$

where c_1 and c_2 are the scale factors of the correlation energies of A^-, A^+ ionic terms and $c_1 + c_2 = 2$, which means that the values of $E_{corr}(A_2)$ can be reasonablly obtained by adjusting the proportion of two correlation energy values of ionic terms $E_{corr}(A^-)$ and $E_{corr}(A^+)$. Now the most important problem involved in obtaining $E_{corr}(A_2)$ is how to determine the scale factors c_1 and c_2 in the above equation. As shown in the mathematical analysis in Ref. 10, these two scale factors depend on the values of $E_{corr}(A^-)$ and $E_{corr}(A^+)$ terms and there exists $c_1 > c_2$.

Let $c_1 = E_{corr}(A^-)/E_{corr}(A^+)$ for these two molecules and obtain c_1, c_2 scale factors for Na_2 and H_2NNH_2, thus the estimation equations are as follows,

$$E_{corr}(Na_2) = 1.10 E_{corr}(Na^-) + 0.90 E_{corr}(Na^+) \qquad (4)$$

and

$$E_{corr}(H_2NNH_2) = 1.43 E_{corr}(NH_2^-) + 0.57 E_{corr}(NH_2^+) \qquad (5)$$

The estimated results of Na_2 and H_2NNH_2 systems obtained by using the above equations are listed in Table 3. For comparison, the direct calculated correlation results of these two systems are also given in Table 3. As seen from the comparison, the absolute deviations of

Table 2 Pair correlation contributions and total correlation energies of H_2NNH_2, NH_2^-, NH_2^- and $NH_2^.$ systems ($-$mh)

	H_2NNH_2		NH_2^- ($^1A_1$)	$NH_2^.$	NH_2^-
$E_{corr}[1a^2(1s_N^2)]$	17.40	$E_{corr}[1a_1^2(1s_N^2)]$	16.79	17.46	17.365
$E_{corr}[2a^2(2s_N^2)]$	41.955	$E_{corr}[2a_1^2(2s_N^2)]$	45.75	47.31	43.645
$E_{corr}[3a^2(2p_N\text{-}1s_H)]$	60.225	$E_{corr}[3a_1^2(2p_N\text{-}1s_H)]$	56.41	56.155	59.975
$E_{corr}[4a^2(2pN\text{-}2pN)]$	73.50	$E_{corr}[1b_2^2(2p_N\text{-}1s_H)]$	48.89	54.285	56.865
$E_{corr}[5a^2(2p_N\text{-}1s_H)]$	64.485	$E_{corr}[1b_1^{0,1,2}(2p_N)]$	—	20.45	61.62
$E_{corr}[1b^2(1s_N^2)]$	17.755		—	—	—
$E_{corr}[2b^2(2s_N^2)]$	46.31		—	—	—
$E_{corr}[3b^2(2p_N\text{-}1s_H)]$	56.92		—	—	—
$E_{corr}[4b^2(2p_N\text{-}1s_H)]$	62.98		—	—	—
E_{corr}(total)	441.89	E_{corr}(total)	167.84	195.66	239.46

Table 3 Comparison of results $c_1 E_{corr}(A^-) + c_2 E_{corr}(A^+)$ with $E_{corr}(A_2)$ in H_2NNH_2 and HOOH systems (mh) calculated by MP2-OPT2 method

	$E_{corr}(A^-)$	$E_{corr}(A^+)$	$c_1 E_{corr}(A^-) + c_2 E_{corr}(A^-)$	$E_{corr}(A_2)$	Absolute deviation	Relative error/%
Na_2	162.06	142.17	303.38	297.74	5.64	1.89
H_2NNH_2	239.46	167.84	438.09	441.89	-3.80	0.86

the estimated results are 5.64 mh (14.78 kJ/mol) for Na_2 and -3.80 mh (-9.96 kJ/mol) for H_2NNH_2. Therefore, it is indicated that it is simple to obtain the total correlation energy of symmetrical A_2 molecules by our scaling ionic partition scheme. However, it should be pointed out that although the absolute deviations of estimated results for these two molecules are relatively large, it is still within an acceptable range of the calculation error. The most important point is that this is the first time for us to get the solution of the exact relationship of the coefficients c_1 and c_2 with the values of $E_{corr}(A^-)$ and $E_{corr}(A^+)$. However, these are two particular cases rather than a generalization for symmetrical A_2 molecules. At present, the parameters c_1 and c_2 of each symmetrical A_2 molecule should be examined individually. In our future research work, we are planning to select a large number of molecules to determine the general rule for the coefficients in the estimation equations of A_2 type molecules. It is especially important because this simple scheme can save more than 90% of the computational work, which enables us to get the total correlation energy of large molecules without considering the limitation of the present computation ability. Therefore it is hopeful that the logically simple approach "Separating Large System into Smaller Ones" would be a useful means to solve the bottleneck problem of correlation energies of large molecular systems.

Conclusion

With the analysis of pair correlation energy contribution values in two typical examples Na_2 and H_2NNH_2 of symmetrical A_2 type systems and the numerical comparison of the correlation energy of A_2 with those of $(A^- + A^+)$ and $(A^{\cdot} + A^{\cdot})$ systems, it is confirmed that the ionic partition scheme is the more reasonable way to obtain the total correlation energy of A_2 molecules. The estimated results are within an acceptable deviation but it saves more than 90% computational work. From the further discussion of the method to determine the coefficients c_1 and c_2 in the estimation equation, a clue in solving the calculation problem of correlation energy for A_2 type molecules with the *ab initio* correlation energy of A^- and A^+ ionic systems is suggested.

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