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The Scaling Ionic Partitioning Scheme for Estimating Electron Correlation Energy of A_2-like and AX-Type Molecules

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Based on the definition of pair correlation contribution of the individual electron pair to the system in the text and the investigation of the transferablility of some pair correlation contributions in the respective covalent systems, the total correlation energies of A_2-like covalent molecules (H_2NNH_2, HOOH) and AX-type polar covalent molecules (CH_3X (X = F, OH, NH_2)) have been approximated using our simple scaling ionic partitioning scheme. The estimation results show that the absolute deviations are less than 2 kcal/mol; however, in this way, more than 90% of computational work can be saved. Incorporating our early work on the strong ionic compounds MA, we summarized the general formula to estimate the total correlation energy for different kinds of chemical bonding systems. The comparison of the numerical values of the ratio of the scaling coefficients for MA strong ionic compounds, AX polar covalent molecules, and A_2 typical standard covalent molecules shows that the ratio of the scaling coefficients depends on the ionic property of the system.

1. Introduction

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.[1,2] Some well-known classical methods for the calculation of the correlation energy are the second-, third-, and fourth-order Moller−Plesset perturbation methods (MP2, MP3, or MP4).[3] Coupled-cluster methods (CCSD or CCSD(T))[4] and the full configuration interaction (CI) method have been established to calculate the correlation energy.[5] However, the application of these methods is strictly limited by the large disk demand, slow convergence, or divergence and by the huge computational demand for large molecules. Since 1995, Sandor Kristyan, Gabor I. Csonka, and others have developed a method called RECEP (rapid estimation of correlation energy from partial charges).[6−10] This approach is used to estimate the atomic correlation parameters for all atoms in a molecule from complete CI or B3LYP atomic correlation energies and the partial charges of atoms in the molecule and obtain the total correlation energy of the molecule from these atomic correlation parameters. They have applied the RECEP method to part of the G2 and G3 database[11−14] and obtained reasonable correlation energy values. However, in this approach, it is not possible to get accurate correlation energies for systems in which the partial charges of atoms are zero in the molecule. For example, calculating the correlation energy of homonuclear A_2 molecule, RECEP method reduces it to $E_{\mathrm{corr}}(A_2) = 2E_{\mathrm{corr}}(A)$, which is obviously an inaccurate treatment of this kind of homonuclear diatomic molecule. As it has been known, if the correlation energy was perfectly linear in the number of electrons in the system, there would be no need for further requirement in electron correlation correction to the bonding.[15] This is a possible reason the RECEP method gives an unreasonable result for A_2 series diatomic molecules because the basic assumption of the RECEP method is constructed from the idea that the electron correlation energy is roughly proportional to the number of electrons in the system.[8] On the other hand, another characteristic property of RECEP method is that its parameters are empirical parameters, while our method below is partly an exact ab initio calculation. In our previous works, on the basis of the analysis of the weak correlation effect between M^+ and A^- in strong ionic compounds MA, we proposed a simple scheme called "separating large system into smaller ones" to estimate the correlation energy for a strong ionic compound by summarizing the correlation energies of its component ions.[16−19] 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. Furthermore, to solve the problem of large covalent molecules, we have analyzed the applicability of our strategy to estimate the correlation energies of homonuclear diatomic covalent molecules, such as F_2 and O_2^{2-}, and the A_2-like molecule CH_3CH_3 by partitioning the A_2-type molecules into A^+ and A^- singlet ionic units and found that this procedure yields the optimal estimation results for these covalent molecules.[20] Inspired by these achievements, in this present study, first, we continue to test the applications of the ionic partitioning scheme to A_2-like molecules, such as HOOH and H_2NNH_2 systems, to confirm that our simple scheme "separating large system into smaller ones" is applicable to both strong ionic MA compounds and the A_2-like covalent molecules. Second, illuminated by the idea that from the viewpoint of chemical bonding the AX-type polar covalent molecule is just between the strong ionic MA compounds and the typical A_2 covalent molecules, this simple ionic partitioning scheme can also be extended to the AX-type covalent molecules. Thus, we chose CH_3X (X = F, OH, NH_2) series molecules to assess the reliability of the ionic partitioning scheme. At last, we summarize the relationship of the estimation equations of these three kinds of bonding systems, for example, strong ionic compounds

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MA, AX polar covalent molecules, and A_2 typical covalent molecules, and obtain a general estimation equation. Besides its theoretical interest, the importance of this work in practical application is evident, because it can enable researchers to estimate the correlation energies of large systems a priori with some degree of confidence.

2. Computation Method

The method used in the calculation of the intrapair and interpair correlation energies has been outlined in ref 21. On the basis of the intrapair and interpair correlation energies, the pair electron correlation contribution to a system is defined as the sum of the intrapair correlation energy plus half of the sum of the interpair correlation energies of one electron pair in the system, that is,

$$E_{\mathrm{corr}}(i) = E_{\mathrm{corr}}(ii) + {}^{1}/_{2}\sum_{j} E_{\mathrm{corr}}(ij) \qquad (1)$$

Here $E_{\mathrm{corr}}(i)$ is the pair correlation contribution of ith electron pair to the system, $E_{\mathrm{corr}}(ii)$ is the intrapair correlation energy of ith electron pair, and $E_{\mathrm{corr}}(ij)$ is the interpair correlation energy between ith and jth elctron pairs in the system. As it can be seen, eq 1 partitions the correlation effect among molecular orbitals. It should be noted that a single electron in an orbital is treated the same as an electron pair to get the correlation contribution of that single electron to the system. In this way, the total correlation energy of a system can be obtained by summarizing the pair correlation contributions from all electron pairs in the system, that is,

$$E_{\mathrm{corr}}(\mathrm{total}) = \sum_{i} E_{\mathrm{corr}}(i) \qquad (2)$$

in which i runs from 1 to $N/2$ and N is the total number of electrons. For simplicity, $E_{\mathrm{corr}}(i)$ is called the pair correlation contribution of i electron pair.

All geometry structures of the systems studied in this paper are optimized by Gaussian 98 program[22] at HF/6-311++G(d) level. In the calculation of intrapair and interpair correlation energies of systems studied in this work, MP2-OPT2 method[23,24] with 6-311++G(d) split-valence polarization basis set are used for these systems. All calculations of the pair electron correlation energy are performed using the MELD[25] suite of electron code developed by Davidson et al. The pair correlation contributions of all electron pairs in the above systems are obtained by eq 1, which partitions the correlation effect among molecular orbitals. And the molecular orbitals used are the ROHF canonical orbitals described in ref 23.

3. Computation Results and Discussion

On the basis of the general chemical sense, in estimating the correlation energy of a given AB molecule, two partitioning schemes should be examined, that is, the ionic partitioning scheme AB → ($A^+ + B^-$) and the diradical partitioning scheme AB → (A + B), where the parentheses indicate that we make a separation in the calculation only and that is not a chemical dissociation. The ionic partitioning scheme, either ($A^+ + B^-$) or ($A^- + B^+$), is based on the actual electron content in AB, which comes from chemical experience. Because it is known that the correlation energy is very sensitive to spin pairing effects and the opposite spin electrons have different correlation energy from the parallel spin electrons, the electronic state of both A^+ and B^- ionic units adopted in the ionic partitioning scheme should be singlet so as to simulate the electron correlation pattern in $A^{\delta+}B^{\delta-}$ molecule.

TABLE 1: Pair Correlation Contributions and Total Correlation Energies of H_2NNH_2, NH_2^-, NH_2^+, and $NH_2^{\bullet}$ Systems (−mhartree)

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

3.1. Simple Ionic Partition Scaling Approach To Estimate the Total Correlation Energy of A_2-like Covalent Molecules. Symmetry A_2-like molecules are the specific systems of AB-type molecules. First, let us take two A_2-like molecules, H_2NNH_2 and HOOH, as examples to analyze the pair correlation contributions in these two systems and to compare with those values in ($A^+ + A^-$) and (A + A) hypothetical systems.

3.1.1. Pair Correlation Contributions in H_2NNH_2 and the Comparison with Those in ($NH_2^- + NH_2^+$) and ($NH_2^{\bullet} + NH_2^{\bullet}$) Systems. Table 1 gives the results of pair correlation contributions in H_2NNH_2, NH_2^+, $NH_2^{\bullet}$, and NH_2^- systems obtained by eq 1 with intrapair and interpair correlation energy results of MP2-OPT2 method in MELD program using 6-311++G(d) basis set. As it is seen in Table 1, the inner core pair correlation contribution of $1s_N^2$ of N atom, which are between −16.79 and −17.755 mhartree in the above NH-containing systems, change little. The $2s_N^2$ pair correlation contributions in H_2NNH_2, NH_2^-, NH_2^+, and $NH_2^{\bullet}$ are within −41.955 ∼ −47.31 mhartree. From the above results, it is shown that the pair correlation contributions of inner shell electron pairs have somewhat transferable property in these NH-containing systems.

To investigate the simple approach to estimate the correlation energy for H_2NNH_2 by its component units, the two partitioning schemes are either the ionic partitioning scheme, H_2NNH_2 → ($NH_2^+ + NH_2^-$), or the diradical partitioning scheme, H_2NNH_2 → ($NH_2^{\bullet} + NH_2^{\bullet}$). In addition, the further comparison of the correlation energies in H_2NNH_2, ($NH_2^+ + NH_2^-$), and ($NH_2^{\bullet} + NH_2^{\bullet}$) systems, which are − 441.89, − 407.30, and − 391.32 mhartree, respectively, shows that the following relationship is correct for the above systems, that is,

$$|E_{\mathrm{corr}}(H_2NNH_2)| > |E_{\mathrm{corr}}(NH_2^+ + NH_2^-)| > |E_{\mathrm{corr}}(NH_2^{\bullet} + NH_2^{\bullet})| \qquad (3)$$

Combining the above relationship in H_2NNH_2, ($NH_2^+ + NH_2^-$), and ($NH_2^{\bullet} + NH_2^{\bullet}$) systems and the analysis of intrapair and interpair correlation results in Table 1, 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 ($NH_2^{\bullet} + NH_2^{\bullet}$) system, because there is no unpaired electron in both H_2NNH_2 molecule and ($NH_2^+ + NH_2^-$) system, while there is one in ($NH_2^{\bullet} + NH_2^{\bullet}$) system and the number of electron pairs in H_2NNH_2 is equal to the sum of electron pairs in ($NH_2^+ + NH_2^-$) ionic units, as well. Thus, it is more suitable to approximate the total correlation energy of H_2NNH_2 by using the ionic partitioning scheme than by using the diradical partitioning scheme.

3.1.2. Pair Correlation Contributions in HOOH and the Comparison with Those in ($OH^+ + OH^-$) and ($OH^{\bullet} + OH^{\bullet}$)

TABLE 2: Pair Correlation Contributions and Total Correlation Energies of HOOH, OH^-, OH^+, and $OH^\bullet$ Systems (−mhartree)

HOOH			$OH^+(^1A_1)$	$OH^\bullet$	OH^-
$1a^2(1s_O{}^2)$	17.66	$1a_1{}^2(1s_O{}^2)$	16.06	17.61	17.535
$2a^2(2s_O{}^2)$	45.04	$2a_1{}^2(2s_O{}^2)$	46.245	49.91	46.48
$3a^2(2p_O-1s_H)$	78.175	$3a_1{}^2(2p_O-1s_H)$	49.24	62.045	66.855
$4a^2(2p_O-2p_O)$	78.565	$1b_2{}^2(2p_O)$	66.685	58.10	66.635
$5a^2(2p_O)$	75.255	$1b_1{}^{0,1,2}(2p_O)$		22.545	66.635
$1b^2(1s_O{}^2)$	17.675				
$2b^2(2s_O{}^2)$	51.19				
$3b^2(2p_O-1s_H)$	61.165				
$4b^2(2p_O)$	71.075				
E_{corr}(total)	495.80	E_{corr}(total)	178.23	210.22	264.15

Systems. HOOH is another example to use in confirming that either the ionic partitioning scheme or the diradical partitioning scheme is more reasonable in this simple approximation of total correlation energy of A_2-like covalent molecules. Table 2 gives the results of pair correlation contributions in HOOH, OH^+, OH, and OH^- systems using the same method with 6-311++G(d) basis set. As it can be seen in Table 2, the pair correlation contributions of inner shell electron pairs also show somewhat transferable property in these OH-containing systems, such as the two pair correlation contributions of $1s_O{}^2$ in HOOH molecule, which are −17.66 and −17.675 mhartree, and the pair correlation contributions of $1s_O{}^2$ in OH^-, OH^+, and $OH^\bullet$, which are −17.535, −16.06, and −17.61 mhartree, respectively. The $2s_O{}^2$ pair correlation contributions are between −45.04 and −51.19 mhartree in OH^-, OH^+, $OH^\bullet$, and HOOH systems. The further comparison of correlation energy results of HOOH, ($OH^+ + OH^-$), and ($OH^\bullet + OH^\bullet$) systems, which are −495.80, −442.38, and −420.44 mhartree, respectively, also shows that the similar relationship obtained for two partitioning schemes of H_2NNH_2 system remains the same order for two partitioning shemes of HOOH system, that is,

$$|E_{corr}(HOOH)| > |E_{corr}(OH^+{+}OH^-)| > |E_{corr}(OH^\bullet{+}OH^\bullet)| \tag{4}$$

With all of the above analysis and the relationships in eqs 3 and 4, it is suggested that the more reasonable way to reproduce the correlation energies of A_2-like covalent molecules is using the ionic partitioning scheme rather than using the diradical partitioning scheme because all electrons in ($A^+ + A^-$) systems are paired up and the low-spin states adopted in the ionic terms are nearer the electron correlation pattern to the equilibrium molecular environments.

3.1.3. Simple Scaling Approach of A_2-like Covalent Molecules by the Ionic Partitioning Scheme ($A^+ + A^-$). In general, we believe that a logically simple approach would be obtained to provide the total correlation energy for the general AB-type molecules by the ionic partitioning scheme. The wave function of a given AB molecule thus can be expressed as

$$\Psi(AB) = a_1\Phi(A^+) + a_2\Phi(B^-) \tag{5}$$

where $\Phi(A^+)$ and $\Phi(B^-)$ stand for the wave functions of A^+ and B^-.

In specific conditions, the following formula to estimate the correlation energy of AB molecules should be valid, that is,

$$E_{corr}(AB) = c_1E_{corr}(A^+) + c_2E_{corr}(B^-) \tag{6}$$

where c_1 and c_2 are the scale factors of the correlation energies of A^+ and B^- ionic terms, which means that the values of E_{corr}(AB) can be obtained by adjusting the proportion of two correlation energy values of ionic terms $E_{corr}(A^-)$ and $E_{corr}(A^+)$. Therefore, it is reasonable that by judicious choice of the coefficients in the energy expression of eq 6 type, the nondiagonal contribution can be estimated by modified diagonal contributions. Now the most important problem involved in obtaining E_{corr}(AB) is how to determine the scale factors c_1 and c_2 in the above equation. As shown in our mathematical analysis,[20] these two scale factors depend on the values of $E_{corr}(A^+)$ and $E_{corr}(B^-)$ terms, and the proportion of the scale factors c_1 and c_2 is relative to $E_{corr}(A^+)$ and $E_{corr}(B^-)$. In addition, we obtained $c_2 > c_1$ and let $c_1 + c_2 = 2$.

Applying eq 6 to the above two A_2-like molecules, H_2NNH_2 and HOOH, the following equations were obtained:

$$E_{corr}(H_2NNH_2) = 0.54E_{corr}(NH_2{}^+) + 1.46E_{corr}(NH_2{}^-) \tag{7}$$

and

$$E_{corr}(HOOH\ ) = 0.36E_{corr}(OH^+) + 1.64E_{corr}(OH^-) \tag{8}$$

The estimated results of H_2NNH_2 and HOOH systems 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 the estimated results are −1.63 mhartree (−1.02 kcal/mol) for H_2NNH_2 and 1.56 mhartree (0.98 kcal/mol) for HOOH. Therefore, by use of eq 6 it is simple to obtain the total correlation energy of A_2-like covalent molecules by scaling the correlation energies of its ionic terms derived from the ionic partitioning scheme.

To recall the scaling estimation equation for CH_3CH_3 system,

$$E_{corr}(CH_3CH_3) = 0.67E_{corr}(CH_3{}^+) + 1.33E_{corr}(CH_3{}^-) \tag{9}$$

By comparing the ratios of c_2/c_1 for HOOH, H_2NNH_2, and CH_3CH_3 given in Table 3, we found that this ratio is related to the affinity of the heavy atom and the number of H atoms in the system, for example, when the electron affinity of the heavy atom is larger, the ratio of c_2/c_1 is smaller, whereas when there are fewer H atoms in the molecule, the ratio of c_2/c_1 is smaller, as well.

3.2. Simple Ionic Partition Scaling Approach To Estimate the Total Correlation Energy of AX Covalent Molecules. Attempting to extend the investigations of the ionic partitioning scheme to AX polar molecules, we have chosen CH_3F, CH_3OH, and CH_3NH_2 of AX-type molecules to derive the scaling calculation formula for estimating the total electron correlation energy. The calculation results of pair correlation energy contributions of $CH_3{}^+(^1A')$, F^-, OH^-, and $NH_2{}^-$ and CH_3F, CH_3OH, and CH_3NH_2 systems are given in Tables 4 and 5.

3.2.1. Comparison of $CH_3{}^+$ with $CH_3{}^{\delta+}$ in CH_3X (X = F, OH, NH_2) Molecules. As it can be seen in Tables 4 and 5, the pair correlation energy contribution of $1s_C{}^2$ in the $CH_3{}^+$ system is −17.08 mhartree, while those corresponding values in CH_3F, CH_3OH, and CH_3NH_2 systems are −17.535, −17.56, and −17.565 mhartree, respectively. These values change little, which indicates the transferable property of the innermost $1s_C{}^2$ electron pair in these systems. The average value of correlation energy contribution of C−H bonding electron pairs in the $CH_3{}^+$ system is −41.36 mhartree, whereas those corresponding values in CH_3F, CH_3OH, and CH_3NH_2 systems are −53.08, −52.366, and −50.398 mhartree, respectively. There is a large increase of electron correlation energy of the C−H bonding pair from $CH_3{}^+$ to $CH_3{}^{\delta+}$ in CH_3X (X = F, OH, NH_2) systems. The reason is that the number of electron pairs in $CH_3{}^+$ system is four while

TABLE 3: Comparison of Results $c_1E_{corr}(A^-) + c_2E_{corr}(A^+)$ with $E_{corr}(A_2)$ in H_2NNH_2 and HOOH Systems (−mhartree) Calculated by MP2-OPT2 Method

	$E_{corr}(A^-)$	$E_{corr}(A^+)$	$c_1E_{corr}(A^+) + c_2E_{corr}(A^-)$	c_2/c_1	$E_{corr}(A_2)$	absolute deviation	relative error (%)
CH_3CH_3	203.07	141.15	364.65	2.00	364.89	0.23	0.06
H_2NNH_2	239.46	167.84	440.26	2.70	441.89	−1.63	0.36
HOOH	264.15	178.23	497.48	4.56	495.79	1.56	0.31

TABLE 4: Pair Correlation Contributions and Total Correlation Energies of $CH_3^+(^1A')$, F^-, OH^-, and NH_2^- Systems (−mhartree)

	$CH_3^+(^1A')$		F^-		OH^-		NH_2^-
$E_{corr}(1s_C^2)$	17.08	$1s_F^2$	17.865	$1a_1^2(1s_O^2)$	17.535	$1a_1^2(1s_N^2)$	17.365
$E_{corr}(C-H)$	39.30	$2s_F^2$	44.69	$2a_1^2(2s_O^2)$	46.48	$2a_1^2(2s_N^2)$	43.645
	42.48	$2p_F^2$	70.085	$3a_1^2(2p_O-1s_H)$	66.855	$3a_1^2(2p_N-1s_H)$	59.975
	42.29	$2p_F^2$	70.085	$1b_2^2(2p_O)$	66.635	$1b_2^2(2p_N-1s_H)$	56.865
	(41.36)	$2p_F^2$	70.085	$1b_1^2(2p_O)$	66.635	$1b_1^2(2p_N)$	61.62
E_{corr}(total)	141.15		272.81		264.15		239.46

TABLE 5: Pair Correlation Energies of Individual Electron Pairs in CH_3F, CH_3OH, and CH_3NH_2 with 6-311++G(d) Basis Sets

	$E_{corr}(C_{1s2})$	$E_{corr}(C-H)$	$E_{corr}(C-Y)$	$E_{corr}(Y-H)$	$E_{corr}(Y_{1s2})$	$E_{corr}(Y_{2s2})$	$E_{corr}(Y_{2p2})$	E_{corr}(total)
CH_3F	17.535	44.61, 57.265, 57.15, (53.08)	78.345		17.965	44.445	58.15, 58.025, (58.088)	433.50
CH_3OH	17.56	44.60, 51.285, 61.215, (52.366)	65.925	63.51	17.835	44.625	62.375	428.94
CH_3NH_2	17.565	42.035, 50.775, 58.385, (50.398)	61.835	55.035, 60.85, (57.94)	17.76	40.87		405.07

that of CH_3X (X = F, OH, NH_2) systems is nine. Thus, the electron pairs of X group produce essentially a nearest-neighbor correlation effect in $CH_3^{\delta+}$ group. However, if only considering these CH_3X (X = F, OH, NH_2) isoelectronic systems, not only the pair correlation energy contribution of $1s_C^2$ is transferable in these systems, but also the C−H bonding correlation energy of $CH_3^{\delta+}$ is fairly transferable in this series molecules.

3.2.2. Comparison of X^- with $X^{\delta-}$ in CH_3X (X = F, OH, NH_2) Molecules. Let us denote by Y the heavy atom in the substituent group X in CH_3X (X = F, OH, NH_2) systems. By inspecting the results in Tables 4−5, we found that the pair correlation energy contributions of $1s_Y^2$ of Y atoms (Y = F, O, N) change little from X^- to $X^{\delta-}$ in CH_3X (X = F, OH, NH_2) molecules, for example, $E_{corr}(1s_F^2) = -17.865 \rightarrow -17.965$ mhartree from F^- to $F^{\delta-}$ in CH_3F, $E_{corr}(1s_O^2) = -17.535 \rightarrow -17.835$ mhartree from OH^- to $OH^{\delta-}$ in CH_3OH, and $E_{corr}(1s_N^2) = -17.365 \rightarrow -17.76$ mhartree from NH_2^- to $NH_2^{\delta-}$ in CH_3NH_2. The pair correlation energy contributions of $2s_Y^2$ of Y atoms (Y = F, O, N) also demonstrate tiny difference from X^- to $X^{\delta-}$ in CH_3X (X = F, OH, NH_2) molecules, for example, $E_{corr}(2s_F^2) = -44.69 \rightarrow -44.445$ mhartree, $E_{corr}(2s_O^2) = -46.48 \rightarrow -44.625$ mhartree, and $E_{corr}(2s_N^2) = -43.645 \rightarrow -40.87$ mhartree. All of these results show the transferability of these pair correlation energies. However, the values of $2p_Y$ for O−H and N−H electron pairs change somewhat largely because of the formation of C−Y bonds in CH_3X (X = F, OH, NH_2) systems.

From the detailed comparison of pair correlation contributions of $CH_3^+X^-$ with those in $CH_3^{\delta+}X^{\delta-}$ systems, it is observed that $X^{\delta-}$ in CH_3X (X = F, OH, NH_2) systems is more close to the isolated X^-. However, $CH_3^{\delta+}$ in CH_3X (X = F, OH, NH_2) is somewhat different from free CH_3^+ system, which might depend on a number of reasons, for example, number of electron pairs, geometry parameters, and group charges.

3.2.3. Simple Scaling Approach To Estimate the Total Correlation Energy of AX Covalent Molecules by Scaling Correlation Energies of Ionic Terms A^+ and X^-. On the basis of the above analysis of CH_3X (X = F, OH, NH_2) isoelectronic systems, it is observed that the electron correlation energy contribution of $CH_3^{\delta+}$ group is transferable in these three CH_3X series systems and $X^{\delta-}$ substituent group in CH_3X (X = F, OH, NH_2) systems is more close to the isolated X^- ionic term. Therefore, according to eq 6, it is reasonable to obtain the total correlation energies of CH_3X molecules by scaling the correlation energies of its ionic terms CH_3^+ and X^-,

$$E_{corr}(CH_3X) = c_1E_{corr}(CH_3^{\ +}) + c_2E_{corr}(X^-) \qquad (10)$$

where c_1 and c_2 are the scale factors of the correlation energies of the corresponding ionic terms, which are relative to the correlation energies of the corresponding CH_3^+ and X^-.

From the above analysis of CH_3X (X = F, OH, NH_2) systems, it is clear that the proportion of the scale factors c_1 and c_2 is relative to the values of $E_{corr}(CH_3^+)$ and $E_{corr}(X^-)$. We let $c_2 > c_1$, and $c_1 + c_2 = 2$, Therefore, the following equations were obtained for these CH_3X (X = F, OH, NH_2) systems:

$$E_{corr}(CH_3F) = 0.84E_{corr}(CH_3^{\ +}) + 1.16E_{corr}(F^-) \qquad (11)$$

$$E_{corr}(CH_3OH) = 0.81E_{corr}(CH_3^{\ +}) + 1.19E_{corr}(OH^-) \qquad (12)$$

and

$$E_{corr}(CH_3NH_2) = 0.75E_{corr}(CH_3^{\ +}) + 1.25E_{corr}(NH_2^{\ -}) \qquad (13)$$

The estimated results of CH_3X (X = F, OH, NH_2) systems by using the above equations are listed in Table 6. For comparison, the direct calculated correlation results of these systems are also given in Table 6. As seen from the comparison, the largest absolute deviations of the three estimated results are −1.52 mhartree (−0.95 kcal/mol) for CH_3X (X = F, OH, NH_2) systems, while the other two absolute deviations are only −0.27 and 0.11 mhartree, respectively. It is indicated that the total correlation energies of the AX polar covalent molecules can also be obtained by scaling the correlation energies of its ionic terms A^+ and X^- derived from the ionic partitioning scheme. In addition, it should be noted that the ratio of c_2/c_1 in the above equations given in Table 6 are relative to the difference between

TABLE 6: Comparison of Results $c_1E_{corr}(A^+) + c_2E_{corr}(B^-)$ with $E_{corr}(AB)$ in CH_3X (X = F, OH, NH_2) Systems (−mhartree) Calculated by MP2-OPT2 Method

	$E_{corr}(A^+)$	$E_{corr}(B^-)$	$c_1E_{corr}(A^+) + c_2E_{corr}(B^-)$	$E_{corr}(AB)$	c_1/c_2	absolute deviation	relative error (%)
CH_3F	141.15	272.81	435.02	433.50	1.38	1.52	0.35
CH_3OH	141.15	264.15	428.67	428.94	1.47	−0.27	0.06
CH_3NH_2	141.15	239.46	405.18	405.07	1.67	0.11	0.02

the affinity of C and Y (Y = F, O, N) atoms in the system, that is, when the difference between the affinity of C and Y atoms is larger, the ratio of c_2/c_1 in the estimation equation is smaller.

3.3. Comparison of the Ionic Scaling Estimation Equations of Different Kinds of Chemical Bonding Systems, MA, AX, and A_2-like Molecules. So far, we have applied our simple scheme “separating large system into smaller ones” to the strong ionic compounds MA, polar covalent molecules AX, and symmetry covalent molecules A_2. As stated above, opposite to the symmetry A_2-like molecules, strong ionic compounds MA are the other specific systems of AB-type molecules in which the bonding electron pair completely belongs to the B atom. To summarize all of the situations, in the estimation of the total correlation energy of a given molecule, eq 6 is valid for the general AB-type molecules including strong ionic compounds MA, polar covalent molecules AX, and symmetry A_2-like covalent molecules, as well, that is,

$$E_{corr}(AB) = c_1E_{corr}(A^+) + c_2E_{corr}(B^-) \qquad (14)$$

This means that no matter what kind of chemical bonding in the system, the total correlation energy can be obtained by scaling the correlation energies of the ionic fragments by the ionic partitioning scheme.

However, the ratio of scaling coefficients, c_2/c_1, shows different characteristics for different kinds of bonding systems. For instance, as seen in the discussion of strong ionic compounds MA, the above equation becomes

$$E_{corr}(MA) \approx E_{corr}(M^+) + E_{corr}(A^-) \qquad (15)$$

That means $c_2/c_1 \approx 1$ for MA strong ionic systems.

For symmetry A_2 covalent molecules, the ratios of scaling coefficients c_2/c_1 of HOOH, H_2NNH_2, and CH_3CH_3 shown in Table 3 are 4.56, 2.70, and 2.00, respectively. If we recall the ratio of c_2/c_1 in the estimation equations for F_2 and O_2^{2-} system with cc-pV5Z* basis set, which are 3.25 and 4.00, it is indicated that the value of c_2/c_1 for A_2 covalent molecules is much larger than 1.

For AX polar covalent molecules CH_3X (X = F, OH, NH_2), the values of c_2/c_1 ratio shown in Table 6 are 1.38, 1.47, and 1.67, respectively.

The comparison of the ratio of c_2/c_1 for MA, AX, and A_2 systems shows that the values of c_2/c_1 of AX polar systems are larger than those of MA strong ionic compounds but smaller than those of A_2 covalent molecules. It is reasonable to rationalize that when AX polar systems have more ionic property, the ratio of c_2/c_1 is much smaller, while when the chemical bonding in AX systems becomes completely ionic, the ratio of c_2/c_1 will be nearer to 1. Therefore, the relative relationship of the c_2/c_1 for MA, AX, and A_2 systems is proportional to the ionic strength of the system, that is,

$$c_2/c_1(A_2) > c_2/c_1(AX) > c_2/c_1(MA)$$

According to the above analysis, it is obvious that the scaling ionic partitioning scheme paves a way of the chemical thinking.

In summary, because the scaling estimation approach by ionic partitioning scheme for large molecules are ab initio calculations and well-sounded from the theoretical point of view, in the future, we plan to further test the scaling ionic partitioning scheme on larger molecules to define the scope of this simple scheme. We believe that the simple scheme “separating large system into smaller ones” would be a useful means to solve the bottleneck problem of the calculation of the electron correlation energy of larger molecules.

4. Conclusions

On the basis of our calculation results and the above analysis, the principle conclusions can be obtained as follows: (1) With the analysis of pair correlation contribution values in H_2NNH_2 and HOOH molecules, it is confirmed that the ionic partitioning scheme ($A^- + A^+$) is the reasonable way to estimate the correlation energies of A_2-like covalent molecules. Thus, the total correlation energy of A_2-like covalent molecule can be obtained by scaling the correlation energies of its singlet ionic terms A^- and A^+ derived from the ionic partitioning scheme. (2) On the basis of our discussion of the pair correlation contributions of CH_3X (X = F, OH, NH_2) systems, it is observed that our simple scheme “separating large system into smaller ones” can also be applied in AX polar covalent molecules, for example, the total correlation energy of AX molecules can be obtained by scaling the correlation energies of its ionic terms A^+ and X^-. The estimated results of these CH_3X (X = F, OH, NH_2) systems are within a small derivation compared with the direct calculation results. (3) The general formula of the scaling ionic partitioning scheme for estimating the total correlation energy of a given system AB can be expressed as

$$E_{corr}(AB) = c_1E_{corr}(A^+) + c_2\,E_{corr}(B^-)$$

For the strong ionic compounds MA, polar covalent molecules AX, and symmetry covalent molecules A_2, there exists the following relationship among the ratio of the scaling coefficients c_2/c_1 in the estimation equations,

$$c_2/c_1(A_2) > c_2/c_1(AX) > c_2/c_1\ (MA)$$

Therefore, it can be concluded that the scaling ionic partitioning scheme is justifiable in a general perspective of chemistry.

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