5492 *J. Phys. Chem. A* **2005,** *109,* 5492−5497

# On the Representation of Molecular Quadrupole Moments in Terms of Atomic Moments

**James F. Harrison***

*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322*

*Received: February 15, 2005*

The magnitude and algebraic sign of the molecular quadrupole moments of the homonuclear diatomic molecules $N_2$, $O_2$, $F_2$, $P_2$, $S_2$ and $Cl_2$ are analyzed by expressing them as a sum of the quadrupole moments of the free atoms and an induced molecular quadrupole due to bond formation. This induced molecular quadrupole is further analyzed in terms of in situ atomic dipole and quadrupole moments constructed following the electron partitioning method suggested by Hirshfeld. These in situ moments are interpreted in terms of the $\sigma$ and $\pi$ character of the chemical bonds and are compared with those predicted by the DMA method of Stone (*The Theory of Intermolecular Forces*; Clarendon: Oxford, 1996).

## Introduction

The multipole moments of a molecule play a crucial role in our understanding of intermolecular forces,[1] arguably one of the lynch pins of modern chemistry. Additionally they provide valuable insight into the charge distribution in molecules, and this insight allows us to develop our intuition regarding the relationships between charge distributions and theories of chemical bonding. One tends to interpret the molecular multipole moments in terms of local atomic moments and most often this means the net charge on an atom. A typical scenario is to assume that the in situ atoms are spherically symmetric and the only local moment they possess is the zero moment or a net atomic charge. Either molecular moments are computed from a point charge model or the charge is fixed to reproduce the lowest nonzero molecular moment. For example, the dipole moment of HF at the MRCI level with an aug-cc-pV5Z basis is 0.7048 au, which, in this model, predicts a charge of 0.407 e on the H atom. However the *zz* component of the quadrupole moment at this level is 1.6921 $ea_0^2$, which predicts a H atom charge of 0.627 e. Clearly the atoms are not spherical, and one cannot find charges that reproduce both moments. This may or may not be a problem depending on ones interest. If one is interested in simulating the long range electrostatic potential of HF, then the dipole term may be all that is needed and the inconsistency with the quadrupole moment is not important. However, if one is interested in developing a deeper understanding of the electrostatic moments, then one must go beyond the spherical atom model and recognize their asymmetry. One then immediately confronts the arbitrariness of partitioning the electron density among the nuclear positions, e.g., writing the electron density in the form $\eta^{\mathrm{mol}} = \sum_{k=1}^{\mathrm{nuclei}} \eta_k^{\mathrm{atom}}$. While there are an infinite number of ways of doing this, only a few are physically sensible. One could assign regions of space to a particular atom using a Voronoi[2,3] or Bader[4] approach, and whatever density is in that region belongs to that atom. This method of defining an in situ atom is compelling because of the exclusivity of the partitioning and the similarity to the ubiquitous space filling representations of molecules. However, the exclusivity of the partitioning seems a bit unphysical in the sense that if one were to take a diatomic molecule and turn off the interactions between the two centers the sum of the resulting noninteracting atomic densities would look very similar to the molecular density. The electron density on one atom would have a significant value at the nucleus of the second atom, suggesting that one consider partitioning in which the in situ atoms have overlapping charge densities.

A method of doing this was suggested by Hirshfeld[5] and is the method we will investigate in this report. Hirshfeld[5] defines a protomolecule as a collection of noninteracting or free atoms located at the appropriate equilibrium positions in the molecule of interest. The corresponding protomolecule density is simply the sum of the free atom densities, $\eta^{\mathrm{pm}} = \sum_{k=1}^{\mathrm{nuclei}} \eta_k^0$, where $\eta_k^0$ is the free atom density on center *k*. He suggested that if one wants to partition the electron density in a molecule among the various atomic centers, one allocates the molecular density at a point in the molecule to the constituent atoms in proportion to the fraction of the corresponding free atom density to the proto molecule density at this point. This fraction is $W_k = \eta_k^0/\eta^{\mathrm{pm}}$, an in situ atomic density is given by $\eta_k = W_k \eta^{\mathrm{mol}}$, and the local moments are computed using $\eta_k$. Since the Voronoi,[2,3] Bader,[4] and Hirshfeld[5] methods all partition the electron density directly, they will each converge to a specific, albeit different, result as the density converges. In contrast to this physical partitioning of the electron density, one has methods such as Mulliken's[6] population analysis and Stone's[1,7] distributed multipole analysis, which allocate the density to various centers based on an algorithm that is basis set dependent and which may not converge in sync with the electron density. These methods tend to be sensitive to the basis set used and, in particular, to the presence of diffuse functions typically used in modern computational chemistry.

Several studies[3,8] have shown that the Hirshfeld partitioning results in charges that are chemically sensible and relatively insensitive to the choice of basis set. There have been fewer studies of the in situ higher atomic moments.[5,8,9] The molecular moments of interest in this report are the quadrupole moments of the homonuclear diatomics $N_2$, $O_2$, $F_2$, $P_2$, $S_2$, and $Cl_2$ in their ground state. These are of particular interest because of the difficulty in representing them using a point charge model.[1]

---

* E-mail: harrison@chemistry.msu.edu. Phone: 517-355-9715 ext 295. Fax: 517-353-1793.

10.1021/jp058050j CCC: $30.25

For example, to do so one assigns identical nonzero charges to the two atoms and places a compensating charge somewhere, usually at the bond midpoint, and this seems nonphysical. The Hirshfeld partitioning of the electron density allows one to represent these quadrupole moments in terms of the in situ atomic dipoles and quadrupoles, and while these are not as intuitive as atomic charges, they are, in this context, more physically sensible. Additionally, because of its widespread use, we will compare these results with the DMA analysis of Stone.[1,7]

## Preliminaries

Following Buckingham,[10] we may write the $zz$ component of the molecular quadrupole moment tensor as the sum of an electronic and a nuclear contribution:

$$\Theta_{zz}^{\mathrm{mol}} = \Theta^{\mathrm{mol}} = -\frac{1}{2}\int (3z^2 - r^2)\eta^{\mathrm{mol}}(\vec{r})\,\mathrm{d}V + \frac{ZR^2}{2}$$

where $Z$ is the atomic number of the nuclei, which we place along the $z$ axis at $\pm R/2$. Writing the molecular density as the sum of the insitu density on the left and right atoms

$$\eta^{\mathrm{mol}} = \eta_{\mathrm{L}} + \eta_{\mathrm{R}}$$

and shifting the origin to the left and right atom as appropriate results in

$$\Theta^{\mathrm{mol}} = \Theta_{\mathrm{L}} + \Theta_{\mathrm{R}} - R(\mu_{\mathrm{L}} - \mu_{\mathrm{R}})$$

where the quadrupole moment on the left atom is

$$\Theta_{\mathrm{L}} = -\frac{1}{2}\int (3z^2 - r^2)\eta_{\mathrm{L}}(\vec{r})\,\mathrm{d}V$$

with the dipole moment on the left atom given by

$$\mu_{\mathrm{L}} = -\int z\eta_{\mathrm{L}}(\vec{r})\,\mathrm{d}V$$

By symmetry $\Theta_{\mathrm{L}} = \Theta_{\mathrm{R}}$ and $\mu_{\mathrm{L}} = -\mu_{\mathrm{R}}$ and so

$$\Theta^{\mathrm{mol}} = 2\Theta_{\mathrm{L}} - 2R\mu_{\mathrm{L}}$$

If we define the density difference function $\delta\eta_L(\vec{r})$ as the difference between the number density of electrons on the left atom when in situ and when free, $\delta\eta_{\mathrm{L}}(\vec{r}) = \eta_{\mathrm{L}}(\vec{r}) - \eta_{\mathrm{L}}{}^0(\vec{r})$, we may write the local quadrupole moment as the sum of the free atom quadrupole and a quantity that reflects the change in the molecular quadrupole moment on the atom due to bond formation.[11−14]

$$\Theta_{\mathrm{L}} = \Theta^{\mathrm{atom}} + \delta\Theta_{\mathrm{L}}$$

where

$$\delta\Theta_{\mathrm{L}} = -\frac{1}{2}\int (3z^2 - r^2)\delta\eta_{\mathrm{L}}(\vec{r})\,\mathrm{d}V$$

Since the free atom does not have a dipole moment, we may write

$$\mu_{\mathrm{L}} = \delta\mu_{\mathrm{L}} = -\int z\delta\eta_L(\vec{r})\,\mathrm{d}V$$

Our final expression for the total molecular quadrupole moment partitions it into a term representing the sum of the free atom quadrupoles and a term representing the change due to the induced local moments created when a bond forms.

$$\Theta^{\mathrm{mol}} = 2\Theta^{\mathrm{atom}} + \delta\Theta^{\mathrm{mol}}$$

where

$$\delta\Theta^{\mathrm{mol}} = 2\delta\Theta_{\mathrm{L}} - 2R\delta\mu_{\mathrm{L}}$$

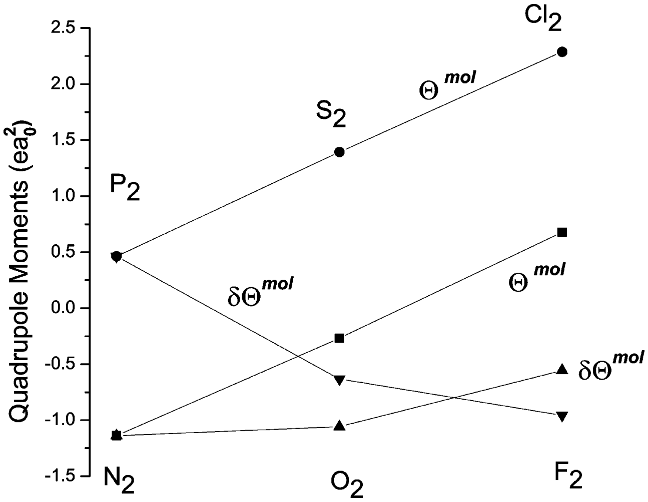

**Figure 1.** Molecular Quadrupole Moments $\Theta^{\mathrm{mol}}$ and the induced quadrupole moment $\delta\Theta^{\mathrm{mol}} = \Theta^{\mathrm{mol}} - \Theta^{\mathrm{atoms}}$ of $N_2$, $O_2$, $F_2$, $P_2$, $S_2$, and $Cl_2$.

In Figure 1 we plot $\Theta^{\mathrm{mol}}$ and $\delta\Theta^{\mathrm{mol}}$ as a function of bond order for the diatomics of interest. The molecular quadrupole moments are calculated using a MRCI (CASSF+1+2) wave function constructed at the experimental equilibrium internuclear separation using an uncontracted aug-cc-pV5Z basis.[15] Note that $\delta\Theta^{\mathrm{mol}}$ was calculated by subtracting the atomic from the molecular quadrupole moments and no particular partitioning of the electron density has been used. For simplicity we have used SCF wave functions for the atomic quadrupoles, which constrains us in the subsequent analysis to use the sum of the SCF electron densities to construct the proto-molecule density. All wave functions are constructed using MOLPRO.[16]

Note that from Figure 1, in all cases $\delta\Theta^{\mathrm{mol}} \le 0$, the zero obtaining where $\Theta^{\mathrm{atoms}} = 0$. Also, $\delta\Theta^{\mathrm{mol}}$ is much larger for the second row diatomics, $S_2$ and $Cl_2$ than for the first row analogues, $O_2$ and $F_2$. This is consistent with the larger polarizabilities and internuclear separations of the second row diatomics. The calculated quadrupole moments are in excellent agreement with the experimental values.

## Hirshfeld Partitioning

As noted above, Hirshfeld defines the electron density of an in situ atom in a diatomic as $\eta_{\mathrm{L}} = W_{\mathrm{L}}\eta^{\mathrm{mol}}$, where $W_{\mathrm{L}} = \eta_{\mathrm{L}}{}^0/(\eta_{\mathrm{L}}{}^0 + \eta_{\mathrm{R}}{}^0)$ with $\eta_{\mathrm{L}}{}^0$ and $\eta_{\mathrm{R}}{}^0$ being the electron densities of the free atoms. In a similar way the change in the density of the in situ atom relative to the free atom is $\delta\eta_{\mathrm{L}} = W_{\mathrm{L}}\delta\eta^{\mathrm{mol}}$. In what follows we will construct $W_{\mathrm{L}}$ using oriented atomic SCF densities on both centers, calculated using the aug-cc-pV5Z basis. With $z$ as the internuclear line, this means that for Cl, for example, we construct the protomolecule density consistent with $1s^22s^22p^63s^23p_x{}^23p_y{}^23p_z{}^1$. For O and S we symmeterize the density according to $1s^22s^22p_x{}^{1.5}2p_y{}^{1.5}2p_z{}^1$ & $1s^22s^22p^63s^23p_x{}^{1.5}3p_y{}^{1.5}3p_z{}^1$, respectively.

Figure 2 shows contours of the total electronic density in the $S_2$ molecule and the associated in situ density of the S atom on the left as determined using the Hirshfeld partitioning. Note that

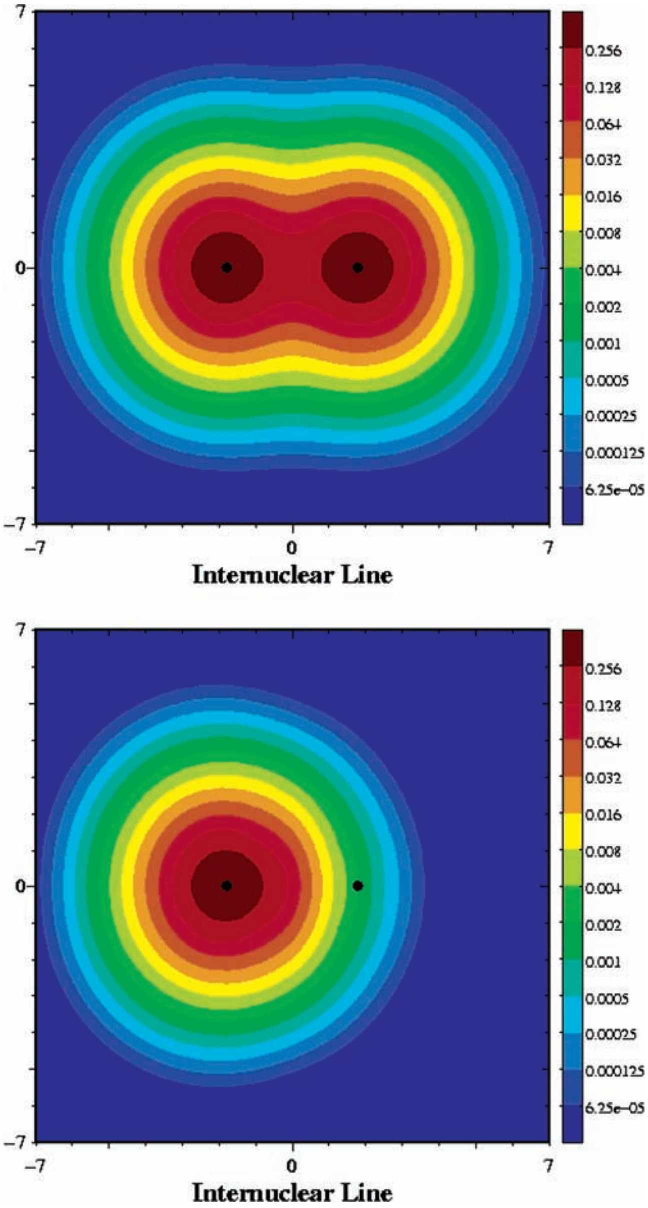

**Figure 2.** Electron density in the $S_2$ molecule (top) and in the in situ S atom (bottom).

some of the in situ atomic density encompasses the other nucleus. Figure 3 shows the density difference $\delta\eta^{\mathrm{mol}}$ in $S_2$ and the associated in situ atomic density difference, $\delta\eta_{\mathrm{L}}$.

After obtaining $\delta\eta_{\mathrm{L}}$ as described above, the induced local atomic moments are computed from

$$\delta M_{\mathrm{L}}{}^{l} = -\int r^{l} P_{l}(\cos\theta)\delta\eta_{\mathrm{L}}(\vec{r})\,\mathrm{d}V$$

This integral is evaluated numerically by placing the atomic center of interest at the origin and observing that for a molecule in a $\Sigma$ electronic state, the integrand is independent of the azimuthal angle. The integration over the polar angle is done using a 40-point Gauss−Legendre quadrature,[17] and the resulting radial integration was done using Simpson's rule.[17] The molecular quadrupole moments computed as expectation values and as a sum of local moments agree to five significant figures.

## Discussion

The difference between the molecular quadrupole moment and the sum of the free atom quadrupoles depends on the induced atomic dipole and quadrupole moments. The induced atomic quadrupole contribution to $\delta\Theta^{\mathrm{mol}}$ is simply the sum of the induced atomic quadrupoles, $2\delta\Theta_{\mathrm{L}}$, while the induced atomic dipole contribution depends on the bond length as well as the induced atomic dipole as $-2R\delta\mu_{\mathrm{L}}$. $\delta\Theta^{\mathrm{mol}}$, and its two components, are plotted in Figures 4 and 5 for the molecules of interest. For $N_2$, $O_2$, and $F_2$, and $Cl_2$, both the atomic dipole and quadrupole contribution to $\delta\Theta^{\mathrm{mol}}$ are negative, while for $P_2$ and $S_2$, the two contributions have opposite signs, reflecting the different sense of the induced dipoles relative to the first row sequence and $Cl_2$. $\delta\mu_{\mathrm{L}}$ points toward the region of reduced electron density, and so a positive $\delta\mu_{\mathrm{L}}$ suggests that the electron density shift in the in situ atom is larger on the lone pair side than on the bond side with the converse for a negative $\delta\mu_{\mathrm{L}}$. To pursue this interpretation we plot $\delta\mu_{\mathrm{L}}$ for the molecules of interest in Figures 6 and 7. Note that because $\delta\mu_{\mathrm{L}}$ depends linearly on $\delta\eta_{\mathrm{L}}$ we may partition it into its $\sigma$ and $\pi$ components $\delta\mu_{\mathrm{L}}^{\sigma}$ and $\delta\mu_{\mathrm{L}}^{\pi}$, and these are also shown. Most interestingly both components behave similarly as a function of bond order in the two sequences. $\delta\mu_{\mathrm{L}}^{\sigma}$ is always positive, decreasing with decreasing bond order, tracking the decreasing spatial extent

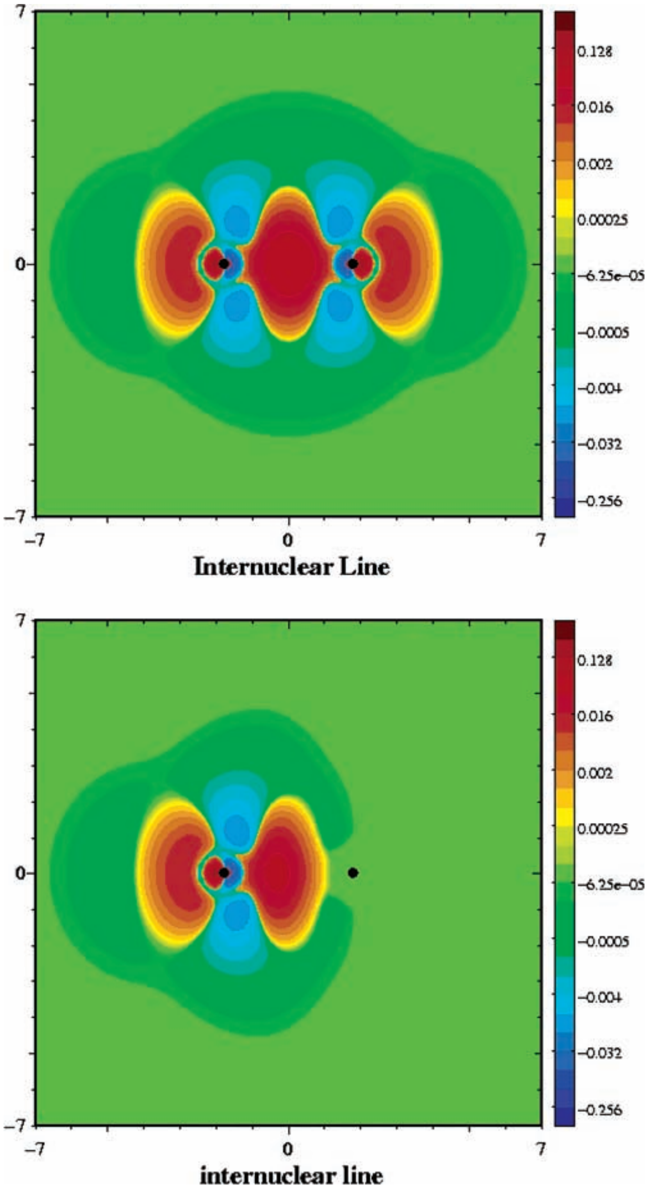

**Figure 3.** Electron density difference in the $S_2$ molecule (top) and in the in situ S atom (bottom).

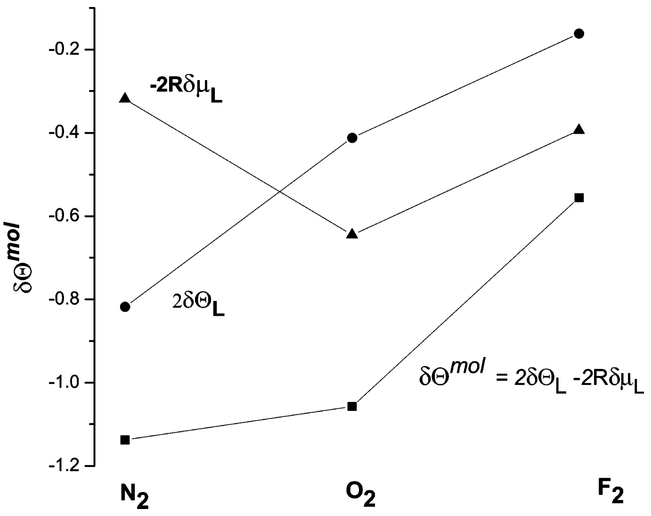

**Figure 4.** Induced molecular quadrupole moment $\delta\Theta^{mol}$ of $N_2$, $O_2$, and $F_2$ and its in situ atomic components.

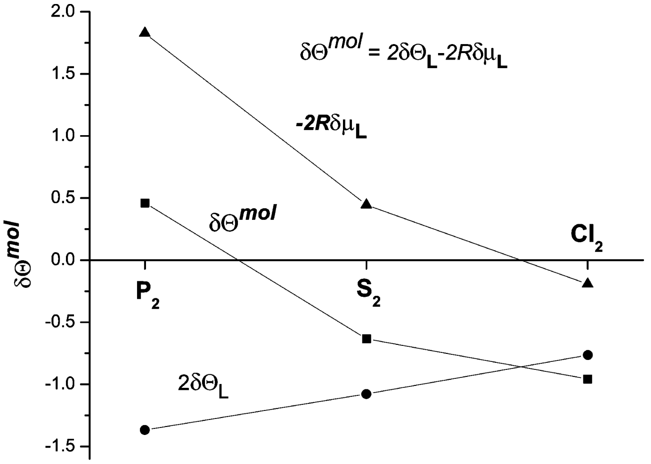

**Figure 5.** Induced molecular quadrupole moment $\delta\Theta^{mol}$ of $P_2$, $S_2$, and $Cl_2$ and its in situ atomic components.

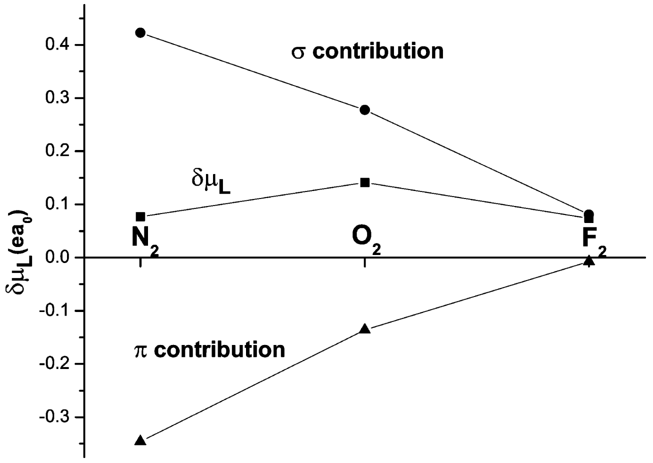

**Figure 6.** Induced atomic dipole moment in $N_2$, $O_2$, $F_2$, and its $\sigma$ and $\pi$ components.

of the lone pair electrons. On the other hand, $\delta\mu_L^\pi$ is always negative and becomes less so as the bond order decreases. This contribution tracks the decreasing importance of $\pi$ bonding with decreasing bond order. The resultant sign of the induced local dipole moment is determined by the relative magnitudes of these shifts.

The induced atomic quadrupoles along with their $\sigma$ and $\pi$ components are shown in Figures 8 and 9 and are always

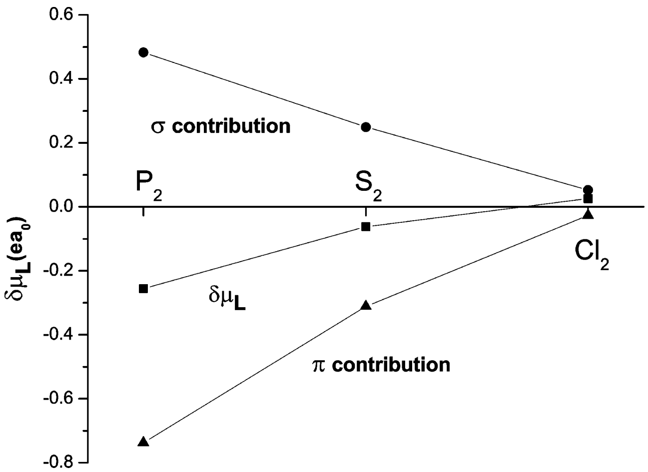

**Figure 7.** Induced atomic dipole moment in $P_2$, $S_2$, and $Cl_2$ and its $\sigma$ and $\pi$ components.

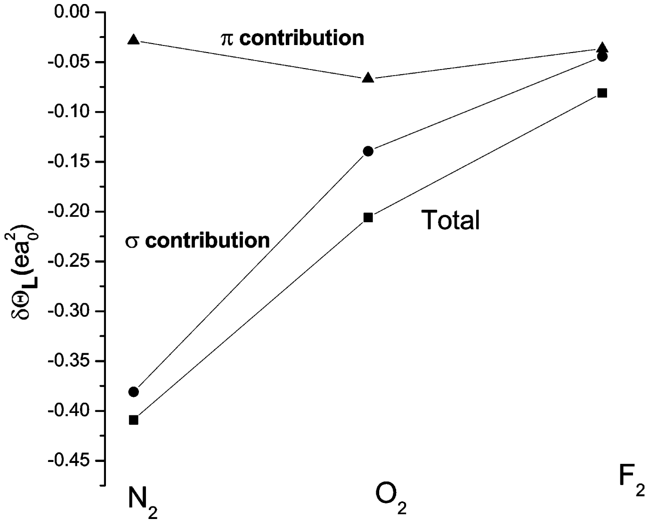

**Figure 8.** Induced atomic quadrupole moment in $N_2$, $O_2$, and $F_2$ and its $\sigma$ and $\pi$ components.

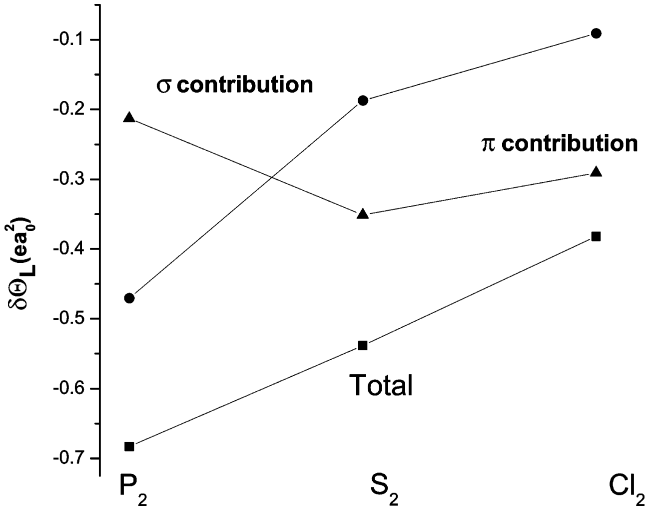

**Figure 9.** Induced local quadrupole moment in $P_2$, $S_2$, and $Cl_2$ and its $\sigma$ and $\pi$ components.

negative, suggesting an elongation of $\delta\eta_L$ in the $\sigma$ direction relative to the $\pi$. $\delta\Theta_L$ becomes less negative for both sequences at the bond order decreases. For the $N_2$, $O_2$, and $F_2$ sequence, the $\pi$ contribution is small and $\delta\Theta_L$ is dominated by the $\sigma$ component. This is not the case for $P_2$, $S_2$, and $Cl_2$, where the

**TABLE 1: In Situ Atomic Moment Composition of the Molecular Quadrupole Moment and Their $\sigma$ and $\pi$ Components as Predicted by the Hirshfeld Partioning of the Electron Density**

| molecule | | $\Theta^{\mathrm{atom}}$ | $\delta\,\Theta_{\mathrm{L}}$ | $\delta\,\mu_{\mathrm{L}}$ | $-2R\delta\,\mu_{\mathrm{L}}$ | $\delta\,\Theta^{\mathrm{mol}}$ | $\Theta^{\mathrm{mol}}$ |
|---|---|---|---|---|---|---|---|
| $N_2$ | total | 0.0 | −0.4091 | 0.0769 | −0.3191 | −1.1374 | −1.1374 |
| | $\sigma$ | | −0.3809 | 0.4228 | −1.7546 | −2.5163 | |
| | $\pi$ | | −0.0283 | −0.3459 | 1.4355 | 1.3790 | |
| $O_2$ | total | 0.3948 | −0.2060 | 0.1414 | −0.6454 | −1.0574 | −0.2678 |
| | $\sigma$ | | −0.1392 | 0.2774 | −1.2665 | −1.5449 | |
| | $\pi$ | | −0.0668 | −0.1360 | 0.6211 | 0.4874 | |
| $F_2$ | total | 0.6170 | −0.0808 | 0.0739 | −0.3943 | −0.5560 | 0.6780 |
| | $\sigma$ | | −0.0443 | 0.0812 | −0.4334 | −0.5220 | |
| | $\pi$ | | −0.0366 | −0.0073 | 0.0391 | −0.0340 | |
| $P_2$ | total | 0.0 | −0.6831 | −0.2555 | 1.8281 | 0.4620 | 0.4620 |
| | $\sigma$ | | −0.4703 | 0.4827 | −3.4543 | −4.3949 | |
| | $\pi$ | | −0.2128 | −0.7382 | 5.2825 | 4.8569 | |
| $S_2$ | total | 1.0125 | −0.5385 | −0.0623 | 0.4446 | −0.6323 | 1.3928 |
| | $\sigma$ | | −0.1871 | 0.2492 | −1.7793 | −2.1534 | |
| | $\pi$ | | −0.3514 | −0.3115 | 2.2238 | 1.5211 | |
| $Cl_2$ | total | 1.6231 | −0.3821 | 0.0257 | −0.1928 | −0.9569 | 2.2892 |
| | $\sigma$ | | −0.0912 | 0.0525 | −0.3944 | −0.5767 | |
| | $\pi$ | | −0.2909 | −0.0268 | 0.2016 | −0.3802 | |

**TABLE 2: Comparison of the Hirshfeld and DMA in Situ Atomic Moments**

| | $\delta\Theta^{\mathrm{mol}} = \Theta^{\mathrm{mol}} - 2\Theta^{\mathrm{atom}}$ | | $-R\delta\mu_{\mathrm{L}}$ | | $\delta\Theta_{\mathrm{L}}$ | | $\delta\mu_{\mathrm{L}}$ | |
|---|---|---|---|---|---|---|---|---|
| molecule | Hirshfeld | DMA | Hirshfeld | DMA | Hirshfeld | DMA | Hirshfeld | DMA |
| $N_2$ | −1.1374 | −1.3750 | −0.1596 | −0.4563 | −0.4091 | −0.1125 | 0.0769 | 0.2119 |
| $O_2$ | −1.0574 | −1.0574 | −0.3227 | −0.6381 | −0.2060 | 0.1094 | 0.1414 | 0.2795 |
| $F_2$ | −0.5560 | −0.5560 | −0.1972 | −0.3683 | −0.0808 | 0.0903 | 0.0739 | 0.1380 |
| $P_2$ | 0.4620 | 0.4619 | 0.9141 | 0.9715 | −0.6831 | −0.7406 | −0.2555 | −0.2715 |
| $S_2$ | −0.6323 | −0.6333 | 0.2223 | 0.0185 | −0.5385 | −0.3351 | −0.0623 | −0.0052 |
| $Cl_2$ | −0.9569 | −0.9567 | −0.0964 | −0.4338 | −0.3821 | −0.0446 | 0.0256 | 0.1155 |

$\pi$ contribution is much more significant. The $\sigma$ and $\pi$ contributions in both sequences vary in a similar way with bond order. Indeed, the $\sigma$ component is numerically comparable in both sequences, and the primary difference is the much larger $\pi$ contribution in the $P_2$ sequence. We collect in Table 1 the in situ atomic dipole and quadrupole moments of these molecules, as well as their $\sigma$ and $\pi$ components, and augment them with the corresponding results for $P_2$, $S_2$, and $Cl_2$.

It is interesting that the quadrupole moment of $P_2$ is positive while that of $N_2$ is negative. In a previous study[13] we have identified this with the different contribution of the $\pi$ electrons, and the present study permits us to sharpen this interpretation and assign the difference in the $\pi$ contribution to the in situ atomic dipole moment. The $\sigma$ contribution to the in situ atomic dipole always points toward the molecular midpoint while the $\pi$ contribution points toward the lone pair region. In $N_2$ the $\pi$ contribution is less than that of the $\sigma$ electrons while in $P_2$ the $\pi$ contribution is much larger. This difference changes the sign of the contribution of the in situ atomic dipole to the molecular quadrupole moment and results in $N_2$ and $P_2$ having molecular quadrupole moments with opposite signs.

## Comparison with the Distributed Multipole Analysis

The distributed multipole moment analysis of Stone[1,7] is an alternative method of defining localized atomic moments. The DMA approach, as generally used, depends on using Gaussian basis sets and allocates these functions to the nuclei in this system according to an algorithm, which depends on the exponents of the Gaussians. Accordingly, the DMA can be sensitive to the composition of the basis, and the computed local moments may not reflect the convergence properties of the electron density. In contrast, the Hirshfeld approach partitions the electron density directly and it is less sensitive to the vagaries of basis sets and the associated local moments should reflect the convergence properties of the electron density. In a previous study[13] we have compared the convergence properties of the two methods for the first six local moments of $N_2$, $O_2$, and $F_2$.

Since both partitionings result in the same molecular quadrupole moment, the atomic moments are constrained by

$$\delta\Theta^{\mathrm{mol}} = 2\delta\Theta_{\mathrm{L}} - 2R\delta\mu_{\mathrm{L}}$$

In Table 2 we collect the Hirshfeld and DMA results for the induced atomic dipole and quadrupole moments for the two sequences. Both methods result in induced atomic dipoles with the same sign but, with the exception of $P_2$, they have very different magnitudes. The induced quadrupole moments vary significantly, except once again for $P_2$. The different physical content of the two partitionings is evident. For example, the change in the quadrupole moment of $Cl_2$ relative to the sum of the quadrupole moments of the separated atoms, $\delta\Theta^{\mathrm{mol}}$, is $-0.957$ $ea_0^2$. The DMA analysis suggests that most of this, $-0.8676$ $ea_0^2$, comes from an induced dipole moment on the two Cl atoms, with $-0.0892$ $ea_0^2$ coming from the induced quadrupole moments on the two Cl atoms. In contrast, the Hirshfeld analysis allocates $-0.1928$ $ea_0^2$ from the induced dipoles and $-0.7642$ $ea_0^2$ from the induced quadrupoles. Since both methods give the same total molecular moment the question at hand is whether one set of atomic moments is preferable. This seems to be a question that will be answered by appealing to chemical intuition and experience but, unlike the situation with atomic charges, there seems to be little experience or intuition about higher moments of in situ atoms. One argument in favor of the Hirshfeld partitioning is that these local moments converge to values representative of the accuracy of the electron density used in their calculation. This in turn permits the development of an intuition as to the magnitudes and algebraic signs of these atomic moments and their relation to the electronic structure of the corresponding molecules. We are pursuing this goal.

## Summary

The magnitude and algebraic sign of the molecular quadrupole moments of the homonuclear diatomic molecules $N_2$, $O_2$, $F_2$, $P_2$, $S_2$, and $Cl_2$ have been analyzed by expressing them as a sum of the quadrupole moments of the free atoms and an induced molecular quadrupole due to bond formation. This induced molecular quadrupole, $\delta\Theta^{\text{mol}}$, is further analyzed in terms of in situ atomic dipole and quadrupole moments constructed following the electron partitioning method suggested by Hirshfeld, and is expressed as $\delta\Theta^{\text{mol}} = 2\delta\Theta_L - 2R\delta\mu_L$. We find that the induced atomic quadrupole moments are all negative while $\delta\mu_L$ is positive for $N_2$, $O_2$, $F_2$, and $Cl_2$ and negative for $P_2$, and $S_2$. These signs in turn are shown to be a consequence of the opposite contributions of the $\sigma$ and $\pi$ electrons. These in situ moments are interpreted in terms of the $\sigma$ and $\pi$ character of the chemical bonds and are compared with those predicted by the DMA method of Stone. Both methods result in in situ atomic dipoles with the same sign but with the exception of $P_2$ they have significantly different magnitudes. The induced atomic quadrupole moments also vary significantly except again for $P_2$. Since both the Hirshfeld and DMA methods give the same molecular moments, we suggest that deciding which set of atomic moments is preferable will be answered by appealing to chemical intuition and experience. A strong argument in favor of the Hirshfeld moments is that they converge to values representative of the accuracy of the density used in their calculation. This in turn permits the development of an intuition about the relationship of the atomic moments to the electronic structure of the corresponding molecules.

## References and Notes

(1) Stone, A. J. *The Theory of Intermolecular Forces*; Clarendon Press: Oxford, U.K., 1996.

(2) Voronoi, G. F.; Reine, Z. *Angew. Math.* **1908**, *134*, 198.

(3) Guerra, C. F.; Handgraaf, J.; Baerends, E. J.; Bickelhaupt, F. M. *J. Comput. Chem.* **2003**, *25*, 189.

(4) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.

(5) Hirshfeld, F. L. *Theo. Chim. Acta* **1977**, *44*, 129.

(6) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. (b) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841. (c) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2338. (d) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2343.

(7) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56*, 1047.

(8) Davidson, E. R.; Chakravorty, S. *Theo. Chim. Acta* **1992**, *83*, 319.

(9) Harrison, J. F. *Mol. Phys.* **2005**, *103*, 1099.

(10) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.

(11) Harrison, J. F. *J. Chem. Phys.* **2003**, *119*, 8763.

(12) Lawson, D. B.; Harrison, J. F. *J. Phys. Chem. A* **1997**, *26*, 4781.

(13) Lawson, D. B.; Harrison, J. F. *Mol. Phys.* **1998**, *93*, 519.

(14) Gearhart, D. J.; Harrison, J. F.; Hunt, K. L. C. *Int. J. Quantum Chem.* **2003**, *95*, 697.

(15) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(16) Werner, H. J.; Knowles, P. J.; Almof, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Lindh, R.; Mura, M. E.; Thorsteinsson, T. MOLPRO, a package of ab initio programs.

(17) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover Publications: New York, 1970.