

## Hellmann-Feynman Constraint on Charge Densities, an Experimental Test

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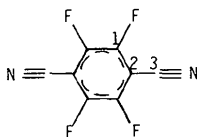
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### Abstract

A deformation density refinement on tetrafluoroterephthalonitrile against the low-temperature X-ray data of Seiler, Schweizer & Dunitz [*Acta Cryst.* (1984), B40, 319-327] has been constrained to yield vanishing electric fields at all nuclear positions. The constraint has produced sharp dipoles on the atoms, correlated with small atomic displacements, but has left the rest of the deformation map virtually unaltered.

Schwarzenbach & Lewis (1982) have proposed that charge-density models for refinement against X-ray diffraction data may be constrained to make the electric field vanish at every nucleus in accordance with the Hellmann-Feynman theorem. Theoretical studies on small molecules have shown that a major contribution to the field at an atomic nucleus often arises from a very sharp polarization of its own cusp density (Hirshfeld & Rzotkiewicz, 1974). Hence the possibility of such polarization must be allowed in the deformation model if it is to satisfy the Hellmann-Feynman constraint in a realistic manner. However, the coefficients of any sharp dipole functions would, if refined against X-ray data alone, be strongly correlated with the corresponding atomic coordinates and thus virtually indeterminate. This means that we may expect these coefficients to be determined, in effect, solely by the Hellmann-Feynman constraint and to have no appreciable effect on the X-ray structure factors or on the other charge-density parameters.

An excellent opportunity to check this expectation was provided by the very precise low-temperature X-ray data for tetrafluoroterephthalonitrile measured by Dunitz and coworkers (Dunitz, Schweizer & Seiler,



1982; Seiler, Schweizer & Dunitz, 1984). A standard deformation refinement with the program *LSEXP* (Hirshfeld, 1977) had led to a highly accurate static deformation density in nearly quantitative agreement

with experimental and theoretical maps for several related molecules (Hirshfeld, 1984). The map showed very little density in the C-F bond and the electric field at the F nucleus, derived from this deformation density, was found to be several times more repulsive than in the promolecule. It was concluded that the required electrostatic balance must come from a strong forward polarization in the immediate vicinity of the nucleus, too sharply localized to be detectable by the X-ray experiment.

The deformation model already contained, in the expansion of the static deformation density, cusp functions on the several atoms of the form

$$\rho_0(\mathbf{r}) = N_0 \exp(-\alpha_0 r),$$

where the exponential factor  $\alpha_0$  is given by the Kato cusp condition  $\alpha_0 = 2Z/a_0$ . These functions have the same form as the cusp densities of the free atoms (Steiner, 1963). Polarization of such a cusp density may be most simply expressed by addition of a sharp dipole function of the form

$$\rho'_0(\mathbf{r}) = N'_0 r \exp(-\alpha_0 r) \cos \theta,$$

where the angle  $\theta$  is measured from an axis marking the direction of polarization. This matches the relation derived by Bingel (1967) for the Coulomb cusp in an electric field due to other nuclei and electrons in the molecule.

Accordingly, the standard deformation model was extended to include a sharp dipole function  $\rho'_0$  on each atomic center, whose coefficient was constrained to yield a vanishing net field at the nucleus. The net field  $E_a$  at nucleus  $a$  comprises a sum of contributions  $E_{p,a}$  from the promolecule and  $E_{\Delta,a}$  from the deformation density. Three approximations greatly simplified the present calculations:

(a) Since each atom lies on a local twofold axis of pseudosymmetry, the polar axes of the functions  $\rho'_0$  were fixed to lie along these pseudosymmetry axes and the Hellmann-Feynman constraint was imposed only on the field components along these axes.

(b) The fields due to the promolecule were derived from the vibration-corrected molecular dimensions from the original unconstrained refinement.

(c) The value of the deformation field  $E_{\Delta,a}$  at each atom was calculated from the deformation functions centered on that atom alone; these contribute fields that are many times larger than those arising from

multipole functions on neighboring atomic centers. The polar functions

$$\rho_{1,k} = (\alpha^4/12\pi)r \exp(-\alpha r) \cos \theta_k,$$

$$\rho_{3,k} = (\alpha^6/120\pi)r^3 \exp(-\alpha r) \cos^3 \theta_k$$

produce electric fields at the origin of magnitudes

$$E_1 = \alpha^2/9, E_3 = \alpha^2/25,$$

respectively, in the appropriate  $k$  directions. The cusp polarizing functions  $\rho'_0$  are, of course, similar to  $\rho_{1,k}$  but for the larger exponents  $\alpha_0$ .

The coefficient  $c'_0$  of each of the functions  $\rho'_0(\mathbf{r})$  was expressed, *via* the Hellmann-Feynman constraint, as an explicit function of the coefficients and the exponent  $\alpha$  of the  $\rho_{1,k}$  and  $\rho_{3,k}$  functions on the same atom. The derivatives of the structure factors with respect to these independent parameters were adjusted accordingly to take account of the contributions of the dependent parameters  $c'_0$ . When the sharp dipoles were introduced, with all other parameters at their previous values, the weighted discrepancy index  $R_w(F^2)$  showed an expected moderate rise from 0.01893 to 0.01939. But refinement of all parameters under the Hellmann-Feynman constraint brought this back to its original value of 0.01893. The only parameter shifts that exceeded their estimated standard deviations were the coordinates of atoms C(3)

Table 1. *Electric fields in radial directions at several atomic nuclei ( $e\text{\AA}^{-2} \times 10^3$ ), arising from promolecule ( $E_p$ ) and from deformation density ( $E_\Delta$ ) after unconstrained and constrained refinements, the latter divided into contributions from diffuse multipoles ( $E_{\text{dif}}$ ) and from sharp dipoles ( $E_{\text{sh}}$ )*

Estimated standard deviations are in parentheses - note that as the sum  $E_\Delta = E_{\text{dif}} + E_{\text{sh}}$  was constrained to equal  $-E_p$ ,  $\sigma(E_{\text{sh}}) = \sigma(E_{\text{dif}})$ .

		Unconstrained	Constrained refinement	
	$E_p$	$E_\Delta$	$E_{\text{dif}}$	$E_{\text{sh}}$
C(1)	143	-546 (73)	-539 (69)	396
C(2)	31	-693 (172)	-703 (169)	672
C(3)	-240	776 (139)	773 (145)	-533
F	314	1588 (327)	1532 (319)	-1845
N	640	613 (421)	613 (431)	-1252

and F, which moved 0.0006 (3) and 0.0007 (2)  $\text{\AA}$ , respectively, in directions close to radially outward. Changes in the static deformation density were virtually imperceptible except for the innermost contours around the nuclear sites (Fig. 1).

Table 1 shows the several contributions to the electric fields at the nuclei before and after introduction of the Hellmann-Feynman constraint. While the standard refinement severely violates the requirement that  $E_p + E_\Delta = 0$ , the apparent precision of  $E_\Delta$  is very poor since these quantities are most sensitive to static deformation features very close to the nuclei. Inclusion of the sharp dipole functions under the Hellmann-Feynman constraint causes insignificant changes in the coefficients of the standard deformation functions and, therefore, in their contributions  $E_{\text{dif}}$  to the fields at the nuclei. The electrostatic imbalance from the unconstrained refinement is remedied almost entirely by the fields  $E_{\text{sh}} = c'_0 \alpha_0^2/9$  arising from the cusp polarization. Accordingly, the constrained refinement has done little more than superimpose a set of sharp dipoles, of predictable magnitudes, on the unconstrained static deformation density.

The Fourier transforms of the functions  $\rho'_0(\mathbf{r})$  are given by

$$\varphi'_0(S) = (8i/3)x \cos \psi / (1+x^2)^3$$

(Hirshfeld, 1971), where  $S = 2 \sin \theta/\lambda$ ,  $x = 2\pi S/\alpha_0 = \pi a_0 S/Z$ , and  $\psi$  is the angle between the scattering vector  $S$  and the axis of polarization. These imaginary scattering factors have their maximum amplitudes at  $S = 0.2690Z \text{\AA}^{-1}$ , which for C, N, and F equals, respectively, 1.614, 1.883, and 2.421  $\text{\AA}^{-1}$ . With the X-ray data of Dunitz *et al.* extending to  $S = 2.30 \text{\AA}^{-1}$ , only for F does the scattering factor of the cusp polarizing function, before vibrational smearing, reach its maximum value beyond the limit of the input data. And even for the F atom, the mean square vibrational amplitude - 0.00845  $\text{\AA}^2$  in the C-F bond direction - shifts the maximum in the thermally smeared scattering factor down to 1.379  $\text{\AA}^{-1}$ . Thus

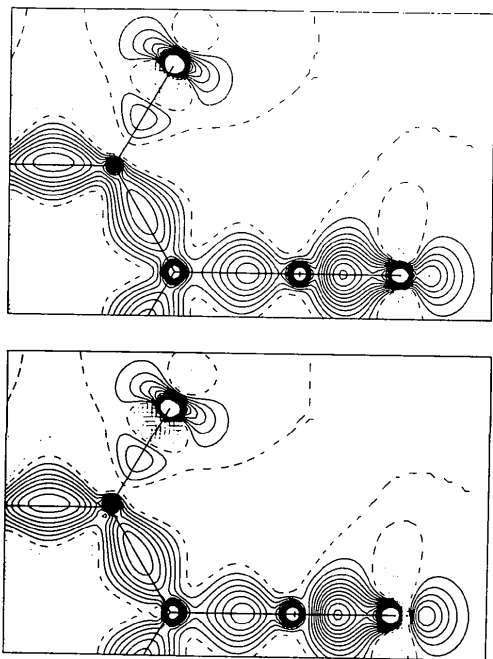


Fig. 1. Static deformation density in mean molecular plane from unconstrained (top) and Hellmann-Feynman-constrained (bottom) refinements. Contour interval 0.1  $e\text{\AA}^{-3}$ .

the insensitivity of  $R_w(F^2)$  to the polarizing functions is evidently attributable primarily to their strong correlations with the atomic coordinates rather than to their inaccessibility with the present X-ray data. These correlations are a consequence of an overall similarity between the scattering factors  $\varphi'_0$  and the derivatives of the structure factors (of the static density) with respect to the corresponding atomic coordinates. They are therefore unlikely to be substantially reduced even at much lower temperatures and with much higher resolution. A more promising strategy might be the collection of extremely precise neutron data sufficient to establish the nuclear positions to within about 0.0001 Å. If the core polarization is indeed of the form given by the functions  $\rho'_0$  defined above, an uncertainty  $\Delta r$  in atomic position corresponds to an approximate uncertainty in electric field, due to the correlation between them, of

$$\Delta E \sim 2Z^3 \Delta r / 3a_0^3.$$

This assumes an error in the coefficient of  $\rho'_0$  sufficient

to displace the centroid of the two-electron core by  $\sim \Delta r$ . For the atoms C, N, and F, an error in position of 0.0001 Å as derived by neutron diffraction would lead to an error of about 0.10, 0.15, and 0.33 eÅ<sup>-2</sup>, respectively, in the field at the nucleus from this source alone if the coefficients  $c'_0$  were refined without constraint.

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