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A Class IV Charge Model for Boron Based on Hybrid Density Functional Theory

Joseph M. Brom,[†] Brian J. Schmitz, Jason D. Thompson, Christopher J. Cramer,* and Donald G. Truhlar*

Department of Chemistry and Supercomputer Institute, 207 Pleasant Street SE, University of Minnesota, Minneapolis, Minnesota 55455-0431

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We present a class IV charge model, in particular charge model 3 (CM3), for molecules containing boron. The model is designed to be able to obtain particularly useful partial atomic charges by mapping (class II) partial atomic charges obtained by Löwdin population analysis into improved (class IV) charges that reproduce accurate charge-dependent observables. To train the model, we mainly use dipole moments as the observables, and we have developed a training set of 43 accurate dipole moments and one quadrupole moment for molecules containing B in addition to H, C, N, O, and/or F. In the present paper we report CM3 parameters for use with hybrid density functional theory, in particular with Adamo and Barone's modified Perdew−Wang (mPW) gradient-corrected exchange functional, the PW91 gradient-corrected correlation functional, 25% Hartree−Fock exchange, and the popular 6-31G* basis set. Dipole moments of boron-containing molecules computed from CM3 atomic point charges have root-mean-square errors of only 0.13 D and mean unsigned errors of 0.10 D as compared to experiment or high level of theory.

1. Introduction

Partial atomic charges are used for modeling electrostatic potential fields,[1] intermolecular interaction potentials and heats of formation,[2] and solvation energies[3] and are also used as solute descriptors in quantitative structure−activity relationships.[4] Class IV partial atomic charges[5] are designed to be more accurate than those obtained by population analysis methods of Mulliken[6] and Löwdin[7] or electrostatic fitting.[8] In other words, class IV partial atomic charges reproduce accurate charge-dependent observables such as dipole moments or quadrupole moments. A recently developed class IV charge model called charge model 3 (CM3) is more stable than previous models with respect to unphysical fluctuations in calculated bond orders and is better suited for use with extended basis sets.[9] CM3 has been parametrized against a larger, more diverse training set than previous class IV charge models for H, Li, C, N, O, F, Si, P, S, Cl, and Br, and in the present article we extend the parametrization to boron.

Class IV charges are obtained by a parametrized mapping of charges obtained by a population analysis, and the parameters depend on which method and basis set is used to calculate the wave function that provides the unmapped populations. In the present paper we have chosen Adamo and Barone's[10] modified Perdew−Wang 1-parameter exchange (the parameter is the percentage of Hartree−Fock exchange, which is 25%) and Perdew−Wang-1991 correlation (mPW1PW91) hybrid density functional method with the popular[11] 6-31G* basis set.

Our parametrization will be based primarily on dipole moments. The conventional way to calculate molecular dipole moments is to calculate the expectation value of the dipole operator over the electron density $|\Psi|^2$, where Ψ is an approximate wave function. A dipole moment calculated this way would be called a density dipole moment. Given a set of partial atomic charges, one can also calculate the dipole moment by classical electrostatics. We call this a point-charge dipole moment. A key advantage of class IV partial atomic charges is that, for a given Ψ, the class IV point-charge dipole moment calculated with that Ψ is usually more accurate than the density dipole moment calculated with the same Ψ.

Boron offers a challenge to semiempirical theories because of its wide diversity of bonding configurations. Thus the difficulty in developing useful semiempirical methods for boron is the creation of a diverse and representative test set of data that can be used to train and validate the theory. Section 2 presents a data set of dipole moments for boron in which we attempt to meet this challenge. Section 3 presents the methods used for parametrization. Section 4 gives the results, section 5 presents discussion, and section 6 gives conclusions.

2. Data Set

This section presents a data set of dipole moments for boron-containing compounds that will be used to train and validate the CM3 model for boron. Our goal is that the data set should include boron in a variety of coordination environments, charge states, and hybridization states. To determine the optimal set of charge model parameters, we use a test set of molecules containing boron bonded to H, C, N, O, and/or F. The test set consists of 43 polar molecules as well as the nonpolar boron trifluoride molecule. Chart 1 illustrates all the molecules in the test set and assigns a canonical structure number to each. Each polar molecule in the test set has been assigned an experimental dipole moment or a high-level theoretical dipole moment.

Experimental dipole moments are available for 14 of the molecules in the test set. We used these experimental data in the parametrization, and in addition we used these experimental data to validate a theoretical method for calculating accurate dipole moments of other molecules in the test set, i.e., those

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* Corresponding authors. C.J.C.: phone 612-624-0859, fax 612-626-2006, e-mail cramer@chem.umn.edu. D.G.T.: phone 612-624-7555, fax 612-626-9390, e-mail truhlar@umn.edu.

[†] Permanent address: Department of Chemistry, University of St. Thomas, St. Paul, MN 55105.

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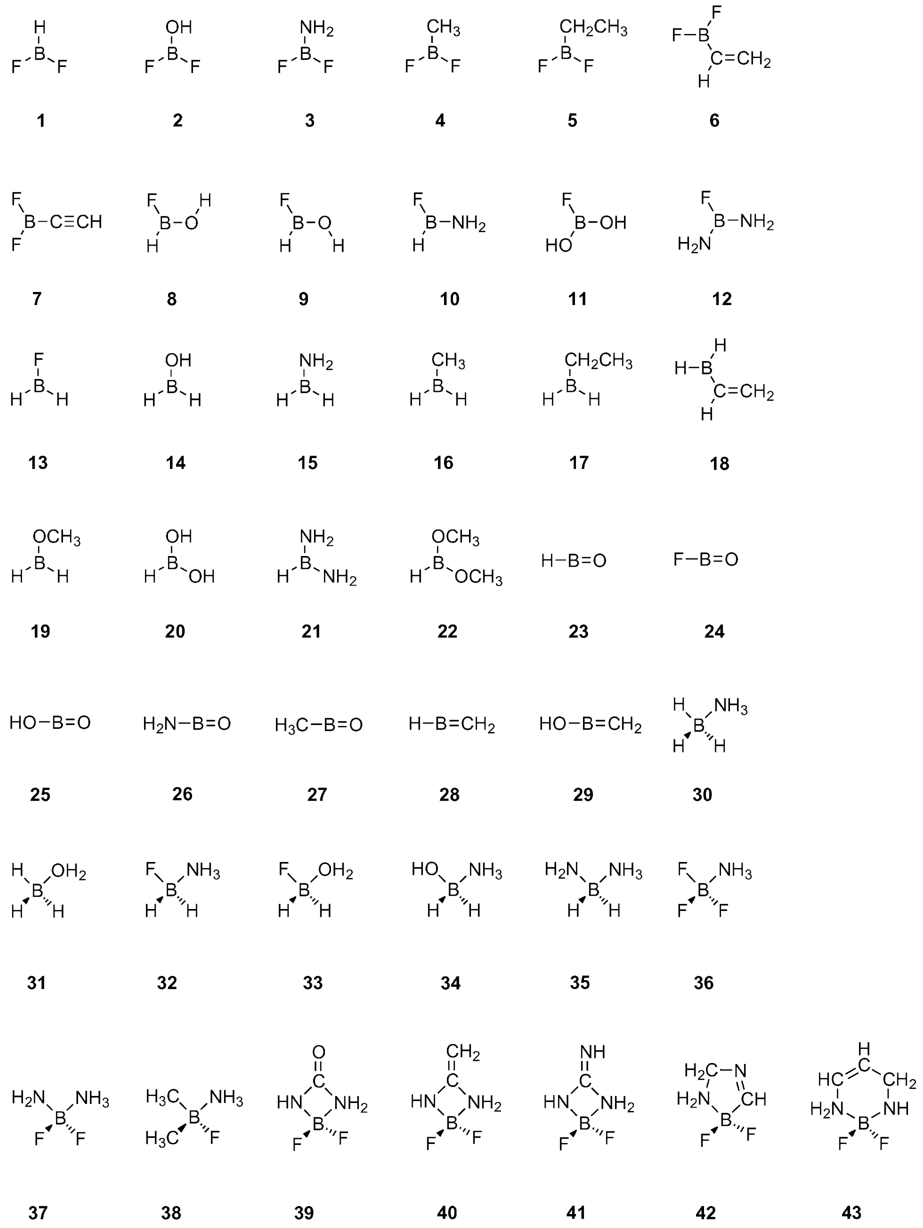
CHART 1: Structures of the Boron-Containing Molecules in the Training Set



molecules without available experimental data. The theoretical method chosen is to calculate density dipole moments using mPW1PW91 hybrid density functional theory with an extended basis set, namely the modified Gaussian-3 semidiffuse basis set (MG3S[12]), which has previously been shown[13] to provide very accurate dipole moments. For the atoms in this study, i.e., H, C, N, O, F, and B, the MG3S basis is identical to the older 6-311+G(2df,2p) basis.[14] As noted in the Introduction, density dipole moments are determined in the usual way, i.e., as expectation values of the dipole operator using the calculated electron density $|\Psi|^2$; we use this term to differentiate this kind of calculated dipole moment from population-analysis dipole moments (calculated by Löwdin[7] population analysis) or from class IV dipole moments (calculated from CM3 partial atomic charges).

For each molecule in the training set we used geometries optimized at the mPW1PW91/MG3S level.

Experimental dipole moments have been obtained from several sources.[15−17] Table 1 compares 14 experimental dipole moments to the theoretical mPW1PW91/MG3S density dipoles. When these experimental dipoles are compared to the high-

TABLE 1: Comparison of Experimental Dipole Moments (Debyes) to Density Dipole Moments Using the mPW1PW91/MG3S Wavefunction

molecule	μ(expt)	μ(density)
BF_2H	0.971	0.929
BF_2OH	1.86	1.995
BF_2NH_2	2.595	2.725
BF_2CH_3	1.668	1.723
$BF_2CH_2CH_3$	1.69	1.751
BF_2CHCH_2	1.74	2.114
BF_2CCH	1.876	1.980
$BF(OH)_2$	1.818	1.896
BH_2OH	1.506	1.561
BH_2NH_2	1.844	1.899
$BH(OH)_2$	1.47	1.541
$BH(NH_2)_2$	1.25	1.330
BF_3NH_3	5.903	6.158
BH_3NH_3	5.216	5.363
MSE[a]		−0.11
MUE[b]		0.12
RMS[c]		0.15

[a] Mean signed error. [b] Mean unsigned error. [c] Root-mean-square error.

TABLE 2: Dipole Moments (Debyes) for Boron-Containing Molecules Comprising the Training Set

molecule	μ	molecule	μ
BF_2H	0.971	HBO	2.808
BF_2OH	1.86	FBO	2.171
BF_2NH_2	2.595	HOBO	3.891
BF_2CH_3	1.668	NH_2BO	4.598
$BF_2CH_2CH_3$	1.69	CH_3BO	3.781
BF_2CHCH_2	1.74	$HBCH_2$	0.611
BF_2CCH	1.876	$HOBCH_2$	2.370
s-cis-BF(H)OH	2.468	BH_3NH_3	5.216
s-trans-BF(H)OH	1.035	BH_3OH_2	4.387
$BF(H)NH_2$	2.405	BH_2FNH_3	5.654
$BF(OH)_2$	1.818	BH_2FOH_2	4.068
$BF(NH_2)_2$	2.343	BH_2OHNH_3	4.893
BH_2F	0.786	$BH_2NH_2NH_3$	3.735
BH_2OH	1.506	BF_3NH_3	5.903
BH_2NH_2	1.844	$BF_2NH_2NH_3$	4.433
BH_2CH_3	0.687	$BF(CH_3)_2NH_3$	5.083
$BH_2CH_2CH_3$	0.784	$F_2BNH_2C(O)NH$	1.629
BH_2CHCH_2	1.322	$F_2BNH_2C(CH_2)NH$	3.480
BH_2OCH_3	1.670	$F_2BNH_2C(NH)NH$	1.972
$BH(OH)_2$	1.47	$F_2BNH_2CH_2NCH$	4.790
$BH(NH_2)_2$	1.25	$F_2BNH_2CHCHCH_2NH$	4.631
$BH(OCH_3)_2$	1.580	BF_3[a]	0.0

[a] In the final fit, this equilibrium geometry value was replaced by the four nonzero values in Table 3. See section 3.

level theoretical dipoles, the mean unsigned deviation is only 0.12 D (note: 1 D = 1 Debye = 10^{-18} esu cm = 3.3356 × 10^{-30} C *m* = 0.39343 atomic unit). This result is acceptably small and validates the use of mPW1PW91/MG3S density dipoles as accurate values for molecules where experimental dipole moments are unavailable.

The complete set of accurate dipole moments used in this work to obtain CM3 parameters for boron is given in Table 2. Experimental dipoles are used when available; otherwise the values in Table 2 are theoretical density dipoles at the mPW1PW91/MG3S level. Experimental dipole moments in Tables 1 and 2 are presented with the precision found in the literature whereas mPW1PW91/MG3S density dipoles are given to three significant digits after the decimal.

3. Parametrization

The CM3 charge model is defined by the following mapping:

$$q_k^{\mathrm{CM3}} = q_k^{\mathrm{PA}} + \sum_{k' \neq k} (D_{Z_k Z_{k'}} B_{kk'} + C_{Z_k Z_{k'}} B_{kk'}^2) \tag{1}$$

where

$$C_{ZZ'} = -C_{Z'Z} \tag{2}$$

and

$$D_{ZZ'} = -D_{Z'Z} \tag{3}$$

and where q_k^{CM3} is the CM3 partial atomic charge on atom k, q_k^{PA} is the value obtained by population analysis, Z_k is the atomic number of atom k, $B_{kk'}$ is the Mayer bond order[18-20] connecting atoms k and k', and $D_{ZZ'}$ and $C_{ZZ'}$ are the parameters to be determined. For q_k^{PA} we use Löwdin populations.[7]

An important aspect of parametrizing the CM3 method is that the number of nonzero $C_{ZZ'}$ parameters is restricted to the smallest number that gives a good fit to the test data set. (The reason for this is to minimize the number of quadratic terms in eq 1 because such terms are more sensitive to unphysical fluctuations in the Mayer bond orders.) Furthermore, given the molecules in the training set, the most critical charge parameters are those between B and F, followed closely by those between B and H. It is essential that the charge model be "physical", and in particular it should follow expectations based on electronegativity differences between the elements. Given these considerations, we determined the optimum parameters by the following strategy.

TABLE 3: Comparison of Density Dipole Moments[a] (Debyes) to CM3 Dipole Moments[b] for Trigonal Pyramidal Distortions of BF_3

FBF angle (deg)	BF bond length (Å)	energy (kcal/mol)	μ(density)	μ(CM3)
120.0	1.308	0.0	0.0	0.0
119.0	1.310	3.3	0.624	0.621
118.0	1.312	6.7	0.886	0.885
117.0	1.314	10.1	1.089	1.093
114.7	1.319	18.4	1.460	1.482

[a] Calculated using the mPW1PW91/MG3S wave function for fixed bond angle and minimized bond length. [b] Calculated using the mPW91PW91/6-31G*//mPW1PW91/MG3S wave function.

We found that a simple minimization of the average error with respect to the parameters was insufficient to satisfy the above considerations in that not only are there a variety of local minima, but some of them, even the one with the smallest error, could be recognized as unphysical. However, we did find a strategy that does appear successful in yielding a physical model. This strategy begins by considering the atomic charge distribution in boron trifluoride. This might seem surprising because the molecular dipole moment of BF_3 is zero by symmetry and therefore any B−F polar bond charge distribution would give the correct molecular dipole moment. However, the molecular quadrupole moment of BF_3 is not zero, and the physically correct B−F charge distribution should be consistent with the nonzero quadrupole moment.

The molecular quadrupole moment θ_{zz} of BF_3 calculated at the mPW1PW91/MG3S level, which is considered to be accurate, is 4.01 B (note: 1 B = 1 Buckingham = 10^{-26} esu cm^2 = 3.3356 × 10^{-40} C m^2 = 0.74347 atomic unit). The best experimental value[21] is $\theta_{zz}(BF_3)$ = 3.37 B estimated from Stark effect measurements of the dipole moments of several van der Waals complexes of BF_3. Considered as an array of atomic partial charges centered on the nuclei, the electrostatic quadrupole moment for BF_3 is

$$\theta_{zz} = \frac{3}{2} q R^2 \tag{4}$$

where $-q$ is the partial atomic charge on each of the three F atoms and R is the B−F bond length. With the B−F bond length (1.308 Å) and quadrupole moment calculated at the mPW1PW91/MG3S geometry, the partial atomic charge at each F was determined as −0.325. This value was used to determine an estimate of 0.249 for the value of the B−F CM3 parameter D_{BF} (with $C_{\mathrm{BF}} = 0$), and we then tested this against calculated dipole moments for nonplanar BF_3 configurations possessing trigonal pyramidal geometries. Table 3 compares density dipole moments, calculated at the mPW1PW91/MG3S level, to CM3 ones, calculated at the mPW1PW91/6-31G* level, for BF_3 with C_{3v} symmetry and with various fixed bond angles. The close agreement between these dipole moments provides confidence in these D_{BF} and C_{BF} parameters, which were then fixed temporarily as constraints on the nonlinear optimization for the remaining boron CM3 parameters.

TABLE 4: CM3 Parameters for B with mPW1PW91/6-31G* Wavefunctions

	$D_{ZZ'}$	$C_{ZZ'}$
H−B	−0.239	0.0
B−C	0.134	0.0
B−N	0.441	−0.163
B−O	0.211	0.0
B−F	0.200	0.0

With D_{BF} and C_{BF} fixed for the moment, we optimized the remaining CM3 parameters to minimize the root-mean-square error in the dipole moments of Table 2. The scalar dipole moment, μ, is calculated from the atomic charges, q_k^{CM3}, by

$$\mu = \sqrt{(\sum_k q_k^{CM3} x_k)^2 + (\sum_k q_k^{CM3} y_k)^2 + (\sum_k q_k^{CM3} z_k)^2} \quad (5)$$

where x_k, y_k, and z_k are the Cartesian coordinates of atom k. Optimization of the parameters is done by the nonlinear adjustment of the $D_{ZZ'}$ and $C_{ZZ'}$ in eq 1. The minimization was carried out by using standard NAG Fortran 90 routines[22] with a variety of initial CM3 parameters for the search. First we optimized the H−B and B−O parameters using 14 molecules from the training set that contained only H−B and B−O bonds in addition to B−F bonds. A good fit was obtained using only D_{HB} and D_{BO} parameters with the C_{HB} and C_{BO} parameters set to zero. With these additional parameters temporarily fixed, we next optimized B−N parameters for 12 molecules in the training set that contained B−N bonds in addition to B−F, B−H, and/or B−O bonds. In this case there was significant improvement in the quality of the fit when a nonzero C_{BN} parameter was included with the D_{BN} parameter. These parameters were also fixed temporarily, and 10 molecules from the training set containing B−C bonds in addition to B−F, B−O, B−H, and/or B−N bonds were used to determine a good estimate to the D_{BC} parameter. The C_{BC} parameter was fixed at zero.

The final fit for CM3 parameters used the estimates obtained above as initial guesses in the fitting routine, and all six nonzero parameters were optimized simultaneously against 47 data. The entire 43 polar molecule training set, as well as the four trigonal pyramidal conformations of BF_3, were used in this final fit.

4. Results

The boron CM3 parameters for mapping the Löwdin charges of the mPW1PW91/6-31G* wave functions for the molecules in the training set are listed in Table 4. The absolute value of all of the parameters is greater than 0.1. This is a reflection of the fact that the dipole moments calculated from Löwdin charges using 6-31G-type basis sets are significantly in error.[9] In fact, the root-mean-square (RMS) error in the Löwdin dipole moments for the 43 polar molecules in the training set is 0.54 D, and the mean unsigned error is 0.42 D. In comparison, the calculated CM3 dipoles show a RMS error of only 0.13 D and a mean unsigned error of only 0.10 D. Simply put, the Löwdin partial atomic charges do not reproduce accurate dipole and quadrupole moments well whereas the CM3 partial atomic charges are accurate in this regard.

As indicated above, the only nonzero $C_{ZZ'}$ parameter that we use is the one for B−N bonds. If only the D_{BN} parameter were used for such bonds, then the RMS error for the dipole moments of the 12 molecules with B−N bonds used to provide close parameter estimates would be increased by a factor of 5 over the fit that included the C_{BN} parameter. The diversity of the training set of molecules seems to demand the quadratic term in the atomic charge model for bonds between boron and nitrogen.

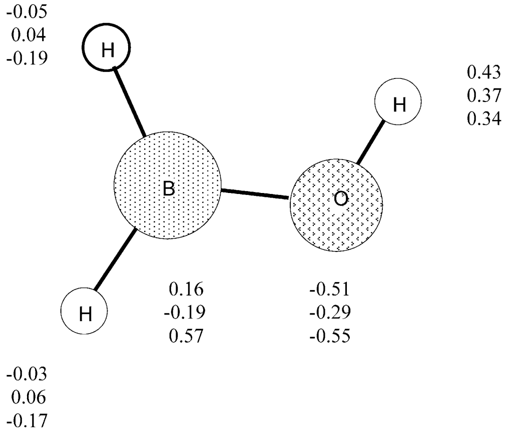


Figure 1. Mulliken (top), Löwdin (middle), and CM3 (bottom) partial atomic charges in borinic acid.

5. Discussion

Because partial atomic charges are not unique, it is interesting to compare different models for obtaining partial atomic charges in molecules containing boron. Boron trifluoride is an important example. At the planar triangular equilibrium geometry of BF_3, the mPW1PW91/6-31G* class IV CM3 charge calculated for B is 0.80 (for F it is −0.27). In contrast, the class II Mulliken charge for B is 0.66 (for F it is −0.22) and the class II Löwdin charge for B is 0.075 (for F it is −0.025). Using the CM3 point charges the calculated molecular quadrupole moment of BF_3 is 3.3 B compared to the previously mentioned high-level theoretical value of 4.0 B. As can be seen, using the Löwdin charges here would seriously underestimate the quadrupole moment. Further comparisons can be made with class III charges calculated for BF_3. Generalized Atomic Polar Tensor (GAPT) charges have recently been published for BF_3 at the MP2/6-311++G(3d,3p) level of theory.[23] The GAPT charge on B is found to be 1.52, considerably higher than the present CM3 charge. Atoms-in-molecules (AIM) charges for BF_3 have also been published recently[24] and the AIM charge on B is 2.43 at the B3LYP/6-311+G(2d,p) level of theory. These large positive charges would seriously overestimate the quadrupole moment of BF_3. Finally, we have also calculated atomic charges obtained by fitting the electrostatic potential of BF_3 according to the charges from electrostatic potentials (ChElPG) scheme[25] and the MP2/MG3S wave function. The ChElPG charge obtained for B is 1.05, about 30% higher than the CM3 charge. The quadrupole moment calculated using the ChElPG charges for BF_3 is 4.3 B and is close to the experimental value. One can see that the high-level ChElPG charge for B agrees better with the CM3 charge than do any of the other models.

Figure 1 gives a comparison of the Mulliken, Löwdin, and CM3 partial atomic charges for each atom in the BH_2OH molecule (borinic acid), and Figure 2 shows the comparison for the $BH(OH)_2$ molecule (boronic acid). The CM3 charges are consistent with expectations based on the Pauling electronegativity scale. The expected increase in the partial charge at B in boronic acid over borinic acid is found although the increase is rather slight. Figure 3 shows the partial atomic charges for each atom in the BF_2OH molecule (difluoroborinic acid). Here, again as expected, there is a significant increase in the partial charge at B over that found in the unsubstituted acid.

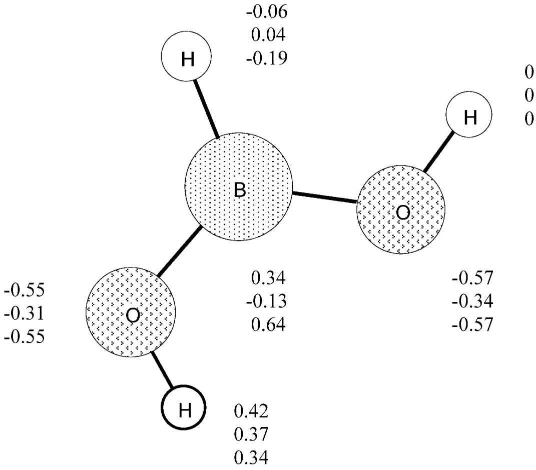


Figure 2. Mulliken (top), Löwdin (middle), and CM3 (bottom) partial atomic charges in boronic acid.

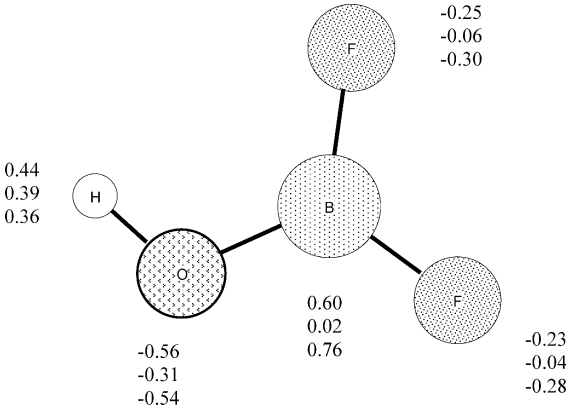


Figure 3. Mulliken (top), Löwdin (middle), and CM3 (bottom) partial atomic charges in difluoroborinic acid.

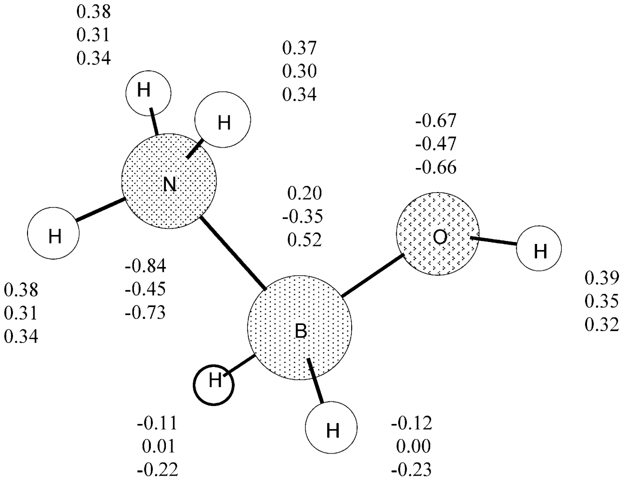


Figure 4. Mulliken (top), Löwdin (middle), and CM3 (bottom) partial atomic charges in the ammonia-borinic acid adduct.

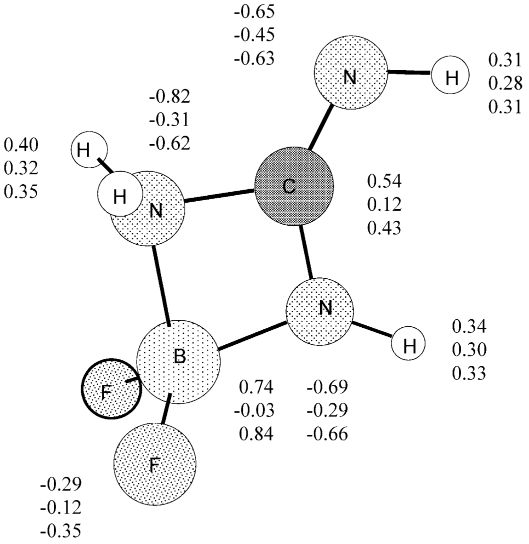


Figure 5. Mulliken (top), Löwdin (middle), and CM3 (bottom) partial atomic charges for the symmetrically independent atoms in the four-membered heterocyclic **41**.

The electronegativity of B should depend on the orbital hybridization utilized in bonding to other elements. Figure 4 shows the partial atomic charges for each atom in the NH_3BH_2OH molecule of the ammonia−borinic acid donor−acceptor complex. The dative B−N bond is long and weak with a recently reported bond dissociation energy of 11.23 kcal/mol.[26] In the present work the B−N bond order is found to be 0.52. Nevertheless, as the geometry about B changes from planar trigonal toward tetrahedral, the electronegativity of B is expected to decrease due to a drop in the s character of B orbital hybridization. As seen in Figure 4, the decrease in electronegativity of B results in substantial increases of negative charges at the oxygen and hydrogen atoms bonded to B as compared to borinic acid alone.

The training set includes four-membered heterocycles **39**−**41** modeled from a recent study of [2+2] cycloaddition reactions of isocyanates, ketimines, and carbodiimides to a nominal B−N double bond.[27] Figure 5 gives the structure and partial atomic charges for the model ring complex **41** that can be visualized as the [2+2] complex between difluoroaminoborane (**3**) with a carbodiimide, HNCNH. As can be seen, all of the bonds in the complex are quite polar even though the symmetric arrangement of the bonds results in only a modest molecular dipole moment of 1.97 D, smaller than the 2.60 D dipole moment of difluoroaminoborane alone.

6. Conclusions

We have presented a model for the prediction of partial atomic charges based on hybrid density functional theory with the 6-31G* basis set for molecules containing boron. A direct comparison between theoretically calculated and experimentally measured quantities has been made. Dipole moments for 43 polar molecules, and the quadrupole moment for BF_3, compare closely to values obtained from experiment or high levels of theory. In this regard the partial atomic charges calculated using CM3 parameters for molecules containing boron are accurate and should prove to be useful in applications such as solvation models.[3]

Availability. The CM3 model including parameters for boron is available in the latest versions of HONDOPLUS-v4.4[28] and MN-GSM,[29] which is an add-on to GAUSSIAN98.[30]

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