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## LETTERS

**Correlated Capped Subsystem Method for the Calculation of Substituent Effects on Bond Energies**

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The correlated capped small system strategy has been demonstrated to be a valuable method for the calculation of bond energies and substituent effects on bond energies. By using the integrated molecular orbital–molecular orbital formulation, this strategy provides a means for introducing electron correlation effects in cases where a correlated calculation on the entire system is not affordable, but both electron correlation on a part of the system and substituent effects from another part are required for obtaining accurate results. To apply this dual-level strategy to very large systems, one may consider various lower levels for which the calculation on the whole system is affordable. In the present work, we examine the behavior of several such lower levels, in particular semiempirical molecular orbital methods based on neglect of diatomic differential overlap, *ab initio* Hartree–Fock calculations with small basis sets, and density functional theory. The methods are tested for calculating C–H bond energies and substituent effects in a series of substituted ethanes with the general formula  $\text{CH}_3\text{CH}_2\text{X}$ . The entire systems considered here are ethane ( $\text{X} = \text{H}$ ), propane ( $\text{X} = \text{CH}_3$ ), ethanol ( $\text{X} = \text{OH}$ ), ethylamine ( $\text{X} = \text{NH}_2$ ), and fluoroethane ( $\text{X} = \text{F}$ ). For 11 of the 13 dual-level methods that we tested, bond energies are more accurate in the dual-level calculation than in either single-level calculation (high level on capped small system or low level on entire system); thus, integrating the levels is found to be a successful strategy. Substituent effects are also more accurate with the dual-level strategy.

**Introduction**

High-level quantum chemical methods have been so successful at predicting the structures, energetics, and reactivity of small systems<sup>1–3</sup> that there is considerable interest in extending such methods to large systems. This in turn raises issues of computational efficiency. It is clear that any parts of a large system involved in bond breaking or bond making should be treated at a high level, and there is great interest in discovering the best way to combine high-level calculations on a subsystem with a lower-level treatment of the rest of the system.

Considerable effort has been expended on combining low-level molecular orbital theory for a subsystem with molecular mechanics for the rest of a large system,<sup>4</sup> but our interest is focused on high-level correlated methods<sup>2,3</sup> for a subsystem.

The use of localized orbitals for correlated calculations is certainly one promising route;<sup>5</sup> with such methods the noncorrelated part of the large system is treated at the *ab initio* Hartree–Fock level,<sup>6</sup> which is more expensive than molecular mechanics, but which has the advantage that it can treat electronic substituent effects (inductive effects) much more reliably. Two alternatives to *ab initio* Hartree–Fock theory for treating electronic substituent effects of a large subsystem on a smaller one are semiempirical molecular orbital theory<sup>7</sup> and density functional theory,<sup>8</sup> and in the present paper we wish to explore these alternatives and compare them to *ab initio* Hartree–Fock calculations with the kind of basis sets that might be employed for very large systems.

A method that appears very promising to us for dual-level calculations based on the highest levels of correlated theory is the use of correlated capped small systems<sup>9,10</sup> (CCSS), which is a special case of the integrated molecular orbital–molecular

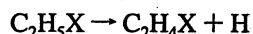
<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1997.

orbital (IMOMO) method of Maseras and Morokuma.<sup>11</sup> In this method one can easily combine high-level *ab initio* correlated calculations for a small subsystem with any other method for treating the other subsystem.<sup>9–12</sup> Both geometry optimizations and energy calculations are possible, and there is no formal difficulty in handling even bond breaking and chemical reactions. The ultimate use one would envision of this method is where the uncorrelated subsystem is fairly large, or at least so large that applying the correlated calculation to the whole system is prohibitively costly. (Actually, for high enough levels to achieve quantitative accuracy, one reaches the large system boundary even for fairly small systems with less than 10 atoms,<sup>13</sup> but one can also envisage this kind of approach being applied not only to systems with sizes on the order of 10 atoms but also to systems with hundreds of atoms or more.<sup>14</sup>) Nevertheless, for testing the method, one is interested in exploring its behavior in well-designed tests for smaller systems. In the present paper we present a series of systematic tests of the ability of CCSS calculations to treat carbon–hydrogen bond dissociation energies and electronic substituent effects on such bond energies.

### Theory

As mentioned in the Introduction, we are focusing here on energies. Thus, although one critical advantage of the CCSS protocol is that it may be used to optimize geometries,<sup>9</sup> in this paper we use standard geometries and concentrate entirely on energies.

Consider the bond-breaking process



where X is an arbitrary substituent. Let  $D_e$  denote the equilibrium bond dissociation energy, by which we mean the change in electronic energy  $E$ , including nuclear repulsion, when the system dissociates from the classical equilibrium structure of  $\text{C}_2\text{H}_5\text{X}$  to the classical equilibrium structure of  $\text{C}_2\text{H}_4\text{X}$ , excluding quantal zero-point energies. In general the bond energy is

$$D_e = E(\text{C}_2\text{H}_4\text{X}) + E(\text{H}) - E(\text{C}_2\text{H}_5\text{X}) \quad (1)$$

We define the substituent effect on the bond energy as

$$\Delta D_e(\text{Y}) = D_e(\text{X}=\text{Y}) - D_e(\text{X}=\text{H}) \quad (2)$$

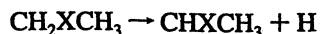
For a CCSS calculation, we define a high level (HL) and a low level (LL). We denote the capped small system (model system) as CSS and the entire system as ES. The final estimate of the energy of the entire system is denoted the integrated energy and is given by<sup>9,10</sup>

$$E(\text{I:HL:LL,ES}) = E(\text{HL,CSS}) - E(\text{LL,CSS}) + E(\text{LL,ES}) \quad (3)$$

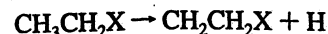
Combining eqs 1 and 2 yields

$$D_e(\text{I:HL:LL,ES}) = D_e(\text{HL,CSS}) - D_e(\text{LL,CSS}) + D_e(\text{LL,ES}) \quad (4)$$

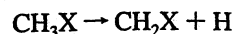
We now specialize to two types of substituent effects,  $\alpha$  and  $\beta$ , given respectively by



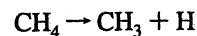
and



and we define the capped small system as



in the  $\alpha$  case and



in the  $\beta$  case. For  $\alpha$  substituent effects the substituent appears in the capped subsystem, and we get

$$\Delta D_e(\text{I:HL:LL,X}) = \Delta D_e(\text{HL,CSS}) - \Delta D_e(\text{LL,CSS}) + \Delta D_e(\text{LL,ES}) \quad (5)$$

For  $\beta$  substituent effects the same formula applies but  $\Delta D_e(\text{HL,CSS})$  is zero. Thus for  $\beta$  effects, the HL calculation affects  $D_e$  but not  $\Delta D_e$ .

In this Letter we examine  $\alpha$  and  $\beta$  substituent effects in four different entire systems: fluoroethane ( $\text{X} = \text{F}$ ), ethanol ( $\text{X} = \text{OH}$ ), ethylamine ( $\text{X} = \text{NH}_2$ ), and propane ( $\text{X} = \text{CH}_3$ ).

### Calculations

As was already pointed out, we are focusing our attention here on the calculation of energies. Thus, all the geometries employed in this work are calculated at the MP2(full)/6-311G(d,p) level, where MP2<sup>15</sup> and the basis set<sup>16</sup> are explained elsewhere. The notation “(full)” means the core is not frozen.

For the present study we take the high level as quadratic configuration interaction with all single and double excitations and perturbative inclusion of connected triple excitations, usually denoted QCISD(T),<sup>17</sup> with the 6-311G(d,p)<sup>16</sup> and cc-pVTZ<sup>18</sup> basis sets. We examine several low levels, drawn from three different classes identified in the Introduction, namely, semiempirical molecular orbital (MO) theory, *ab initio* Hartree–Fock (HF) theory, and density functional theory (DFT). Within the semiempirical MO framework, we limit ourselves to the three most widely employed general parameterizations, namely, the modified neglect of differential overlap (MNDO) method,<sup>19</sup> the Austin model 1 (AM1),<sup>20</sup> and the parametrized model 3 (PM3);<sup>21</sup> these may all be classified as neglect of diatomic differential overlap<sup>22</sup> (NDDO) methods. Within the HF class of models we have used the restricted and unrestricted formalisms<sup>6</sup> for the closed and open-shell systems involved in the calculations, respectively. A set of five different basis sets has been used for the lower level: STO-3G,<sup>23</sup> 3-21G,<sup>24</sup> 3-21G(d),<sup>25</sup> MIDI,<sup>26</sup> and the 6-31G(d).<sup>27</sup> Within the DFT framework we have selected the B3PW91 density functional—which is the Becke three-parameter hybrid method<sup>28</sup> with the 1991 nonlocal correlation expression of Perdew and Wang<sup>29</sup> (PW91, also called PW GGA-II)—with the STO-3G, 3-21G(d), 6-31G(d), 6-31G(d,p),<sup>27</sup> and 6-311G(d,p) basis sets. The selection of the B3PW91 density functional was based on the results of a series of preliminary calculations performed using the STO-3G basis set with six different density functionals: three based on Becke’s 1988 exchange functional<sup>30</sup> combined with various local and nonlocal correlation functionals—the Vosko–Wilk–Nusair V functional,<sup>31</sup> Perdew’s 1981 nonlocal functional,<sup>32</sup> and the Lee–Yang–Parr<sup>33</sup> functional—and three based on Becke’s three-parameter hybrid method combined with the LYP and PW91 correlation functionals and with Perdew’s 1986 local correlation functional.<sup>34</sup> All six density functionals considered give similar results for bond energies and substituent effects, with the B3PW91 choice being slightly better (taking our highest-level calculations as a reference) than the others.

TABLE 1: Bond Energy Using QCISD(T)/cc-pVTZ as the High Level and as the Accurate Value (kcal)

		$\alpha$ substituents					$\beta$ substituents				
		ethane	F	OH	NH <sub>2</sub>	CH <sub>3</sub>	F	OH	NH <sub>2</sub>	CH <sub>3</sub>	average  error
accurate value		108.1	105.6	101.1	96.6	105.5	110.0	110.7	106.4	108.3	
HL/model system		111.3	107.2	102.1	97.3	108.1	111.3	111.3	111.3	111.3	2.1
LL/entire system											
NDDO	MNDO	82.2	75.5	73.2	72.7	76.6	84.4	83.3	81.4	82.2	26.8
	AM1	84.8	79.2	79.4	69.8	81.1	88.4	88.8	84.4	85.4	23.4
	PM3	85.2	79.3	75.0	70.6	79.2	89.2	88.3	84.3	85.7	23.9
HF	HF/STO-3G	111.4	102.2	101.7	100.4	107.5	111.7	112.5	108.9	111.5	2.5
	HF/3-21G	84.3	82.2	79.4	74.4	82.2	86.5	86.4	82.8	84.5	23.3
	HF/3-21G(d)	85.2	81.3	78.6	75.3	82.7	87.6	87.7	82.8	85.3	22.9
	HF/MIDI!	81.6	78.6	75.8	72.7	79.2	83.7	83.9	79.7	81.9	26.1
	HF/6-31G*	83.9	82.1	78.6	74.6	81.2	85.6	85.8	81.8	83.9	23.9
DFT	B3PW91/STO-3G	136.6	119.5	118.5	117.6	131.4	135.8	137.6	134.0	136.7	23.9
	B3PW91/3-21G(d)	108.8	101.1	97.4	93.6	104.9	111.5	112.1	106.5	111.5	2.1
	B3PW91/6-31G*	107.1	102.3	98.1	93.3	103.0	109.1	109.6	105.1	109.1	1.9
	B3PW91/6-31G**	107.6	103.0	98.6	93.9	103.5	109.7	110.3	105.7	109.7	1.5
	B3PW91/6-311G**	105.9	102.4	97.3	92.4	102.0	108.0	108.7	104.3	108.0	2.6
dual-level/CCSS method											
NDDO	MNDO	105.2	102.5	97.4	92.3	102.6	107.4	106.3	104.5	105.2	3.2
	AM1	106.0	104.4	99.6	94.0	104.5	110.0	110.0	105.6	106.7	1.3
	PM3	103.3	101.6	97.1	91.8	102.2	107.3	106.5	102.4	103.9	4.0
HF	HF/STO-3G	107.6	104.1	99.0	94.0	102.4	107.9	108.6	105.1	107.6	1.8
	HF/3-21G	108.9	105.6	100.8	97.0	106.1	111.2	111.1	107.5	109.1	0.6
	HF/3-21G(d)	108.8	105.4	100.5	96.1	105.6	111.2	111.3	106.4	108.9	0.5
	HF/MIDI!	108.5	105.5	100.6	96.4	105.7	110.5	110.8	106.6	108.8	0.3
	HF/6-31G*	108.6	105.2	100.3	95.9	105.4	110.3	110.5	106.6	108.6	0.4
DFT	B3PW91/STO-3G	105.9	103.6	98.5	93.6	103.0	105.2	107.0	103.4	106.1	2.9
	B3PW91/3-21G(d)	106.8	104.8	100.0	95.6	104.3	109.6	110.2	104.5	107.1	1.0
	B3PW91/6-31G*	106.7	104.4	99.6	95.3	104.0	108.6	109.2	104.7	106.7	1.5
	B3PW91/6-31G**	106.6	104.5	99.7	95.4	104.0	108.7	109.2	104.7	106.7	1.4
	B3PW91/6-311G**	106.7	104.8	100.2	92.8	104.2	108.8	109.5	105.1	106.8	1.5

TABLE 2: Substituent Effects on Ethane Using QCISD(T)/cc-pVTZ as the High Level and as the Accurate Value (kcal)

		$\alpha$ substituents				$\beta$ substituents				average  error
		F	OH	NH <sub>2</sub>	CH <sub>3</sub>	F	OH	NH <sub>2</sub>	CH <sub>3</sub>	
accurate value		-2.5	-7.0	-11.5	-2.6	1.9	2.6	-1.7	0.1	
HL/model system		-4.1	-9.1	-14.0	-3.2	0.0	0.0	0.0	0.0	1.6
LL/entire system										
NDDO	MNDO	-6.6	-8.9	-9.5	-5.6	2.3	1.1	-0.7	0.0	1.8
	AM1	-5.5	-5.3	-15.0	-3.6	4.0	4.0	-0.4	0.7	1.8
	PM3	-5.9	-10.2	-14.6	-6.0	4.0	3.2	-0.9	0.6	2.1
HF	HF/STO-3G	-9.2	-9.7	-11.0	-3.9	0.3	1.1	-2.5	0.1	1.9
	HF/3-21G	-2.1	-4.9	-9.8	-2.0	2.3	2.2	-1.5	0.2	0.7
	HF/3-21G(d)	-3.9	-6.6	-9.8	-2.5	2.4	2.5	-2.4	0.1	0.6
	HF/MIDI!	-3.1	-5.8	-9.0	-2.4	2.0	2.3	-1.9	0.3	0.7
	HF/6-31G*	-1.8	-5.3	-9.3	-2.7	1.7	1.9	-2.1	0.0	0.8
DFT	B3PW91/STO-3G	-17.0	-18.0	-19.0	-5.1	-0.7	1.1	-2.5	0.2	5.1
	B3PW91/3-21G(d)	-7.7	-11.4	-15.2	-3.9	2.7	3.4	-2.3	2.7	2.4
	B3PW91/6-31G*	-4.8	-9.0	-13.8	-4.1	2.0	2.5	-2.0	2.0	1.3
	B3PW91/6-31G**	-4.7	-9.1	-13.8	-4.1	2.1	2.6	-1.9	2.1	1.3
	B3PW91/6-311G**	-3.5	-8.6	-13.5	-3.9	2.1	2.8	-1.6	2.1	1.1
dual-level/CCSS method										
NDDO	MNDO	-2.6	-7.8	-12.9	-2.6	2.3	1.1	-0.7	0.0	0.7
	AM1	-1.7	-6.4	-12.0	-1.5	4.0	4.0	-0.4	0.7	1.1
	PM3	-1.7	-6.2	-11.5	-1.2	4.0	3.2	-0.9	0.6	0.9
HF	HF/STO-3G	-3.5	-8.6	-13.6	-5.2	0.3	1.1	-2.5	0.1	1.4
	HF/3-21G	-3.3	-8.1	-11.9	-2.8	2.3	2.2	-1.5	0.2	0.5
	HF/3-21G(d)	-3.4	-8.3	-12.8	-3.2	2.4	2.5	-2.5	0.1	0.7
	HF/MIDI!	-3.0	-7.9	-12.1	-2.8	2.0	2.3	-1.9	0.3	0.4
	HF/6-31G*	-3.5	-8.4	-12.8	-3.2	1.7	1.9	-2.1	0.0	0.7
DFT	B3PW91/STO-3G	-2.3	-7.5	-12.4	-2.9	-0.7	1.1	-2.5	0.2	0.9
	B3PW91/3-21G(d)	-2.0	-6.9	-11.2	-2.6	2.8	3.4	-2.3	0.2	0.4
	B3PW91/6-31G*	-2.2	7.1	-11.4	-2.6	2.0	2.5	-2.0	0.1	0.1
	B3PW91/6-31G**	-2.1	-6.9	-11.2	-2.6	2.1	2.6	-1.9	0.1	0.2
	B3PW91/6-311G**	-2.0	-6.6	-13.9	-2.5	2.1	2.8	-1.6	0.1	0.5

In order to test the methods, we carried out QCISD(T)/cc-pVTZ calculations not only on the capped small system but also on the entire systems.

All calculations were carried out using the GAUSSIAN94 computer package.<sup>35</sup>

## Results

The results are given in Tables 1–3. In all cases we take the QCISD(T)/cc-pVTZ calculation as “accurate” for reference purposes. This does not imply that the error is zero in that calculation. Rather it allows us to answer the question: can

**TABLE 3: Mean Unsigned Errors (kcal) in CCSS Substituent Effects for Classes of Methods As Calculated from Table 2**

type of lower level	$\alpha$ effects	$\beta$ effects
NDDO methods	0.7	1.0
minimum basis set HF or DFT methods	1.2	1.1
extended basis set HF methods	0.8	0.3
extended basis set DFT methods	0.4	0.2

we obtain the high accuracy of the QCISD(T)/cc-pVTZ calculation from simpler CCSS calculations in which correlated calculations are limited to a five- to eight-atom capped small system, and only low-level calculations are carried out on the entire system, which in our test cases has three to six more atoms than the capped small system, but which in eventual applications might be considerably larger? Table 1 answers this question for bond energies themselves, and Tables 2 and 3 answer the question for substituent effects.

In each table we give the bond energy or substituent effect in all columns but the last, and the last column gives the mean unsigned error across the eight test cases. The first row of each table in the accurate reference value used for assessing the error. The next row gives the result we would obtain if we only performed the high-level calculation on the capped small system, which is called the "model system" in the tables. The next 13 rows give the results we would obtain if we performed only the low-level calculation on the entire system. The final 13 rows give the results obtained by the dual-level methods.

### Discussion

The ultimate test of theory is comparison with experiment, but in the present case that would only complicate things for two reasons. First, one might find cancellation of errors between the ability of the dual-level calculations to reproduce the high-level results (which is probably the best we can expect in

general) and the ability of the high-level results to predict experiment. Second, one typically finds that uniformly accurate experimental values are not available for a systematic series of substituents effects. Thus our test of the dual-level methods is based entirely on their ability to reproduce the high-level calculations on the entire system.

In order for the dual-level approach to be considered successful, we require that it leads to smaller errors than either of the two single-level approaches (high level on capped small system and low level on entire system). That is, the extra effort of performing both kinds of single-level calculations and combining them as in eqs 3, 4, or 5 is warranted only if the resulting combination yields smaller errors than the individual terms. Thus, for example, the I:QCISD(T)/cc-pVTZ:AM1 result in Table 1 is considered a success only if its average error (1.5 kcal) is smaller than the average errors obtained by both the AM1 (entire system) calculations and the QCISD(T)/cc-pVTZ (model system) calculations. Since the latter values are 23.5 kcal and 2.5 kcal, respectively, the dual-level method passes the test and is considered successful. Applying this test to the other 12 methods in Table 1 shows that the dual-level strategy is successful for 11 of the 13 low levels tested. The most successful combination of all is the I:QCISD(T)/cc-pVTZ:HF/MIDI! method. In general, for any of the three basis sets for which we can directly compare HF and DFT calculations, the integrated calculations are more accurate when HF is employed as the low level (errors of 2.0 kcal vs 3.0, 0.6 vs 1.1, and 0.5 vs 1.5), although if the high-level calculation is omitted, DFT is considerably more accurate in two cases out of three (errors of 2.6 vs 22.9 and 2.2 vs 23.9 kcal). This provides a dramatic illustration of a maxim well-known in the fashion industry and home decorating, which apparently also applies to dual-level CCSS methods: it is not sufficient to mix components indiscriminately, one must "mix and match."

**TABLE 4: Substituent Effects on Ethane Using QCISD(T)/6-311G(d,p) as the High Level and QCISD(T)/cc-pVTZ as the Accurate Value**

		$\alpha$ substituents				$\beta$ substituents				average  error
		F	OH	NH <sub>2</sub>	CH <sub>3</sub>	F	OH	NH <sub>2</sub>	CH <sub>3</sub>	
accurate value		-2.5	-7.0	-11.5	-2.6	1.9	2.6	-1.7	0.1	
HL/model system		-3.3	-8.5	-14.2	-2.7	0.0	0.0	0.0	0.0	1.4
LL/entire system										
NDDO	MNDO	-6.6	-8.9	-9.5	-5.6	2.3	1.1	-0.7	0.0	1.8
	AM1	-5.5	-5.3	-15.0	-3.6	4.0	4.0	-0.4	0.7	1.8
	PM3	-5.9	-10.2	-14.6	-6.0	4.0	3.2	-0.9	0.6	2.1
	HF/STO-3G	-9.2	-9.7	-11.0	-3.9	0.3	1.1	-2.5	0.1	1.9
HF	HF/3-21G	-2.1	-4.9	-9.8	-2.0	2.3	2.2	-1.5	0.2	0.7
	HF/3-21G(d)	-3.9	-6.6	-9.8	-2.5	2.4	2.5	-2.4	0.1	0.6
	HF/MIDI!	-3.1	-5.8	-9.0	-2.4	2.0	2.3	-1.9	0.3	0.7
	HF/6-31G*	-1.8	-5.3	-9.3	-2.7	1.7	1.9	-2.1	0.0	0.8
DFT	B3PW91/STO-3G	-17.0	-18.0	-19.0	-5.1	-0.7	1.1	-2.5	0.2	5.1
	B3PW91/3-21G(d)	-7.7	-11.4	-15.2	-3.9	2.7	3.4	-2.3	2.7	2.4
	B3PW91/6-31G*	-4.8	-9.0	-13.8	-4.1	2.0	2.5	-2.0	2.0	1.3
	B3PW91/6-31G**	-4.7	-9.1	-13.8	-4.1	2.1	2.6	-1.9	2.1	1.3
	B3PW91/6-311G**	-3.5	-8.6	-13.5	-3.9	2.1	2.8	-1.6	2.1	1.1
dual-level/CCSS method										
NDDO	MNDO	-1.9	-7.1	-12.8	-2.2	2.3	1.1	-0.7	0.0	0.7
	AM1	-0.9	-5.7	-11.7	-0.7	4.0	4.0	-0.4	0.7	1.3
	PM3	-0.9	-5.5	-11.2	-0.7	4.0	3.2	-0.9	0.6	1.2
	HF/STO-3G	-2.7	-7.0	-13.6	-2.9	0.3	1.1	-2.5	0.0	1.0
HF	HF/3-21G	-2.5	-7.4	-11.9	-2.4	2.3	2.2	-1.4	0.2	0.3
	HF/3-21G(d)	-2.6	-7.6	-12.8	-2.7	2.4	2.5	-2.5	0.1	0.4
	HF/MIDI!	-2.2	-7.2	-12.2	-2.3	2.0	2.3	-1.9	0.3	0.3
	HF/6-31G*	-2.7	-7.7	-12.8	-2.8	1.7	1.9	-2.1	0.0	0.5
DFT	B3PW91/STO-3G	-1.5	-6.8	-12.4	-2.5	-0.7	1.1	-2.5	0.2	0.9
	B3PW91/3-21G(d)	-1.2	-6.2	-11.3	-2.1	2.7	3.4	-2.3	0.2	0.6
	B3PW91/6-31G*	-1.4	-6.4	-11.4	-2.2	2.0	2.5	-2.0	0.0	0.4
	B3PW91/6-31G**	-1.3	-6.2	-11.3	-2.2	2.1	2.6	-1.9	0.0	0.4
	B3PW91/6-311G**	-1.2	-5.9	-10.9	-2.1	2.1	2.8	-1.6	0.0	0.5

In Table 2 we tested the dual-level strategy for substituent effects. Substituent effects are expected to be more accurate than bond energies themselves when a portion of the error in the bond energies is systematic and cancels out. Comparing Table 2 to Table 1 shows that this cancellation usually (but not always) occurs for the low-level calculations on the entire system and does not occur for the problems addressed here for high-level calculations on the capped small systems. For the dual-level calculations, the substituent effects are more accurate than the bond energies for all three semiempirical MO methods, for the small-basis *ab initio* Hartree–Fock methods, and for the DFT methods with all basis sets studied, but not for the *ab initio* Hartree–Fock calculations with polarized basis sets. The really dramatic results are the dual-level calculations based on DFT lower levels; the average errors in substituent effects in these CCSS calculations are 0.2–0.9 kcal for all but the smallest basis set.

Twelve of the dual-level methods tested in Table 2 yield better accuracy for substituent effects than either of their component single-level methods. In eight of the cases the dual-level method decreases the mean error in the substituent effects by a factor of 2 or more compared to the single-level calculation on the entire system.

The mean unsigned errors in the CCSS substituent effects are compared for four classes of methods in Table 3. When NDDO and minimum basis set methods are used for the lower level, the average error is about the same for  $\alpha$  and  $\beta$  substituent effects, whereas when extended basis sets (double  $\zeta$  or better) are used for the lower level, the average error is only about half as large for  $\beta$  effects as for  $\alpha$  effects.

Table 4 shows that the smallness of the CCSS errors found in this paper are not solely a consequence of using the same method for accurate calculations as a reference and for the high level on the capped small system. The errors in Table 4, which uses a less accurate high level for the capped small system than was used for Table 2, are qualitatively and quantitatively similar to those in Table 2.

## Conclusions

The dual-level strategy is successful for both bond energies and substituent effects.

Depending on the size of the system, several dual-level combinations are found to provide economically attractive ways to correlate a portion of a large system and treat the entire system quantum mechanically with good accuracy both for absolute bond energies in the correlated subsystem and also for electronic substituent effects from the rest of the system. For medium-sized systems, the B3PW91/3-21G(d) method may be recommended as a lower level, for large systems the HF/3-21G and HF/MIDI! methods can be recommended as a lower level, and for very large systems, the MNDO and AM1 methods can be recommended.

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**Supporting Information Available:** Table of QCISD(T)/6-311G(d,p)/MP2/6-311G(d,p) and QCISD(T)/cc-pVTZ/MP2/6-311G(d,p) absolute bond energies in hartrees. (1 page). Ordering information is given on any current masthead page.

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