letters to the editor

Comment on *On the calculation of the electrostatic potential, electric field and electric field gradient from the aspherical pseudoatom model* by Volkov, King, Coppens & Farrugia (2006)

Mark A. Spackman

Chemistry - M313, School of Biomedical, Biomolecular & Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia. Correspondence e-mail: mas@cyllene.uwa.edu.au

The determination of relevant physical properties from the aspherical pseudoatom model and comparison with independent experimental and/or computational results remains a key objective of many modern charge-density studies based on high-resolution low-temperature X-ray diffraction data. The recent paper published by Volkov, King, Coppens & Farrugia [*Acta Cryst.* (2006), A62, 400–408] (referred to as VKCF in the following) represents an important step towards realizing this goal in routine charge-density analyses. It presented new and improved formulae for calculating the electrostatic potential (ESP), electric field (EF) and electric field gradient (EFG) from the aspherical pseudoatom model, with applications made to both experimental and model sets of structure factors. Of considerable practical importance, these expressions have been incorporated in a new version of *XDPROP*, part of the *XD* package now in widespread use (Koritsanszky *et al.*, 2003). This Letter aims to complement the work described by VKCF by providing a broader perspective on some of the issues raised in that work, and commenting on some of the results presented by them.

VKCF write (p. 401) that 'Various methods for calculating the ESP from X-ray diffraction data have been described and consequently applied in the literature. These methods can basically be split into two very different groups: (i) directly from experimentally measured structure factors (Bertaut, 1978; Schwarzenbach & Thong, 1979; Stewart, 1979) and (ii) from static models of the electron density.' It is important to recognize that the group identified as (i) is not restricted to experimental measurements, and can be applied much more broadly to any set of valid structure factors (*e.g.* static, computed from the aspherical pseudoatom model, as discussed further below). Moreover, there is an intimate relationship between approaches (i) and (ii), and many properties *in the crystal* are most advantageously computed *via* a combination of the two approaches. This aspect of the determination of the ESP, EF and EFG from X-ray diffraction data was clearly outlined several decades ago by R. F. Stewart, and Stewart's paper cited by VKCF discussed the determination of 'inner moments' (*i.e.* averages that involve negative powers of **r**, as opposed to 'outer moments' such as the dipole and quadrupole moments, which involve zero and positive powers of **r**) from X-ray diffraction data, with a focus on Fourier summation techniques (Stewart, 1979). That work presented comprehensive expressions for the determination of the ESP, EF, EFG, charge density (*i.e.* including nuclei), gradient of the EFG and gradient of the charge density. Importantly, it also provided details of the method (which can be generalized to inner moments of higher order), discussed the origin term for the ESP, the finite resolution of experimental data (and hence convergence behaviour of the various properties and the effects of series termination), and observed that results based on Fourier coefficients

incorporating vibrational (or thermal) averaging of deformation electron densities closely approximate static results in regions far from the nuclei.

A number of papers that emerged from Stewart's group in the early 1980s outlined Fourier summation, direct space and combined strategies for the computation of the ESP, EF and EFG, with examples drawn from pseudoatom multipole fits to experimental data for imidazole and 9-methyladenine measured by Craven's group at the University of Pittsburgh (Spackman & Stewart, 1981; Stewart, 1982; Spackman & Stewart, 1984). Later applications of this kind included a combined Fourier/direct-space approach to mapping the total ESP in sodium zeolite A (Spackman & Weber, 1988), and a detailed presentation of ESP maps for molecules and molecular clusters of urea, imidazole, 9-methyladenine and benzene (Stewart, 1991). All of these results were based on algorithms developed by Stewart that were unfortunately not published at the time. They were incorporated into early versions of *VALRAY*, and the 1983 version of *VALRAY* implemented the entire suite of Fourier, direct-space and combined approaches to the computation of the ESP, EF and EFG for isolated molecules, clusters or the crystal. Stewart's expressions for the direct-space computation of the ESP from the parameters of the pseudoatom model were also incorporated into *MOLPOT*, part of the series of programs known as the 'POP procedure' (He, 1984; Craven *et al.*, 1987; Craven, 1988). *MOLPOT* in turn formed the basis for *ELECTROS* (Ghermani *et al.*, 1992), and Ghermani *et al.* (1993) have published an independent derivation of the relevant expressions for the ESP.

Su & Coppens (1992) published the first complete derivation and expressions for computing not only the ESP but also the EF and EFG from pseudoatom model parameters, including penetration (peripheral) contributions, based on a generalization of the Fourier convolution approach used by Epstein & Swanton (1982). Their expressions were exceedingly complex, and according to VKCF involved 'the evaluation of fairly complicated one-electron two-centre integrals', and further comments in the recent paper suggest that their incorporation into the *XD* suite was never fully satisfactory. The VKCF paper presents a careful review of the derivation of the expressions published by Ghermani *et al.* (1993) and, instead of the Green function approach used by Ghermani *et al.*, VKCF expand $|\mathbf{r} - \mathbf{r}'|^{-1}$ directly in real spherical harmonics, along the lines of previous work (Bentley, 1981; te Velde, 1990; De Bondt *et al.*, 1993; te Velde *et al.*, 2001).

Stewart's detailed derivation for the ESP was published in conjunction with Craven in a study on γ-aminobutyric acid (Stewart & Craven, 1993). It presents Stewart's beautiful and elegant derivation of the same expressions published by others, including the closed

forms of equations (22) and (23) in VKCF, and based on the Fourier convolution approach. The key difference between this and other derivations is that Stewart's makes use of his intimate knowledge of Bessel functions and their inter-relationships. This is more than a mathematical curiosity; it enabled relatively straightforward extension of the same approach to the derivation of expressions for the EF and EFG, yielding separate expressions for all three components of the EF, and for all five components of the traceless EFG tensor. As noted above, these latter derivations and expressions were never published in the peer-reviewed literature, but they were incorporated in Appendix C of the *VALRAY* manual in 2000 (Stewart *et al.*, 2000). As that manual has not been widely circulated, in the interests of wider dissemination of those important results, that Appendix is provided in PDF format as supplementary material accompanying this communication.[1]

This Letter concludes with some remarks pertaining to the results and discussion in §4 of the paper by VKCF. The first concerns the EF, and in particular the map of EF projected onto the plane of the formamide molecule (Fig. 1 of VKCF), based on a pseudoatom modelling of theoretical structure factors. The contribution of the 'central' molecule has been omitted from the map and, as VKCF emphasize, the resulting map very nicely demonstrates how the 'central' molecule experiences an EF due to surrounding molecules that is closely parallel to its own dipole moment vector. This is an important result, and the strategy used to obtain it, namely subtracting the contribution from a particular molecule (or atom or ion), deserves to be used more widely. In light of the comments above, it is worth noting that the map presented by VKCF is based on a direct-space summation of contributions from only the eight nearest neighbours in the crystal. The computation of the EF *in the crystal* due to point dipoles is well known to require lattice summation techniques to achieve convergence (Cummins *et al.*, 1976), and that is one reason why Stewart advocated combined Fourier/direct-space approaches to computing some properties, and these combined approaches are entirely analogous to the Ewald approach used to achieve rapid convergence of lattice sums. Thus, computation of the ESP and EF *in the crystal* are best achieved with an approach involving both summation over appropriate Fourier coefficients (*e.g.* those due to the deformation density) as well as a direct-space calculation (*e.g.* over spherical atoms, including nuclei).

Regarding the EFG, VKCF write (p. 401): 'Several methods for the calculation of the ESP/EFG were proposed by Brown & Spackman (1994)', and 'While giving more or less reasonable results, these methods are either too computationally demanding or have convergence problems with Fourier sums.' These comments rather miss the point of the calculations presented in that paper. We noted in that paper that, at that time, the direct-space EFG code in *VALRAY* had never been tested fully, and the purpose of the various computational routes to the EFG was simply to validate that code in *VALRAY* (*not* the algorithms). Thus, we compared results and convergence behaviour of the direct-space EFG with: (i) a combined Fourier/direct-space approach as described above for the EF; and (ii) numerical second differentiation of both the direct-space and combined Fourier/direct-space approaches to the ESP. It was never our intention that any approach other than the direct-space calculation be used to compute the EFG from the pseudoatom model; we did locate minor bugs and proceeded to validate the corrected code.

Also on p. 401, VKCF state that 'the method of Su & Coppens only allows calculation of the *traceless* EFG tensor at the nuclear positions'. Equation (1) of their paper, Poisson's equation, relates the Laplacian of the ESP to the electron density, and hence any code that computes the electron density and the traceless EFG can also provide the complete EFG tensor, although only the traceless EFG tensor is relevant in the computation of quantities such as nuclear quadrupole coupling constants measured in NMR or NQR experiments (Cohen & Reif, 1957). In their comparison between EFG results derived from pseudoatom modelling of theoretical structure factors for formamide (labelled XD/PBE/6-31G** in their tables) and those directly from the *ab initio* wavefunction (labelled PBE/6-31G**), VKCF use the whole EFG tensor (*i.e. not* the traceless tensor), which appears to obscure any agreement between the two. Although VKCF (p. 405) conclude that agreement between the two is 'very good, taking into account the differences between Gaussian- and Slater-type functions', this reflects the systematic differences between *electron densities* at the nuclei. Converting their results (reported in their Tables 4 and 5) to traceless form reveals that for H atoms their XD/PBE/6-31G** results are in almost perfect agreement with those obtained directly from the wavefunction, and that (to only the single significant figure available) a similar result holds for the C atom, but agreement gets progressively worse for N and O, atoms with more contracted electron densities. These conclusions are in excellent agreement with our own detailed model studies on a number of molecular crystals (Spackman & Byrom, 1996; Spackman *et al.*, 1999), with our earlier work on benzene and corundum (Brown & Spackman, 1994), and they clearly echo conclusions by Epstein *et al.* (1977), based on generalized scattering factor (g.s.f.) expansions for diatomic molecules.

A final comment concerns the use of Sternheimer corrections by VKCF in their computation of the EFG tensor at the Fe nucleus based on multipole modelling of X-ray data for iron pentacarbonyl. The use of Sternheimer corrections was never discussed by Stewart, nor in our own work, yet appears in analyses by Coppens and co-workers [for a detailed discussion and summary of many results, see Section 10.3 of Coppens's monograph (Coppens, 1997), and Section VII.C of the review article by Koritsanszky & Coppens (2001)], and has been used without question in recent analyses (Dahaoui *et al.*, 2001). However, the use of Sternheimer corrections deserves to be questioned, as they were introduced to describe so-called 'core polarization' at a time when EFGs in solids were estimated using point charges on atomic sites. VKCF incorporate both a shielding factor, R^{core}, and an antishielding factor, γ_∞, resulting in an expression for the EFG tensor components for the Fe nucleus, $E_{\alpha\beta}(\mathbf{r}) = 0.927E_{\alpha\beta}^{central}(\mathbf{r}) + 9.933E_{\alpha\beta}^{peripheral}(\mathbf{r})$. Thus, the contribution from the nucleus-centred quadrupole functions is *reduced* by ~7%, and the (generally much smaller) peripheral (penetration) contribution is *enhanced* by an order of magnitude by including these correction factors. Tsirelson & Ozerov (1996) have argued that the antishielding correction should only be included when the peripheral term is approximated by a point-charge model, and this makes a great deal of sense. It is also arguable that even the shielding contribution should be included. Coppens (1997) argued that its use takes into account the fact that the pseudoatom model uses a frozen core approximation, and thus cannot describe core polarization effects. However, Schwarz, Blaha and co-workers have performed accurate all-electron theoretical calculations of EFGs in a variety of complex solids using a full-potential linearized augmented plane-wave method (FP LAPW) and make no use of any Sternheimer corrections (Blaha *et al.*, 1985; Schwarz & Blaha, 1992; Dufek *et al.*, 1995; Blaha *et al.*, 2000; Schwarz & Blaha, 2003). Most importantly, their calculations

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provide a breakdown of the EFG tensors into contributions from semi-core (SC) and valence states. For a series of Al_2SiO_5 polymorphs (Iglesias *et al.*, 2001), they conclude that the 'main contribution to the EFG comes from the distortion from spherical symmetry of the respective valence *p* electrons', although for Al and Si important contributions come from the low-lying semi-core states on Al (2*p*) and O (2*s*). Similarly, results for a series of Fe-containing solids indicate that 'usually the Fe 3*p* SC state contribution is less than 10% of the valence part' (Dufek *et al.*, 1995). This is not intended to suggest that core polarization is negligible, but it seems likely that more important factors currently hamper determination of accurate EFG tensors for heavy atoms from X-ray diffraction data (*e.g.* a complete and accurate description of the thermal motion of the nucleus, limited flexibility of radial functions in the pseudoatom model, and inherent limits on the resolution of the X-ray diffraction data), and the use of Sternheimer shielding factors is likely to obscure any attempts at improvement in these areas.

It is worth reiterating that the new expressions and algorithms presented by VKCF and especially their incorporation into *XD* – now used in more than three-quarters of published experimental charge-density studies – represents an important step towards the routine determination and presentation of ESP, EF and EFG results based on modern charge-density studies. In particular, it would be a suitably fitting outcome of the incorporation of the new expressions by VKCF into *XD* if attention could be focused on the EFG tensor once again, with the aim of seeking quantitative agreement with NQR results where possible, as advocated by Stewart (1977) nearly 30 years ago.

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Response to Spackman's comment on *On the calculation of the electrostatic potential, electric field and electric field gradient from the aspherical pseudoatom model*

Anatoliy Volkov* and Philip Coppens*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260-3000, USA.
Correspondence e-mail: volkov@chem.buffalo.edu, coppens@buffalo.edu

We fully agree with Spackman's tribute to the considerable contribution of R. F. Stewart to the field of charge-density analysis and will restrict our comments to the second half of his letter which discusses a number of issues relevant to the results presented in our paper (Volkov, King *et al.*, 2006).

Mark Spackman (MS) states that 'it is worth noting that the map presented by VKCF is based on a direct-space summation of contributions from only the eight nearest neighbours in the crystal', implying that the figure presented will change significantly if more neighbouring molecules are included in the calculation. In Fig. 1 below, we present analogous maps obtained by taking into account the contributions of pseudoatoms within several unit cells (this option was available in the latest version of *XD2006* at the time our original paper was published). Only small changes are observed on the periphery of the map, which do not in any way change any of the conclusions presented in our paper. For the calculation of the electrostatic potential (ESP), electric field (EF) and electric field gradient (EFG), we use the same EPMM approach (Volkov *et al.*, 2004) developed for calculation of the electrostatic interaction energy. Exact formulae are used for atoms located within a certain distance (typically ~6 Å for the ESP, EF and EFG in organic systems) from the point at which the properties are calculated. Beyond that distance, approximate formulae, based on the expansion of the ESP, EF and EFG in atomic multipole moments, are used. Table 1 includes a comparison between exact and EPMM methods, demonstrating the satisfactory accuracy of the much faster (Table 2) EPMM method. Table 3 shows the convergence of the x and y components of the EF vector in the plane of the map *versus* the number of unit cells included in the calculation. An excellent convergence is achieved when including atoms with fractional coordinates of $-1 < x, y, z < 2$, while the inclusion of eight neighbouring cells is also quite satisfactory, *i.e.* the r.m.s. deviation is only 0.02–0.03 e Å^{-2}, which is less than 1% of the r.m.s. values of the E_x (~5.4 e Å^{-2}) and E_y (~6.5 e Å^{-2}) components of the EF vector in the plane of the map. Note that a similar direct-space approach is used for the calculation of the electrostatic binding energy in the crystal (Volkov *et al.*, 2007), which has also been implemented in *XD2006* (Volkov, Macchi *et al.*, 2006). The efficient combination of the exact formulae and the multipole moment approximation eliminates the convergence problems inferred by MS.

MS quotes Cummins *et al.* (1976) that 'computation of the EF in the crystal due to point dipoles is well known to require lattice summation techniques to achieve convergence' and adds that 'these combined approaches are entirely analogous to the Ewald approach used to achieve rapid convergence of lattice sums.' We are of course well aware of the existence of the Ewald summation techniques which we used previously in the calculation of the lattice energy of ionic (Su & Coppens, 1995) and molecular (Abramov, Volkov, Wu & Coppens, 2000a,b; Abramov, Volkov & Coppens, 2000) crystals. However, the direct-space summation was found to be advantageous in terms of both speed and ease of implementation when combined with the new EPMM method (Volkov *et al.*, 2007).

MS states that we misunderstand the purpose of the methods described by Brown & Spackman (1994) as several algorithms published in this paper were used only for debugging of the *VALRAY* code and should not be considered of practical importance.

Table 1
Root-mean-squared differences in electric field components E_x and E_y (e Å^{-2}) in the plane of the map between exact and EPMM calculations .

(R.m.s. values of E_x and E_y are ~5.4 and ~6.5 e Å^{-2}, respectively.)

	8 neighboring molecules	All atoms with $-1 < x, y, z < 2$	All atoms with $-2 < x, y, z < 3$	All atoms with $-3 < x, y, z < 4$
R.m.s.(E_x)	2×10^{-6}	1×10^{-5}	1×10^{-5}	1×10^{-5}
R.m.s.(E_y)	2×10^{-6}	7×10^{-6}	1×10^{-5}	1×10^{-5}

Table 2
Number of atoms and elapsed time (s) for each of the calculations (calculations were performed using Athlon64 3400+ 2.2 GHz processor with 1MB of L2 cache).

Calculation	Elapsed CPU time (s) Exact formulae	Elapsed CPU time (s) EPMM	Number of atoms used in the calculation
8 neighboring molecules	5.2	4.3	48
All atoms with $-1 < x, y, z < 2$	54.5	13.6	642
All atoms with $-2 < x, y, z < 3$	254.5	40.7	2994
All atoms with $-3 < x, y, z < 4$	713.8	100.8	8226
All atoms with $-4 < x, y, z < 5$	–	216.5	17490

Table 3
Root-mean-squared differences in electric field components E_x and E_y (e Å^{-2}) in the plane of the map relative to the values from calculation that included all atoms with $-4 < x, y, z < 5$ (all from EPMM calculations).

(R.m.s. values of E_x and E_y are ~5.4 and ~6.5 e Å^{-2}, respectively.)

	8 neighboring molecules	All atoms with $-1 < x, y, z < 2$	All atoms with $-2 < x, y, z < 3$	All atoms with $-3 < x, y, z < 4$
R.m.s.(E_x)	0.02	0.006	0.0007	0.00020
R.m.s.(E_y)	0.03	0.004	0.0004	0.00009

Table 4
Components of the *traceless* EFG tensor at the nuclear positions in formamide (atomic units) from different methods.

	XX	XY	XZ	YY	YZ	ZZ
O(1)						
PBE/6-31G**	−0.43	−1.52	0.04	1.44	0.02	−1.01
PBE/aug-cc-pVDZ	−0.41	−1.50	0.03	1.37	0.02	−0.96
PBE/aug-cc-pVDZ	−0.34	−1.49	0.03	1.44	0.02	−1.09
XD/PBE/6-31G**	−0.27	−1.21	−0.04	1.25	0.07	−0.98
N(2)						
PBE/6-31G**	−0.61	−0.03	−0.05	−0.66	−0.01	1.27
PBE/aug-cc-pVDZ	−0.58	−0.04	−0.05	−0.63	−0.01	1.20
PBE/aug-cc-pVDZ	−0.56	−0.03	−0.05	−0.59	−0.01	1.15
XD/PBE/6-31G**	−0.39	−0.02	−0.02	−0.45	−0.02	0.85
C(3)						
PBE/6-31G**	0.13	0.08	0.00	0.33	0.00	−0.46
PBE/aug-cc-pVDZ	0.16	0.08	0.00	0.34	0.00	−0.49
PBE/aug-cc-pVDZ	0.19	0.08	0.00	0.39	0.00	−0.59
XD/PBE/6-31G**	0.25	0.07	0.00	0.27	−0.02	−0.52
H(4)						
PBE/6-31G**	−0.32	−0.42	−0.02	−0.06	−0.01	0.37
PBE/aug-cc-pVDZ	−0.31	−0.43	−0.02	−0.05	−0.01	0.37
PBE/aug-cc-pVDZ	−0.31	−0.42	−0.02	−0.05	−0.01	0.36
XD/PBE/6-31G**	−0.33	−0.44	−0.02	−0.04	−0.01	0.37
H(5)						
PBE/6-31G**	0.25	0.07	0.00	−0.60	0.00	0.35
PBE/aug-cc-pVDZ	0.26	0.07	0.00	−0.60	0.00	0.35
PBE/aug-cc-pVDZ	0.25	0.07	0.00	−0.60	0.00	0.34
XD/PBE/6-31G**	0.27	0.07	0.00	−0.62	0.00	0.35
H(6)						
PBE/6-31G**	0.21	0.01	0.00	−0.44	−0.01	0.23
PBE/aug-cc-pVDZ	0.22	0.02	0.00	−0.47	−0.01	0.24
PBE/aug-cc-pVDZ	0.20	0.01	0.00	−0.43	−0.01	0.23
XD/PBE/6-31G**	0.21	0.01	0.00	−0.46	0.00	0.24

Nevertheless, the methods were published and are thus in the public domain and subject to further discussion.

The 1957 statement that 'only the traceless EFG tensor is relevant in the computation of quantities such as nuclear quadrupole coupling constants measured in NMR or NQR experiments (Cohen & Reif, 1957)' is the basis for criticism of our comparison of the elements of the unabridged tensor elements. The point was to *verify* that our expressions yield correct values, for which the unabridged tensor provides a more stringent test. Going from the total to the traceless definition is of course trivial. In fact *XD2006*, like *Gaussian 03* (2004), automatically prints out both total and traceless components of the EFG tensor as well as the corresponding eigenvalues (Appendix *A*, Supplementary Material).[1] For completeness, the components of the traceless EFG tensor and its eigenvalues for formamide are given in Tables 4 and 5. They in no way contradict any of the statements presented in our original paper.

We agree that use of the Sternheimer correction (Sternheimer, 1986) is questionable and should be re-examined. However, any disagreement between our value and the most precise up-to-date determination of $Q(^{57}Fe^m)$ (Dufek *et al.*, 1995) is unlikely to be due to the use of the correction, which adds only 0.01×10^{-28} m^2 to the uncorrected value of $Q(^{57}Fe^m) = 0.11 \times 10^{-28}$ m^2 (less than 10%). Any disagreement is more likely to be due to experimental errors in the data, which are larger than the Sternheimer correction, as shown in our paper. Of course, this does not eliminate the need for more

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[1] Supplementary material for this paper is available from the IUCr electronic archives (Reference: SH0187). Services for accessing this material are described at the back of the journal.
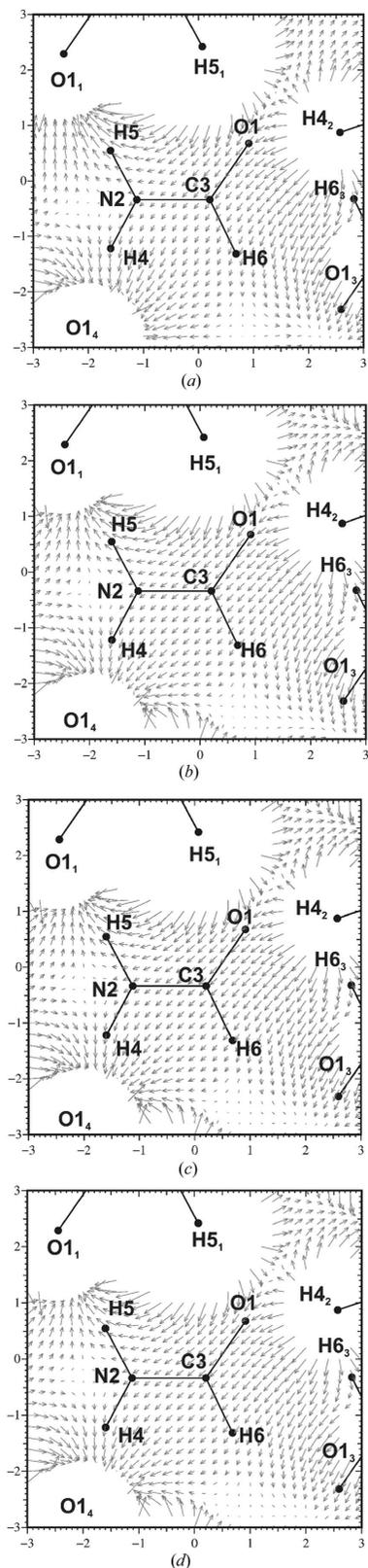

Figure 1
Electric field (EF) vectors in the N2—C3—O1 plane of the 'central' formamide molecule due to (*a*) the eight nearest-neighbouring molecules in the crystal, and all atoms with fractional coordinates (*b*) $-1 < x, y, z < 2$, (*c*) $-2 < x, y, z < 3$ and (*d*) $-4 < x, y, z < 5$ (the contribution of the 'central' molecule to EF is not included). Subscripts of atom names identify the neighbouring molecules. Vectors with magnitudes larger than 0.15 e Å^{-2} are omitted for clarity. The size of the map is 6×6 Å with a grid spacing of 0.2 Å.

Table 5
Eigenvalues of the *traceless* EFG tensor at the nuclear positions in formamide (atomic units) from different methods.

	λ_1	λ_2	λ_3
O(1)			
PBE/6-31G**	−1.29	−1.00	2.29
PBE/aug-cc-pVDZ	−1.27	−0.95	2.22
PBE/aug-cc-pVDZ	−1.20	−1.08	2.28
XD/PBE/6-31G**	−0.98	−0.94	1.92
N(2)			
PBE/6-31G**	−0.68	−0.59	1.27
PBE/aug-cc-pVDZ	−0.65	−0.56	1.20
PBE/aug-cc-pVDZ	−0.61	−0.54	1.15
XD/PBE/6-31G**	−0.46	−0.39	0.85
C(3)			
PBE/6-31G**	−0.46	0.10	0.35
PBE/aug-cc-pVDZ	−0.49	0.13	0.37
PBE/aug-cc-pVDZ	−0.59	0.16	0.42
XD/PBE/6-31G**	−0.52	0.19	0.33
H(4)			
PBE/6-31G**	−0.63	0.26	0.37
PBE/aug-cc-pVDZ	−0.63	0.26	0.37
PBE/aug-cc-pVDZ	−0.63	0.26	0.37
XD/PBE/6-31G**	−0.65	0.28	0.37
H(5)			
PBE/6-31G**	−0.61	0.25	0.35
PBE/aug-cc-pVDZ	−0.61	0.26	0.35
PBE/aug-cc-pVDZ	−0.60	0.26	0.35
XD/PBE/6-31G**	−0.62	0.28	0.35
H(6)			
PBE/6-31G**	−0.44	0.21	0.23
PBE/aug-cc-pVDZ	−0.47	0.22	0.24
PBE/aug-cc-pVDZ	−0.43	0.20	0.23
XD/PBE/6-31G**	−0.46	0.21	0.24

accurate experimentation and re-examination of the importance of the core polarization.

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