

A Quick Estimate of the Correlation Energy for Alkanes

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Within the localized molecular orbital description, the intra- and interorbital pair correlation energies calculated with the coupled cluster doubles (CCD) theory have been obtained for methane, ethane, propane, butane, isobutane, pentane, isopentane and neopentane using the 6-31G* basis set. The results showed the quantitative transferability of pair correlation energies and gross orbital correlation energies within this series of molecules. Based on the gross orbital correlation energies of five sample alkanes (butane, isobutane, pentane, isopentane and neopentane), we have derived a simple linear relationship to estimate the CCD correlation energy for an arbitrary large alkane. The correlation energy predicted by this simple relationship remarkably recovers more than 98.9% of the exact CCD correlation energy for a number of alkanes containing six to eight carbon atoms. The relative stability of less branched isomers can be correctly predicted.

Keywords correlation energy, pair correlation, localized orbitals, coupled cluster theory, alkanes

Introduction

The electron correlation energy, the difference between the exact nonrelativistic energy of the system and the Hartree-Fock (HF) energy,¹ is critical for the accurate and quantitative evaluation of molecular energies. During the past two decades the coupled cluster (CC) theories²⁻⁷ have proven to be among the most successful methods for calculating electron correlation energies of molecules. Traditionally, the CC equations are solved in a basis of HF canonical molecular orbitals (CMOs). Since CMOs are generally delocalized over the entire system, the computational effort of CC calculations increases steeply with increasing the molecular size.⁵⁻⁷ Apparently, for large molecules the conventional CC calculations with delocalized CMOs are hopeless. To allow CC calculations computationally feasible for large systems, several lower-order even linear scaling local correlation (LC) CC methods⁸⁻¹¹ have been developed. These methods are demonstrated to be capable of recovering more than 98% of the correlation energy obtained in the corresponding conventional CC calculation. Therefore, one can expect that with various LC approaches it may be possible in the near future to accu-

rately calculate the correlation energy for very large systems. Nevertheless, at present the computational task is still substantial since these LC methods achieve linear scaling only in the large molecule asymptote.⁸⁻¹¹

Although the accurate CC calculations are indispensable for a single molecule, a simple procedure for estimating the correlation energy for a group of structurally similar molecules is also desirable. Actually, the success of various LC CC methods provides some clues for such a procedure. The theoretical grounds underlying these approaches^{8,9,11} include: (1) the correlation energy can be partitioned into pair contributions; (2) within the localized molecular orbital (LMO) description those interorbital pair contributions from distant localized orbitals may be neglected without much loss of accuracy. Clearly, the additivity of the correlation energy and the fast decay of pair correlation energies with the distance between orbitals must be employed in building a simple model for estimating the correlation energy for a large molecule. On the other hand, our chemical intuition suggests that in a localized description pair correlation energies might be transferred in a homologous series if the involved two (or one) localized orbitals are situated at similar molecular fragments. Obviously, this transferability is also essential in the estimate of the correlation energy for homologous molecules. From the above discussions, a plausible strategy for estimating the correlation energy of homologous molecules has emerged. It consists of three steps: (1) calculate the pair correlation energies for small members of a homologous series; (2) transfer the resultant pair energies to larger members of the series; (3) sum those significant pair correlation energies to obtain an estimate of the total correlation energy. To our knowledge, the simple strategy outlined above for quantitatively evaluating the total correlation energy for homologous molecules has not been established within the CC theories. Within the Møller-plesset perturbation theory (second to fourth-order, denoted as MP2-MP4), it has been demonstrated that intraorbital and interorbital pair energies are quite transferable for structurally similar molecules,¹²⁻²⁰ but no further applications have been reported.

In this work, our primary aim is to establish a simple

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model by using the simple procedure outlined above for effectively estimating the correlation energy of alkanes. First, we introduce an implementation of the CCD method, in which both CMOs and LMOs can be employed. Then, we present intraorbital and interorbital pair correlation energies calculated with the CCD theory, and discuss the dependence of the pair correlation energy with the distance between two localized orbitals. Analyses on the transferability of pair correlation energies and gross orbital correlation energies are followed. Based on gross group (or orbital) correlation energies obtained from five sample alkanes (butane, isobutane, pentane, isopentane and neopentane), we have derived a simple relationship for estimating the total correlation energy of an arbitrary large alkane. For alkanes containing up to eight carbon atoms, the correlation energies predicted by this simple formula are compared with those computed with the conventional CCD calculations.

Coupled cluster doubles theory

The CCD wave function is represented in the cluster expansion form²⁻⁴

$$\Psi_{\text{CCD}} = e^{\hat{T}_2} \Psi_0 \quad (1)$$

where Ψ_0 is the HF determinantal wave function

$$\Psi_0 = (N!)^{-1/2} |\phi_1 \phi_2 \dots \phi_N| \quad (2)$$

with $\phi_1 \dots \phi_N$ being spin orbitals occupied by N electrons, and \hat{T}_2 represents a complete double excitation operator

$$\hat{T}_2 = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} a_i^+ a_j^+ a_b^- a_a^- \quad (3)$$

where t_{ij}^{ab} are antisymmetrized double excitation amplitudes to be determined. Here and in the following labels i, j are used to denote occupied spin orbitals and a, b for virtual ones.

The explicit equations for the amplitudes are obtained by projecting the Schrödinger equation onto Ψ_0 and the space of doubly excited determinants²⁻⁴

$$\Psi_0 | H - E | \Psi_{\text{CCD}} = 0 \quad (4)$$

$$\Psi_{ij}^{ab} | H - E | \Psi_{\text{CCD}} = 0 \quad (5)$$

and

$$\Psi_{ij}^{ab} = a_a^+ a_i a_b^+ a_j | \Psi_0 \quad (6)$$

Substituting the expression of Ψ_{CCD} [Eq. (1)] into Eqs. (4) and (5) leads to a set of coupled non-linear equations, which have been discussed in our previous work,¹¹ for determining all double excitation amplitudes.⁴⁻⁷ Once

the amplitudes are known, the CCD correlation energy can be obtained by

$$\Delta E^{\text{CCD}} = E^{\text{CCD}} - E^{\text{HF}} = \sum_{\substack{i>j \\ a>b}} ab || ij t_{ij}^{ab} \quad (7)$$

For restricted closed-shell molecules like saturated alkanes under investigation, it is computationally preferable to transform the spin orbital expression of each term in Eq. (7) into the corresponding spatial orbital form.⁷ For instance, Eq. (7) can be transformed as

$$\Delta E^{\text{CCD}} = \sum_{\substack{i>j \\ a>b}} ij || ab 2\bar{t}_{ij}^{ab} + \sum_{\substack{ij \\ ab}} ia | jb \tilde{t}_{ij}^{ab} \quad (8)$$

Here the variables $\bar{t}_{ij}^{ab} = t_{iajb}^{ab}$ and $\tilde{t}_{ij}^{ab} = t_{iajb}^{ab}$ are introduced, and the relationships $t_{iaja}^{aba} = t_{ijj\beta}^{a\beta\beta}$ and $t_{ij}^{ab} = \tilde{t}_{ji}^{ba}$ due to the spin inversion symmetry are employed. From now on, labels i, j will denote occupied spatial orbitals and a, b for virtual ones. We have completed an *ab initio* implementation of the restricted closed-shell CCD method. In our program, both LMOs and CMOs can be used although the use of LMOs usually needs a few more iterations. Boys' localization procedure²¹ is employed to obtain occupied and virtual LMOs, separately, because it computationally scales as the third power of the number of basis functions (N_b), while the localization method of Edmiston and Ruedenberg²² is a N_b^5 procedure. Our test calculations on several small molecules reproduced the CCD correlation energies given by the Gaussian 98 package.²³

It is obvious from Eq. (8) that the total correlation energy may be partitioned into a sum of pair correlation energies as shown in Eq. (9), each term characteristic of two occupied orbitals.

$$\Delta E^{\text{CCD}} = \sum_{i \geq j} \epsilon(ij) \quad (9)$$

with

$$\epsilon(ii) = \sum_{a,b} ia | ib \tilde{t}_{ii}^{ab} \quad (10)$$

$$\epsilon(ij) = \sum_{a>b} ij || ab 2\bar{t}_{ij}^{ab} + \sum_{\substack{a,b \\ j a}} [ia | jb \tilde{t}_{ij}^{ab} + ja | ib \tilde{t}_{ji}^{ab}] \quad (i \neq j) \quad (11)$$

Here $\epsilon(ii)$ stands for the intraorbital correlation contribution involving two electrons in the same orbital ϕ_i , and $\epsilon(ij)$ stands for the interorbital correlation contribution involving one electron from ϕ_i and one from ϕ_j . Clearly, both canonical and localized MOs are applicable in the decomposition of the total correlation energy. However, it is preferable to carry out the decomposition with the localized MOs since the associated pair correlation energies might be quite transferable for structurally analogous compounds, as shown within the many-body perturbation theory.¹²⁻²⁰ More

importantly, this transferability of pair correlation energies makes it possible to approximately estimate the total correlation energy for large members of a homologous series from calculations on its small members. On the other side, one may notice that there is no unique way of constructing LMOs and the pair correlation energies will depend on to some extent the choice of localization procedures. Nevertheless, in the present work, since our purpose is to evaluate the total correlation energy for a homologous series based on the transferability of pair correlation contributions, the use of different localization methods should have little effect on the final results.

Results and discussion

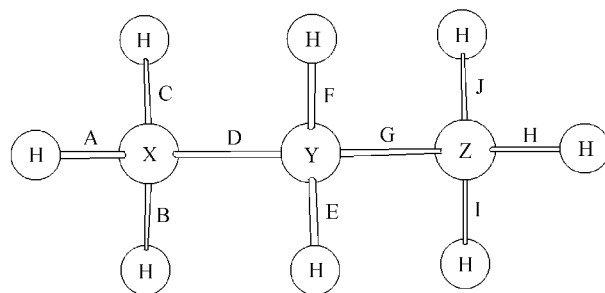
To evaluate the correlation energy for large members of a homologous series from calculations on its first few members, two premises should be satisfied: one is the fast decay of pair correlation energies with the distance between orbitals, the other is the transferability of pair correlation energies and gross orbital correlation energies within the given series. For alkanes, we will discuss these two premises first, and then introduce a simple formula for estimating the correlation energy of an arbitrary long alkane.

The fast decay of pair correlation energies with the distance between orbitals

Table 1 shows the intra- and interorbital pair correlation energies for the ground state of propane at the CCD/6-31G*//HF/6-31G* level, with the labels of core and valence localized orbitals listed in Scheme 1. In our CCD calculations all electrons are included. Since for ground-state alkanes the localized molecular orbitals cleanly resemble bicentric bonds or atomic cores, we will describe a specific LMO by its associated chemical bond or core orbital in the subsequent sections for simplicity. As expected, the intraorbital pair correlation energies for the carbon core orbitals are only about 2.5 milliHartree (mH). The

intraorbital pair correlation energies for C—H bonds are approximately constant, varying from -22.8 mH to -23.0 mH. The intraorbital pair correlation energy of a single C—C bond is about -22.9 mH, similar to that of a single C—H bond. For interorbital pairs, the absolute pair correlation energy decreases rapidly with the interorbital separation. For a given core orbital, the pair correlation energies between this orbital and its adjacent valence orbitals have values from 0.53 mH to 0.55 mH, but all other interorbital correlation energies are nearly zero. If the localized orbitals share one atom, such as A and B in Scheme 1, the interorbital pair energies are found to be in the range from -10 to -12 mH. The absolute pair correlation energies are all less than 1 mH for those orbitals separated by one bond, exemplified by A and E in Scheme 1, and even smaller if those orbitals are two or more bonds far apart. The fast decay of pair correlation energies with the distance between orbitals, obtained here within the CCD theory, is quite similar to that observed at various orders of many-body perturbation theory.^{16,17}

Scheme 1



The transferability of correlation energies in alkanes

The transferability of pair correlation energies for structurally similar systems has been discussed for some molecules within the many-body perturbation theory,¹²⁻²⁰ but no in-depth analysis has been reported within the CCD theory for a homologous series and their isomers. Here,

Table 1 Negative of pair correlation energies (in milliHartree) for the ground state of propane at the CCD(full)/6-31G*//HF/6-31G* level

	X	Y	Z	A	B	C	D	E	F	G	H	I	J
X	2.48												
Y	0.00	2.55											
Z	0.00	0.00	2.48										
A	0.54	0.01	0.00	22.84									
B	0.53	0.01	0.00	11.14	22.81								
C	0.53	0.01	0.00	11.14	11.13	22.81							
D	0.53	0.54	0.01	10.55	10.58	10.58	22.88						
E	0.01	0.55	0.01	0.73	0.73	0.83	10.58	22.99					
F	0.01	0.55	0.01	0.73	0.83	0.73	10.58	11.19	22.99				
G	0.01	0.54	0.53	0.79	0.68	0.68	9.93	10.58	10.58	22.88			
H	0.00	0.01	0.54	0.22	0.17	0.17	0.79	0.73	0.73	10.55	22.84		
I	0.00	0.01	0.53	0.17	0.26	0.15	0.68	0.73	0.83	10.58	11.14	22.81	
J	0.00	0.01	0.53	0.17	0.15	0.26	0.68	0.83	0.73	10.58	11.14	11.13	22.81

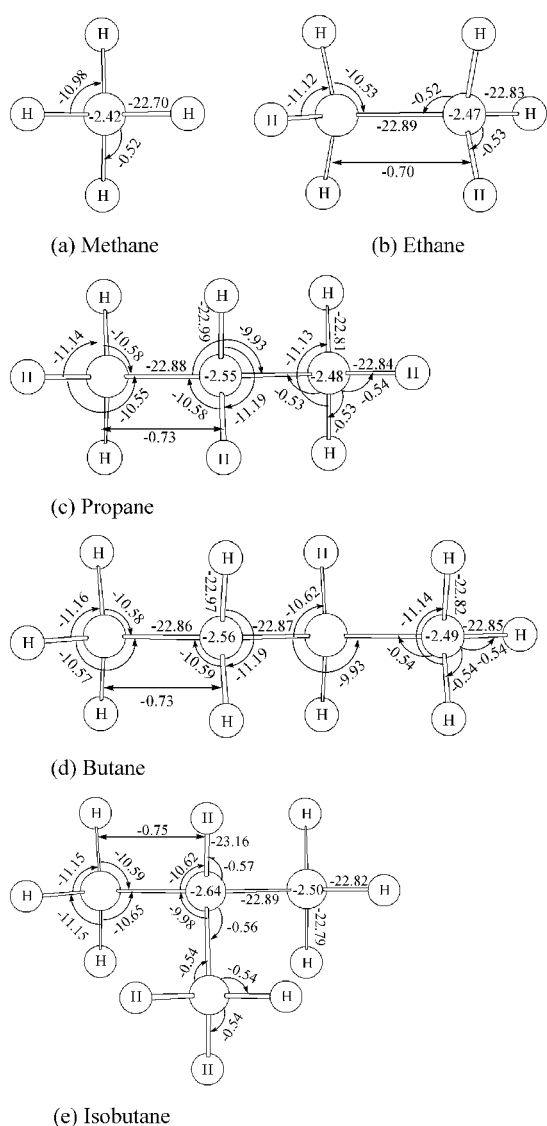


Fig. 1 Intraorbital and interorbital pair correlation energies (in milliHartree) of significant pairs for (a) methane, (b) ethane, (c) propane, (d) butane and (e) isobutane at the CCD(full)/6-31G*//HF/6-31G* level.

Fig. 1 shows intraorbital correlation energies and interorbital correlation energies of significant pairs for methane, ethane, propane, butane and isobutane at the CCD(full)/6-31G*//HF/6-31G* level. One may note that intraorbital correlation energies for core orbitals of the primary carbon vary by about 0.05 mH from methane to ethane but almost keep unchanged from ethane to butane and isobutane. The interorbital correlation energies between a primary carbon core orbital and its neighboring bond orbitals are nearly constant from propane to butane and isobutane. The intraorbital correlation energies for primary C—H bonds vary by about 0.1 mH from methane to ethane, and remain almost unchanged from ethane to butane, and isobutane. Similarly, negligible change in the intrapair contribution occurs for secondary C—H bonds and C—C bonds in CH₃CH₂—fragments from propane to butane. The interorbital contributions between neighboring primary

C—H bonds vary by 0.1 mH from methane to ethane, but by only 0.01—0.02 mH from ethane to propane and remain almost the same from butane to isobutane. From propane to butane, the interpair correlation energy between a primary C—H bond and its neighboring C—C bond, is consistent within the 0.03 mH. The interpair contribution between neighboring C—C bonds in propane is essentially the same as that in butane but decreases by 0.05 mH (from -9.93 to -9.98) from butane to isobutane. To conclude, we find that if the local environment of a certain type of bond is similar in two different molecules, the intraorbital correlation energy for this type of bond will be nearly constant in these two molecules. If both of two bonds have very analogous neighboring bonds in two different molecules, the interorbital contribution between these two bonds is also highly transferable.

Instead of partitioning the total correlation energy into intraorbital correlation energies and interorbital correlation energies for pairs of orbitals, it is convenient for later discussions to apportion the total correlation energy among the orbitals only. This can be done by splitting each interorbital correlation energy $\epsilon(ij)$ equally between the orbitals i and j . For each occupied orbital i , this defines a gross orbital correlation energy $\Delta\epsilon(i)$, which is shown in Eq. (12)

$$\Delta E^{\text{CCD}} = \sum_i \Delta\epsilon(i) \quad (12)$$

with

$$\Delta\epsilon(i) = \epsilon(ii) + \frac{1}{2} \sum_{j \neq i} \epsilon(ij) \quad (13)$$

As done in the preceding section, we will investigate whether gross orbital correlation energies are also highly transferable for orbitals in small alkane molecules. Fig. 2 shows gross orbital correlation energies for ethane, propane, butane and pentane. First, we note that gross orbital correlation energies for the primary carbon core orbitals remain almost unchanged from ethane to pentane. Gross orbital correlation energies for the primary C—H bond orbitals vary by about 0.35 mH from ethane to propane but only 0.09 mH from propane to butane and 0.01 mH from butane to pentane. Similarly, gross orbital correlation energies for C—C bond orbitals in CH₃CH₂—fragments change by 0.27 mH from propane to butane but only 0.07 mH from butane to pentane. Therefore, we find that if the local environment of a certain occupied orbital is similar in two different molecules, the gross orbital correlation energies in these two molecules are quite transferable. Of course, the transferability of gross orbital correlation energies depends on to some extent how two orbitals are judged to have similar local environments. More discussions on this issue are given in the following section.

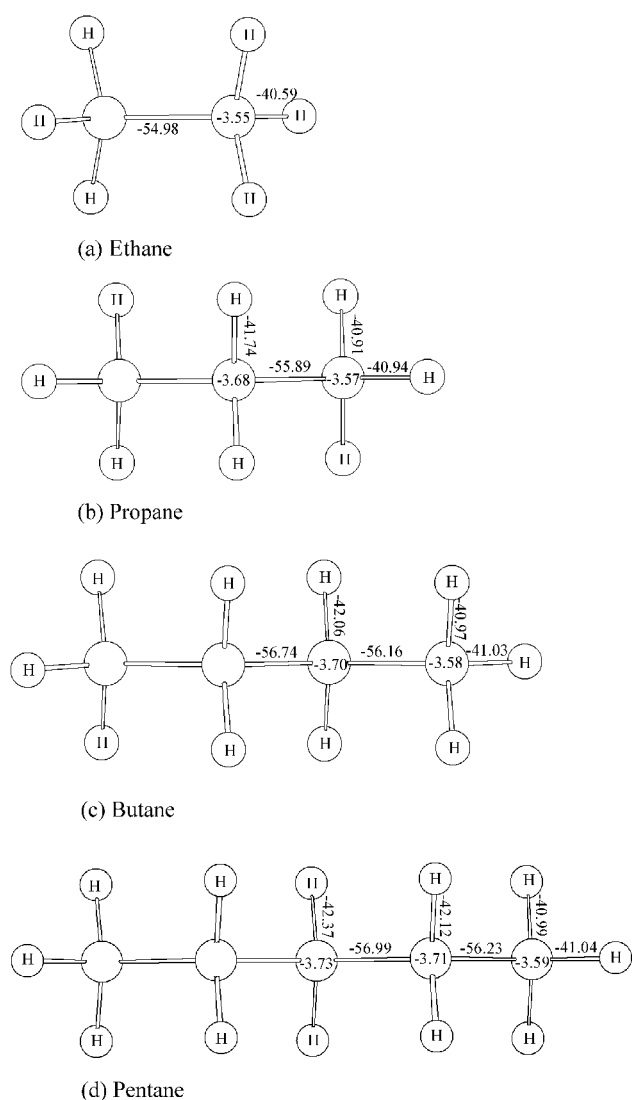


Fig. 2 Gross orbital correlation energies (in milliHartree) for core and bond orbitals in (a) ethane, (b) propane, (c) butane and (d) pentane at the CCD(full)/6-31G*//HF/6-31G* level.

The estimate of the correlation energy for large alkanes

In order to derive a simple formula to estimate the total correlation energies for large alkanes, it is useful to define a gross group correlation energy as the sum of gross orbital correlation energies within a certain group, which may consist of several orbitals. For simple alkyl groups such as CH₃, the gross group correlation energy is just the addition of gross orbital correlation energies for a carbon core orbital and its adjacent C—H bond orbitals. Obviously, the total correlation energy of a large alkane can be estimated by adding gross group correlation energies for alkyl groups and gross orbital correlation energies for C—C bond orbitals, which are derived from small alkane molecules. To ensure the transferability of gross group (or orbital) correlation energies of alkyl groups (or C—C bond orbitals) as high as possible, we use gross orbital correlation energies and gross group correlation energies from five

sample molecules: butane, isobutane, pentane, isopentane (2-methyl-butane) and neopentane (2,2-dimethyl-propane) (see Fig. 3).

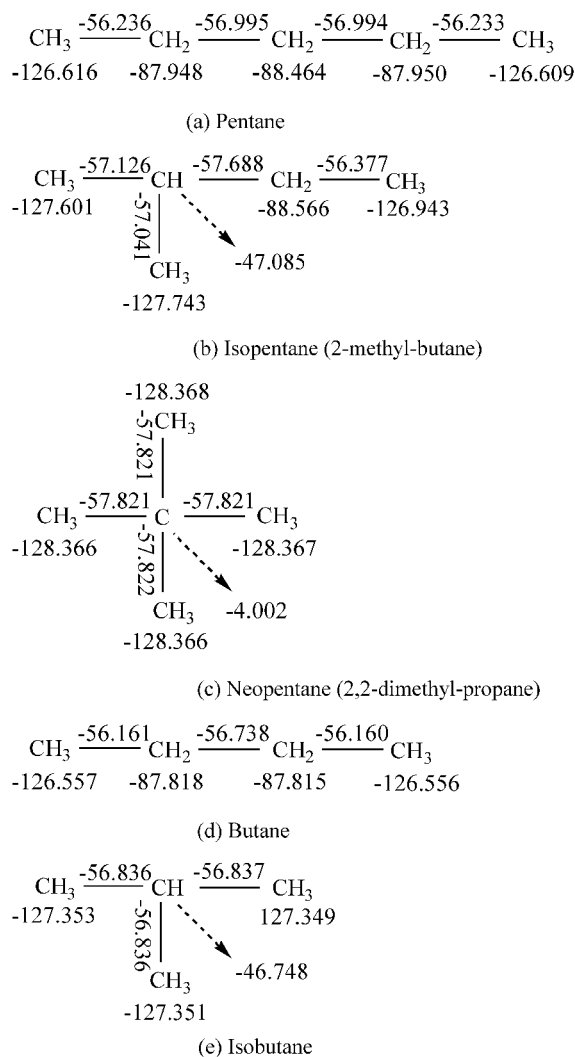


Fig. 3 Gross group correlation energies of alkyl groups and gross orbital correlation energies of C—C bond orbitals (in milliHartree) for (a) pentane, (b) isopentane, (c) neopentane, (d) butane and (e) isobutane at the CCD(full)/6-31G*//HF/6-31G* level.

From Fig. 3, one can notice that the gross orbital correlation energies for C—C bond orbitals depend on the number of the hydrogen atoms bonded to these two carbons, but those with the same number of adjacent hydrogen atoms are close to each other. Thus for C—C bonds with the same number of adjacent hydrogen atoms, the average of the corresponding values obtained from three sample molecules (pentane, isopentane and neopentane) is assumed to be transferable in large alkanes. This assumption gives the gross orbital correlation energy to be -56.306 mH, -57.040 mH, -57.755 mH for C—C bonds with five, four, three adjacent hydrogen atoms, respectively. Interestingly, we find that the average gross orbital correlation energies for C—C bonds approximately depend linearly on the number of adjacent hydrogen

atoms. A least-squares procedure gives a good linear relationship below between the gross orbital correlation energies of C—C bond orbitals with the number of adjacent hydrogen atoms m

$$\Delta E_{C-\alpha(m)} = -60.065 + 0.757m \text{ (mH)} \quad (14)$$

This formula will be used to predict the gross orbital correlation energies for those C—C bonds in large alkanes with the number of adjacent hydrogen atoms not covered in three selected sample molecules. Similarly, we find that the gross group correlation energy for a selected alkyl (CH_3 , CH_2 , CH) is also affected by the number of the hydrogen atoms in adjacent alkyl groups linked to this group, but those with the same number of adjacent hydrogen atoms are similar. By adding butane and isobutane as two additional sample molecules and using least-squares procedures, we have also derived the linear relationships between the gross group correlation energies of alkyl groups with the number of their adjacent hydrogen atoms m , which are collected in Table 2. In Table 2, for quaternary carbon atoms the gross group correlation energy is just the gross orbital correlation energy for there is only a carbon core orbital within the group. For quaternary carbon atoms, we have assumed the gross group correlation energy calculated from neopentane to be transferable in large alkanes. Now, it is straightforward to estimate the total correlation energy of an arbitrary large alkane from the gross group correlation energies and gross orbital correlation energies discussed above

$$\Delta \sum_{\text{CCD}} = \sum_{m=0}^5 n_{C-\alpha(m)} \times \Delta E_{C-\alpha(m)} + \sum_{m=0}^2 n_{\text{CH}_3(m)} \times \Delta E_{\text{CH}_3(m)} + \sum_{m=0}^5 n_{\text{CH}_2(m)} \times \Delta E_{\text{CH}_2(m)} + \sum_{m=0}^8 n_{\text{CH}(m)} \times \Delta E_{\text{CH}(m)} + \sum_{m=0}^{11} n_{\alpha(m)} \times \Delta E_{\alpha(m)} \quad (15)$$

Here $n_{C-\alpha(m)}$ is the number of adjacent hydrogen atoms for a given C—C bond and $\Delta E_{C-\alpha(m)}$ is the fitted gross orbital correlation energy for this C—C bond. The other items have similar meanings.

The correlation energies for several large members of alkanes have been predicted by using Eq. (15), with the results presented in Table 3. The calculated correlation energies at the CCD(full)/6-31G*//HF/6-31G* level for these molecules are also collected in Table 3 for comparison. Very encouragingly, for each molecule from hexane to octane and their isomers the predicted CCD correlation energy accounts for more than 99.0% of the exact CCD correlation energies in the 6-31G* basis set. Hence, we are confident that the simple relationship, Eq. (15), can be employed to yield a relatively accurate estimate to the exact CCD correlation energy for an arbitrary alkane (no less than pentane) in the 6-31G* basis set.

From Table 3, one can notice that the correlation energy is important in predicting the relative stability of





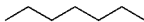



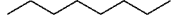
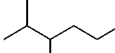


Table 2 Relationships of gross orbital correlation energies (in milliHartree) of C—C bonds and gross group correlation energies of alkyl groups with the total number of hydrogen atoms (m) from least-squares procedure. For C—C bonds m is the total number of hydrogen atoms bonded to two carbon atoms, and for an alkyl group m stands for the total number of hydrogen atoms on its neighboring alkyl groups

C—C bonds or alkyl groups	m	Correlation energy	Relationship
C—C	5	-56.282	$\Delta E_{C-\alpha(m)} = -60.065 + 0.757m$
	4	-57.039	
	3	-57.795	
	2	-126.656	
CH_3 —	1	-127.479	$\Delta E_{\text{CH}_3(m)} = -128.356 + 0.856m$
	0	-128.367	
— CH_2 —	5	-87.883	$\Delta E_{\text{CH}_2(m)} = -91.043 + 0.632m$
	4	-88.515	
— CH — 	9	-46.748	$\Delta E_{\text{CH}(m)} = -49.781 + 0.337m$
	8	-47.085	
— C — 	—	-4.002	$\Delta E_{\text{C}} = -4.002$

alkane isomers. At the HF/6-31G* level normal alkanes are found to be the most stable in their isomeric species from hexane to octane. However, at the CCD(full)/6-31G*//HF/6-31G* level, species **4**, **8**, **11**, are the most stable among their four isomers. For hexane and its isomers, their relative stability predicted by the estimated CCD energies is in accord with that from exact CCD calculations. For seven-carbon alkanes, the relative stability of the first three species **5**–**7** is correctly predicted by the empirical formula Eq. (15). Nevertheless, the most stable isomer predicted by Eq. (15) is normal heptane, but exact CCD calculations show that **8** (2,2,3-trimethyl-butane) has the lowest energy in the four isomers. Similarly, the most stable species among octane and its isomers could not be predicted by the estimated CCD energies. There-

fore, we note that for highly branched alkanes the empirical formula Eq. (15) with the parameters listed in Table 2 is not sufficiently accurate. For example, for the studied most branched alkane, 2,2,3,3-tetramethyl-butane, the predicted correlation energy only accounts for 98.98% of exact CCD correlation energy, a percentage significantly less than those obtained for other eight-carbon isomers. The reason behind the failure of our simple prediction may be ascribed to the fact that selected sample alkanes for deriving the gross group (or orbital) correlation energies for alkyl groups (or C—C bonds) are linear or less branched, and are limited with no more than five carbons. Thus, to improve the accuracy of our simple approach, larger sets of sample alkanes are required, and it will be considered in our future work.

Table 3 A comparison of predicted and calculated CCD correlation energies for several alkanes at the CCD(full)/6-31G*//HF/6-31G* level

Species	Structure	$E(\text{HF})(\text{a.u.})$	Correlation energy (a.u.)		$E(\text{CCD-full})(\text{a.u.})$	
			Calculated	Predicted ^b	Calculated	Predicted
1		0.000000	0.890304	0.889755 (99.94%)	-0.890304	-0.889755
2		0.003488	0.893137	0.890425 (99.70%)	-0.889649	-0.886937
3		0.004730	0.895140	0.891543 (99.60%)	-0.890410	-0.886813
4		0.003187	0.896247	0.893074 (99.65%)	-0.893060	-0.889887
5		0.000000	1.036569	1.035307 (99.88%)	-1.036569	-1.035307
6		0.008866	1.040529	1.035458 (99.51%)	-1.031663	-1.026592
7		0.007781	1.043907	1.037546 (99.39%)	-1.036126	-1.029765
8		0.008880	1.045740	1.038593 (99.32%)	-1.036860	-1.029713
9		0.000000	1.182834	1.180859 (99.83%)	-1.182834	-1.180859
10		0.008406	1.188909	1.182128 (99.43%)	-1.180503	-1.173722
11		0.008653	1.191873	1.185367 (99.45%)	-1.183220	-1.176714
12		0.016043	1.197217	1.184969 (98.98%)	-1.181174	-1.168926

^a The energies are differences with respect to the RHF energies of corresponding normal alkanes. ^b Percentage relative to the calculated CCD energy given in parentheses.

Conclusions

Within the localized molecular orbital description, the intra- and interorbital pair correlation energies calculated with the CCD theory have been obtained for methane, ethane, propane, butane, pentane and their isomers using the 6-31G* basis set. The results have shown the rapid decrease of interorbital pair correlation energies with the orbital separation, and the quantitative transferability of pair correlation energies and gross orbital correlation energies within these molecules, which provide the theoretical grounds for a simple estimate of the total correlation energy for larger alkanes. Based on the gross group correlation energies for alkyl groups and gross orbital correlation energies for C—C bonds derived (or extrapolated) from five sample alkanes (butane, isobutane, pentane, isopentane, and neopentane), we have derived a simple linear relationship to evaluate the approximate CCD correlation energy for an arbitrary large alkane. The correlation energy predicted by this linear relationship remarkably recovers more than 98.9% of the exact CCD correlation energy in the 6-31G* basis set for a number of alkanes containing six to eight carbon atoms. Our results show that for alkanes not highly branched this simple approach with the parameters presented in this work is able to give correct predictions on the relative stability among isomeric species.

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