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Simple Approximation of Core-Correlation Effects on Binding Energies

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We present a method for estimating the core-correlation contribution to the binding energy of molecules without electronic structure calculations. The method is parametrized for molecules containing H, Li, Be, B, C, N, O, F, Al, Si, P, S, and Cl. This method can be used for the prediction and estimation and thermochemical properties of large molecules.

1. Introduction

The majority of the ab initio electronic structure calculations that are performed today include the correlation energy of only the valence electrons. This is sometimes called the frozen-core (FC) approximation. Even when correlated calculations are carried out without the FC approximation, one cannot make a realistic estimate of core correlation energy unless one adds extra basis functions in the core region, and standard basis sets[1] do not include these. The idea that only the valence electrons contribute to binding has a long and venerable history, dating to the early days of quantum chemistry, and it is essentially correct, rightfully constituting one of the key elements for understanding why the periodic table explains so much of chemistry.[2] However recent years have seen great progress in the calculation of molecular binding energies,[3] and in some cases errors due to neglecting the contribution of core correlation energy may exceed all other errors combined. In fact, over the past few years a number of researchers[4−17] have shown that the change in correlation energy of core electrons must be accounted for quantitatively to predict accurate molecular structures or energetics. Accounting for the correlation energy of core electrons by explicitly including them in correlated electronic structure calculations increases the computational cost by a very significant amount, due both to the need for larger one-electron basis sets and also to the larger number of many-electron configurations that need be considered. This is prohibitively expensive for larger molecules. The purpose of the present paper is to point out that one can formulate a useful approximation to core correlation effects on binding energies by counting the heavy-atom bonds in a molecule.

2. Theory

The core-correlation binding energy, D_{CC}, is defined as minus the difference between the core-correlation energy of a molecule and the core-correlation energy of all its constituent atoms. It is approximated as a sum over all the atoms, α, in a given molecule

$$D_{\mathrm{CC}} = \sum_{\alpha} D_{Z_\alpha} n_\alpha \tag{1}$$

where D_{Z_α} is the average core-correlation binding energy per bond contributed by a given atom α with atomic number Z_α, and n_α is the number of bonds that the atom α makes with other atoms in the molecule. We do not count the number of bonds that each hydrogen makes because there is no core energy for hydrogen (i.e., $D_1 = 0$); however, we do count the number of bonds that a heavy atom makes with hydrogen. Notice that a positive sign on D_{CC} indicates that it *increases* the binding energy (which is the usual case).

3. Calculations and Results

Accurate core-correlation binding energies have been compiled from the literature[4−16] to yield 115 pieces of data for 72 molecules. This data set is summarized in full in Supporting Information. In general it appears that the more recent calculations are more accurate than the less recent ones; therefore, in the cases where more than one core-correlation binding energy was found for a given molecule, with the exception of CN, the most recent one was used; these are given in Table 1. In the case of CN, the value of D_{CC} was taken from ref 5 because the calculation is better than the one given in ref 14.

For each of the 72 molecules, the number, n_α, of bonds were counted for each heavy atom (atoms larger than H) in the molecule. Using linear regression techniques and eq 1, we found a set of D_Z values that best fit the data; these are given in Table 2. The results predicted by eq 1 with these parameters are compared to the accurate values in Table 1. The corresponding mean signed errors (MSEs) and mean unsigned errors (MUEs) in D_{CC} for molecules containing each atom type are also given in Table 2, along with the mean unsigned value of D_{CC} for all molecules containing a given atom type.

4. Discussion

The mean signed error and mean unsigned error over the entire data set of 72 molecules are −0.02 and 0.20 kcal/mol, respectively. Averaging the absolute values of the core-correlation binding energy for the 72 molecules yields a value of 1.21 kcal/mol. Thus the extremely simple eq 1 can be used to reduce the mean unsigned error in a binding energy calculation by a factor of 6 as compared to neglecting core-correlation energy. The final mean unsigned error of 0.20 kcal/mol is comparable to the reliability of the full calculations in the literature. In fact, in 26 cases where refs 4−16 provide two or more ab initio estimates of D_{CC} for a given molecule, the mean unsigned deviation between the largest and smallest values is 0.24 kcal/mol, which means that our fit, on average, is comparable to the quality of the calculations themselves.

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TABLE 1: Accurate and Predicted Core-Correlation Binding Energies (kcal/mol)

molecule	accurate	eq 1	molecule	accurate	eq 1
AlF	0.30[a]	0.19	$CH_2(^1A_1)$	0.45[e]	0.65
AlH	−0.18[a]	−0.07	$CH_2(^3B_1)$	0.79[b]	0.65
B_2	1.10[b]	0.84	*cyclo*-$CH_2CH_2C(^1A_1)$	3.38[e]	3.26
BF	0.70[c]	0.67	*cyclo*-$CH_2CH_2C(^3B_1)$	3.39[e]	3.26
BF_3	1.92[c]	2.01	CH_3	1.04[b]	0.98
BH	0.16[d]	0.42	CH_3OH	2.05[e]	1.55
BH_2	0.79[d]	0.84	CH_4	1.25[b]	1.30
BH_3	1.05[d]	1.26	*cyclo*-$CHCHCH_2$	3.80[e]	3.91
BeH	0.50[d]	0.45	Cl_2	0.48[a]	0.48
BeH_2	0.89[d]	0.90	CN	1.18[g]	1.40
C_2	1.50[b]	1.30	CO	0.96[f]	1.35
C_2H	2.05[e]	2.28	CO_2	1.78[f]	1.81
C_2H_2	2.44[f]	2.60	CS	0.73[a]	0.90
C_2H_3	2.21[e]	2.28	F_2	−0.07[c]	0.50
C_2H_4	2.36[f]	2.60	FCCH	2.43[h]	2.85
C_2H_5	2.42[e]	2.28	FH	0.18[b]	0.25
C_2H_6	2.61[e]	2.60	FLi	1.13[e]	0.58
cyclo-$C_3H_2(^1A_1)$	3.24[e]	2.60	H_2CO	1.32[f]	1.55
cyclo-$C_3H_2(^3B_1)$	3.18[e]	3.26	H_2O	0.38[b]	0.25
cyclo-C_3H_3	3.60[e]	3.58	H_2O_2	1.27[e]	0.76
cyclo-C_3H_5	3.87[e]	3.58	H_2SiO	0.09[i]	0.09
cyclo-C_3H_6	4.07[e]	3.91	HCl	0.15[a]	0.24
CCH_2	1.86[e]	1.95	HCN	1.67[f]	1.73
CH	0.14[b]	0.33	HCO	1.46[e]	1.23
HLi	0.32[b]	0.33	P_2	0.60[a]	0.60
HNO	0.48[f]	0.68	PN	0.71[a]	0.73
Li_2	0.43[e]	0.65	SiF	0.57[k]	0.21
N_2	0.85[f]	0.85	SiF^+	0.67[k]	0.21
N_2H_4	1.68[e]	0.71	SiH	−0.04[l]	−0.04
N_2O	1.26[f]	0.68	$SiH_2(^1A_1)$	−0.11[i]	−0.08
NH	0.11[b]	0.14	$SiH_2(^3B_1)$	−0.56[i]	−0.08
NH_2	0.31[b]	0.28	SiH_3	−0.22[l]	−0.12
NH_3	0.66[b]	0.43	SiH_4	−0.31[l]	−0.16
NO	0.42[j]	0.80	SiO	0.72[i]	0.26
O_2	0.30[c]	0.50	SO	0.77[m]	0.20
OH	0.14[b]	0.13	SO_2	0.40[m]	0.40

[a] Ref 9. [b] Ref 10. [c] Ref 12. [d] Ref 5. [e] Ref 14. [f] Ref 11. [g] Ref 15. [h] Ref 6. [i] Ref 7. [j] Ref 13. [k] Ref 4. [l] Ref 13. [m] Ref 8.

TABLE 2: Parameters (kcal/mol), Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Number of Data Points for Each Atom

atom type	Z	D_Z	no. data[a]	MSE[b]	MUE[b]	MSV[c]	MUV[c]
H	1	0.000	47	−0.01	0.17	1.35	1.41
Li	3	0.327	3	−0.11	0.26	0.63	0.63
Be	4	0.448	2	−0.02	0.03	0.70	0.70
B	5	0.419	6	0.05	0.15	0.95	0.95
C	6	0.326	30	0.01	0.19	2.11	2.11
N	7	0.142	11	−0.08	0.25	0.85	0.85
O	8	0.126	16	−0.10	0.28	0.86	0.86
F	9	0.250	9	−0.04	0.30	0.87	0.89
Al	13	−0.065	2	0.00	0.12	0.06	0.24
Si	14	−0.040	9	−0.06	0.23	0.09	0.37
P	15	0.100	2	0.01	0.01	0.66	0.66
S	16	−0.026	3	−0.13	0.25	0.63	0.63
Cl	17	0.240	2	0.05	0.05	0.32	0.32
entire data set			72	−0.02	0.20	1.17	1.21

[a] Number of molecules containing this atom type. [b] Mean errors (kcal/mol) for molecules containing this atom type. [c] Mean signed and unsigned value of D_{CC} (kcal/mol) for all molecules containing this atom type.

Caution should be taken when using the values of D_Z for atoms where only 2 or 3 data points were used for the fit, but results for B, C, N, O, F, and Si are all based on six or more data and should be reasonably robust. If we consider only molecules composed of H, B, C, N, O, F, and Si, there are 58 molecules with a mean unsigned value of 1.37 kcal/mol for D_{CC}. For these 58 molecules, eq 1 fits the data with a mean unsigned error of 0.21 kcal/mol, based on six parameters for 58 data. (The mean unsigned error would of course be even less if we had adjusted the six parameters to fit only that data.)

Another way to look at the performance of the present method is to calculate the error per bond. The 72 molecules examined here have a total of 230 bonds. Therefore the mean unsigned error per bond is only 0.06 kcal/mol. It will be very hard to do better.

The present paper has been concerned with core-correlation contributions at the equilibrium internuclear geometry. This is the relevant quantity for the calculation of heats of formation, but for modeling potential energy surfaces one needs to know the dependencies on geometry. It seems reasonable to assume that the dependence of D_{CC} on internuclear distances would be well modeled by exponential functions, at least at short distances, but so far there is little data on this. At large internuclear distances, the correlation energy contributions to core−core interaction energy may be treated by standard theories for dispersion forces, but core−valence interactions[18] are more complicated.

5. Conclusion

We have presented a simple formula that can be used to estimate core-correlation binding energies quite accurately, and we have used it to fit atomic parameters for B, C, N, O, F, Si, and six other atoms. We believe that the parameters reported here can be useful for a wide variety of thermochemical applications.

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Supporting Information Available: Tables of core-correlation binding energies (kcal/mol) and the number of bonds to heavy atoms of each type for each molecule. This material is available free of charge via the Internet at http://pubs.acs.org.

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