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Supporting information for article:

A first prototype of a multi-determinant X-ray constrained wavefunction approach: the X-ray constrained extremely localized molecular orbital–valence bond method

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Supporting information for “A first prototype of multi-determinant X-ray constrained wave function approach: the X-ray constrained Extremely Localized Molecular Orbital-Valence Bond method”

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S1. Unconstrained Extremely Localized Molecular Orbitals

The Extremely Localized Molecular Orbital (ELMO) method devised by Stoll *et al.* (Stoll, H., Wagenblast, G. & Preuss, H. (1980). *Theoret. Chim. Acta* **57**, 169-178) is a technique that enables to determine Molecular Orbitals strictly localized on elementary molecular fragments/subunits (i.e., atoms, bonds or functional groups) in which a $2N$ electron closed-shell molecule has been preliminarily fragmented according to a chemically meaningful localization scheme (see, for example, Figure S1).

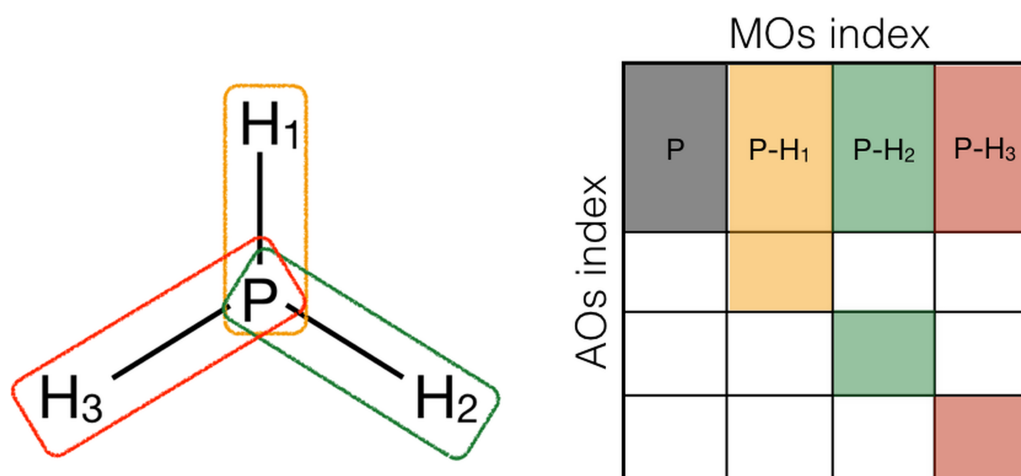


Figure S1 Localization scheme (left) and block-structured matrix of the ELMO coefficients (right) for the phosphine molecule. In the localization scheme, the three overlapping bond fragments P-H₁, P-H₂ and P-H₃ are explicitly shown, while, for the sake of clarity, the atomic fragment P, which describes the core and lone-pair electrons of the phosphorus atom, is not depicted.

After the definition of the localization pattern, each subunit j is associated with a local basis-set $\beta_j = \{|\chi_{j\mu}\rangle\}_{\mu=1}^{M_j}$ consisting of the only basis functions centred on the atoms that belong to the fragment. Therefore, the ELMOs associated with the different subunits are expanded only on the corresponding local sets of basis functions and, for instance, the generic γ -th ELMO of the j -th fragment can be simply written as follows:

$$|\varphi_{j\gamma}\rangle = \sum_{\mu=1}^{M_j} C_{j\mu,j\gamma} |\chi_{j\mu}\rangle \quad (\text{S1})$$

According to Stoll, the closed-shell system under exam can be described by a normalized single Slater determinant constructed with Extremely Localized Molecular Orbitals (ELMO wave function):

$$|\Psi_{ELMO}\rangle = \aleph \hat{A} \left[\varphi_{11} \bar{\varphi}_{11} \dots \varphi_{1n_1} \bar{\varphi}_{1n_1} \dots \varphi_{f1} \bar{\varphi}_{f1} \dots \varphi_{fn_f} \bar{\varphi}_{fn_f} \right] \quad (\text{S2})$$

where \hat{A} is the antisymmetrizer, n_j is the number of occupied ELMOs for the j -th fragment, $\varphi_{j\gamma}$ is a spin-orbital with spatial part $\varphi_{j\gamma}$ and spin part α and $\bar{\varphi}_{j\gamma}$ is a spin-orbital with spatial part $\varphi_{j\gamma}$ and spin part β . Finally, \aleph is a normalization constant that can be written as:

$$\aleph = \frac{1}{\sqrt{(2N)! \det[\mathbf{S}]}} \quad (\text{S3})$$

with $\det[\mathbf{S}]$ as the determinant of the overlap matrix between the occupied ELMOs.

The ELMOs in Slater determinant (S2) are obtained variationally minimizing the following functional

$$E[\boldsymbol{\varphi}] = \langle \Psi_{ELMO} | \hat{H} | \Psi_{ELMO} \rangle \quad (\text{S4}),$$

which is simply the energy corresponding to the ELMO wave function.

Following Stoll, it is possible to show that the minimization of functional (S4) is actually equivalent to solving the following modified Hartree-Fock equation for each subunit:

$$\hat{F}^j |\varphi_{j\gamma}\rangle = \epsilon_{j\gamma} |\varphi_{j\gamma}\rangle \quad (\text{S5})$$

where \hat{F}^j is the modified Fock operator for the generic j -th fragment, namely

$$\hat{F}^j = (1 - \hat{\rho} + \hat{\rho}^{j\dagger}) \hat{F} (1 - \hat{\rho} + \hat{\rho}^j) \quad (\text{S6})$$

with \hat{F} as the usual Fock operator, $\hat{\rho}^j$ as the local density operator for the subunit j , which depends only on the occupied ELMOs of the fragment, and $\hat{\rho}$ as the global density operator, which depends on

all the occupied ELMOs of the investigated closed-shell system and which consequently couples the eigenvalue-equations associated with the different subunits.

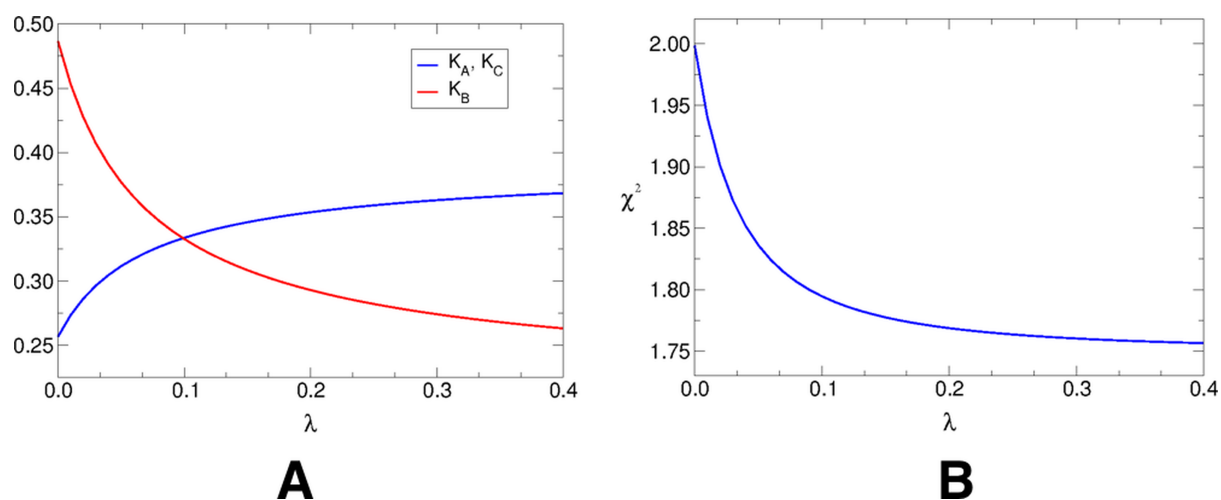


Figure S2 (A) Chirgwin-Coulson weights (K_A , K_C in blue and K_B in red) and (B) χ^2 statistical agreement in function of the external multiplier λ for the XC-ELMO-VB calculations performed on the naphthalene crystallographic structures determined at 135 K.

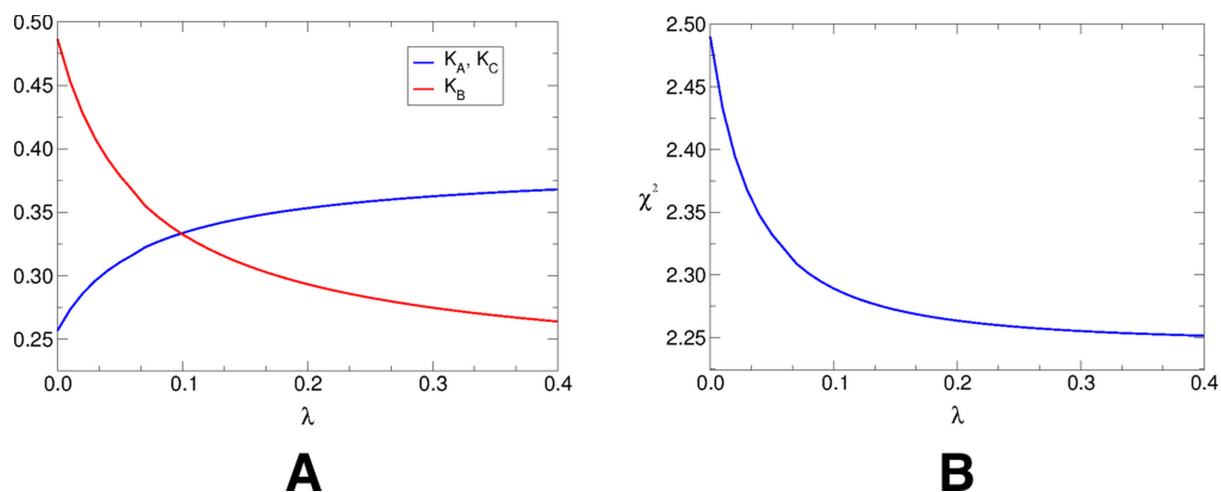


Figure S3 (A) Chirgwin-Coulson weights (K_A , K_C in blue and K_B in red) and (B) χ^2 statistical agreement in function of the external multiplier λ for the XC-ELMO-VB calculations performed on the naphthalene crystallographic structures determined at 170 K.

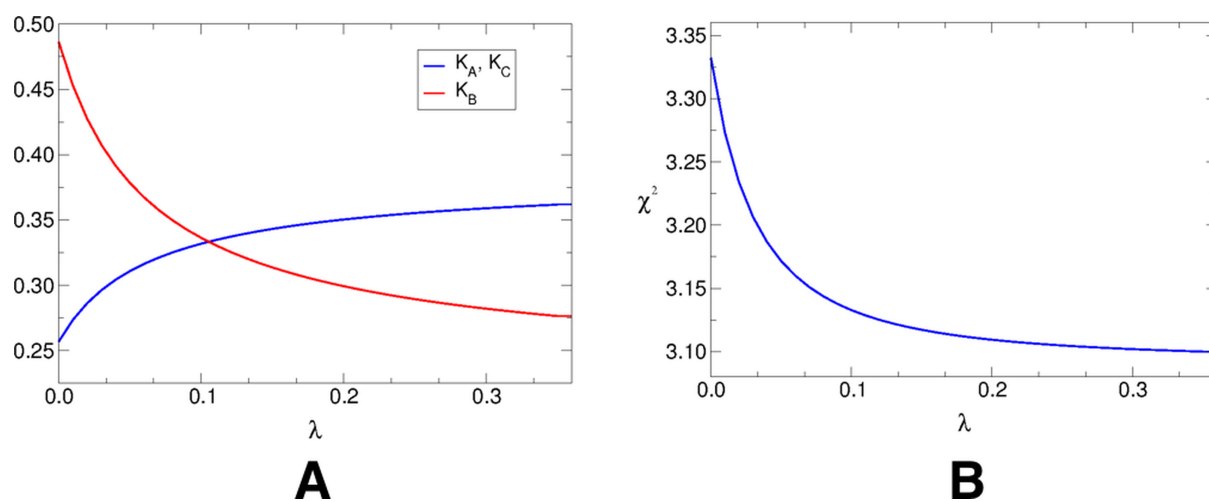


Figure S4 (A) Chirgwin-Coulson weights (K_A , K_C in blue and K_B in red) and (B) χ^2 statistical agreement in function of the external multiplier λ for the XC-ELMO-VB calculations performed on the naphthalene crystallographic structures determined at 205 K.