

wavefunction of an ideal system and that, quite often more limited, but referred to a real system, obtained from an experimental ρ derived from X-ray diffraction data.

The potential uses of the SF are, however, yet not fully explored. In a preliminary work, we addressed the question of whether the SF is or is not capable to reveal electron conjugation [3]. Question arose because of a recent claim [4] according to which “ π -electron delocalization in the benzene ring is not manifest in the SF when the reference point (rp) - the point at which the atomic sources for its density are calculated - is taken at the C-C bond critical point (bcp)”. Reasoning behind this statement is the null contribution from π molecular orbitals (MOs) to ρ in their nodal plane. However, since σ - and π -distributions are not independent, but self-consistently interrelated, we conjectured that some, albeit small, effect of electron conjugation could also be manifest when the rp lies in the π -nodal plane, even though π -orbitals do not obviously yield *direct* contributions to ρ in that plane. Results on a series of increasingly π -conjugated systems demonstrate that *this is actually the case*. By looking at the C-C bcp electron density for the shortest bond(s) in cyclohexene, cyclohexadiene, benzene, i.e. those bonds with largest double-bond character, one observes that both the SF and the SF% contributions of the C atoms other than those directly involved in such a bond increase with decreasing double bond character and electron localization of the bond. The enhanced S% value then becomes largely more evident when analysed using rps for which the effect of π -electron conjugation takes place directly through π -electron distribution rather than, indirectly, through σ - π electron interdependency.

In this work, the analysis is extended to more complex systems, formed by more than one ring, with fully conjugated or partially interrupted sequence of formal double-bonds and with planar or non planar geometry. In the case of benzene, the analysis is also performed on a ρ derived through multipole refinement of a set of X-ray diffraction data taken on a benzene molecular crystal. In the inspected cases and regardless of the theoretical or experimental origin of ρ , the SF reveals capable to detect electron conjugation. Such an ability is independent from a σ and π separation of ρ , since the SF tool was applied to the *total* ρ . This observation is important in view of the possibility to recover electron conjugation effects *using both ρ 's derived experimentally* (hence without σ and π separation being allowed) and ρ 's where *the departure from symmetry inhibits a proper separation* of σ and π contributions. Using a MO approach, the σ and π contributions to the SF values can also be revealed and quantified.

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Descriptors of charge density for estimating the energy of coordinate bonds

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Various quantum descriptors have been employed in establishing the QSAR/QSPR relationship in chemistry and biochemistry, but the main objective of this approach is to relate the electronic properties derived from calculations for isolated molecules with their macroscopic properties. The useful bridge between these two steps is the investigation of experimental charge density distribution function ($\rho(r)$) via high-resolution X-ray diffraction analysis and extracting the

necessary quantum descriptors of charge density from this data to relate them with more sound physical quantities.

The quantum theory of *Atoms in Molecules* [1] together with Espinosa's correlation scheme [2] provides the unique opportunity of estimating the energy of weak closed-shell interactions from first principles on the basis of one of the descriptors of molecular structure, namely, the value of potential energy density ($v(r)$) in the corresponding bond critical point. Recently the application of this approach was extended to the case of strong hydrogen bonds, in other words, the interactions of intermediate type [3]. The topological analysis of various coordination bonds based on the experimental $\rho(r)$ showed the similarity of strong hydrogen bonds and semipolar bonds of a moderate strength from the quantum descriptors' point of view [4].

We tested the applicability of this approach to estimate the dissociation of AuCl-PPh₃ complex [5]. The Au-P bond energy estimated via Espinosa correlation (57.9 kcal/mol) was close to the dissociation energy of the complex according to MP2 calculation (53.2 kcal/mol). This finding as well as the recent data for lanthanide complexes [4] showed this approach can be used at least for the semi-quantitative description of the coordination bonds.

To generalize the usage of quantum descriptors for the estimation of the metal-to-ligand binding energies, we performed the systematic high-resolution XRD analysis of a wide range of coordination and organometallic complexes and examined the relative strength of different metal-ligand bonds. Results will be presented for ruthenocene [6], cymantrene [7], and various coordination complexes of titanium, copper, zinc, palladium, and cadmium [8]. They cover a wide range of interactions - from the weakest metal...hydrogen ones to strong metal-carbon bonds. We also investigated the influence of intermolecular interactions on the bonding within first coordination sphere of metal atoms.

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The atomic energy as the descriptor for the stereoelectronic interactions

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The term 'stereoelectronic effect' comes from the molecular mechanics approach and defines a conformational preference not explainable in terms of steric effects. One of the most fundamental of such effects is the generalized anomeric effect which dictates that in the R-X-C-Y systems, where X is bearing a lone pair (lp), and Y is more electronegative than carbon atom, the gauche conformation is generally the most stable [1]. It is explained in terms of lp-X-C-Y stereoelectronic interaction (SEI): the charge transfer from X's lone pairs to the σ^*_{C-Y} antibonding orbital. Until recently the study of energetic characteristics of SEI was limited to second-order perturbation analysis