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Abstract

This study investigates the possibility of detecting relativistic effects and electron correlation in single-crystal X-ray diffraction experiments using the examples of diphenyl mercury (HgPh₂) and triphenyl bismuth (BiPh₃). In detail, the importance of electron correlation (ECORR), relativistic effects (REL) [distinguishing between total, scalar and spin-orbit (SO) coupling relativistic effects] and picture change error (PCE) on the theoretical electron density, its topology and its Laplacian using Infinite Order Two Component (IOTC) wavefunctions is discussed. This is to develop an understanding of the order of magnitude and shape of these different effects as they manifest in the electron density. Subsequently, the same effects are considered for the theoretical structure factors. It becomes clear that SO and PCE are negligible, but ECORR and scalar REL are important in low- and medium-order reflections on absolute and relative scales - not in the high-order region. As a further step, Hirshfeld atom refinement (HAR) and subsequent X-ray constrained wavefunction (XCW) fitting have been performed for the compound HgPh₂ with various relativistic and non-relativistic wavefunctions against the experimental structure factors. IOTC calculations of theoretical structure factors and relativistic HAR as well as relativistic XCW fitting are presented for the first time, accounting for both scalar and spin-orbit relativistic effects.

Introduction

Relativistic effects play an important role in chemistry. They are responsible for macroscopic properties of heavy elements, such as the color and properties of gold,¹⁻³ or the liquid aggregation state of mercury,⁴ they explain the high voltage of lead-acid batteries,⁵ the geometries of heavy-element containing molecules⁶ and the reactive behaviour of heavy elements.⁷,⁸ The observed effects are normally attributed to a contraction of the inner shells of the heavy elements when electrons are reaching speeds close to the speed of light, which in turn influences the outer core shells and changes ionisation potentials and other physical properties.⁹⁻¹¹ The
influence of relativistic effects on chemistry is therefore identifiable through shifts of spectroscopic properties with respect to non-relativistic expectations/models which are related to the energetic levels of the shell structure of atoms,\textsuperscript{12} and also in nuclear magnetic resonance experiments.\textsuperscript{13,14} Importantly, the simple but wide-spread notion that the innermost electrons are influenced by relativity most severely and the outermost electrons the least is not maintainable. In contrast, Pyykkö points out:\textsuperscript{6} "Due to interacting relativistic and shell-structure effects, the higher s shells' contraction can in fact be even larger; for gold, the 6s shell has a larger (percentual) relativistic effect than the 1s shell." This leads us to the question if relativistic effects are likewise significant for the bonding electron density in heavy-element containing molecules so that they can probably be detected and modeled in single-crystal X-ray diffraction data.

Experimental electron density investigations are normally based on Hansen-Coppens multipole modelling\textsuperscript{15} of structure factors from low-temperature single-crystal X-ray diffraction.\textsuperscript{16,17} The total electron density distribution is constructed from a superposition of pseudo-atoms, which are aspherical atom-centered electron densities built up by spherical-harmonic functions up to hexadecapole level and single-zeta Slater-type radial functions. The radial contraction due to relativistic effects can be accounted for in the modeling when using radial functions introduced by Macchi and Coppens.\textsuperscript{18} This only covers scalar contributions to relativistic effects and not the spin-orbit coupling contributions, but it will be shown below that scalar relativity is the major effect. Nevertheless, it is known that the multipole formalism is not flexible enough to model heavy elements.\textsuperscript{19,20} Stevens and Coppens have pointed out already in 1976\textsuperscript{21} that "transition metals are not fully suitable for charge density analysis because most of the X-ray scattering comes from the core electrons." Already with third-row atoms such as sulfur, non-negligible residual electron densities in the core region can occur even if the measurement is of high quality (see e.g. Novakovic \textit{et al.}\textsuperscript{22} and references therein). For measurements of extremely high quality and extremely high resolution, the extended Hansen-Coppens formalism\textsuperscript{23} can be employed that is able to model
core deformation and core polarisation through an additional set of refinable multipole and expansion-contraction parameters. Successful applications of the extended Hansen-Coppens model refer to data of light-atom structures measured with powder-diffraction techniques that are of the highest quality and resolution achievable today. However, a similar approach has been used recently to attempt multipole modelling of cesium uranyl chloride. It is questionable if this approach can distinguish between different physical effects, and can lead to an experimental description of relativistic effects in the electron density.

X-ray wavefunction refinement (XWR) is an alternative approach for the modelling of experimental electron density. It consists of Hirshfeld atom refinement (HAR) and X-ray constrained wavefunction fitting (XCW) (established in 1998 and extended in 2001), so it refines geometry and fits the electron density against the measured structure factors. For more details, see below. Within XWR, a quantum-mechanical model is employed in the description of the diffraction experiment, so that any flexibility of the basis set is possible. Hence, intrinsically the method should be able to deal with heavy elements in contrast to the multipole model, making use of modern quantum-mechanical developments. Through an appropriate choice of the method (HF, DFT, IOTC, see below) physical effects such as electron correlation and relativity can be excluded or included in the QM ansatz used for XWR. It should therefore be possible to distinguish between these effects and compare their size to the information content of the actual experimental data. It has already been studied how electron correlation affects the theoretical structure factors, which is important from the perspective of possible ambiguities of XCW fitting results due to the choice of an electron correlation method. Currently, investigations into electron correlation are also underway by Genoni et al. within their recent implementation of XCW fitting which is extended for the option of using extremely localized molecular orbitals.

The pilot work on XCW and relativistic effects by Hudak et al. was performed for copper and iron complexes. The extent of relativistic effects in electron/spin densities and structure factors was analyzed at low resolution, without being able to conclude with confi-
dence towards the extraction of relativistic effects from experimental data. However, it was shown previously that relativistic effects have a non-negligible influence on the topology of the electron density distribution according to the Quantum Theory of Atoms in Molecules (QTAIM). The concept of a zero flux surface of electron density remains a natural choice of defining a QTAIM atom in a molecule also in the relativistic domain. This was found by Anderson and Ayers for the quasirelativistic Zero Order Regular Approximation Hamiltonian. Nevertheless, Cioslowski and Karwowski commented on a degree of arbitrariness in the expression for the relativistic Lagrangian density as well as for the atomic surface choice itself. The Dirac-Coulomb Hamiltonian difference electron density and Laplacian were considered with respect to Zeroth-Order-Regular Approximation, 10th order Douglas-Kroll-Hess Hamiltonian and the non-relativistic Hamiltonian for the series TM(C_2H_2) (TM = Ni, Pd and Pt). Batke and Eickerling have studied the extent of relativistic effects in electron density as well as structure factors and residual density for the same series of TM(C_2H_2) compounds (where TM = Ni, Pd and Pt) including a direct comparison of experimental and theoretical data for Pd(C_2H_2). They have shown, that relativistic effects are discernible theoretically in the structure factors of heavy element complexes, but being at the limit of the experimental error. Similar analyses of relativistic effects, distinguishing between scalar and spin-orbit relativistic contributions to the electron density topology of a ruthenium and an osmium complex showed that the relativistic effects for 5d-transition metal complexes are affecting the valence electron density and/or the bonding situation between the transition metal and the ligand atoms. However, it has not been possible so far to experimentally determine and quantify the extent of relativistic effects in the electron density of a heavy-element containing compound. Hereby, we do not mean that relativistic reality can be turned on and off in an experiment. Nevertheless, it should be possible to analyse in detail the experimentally determined structure factors and electron densities with respect to relativistic and non-relativistic reference models which can be based on theoretical calculations. In other words, in the reconstruction of the experimental diffraction pattern
different models can be used in which relativity can be switched on and off (by means of 
either taking the velocity of light to infinity or not) in the same way that electron correlation 
can be switched on and off in the model. Hence, significance, affected regions, source and 
origin of the given effect can be deconvoluted in the experimental electron density.

Thus the exploration of relativity (as a physical effect) and electron correlation (as a 
methodological effect) with respect to experimental observables (structure factors) directly 
transferable to electron density are worth to be considered further from the theoretical side 
with the aim to predict preferable conditions and suitable compounds to make these effects 
discernible in the diffraction experiment. Hence, it is not the aim of this study to experimentally determine relativistic effects and electron correlation in the electron density, but 
to investigate if this is feasible in principle, and to identify properties, methodologies and 
methods which make it possible. The influence of relativistic effects on molecular structure 
and spectroscopic properties of triphenyl bismuth BiPh$_3$ has recently been investigated carefully, 
so that we chose the same compound as a model compound for our investigation and 
extend the comparison to include diphenyl mercury HgPh$_2$. Through a combination of vari-
ous methods, difference densities and structure factors are theoretically calculated that can 
be attributed to the pure effects of electron correlation, relativity (distinguishing between 
total, scalar and spin-orbit coupling contributions) and the picture change error.

Methods

Relativistic effects

The relativistic expression for the energy of a free particle (including kinetic and rest mass 
energy) reads:

\[ E^2 = m^2 c^4 + c^2 p^2 \]  \hspace{1cm} (1)
where \( m \) is the rest mass, \( c \) the speed of light and \( p \) the momentum of the particle. To obtain a suitable expression of the single particle energy for the insertion into the Hamiltonian, Dirac has linearized equation (1). The free-particle 4-component relativistic Dirac Hamiltonian can be expressed in the following way:

\[
\hat{H}_D = c\alpha \cdot \hat{p} + \beta mc^2
\]

(2)

where \( \alpha_{x,y,z} \) and \( \beta \) are \( 4 \times 4 \) matrices which satisfy equation 1.\(^{48-52}\)

In atoms and molecules, treating the electron-nucleus attraction \( (V) \) and the electron-electron repulsion \( via \) Coulombic interaction \( (\sum_{ij}r_{ij}^{-1}) \) leads to the Dirac Coulomb Hamiltonian \( (\hat{H}_{DC}) \).

\[
\hat{H}_{DC} = \sum_i [c\alpha \cdot \hat{p}_i + \beta mc^2] + V + \sum_{ij} r_{ij}^{-1}
\]

(3)

where \( V \) is the electron - nucleus potential, \( i.e. \ V = -\sum_{i,A} Z_A / r_{iA} \) (where \( A \) labels the nuclei and \( i \) labels the electrons). A Dirac Coulomb Hamiltonian eigenvector \( \Psi \) according to Dirac’s Equation \( (\hat{H}_{DC}\Psi = E\Psi) \) will have four components \( (4c) \), accounting formally for spin \( (\text{up/down}) \) and energy \( (\text{positive/negative}) \) degrees of freedom:

\[
\Psi = \begin{pmatrix}
\Psi_{L,\alpha} \\
\Psi_{L,\beta} \\
\Psi_{S,\alpha} \\
\Psi_{S,\beta}
\end{pmatrix}
\]

(4)

where \( L \) and \( S \) denote the Large and Small component (due to their contribution to the electronic states) and \( \alpha \) and \( \beta \) denote the expansion of the spin degree of freedom in terms of the particular Pauli \( \hat{S}_z \) eigenvectors (not to be confused with the spin labels in the non-relativistic sense).

Because of the enormous computational cost of the 4c-approach, it is customary to simplify the 1-electron Dirac Coulomb Hamiltonian to 2-component \( (2c) \) or even 1-component
forms (both being considered as quasirelativistic Hamiltonians). In the 2c approximation, the block diagonalization of the one-electron Dirac Coulomb Hamiltonian is achieved by the unitary matrix $U$, which will be herein referred to as the Infinite Order Two Component (IOTC) quasirelativistic approach$^{53–59}$ with

$$\hat{H}^{\text{decoupled}} = U \hat{H}_{DC} U^+ = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}$$

(5)

where $h_+$ and $h_-$ are the decoupled Hamiltonians of the positive energy (electrons) and negative energy (positrons) spectra, respectively, and $U$ is the exact Foldy-Wouthuysen transformation matrix$^{43,60–62}$ which is expected to be found upon the condition to diagonalize $\hat{H}_{DC}$. (The full transformation should account for the 2-electron Coulomb repulsion,$^{57,59}$ but this is computationally as demanding as the 4c approach itself.) The change in the wavefunction caused by application of the unitary matrix $U$ can be expressed as follows

$$\tilde{\Psi} = U \Psi$$

(6)

and the Schrödinger equation becomes

$$\hat{H}^{\text{decoupled}} \tilde{\Psi} = E \tilde{\Psi}.$$  

(7)

In the no-pair restriction no creation of electron-positron pairs $h_-$ is left out of consideration, so that the Large component part is expressed only in terms of the positive energy spectrum, i.e. the electronic solutions result into the positive energy spectrum quasirela-
tivistic wavefunction $\tilde{\Psi}_+$ according to

$$\tilde{\Psi}_{\text{no-pair}} = \begin{pmatrix} \tilde{\Psi}_{+,\alpha} \\ \tilde{\Psi}_{+,\beta} \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \tilde{\Psi}_+ \end{pmatrix}$$

\hspace{1cm} (8)

The IOTC approach decouples the Large and Small components exactly and thus belongs to the eXact 2-Component (X2C) class of quasirelativistic Hamiltonians.\textsuperscript{62–67} The 2-component approaches, which self-consistently treat spin-orbit (SO) relativistic effects, are nowadays becoming part of numerous quantum chemistry packages.\textsuperscript{68–71} More details can be found in reviews\textsuperscript{48,50,72,73} and text books.\textsuperscript{51,52}

In regards to distinguish the scalar and spin-orbit relativistic effects, as well as to allow for the straightforward implementation of scalar relativity into existing non-relativistic codes, the following identity is employed:

$$\sigma \cdot \hat{p} V \sigma \cdot \hat{p} = \hat{p} V \cdot \hat{p} + \sigma \cdot (\hat{p} V \times \hat{p})$$

\hspace{1cm} (9)

where $\hat{p}$ is the momentum operator, $\sigma$ is the Pauli $\sigma$ vector and $V$ is the electron - nucleus potential. In the case of scalar relativity [often denoted as 1-component (1c) or spin-free approaches], only the first term $\hat{p} V \cdot \hat{p}$ on the right hand side of eq. (9) is employed, which requires to have available the $\hat{p}_x V \hat{p}_x$, $\hat{p}_y V \hat{p}_y$ and $\hat{p}_z V \hat{p}_z$ integrals.\textsuperscript{74} Scalar adapted quasirelativistic classics are the Douglas-Kroll-Hess 2nd order (DKH2)\textsuperscript{74–79} and Zero-Order Regular-Approximation (ZORA)\textsuperscript{42,43} Hamiltonians. Nevertheless, the same is possible to do with the IOTC Hamiltonian whose scalar (sr) version (without the inclusion of the one electron spin orbit term) will be denoted as sr-IOTC.

More details on the derivation of the IOTC approach can be found in the original papers of Sadlej & Barysz,\textsuperscript{54,55} in IOTC related papers\textsuperscript{56–59} and the basics of this method are
summarized also in Supporting Information. Herein, the IOTC and sr-IOTC Hamiltonians will be preferably employed to include relativity.

**Picture change error of properties**

According to equation 6, diagonalization of the Dirac Coulomb Hamiltonian simultaneously accounts for a change of the resulting quasirelativistic wavefunction $\tilde{\Psi}$.\textsuperscript{54,80,81} This was recognized in the physics realm already with the introduction of the free particle Foldy-Wouthuysen transformation,\textsuperscript{82} and has been later explored also in the quantum chemistry community.\textsuperscript{83,84} Why picture change affects a particular property at the quasirelativistic level of theory can be understood by the inspection of the formal mapping between the expectation value of a general property operator $\hat{X}$ in the Dirac picture ($\Psi$) and the unitary transformed IOTC picture ($\tilde{\Psi}$):\textsuperscript{54,58,80,81}

$$
\langle \Psi | \hat{X} | \Psi \rangle = \langle \Psi | U \hat{X} U^+ U | \Psi \rangle = \langle \tilde{\Psi} | U \hat{X} U^+ | \tilde{\Psi} \rangle 
$$

(10)

To avoid an error in the 1c/2c calculations of properties when using $\tilde{\Psi}$ (the so-called picture change error PCE), the property operator and/or its matrix representation has to be transformed as shown in equation (10) (PCE correction), \textit{i.e.} it has to be moved to the 1c/2c quasirelativistic level of theory. Picture change error itself is defined as the difference between the properly treated expectation value $< U \hat{X} U^+ >$ [as shown in eq. (10)] and the expectation value which uses $\tilde{\Psi}$ with untreated operator $\hat{X}$:

$$
X_{PCE} = < U \hat{X} U^+ > - < \hat{X} > 
$$

(11)

In the following three subchapters, treatment of PCE in electron density, Laplacian of electron density and the Fourier transform of electron density (structure factors) is briefly presented. In general, it has been found that PCE dominantly affects the core electron density and properties related to electron density in the vicinity and/or at the nucleus, such as
hyperfine coupling,\(^85,86\) quadrupole moments,\(^87\) contact densities\(^36,59,88\) and effective densities.\(^89,90\) Properties related to electron density in the valence region (e.g. dipole moments and/or polarizabilities)\(^91–95\) are not affected by PCE and the same is found for the electron density itself.\(^39,58,80,88\) Nevertheless, a common exploration of PCE in electron density, its Laplacian or Fourier transform for compounds of heavy elements is being worthwhile. Foremost, the direct comparison to the relativistic as well as electron correlation effects is to be addressed, including the radial significance with respect to the core region and the relevance on differences in structure factors with respect to \(sin(\theta)/\lambda\). For a more detailed reading on PCE see also references.\(^54,72\)

**Electron density**

For the purpose of this paper, the electron density \((\rho_e)\) is of central interest. The operator of electron density is an even (diagonal) operator which reads:\(^96\)

\[
\hat{\rho}_e = \sum_{i=1}^{N} \delta^{(3)}(r_i - r)
\]  

(12)

where \(r\) is the general position, \(r_i\) denotes the position of the \(i\)-th electron and \(\delta^{(3)}(r - r_i)\) is the Dirac \(\delta\) function. Because the \(\delta\) function is a function of position, the momentum operator, which is inherently present in the unitary transformation \(U\) (and/or \(Y\) in eq. (8) in Supporting Information), does not commute with \(\hat{\rho}_e\). More detail on the PCE correction of electron density can be found elsewhere.\(^39,58,97\)

**Laplacian of electron density**

There are two possible ways to treat the PCE for properties based on electron density: I. correcting the matrix representation of both operator and density; II. correcting only the density and evaluating the property afterward. In the case of the Laplacian of electron density \(L(r) = \nabla^2 \rho_e\), the PCE correction for \(L(r)\) is essentially the same as the Laplacian
of the PCE corrected \( \rho_e \), because \( \nabla^2 \) commutes with \( U \), i.e.:

\[
UL(r)U^+ = U\nabla^2 \hat{\rho}_e U^+ = U\nabla^2 \delta^{(3)}(r_i - r)U^+ = \nabla^2 U\delta^{(3)}(r_i - r)U^+. \tag{13}
\]

Nevertheless, even for the Laplacian it seems more rigorous to stack formally to option II, which means that we evaluate the non-relativistic Laplacian of the PCE corrected electron density, interpreting the electron density depletion/accumulation with no relation to the kinetic energy and/or kinetic energy density terms.

**Fourier transform of electron density - structure factors**

As already discussed for the Laplacian of \( \rho_e \), a PCE correction of Fourier transform of \( \rho_e \) has to be done via \( \rho_e \) itself. E.g., structure factors are expressed as Fourier transforms of \( \rho_e \):

\[
F_j = \int_{\text{cell}} \rho(r) \exp(2\pi i \mathbf{q}_j \cdot \mathbf{r}) \, d\mathbf{r} \tag{14}
\]

where \( \mathbf{q} \) is the scattering vector and \( \rho(\mathbf{r}) \) is the particular electron density. PCE correction of structure factors has been performed in the following manner:

\[
UF_j U^+ = U \hat{\rho}_e U^+(\mathbf{r}) \exp(2\pi i \mathbf{q}_j \cdot \mathbf{r}) \tag{15}
\]

This means, that the quasirelativistic PCE corrected electron density is used within the non-relativistic framework of evaluation of structure factors *via* the Fourier transform (herein we are not considering the possibility of evaluating structure factors fully relativistically). The analytic PCE correction of electron density within the evaluation of structure factors requires the pVp integrals analogous to the Fourier transform of two Gaussian functions, *i.e.* \( UFU^+ [\nabla g(x; a, \alpha, A) \nabla g(x; b, \beta, B)] \) whose implementation is based upon the original paper on the Fourier transform integrals \( F[g(x; a, \alpha, A)g(x; b, \beta, B)] \).
PCE and relativity remarks

Current implementation of PCE correction for structure factors accounts only for the sr-IOTC approach. PCE correction of structure factors is not treated at the 2c level of theory. Evaluation of PCE contaminated (i.e. not corrected) IOTC structure factors employs all four blocks of the 2c density matrix within the ordinary evaluation of structure factors. Furthermore, the evaluation of PCE contaminated sr-IOTC electron density, Laplacian and structure factors is exactly the same as in the non-relativistic domain so after converging the sr-IOTC SCF, one can evaluate the desired properties, with bearing in mind that one gets PCE contaminated values. In addition, PCE is reported to be non-negligible for properties related to contact density (electron/spin density in the vicinity of nuclei), but decays quickly with distance from the nucleus. Nevertheless, a critical assessment of these effects in respect to electron correlation and relativistic effects is worthwhile, as is mentioned in the latter.

Hirshfeld atom refinement

Hirshfeld Atom Refinement (HAR) was developed by Jayatilaka & Dittrich in 2008 and further extended by Capelli et al. HAR is a method to refine structural parameters from single-crystal X-ray diffraction data based on aspherical atomic scattering factors which are obtained from Fourier transforms of thermally smeared quantum-mechanical aspherical atoms based on Hirshfeld’s stockholder partitioning. In the same way as in the 100-year old Independent Atom Model (IAM) least-squares refinements of coordinates and atomic displacement parameters are carried out using theoretically calculated scattering factors. The difference between IAM and HAR is that in the IAM those scattering factors are calculated for isolated spherical atoms and are tabulated, whereas in HAR they are tailor-made for an aspherical atom in its molecular environment, and hence recalculated iteratively after each refinement step, but never tabulated. Therefore, the experimentally refined structure obtained with HAR is normally much improved compared to IAM, especially pertaining to
the positions and displacement parameters of hydrogen atoms.\textsuperscript{109–111}

Currently, HAR is possible with aspherical scattering factors from HF and BLYP calculations. In this study, we have not accounted for PCE correction inside the quasirelativistic IOTC HAR approach. Hence, there is no need to make any changes in HAR with respect to the usage of sr-IOTC, because MOs and the density matrices from non-relativistic HF and sr-IOTC have exactly the same forms. Herein, we report HAR only at the sr-IOTC-BLYP, sr-IOTC and non-relativistic HF levels of theory. Nevertheless, in order to allow for treating heavy elements and the usage of tight Gaussian basis functions, the HAR approach had to be extended to allow for the usage of spherical basis sets.

**X-ray constrained wavefunction fitting**

X-ray constrained wavefunction (XCW) fitting was introduced by Jayatilaka in 1998\textsuperscript{30} and extended in 2001.\textsuperscript{31} Based on a fixed experimental geometry (either from IAM refinement, HAR or multipole modelling) the molecular orbital coefficients of a molecular wavefunction are adjusted to reproduce the experimental diffraction pattern with the highest possible agreement in terms of $\chi^2$ statistics, while simultaneously minimising the electronic energy of the molecule. In this way, information from the experimental structure factors that go beyond the quantum-mechanical ansatz used are transferred into the single-determinantal wavefunction and enhance its information content. We plan to make use of this approach to extract information of relativistic effects. Perhaps a comment worth at this place has to be made with respect to X-ray constrained fitting using DFT, where speaking of wavefunction fitting is not well suited. Surely, denoting such an approach X-ray constrained density fitting would be far more appropriate. Nevertheless, to keep the notation simple we will use the abbreviation XCW for both Hartree-Fock and DFT based fitting.

Relativistic XCW fitting, similar to the HAR case, was performed without treating PCE correction for structure factors or for $\chi^2$ variation within the XCW approach itself. Therefore, the XCW approach remains unchanged for scalar relativistic calculations with respect to the
ordinary non-relativistic level of theory. However, essentially, one needs to use spherical basis sets to treat heavy elements with sufficiently large basis sets, but avoiding linear dependency issues. In addition, the full 2-component (2c) IOTC XCW approach has been also made available to study the impact of spin-orbit effects in XCW fitting. As mentioned for the evaluation of PCE-contaminated 2c structure factors above, our implementation of 2c XCW fitting makes use of the complex 2c density matrix and works in a completely analogous way with the non-relativistic code except that the four 2c density matrix blocks are defined as complex entities.

**Mulliken-like analysis of structure factors**

Mulliken-like analysis of structure factors that we introduce here is a direct analog of Mulliken-charge analysis. In our procedure, we use the atomic orbitals (AO) matrix representation of each structure factor \(F_{j\mu\nu}\) instead of the overlap matrix \(S_{\mu\nu}\) which is used in the classical Mulliken procedure. Thus, the Mulliken gross (population) contribution of atom \(A\) to a given structure factor \(F_j\) reads:

\[
F^i_A = \sum_{i}^{\text{occ}} \sum_{\mu \in A} N_i c_{\mu i} \left( \sum_{\nu \in A} c_{\nu i} F^j_{\nu \mu} + \sum_{B \notin A} \sum_{\nu} c_{\nu i} F^j_{\nu \mu} \right)
\]

where \(A, B\) represent labels of atomic centres; \(\mu, \nu\) are the AO labels; \(i\) labels the occupied orbitals (with the appropriate occupation numbers \(N_i\) being equal to two in the closed shell regime); \(c_{\mu i}\) is the \(i\)-th molecular orbital coefficient of AO \(\mu\) at a given centre; and \(F^j_{\nu \mu}\) is the matrix element of the Fourier transform representation of the particular structure factor \(j\) in the AO space. This matrix element of the Fourier transform representation in the AO space is given by:

\[
F^j_{\nu \mu} = \int_{\text{cell}} \chi_{\nu}(r) \chi_{\mu}(r) \exp(2\pi i \mathbf{q}^j \cdot \mathbf{r}) d\mathbf{r}
\]

with \(\mathbf{q}^j\) being the scattering vector and \(\chi_{\mu}, \chi_{\nu}\) are the finite (Gaussian) basis set AO functions. The Mulliken gross population analysis has to be performed for each structure factor.
individually.

**Experimental and Computational details**

**Experimental details**

As input for the theoretical calculations the experimental geometry of HgPh$_2$ was taken from the X-ray structure determination at Independent Atom Model (IAM) level published in Glidewell *et al.* For BiPh$_3$ the IAM geometry comes from our own X-ray diffraction measurement at the in-house (CMCA, University of Western Australia) Oxford Gemini diffractometer with Molybdenum K$_{\alpha}$ radiation at a temperature of 104 K. Previous X-ray structure determinations of BiPh$_3$ are reported in Hawley *et al.* and Jones *et al.*

The HgPh$_2$ molecule is of C$_i$ symmetry with an inversion center on the mercury atom, and BiPh$_3$ is of C$_1$ symmetry. The experimental structure factors for comparison with the calculated ones and for use in the Hirshfeld Atom Refinement and X-ray constrained wavefunction fitting procedures are also taken from the publication of Glidewell *et al.* for HgPh$_2$ and from our own determination for BiPh$_3$. In both cases resolutions are limited to low-order reflections (d = 0.77Å for HgPh$_2$ and 0.60Å for BiPh$_3$), which means that data sets of this quality and resolution are routinely obtainable at normal in-house diffractometers with conventional X-radiation sources. As mentioned in the Introduction, it is not the aim of this study to experimentally determine relativistic effects in the electron density, but to investigate if this is feasible in principle, for which routine data are sufficient. However, careful treatment of absorption is necessary since the effects of unmodelled absorption interfere with the effects of relativity in the outer core region of the heavy metals. Therefore, for BiPh$_3$, in addition to the Multi-scan Empirical Absorption (MEA) correction (data set MEA) using spherical harmonics as implemented in the SCALE3 ABSPACK scaling algorithm of the software CrysAlisPRO, Analytical Numeric Absorption (ANA) correction using a multifaceted crystal was carried out according to Clark & Reid (data set ANA).
More details can be found in the CIFs deposited with the Cambridge Structural Data Base (CCDC-1468789 for model MEA and CCDC-1468907 for model ANA) and included within Supporting materials of this paper (BiPh3_cifs.zip). Glidewell et al.\textsuperscript{113} report that for HgPh$_2$ multi-scan absorption correction was carried out with the software SADABS.\textsuperscript{119}

**Computational details**

The Infinite order two component (IOTC) Hamiltonian\textsuperscript{53–56} was employed within the presented study. Spin-orbit (SO) coupling relativistic effects were only accounted for in the 2c General Complex Hartree-Fock (GCHF) quasi-relativistic calculations (IOTC). The electron-electron interaction was described by the Coulombic potential. The Atomic Mean Field spin-orbit operator (AMFI)\textsuperscript{120–122} and/or the 2e spin-orbit interaction were not accounted for in the calculations. The point charge model of the nucleus was employed in the evaluation of electron-nucleus potential ($V$). Electron correlation was treated via the BLYP\textsuperscript{123,124} functional at the sr-IOTC and non-relativistic levels of theory (denoted sr-IOTC-BLYP and NR-BLYP).

An overview of the methods used, their acronyms, the effects they include and their Hamiltonians is given in the first part of Table 1. In the second part of Table 1, the effects visible through difference densities and other difference properties are summarized.
Table 1: Abbreviations for methods used

<table>
<thead>
<tr>
<th>acronym</th>
<th>SCF</th>
<th>effects included</th>
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</thead>
<tbody>
<tr>
<td>NR</td>
<td>non-relativistic HF</td>
<td>none</td>
</tr>
<tr>
<td>NR-BLYP</td>
<td>non-relativistic BLYP</td>
<td>ECORR</td>
</tr>
<tr>
<td>IOTC</td>
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<td>sr and SO with PCE correction</td>
</tr>
<tr>
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<td>full Infinite Order Two Component HF</td>
<td>sr and SO without PCE correction</td>
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<tr>
<td>sr-IOTC</td>
<td>scalar Infinite Order Two Component HF</td>
<td>sr with PCE correction</td>
</tr>
<tr>
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<td>scalar Infinite Order Two Component HF</td>
<td>sr without PCE correction</td>
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<tr>
<td>sr-IOTC-BLYP</td>
<td>scalar Infinite Order Two Component BLYP</td>
<td>ECORR and sr with PCE correction</td>
</tr>
<tr>
<td>sr-IOTC-BLYP&lt;sub&gt;PCE&lt;/sub&gt;</td>
<td>scalar Infinite Order Two Component BLYP</td>
<td>ECORR and sr without PCE correction</td>
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<table>
<thead>
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<th>abbreviation of effect observed</th>
<th>difference between methods</th>
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<tr>
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<td>experiment minus sr-IOTC-BLYP</td>
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<tr>
<td>SIGMA</td>
<td>experimental error</td>
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<td>electron correlation</td>
<td>sr-IOTC-BLYP minus sr-IOTC</td>
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<td>REL</td>
<td>total relativistic effects</td>
<td>IOTC minus NR</td>
</tr>
<tr>
<td>sr</td>
<td>scalar relativistic effects</td>
<td>sr-IOTC minus NR</td>
</tr>
<tr>
<td>SO</td>
<td>spin-orbit coupling</td>
<td>IOTC minus sr-IOTC</td>
</tr>
<tr>
<td>PCE</td>
<td>picture change error (full)</td>
<td>IOTC minus IOTC&lt;sub&gt;PCE&lt;/sub&gt;</td>
</tr>
<tr>
<td>PCE</td>
<td>picture change error (scalar)</td>
<td>sr-IOTC minus sr-IOTC&lt;sub&gt;PCE&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

For the purpose of electron density, Laplacian, structure factors, HAR and XCW calculations double zeta quality basis sets were employed. Namely, uncontracted cc-pVDZ<sup>125</sup> basis sets were used for H and C atoms and the uncontracted DZ basis sets of Dyall<sup>126–128</sup> were employed for mercury and bismuth. The choice of uncontracted basis sets was motivated by the fact that contracted non-relativistic <i>l</i>-valued basis sets do not have the appropriate flexibility for properly representing SO relativistic effects. In contrast, uncontracted basis sets have this flexibility and in addition they have the appropriate flexibility to describe...
the radial behavior of electron density at both the relativistic and non-relativistic level of theory simultaneously, while in contracted basis sets different contractions have to be used for both cases. To explore the impact of basis set cardinality on the studied effects (electron correlation and relativity) in electron density, negative Laplacian and structure factors, uncontracted TZ basis sets were employed in addition (cc-pVTZ for H and C atoms and Dyall’s TZ basis set for Hg). (In the case of the UTZ basis set the following restrictions had to be utilized: no g-functions on Hg and no f-functions on C). The impact of basis set cardinality considering up to quadruple-zeta basis sets (UDZ-UQZ) on the electron density and the negative Laplacian of benzene and Hg(CN)$_2$ are investigated in Supporting Information.

Calculations of electron density, Laplacian of electron density and structure factors were performed in a development version of the Tonto software suite.\textsuperscript{70,129} Calculations of structure factors and XCW are performed for both the fixed IAM- and HAR-derived geometries without treating the effects of the surrounding molecules in the crystal. Visualization of two-dimensional properties were produced using the XCrysDen program package,\textsuperscript{130,131} one-dimensional plots were produced with the GNUPLOT package.

HAR and XCW were performed using the DZ basis sets with and without the use of cluster charges (plus cluster dipoles) of the neighboring molecules, for HgPh$_2$ only. Both the original IAM geometry and the HAR-derived geometries were used in XCW. The XCW fitting parameter $\lambda$ was in the range 0.0 to 1.0 with a varying step size (0.0 to 1.0 with a 0.01 step) for the IAM geometry (HAR-derived geometries). Coppens’ thermal smearing\textsuperscript{132} model was employed for the calculation of structure factors to allow for treating PCE correction and thermal smearing, while in the HAR study, which did not account for PCE, Hirshfelds thermal smearing was used.

Quantum Theory of Atoms In Molecules (QTAIM) analysis\textsuperscript{40} was performed with the AIMAll package,\textsuperscript{133} using the g09\textsuperscript{68} fchk for NR approaches and the wfn file from Tonto for sr-IOTC approaches. [Numerical issues of sr-IOTC calculations, which had to use Cartesian basis sets (causing occurrence of linear dependencies for $S^{-1/2}$) when producing wfn files in
the Tonto package, are considered in Supporting Information.

Results and discussion

Electron density

Figs. 1 and 2 present the ECORR, REL, SO, and PCE effects in the electron density. (Note that REL accounts for both the scalar and SO relativistic effects.)

The sr-IOTC-BLYP, IOTC, sr-IOTC, sr-IOTC_{PCE} and NR distributions of electron density along the Hg-C1 and Bi-C1 bonds are shown in Fig. 1, where the inlets represent difference densities of the particular effects. Figs. 1(a) and 1(b) show the behavior of electron density close to the nuclei of Hg and Bi. As already shown in the literature,\textsuperscript{59,73,87,89,90,96,101–106} PCE and REL effects are dominant at the nucleus, while the SO and ECORR effects are hardly discernible at such large scale. Further from the nucleus (in the range from 0.01 to 0.05 Å, see Figs. 1(c) and 1(d)), the NR curve is shifted from all the remaining curves, \textit{i.e.} especially scalar REL effects are dominant in this region,\textsuperscript{104} but PCE is also discernible in the difference densities (see inlets). Electron correlation (BLYP vs. HF) becomes significant in the region 0.1 - 0.3 Å (see Figs. 1(e) and 1(f)) as well as in the valence or bonding region (around 1.2 Å, see Figs. 1(g) and 1(h)). Relativistic effects are also well discernible in the valence region in Figs. 1(g) and 1(h). Thus, REL and ECORR effects are considerably affecting the distribution of electron density along the metal-carbon bond. Note that the minimum of density along the metal-carbon bond has a larger value for HgPh\textsubscript{2} in comparison to BiPh\textsubscript{3} (see Figs. 1(g) and 1(h)).

Difference electron density plots in the chosen metal - phenyl plane (built of Hg-C1-C2 atoms) are shown in Fig. 2. Considered effects in 2D difference electron densities in Fig.

20
Figure 1: 1D plots of electron density along the Hg-C and Bi-C bonds; HgPh$_2$ left and BiPh$_3$ right column, respectively. Inlets represent difference electron density along the Hg-C and Bi-C bonds. On the x axis is the distance between the metal atom and carbon C1 (in Å) and on the y-axis is the electron density (in e bohr$^{-3}$). Labels of Fig 1(a) are valid for all remaining pictures and inlets of Figs. 1.
have the same spatial expansion as found for the electron density distributions along the metal carbon bond in Fig. 1. ECORR is dominating over the whole backbone of the metal-phenyl moieties in the studied compounds. REL effects dominate especially in the metal core region, but are also well discernible in the metal-carbon bond region. Hence, relativistic effects will be unavoidable for modelling of metal ligand interactions, core polarization and reconstruction of diffraction data of heavy-element compounds. This will have important consequences for any future extension of experimental electron density works related to heavy elements.

In contrast, SO relativistic effects and PCE are very local in that they only occur in the inner core of the heavy elements whereas (scalar+SO) REL effects occur in the inner core, outer core, and valence region. Thus scalar relativity dominates over SO effects in the case of the REL results. SO effects expand a little bit further out in the metal inner core compared to PCE, however, PCE is relevant also for the carbon cores, whereas SO is not. Thus, the PCE is important for the core of every atom, but SO effects only for heavy atoms. For experimental diffraction studies, both PCE and SO are negligible since the effects are beyond the experimentally achievable accuracy and resolution. The small or negligible extent of SO and PCE for diffraction studies will be further advocated in a separate subchapter devoted solely to the evaluation of structure factors at different levels of theory, see below.

The impact of basis set quality (cardinality number) on the electron density of HgPh$_2$ is presented in Fig. 3. On one hand, the difference in the total electron densities for the UDZ and UTZ basis sets is indeed significant on an absolute scale, see Fig. 3(a). Nevertheless, the UTZ difference electron density and Laplacian maps presenting ECORR and REL effects are almost identical to those from the UDZ calculation which are presented above (compare Fig. 3(c) with 2(a) and 3(e) with 2(c)). This means that for the analysis of the ECORR,
Figure 2: 2D plots of difference electron densities; HgPh$_2$ left and BiPh$_3$ right column, respectively. Color scale is in the range -0.01 (blue) to 0.01 (red) e bohr$^{-3}$, with a contour interval of 0.0025 e bohr$^{-3}$. 
REL effects - which are differences by definition, see Table 1 - the UDZ basis set is sufficient (the same holds for SO and PCE effects, basis set dependence is not shown).

![2D difference plots of HgPh₂ obtained for different basis sets, difference electron density in the left column and difference Laplacian in the right column, respectively. Color scale is the same as in Figs. 2 and 5](image)

**Figure 3:** 2D difference plots of HgPh₂ obtained for different basis sets, difference electron density in the left column and difference Laplacian in the right column, respectively. Color scale is the same as in Figs. 2 and 5

**Negative Laplacian of electron density**

Figs. 4 and 5 present the ECORR, REL, SO, and PCE effects in the negative Laplacian of electron density. (Note that REL accounts for both the scalar and SO relativistic effects.)

The sr-IOTC-BLYP, IOTC, sr-IOTC, sr-IOTC\(_{PCE}\) and NR distributions of the negative Laplacian of the electron density along the Hg-C1 and Bi-C1 bonds are shown in Fig. 4, the inlets show the difference negative Laplacians. The distribution of negative Laplacian
of electron density \((L(r))\) along the metal-carbon bonds is considered from 0.2 Å away from the metal atoms.

In all pictures in Fig. 4, the red curve represents the NR model, i.e. missing treatment of relativistic effects, and in the inlets, the red curve represents the REL effect as the difference between IOTC and NR models. The black curve in pictures and inlets of Fig. 4 shows the effect of electron correlation ECORR. It is obvious that these two effects, REL and ECORR, dominate the behavior of the distribution of the negative Laplacian along the metal-carbon bond. A relativistic contraction can be seen in the region between 0.2 and 0.3 Å in Figs. 4(a) and 4(b) in that the minimum representing an electron depletion between two core shells is shifted closer to the nucleus in all methods treating relativistic effects compared to the red NR curve. The effect of relativity (red REL curve in the inlets of Figs. 4(a) and 4(b)) in the core region has magnitudes of some hundred \(\text{e bohr}^{-5}\), exceeding 500 \(\text{e bohr}^{-5}\), the effect of electron correlation (black ECORR curve in the inlets) can be as high as 200 \(\text{e bohr}^{-5}\).

A maximum in the curve at around 0.5Å (Figs. 4(c) and 4(d)) can be referred to as the outer core region of the metal atom. It is more affected by REL effects than by ECORR effects. The maximum is significantly more pronounced in the red NR curve than in all the others, meaning that relativistic effects lead to a reduction of electron concentration in the outer core region. Values of the negative Laplacian slightly above and below zero in the bonding region (Figs. 4(e) and 4(f)) with discernible valence shell charge concentrations (VSCCs, maxima in the negative Laplacian) for the carbon but not for the metal atoms show that the M-C bonds are of polar covalent character. The same relativistic reduction of charge concentration is true for the VSCC at the carbon atom in the region around 1.6 Å to 1.8 Å, however, the difference for the metal outer core region is big enough to be experimentally detectable, whereas for the carbon VSCC it is below the experimental accuracy. It can be concluded that the scalar relativistic effects dominate over SO ones, when comparing the REL and SO results of Fig. 4 as holds also for electron density.

When comparing the features in the \(L(r)\) distributions between the two different com-
pounds, it stands out that the sr-IOTC-BLYP minimum of $L(r)$ at approx. 0.27 Å lies below the sr-IOTC one in the case of HgPh$_2$, while for BiPh$_3$ the sr-IOTC-BLYP minimum is above the sr-IOTC minimum (see Figs. 4(a) and 4(b)). Note also that the minimum of the sr-IOTC curve of HgPh$_2$ is shifted from the particular sr-IOTC minimum in BiPh$_3$ by about 300 e bohr$^{-5}$ (note, different scale on the y-axis). Further significant differences are found for the outer core in the region 0.5 Å. These maxima in the HgPh$_2$ $L(r)$ curves (Fig. 4(c)) are shifted by about 4 e bohr$^{-5}$ below the particular maxima of the BiPh$_3$ $L(r)$ curves (Fig. 4(d)). In addition, the sr-IOTC-BLYP $L(r)$ curve of HgPh$_2$ contains only an inflex and no maximum. Thus, the $L(r)$ distribution recovers notable qualitative and quantitative differences between the Hg and Bi phenyl compounds. This behavior can be related to the difference in the nature of the valence shells of the metal atoms which participate in the metal carbon bonds, i.e. [Xe]5d$^{10}$6s$^2$ and [Xe]5d$^{10}$6s$^2$6p$^3$ for Hg and Bi atoms, respectively. Even in the bonding region (see Figs. 4(e) and 4(f)) there are discernible differences for the $L(r)$ distribution along the Hg-C and Bi-C bonds, especially for relativistic effects. The NR $L(r)$ curve is below the IOTC $L(r)$ curves in the region 0.9 - 1.5 Å for HgPh$_2$, while for BiPh$_3$ this region spans between 0.9 - 1.1 Å. Note also that the carbon VSCC in Figs. 4(e) and 4(f) is shifted for BiPh$_3$ in comparison to HgPh$_2$ due to the longer metal-carbon bond length (which also implies weaker bonding in the case of BiPh$_3$ in comparison to HgPh$_2$).

No clear quantitative and qualitative differences are found in the 2D maps of the negative Laplacian of electron density, when comparing 1c-IOTC-BLYP and NR levels of theory (see Supporting information), with the exception of the core region between 0.5 - 0.6 Å from the metal atom. More detailed insight on the particular effects (ECORR, REL, SO, PCE) in the 2D maps of the negative Laplacian can be gained by the inspection of 2D negative Laplacian difference plots, see Fig. 5. Similar to the 2D difference maps of electron density (Fig. 2), ECORR is dominating over the whole backbone of the metal - phenyl moieties in the studied
Figure 4: 1D plots of negative Laplacian along the Hg-C1 and Bi-C1 bonds; HgPh\textsubscript{2} left and BiPh\textsubscript{3} right column, respectively. Inlets represent difference negative Laplacians along the Hg-C and Bi-C bonds. On the x axis is the distance between the metal atom and carbon C1 (in Å) and on the y-axis is the negative Laplacian (in e \textit{bohr}\textsuperscript{-5}). Labels of Fig 4(a) are valid for all remaining pictures and inlets of Fig. 4
compounds. REL effects dominate again in the metal-carbon region. SO relativistic effects on their own and PCE are very local around the metal atoms although PCE is discernible also in the core region of carbon atoms.

Additional calculations of negative Laplacians of HgPh$_2$ in the UTZ basis set lead to a similar basis set cardinality significance as already found for the electron density itself (Fig. 3. The difference in the total negative Laplacians for the UDZ and UTZ basis sets is indeed significant, see Fig. 3(b). Nevertheless, the UTZ negative Laplacian maps presenting ECORR and REL effects as difference properties are qualitatively the same as those from the UDZ calculations.

**Relativistic effects in the topology of the electron density**

Here we will briefly summarize QTAIM results$^{40}$ for the metal-carbon regions stemming from a topological analysis of the electron densities calculated at the various levels of theory discussed above. As can be seen from Table 2, both REL and ECORR effects are quantitatively affecting the position of the BCP as well as the BCP characteristics, including the delocalization index. Some trends are visible, such as an increase in the negative Laplacian (less negative) for both the ECORR (HF to BLYP) and REL (NR to sr-IOTC) effects as well as an increase in the delocalization index for ECORR and REL. The changes due to REL are more pronounced than those for ECORR. (Please note that in this subsection we consider only scalar relativity due to using sr-IOTC and/or sr-IOTC-BLYP approaches.)
Figure 5: 2D plots of difference negative Laplacian of electron density; HgPh$_2$ left and BiPh$_3$ right column, respectively. Color scale is in the range -0.1 (blue) to 0.1 (red) e bohr$^{-5}$, with a contour interval of 0.025 e bohr$^{-5}$
Table 2: QTAIM bond-critical point (BCP) characteristics of Hg-C2 and Bi-C_{Bi} bonds, including C-BCP, BCP-Hg and BCP-Bi distances, electron density, Laplacian and ellipticity at the BCP ($\rho$, $\Delta \rho$ and $\epsilon$, respectively), and the Delocalization Index (DI) which can be understood as an average number of electron pairs delocalized (shared) between Hg-C and/or Bi-C atoms.\textsuperscript{134} Note that the Bi-C2, Bi-C13 and Bi-C24 bond characteristics are averaged into single Bi-C ones, due to symmetry reasons.

<table>
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<tr>
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<th>d(C-BCP)</th>
<th>d(BCP-Hg)</th>
<th>$\rho$</th>
<th>$-\Delta \rho$</th>
<th>$\epsilon$</th>
<th>DI</th>
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<tr>
<td>[Å]</td>
<td>[Å]</td>
<td>[e bohr$^{-3}$]</td>
<td>[e bohr$^{-5}$]</td>
<td>[-]</td>
<td>[e]</td>
<td></td>
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<tr>
<td>sr-IOTC-BLYP</td>
<td>0.946</td>
<td>1.142</td>
<td>0.130</td>
<td>-0.086</td>
<td>0.055</td>
<td>0.928</td>
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<tr>
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<td>0.135</td>
<td>-0.101</td>
<td>0.052</td>
<td>0.929</td>
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<td>-0.209</td>
<td>0.056</td>
<td>0.900</td>
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<td>0.126</td>
<td>-0.252</td>
<td>0.056</td>
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<th>d(BCP-Bi)</th>
<th>$\rho$</th>
<th>$-\Delta \rho$</th>
<th>$\epsilon$</th>
<th>DI</th>
</tr>
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<td>[Å]</td>
<td>[Å]</td>
<td>[e bohr$^{-3}$]</td>
<td>[e bohr$^{-5}$]</td>
<td>[-]</td>
<td>[e]</td>
<td></td>
</tr>
<tr>
<td>sr-IOTC-BLYP</td>
<td>1.106</td>
<td>1.148</td>
<td>0.097</td>
<td>-0.095</td>
<td>0.065</td>
<td>0.871</td>
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<td>sr-IOTC</td>
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<td>1.138</td>
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<td>-0.105</td>
<td>0.066</td>
<td>0.838</td>
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<tr>
<td>NR-BLYP</td>
<td>1.096</td>
<td>1.159</td>
<td>0.096</td>
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<td>0.072</td>
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<td>NR</td>
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<td>1.129</td>
<td>0.099</td>
<td>-0.162</td>
<td>0.075</td>
<td>0.790</td>
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</table>

Furthermore, we show QTAIM net charges of the two metals Hg and Bi, of carbon atoms bonded to the metal atoms (symmetry-independent carbon C2 for HgPh$_2$, an average for carbons C2, C13, C24 for BiPh$_3$, denoted C$_{Bi}$), averages of the QTAIM net charges for all remaining carbon atoms not bonded to the metals (denoted C$_{ave}$) and averages for all hydrogen atoms, see Table 3. The charges of the metal atoms are strongly affected by both (scalar) REL and ECORR effects. Scalar REL effects are lowering the positive charge of the heavy atoms and so do ECORR effects. Charges of carbons directly bonded to metals are negative and in sum grossly counter-balance the positive charge on the metals; hence, these charges are also affected by scalar REL and ECORR effects significantly. Average charges
of the remaining carbon atoms are positive and affected only by ECORR effects, not REL; the same holds for the negative average charges of the hydrogen atoms. Note also that the C-H bonds are more polarized in the case of HgPh$_2$ in comparison to BiPh$_3$.

Table 3: QTAIM net charges [e] of selected atoms (metal and carbon bonded to metal) and averages for remaining atom types. Note that charges of C2, C13 and C24 atoms which are directly bonded to Bi are averaged to single C$_{Bi}$ values, due to symmetry reasons

<table>
<thead>
<tr>
<th></th>
<th>HgPh$_2$</th>
<th>BiPh$_3$</th>
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<tbody>
<tr>
<td></td>
<td>Atom</td>
<td>sr-IOTC-BLYP</td>
</tr>
<tr>
<td>Hg1</td>
<td>0.477</td>
<td>0.681</td>
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<tr>
<td>C2</td>
<td>-0.214</td>
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</tr>
<tr>
<td>C$_{ave}$</td>
<td>0.083</td>
<td>0.157</td>
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<tr>
<td>H$_{ave}$</td>
<td>-0.088</td>
<td>-0.169</td>
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Structure factors

The agreement statistics for the calculated structure factors compared to the measured structure factors at different levels of theory using the experimental IAM geometries are compiled in Table 4. Agreement statistics for HgPh$_2$ data follow the expectations, i.e. ECORR has the largest influence on the data (lowest values for sr-IOTC-BLYP), followed by the REL effects (all HF IOTC results are significantly lower than NR), while SO relativistic effects and PCE are again of minor significance. The same holds for the BiPh$_3$ MEA data set, although in
comparison to HgPh$_2$ the improvements in the reconstruction of the experimental structure factors when treating REL and ECORR are considerably smaller relative to NR. On the other hand, for the BiPh$_3$ ANA data set, for which the analytical face-indexed absorption correction is thought to be more rigor than the empirical multi-scan absorption correction in the MEA data set, the best agreement statistics are found surprisingly for the NR level of theory. Clearly, the differences in the values between the two different ways of treating absorption in the same measured structure factors (MEA vs. ANA) are significantly bigger than the differences between NR, BLYP and IOTC treatments of the data. In other words, the effect of absorption on the experimental structure factors is much higher than the effect of electron correlation or relativistics. If REL and ECORR effects are to be detected and modelled in the X-ray diffraction experiment, absorption must be avoided by using tiny crystals and high X-ray energies at synchrotrons or even $\gamma$-rays instead of X-rays.

Albeit basis set cardinality is essential for the electron density and the Laplacian, the overall agreement statistics of structure factors for HgPh$_2$ do not improve by using UTZ basis sets compared to UDZ. In the case of sr-IOTC-BLYP and NR calculations with UTZ basis sets the agreement statistics are slightly worse while for IOTC calculations the agreement statistics are only very little improved.
Table 4: Agreement statistics relative to the experimental structure factors

<table>
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<th>sr-IOTC-BLYP</th>
<th>IOTC_{PCE}</th>
<th>sr-IOTC</th>
<th>sr-IOTC_{PCE}</th>
<th>NR</th>
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<td><strong>HgPh_2</strong></td>
<td></td>
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<tr>
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<tr>
<td>R(F)</td>
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<tr>
<td>R(F2)</td>
<td>0.0285</td>
<td>0.0297</td>
<td>0.0297</td>
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<td>0.0298</td>
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<td>Rw(F)</td>
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<tr>
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<tr>
<td>$\chi^2(N_p=1)(F)$</td>
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<tr>
<td>$\chi^2(N_p=1)(F)$ - UTZ</td>
<td>2.5040</td>
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<td>R(F2)</td>
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<td>0.1001</td>
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<tr>
<td>Rw(F)</td>
<td>0.0607</td>
<td>0.0613</td>
<td>0.0612</td>
<td>0.0612</td>
<td>0.0595</td>
</tr>
<tr>
<td>Rw(F2)</td>
<td>0.0707</td>
<td>0.0715</td>
<td>0.0714</td>
<td>0.0714</td>
<td>0.0683</td>
</tr>
<tr>
<td><strong>BiPh_3 - MEA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scale factor</td>
<td>0.9492</td>
<td>0.9486</td>
<td>0.9488</td>
<td>0.9488</td>
<td>0.9564</td>
</tr>
<tr>
<td>R(F)</td>
<td>0.0704</td>
<td>0.0706</td>
<td>0.0706</td>
<td>0.0706</td>
<td>0.0706</td>
</tr>
<tr>
<td>R(F2)</td>
<td>0.0996</td>
<td>0.0998</td>
<td>0.0998</td>
<td>0.0998</td>
<td>0.1002</td>
</tr>
<tr>
<td>Rw(F)</td>
<td>0.0512</td>
<td>0.0517</td>
<td>0.0517</td>
<td>0.0517</td>
<td>0.0517</td>
</tr>
<tr>
<td>Rw(F2)</td>
<td>0.0619</td>
<td>0.0624</td>
<td>0.0625</td>
<td>0.0624</td>
<td>0.0644</td>
</tr>
</tbody>
</table>

The theoretical structure factors are shown (particularly their differences to experiment or among each other) along with experimental errors in Fig. 6 using the same set of hkl indices as measured and therefore the same maximum resolution. The direct difference between the
measured and theoretical structure factors, including the experimental error ($\sigma$), are shown in Figs. 6(a)-6(b). While the EDAT data lie well within the SIGMA values for HgPh$_2$, this is not the case for both MEA and ANA BiPh$_3$ data sets. The ECORR and REL effects are rather a matter to improve the systematic error when compared to either experimental error (SIGMA) or the shift between the experimental and theoretical structure factors (EDAT). SO and PCE are not discernible in Figs. 6(a)-6(b). Thus, scalar relativity is dominant in the overall REL effects in structure factors, as expected from electron density and the negative Laplacian. It must be noted that the experimental data sets chosen are routine low-order data of medium quality. The uncertainties SIGMA on the experimental structure factors can be lowered significantly by using modern detectors, synchrotrons, helium cooling and modern data reduction software, so that the effects ECORR and REL would take shape much more clearly relative to the error - not so SO and PCE which will most probably never be identifiable with X-ray diffraction.

To obtain a better representation and resolution of the studied effects in the structure factors two sets of figures have been produced: Figs. 6(c)-6(d) account for the individual scale factors to experimental data [scale factors are shown in Table 4] while in Figs. 6(e)-6(f) the absolute scale is used. Interestingly, the (scalar) REL effects are much more pronounced and discernible in the absolute scale plots in Figs. 6(e)-6(f) in comparison to the scaled ones (Figs. 6(c)-6(d)). Thus, it can be immediately seen that even for the low resolution data relativity becomes important on the absolute scale. This finding is in close agreement with the recent study of Batke and Eickerling. This importance of REL (red squares in Figs. 6(e)-6(f)) spans the complete range of considered structure factors - from lowest to highest resolution - whereas ECORR (black dots) is dominant only in the resolution range from lowest resolution to about 0.6Å$^{-1}$. This agrees with the observation that ECORR mainly manifests itself in the backbone of the molecule, whereas REL is present in inner core, outer core and valence region of the metal atom. As is expected, SO relativistic effects are found more pronounced for the BiPh$_3$ compound in comparison to HgPh$_2$, i.e. the SO
splitting of the singly occupied 6p orbital into 6p$^{1/2}$ and 6p$^{3/2}$ orbitals of BiPh$_3$ taking part in the bonding interactions with the phenyl groups.

![Graphs showing difference structure factors](image)

**Figure 6**: Difference structure factors; HgPh$_2$ left, BiPh$_3$ right (experimental MEA data is shown). On the x axis is $\sin\theta/\lambda$ (Å$^{-1}$) up to the maximum resolution of the experimental data set; on the y axis is the particular difference of structure factors on different scales. Labels of Fig 6(a) are valid for all remaining pictures of Fig. 6.

In addition, the HgPh$_2$ data in Fig. 6(e) show that from approx. 0.2 Å$^{-1}$ there are two types of structure factors: those which are and those which are not affected by relativistic effects. This seems to be directly related to the weight of the heavy atom for a particular
structure factor. Therefore, we have performed a Mulliken-like analysis of the atomic contributions in the measured structure factors of Glidewell et al.,\textsuperscript{113} see Figs. 7.

In particular the structure factors are split into the following four categories:

1; structure factors larger than 25 in magnitude, and the Hg atom with a Mulliken-like contribution larger than 50%,

2; structure factors smaller than 25 in magnitude, and the Hg atom with a Mulliken-like contribution larger than 50%,

3; structure factors with a Mulliken-like contribution of the Hg atom between 10 % and 50 %, 

4; structure factors with a Mulliken-like contribution of the Hg atom below 10 %.

We will consider the relativistic effects in the absolute

\[
\Delta_j = F_j(IOTC) - F_j(NR) \tag{18}
\]

and relative

\[
\delta_j = (F_j(IOTC) - F_j(NR))/F_j(IOTC) \tag{19}
\]

measures. In addition, the absolute contribution of Hg atom in each structure factor is also presented, i.e.:

\[
\delta_{j,Hg} = F_j(Hg, IOTC)/\sum_{k} |F_j(k, IOTC)| \tag{20}
\]

It can be immediately seen (Fig. 7(a)) that the absolute extent of relativistic effects in the structure factors is essentially ruled by the contribution of the heavy atom (Fig. 7(a)). Naturally, the contribution of the heavy atom (Mulliken-like contribution of the Hg atom larger than 50%) affects proportionally the value (intensity) of the structure factor itself (Fig. 7(b)). The relative extent of REL effects in the structure factors is often larger for small structure factors (Fig. 7(c)). Nevertheless, there is a systematic ordering of structure
factors with large contribution of the Hg atom also with respect to the relative extent of REL effects (Fig. 7(c)). Finally, the Hg atom Mulliken-like contribution to the structure factors is shown as a function of resolution (Fig. 7(d)), recovering that the Mulliken-like contributions of Hg are relatively continuous.

Figure 7: Mulliken like analysis of the extent of relativistic effects for the HgPh\textsubscript{2} data set of measured structure factors: (a) absolute extent of given effect (unitless) in the structure factors with respect to resolution in $\sin \theta / \lambda$; (a) impact of the chosen categorization on the structure factors with respect to resolution in $\sin \theta / \lambda$; (c) relative extent of given effect (%) in the structure factors with respect to resolution in $\sin \theta / \lambda$; (d) Hg Mulliken-like contribution (%) in the structure factors with respect to resolution in $\sin \theta / \lambda$. Labels of Fig 7(a) are valid for all remaining pictures of Fig. 7.

Because of the low resolution in the experimental structure factor data sets, we have produced additional benchmark data sets for HgPh\textsubscript{2} (up to $\sin(\theta)/\lambda$ value of 3.0 Å\textsuperscript{-1}, but including only structure factors larger than 0.025), see Fig. 8. The structure factors were computed at all relevant levels of theory (IOTC, sr-IOTC, sr-IOTC-BLYP and NR; PCE correction was not accounted for), using the experimental geometry and an isolated-molecule
wavefunction. In a very similar way as for the experimental data set, the scaled and unscaled data have a considerably different behavior for the differences in the structure factors. While scaling still hampers the recognition of REL effects in the structure factors, the data in the absolute scale (i.e. unscaled data) highlight the importance of the relativistic effects with respect to $\sin(\theta)/\lambda$. The large importance of REL effects for the low angle data (up to $0.8^{-1}$) is obvious and in accordance with the extent of REL in the experimental data set. This confirms the contribution of scalar relativity which is accounted for in the low angle diffractions. Hence, scalar REL effects are essential for accurate assessment of charge density in the valence region around the heavy atom. Nevertheless, in the range $0.8 - 1.5^{-1}$ the relativistic effects are reaching a value of 0.5 on the unitless structure factor scale. Nevertheless, the relative extent of REL effects are not affected in a similar way as in the absolute differences, i.e. there is no systematic difference between the scaled and unscaled data when considering the relative extent of the studied effects. Albeit it is worth to stress that the relative significance of relativistic effects (up to 25%) is reached again in the range $0.8 - 1.8^{-1}$.

In addition, the full set of sr-IOTC-BLYP structure factors (up to $\sin(\theta)/\lambda$ 3.0 Å$^{-1}$) is shown in Fig. 8(e). As can be seen, even in the absolute value of the structure factors there are two branches of diffraction data at low angle. On the one hand, this agrees with the fact that relativistic effects seem indeed measurable and/or detectable in low-order data. On the other hand, the high angle part is still worth of being accounted for up to 1.5 Å$^{-1}$, where the absolute value of structure factors falls below five, see Fig. 8(f). Hence the accuracy and assessment of the high angle measurement remains of crucial importance to obtain a meaningful statistical ensemble.
Figure 8: Difference structure factors (absolute - abs and relative - rel) and sr-IOTC-BLYP structure factors of HgPh$_2$ up to sinθ/λ = 3.0 (Å$^{-1}$). Labels of Fig 8(a) are valid for all remaining pictures showing difference structure factors.
Hirshfeld atom refinement and X-ray constrained wavefunction fitting

The agreement statistics for Hirshfeld atom refinement (HAR) of HgPh$_2$ at different levels of theory are shown in Table 5. The number of refined parameters was 106, i.e. the number of independent atoms (Hg, 6 x C and 5 x H) times nine (three positional degrees of freedom and six thermal anisotropy degrees of freedom) minus three (center of mass) plus one (scale factor). A comparison of the agreement statistics in Table 5 based on the HAR geometry compared to those in Table 4 based on the IAM geometries clearly shows that HAR improves the agreement significantly and thus confirms the superiority of the HAR treatment using tailor-made aspherical atomic scattering factors compared to the IAM refinement using generalized spherical atomic scattering factors. It can be immediately seen from Table 5 that sr-IOTC-BLYP HAR yields the lowest agreement statistics, whereas sr-IOTC HAR still yields better statistics when compared to NR HAR. This means that relativistic effects improve the reconstruction of the experimental data significantly even for low-resolution data sets. Note that one of the C-H bonds in the HAR geometries is significantly longer than expected (see Supporting Information) which indicates that although the measured data do not seem to suffer from obvious systematic errors the quality of the data set is not sufficient for an experimental quantification of ECORR and REL, which is not the aim of this study but a future project. Robustness of HAR for heavy elements has to be further checked, and highest quality data are crucial.
Table 5: HgPh$_2$ Hirshfeld atom refinement (HAR) $\chi^2$ statistics relative to the experimental structure factors (IOTC structure factors are not PCE corrected)

<table>
<thead>
<tr>
<th></th>
<th>sr-IOTC-BLYP$_{PCE}$</th>
<th>sr-IOTC$_{PCE}$</th>
<th>NR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2(N_p=106)^a$</td>
<td>1.7461</td>
<td>1.7645</td>
<td>1.8479</td>
</tr>
<tr>
<td>$\chi^2(N_p=1)(F)^b$</td>
<td>1.5626</td>
<td>1.5790</td>
<td>1.6537</td>
</tr>
<tr>
<td>$\chi^2(N_p=1)(F)^c$</td>
<td>1.5973</td>
<td>1.8151 (1.8112)$^d$</td>
<td>1.8503</td>
</tr>
</tbody>
</table>

$^a$ HAR agreement statistics accounting for 106 parameters in the refinement
$^b$ HAR agreement statistics accounting only for the scale factor (which is close to one)
$^c$ HAR agreement statistics accounting only for the scale factor (which is close to half)
$^d$ IOTC HF level of theory agreement statistics, using the sr-IOTC HAR geometry

X-ray constrained wavefunction fitting (XCW) has been performed for HgPh$_2$ only. The dependence of $\chi^2$ upon the XCW $\lambda$ parameter in the XCW sr-IOTC-BLYP, XCW sr-IOTC and XCW NR calculations of HgPh$_2$ is shown in Fig. 9, for both IAM and HAR-derived geometries. In the case of the IAM geometry, where fitting was performed to a $\lambda$ value up to one, the fact that the deviation between the agreement statistics at different levels of theory is lower with respect to larger $\lambda$ values shows that electron correlation as well as relativity can be accounted for by means of the XCW method. This means that both REL and ECORR effects are incorporated into the wavefunction from the experimental measurement through the fitting procedure. The originally non-relativistic HF wavefunction includes information on REL and ECORR at high lambda values through the fit. However, since the agreement statistics for NR and the methods that already include REL and ECORR in their definition are not identical at high lambda values shows that the NR wavefunction does not absorb all the information about REL and ECORR that are available in the measured data. Whereas REL seems to be captured by the NR wavefunction nearly completely, ECORR only to a small extent. The small difference between the IOTC and sr-IOTC XCW agreement statistics shows again on the dominant contribution of scalar REL effects over SO coupling. Electron
correlation is important over the entire molecule, as shown for the electron density and its negative Laplacian, but the structure factors are dominated by contributions of the heavy element and possibly its nearest environment. Thus, electron correlation might be harder to be assessed via XCW for compounds containing heavy elements. On the other hand, the relativistic effects seem to be possible to be fitted via the XCW NR method. This might be directly related to the fact that scalar REL effects are closely related to the heavy element whose electron density dominates largely in the measured structure factors. Apart from this, the sr-IOTC-BLYP procedure yields the best agreement statistics in the XCW fitting, as it includes significant ECORR contributions already. On the other hand and in light of what has been considered just above, it has a slower convergence with the increasing \( \lambda \)-value in comparison to sr-IOTC and NR XCW procedures. Additional effects such as crystal environment, choice of DFT to model electron correlation, even the meaningfulness of XCW with DFT are topics on their own for future projects. For the case of HAR-derived geometries (Fig. 9(b)), the XCW method leads to an improvement of the agreement statistics, but because of the discussed issue with one of the C-H bond lengths, \( \lambda \) has not been extrapolated too far.

Nevertheless, further sanity checks are required, focusing predominantly on obtaining high angle diffraction data with modest experimental error, including robustness of HAR and XCW treatments for compounds containing heavy atoms. In particular, XCW method has to be explored to greater detail, i.e. whether one gets improved agreement statics for the right reasons and at what \( \lambda \)-value to finish the fitting procedure itself, because of the danger of overfitting.
Figure 9: The dependence of $\chi^2$ (y axis) upon the XCW fitting parameter $\lambda$ (x axis) in the XCW approach for HgPh$_2$: left IAM geometry, right HAR-derived geometries

Conclusions

This study was aimed at exploring the significance of relativistic effects on the electron density distribution in heavy-element containing molecular compounds and compare these to the effect of electron correlation accounted for at the BLYP level of theory. This was done in order to find out if relativistic and/or electron correlation effects are possibly detectable, discernible, and modellable from experimental single-crystal X-ray diffraction structure factors. Diphenyl mercury and triphenyl bismuth served as test molecules for theoretical calculations at various levels of theory including or excluding electron correlation and relativity, respectively, with low-order medium-quality experimental X-ray structure factors being available. It was not within the scope of the study to actually experimentally determine relativistic effects and electron correlation within the electron density, but to find the conditions and methods through which they are discernible experimentally in the future.

The main finding of the study is that relativistic effects are not restricted to the core electron density of heavy elements but are clearly discernible also in the outer core and the valence region within adjacent bonds. Analysis of structure factors shows that the influence of relativistic effects on the low-order data is so significant that they will be quantifiable with high-quality experiments at routine resolution, and, consequently, are not avoidable in
any modelling of structure factors of heavy-element containing compounds.

Plots of the electron density and the Laplacian of the electron density show that electron correlation effects dominate along the backbone of the molecules regardless of the presence or absence of a heavy element in the immediate vicinity. Relativistic effects in contrast are very important in the inner core, outer core and valence region of the heavy elements, but not beyond the immediate vicinity of the heavy element. They have a much more pronounced effect on the valence shell charge concentrations of both the heavy metal and the bonded carbon atom than electron correlation. In contrast, spin-orbit coupling and picture change error are very local effects that are negligible for any experimental electron density considerations. The scalar relativistic effects are confirmed to be the dominating relativistic contribution. Atomic net charges from a topological analysis of the electron density according to the QTAIM method reflect the influence of electron correlation and relativistic effects on different coordination spheres of the heavy element very accurately, whereas properties of bond critical points are less suited to investigate either effect, e.g. $\rho_{BCP}$.

Within theoretically calculated structure factors for HgPh$_2$, relativistic effects are important over the full resolution range, at low and high resolution, however, their absolute impact decreases quickly beyond 1.5Å$^{-1}$ in resolution (albeit being discernible in the full range of the relative comparison). There are in fact two sets of structure factors: those dominated by the heavy element that include relativity, found out through Mulliken-like partitioning into atomic contributions, and those not affected. The effect of electron correlation on the structure factors is in the absolute scale only important at low resolution below 0.6Å$^{-1}$. Both effects are clearly detectable in low-order structure factors and must not be neglected in modelling the observed structure factors.

For a quantification of absolute numbers of electron densities of HgPh$_2$ and BiPh$_3$ double-zeta basis sets are not sufficient as they give significantly different results than triple-zeta basis sets. However, for the qualitative and quantitative analysis of electron correlation and
relativistics in the electron density, which are difference densities, double-zeta basis sets are sufficient. Since neither spin-orbit effects nor picture change error are of importance in the difference densities, PCE contaminated scalar infinite order two component BLYP (sr-IOTC-BLYP$_{PCE}$) is the preferable method out of the methods used in this study to achieve best possible agreement with the measured structure factors at the lowest computational cost.

In this study we have made relativistic X-ray wavefunction refinement - a combination of Hirshfeld atom refinement and X-ray constrained wavefunction fitting against relativistic structure factors - possible for the first time, so that an adequate method to model relativity and electron correlation in the experiment is available. It was shown that inclusion of both effects improves the reconstruction of the low-order experimental structure factors significantly. If the non-relativistic HF method is used, a certain extent of information on relativity and electron correlation can be extracted from the measured structure factors and incorporated into the wavefunction. It seems as if relativity might be captured nearly completely, but electron correlation only to a certain percentage.

Now that relativistic XWR is possible and (scalar) relativistic effects seem to be detectable and measurable, improvements on the experiment need to be made. It is one of the results from this study that the effect of absorption on the site of the heavy element is much more significant than either electron correlation or relativity. Therefore, absorption has to be avoided in the experiment (high-energy synchrotron X-radiation or $\gamma$-radiation, tiny crystals, helium cooling, modern detectors) or corrected for very reliably, otherwise an experimental quantification of relativistic effects in the electron density will be impossible - although we show here that in principle it is clearly detectable in the low- and high-order data, counter to widespread expectation.
Acknowledgement

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Supporting Information Available

Contents of file SupportingInformation.pdf:
Table S1; Abbreviations for methods used
Section S1; IOTC Hamiltonian
Section S2; Basis set dependence
Subsection S2.1; Benzene
Subsection S2.2; Hg(CN)$_2$
Section S3; Hirshfeld atom refinement
Section S4; Additional Douglas-Kroll-Hess (DKH2) calculations
Table S2; Positions (in Å) and anisotropic displacement parameters (in Å$^2$) of HgPh$_2$ refine-
ments

Table S3; Chosen bond lengths (in Å) of HgPh₂ IAM and HAR geometries

Table S4; QTAIM bond-critical point (BCP) characteristics of Hg-C₂ and Bi-C₆ bonds

Table S5; QTAIM net charges [e] of selected atoms

Figure S1; 2D difference plots of benzene molecule for results obtained in different basis sets; difference electron density and difference negative Laplacian plots

Figure S2; 2D difference plots of benzene molecule showing the importance or ECORR effects for different basis sets; difference electron density and difference negative Laplacian plots

Figure S3; 2D difference plots of HgCN₂ for results obtained in different basis sets; difference electron density and difference negative Laplacian plots

Figure S4; 2D difference electron density plots of HgCN₂, showing ECORR, REL and PCE effects

Figure S5; 2D difference negative Laplacian plots of HgCN₂, showing ECORR, REL and PCE effects

Figure S6; 2D plots of negative Laplacian of electron density for HgPh₂ and BiPh₃

Figure S7; 1D plots of electron density and negative Laplacian of HgPh₂ along the Hg-C bond. Inlets present difference electron density and negative Laplacian along the Hg-C bond

References (for Supporting Information)

File BiPh₃_cifs.zip contains: CIFs deposited in the Cambridge Structural Data Base and deposition details. Deposition number CCDC-1468789 refers to model MEA and CCDC-1468907 number to model ANA of BiPh₃ compound

The following files are available free of charge.

• SupportingInformation.pdf: Supporting Information materials

• BiPh₃_cifs.zip: Cambridge Structural Data Base deposition details

This material is available free of charge via the Internet at http://pubs.acs.org/.
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Graphical TOC Entry

- Electron correlation in electron density
- Relativistic effects in electron density
- Relativistic effects in structure factors