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Relationships between dipole moments of diatomic molecules

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Abstract

The dipole moment is one of the most important physical properties of a molecule. We present a combination rule for the dipole moments of related diatomic molecules. For molecules AB, AX, BY, and XY from two different element groups in the periodic table, if their elements make a small parallelogram, reliable predictions can be obtained. Our approach is particularly useful for systems with heavy atoms. For a large set of molecules tested, the average of difference of the prediction from experimental data is less than 0.2 debye (D). The dipole moments for heavy molecules such as GaCl, InBr, SrCl, and SrS, for which no experimental data are available at present, are predicted to be 3.17, 3.76, 3.85 and 11.54 D, respectively.

Keywords: dipole moment; equilibrium geometry, diatomic molecule

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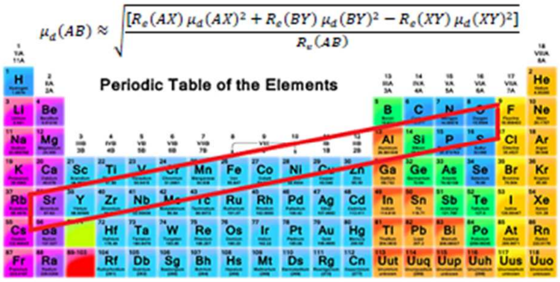
Graphical abstract

Accurate dipole moments for heavy polar molecules can be obtained from those of other related molecules.



Dipole moments are important in many areas of molecular physics and molecular spectroscopy.[1,2] Dipole moments can be obtained from various empirical approaches[3-5] and *ab initio* or density functional (DFT) methods.[6-12] For typical ionic molecules, empirical approaches can produce high quality results even comparable to those from high quality *ab initio* calculations. In principle, dipole moments for all small molecules can be obtained with acceptable accuracy using modern theoretical approaches, as long as proper basis sets and the required computational resources are available. In practice, however, high quality computations are still limited to systems with a relatively small number of electrons for various technical reasons. For molecules with heavy atoms, it is still not easy to obtain accurate dipole moments from high level *ab initio*/DFT approaches.

One of the simplest relationships between dipole moments and atomic or polarized charges in diatomic molecules can be expressed as $\mu_\mathrm{d} = q \cdot R_e$, where q is the effective atomic charge, R_e is the equilibrium internuclear separation, and μ_d is the dipole moment. The problem with this relation is that it does produce correct effective atomic charges, even for typical ionic systems. If this simple relationship is used to predict dipole moments based on some chemical similarity, the quality of the predicted results is not reliable or stable. For typical highly ionic molecules, such as the alkali halides, reasonable results can be obtained for most species; but, for general molecules, the errors from this approach are much larger (e.g., the error is greater than 15% for AgCl estimated from the dipole moment of AgF). Moreover, the results tend to be very irregular so it is difficult to estimate the quality of the predicted data. A better semi-empirical approach is needed to organize the observed dipole moment patterns and to predict dipole moments not yet measured.

Recently we found an empirical relationship (Eqn (1) in this work) between dipole moments, harmonic vibrational frequencies (or force constants) and atomic charges in diatomic molecules at their equilibrium geometries.[13] It has been demonstrated with dozens of molecules that this new relationship can produce reliable atomic charges comparable to high quality *ab initio*/DFT calculations. For arbitrary diatomic molecules, since their atomic charges are unknown, accurate dipole moments cannot be predicted directly using this relationship. However, since the relationship connects dipole moments with molecular force constants, it can be used to explore the relationship between dipole moments of different molecules.

The main motivation of the present paper is to explore such a combination relationship so that accurate dipole moments can be predicted for both highly ionic and general diatomic molecules. The positive result for large numbers of diatomic molecules, especially for those with heavy atoms, demonstrates that the dipole moment relationship from Ref. 13 (Eqn (1) in this work) can also be used to predict reliable dipole moments for general molecules.

Within the harmonic oscillator approximation an empirical relationship between dipole moments and harmonic vibrational frequencies can be expressed as[13]

$$\mu_d = b \cdot q^2/\sqrt{R_e \mu_A \omega_e^2}, \qquad (1)$$

where $b = 19009.3405$ for dipole moments μ_d in debye (D), atomic charge q in units of an electron charge *e*, R_e in Å, harmonic vibrational frequency ω_e in cm^{-1}, and reduced mass μ_A in atomic mass units. The molecular force constants, *k*, can be expressed as $\mu_A\omega_e^2$, so Eqn (1) is also a relationship between dipole moments and molecular force constants. Note that the distance between the centers of effective atomic charges is equal to Eqn (1) divided by *q*, which is different than R_e. In other words the dipole moment of a diatomic molecule is given by $\mu_d=qR_d$, in which R_d is the difference between the effective centers of charge.

Several empirical relationships between force constants of different molecules have been reported and discussed in Ref. 14. In the present work, we adopt the relationship from the AB{AX+BY-XY} scheme, which can produce accurate force constants for polar molecules from different groups. The AB{AX+BY-XY} scheme can be expressed using the following relation between diatomic force constants, k:

$$\frac{1}{k_{AB}} = \frac{1}{k_{AX}} + \frac{1}{k_{BY}} - \frac{1}{k_{XY}}. \qquad (2)$$

Eqn (2) shows that the force constant of molecule AB, k_{AB}, can be estimated from the force constants of molecules with related atoms, *i.e.*, AX, BY, and XY. For the case that A and Y belong to one group, and B and X belong to another group of the periodic table, Eqn (2) can produce reliable results.

Based upon Eqns (1) and (2), we have

$$\mu_d(AB) = \left\{\left(\frac{R_e(AX)\,\mu_d(AX)^2}{q(AX)^4} + \frac{R_e(BY)\,\mu_d(BY)^2}{q(BY)^4} - \frac{R_e(XY)\,\mu_d(XY)^2}{q(XY)^4}\right)\left(\frac{q(AB)^4}{R_e(AB)}\right)\right\}^{1/2} . \qquad (3)$$

In practice, it is not easy to obtain accurate atomic charges q in molecules. To make Eqn (3) more useful, some simplifications are needed.

For given sets of polar molecules, if the atomic charges $q(AB)$ *etc.* are approximately equal to each other, that is,

$$q(AB) \approx q(AX) \approx q(BY) \approx q(XY), \qquad (4)$$

then Eqn (3) can be written as

$$\mu_d(AB) \approx \sqrt{\frac{[R_e(AX)\,\mu_d(AX)^2 + R_e(BY)\,\mu_d(BY)^2 - R_e(XY)\,\mu_d(XY)^2]}{R_e(AB)}}. \qquad (5)$$

Both Eqn (3) and Eqn (5) are adopted to investigate the relationship between dipole moments of different molecules.

There are no force constants or harmonic vibrational frequencies involved in Eqns (3) and (5), so they are direct relationships between dipole moments at equilibrium geometries. It is expected that Eqn (3) will be more reliable than Eqn (5).

According to Eqn (4), we need to be careful in selecting the relative values of the atomic charges to make Eqn (5) more reliable. Based on general chemistry knowledge, the molecules involved in the set {AB, AX, BY, XY} should have some similarities, which can be estimated based on the relative positions of the elements in the periodic table. For example the relative atomic charges can be estimated based on the differences between the electronegativities of relevant atoms.[15,16] One of the easiest ways to select AX, BY, and XY molecules, is to choose atoms A and Y from one group, and B and X from another group. If the atoms {A,Y} and {B,X} are selected to make the smallest parallelogram in the periodical table, then relation (4) will be approximately satisfied.

Many molecules are investigated using Eqns (3) and (5). All experimental dipole moments μ_d and equilibrium distances R_e are taken from Ref. 17 except those indicated. For the sake of clarity, the results for the alkali halide molecules are presented as detailed examples.

For the alkali halide molecules (A=Li, Na, K, Rb and Cs; X=F, Cl, Br and I), all the $C_2^5 \times C_2^4 = 60$ sets of molecules are tested using equations (3) and (5). Notice that each set of four molecules can be used to predict four dipole moments. The details are presented in Table S1 provided as supplementary data. Adopting the atomic charges in Ref. 13, which are estimated from Eqn (1) based on experimental dipole moments, the average difference between the values estimated using Eqn (3) and the observed data is 7.05% for all of the 240 predictions for the 20 alkali halide molecules. This discrepancy decreases to 5.58% for 228 predictions if 12 predictions for LiF are excluded. The relative errors in the observed dipole moments are less than 1%,[17] the errors in R_e are far less than 1%, so the influence of experimental errors can be ignored at present.

If the differences between atomic charges in the molecules are ignored, the corresponding results from Eqn (5) are not as good as those from Eqn (3). The average error for the 20 alkali halide molecules (227 predictions in total) is 15%. There are also some unphysical results (13 predictions in total) for some light molecules, including LiF, LiCl, and NaF. (The detailed data are presented in supplementary files.)

The relative positions in the periodic table of the atoms chosen in a given set influence the quality of the predictions. For the dipole moment prediction for AB from scheme {AX+BY-XY}, we use n_Y-n_A and n_X-n_B or their absolute values $\Delta n_A=|n_Y-n_A|$ and $\Delta n_B=|n_X-n_B|$ to indicate the relative positions of the elements in the periodic table, where n are the periodic vertical numbers of the corresponding atoms. For all the molecules tested, the $(\Delta n_A,\Delta n_B)=(1,1)$ schemes produce the most reliable results in general. As an example, the results for CsBr from all possible schemes are presented in Figure 1.

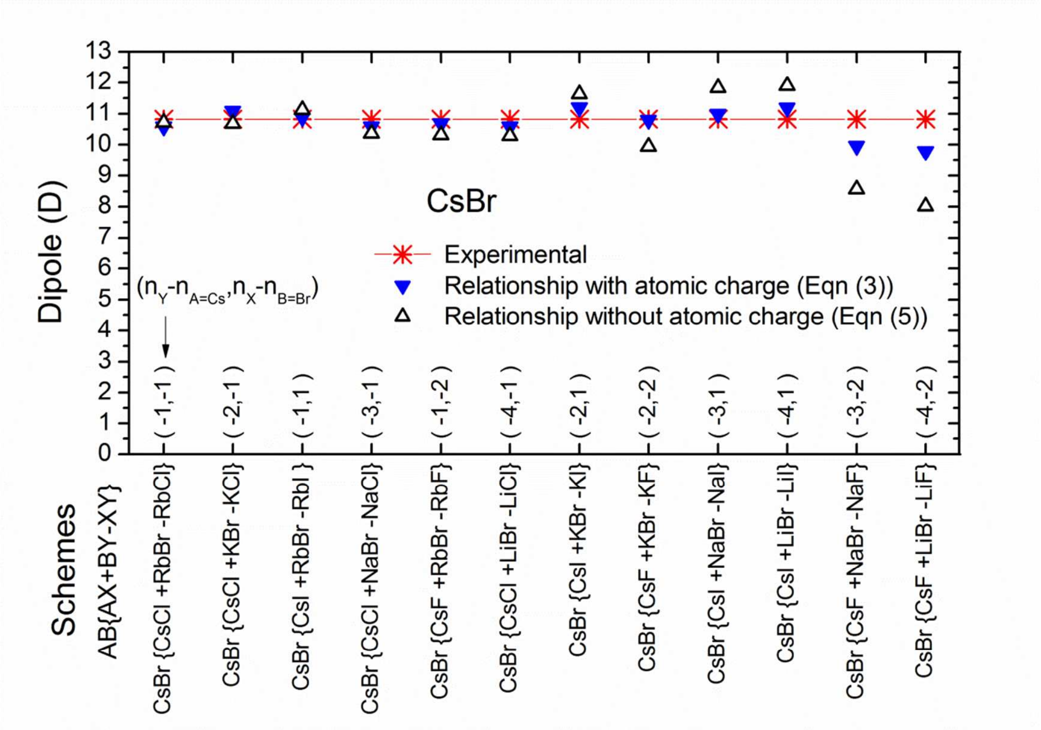


Figure 1. Comparison between experimental dipole moment and the predicted results from all possible schemes with alkali halides for the ground state of CsBr. The relative positions of related atoms are indicated with relative periodic numbers to Cs and Br in the periodic table of the elements. The experimental uncertainties for CsI, CsBr, RbI, RbBr, and KI are ±0.1 D,[17(c)] compared with the large observed values (≥ 10.8 D), the relative errors are less than 1%. For other molecules the relative experimental errors are less than 1%.[17(a)]

A collection of some $(\Delta n_A,\Delta n_B)=(1,1)$ results are plotted in Figure 2. The atomic charges are also plotted for comparison. For molecules in the same set {AB, AX, BY, XY}, if the dipole moment of each molecule is predicted from those of the other molecules, the results show that the errors for heavy molecules are smaller than those of the light ones, even when atomic charges are not considered. For heavier systems, such as molecules in sets {RbCl, CsCl, RbBr, CsBr}, {NaBr, KBr, NaI, KI} and {RbBr, CsBr, RbI, CsI}, the discrepancies for all the predicted dipole moments are within ~3%.

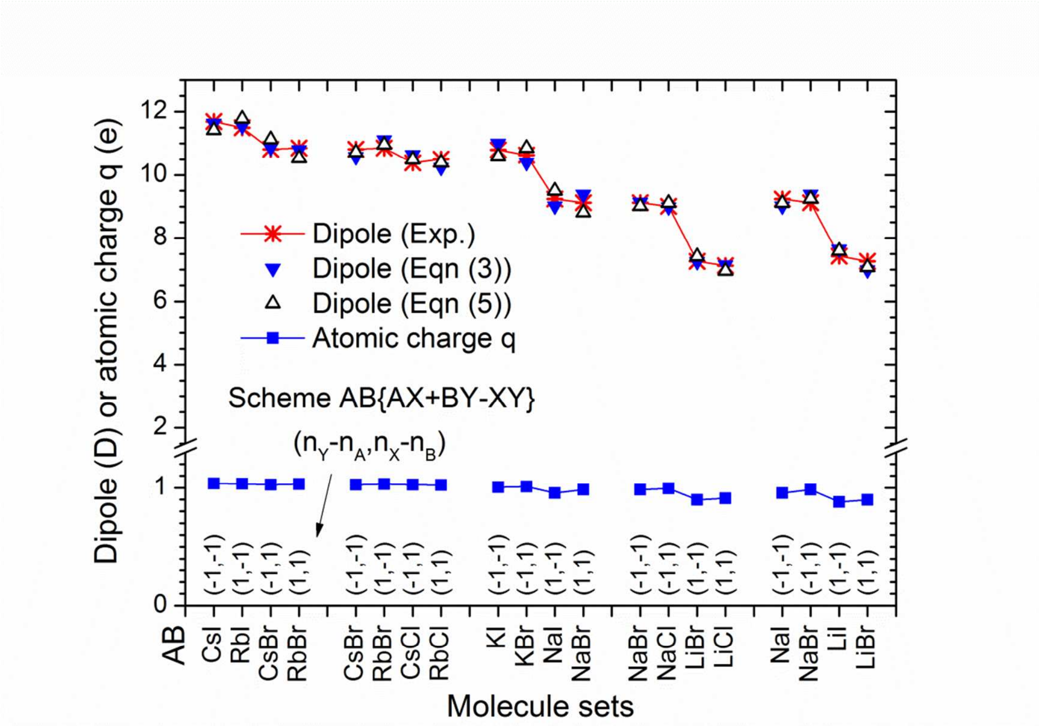


Figure 2. Predicted dipole moments for some alkali halide molecules in the same molecule sets. In each set the dipole moment of one molecule is predicted from the relevant data of all the other molecules from relationships with (Eqn (3)) and without (Eqn (5)) atomic charges. In each set the relative periodic numbers to the related atoms are equal to ±1. Atomic charges adopted are listed for comparison, which are taken from Ref. 13.

Figures 1 and 2 show that the $(\Delta n_A,\Delta n_B)=(1,1)$ schemes provide the best predictions in general. However, the results of CsBr{CsCl+KBr-KCl} ($(\Delta n_A,\Delta n_B)=(2,1)$) in Figure 1 also show that some accurate predictions are also produced by schemes with

$\Delta n_A \bullet \Delta n_B > 1$. The detailed results with (Δn_A, Δn_B) for every molecule from each molecule set (scheme) are presented in Figures S1-S10. These figures show that accurate dipole moments for heavy molecules can be obtained from light systems, and the smaller $\Delta n_A \bullet \Delta n_B$ give better predictions. For all molecules except fluorides there are some different choices that provide reliable predictions. For molecules in a given (Δn_A, Δn_B) molecule set, heavier molecules have better predictions in general.

The quality of Eqns (3) and (5) is also tested using other possible molecule sets, including AB from {A=Si, Ge, Sn, Pb; B=O, S, Se, Te}, {A=In, Tl; B=F, Cl}, {A=Li, Na; B=K, Rb} and {A=F, Cl; B=Br, I}. The results for SiO, SiS, SnO, and SnS from all schemes are plotted in Figure 3 as an example. The data also demonstrate that the (Δn_A,Δn_B)=(1,1) schemes provide the best predictions. More detailed results are presented in Table S2 and Figures S11-S14.

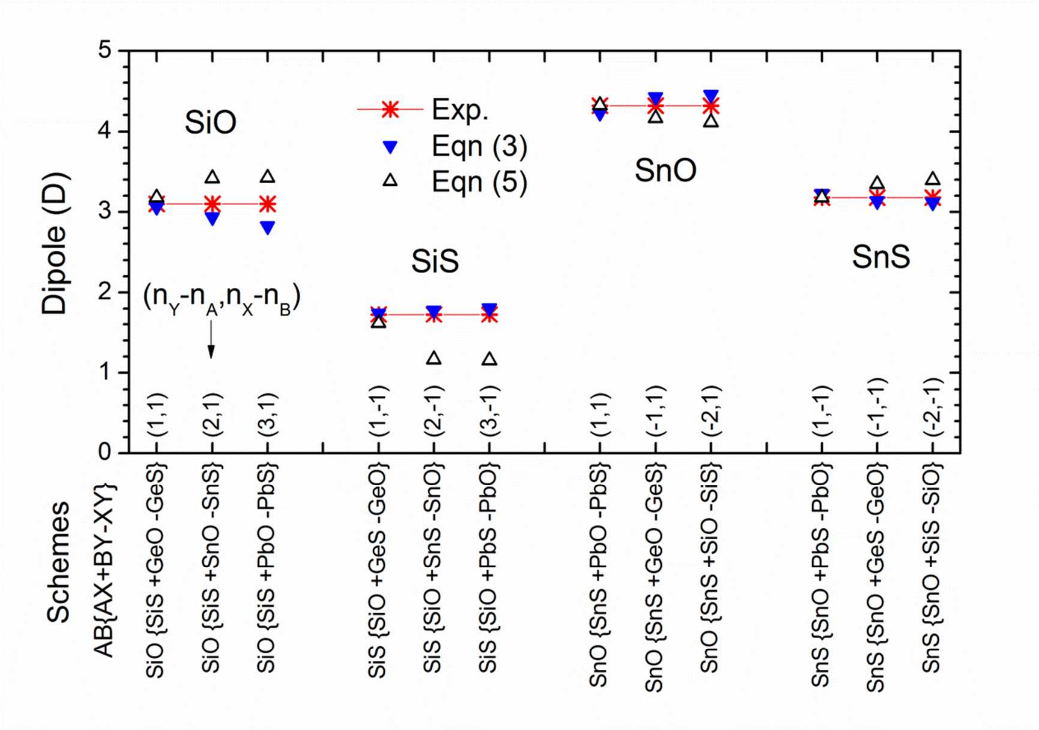


Figure 3. Predicted dipole moments for the ground states of SiO, SiS, SnO, and SnS from schemes with (Eqn (3)) and without (Eqn (5)) atomic charges. The relative positions of the elements considered are indicated with relative periodic numbers.

The results for six sets of the general molecules are presented in Figure 4. The atomic charges are also plotted for reference. Comparison between atomic charges in a molecule set shows that the largest discrepancies generally correspond to the molecules with the relatively smallest atomic charges, such as the GeS in {SnO (0.975 *e*), GeO (0.887 *e*), SnS (0.780 *e*), GeS (0.736 *e*)}. Similar results are also obtained for relatively weakly-bonded molecules such as LiRb, NaRb, in {LiK, NaK, LiRb, NaRb} and BrF, IF, and ICl in {BrF, IF, ICl, BrCl} (the corresponding data are presented in Table S3 and Figures S13 & S14). In fact a similar pattern also occurs for the alkali halides, such as for the sets involving the lithium halides. The case for AgF and AgCl from {AgF, AgCl, HF, HCl} in Figure S14 is just a test for elements (Ag and H) not from the same group but with a chemical similarity. The relative errors are less than 6%.

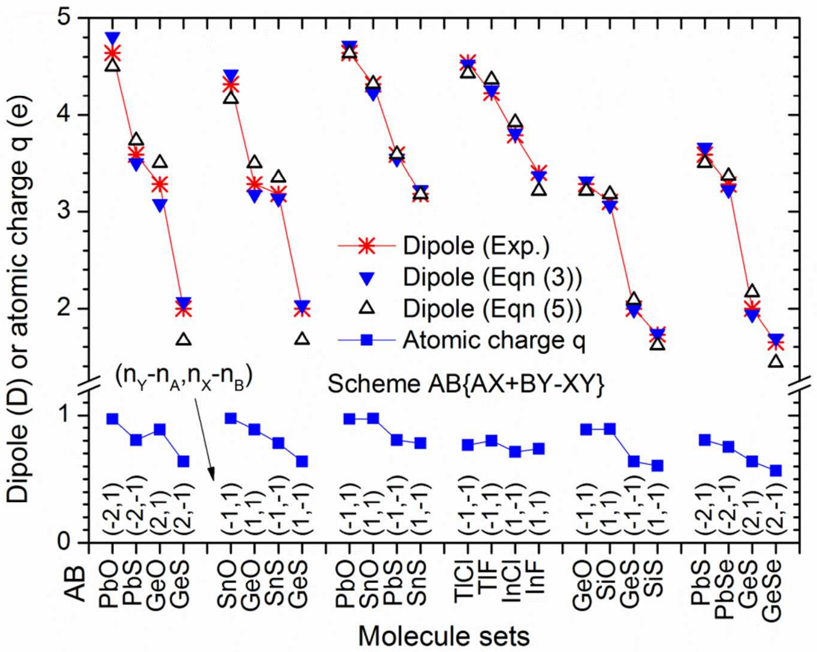


Figure 4. Predicted dipole moments for some general polar molecules in different sets. In each set the dipole moment of one molecule is predicted from the relevant data of all the other molecules from relationships with (Eqn (3)) and without (Eqn (5)) atomic charges. In each set the relative periodic numbers are presented with each molecule.

Atomic charges adopted are also listed for comparison, which are taken from Ref. 13.

The results for alkali halides make it clear that it is difficult to obtain accurate predictions from Eqn (5) for light elements, e.g. for LiF from the {LiF, LiCl, NaF, NaCl} set. The relative discrepancy is ~-20%, even though it is the best of all the 12 possible schemes using alkali halide molecules. This error however is ~10% for LiCl, and less for NaF (8.6%) and NaCl (-6.2%) in the same set. When the atomic charges are considered, the results from Eqn (3) are -6.2% (LiF), 4.2% (NaF), 3.4% (LiCl) and -2.7% (NaCl). For such light polar molecules, it is easy to obtain accurate dipole moments from standard quantum chemistry calculations; the errors from the coupled cluster-singles and double (CCSD)[12] method with 6-311++G(3df) basis sets is ~3% or less. But for heavy molecules, the errors are larger for *ab initio* calculations; Eqn (5) is then particularly useful in this case.

For all molecule sets with $(\Delta n_A,\Delta n_B)=(1,1)$, the predicted dipole moments from Eqn (5) are reasonable for heavy systems. The results for molecule sets such as {InCl, TlCl, InF, TlF}, {GeS, GeO, SiS, SiO}, and {PbS, PbO, SnS, SnO} in Figure 4 are typical examples. A comparison between the predicted results from Eqn (5) and CCSD/6-311++G(3df) results from *Gaussian 09* package[18] is presented in Table S3 for many molecules except the alkali fluorides. The results show that for some light molecules, the CCSD predictions are slightly better than those of Eqn (5), but for other molecules, especially heavy polar molecules, the results from Eqn (5) are much better than the CCSD predictions. For GeSe the experimental data for the $(\Delta n_A,\Delta n_B)=(1,1)$ scheme are not available at present; but the $(\Delta n_A,\Delta n_B)=(2,1)$ scheme also gives results with similar quality to the CCSD/6-311++G(3df) calculation. The discrepancy from Eqn (5) on average is 0.14 D for all 37 molecules (excluding alkali fluorides). The corresponding result for 14 molecules from the CCSD/6-311++G(3df) approach is 0.23 D.

Based upon the quality of the above results, Eqn (5) with a scheme with

(Δn_A, Δn_B)=(1,1) is adopted to predict the dipole moments for some heavy molecules, including GaCl, InBr, SrCl, SrS, CuCl and CuBr, for which the experimental dipole moments are not available at present. The results and the corresponding schemes are presented in Table 1. All the experimental dipole moments of the relevant molecules are from Ref. 17; the R_e are from Refs. 17, 19, and 20. Detailed data, including the atomic charges for the molecules from Eqn (1) are presented in Table S4 for reference. We note that for CuBr, since the experimental dipole moment for CuCl is not available, the data estimated from Ref. 13 (~5.74 D) is adopted, which is similar to the recent DFT calculation from Ref. 21 (5.3~6.2 D). The result from the {CuF+AgCl-AgF} scheme is 5.66 D, which is close to that of Ref. 13.

Table 1. Predicted ground state dipole moments using Eqn (5) for some molecules.*

AB	μ_d/D	Re/Å	Scheme	(Δn_A,Δn_B)
GaCl	3.17	2.20169	{InCl+GaF -InF}	(1,1)
InBr	3.76	2.54315	{$Tl^{81}Br$+InCl -TlCl}	(1,1)
SrCl	3.85	2.575848 [19]	{CaCl+SrF -CaF}	(1,1)
SrS	11.54	2.441 [20]	{BaS+SrO -BaO}	(1,1)
CuCl	5.66	2.05118	{CuF+AgCl -AgF}	(1,1)
CuBr	5.20	2.17344	{CuCl[a]+AgBr -AgCl}	(1,1)

* All the experimental dipole moments and Re of the relevant molecules are from Ref. 17 except as indicated.

[a] Theoretical dipole moment of CuCl taken 5.74 D from Ref. 13.

In summary, a reliable connection between dipole moments of different polar molecules is given. The quality of the predictions depends strongly on the relative positions of the elements in the periodic table. For molecules from just two different groups, reliable predictions can be obtained without considering the atomic charges if the positions of the atoms {A, Y} and {B, X} make the smallest parallelogram in the periodic table. For molecules in the same set (also within the same (Δn_A,Δn_B) scheme), the molecule with the largest atomic charge is the one with the smallest relative error in general. The most reliable dipole moments can be predicted for molecules with heavier masses and relatively large atomic charges. The present approach is therefore particularly useful for polar molecules with heavy atoms.

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