research papers

Determination of a one-electron reduced density matrix using a coupled pseudo-atom model and a set of complementary scattering data

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A possible model of one-electron reduced density matrices is presented, adapted from the Hansen–Coppens pseudo-atomic description of electron density [Hansen & Coppens (1978). *Acta Cryst.* A**34**, 909–913]. Potential benefits from a joint refinement of the model from X-ray diffraction and deep inelastic scattering data are illustrated.

1. Introduction

High-resolution X-ray diffraction, convergent-beam electron diffraction, deep inelastic X-ray scattering (Compton scattering), e–$2e$ and γ–e–γ spectroscopies are all directly related to the one-electron reduced density matrix (1-RDM) (Weyrich, 1996). On the other hand, it is well known (Löwdin, 1955; Coulson, 1960) that the 1-RDM contains all the information about the electronic structure available at the one-electron level. Unfortunately, and to our best knowledge, few attempts to refine 1-RDM models have been carried out (Clinton & Massa, 1972; Massa *et al.*, 1985; Aleksandrov *et al.*, 1989; Howard *et al.*, 1994; Snyder & Stevens, 1999; Jayatilaka & Grimwood, 2001). With the exceptions of Schmider (Schmider *et al.*, 1992, 1993) for atomic systems, and Schulke and co-workers (Schulke *et al.*, 1981), only X-ray diffraction data were employed as experimental references.

The purpose of this paper is to study to what extent the successful decomposition of the electron density into aspherical pseudo-atomic contributions (Hansen & Coppens, 1978) can be adapted to the 1-RDM case. Furthermore, we intend to show that, with such a model, the complementarity between very different experiments can be better exploited through a joint refinement.

2. Density matrices and X-ray scattering experiments

We briefly recall essential points about density matrices and their relationships with diffraction and inelastic scattering experiments.

For a pure state, the so-called one-electron reduced density matrix is defined from an N-electron wavefunction with the expression

$$\Gamma(\mathbf{x}'_1, \mathbf{x}_1)$$
$$= N \int \psi^*(\mathbf{x}'_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\psi(\mathbf{x}'_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\,d\mathbf{x}_2 \ldots d\mathbf{x}_N, \quad (1)$$

where $\mathbf{x}_i$ stands for the spin and position variables of particle i. In this paper, we will use a 'spin-traced' density matrix:

$$\Gamma(\mathbf{r}', \mathbf{r}) = \int \Gamma(\mathbf{x}', \mathbf{x})_{\sigma'=\sigma}\,d\boldsymbol{\sigma}, \quad (2)$$

where $\boldsymbol{\sigma}$ is the spin variable. Definition (1) implies that a legitimate model of a 1-RDM is expected be related to an N-electron wavefunction, *i.e.* to be 'N-representable'. In the case of a pure state, one step towards this property is to request that the 1-RDM should at least be 'idempotent', *i.e.* $\int \Gamma(\mathbf{r}', \mathbf{r}'')\Gamma(\mathbf{r}'', \mathbf{r})\,d\mathbf{r}'' = \Gamma(\mathbf{r}', \mathbf{r})$.

Structure factors are Fourier transforms of the thermal average of the charge density, $\langle\rho(\mathbf{r})\rangle_T$, and hence also of the *diagonal part of the 1-RDM* in position representation,

$$F(\mathbf{Q}) = \int_v \langle \Gamma(\mathbf{r}', \mathbf{r})_{\mathbf{r}'=\mathbf{r}}\rangle_T \exp(i\mathbf{Q} \cdot \mathbf{r})\,d\mathbf{r}. \quad (3)$$

As a consequence of this relationship, in a refinement using only X-ray diffraction data, and unless strong mathematical constraints are applied to the model, one should not expect the resulting experimental 1-RDM to have any meaningful *off-diagonal elements*. In particular, N-representability or even idempotency may not be satisfied.

Most of the inelastic scattering experiments cited in the *Introduction* provide projections of the electron momentum density, and therefore mostly probe the *off-diagonal part* of the 1-RDM. This is the case, within the so-called 'impulse approximation' (Platzman & Tzoar, 1965), for the directional Compton profiles (DCP):

$$J(\mathbf{u}, q) = \frac{1}{2\pi\hbar} \int \Gamma(\mathbf{r}, \mathbf{r} + (\mathbf{u} \cdot \mathbf{s})\mathbf{u}) \exp(iq\mathbf{u} \cdot \mathbf{s})\,d\mathbf{r}\,d\mathbf{s}, \quad (4)$$

where $\mathbf{u}$ is a unit vector collinear to the inelastic scattering vector. It is essential to note that the ever-increasing brightness of synchrotron-radiation sources allows for a collection of a large number of DCPs, at 0.1 a.u. resolution. Hence, reliable momentum density reconstructed in two or three dimensions is becoming available and should also be considered.

Expressions (3) and (4) clearly show that a dual approach of position and momentum spaces reveals the strong complementarity of the different experiments, probing at different parts of the 1-RDM. This was first beautifully illustrated by

Schmider *et al.* (1992). Bragg scattering has a solid reputation in its ability to describe the local distribution of the electron density in the neighborhood of atomic sites. However, it can suffer greatly from disorder, temperature and multiple scattering effects. On the contrary, because Compton scattering relies on an incoherent process, it is much less sensitive to crystalline quality. DCPs are more adapted to the study of delocalized electrons and, far from a phase transition, low momentum electrons are hardly affected by thermal vibrations. We should hence expect that a wider diversity in scattering data should enrich our experimental knowledge of the 1-RDM.

3. A coupled pseudo-atom model

Most of the 1-RDM models that have been proposed to date were built with the unique purpose of fitting experimental structure factors. Off-diagonal elements were either considered as a by-product for idempotence requirements (Howard *et al.*, 1994) or to yield a minimum energy of the electronic part of the system (Jayatilaka & Grimwood, 2001).

We here propose to modify the electron-density model as a sum of pseudo-atomic and multipole contributions elaborated by Hansen & Coppens (1978) to construct a 'generic' 1-RDM as

$$\Gamma(\mathbf{r}', \mathbf{r}) = \sum_a \Gamma_a(\mathbf{r}', \mathbf{r}) + \sum_{(a,b)} \Gamma_{ab}(\mathbf{r}', \mathbf{r}), \qquad (5)$$

where a labels the purely atomic contributions and (a, b) stands for any couple of close neighboring atoms following a 'nearsightedness' principle (Kohn, 1996; Ragot *et al.*, 2002).

This model presents at least two strong advantages. The pseudo-atom decomposition has been shown to be flexible enough for applications to X-ray diffraction experiments and nevertheless linearly scales with the size of the system. Secondly, it provides on its own an intuitive, but not unique, and handy partitioning of the electron distribution in terms of atomic and bond contributions with a proved efficiency for deconvoluting most of the thermal effects (Tanaka, 1988).

In practice, the atomic contribution is built up from an isotropic core (usually frozen), Γ_a^{core}, and a valence, Γ_a^{val}, component, constructed from the isolated atom orbitals $\{\psi_i(\mathbf{r})\}$. The latter are expanded on a set of basis functions $\phi_j(\mathbf{r})$. The anisotropic distortion is described by a hybridization term, Γ_a^{hyb}, obtained from products of basis functions with different azimuthal quantum numbers. We thus write

$$\Gamma_a^{\mathrm{val}}(\mathbf{r}', \mathbf{r}) = (\kappa_a)^3 \sum_{i \in \mathrm{val}(a)} n_i^a \psi_i^*(\kappa_a(\mathbf{r}' - \mathbf{R}_a)) \psi_i(\kappa_a(\mathbf{r} - \mathbf{R}_a))$$

$$(6a)$$

$$\Gamma_a^{\mathrm{hyb}}(\mathbf{r}', \mathbf{r}) = (\kappa_a')^3 \sum_{(i,j)\in a} P_{ij}^a \widehat{S}[\phi_i^*(\kappa_a'(\mathbf{r}' - \mathbf{R}_a))\phi_j(\kappa_a'(\mathbf{r} - \mathbf{R}_a))],$$

$$(6b)$$

where $\widehat{S}$ symmetrizes the products of eigenfunctions with respect to a permutation of $(\mathbf{r}', \mathbf{r})$. The two-center contributions to the 1-RDM, denoted Γ_{ab}, are very similar to the

hybridization component with the two basis functions pertaining to different atoms:

$$\Gamma_{ab}(\mathbf{r}', \mathbf{r}) = (\kappa_a'' \kappa_b'')^{(3/2)}$$
$$\times \sum_{i\in a, j\in b} P_{i,j}^{ab} \widehat{S}[\phi_i^*(\kappa_a''(\mathbf{r}' - \mathbf{R}_a))\phi_j(\kappa_b''(\mathbf{r} - \mathbf{R}_b))].$$

$$(7)$$

These coupling terms were already considered for refinement in a previous work by Coppens and co-workers (Coppens *et al.*, 1971). The authors emphasized the difficulties arising from using such quantities for interpreting experimental X-ray structure factors. However, it has been shown that the products of orbitals centered on different sites are essential for explaining oscillations of the autocorrelation functions, *i.e.* the Fourier transforms of directional Compton profiles.

The resulting 1-RDM is thus, by construction, real symmetrical. Nuclei positions, $\mathbf{R}_a$, occupation numbers, n_i^a, hybridization coefficients (real-valued and symmetrical), P_{ij}^a, as well as the scaling parameters, $\kappa, \kappa', \kappa''$, are expected to be determined from comparison with experimental data.

4. Pseudo-data and minimization

We wish to test the ability of such a 1-RDM model based on coupled pseudo-atoms to absorb information from two data sets issuing from experiments as different as X-ray diffraction and Compton scattering.

We present here the results of the refinement of model (5) on two diatomic systems, hydrogen fluoride and carbon monoxide. To allow for a fair estimate of the accuracy of the refinement process, we decided to start from a known (calculated) 1-RDM, $\Gamma^{\mathrm{exp}}(\mathbf{r}', \mathbf{r})$ from which pseudo-data sets were derived. Using realistic experimental values, thermal smearing, by means of one- and two-center Debye–Waller factors, were then applied to the structure factors. In both cases, the molecule was placed in a unit cell ($1 \times 1 \times 3$ Å) defining the sampling in reciprocal space. Convolution by a pseudo-instrumental resolution, mis-centering and slope error (from possible ill background subtraction) were applied to the directional Compton profiles. Gaussian distributions of noise corresponding to usual statistical errors were finally added to the resulting structure factors and DCPs. In order to account for the finite experimental resolution, 505 structure factors were considered, corresponding to a truncation at $\sin(\theta)/\lambda = 1.3$ Å^{-1}. As for DCPs, 70 points, equally spaced, up to 7 a.u. were used. The final pseudo-data sets are hereafter denoted $\{F^{\mathrm{exp}}(\mathbf{Q})\}$ and $\{J^{\mathrm{exp}}(\mathbf{u}, q)\}$.

The original 1-RDM, $\Gamma^{\mathrm{exp}}(\mathbf{r}', \mathbf{r})$, was calculated at the Hartree–Fock level with a minimal basis set for the two diatomic molecules hydrogen fluoride and carbon monoxide (Fig. 1). The 1-RDM model, hereafter denoted $\Gamma^{\mathcal{M}}(\mathbf{r}', \mathbf{r})$ is constructed from atomic eigenfunctions also computed at the Hartree–Fock level, in a so-called 'single-zeta' basis set. For each atom, refined parameters are: the κ_a, κ_a' and κ_a'' atomic extension parameters, the n_i^a valence orbitals occupancies, the P_{ij}^a and P_{ij}^{ab}, respectively hybridization and interatomic

coupling parameters. In this work, the positions of nuclei were not refined and theoretical values were used.

Details of strategies for combining experimental data in a unique model for electronic structure investigation were given in previous publications (Gillet *et al.*, 2001; Gillet & Becker, 2004). In this work, two quantities were considered for minimization:

$$\mathcal{L}_s = \chi_F^2 + \chi_J^2 \tag{8a}$$

$$\mathcal{L}_p = (\chi_F^2)^{N_F}(\chi_J^2)^{N_J}, \tag{8b}$$

where $N_{\mathcal{P}}$ refers to the number of data in a given set and $\chi_{\mathcal{P}}^2$ has the usual definition in statistics for a given property $\mathcal{P}$. Though not as intuitive as (8a), the second expression (8b) was introduced to compensate for an unfair weighting due to an overwhelming number of data points or a possible inaccuracy of the absolute values of data error bars in one set (Sivia, 1996). In this work, both quantities yielded identical results when the two sets had a comparable number of data points with a significantly faster convergence using (8a). However,

for the sake of homogeneity, all the results presented in the following were obtained by means of (8b), which turned out to be more stable with respect to a change of the number of data points in each set.

At this stage, no constraint on the number of electrons or idempotence was introduced on $\Gamma^{\mathcal{M}}(\mathbf{r}', \mathbf{r})$ to 'let the nature speak' with the conviction that these conditions would be automatically fulfilled with the agreement to (pseudo-) experimental values. Nevertheless, and strictly speaking, idempotence is not to be expected when thermal effects are present nor when, in the real case, data from an interacting many-electron system are used.

5. Results and discussion

In order to illustrate the potential benefits brought by joint refinements, we first consider refinements using either χ_F^2 or χ_J^2 separately. As expected, the resulting 1-RDM from refinements on structure factors only (see Fig. 2) yield very satisfactory qualitative agreements with the original on the diagonal parts ($s = 0$). However, essential features on the off-diagonal regions are clearly not reproduced. It thereby shows that, despite the fact that the model with such refined parameters perfectly matches the pseudo-experimental
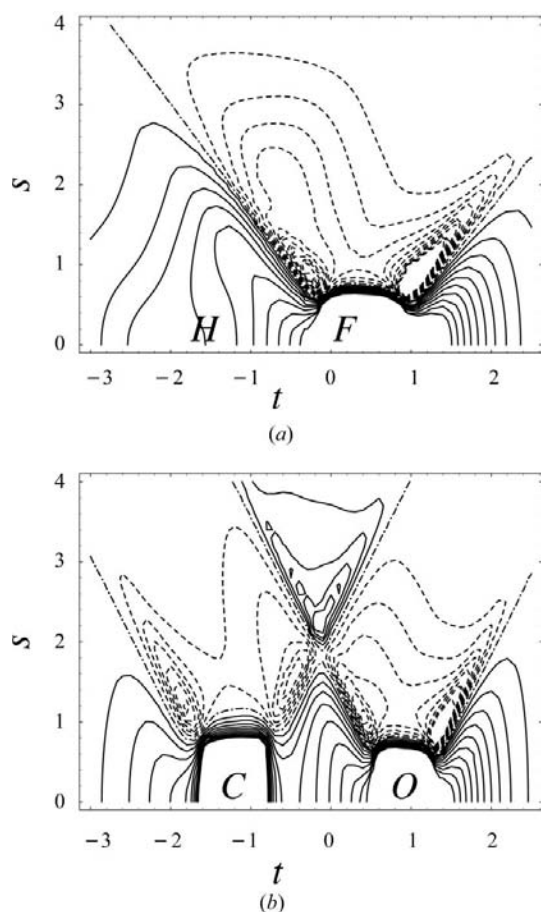
Figure 1
Pseudo-experimental reduced density matrices, $\Gamma^{exp}(\mathbf{r}', \mathbf{r})$, for the hydrogen fluoride molecule (top) and carbon monoxide molecule (bottom) in extracular–intracular representation taken along the bond axis. Extracular and intracular coordinates are respectively $t = (z + z')/2$ and $s = z - z'$ in a.u. Positive (solid) and negative (dashed) contours are plotted every 0.1 a.u. Contours for values higher than 1.0 a.u. are not shown.
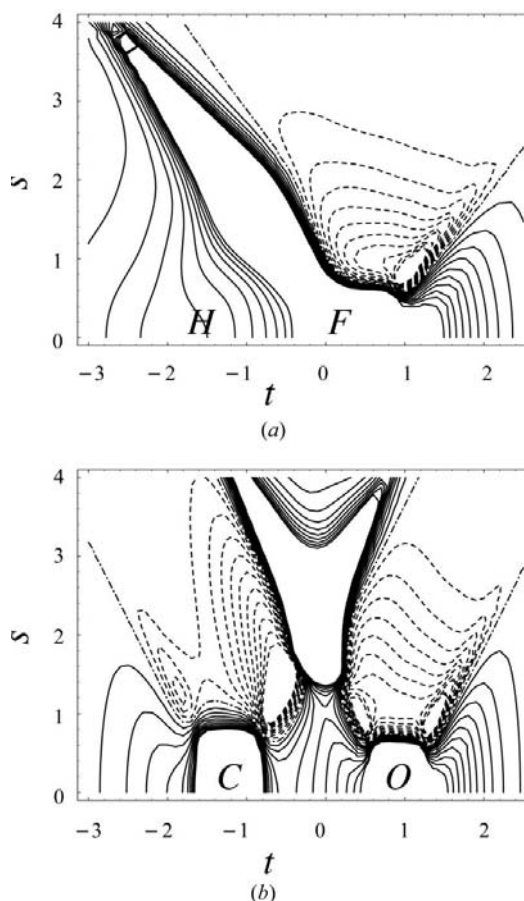
Figure 2
Refined 1-RDM for HF molecule (top) and CO molecule (bottom) using only the pseudo-experimental structure factors.

diffraction data, it does not account for the details of the chemical bond structure. More specifically, the off-diagonal positive peak, representing a covalent signature of the C—O bond, is far too intense, showing that structure factors do not automatically allow for a correct description of delocalized electrons in terms of coherent couplings between atomic sites. A change in the amplitude of the error bars amplifies this effect (not shown here) and therefore confirms that this is a limitation that is intrinsic to a diffraction measurement.

On the other hand, the sole use of a limited number of directional Compton profiles in the refinement does also suffer from similar artifacts (see Fig. 3). This is of course true on the diagonal close to the hydrogen site, and even more obvious on both atomic sites in the CO molecule. The results here obviously lack the precious ability of diffraction measurements to account for the local arrangement of the charge density in the vicinity of nuclear sites. It should be noted that the covalent CO bond peak is clearly not rendered. This behavior can be attributed to the difficulty, in momentum space, to separate atomic hybridization from site coupling contributions.

We now turn to the use of expressions (8). Joint refinements gathering structure factors and Compton profiles allow the model for a good reproduction of the original 1-RDM. Charge density as well as iono-covalent features of the off-diagonal regions are clearly shown with the correct magnitude (Fig. 4). The covalent peak for the CO molecule could partly be recovered with five DCPs pointing in non-equivalent directions in addition to $\{F^{exp}(\mathbf{Q})\}$.

Even though idempotence was clearly not at the center of this study, it turns out that the joint refinement brings enough constraints to reach almost perfect identity between $\int \Gamma^{\mathcal{M}}(\mathbf{r}', \mathbf{r}'')\Gamma^{\mathcal{M}}(\mathbf{r}'', \mathbf{r}) \, d\mathbf{r}''$ and $\Gamma^{\mathcal{M}}(\mathbf{r}', \mathbf{r})$ with typical mean-square deviations of 5×10^{-4} a.u. for HF and 6.5×10^{-4} a.u. for CO along their bond directions. At this point, no prior constraint was applied to the model to ensure that the 1-RDM is N-representable. It was merely checked that all the occupation numbers of the natural orbitals were not noticeably out of the $[0, 1]$ range.

6. Conclusions

Inspired by the Hansen & Coppens electron-density model, we have shown that a generic model of the one-electron reduced density matrix can be used efficiently for retrieving important features of the chemical bonds if data from complementary experiments are employed. This work illustrates a test of the model on two rather different diatomic
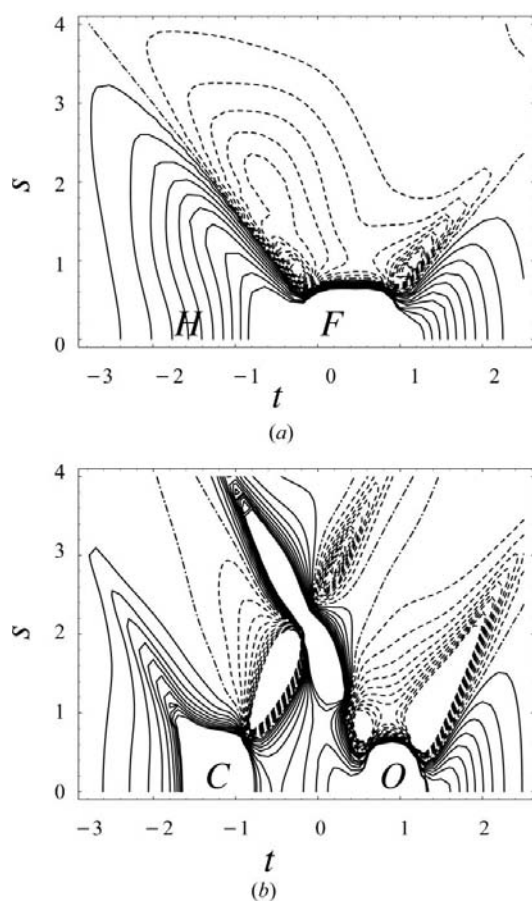
Figure 3
Refined 1-RDM for HF molecule (top) and CO molecule (bottom) using only two directional Compton profiles.
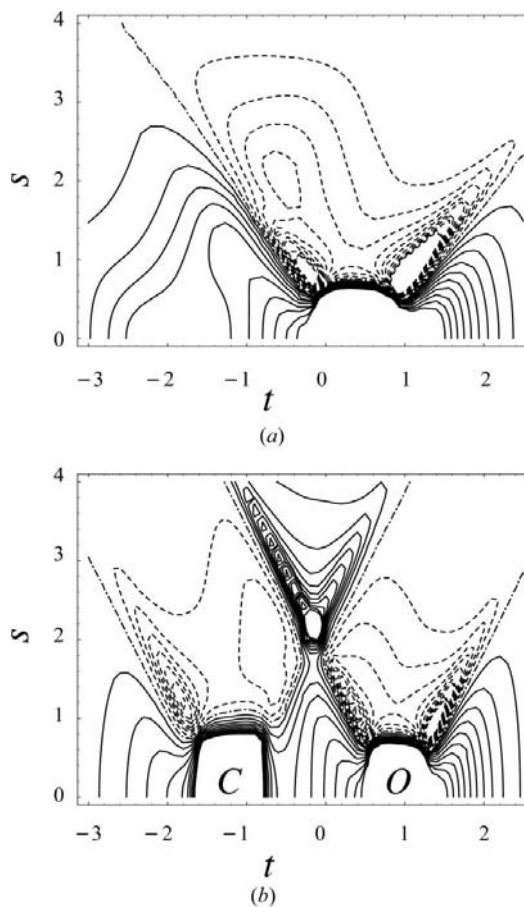
Figure 4
Refined 1-RDM for HF and CO molecules obtained by combining structure factors and directional Compton profiles.

systems HF and CO. In the case of a more structured covalent bond, a larger set of directional Compton profiles is required so that the richness of a reconstructed momentum density can be exploited simultaneously with X-ray structure factors.

For accurate comparison with the pseudo-experimental structure factors, one- and two-center Debye–Waller parameters had to be included in the model. As expected, correlations with the κ parameters increased the difficulty in reaching convergence from the sole use of $\{F^{\exp}(\mathbf{Q})\}$. However, the introduction of Compton scattering data yielded a more stable result with better confidence intervals.

Further studies (the details of which will be reported in a forthcoming paper) have shown that joint refinements are more sensitive to the quality and flexibility of the model than when a unique type of experiment is considered.

The joint refinement method for retrieving information on density matrices is of course appropriate when position and momentum space densities can reliably be measured. Limitations are therefore the same as those currently encountered by high-resolution crystallography augmented by the difficulty of interpreting inelastic scattering data for many- (and heavy-) atom systems. We thus believe that ionic crystals as well as small hydrogen-bonded molecular crystals (such as urea, ice, . . .) should be considered for first studies.

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