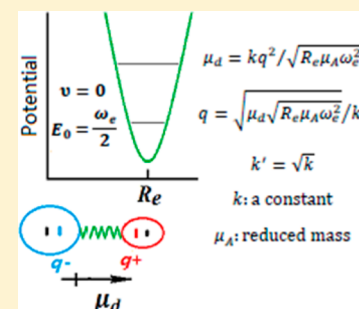


Relationship between Dipole Moments and Harmonic Vibrational Frequencies in Diatomic Molecules

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S Supporting Information

ABSTRACT: Electric dipole moments and harmonic vibrational frequencies are two of the most important molecular properties in many fields of chemistry and physics. With the aid of classical physics, an empirical relationship between them was obtained for diatomic molecules as $\mu_d = kq^2/(R_e\mu_A\omega_e^2)^{1/2}$, where k is a constant and μ_d , q , R_e , μ_A , and ω_e are the dipole moment, atomic charge, equilibrium bond length, reduced mass, and equilibrium vibrational frequency, respectively. This relation also provides the atomic charge q as a function of molecular dipole moment. Comparisons with over 60 molecules were made to test this relationship. For typical ionic molecules such as the alkali halides, the predicted dipole moments are in good agreement with the observed data assuming the atomic charges are $1e$. For general polar molecules, the estimated atomic charges obtained from the electric dipole moments are in good agreement with ab initio results for natural bond orbital and/or Mulliken populations.



Electric dipole moments and harmonic vibrational frequencies play important roles in molecular spectroscopy, molecular physics, and related fields.^{1–3} Theoretically, both dipole moments and harmonic vibrational frequencies depend on the electron distribution in molecules and can be obtained from ab initio and density functional theory (DFT) calculations.^{4–6} Many other molecular parameters in molecules, ranging from equilibrium geometries to atomic charges,^{7–10} can also be obtained using computational techniques. However, it is difficult to obtain a direct relationship between molecular parameters from quantum chemistry. Herein, we report a simple analytic formula based on classical physics and demonstrate with experimental and high-quality ab initio results that there is a close connection between dipole moments, atomic charges, and harmonic frequencies at the equilibrium geometry.

The dipole moment in classical physics is $\mu_d = qR$, where R is the distance between point charges q^+ and q^- . If R is assumed to be the equilibrium nuclear separation R_e , which means that the separated charges are centered at the nuclei of the atoms, the estimated dipole moments are generally much larger than the observed values, even for typical highly ionic diatomic molecules.

In a diatomic molecule, the center of mass of all electrons of an atom is also the center of electronic charge. Considering the electric fields in molecules and the flexibility of the electron clouds around each nucleus, polarized charges are also present. Because of polarization, the effective charge center is not at the nucleus of the atom. The center of mass of each atom lies between its nucleus and the center of mass of the electrons but is very close to the nucleus because of the large nucleus/electron mass ratio (≥ 1836). The separation between the

centers of atomic mass is R_e , which can be obtained from spectroscopic measurements. The separation between the centers of effective atomic charges is R_d , which is, in general, not the same as R_e . From the definition of dipole moments, accurate dipole moments should be estimated as $\mu_d = qR_d$, not $\mu_d = qR_e$. The difference between the center of mass and center of charge is illustrated in Figure S1 in the Supporting Information (SI).

For an ionic molecule $A^qB^{q'}$, we assume the following empirical relationship (SI units)

$$\frac{q^2}{4\pi\epsilon_0 R_d^2} = \frac{1}{\hbar^2\mu_A R_e E_0^2} \quad (1)$$

where μ_A is the reduced mass of the molecule, ϵ_0 is the permittivity of a vacuum, \hbar is the Planck constant h divided by 2π , and E_0 is the zero-point energy (ZPE). We present eq 1 without theoretical justification; it should be treated as an empirical relationship. The justification for eq 1 is based on the quality of its predictions, as demonstrated below.

To obtain a simple relationship, we employ the harmonic approximation. Within the harmonic approximation, $E_0 = h\omega_e/2$, where ω_e is the equilibrium vibrational frequency in wavenumbers (m^{-1} in SI) and c is the speed of light in a vacuum. Substituting this relationship into eq 1 and taking ω_e in cm^{-1} , atomic charge q in e , R_e and R_d in \AA , and the reduced mass μ_A in atomic mass units, we have

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$$R_d = 3957.6371q / \sqrt{R_e \mu_A \omega_e^2} \quad (2)$$

All fundamental constants were taken from ref 11. The corresponding dipole moment μ_d (in D) is

$$\mu_d = 4.8032qR_d \quad (3)$$

From eqs 2 and 3, we have

$$\mu_d = 19009.3405q^2 / \sqrt{R_e \mu_A \omega_e^2} \quad (4)$$

From eq 4 and the dipole moments μ_d , the effective charges can be estimated as

$$q = \sqrt{\mu_d \sqrt{R_e \mu_A \omega_e^2}} / 137.87436 \quad (5)$$

The signs of the atomic charges can be determined by comparison with the electronegativities of the atoms. Note that eqs 2, 4, and 5 are isotopically invariant within the Born–Oppenheimer approximation, because $\mu_A \omega_e^2$, the molecular force constant, is isotopically invariant. This also means that eqs 4 and 5 express a relationship among dipole moments, atomic charges, and molecular force constants.

Equations 4 and 5 were applied to over 90 diatomic molecules that have reliable experimental dipole moments in their ground electronic states. The experimental R_e , ω_e , and dipole-moment values were taken from ref 12, except as indicated. Details are presented in Table S1 (SI). The atomic masses were taken from ref 13. For most of the molecules (about 50), the results were compared with ab initio results from the coupled-cluster singles and doubles (CCSD)⁴ approach with the 6-311G(3df) and 6-311++G(3df) basis sets. For a few of the molecules, the aug-cc-pv n z ($n = 2-5$) basis sets^{14,15} and the B3LYP⁶ approach were also tried for comparison. All theoretical data were calculated using the Gaussian 09 package.¹⁵ The detailed results are presented in Tables S1–S4 (SI).

For most of the molecules, the relative errors were within 2%, 5%, and 10% for the calculated R_e , ω_e , and dipole-moment values, respectively. The discrepancies for the atomic charges from eq 5 are not more than 0.1 e or 10% for most of the molecules [Tables S3 and S4 (SI)]. The ab initio/DFT results for about 50 molecules were compared with the results of eq 5 for both experimental and theoretical R_e , ω_e , and dipole-moment values.

For the 16 highly ionic alkali halide molecules AX ($A = \text{Na, K, Rb, Cs}$; $X = \text{F, Cl, Br, I}$), the atomic charges were assumed to be 1 e . The dipole moments estimated from both R_e and R_d are plotted in Figure 1. The dipole moments calculated using $q = 1$ from $\mu_d = 4.8032qR_e$ are plotted as triangles, whereas those obtained from $\mu_d = 4.8032qR_d$, with R_d obtained from eq 2 with $q = 1$ (or from eq 4 with $q = 1$), are plotted as solid circles. The dipole moments from eR_d (also eq 4; solid circles) are in good agreement with the observed data (stars). The maximum and minimum discrepancies are 9.8% (NaI) and -0.36% (RbF), respectively. The discrepancies from the observed dipole moments are -0.2 D (-2.79%), 0.1 D (1.2%), and -0.1 D (-1.36%) for NaF, NaCl, and KF, respectively. The average of the relative errors for all of these molecules is 4.4%. The quality of the dipole moments predicted using eq 4 is similar to that obtained using CCSD approaches [Tables S2 and S4 (SI)] for AX ($A = \text{Na, K}$; $X = \text{F, Cl, Br}$). As expected, the dipole moments estimated directly from eR_e are too large.

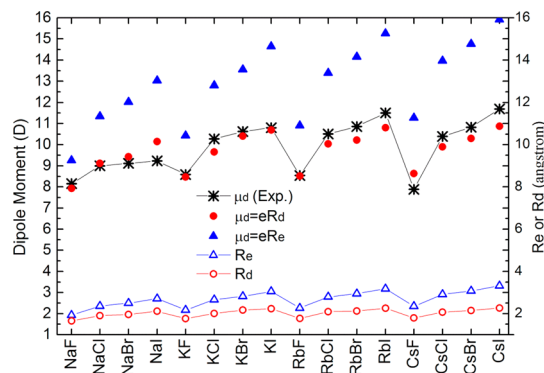


Figure 1. Equilibrium distances R_e , distances between effective charge centers R_d , and dipole moments estimated from them for the ground states of alkali halide molecules. Atomic charges are assumed to be 1 e .

It was also found that the effective atomic charges from eq 5 were close to the natural bond orbital (NBO)⁹ or Mulliken¹⁰ population charges for nearly all of the molecules. The discrepancies from accurate ab initio atomic charges are not larger than 0.1 e or 10%. The corresponding atomic charges from both coupled-cluster (CC) and self-consistent-field (SCF) electron densities are presented in Figures 2–4. The NBO

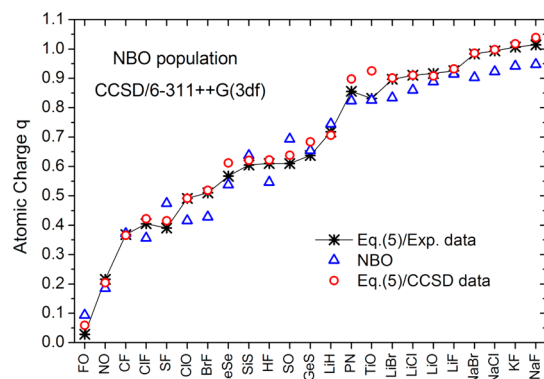


Figure 2. Comparison with the NBO population charges from the CCSD/6-311++G(3df) calculations.

charges from the CCSD/6-311++G(3df) computations are presented in Figure 2 for 22 molecules. The data in Figure 2 show that the atomic charges from the NBO populations are consistent with the atomic charges from eq 5; the discrepancies are within 0.1 e , from both the experimental and the ab initio data for R_e , ω_e , and dipole moments. The results for other basis sets or populations mentioned above are similar to those in Figure 2. Comparisons are presented in Figures 3 and 4; detailed data are presented in Figures S2–S5 and Table S4 of the SI.

Figure 3 presents a comparison between the NBO results and the results of eq 5 from experimental data. Figure 4 presents a comparison between the Mulliken charges and the atomic charge of eq 5 from experimental data. For highly ionic molecules, the NBO atomic charges are close to the results of eq 5, but with some systematic errors, which can also be found in Figure 2 (for NaF, KF, etc.). Figure 4 shows that Mulliken charges also compare well with the results of eq 5. Our results from eq 5 are also in good agreement with literature^{16–18} values [Table S3 (SI)] from other quantum chemistry approaches.

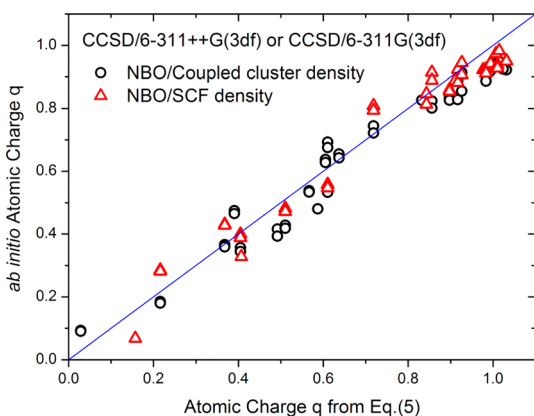


Figure 3. Comparison between atomic charges from NBO populations and the atomic charges of eq 5 from experimental data.

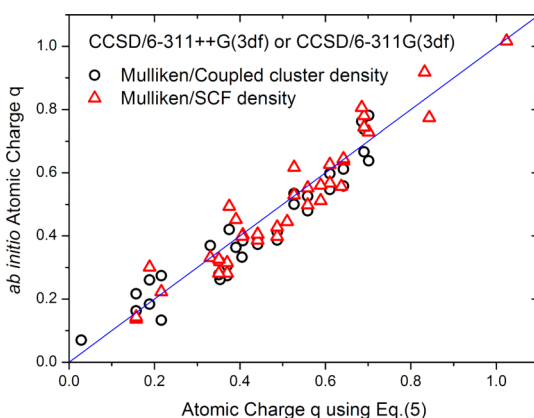


Figure 4. Comparison between atomic charges from Mulliken populations and the atomic charges from eq 5 using experimental data.

The atomic charges were also calculated using the *ab initio* R_e , ω_e and dipole-moment values and were compared with the NBO and Mulliken charges (Figure 2; Figures S2–S5 and Table S4 (SI)). The agreement is similar to that obtained with experimental data.

The predictions of other theoretical approaches are not discussed systematically herein. Some of them produce atomic charges closer to those of eq 5 than the CCSD//6-311G(3df)/6-311++G(3df) results presented. For example, for the ground state of the CrO molecule, the polar tensor charge¹⁹ from the B3LYP/aug-cc-pv5z approach is 0.85 e , which is closer to the eq 5 result (0.90 e) than the data from NBO and Mulliken populations. The quality of this calculation can be assessed by examining the errors in the predictions of R_e (−0.1%), ω_e (−2.1%), and dipole moment (6.9%). For some of the molecules, the detailed results from DFT theory and the data from the aug-cc-pvnz ($n = 2-5$) basis sets are also presented in Table S4 (SI).

For molecules without experimental dipole moments, eq 4 can also be examined with the help of some other models. For example, according to Gordy and Cook²⁰ and Pauling,²¹ the atomic charges can be estimated from the difference in the electronegativities of the atoms. For Cu and Ag, the Pauling electronegativities are 1.90 and 1.93, respectively,¹² so the atomic charges in CuF and AgF should be close to each other. Equation 5 gives the atomic charges as 0.977 and 0.975 (in e) for CuF and AgF, respectively. It is clear that the effective charge $q(F)$ of the fluorine atom in CuF is approximately equal

to the effective charge $q(F)$ in AgF. For the same reason, we employed similar relationships for the CuCl, AgCl, CuBr, and AgBr molecules. The atomic charges from eq 5 are AgCl (0.923 e) and AgBr (0.877 e). Thus, we have $q(Cl, CuCl) \approx q(Cl, AgCl) = 0.923 e$; similarly, $q(Br, CuBr) \approx q(Br, AgBr) = 0.877 e$. With these values and the experimental R_e and ω_e values from ref 12, the dipole moments from eq 4 for CuCl and CuBr are predicted to be 5.74 and 5.32 D, respectively. These data are close to our CCSD/6-311++G(3df) results, which are 5.73 D (CuCl) and 5.57 D (CuBr). The result for CuCl is also close to the high-level DFT values 5.707 D (LC-PBE0-5) and 5.782 D (CAM-B3LYP*) from ref 22. For CuBr, the result is also close to the multireference configuration interaction (MRCI) value of 5.55 D from ref 23. These data also demonstrate that the atomic charges from eq 5 are reliable.

For nearly all of the molecules available to test, the atomic charges from eq 5 are close to the high-quality NBO or the Mulliken population results from quantum mechanical calculations. Equation 5 is particularly useful for heavy molecules, for which calculations are most difficult, because it gives atomic charges based on only the dipole moments and harmonic vibrational frequencies at equilibrium.

There is a long history of semiempirical relationships associated with dipole moments. For example, early workers used molecular beam electric resonance to obtain dipole moments for alkali halides, and Trischka²⁴ derived a relationship, similar in spirit to our equations, relating internuclear distances to dipole moments with the Rittner model. We note that eq 5 also has some utility in undergraduate teaching to help understand the concept of atomic charges in molecules. The incorrect definition of an “experimental atomic charge” given by equations such as $q = \mu_d/R_e$ is often used to teach beginning chemistry students.^{25–27}

In addition, eq 4 can also be used to explore the relationship between dipole moments of different molecules, and accurate results can be obtained especially for heavy polar systems.²⁸ The positive results for over 50 molecules also demonstrate the reliability of eq 4.

To conclude, we have found a simple analytic empirical relationship for estimating dipole moments and atomic charges in diatomic molecules at equilibrium. Over 60 molecules were tested by predicting dipole moments and/or the atomic charges. For typical ionic molecules, this method produces reliable dipole moments; for polar molecules, in general, it produces reliable atomic charges that are close to the values obtained from high-quality *ab initio*/DFT results. The results demonstrate that there is a close connection among dipole moments, atomic charges, and harmonic frequencies at the equilibrium geometry.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental data used in the main text (Table S1), detailed *ab initio*/DFT data for comparison (Tables S2–S4), and related figures (Figures S1–S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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