Acta Cryst. (1999). A**55**, 965–967

On the errors in molecular dipole moments derived from accurate diffraction data

Philip Coppens,[a]* Anatoliy Volkov,[a] Yuriy Abramov[a] and Tibor Koritsanszky[b] *at* [a]*Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14260-3000, USA, and* [b]*Department of Chemistry, University of the Witwatersrand, Johannesburg, WITS 2050, South Africa. E-mail: coppens@acsu.buffalo.edu*

(*Received 13 July 1999; accepted 15 July 1999*)

Abstract

The error in the molecular dipole moment as derived from accurate X-ray diffraction data is shown to be origin dependent in the general case. It is independent of the choice of origin if an electroneutrality constraint is introduced, even when additional constraints are applied to the monopole populations. If a constraint is not applied to individual moieties, as is appropriate for multicomponent crystals or crystals containing molecular ions, the geometric center of the entity considered is a suitable choice of origin for the error treatment.

1. Errors in dipole moments

As the derivation of electrostatic moments from accurate diffraction data has attracted considerable attention since Stewart reported the first X-ray dipole moment for the molecule of uracil (Stewart, 1970) (see for example Spackman, 1992; Coppens, 1997), the uncertainty in the derived quantities merits consideration. Errors in experimental dipole moments are often quoted in the literature, but in the general case the errors in the electrostatic moments are origin-dependent, as pointed out by Spackman (1992). This communication examines the origin dependence of the experimental error in a molecular dipole moment.

It can easily be shown that the dipole moment $\boldsymbol{\mu}$ of a neutral entity is independent of origin. Since $\boldsymbol{\mu}$ is given by

$$\boldsymbol{\mu} = \sum_{i=1}^{N} q_i \mathbf{r}_i + \boldsymbol{\mu}_i, \tag{1}$$

where q_i is the net charge on atom i located at $\mathbf{r}_i$ and $\boldsymbol{\mu}_i$ its local atomic dipole, a shift of origin $\mathbf{r}_o$ leads to

$$\boldsymbol{\mu}' = \sum_{i=1}^{N} [\mathbf{q}_i(\mathbf{r}_i - \mathbf{r}_o) + \boldsymbol{\mu}_i] = \sum_{i=1}^{N} (\mathbf{q}_i \mathbf{r}_i + \boldsymbol{\mu}_i) - \mathbf{r}_o \sum_{i=1}^{N} \mathbf{q}_i. \tag{2}$$

Thus, $\boldsymbol{\mu}' = \boldsymbol{\mu}$ for any neutral entity. In general, a moment is origin independent as long as the moments of lower order of the entity being considered are zero. Thus, for a charged entity the second term on the right-hand side of (2) does not vanish and the moment is origin dependent. In this case, the accepted convention is to refer the dipole moment to the center of mass as origin. As it is desirable that the *errors* associated with the experimental results be reported, their behavior as a function of the origin choice must be analyzed.

In general, the variances and covariances $\mathbf{M}_\mu$ of derived quantities μ are given by

$$\mathbf{M}_\mu = \mathbf{d}\mathbf{M}_x\mathbf{d}^T \tag{3}$$

(see for example Coppens, 1997), in which $\mathbf{M}_x$ is the $m \times m$ variance–covariance matrix of the least-squares variables, and $\mathbf{d}$ a row vector with m elements in the case of a molecular dipole moment or a vector with $3 \times m$ elements in the case that the components of the dipole moment are to be calculated. The elements of $\mathbf{d}$ are given by

$$\mathbf{d}_j = \partial Q/\partial x_j, \tag{4}$$

where Q is the quantity to be derived and the x_j are the least-squares variables.

For the dipole moment μ, the pertinent variables are the positional coordinates of the atoms, the valence monopole populations, and the populations P_{10} and $P_{11\pm}$ of the dipolar terms of the multipole expansion. We will consider the monopole contributions, which dominate the total molecular dipole moment.† Furthermore, as the relative errors in the monopole populations from a diffraction experiment are relatively large compared with those in the more accurately determined positional parameters, we will concentrate our attention on the effect of the charge uncertainties.

With these assumptions, we obtain, with

$$\partial\mu_x/\partial q_i = x_i \tag{5}$$

for the error in the x component of the molecular dipole moment,

$$\sigma^2(\mu_x) = \sum_i \sum_j x_i x_j \rho(q_i q_j), \tag{6}$$

where $\rho(q_i q_j)$ represents the variances ($i = j$) and covariances ($i \neq j$) of the net atomic charges on atoms i and j.

For a shift of origin in the x direction equal to x_o, we obtain

$$\sigma^{2\prime}(\mu_x) = \sum_i \sum_j (x_i - x_o)(x_j - x_o)\rho(q_i q_j), \tag{7}$$

the difference between the two being given by

$$\begin{aligned}\Delta\sigma^2(\mu_x) &= \sigma^{2\prime} - \sigma^2 \\ &= x_o^2 \sum_i \sum_j \rho(q_i q_j) - x_o \sum_i \Big[x_i \sum_j \rho(q_i q_j)\Big] \\ &\quad - x_o \sum_i \Big[x_j \sum_j \rho(q_i q_j)\Big] \\ &= x_o^2 \sum_i \sum_j \rho(q_i q_j) - 2x_o \sum_i \Big[x_i \sum_j \rho(q_i q_j)\Big],\end{aligned} \tag{8}$$

which depends both on the shift x_o and on the atomic coordinates $x_{\rm i}$.

We are interested in the shift x_o, which minimizes the error in the dipole moment, and thus in the value of x_o for which

---

† The contribution from the atomic dipole moments to the total dipole moment is origin independent, as it is obtained by a simple summation over the pseudoatoms.

Acta Crystallographica Section A
ISSN 0108-7673 © 1999

$$\partial\sigma^{2\prime}/\partial x_o = 0. \tag{9}$$

With (7), we obtain

$$\partial\sigma^{2\prime}/\partial x_o = 2x_o \sum_i \sum_j \rho(q_iq_j) - 2\sum_i \left[x_i \sum_j \rho(q_iq_j)\right] = 0 \tag{10}$$

or, for N atoms, with the assumption that all variances σ^2 ($i = j$) and covariances γ ($i \neq j$) are equal:

$$\begin{aligned} \mathrm{d}\sigma^{2\prime} &= 2x_oN\sigma^2 + 2x_oN(N-1)\gamma \\ &\quad - 2\sigma \sum_{i=1,N} x_i - 2(N-1)\gamma \sum_i x_i \\ &= 0 \end{aligned} \tag{11}$$

or

$$2x_oN\sigma^2 + 2x_oN(N-1)\gamma = 2\sigma^2 \sum_i x_i + 2(N-1)\gamma \sum_i x_i \tag{12}$$

or

$$x_oN[2\sigma^2 + 2(N-1)\gamma] = \sum_i x_i[2\sigma^2 + 2(N-1)\gamma], \tag{13}$$

which gives for the shift that minimizes the molecular-dipole-moment error

$$x_o = \sum_i x_i \Big/ N. \tag{14}$$

Thus, under the approximations used here, the dipole-moment error is minimized when the dipole moment is referred to the geometric center of the molecule.

However, for one-component crystals, it is common to apply a molecular eletroneutrality constraint. In this case, the dipole moment becomes origin independent, as shown in the following.

Following Hamilton (1964), the variance–covariance matrix $\overline{\mathbf{M}_x}$ corresponding to the constrained parameter estimates $\bar{\mathbf{x}}$ is

$$\overline{\mathbf{M}_x} = \mathbf{M}_x - \mathbf{M}_x\mathbf{C}^T(\mathbf{C}\mathbf{M}_x\mathbf{C}^T)^{-1}\mathbf{C}\mathbf{M}_x, \tag{15}$$

where $\mathbf{C}$ is the matrix of constraints. If the only constraint applied is to keep the unit cell neutral

$$\mathbf{C} = \mathbf{c}, \tag{16}$$

where $\mathbf{c}$ is a row vector with the nonzero components corresponding to atomic monopole populations equalling 1, then

$$\overline{\mathbf{M}_x} = \mathbf{M}_x - (\mathbf{c}\mathbf{M}_x\mathbf{c}^T)^{-1}\mathbf{M}_x\mathbf{c}^T\mathbf{c}\mathbf{M}_x, \tag{17}$$

since

$$(\mathbf{c}\mathbf{M}_x\mathbf{c}^T)^{-1} = \left(\sum_i \sum_j \rho_{ij}\right)^{-1} \tag{18}$$

is a scalar. Thus,

$$\mathbf{c}\overline{\mathbf{M}_q} = \mathbf{c}\mathbf{M}_q - \mathbf{c}\mathbf{M}_q = \mathbf{0} \tag{19a}$$

$$\overline{\mathbf{M}_q}\mathbf{c}^T = \mathbf{M}_q\mathbf{c}^T - \mathbf{M}_q\mathbf{c}^T = \mathbf{0}^T \tag{19b}$$

$$\mathbf{c}\overline{\mathbf{M}_q}\mathbf{c}^T = \mathbf{c}\mathbf{M}_q\mathbf{c}^T - \mathbf{c}\mathbf{M}_q\mathbf{c}^T = 0, \tag{19c}$$

where $\mathbf{M}_q$ is the variance–covariance matrix of the atomic charges, and $\mathbf{c}$ has been truncated by omitting the zeros corresponding to the noncharge variables.

Equations (19*a*) and (19*b*) imply that the sum over every column (or row) of the constrained variance–covariance matrix equals zero, while (19*c*) gives the corresponding result for the sum over all the elements. It follows that $\Delta\sigma^2(\mu_x)$ as expressed by equation (8) equals zero.†

However, in almost all charge-density analyses, additional constraints are applied, restricting chemically equivalent atoms to carry identical charges. In that case,

$$\mathbf{C} = \begin{pmatrix} \mathbf{c} \\ \mathbf{B} \end{pmatrix}, \tag{20}$$

where $\mathbf{B}$ is the block matrix corresponding to the chemical constraints. In analogy to equation (19):

$$\mathbf{C}\overline{\mathbf{M}_x} = \mathbf{0}, \quad \overline{\mathbf{M}_x}\mathbf{C}^T = \mathbf{0}^T \quad \text{and} \quad \mathbf{C}\overline{\mathbf{M}_x}\mathbf{C}^T = 0, \tag{21}$$

because from (15)

$$\mathbf{C}\overline{\mathbf{M}_x} = \mathbf{C}\mathbf{M}_x - \mathbf{C}\mathbf{M}_x\mathbf{C}^T(\mathbf{C}\mathbf{M}_x\mathbf{C}^T)^{-1}\mathbf{C}\mathbf{M}_x = \mathbf{C}\mathbf{M}_x - \mathbf{C}\mathbf{M}_x = \mathbf{0}. \tag{22}$$

This result also implies that

$$\mathbf{c}\overline{\mathbf{M}_q} = \mathbf{0}, \quad \overline{\mathbf{M}_q}\mathbf{c}^T = \mathbf{0} \quad \text{and} \quad \mathbf{c}\overline{\mathbf{M}_q}\mathbf{c}^T = 0, \tag{23}$$

which means that the error in the dipole moment is origin independent whatever constraint has been applied in addition to the molecular electroneutrality requirement.

To verify the independence of the dipole-moment error for a neutral molecule, we have calculated the error in the molecular dipole moment of 4-amino-4′-nitrobiphenyl, for which the charge density was recently determined using 20 K synchrotron data (Volkov *et al.*, 1999). The charge-density analysis was performed with the program package *XD* (Koritsanszky *et al.*, 1997) and the molecule was constrained to be neutral. The refinement included a number of chemical equivalent constraints. The origin of the dipole moment was varied along a line connecting the two nitrogen atoms at opposite ends of the molecule, starting and ending 5 Å from N(O_2) and N(H_2), respectively. The results confirm the origin independence of the molecular dipole-moment error even when chemical constraints are applied.‡

In summary, the dipole-moment error is origin independent when a molecular neutrality constraint has been applied. But in case such a constraint is inappropriate, or has not been applied, the origin to which electrostatic moments are referred must be carefully selected to give an unambiguous representation of the uncertainties associated with the experimental result. The geometric center as defined here is a suitable, though not unique, choice for the error treatment, and thus also for the origin to which the dipole moment is referred.

We conclude that, except in the case of a neutral molecule for which all atomic charges have been constrained to preserve neutrality, the origin must be specified for both the dipole moment and the associated standard deviations.

APPENDIX *A*

An alternative proof of $\mathbf{C}\overline{\mathbf{M}_x} = \mathbf{0}$ (equation 19*a*) is as follows.

The variance $\rho(i, i)$ is defined as

$$\rho(i, i) = E[\{x(i) - m(i)\}^2], \tag{24}$$

---

† An alternative derivation of equation (19) is given in Appendix *A*.

‡ The current version of *XD* (version 1.2) does not treat the error in the dipole moment appropriately in case chemical constraints have been applied. This error will be corrected in a coming release.

in which E represents the expectation value and m the mean of the variable.

Similarly, for the covariance $\rho(i, j)$:

$$\rho(i, j) = E[\{x(i) - m(i)\}\{x(j) - m(j)\}]. \qquad (25)$$

The sum over the elements of a row of the variance–covariance matrix is thus equal to

$$\begin{aligned}\sum_i \rho(i, j) &= E[\{x(i) - m(i)\}^2] + E[\{m(i) - m(i)\}\{x(j) - m(j)\}] \\ &= E\Big[\{x(i) - m(i)\} \sum_j \{x(j) - m(j)\}\Big]. \qquad (26)\end{aligned}$$

Because of the constraint, for the atomic charges the sum over j equals zero and thus $\sum_i \rho(i, j) = 0$.

Support of this work by the National Science Foundation (CHE9615586) and the Division of Basic Energy Sciences of the US Department of Energy (DE-FG02-86ER45231) is gratefully acknowledged.

References

Coppens, P. (1997). *X-ray Charge Densities and Chemical Bonding.* Oxford University Press.

Hamilton, W. C. (1964). *Statistical Methods in the Physical Sciences.* New York: Ronald Press.

Koritsanszky, T., Howard, S., Su, Z., Mallinson, P. R., Richter, T. & Hansen, N. K. (1997). *XD. Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data.* Free University of Berlin, Germany.

Spackman, M. A. (1992). *Chem. Rev.* **92**, 1769–1797.

Stewart, R. F. (1970). *J. Chem. Phys.* **53**, 205–213.

Volkov, A., Wu, G. & Coppens, P. (1999). *J. Synchrotron Rad.* In the press.