On the error in the nucleus-centered multipolar expansion of molecular electron density and its topology: A direct-space computational study

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The convergence of nucleus-centered multipolar expansion of the quantum-chemical electron density (QC-ED), gradient, and Laplacian is investigated in terms of numerical radial functions derived by projecting stockholder atoms onto real spherical harmonics at each center. The partial sums of this exact one-center expansion are compared with the corresponding Hansen-Coppens pseudoatom (HC-PA) formalism [Hansen, N. K. and Coppens, P., "Testing aspherical atom refinements on small-molecule data sets," *Acta Crystallogr., Sect. A* **34**, 909–921 (1978)] commonly utilized in experimental electron density studies. It is found that the latter model, due to its inadequate radial part, lacks pointwise convergence and fails to reproduce the local topology of the target QC-ED even at a high-order expansion. The significance of the quantitative agreement often found between HC-PA-based (quadrupolar-level) experimental and extended-basis QC-EDs can thus be challenged. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983633>]

INTRODUCTION

Derivation of the static crystalline electron density (ED; ρ) from diffraction data is subject to demanding experimental conditions and to a series of approximations involved in reducing the X-ray scattering intensities to Bragg structure factor amplitudes and modeling the ED associated with these properties. To "fabricate" a closed analytic form for the structure factor, commonly used models invoke the harmonic-convolution approximation.^{2,3} In spite of bypassing the physical correlation between the electronic and the nuclear motion, this method of thermal averaging is adequate at the correct equilibrium nuclear configuration, as it has recently been shown for approximate quantum-chemical electron densities (QC-EDs) expanded over a Gaussian basis set.⁴ The other critical step used in conjunction with the above approach in the standard modeling of Bragg data involves a partitioning of the static ED into fuzzy atomic contributions, each of which is rigidly attached to a single nucleus (the isolated atom being the zero-order approximation). The natural choice for the angular basis of an analytic one-center expansion is a finite set of real spherical harmonics (SPH) at each nucleus, termed by Stewart as the pseudoatom (PA) formalism.⁵ The corresponding inverse problem (extracting the static ED from the Fourier amplitudes related to the "average" ED) is thus reduced, in principle, to the derivation of the PA radial density functions (RDFs). The finiteness of data however dictates the radial basis to be fixed to a pre-assumed analytic form—just like for orbital-based

QC calculations—requiring thus the optimization of only a relatively small number of parameters. Since the least-squares (LS) fitting of these parameters against a finite set of experimental data remains to be a mathematically ill-posed problem, the procedure unavoidably yields a non-unique static PA-ED (or a statistically equivalent set, at the best case). Validation of the outcomes is thus also an unavoidable part of experimental ED studies.

Owing to the interpretive power of the Quantum Theory of Atoms in Molecules (QTAIM),⁶ it has become a standard practice^{7–9} to report the full topological analysis of the "experimental" static PA-ED fitted to the measured structure factor amplitudes. Observed critical-point indices are extensively used not only to characterize the chemical interaction in crystals but also to access the reproducibility¹⁰ of the PA method and even to validate¹¹ it. The topological toolkit has been extended to properties^{12–16} related to the derivatives of the ED that are expected to be one or two orders of magnitude ($\nabla\rho$ and $\nabla^2\rho$, respectively) more sensitive to uncertainties in the LS parameter estimates than the ED itself. The precision of these quantities, as derived via error propagation from the uncertainties of the fitted PA parameter estimates, is notoriously underestimated.¹⁷ In the lack of reliable significance measures, the validation is equivocal and thus substantially relies on the comparison of the experimental PA-ED with a QC-ED computationally derived either for the isolated molecule or for the periodic system via energy minimization.

In this report, we elaborate on the accuracy of two different PA representations of a QC-ED and related local QTAIM properties. The reconstructive analysis, performed in the direct rather than the Fourier-space, compares the exact nucleus-centered multipole expansion (E-PA) and an optimized version of the Hansen-Coppens model (OHC-PA)¹

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which, in its restricted form, is the most popular formalism used in experimental ED analyses. The derivation of the exact-PA is a conceptually new element of our approach. First, we partition the QC-ED, obtained within the clamped-Hamiltonian, molecular orbital (MO) formalism, into “fuzzy atomic” (one-center) density units, and then evaluate the spherical harmonics content of each such unit independently. While the first step is ambiguous (since there is no unique “atomic” partitioning), the second is exact, since it is an orthogonal projection leading to unbiased (uncorrelated) numerical RDFs for each pole at each center for any one-center partitioning. This allows in principle for an *arbitrarily accurate pseudoatom reconstruction of a target QC-ED corresponding to any model Hamiltonian and basis set*.

The paper is structured in the following way: first, the main steps of the direct-space projection of a molecular QC-ED onto PAs are revisited,^{18,19} followed by the demonstration of what it takes to faithfully reproduce fine details of this ED and its topology, including bond-critical-point (BCP) properties, with the two PA models.

COMPUTATIONAL METHODS

Direct-space pseudoatom projection of the molecular electron density

We start with a known QC-ED. While it is not an essential element of the method described, for the sake of simplicity, we target a theoretical ED that is obtained within the single-determinant linear combination of atomic orbital (LCAO-MO) approach,

$$\rho(\mathbf{r}) = \sum_j n_j |\psi_j|^2, \quad (1)$$

where ψ_j is the j th MO with occupation number n_j ($n_j = 2$ for closed shell single determinant MOs).

This ED is partitioned into fuzzy “atomic” contributions (ρ_A),

$$\rho(\mathbf{r}) = \sum_A^N \rho_A(\mathbf{r}_A), \quad (2)$$

where $\mathbf{r}_A = \mathbf{r} - \mathbf{Q}_A$ and the summation runs over all nuclei (N) located at positions $\{\mathbf{Q}_A\}$. The exact multipolar representation of $\rho_A(\mathbf{r}_A)$ is obtained as a finite combination of density units each factored into a normalized radial part ($\rho_{lm}^A(r_A)$) and a real density-normalized SPH (d_{lm}^A),²⁰

$$\rho_A(\mathbf{r}_A) = \sum_{l,m}^L C_{lm}^A \rho_{lm}^A(r_A) d_{lm}^A(\vartheta_A, \varphi_A); \quad -l \leq m \leq l, \quad (3)$$

where

$$\rho_{lm}^A(r_A) = \frac{\langle \rho_A | d_{lm}^A \rangle_{\Omega_A}}{C_{lm}^A}. \quad (4)$$

In the above formula, $\langle \rangle_{\Omega_A}$ stands for angular integration in the A -centered local frame (Ω represents the position on the sphere in terms of polar ϑ and azimuthal φ angles, and l and m are the spherical-harmonic degree and order, respectively) which is performed numerically^{21–23} for a dense set of radial grid points $\{r_A^{(i)}\}$. The corresponding multipole populations are obtained through normalization,

$$C_{lm}^A = \int_0^\infty \langle \rho_A(r_A) | d_{lm}^A(\vartheta_A, \varphi_A) \rangle_{\Omega_A} r_A^2 dr_A. \quad (5)$$

We refer to expansion (Eqs. (3)–(5)) as “exact” (Laplace series) in the sense of its convergence in the $L^2(S^2)$ -norm, that is, the expansion coefficients are uncorrelated and do not depend on the maximal degree of the expansion (L), due to the orthonormality and completeness of the SPH basis (d_{lm}^A). The pointwise converge is also ensured since the QC-ED ($\rho(\mathbf{r})$ and each $\rho_A(\mathbf{r}_A)$) possesses the Lipschitz continuity, except at the nuclear positions (for Slater-type basis functions) where the exact static ED also exhibits cusps.^{24,25} On the other hand, expansion (3) is an approximation because it depends on the maximum degree. Different PA partitioning schemes of the target molecular $\rho(\mathbf{r})$ can, of course, lead to different PA-RDFs, yet, *whatever form Eq. (2) takes, Eq. (3) is unique (orthogonal projection) and thus Eq. (4) and consequently Eq. (5) are exact (for $L \rightarrow \infty$)*.

Because of its simplicity, the stockholder method²⁶ is adapted in this study. Our preliminary investigations¹⁹ showed that this partitioning yields fairly local and transferable “bounded atoms” with the corresponding PA-RDFs exhibiting a “chemical invariance” with respect to connectivity up to the second-neighbor level. We note here that the stockholder method is being successfully used in refinements of experimental structure factors.^{27,28} It is uniquely defined for a given basis set, if that is shared by the promolecular (superposition of isolated atoms) and the molecular QC-EDs.

The Hansen-Coppens model

In the HC-PA formalism, the RDFs are deduced from isolated-atom ground-state Hartree-Fock (HF) wave functions.²⁹ The monopole density is decomposed into a frozen core and a spherically deformed (in terms of the κ parameter) valence part,

$$R_{00}^A(r) = \rho_{core}^A(r) + \kappa^3 P_{00} \rho_{valence}^A(\kappa r), \quad (6)$$

corresponding to the closed inner shell(s) ($\rho_{core}^A(r)$) and the spherically averaged (evenly occupied orbitals) outermost shell densities ($\rho_{valence}^A$) expanded over an extended Slater basis set. The RDFs of the higher-order (deformation) terms in the expansion are simple nodeless Slater functions (S_l) fabricated from minimal-basis HF, isolated-atom valence orbitals with energy-optimized exponents (η_l),

$$R_{lm}^A(r) = P_{lm} S_l(n_l, \eta_l, \kappa' r), \quad S_l(n_l, \eta_l, \kappa' r) = N_{\eta_l} r^{\eta_l} e^{-\kappa' \eta_l r}. \quad (7)$$

Thus the standard HC-PA approximation takes the following form (dropping index A):

$$\rho(\mathbf{r}) = \rho_{core}(r) + \kappa^3 P_{00} \rho_{valence}(\kappa r) + \sum_{l=1}^L S_l(\kappa' r) \sum_{m=-l}^l P_{lm} d_{lm}(\vartheta, \varphi). \quad (8)$$

This model is evidently restricted in all three terms listed above. Since ρ_{core} is kept spherical and frozen during the LS fit of structure factors, it cannot account for core polarizations that are expected to have a significant role in molecules in balancing electrostatic forces.^{30,31} The radial deformation of ρ_{core} has recently been found detectable experimentally for diamond.³² The valence monopole term is “scaled” by a single expansion-contraction parameter (κ) implying uniform radial

deformation for its contributing subshells, whose orbitals however can be involved in different types of bond formations (σ and π). This latter restriction is built also into the valence deformation term (the last one in Eq. (8)), since the RDFs are taken to be order (m)-independent (unlike for those in the E-PA).

When the standard HC-PA formalism is applied to interpret Bragg scattering experiments, the multipole populations (P_{lm}), radial scaling factors (κ and κ'), mean nuclear positions, and anisotropic displacement parameters (ADPs) are LS fitted against observed structure factor amplitudes, while the remaining static density parameters (n_l , η_l , and L) and monopole densities are usually held fixed and identical for all identical atoms (having the same atomic number) irrespective of their actual bonding situation. The HC-PA partitioning is thus implicitly defined by the order-independence and a particular parameterization of the RDFs, that is, “controlled” by the fixed analytic forms of ρ_{core} , $\rho_{valence}$, and S_l (and their parameters), and additional chemical transferability (symmetry) constraints.

Optimal HC radial functions via the exact multipole expansion

The RDF data points obtained through the numerical angular integration (Eq. (4)) can be fitted with a combination of Slater functions to obtain an analytic representation of PA-EDs and scattering factors.¹⁹ This requires several Slater primitives, the actual number of which depends on the accuracy desired and on the maximum degree of expansion. To avoid fitting errors, we applied the numerical RDF data directly (as obtained via Eq. (4)) using a cubic interpolation scheme. Intermediate data points were thus locally estimated from the numerical data instead of using an analytic representation of the entire data, leading to a significant increase of the accuracy of the RDFs and their derivatives. Furthermore, to achieve the maximal consistency between the QC-ED and its two HC-PA representations, optimal m -independent RDFs were derived from the numerical ρ_{lm} data by utilizing a Löwdin type projection technique.³³ This procedure leads to a set of optimized m -independent RDFs and the corresponding HC-PA model (OHC-PA). It is to be emphasized that the OHC-PA RDFs obtained in this way are as close as possible to the E-PA RDFs (in the LS sense), and thus, they are superior to the atomic functions (Eqs. (6) and (7)) used in the standard HC-PA formalism for representing a molecular QC-ED. There are however two important differences between the OHC- and HC-PA representations: (a) the former is a “total-ED” PA model (it also accounts for aspherical core contributions), while the latter treats the spherical core- and aspherical valence-EDs separately (frozen-core approximation); (b) the OHC-PA (just like the E-PA) derived in such a way leads to an orthogonal expansion, which is an important advantage over the standard HC-PA model for LS-fitting (due to minimizing correlations in parameter estimation).

RESULTS AND DISCUSSION

The PA reconstruction of QC-EDs is scrutinized by targeting two small molecules; formamide with bonding situations

typical for organic molecules, and an inorganic molecule, the $\text{H}_2\text{NSO}_2(\text{OH})$ tautomer (non-zwitterion isomer) of sulfamic acid, possessing polarized S—O and S—N bonds.³⁴ The EDs and their local topological properties of the formamide molecule were calculated for the two PA models obtained from the QC-ED at the optimized planar geometry with the ADF program package³⁵ utilizing the BLYP/QZ4P level of theory.^{36,37} We tried to overcome basis-set issues in this way, since the ADF ED (just like its HC-PA image) is based on Slater basis functions.³⁸ Calculations on sulfamic acid are however based on a Gaussian basis set (B3LYP/cc-pVTZ)³⁹ (also for the optimized geometry). The topological analyses of the PA models were performed with a new version of the DENPROP program package⁴⁰ whose functionality has been extended to handle both QC- and PA-EDs, with not only analytic but also numerical RDFs for the latter.

Error of the pseudoatom densities of formamide

Figures 1 and 2 compare the convergence of the E-PA and OHC-PA models as the function of the maximal level of multipole expansion (L) in terms of residual EDs calculated in the plane of the molecule with reference to the target QC-ED ($\Delta\rho^L = \rho_{PA}^L - \rho_{\Psi(\text{ADF})}$, $L = 0, 2, 4, 6$).

The residual features obtained by the two expansions “evolve” quite parallel up to the dipolar order. The two monopole residual EDs are identical, since they share the same monopole RDFs. This is important to avoid biasing higher-order residual maps if we want to reveal convergence issues and the effects of order-dependent RDFs. While at the dipolar level ($L = 1$), the two maps exhibit a good quantitative agreement (not shown in Figures 1 and 2); at ($L = 2$), they differ considerably, especially for the C=O bond, because the OHC-PA model is unable to account for the apparently quadrupolar deformations at the C and O sites. These differences remain pronounced with an increasing order of expansion. At ($L > 4$), the OHC-PA error map exhibits a sharp quadrupolar polarization, especially at the O-site. Furthermore, all bonding contours are equal or larger than $0.05 \text{ e } \text{\AA}^{-3}$. The highest contour for the C—H and N—H bonds remains $0.04 \text{ e } \text{\AA}^{-3}$. However the E-PA model exhibits a consistent convergence; as L increasing from 2 to 6, the maximal residual contour gradually drops from 0.05 to $0.02 \text{ e } \text{\AA}^{-3}$.

Error in local topological properties of formamide

The local topological indices involve the first ($\nabla\rho$) and second derivatives ($\nabla^2\rho$) of the ED that can be evaluated either at the model specific ($\mathbf{r}_{BCP}^{E-PA}$ and $\mathbf{r}_{BCP}^{OHC-PA}$) or at the target ($\mathbf{r}_{BCP}^{\Psi}$) BCP locations. Both comparisons have their own validation power. Being reference free, the former can provide figures indicative of the overall performance of the PA models and thus it parallels practical analyses. The latter way of validation has its merit in making the total absolute errors accessible without biasing the analysis owing to decomposing the error component of the BCP-location mismatch. However, the entries in Table I indicate that the $\mathbf{r}_{BCP}^{\Psi}$ values are well reproduced by both models at ($L > 4$).

While this observation could be of significance for validation purposes and thus deserves a more detailed analysis,

FIG. 1. E-PA residual electron density contour maps in the plane of the formamide molecule for different degrees of expansion (L). (a) $L = 0$, (b) $L = 2$, (c) $L = 4$, (d) $L = 6$. Contour lines are 0.05 for (a) and (b) and 0.01 $e/\text{\AA}^3$ for (c) and (d). Positive: red, zero: black, negative: blue.

we do not address explicitly the issue of correlation between BCP indices and BCP locations in the following discussion; thus the BCP properties referred here correspond to the model specific BCP locations ($\mathbf{r}_{BCP}^{E-PA}$ and $\mathbf{r}_{BCP}^{OHC-PA}$).

Figure 3 visualizes the PA-reconstructions of $\rho_{\Psi}(\mathbf{r}_{BCP})$ and $\nabla^2 \rho_{\Psi}(\mathbf{r}_{BCP})$ indices for formamide in terms of percentage errors for different bonds as a function of L . The corresponding data can be found in the [supplementary material \(S1\)](#).

The rather smooth E-PA graphs (solid lines) show a steady (almost monotone) convergence to zero, while the OHC-PA curves (dotted lines) tend to limit to non-zero errors. Furthermore, occasional cancellations of errors of a different origin (lower degree and order-independence) are observed to occur. For example, for the bonds not involving H-atoms (C=O and C—N), the error in the E-PA ED ($\Delta \rho_{E-PA}(\mathbf{r}_{BCP})$) drops below 1% already at the ($L = 3$) level, while the corresponding OHC-PA error is higher (3.11%) for C=O but much lower (0.23%) for the C—N bond. For the C—H and N—H interactions, the 1% error-threshold is bypassed by the E-PA model only at ($L = 5$) where the OHC-PA performs less favorably ($>1.5\%$). The reconstruction pattern of $\nabla^2 \rho_{\Psi}(\mathbf{r}_{BCP})$ is more in line with the expectations. The error curves (Figure 3(b)) show that the E-PA series consistently outperforms the OHC-PA for ($L > 3$) for all bonds. The rate of convergence is however slow. Taking the “critical” C=O bond as an example, the 1%

error is reached by the E-PA approximation only at ($L = 15$) (0.7%), where the error in the OHC-PA Laplacian exceeds 14%. Considering all bonds, an acceptable reconstruction of the target $\nabla^2 \rho_{\Psi}(\mathbf{r}_{BCP})$ is possible with the E-PA model but only for ($L > 10$). On the other hand, the minimum error reachable by the OHC-PA model at ($L = 16$) is larger than 14, 2, 6, and 13% for the C=O, C—N, N—H, and C—H bonds, respectively.

The eigenvalue λ_3 , corresponding to the bond-parallel Hessian eigenvector, has the largest contribution to the uncertainty in the OHC-PA Laplacian, since this component exhibits a rather erratic behavior that apparently lacks convergence. It thus seems that the error in the Laplacian of the OHC-PA for formamide is mainly due to the numerical instability of λ_3 ($\nabla^2 \rho_{BCP} = \lambda_1 + \lambda_2 + \lambda_3$).

Further details are revealed in Figure 4 where the absolute error at the convergence level of ($L = 16$) in ρ_{PA} (Figures 4(a) and 4(c)) and $\nabla^2 \rho_{PA}$ (Figures 4(b) and 4(d)) is displayed along the path of the C—N (4(a) and 4(b)) and C=O (4(c) and 4(d)) bonds, respectively.

While the E-PA almost completely and entirely replicates the target properties in these important topological domains, the OHC-PA properties are significantly off in core domains and regions of valence shell charge concentrations (VSCCs).

FIG. 2. OHC-PA residual electron density contour maps in the plane of the formamide molecule for different degrees of expansion (L). (a) $L = 0$, (b) $L = 2$, (c) $L = 4$, (d) $L = 6$. Contour lines are 0.05 for (a) and (b) and 0.01 $\text{e}/\text{\AA}^3$ for (c) and (d). Positive: red, zero: black, negative: blue.

TABLE I. Absolute errors of the BCP locations obtained by the two PA models for the bonds of the formamide molecule at different levels of multipole expansion (L). Units are in $\text{\AA}$.

L	C=O		C–N		N–H		C–H	
	E-PA	OHC-PA	E-PA	OHC-PA	E-PA	OHC-PA	E-PA	OHC-PA
0	1.95×10^{-2}	1.95×10^{-2}	5.99×10^{-2}	5.99×10^{-2}	1.02×10^{-2}	1.02×10^{-2}	2.30×10^{-2}	2.30×10^{-2}
1	3.02×10^{-2}	2.83×10^{-2}	3.95×10^{-2}	5.03×10^{-2}	4.51×10^{-2}	4.57×10^{-2}	7.82×10^{-2}	7.58×10^{-2}
2	1.21×10^{-2}	1.59×10^{-2}	4.77×10^{-2}	5.81×10^{-2}	5.31×10^{-2}	4.71×10^{-2}	6.24×10^{-2}	4.16×10^{-2}
3	1.85×10^{-2}	1.02×10^{-2}	2.00×10^{-2}	9.72×10^{-3}	1.38×10^{-2}	8.12×10^{-3}	1.38×10^{-2}	1.69×10^{-2}
4	1.44×10^{-2}	6.10×10^{-3}	2.13×10^{-2}	1.00×10^{-2}	1.10×10^{-2}	5.32×10^{-3}	1.39×10^{-2}	1.50×10^{-2}
5	1.03×10^{-2}	3.15×10^{-3}	1.35×10^{-2}	5.73×10^{-3}	6.55×10^{-3}	3.61×10^{-3}	1.08×10^{-2}	1.13×10^{-2}
6	6.87×10^{-3}	2.22×10^{-3}	1.14×10^{-2}	4.20×10^{-3}	2.06×10^{-3}	7.17×10^{-3}	3.91×10^{-3}	1.61×10^{-2}
7	4.47×10^{-3}	1.05×10^{-3}	8.09×10^{-3}	3.55×10^{-3}	7.29×10^{-4}	7.22×10^{-3}	2.05×10^{-3}	1.72×10^{-2}
8	2.92×10^{-3}	2.16×10^{-3}	4.81×10^{-3}	3.11×10^{-3}	3.49×10^{-4}	7.27×10^{-3}	7.37×10^{-4}	1.80×10^{-2}
9	2.00×10^{-3}	2.99×10^{-3}	3.30×10^{-3}	3.30×10^{-3}	3.97×10^{-4}	7.06×10^{-3}	8.05×10^{-4}	1.74×10^{-2}
10	1.39×10^{-3}	3.52×10^{-3}	2.35×10^{-3}	3.66×10^{-3}	4.65×10^{-4}	6.94×10^{-3}	2.48×10^{-4}	1.74×10^{-2}
11	9.43×10^{-4}	3.84×10^{-3}	1.78×10^{-3}	3.93×10^{-3}	5.40×10^{-4}	6.83×10^{-3}	1.23×10^{-4}	1.75×10^{-2}
12	6.18×10^{-4}	4.06×10^{-3}	1.14×10^{-3}	4.26×10^{-3}	4.47×10^{-4}	6.70×10^{-3}	1.90×10^{-4}	1.76×10^{-2}
13	3.90×10^{-4}	4.21×10^{-3}	8.22×10^{-4}	4.43×10^{-3}	3.81×10^{-4}	6.62×10^{-3}	1.84×10^{-4}	1.75×10^{-2}
14	2.35×10^{-4}	4.33×10^{-3}	6.19×10^{-4}	4.42×10^{-3}	2.79×10^{-4}	6.63×10^{-3}	1.90×10^{-4}	1.76×10^{-2}
15	1.27×10^{-4}	4.40×10^{-3}	3.26×10^{-4}	4.58×10^{-3}	2.07×10^{-4}	6.60×10^{-3}	2.11×10^{-4}	1.76×10^{-2}
16	5.62×10^{-5}	4.45×10^{-3}	2.21×10^{-4}	4.60×10^{-3}	1.75×10^{-4}	6.60×10^{-3}	1.81×10^{-4}	1.76×10^{-2}

FIG. 3. Percent errors of the two PA-EDs and Laplacians at the BCP locations versus the level of expansion (L) for different bonds in the formamide molecule. (a) $\rho(r_{BCP})$, (b) $\nabla^2\rho(r_{BCP})$. Solid lines: E-PA, dotted lines: OHC-PA. Blue: C=O; black: N-H; green: C-N; red: C-H.

Error of the pseudoatom densities of sulfamic acid

The PA-reconstruction of the B3LYP/cc-pVTZ ED of sulfamic acid broadly resembles that found for the formamide molecule but with a slower rate of convergence, as seen in terms of the error maps in Figures 5 and 6 ($\Delta\rho^L = \rho_{PA}^L - \rho_\Psi$) and Figures 7 and 8 ($\Delta\nabla^2\rho = \nabla^2\rho_{PA}^L - \nabla^2\rho_\Psi$, $L = 4, 16$).

Relatively high ED residuals ($0.1 \text{ e } \text{\AA}^{-3}$) are found for the S=O bonds at ($L = 4$), plausibly due to the involvement of f-type functions in the cc-pVTZ basis set. The main differences between the two PA maps for both properties appear however in the vicinity of the N-atom, as exposed by substantial aspherical residual features that continue to dominate the OHC-PA error even at the terminal order ($L = 16$). On the other hand,

FIG. 4. Error curves of the PA-EDs and Laplacians plotted along the inter-nuclear axes of different bonds in the formamide molecule calculated at the ($L = 16$) level of expansion. (a) ρ C-N, (b) $\nabla^2\rho$ C-N, (c) ρ C=O, (d) $\nabla^2\rho$ C=O. X-axis: distance from the C-atom, y-axis: value of the property relative to the QC-ED. Red: OHC-PA; blue: E-PA. Units are in e and $\text{\AA}$.

FIG. 5. E-PA density error maps in the N–S=O plane of the sulfamic acid molecule at different orders (L) of Harmonic expansion. (a) $L = 4$, (b) $L = 16$. Contour lines are 0.05 (a) and 0.01 (b) $e/\text{\AA}^3$. Positive: red, zero: black, negative: blue.

FIG. 6. OHC-PA density error maps in the N–S=O plane of the sulfamic acid molecule at different orders (L) of Harmonic expansion. (a) $L = 4$, (b) $L = 16$. Contour lines are 0.05 (a) and 0.01 (b) $e/\text{\AA}^3$. Positive: red, zero: black, negative: blue.

no bonding features higher than $0.01 e \text{\AA}^{-3}$ ($\Delta\rho$) and $0.02 e \text{\AA}^{-5}$ ($\Delta\nabla^2\rho$) remain at this order for the E-PA expansion.

Error in local topological properties of sulfamic acid

The variations of the present errors in $\rho_{\text{PA}}(r_{\text{BCP}})$ are depicted in Figure 9. The corresponding entries are given in the [supplementary material](#) (S2 and S3). We find that for all BCPs,

but those of the bonds involving H-atoms, the OHC-PA partial ED sums ($L = 4$) are more accurate than those corresponding to the E-PA. For example, the OHC-PA error for the S=O bond at ($L = 4$) is 0.190% compared to 1.185% obtained with the E-PA. The less than 1% error for this bond is reached at ($L1\% = 3$) with the OHC-PA but only at ($L1\% = 5$) with the E-PA. This is however inconsequential (appears to be accidental)

FIG. 7. E-PA Laplacian error maps in the N–S=O plane of the sulfamic acid molecule at different orders (L) of Harmonic expansion. (a) $L = 4$, (b) $L = 16$. Contour lines are $\pm 2k 10^j$ ($k = 1, 2, 3$; $j = -1, 0, 1$) $e/\text{\AA}^5$. Positive: red, zero: black, negative: blue.

FIG. 8. OHC-PA Laplacian error maps in the N-S=O plane of the sulfamic acid molecule at different orders (L) of Harmonic expansion. (a) $L = 4$, (b) $L = 16$. Contour lines are $\pm 2k 10^j$ ($k = 1, 2, 3$; $j = -1, 0, 1$) $e/\text{\AA}^5$. Positive: red, zero: black, negative: blue.

FIG. 9. Percent errors of the PA-EDs at the BCP locations versus the level of expansion (L) for different bonds in the sulfamic acid molecule. (a) OHC-PA, (b) E-PA. Blue: S=O; black: N-H; green: S-N; red: S-O; magenta: O-H.

since the OHC-PA values converge for ($L > 4$) to a final error of only 0.800%. Similar results are obtained for the S-N bond; $L1\% = 4$ and $L1\% = 5$, in the above order. Interestingly, the inadequacy of the OHC-PA expansion is the most pronounced for the O-H and N-H bonds, for which the errors at the maximal order are 1.48% and 1.98%, respectively. On the other hand, the E-PA expansion reproduces the $\rho_{\Psi}(r_{BCP})$ values up

to three decimal points for all bonds at L equal or greater than 14.

As for the Laplacian at the BCPs (Figure 10), the E-PA consistently outperforms the OHC-PA for all bonds and at all orders. The OHC-PA seems to fall short in reproducing this local property within the 1% error margin even at the highest-order expansion, as shown in Table II,

FIG. 10. Percent errors of the PA-Laplacians at the BCP locations versus the level of expansion (L) for different bonds in the sulfamic acid molecule. (a) OHC-PA, (b) E-PA. Blue: S=O; black: N-H; green: S-N; red: S-O; magenta: O-H.

TABLE II. The absolute error of the Laplacian at the BCP for the different bonds in sulfamic acid obtained by the two PA models at the terminal order of expansion.

Bond	OHC-PA	E-PA
S ₁ =O ₂	0.927	0.178
S ₁ =O ₃	1.387	0.177
S ₁ -O ₄	0.046	0.042
S ₁ -N ₆	0.479	0.000
O ₄ -H ₅	3.669	0.248
N ₆ -H ₇	5.055	0.035
N ₆ -H ₈	4.898	0.035

TABLE III. Statistical figures of the PA-based BCP properties of sulfamic acid at different degrees of expansion.

Property (BCP)	L = 4			L = 16		
	$\bar{\Delta}$	σ_{Δ}	R_{Δ}	$\bar{\Delta}$	σ_{Δ}	R_{Δ}
$\rho_{\text{OHC-PA}}$	0.034	0.030	0.044	0.024	0.017	0.029
$\nabla^2 \rho_{\text{OHC-PA}}$	4.687	3.841	5.884	2.352	2.133	3.071
$\rho_{\text{E-PA}}$	0.025	0.007	0.026	0.000		
$\nabla^2 \rho_{\text{E-PA}}$	3.138	1.855	3.577	0.103	0.096	0.136

depicting the terminal ($L = 16$) errors of $\Delta \nabla^2 \rho_{\text{PA}}(\mathbf{r}_{\text{BCP}})$ for all bonds.

A statistical summary of the results is given in Table III in terms of the mean absolute deviations ($\bar{\Delta} = N^{-1} \sum_k^N \Delta_k$), standard deviations ($\sigma_{\Delta} = \left(N^{-1} \sum_k^N (\Delta_k - \bar{\Delta})^2 \right)^{1/2}$), and root-mean-square deviations ($R_{\Delta} = \left(N^{-1} \sum_k^N \Delta_k^2 \right)^{1/2}$) for both BCP properties and for both PA expansions calculated over all bonds ($N = 7$) in sulfamic acid. This simple statistical analysis supports the overall consistency of the E-PA BCP indices in contrast to those obtained by the constrained expansion (OHC-PA) and provides some overall measures setting the limit to the interpretive performance of the pseudoatom method.

CONCLUSIONS

Overall similarities or disagreements between experimental PA-based and theoretical results (QC-ED) are usually visualized in terms of deformation ED maps for each. The qualitative nature of this comparison leaves fine quantitative details hidden that can directly be revealed by difference ED maps, comparing an experimental PA-ED with a QC-ED (this is informative only if the QC-ED is derived for the experimental nuclear geometry). Such difference maps are however not commonly evaluated, instead local topological features are analyzed, assuming point-wise convergence at the quadrupolar level of PA-expansion.

As anticipated, the exact PA recreation of the QC-ED is primarily contingent upon the level of multipole expansion (maximum degree). For formamide, the E-PA method yields an overall accuracy of less than $10.051 \text{ e } \text{\AA}^{-3}$ at the hexadecapolar level ($L = 4$) commonly used as the upper degree-limit of expansion in PA-based experimental analyses. The highest/lowest residual peaks are located at the bonds.

For the OHC-PA model however, the residual features at both the nuclear and bonding regions are more pronounced ($>0.1 \text{ e } \text{\AA}^{-3}$), and they do not diminish with the increasing level of expansion, since the convergence ceases at the octupolar ($L = 3$) level. The overall accuracy reached by the E-PA model is about $0.01\text{--}0.02 \text{ e } \text{\AA}^{-3}$ ($L = 5$) and persistently decreasing with increasing L . Similar results are obtained for sulfamic acid, except for the S=O bond which is inadequately represented by both PA expansions at the quadrupolar degree. For this molecule, we observe a slower convergence rate that is attributable to the extended Gaussian basis set (f-type functions) utilized in the QC-ED. This has also been found in the course of a preliminary study on formamide.⁴¹

It is also expected that the convergence issue is more “delicate” for the local topological properties involving derivatives of the ED. The errors of the E-PA ($L = 4$) are comparable and an order of magnitude higher, for ρ_{BCP} and $\nabla^2 \rho_{\text{BCP}}$, respectively, than the uncertainties typically reported for regular bonds in experimental studies based on the HC-PA parameterization. In fact, it takes an upper limit of ($L = 16$) for the E-PA expansion to faithfully reconstruct all BCP properties of both molecules. It is important to stress in this respect the “uniform” nature of the convergence (not in the strict mathematical sense) of the E-PA that includes all BCP indices. This result is not local, since an almost perfect agreement (for both $\rho_{\text{E-PA}}$ and $\nabla^2 \rho_{\text{E-PA}}$) with the corresponding target QC properties (ρ_{Ψ} and $\nabla^2 \rho_{\Psi}$) can be achieved for the entire bond-profile of each bond of the formamide molecule but only at the highest order ($L = 16$). On the other hand, the OHC-PA formalism, even with the optimized order-independent RDFs, fails to recreate the target ED, yet it can apparently yield correct values for ρ_{BCP} at a lower order. Furthermore, no convergence to zero error can be established in this case. The inconsistency in the $\nabla^2 \rho_{\text{BCP}}$ values for formamide can be attributed to the bond-parallel curvature (λ_3) that appears to carry the largest uncertainty based on the PA models.

A significant finding of this study is the overall inaccuracy of the OHC-PA properties along the bond path, especially in regions of the VSCCs, for the C=O and C—N bonds in formamide. This observation contradicts the results of numerous reports that present much better agreement between experimental HC-PA ($L = 4$) and QC-EDs in terms of bond-path scans.^{42–45} A quadrupole-zeta basis utilized in the formamide analysis, opposed to the triple-zeta basis used in the above cited works, might be one of the reasons for this inconsistency.

This computational study firmly demonstrates that no perfect agreement between topological details of an extended-basis QC-ED and its PA representation can be expected at the usual level of multipole expansion, even if the corresponding densities appear to be statistically equivalent within the usual tolerance level. Thus the results of comparative topological analyses of theoretical and experimental PA densities in terms of local topological indices should be viewed more critically; local (BCP) agreements should not be considered as the absolute validation of the experimental PA-ED, and disagreements should not be attributed solely to crystal-field or data-resolution effects. These findings raise the question of what significance of experimental BCP indices have that would

justify their mass production. Since the topology of the HC-PA Laplacian can possess high uncertainties, strict quantitative conclusions drawn from experimental PA-EDs on reactivity can be especially doubtful. Besides the level of expansion (degree), the order-dependence of the RDFs appears to be essential for convergence.

Additional points to emphasize. (a) The title analysis was done within the stationary-geometry framework; thus correlations between conventional (nuclear positions and ADPs) and static-ED parameters inherent to the experimental protocol were completely bypassed. A more far-reaching issue to be raised here is that the experimental (PA-based) nuclear positions do not necessarily match the optimized theoretical (QC-based) ones. In other words, the “isolated-molecule” QC-ED derived at the experimental geometry does not necessarily correspond (for physical and/or computational reasons) to the stationary situation for which Coulomb forces are balanced and for which important QTAIM statements apply exclusively. Unbalanced forces manifest themselves in local polarizations of the QC-ED that can include both core and valence contributions. This can present an extra uncertainty component to the validation of the standard HC-PA ED that is however not easily tractable. (b) The OHC-PA RDFs used in this study are the least biased representations of the corresponding E-PA functions. The results were “designed” to reveal errors solely due to ignoring the order-dependence of RDFs in the PA expansion of a QC-ED. The OHC-PA discussed here is thus optimized to account for a particular QC-ED and in this respect maximally superior for validation to the conventional (isolated-atom based) HC-PA adopted in X-ray charge density analyses. (c) Our direct-space analysis corresponds to infinite Fourier-space and thus not affected by data-resolution or fitting issues. (d) The restricted flexibility of the HC-PA RDFs adapted in experimental studies has always been considered as the major limiting factor of the accuracy of X-ray charge densities,^{46,47} and considerable efforts have been made to overcome this issue but usually within the single-Slater framework⁴⁸ to keep the number of parameters to be fitted manageable. The analyses of E-PA RDFs projected out of extended-basis QC-EDs however suggest that the structure of these functions is, as expected, more complex than that of the Slater functions (obviously, they cannot be represented by single-Slater functions). How this “inadequacy is transformed” into the Fourier-space (scattering factors), or tempered by thermal smearing, is remained to be explored. Our follow up studies will focus on interpreting Bragg data of molecular crystals in terms of order-dependent E-PA RDFs deduced from QC-EDs of isolated molecules. Using bound rather than isolated-atom scattering factors in X-ray data analyses has the potential of opening new revenues for treating non-centrosymmetric structures, atomic sites with an-harmonic vibration, magnetic scattering, and projecting crystal-field effects onto isolated-molecule QC-EDs.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for Bond Critical Point data for both molecules at different orders of pseudoatom expansion.

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