

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

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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

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)		Number of atoms used in the calculation
	Exact formulae	EPMM	
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

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, 2000*a,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 4

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

	<i>XX</i>	<i>XY</i>	<i>XZ</i>	<i>YY</i>	<i>YZ</i>	<i>ZZ</i>
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 $Q(^{57}\text{Fe}^m)$ (Dufek *et al.*, 1995) is unlikely to be due to the use of the correction, which adds only $0.01 \times 10^{-28} \text{ m}^2$ to the uncorrected value of $Q(^{57}\text{Fe}^m) = 0.11 \times 10^{-28} \text{ m}^2$ (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

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.

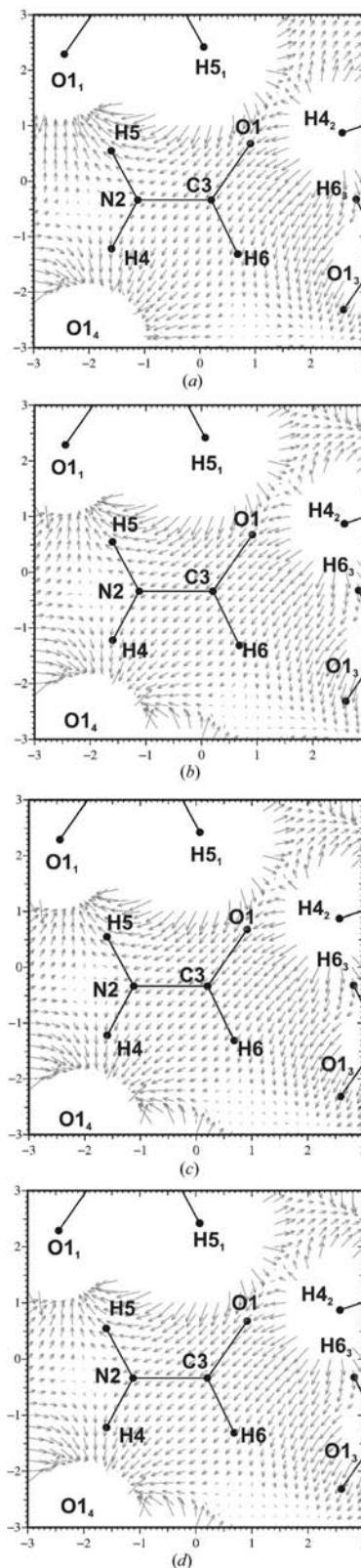


Figure 1

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 \AA^{-2} are omitted for clarity. The size of the map is $6 \times 6 \text{ \AA}$ with a grid spacing of 0.2 \AA .

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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