Supporting information for: "X-Ray Constrained Extremely Localized Molecular Orbitals: Theory and Critical Assessment of the New Technique"

Alessandro Genoni[*,†,‡]

CNRS, Laboratoire SRSMC, UMR 7565, Vandoeuvre-lès-Nancy, F-54506, France, and Université de Lorraine, Laboratoire SRSMC, UMR 7565, Vandoeuvre-lès-Nancy, F-54506, France

E-mail: Alessandro.Genoni@univ-lorraine.fr

---

[*]To whom correspondence should be addressed
[†]CNRS
[‡]Université de Lorraine

Obara-Saika Scheme for the Computation of Fourier Transform Integrals. In order to compute the matrix elements $\left[\mathbf{I_h}\right]_{\mu\nu}$ given by Eq. (17) of the manuscript, it is necessary to evaluate the Fourier Transform Integrals (FTIs) that appear in the just mentioned equation. To accomplish this task we have implemented an Obara-Saika scheme exploiting both vertical and horizontal recurrence relations[1,2] that allows to express each FTI in terms of other integrals of lower angular momentum. In fact, by means of repeated applications of the recurrence formula, all the FTIs can be reduced to integrals involving only zero angular momentum s functions that can be easily evaluated.

Now, since

$$(\mathbf{R}_j\mathbf{r}) \cdot (\mathbf{Bh}) = \mathbf{r} \cdot \left(\mathbf{R}_j^T\mathbf{Bh}\right) \tag{S1}$$

let us focus on the following integral

$$\int d\mathbf{r}\, \chi_\mu(\mathbf{r})\, \chi_\nu(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{S2}$$

where $\mathbf{k} = 2\pi\mathbf{r} \cdot (\mathbf{R}_j^T\mathbf{Bh})$ and where the basis functions $\chi_\mu(\mathbf{r})$ and $\chi_\nu(\mathbf{r})$ are linear combinations of unnomalized Cartesian Gaussian functions (primitives):

$$\chi_\mu(\mathbf{r}) = \sum_{i=1}^{m_\mu} C_{i\mu}\, N_{i\mu}\, \Phi_{i\mu}(\mathbf{r}) \tag{S3}$$

$$\chi_\nu(\mathbf{r}) = \sum_{i=1}^{m_\nu} C_{i\nu}\, N_{i\nu}\, \Phi_{i\nu}(\mathbf{r}) \tag{S4}$$

with m_μ and m_ν as the degrees of the contractions, and $\left\{N_{i\mu}\right\}$ and $\left\{N_{i\nu}\right\}$ as the normalization constants for the primitives.

Considering Eqs. (S3) and (S4), and bearing in mind that a generic unnormalized Cartesian Gaussian function can be expressed like this

$$\begin{aligned}
\Phi\left(\mathbf{r}; \alpha, A, \mathbf{a}\right) &= \left(x - A_x\right)^{a_x}\left(y - A_y\right)^{a_y}\left(z - A_z\right)^{a_z} e^{-\alpha(\mathbf{r}-\mathbf{A})^2}\\
&= \left(x - A_x\right)^{a_x}\left(y - A_y\right)^{a_y}\left(z - A_z\right)^{a_z} e^{-\alpha\left[(x-A_x)^2+(y-A_y)^2+(z-A_z)^2\right]}
\end{aligned} \tag{S5}$$

where $\mathbf{A} = \left(A_x, A_y, A_z\right)$ is the center of the primitive, $\mathbf{a} = \left(a_x, a_y, a_z\right)$ is the vector of the angular

momentum indexes and α is the Gaussian exponent, it is easy to show that the FTI given by Eq. (S2) is a simple linear combination of integrals that have the following form:

$$I = \int d\mathbf{r} \; \Phi_a(\mathbf{r}; \alpha, A, \mathbf{a}) \; \Phi_b(\mathbf{r}; \beta, B, \mathbf{b}) \; e^{i\mathbf{k} \cdot \mathbf{r}} \tag{S6}$$

Since it is well known that

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2} e^{-\beta(\mathbf{r}-\mathbf{B})^2} = E_{AB} \; e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2} \tag{S7}$$

with

$$E_{AB} = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} \tag{S8}$$

and

$$\mathbf{P} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha+\beta} \tag{S9}$$

the integral I (see Eq. (S6)) becomes

$$
\begin{aligned}
I \;=\; & E_{AB} \int dx \, (x-A_x)^{a_x} (x-B_x)^{b_x} e^{-(\alpha+\beta)(x-P_x)^2} e^{ik_x x} \times \\
& \int dy \, (y-A_y)^{a_y} (y-B_y)^{b_y} e^{-(\alpha+\beta)(y-P_y)^2} e^{ik_y y} \times \\
& \int dz \, (z-A_z)^{a_z} (z-B_z)^{b_z} e^{-(\alpha+\beta)(z-P_z)^2} e^{ik_z z} = \\
\;=\; & E_{AB} \, I_x(a_x, b_x) \, I_y(a_y, b_y) \, I_z(a_z b_z)
\end{aligned}
\tag{S10}
$$

where we have explicitly indicated the functional dependence on the Cartesian angular components.

Without loss of generality, let us simply consider $I_x(a_x, b_x)$:

$$I_x(a_x, b_x) = \int dx \, (x-A_x)^{a_x} (x-B_x)^{b_x} e^{-(\alpha+\beta)(x-P_x)^2} e^{ik_x x} \tag{S11}$$

It is possible to show that

$$(x-A_x)^{a_x} (x-B_x)^{b_x} = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (x-P_x)^{i_x+j_x} (P_x-A_x)^{a_x-i_x} (P_x-B_x)^{b_x-j_x} \tag{S12}$$

and, therefore, Eq. (S11) can be rewritten like this:

$$I_x(a_x, b_x) = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x - i_x} (P_x - B_x)^{b_x - j_x} \times$$

$$\int dx \, (x - P_x)^{i_x + j_x} e^{-(\alpha + \beta)(x - P_x)^2} e^{ik_x x} \qquad \text{(S13)}$$

Bearing in mind that:

$$\int dx \, (x - P_x)^l \, e^{-\eta(x - P_x)^2} \, e^{ik_x x} = \sqrt{\frac{\pi}{\eta}} \left(\frac{i}{2\sqrt{\eta}}\right)^l H_l\left[\frac{k_x}{2\sqrt{\eta}}\right] e^{-\frac{k_x^2}{4\eta}} e^{ik_x P_x} \qquad \text{(S14)}$$

and that $H_l\left[\frac{k_x}{2\sqrt{\eta}}\right]$ represents a Hermite polynomial having this form

$$H_n[y] = (-1)^n \, e^{y^2} \frac{d^n}{dy^n} e^{-y^2} = n! \sum_{j=0}^{\lfloor n/2 \rfloor} \frac{(-1)^j (2y)^{n-2j}}{j!(n-2j)!} \qquad \text{(S15)}$$

the integral $I_x(a_x, b_x)$ becomes

$$I_x(a_x, b_x) = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \gamma\left(i_x, j_x, \alpha, \beta, k_x\right) \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x - i_x} (P_x - B_x)^{b_x - j_x} e^{ik_x P_x} \quad \text{(S16)}$$

with

$$\gamma\left(i_x, j_x, \alpha, \beta, k_x\right) = \sqrt{\frac{\pi}{\alpha + \beta}} \left(\frac{i}{2\sqrt{\alpha + \beta}}\right)^{i_x + j_x} H_{i_x + j_x}\left[\frac{k_x}{2\sqrt{\alpha + \beta}}\right] e^{-\frac{k_x^2}{4(\alpha + \beta)}} \qquad \text{(S17)}$$

Now, considering Eq. (S11), the derivatives of the integral $I_x(a_x, b_x)$ with respect to A_x and B_x are respectively given by:

$$\frac{\partial I_x(a_x, b_x)}{\partial A_x} = -a_x I_x(a_x - 1, b_x) + 2\alpha I_x(a_x + 1, b_x) + 2\alpha (A_x - P_x) I_x(a_x, b_x) \qquad \text{(S18)}$$

and

$$\frac{\partial I_x(a_x, b_x)}{\partial B_x} = -b_x I_x(a_x, b_x - 1) + 2\beta I_x(a_x, b_x + 1) + 2\beta (B_x - P_x) I_x(a_x, b_x) \qquad \text{(S19)}$$

If we take into account Eq. (S16), the expressions for the derivatives are:

$$\frac{\partial I_x(a_x, b_x)}{\partial A_x} = a_x \left(\frac{\alpha}{\alpha + \beta} - 1 \right) I_x(a_x - 1, b_x) + b_x \frac{\alpha}{\alpha + \beta} I_x(a_x, b_x - 1) + i k_x \frac{\alpha}{\alpha + \beta} I_x(a_x, b_x)$$

(S20)

and

$$\frac{\partial I_x(a_x, b_x)}{\partial B_x} = b_x \left(\frac{\beta}{\alpha + \beta} - 1 \right) I_x(a_x, b_x - 1) + a_x \frac{\beta}{\alpha + \beta} I_x(a_x - 1, b_x) + i k_x \frac{\beta}{\alpha + \beta} I_x(a_x, b_x)$$

(S21)

Comparing Eq. (S18) with Eq. (S20), we obtain the first vertical recurrence relation

$$I_x(a_x + 1, b_x) = \left(P_x - A_x + \frac{i k_x}{2(\alpha + \beta)} \right) I_x(a_x, b_x) + \frac{a_x}{2(\alpha + \beta)} I_x(a_x - 1, b_x) +$$
$$\frac{b_x}{2(\alpha + \beta)} I_x(a_x, b_x - 1)$$

(S22)

while, comparing Eq. (S19) with Eq. (S21), we have the second vertical recurrence relation

$$I_x(a_x, b_x + 1) = \left(P_x - B_x + \frac{i k_x}{2(\alpha + \beta)} \right) I_x(a_x, b_x) + \frac{a_x}{2(\alpha + \beta)} I_x(a_x - 1, b_x) +$$
$$\frac{b_x}{2(\alpha + \beta)} I_x(a_x, b_x - 1)$$

(S23)

Finally, rearranging Eqs. (S22) and (S23), we respectively obtain:

$$I_x(a_x + 1, b_x) + \left(A_x - P_x - \frac{i k_x}{2(\alpha + \beta)} \right) I_x(a_x, b_x) = \frac{a_x}{2(\alpha + \beta)} I_x(a_x - 1, b_x) +$$
$$\frac{b_x}{2(\alpha + \beta)} I_x(a_x, b_x - 1) \quad \text{(S24)}$$

$$I_x(a_x, b_x + 1) + \left(B_x - P_x - \frac{i k_x}{2(\alpha + \beta)} \right) I_x(a_x, b_x) = \frac{a_x}{2(\alpha + \beta)} I_x(a_x - 1, b_x) +$$
$$\frac{b_x}{2(\alpha + \beta)} I_x(a_x, b_x - 1) \quad \text{(S25)}$$

and subtracting Eq. (S25) from Eq. (S24) the last two equations we have the horizontal recur-

rence relation for our integrals:

$$I_x\big(a_x, b_x + 1\big) = I_x\big(a_x + 1, b_x\big) + \big(A_x - B_x\big) I_x\big(a_x, b_x\big) \tag{S26}$$

Hence, through proper and repeated applications of Eqs. (S22), (S23) and (S26), the generic FTI $I_x\big(a_x, b_x\big)$ can be expressed in function of the only integral $I_x\big(0, 0\big)$ that involves only two primitive s functions and that is equivalent to:

$$I_x\big(0, 0\big) = \int dx\, e^{-(\alpha+\beta)\,(x-P_x)^2}\, e^{ik_x x} = \sqrt{\frac{\pi}{\alpha+\beta}}\, e^{-\frac{k_x^2}{4(\alpha+\beta)}}\, e^{ik_x P_x} \tag{S27}$$

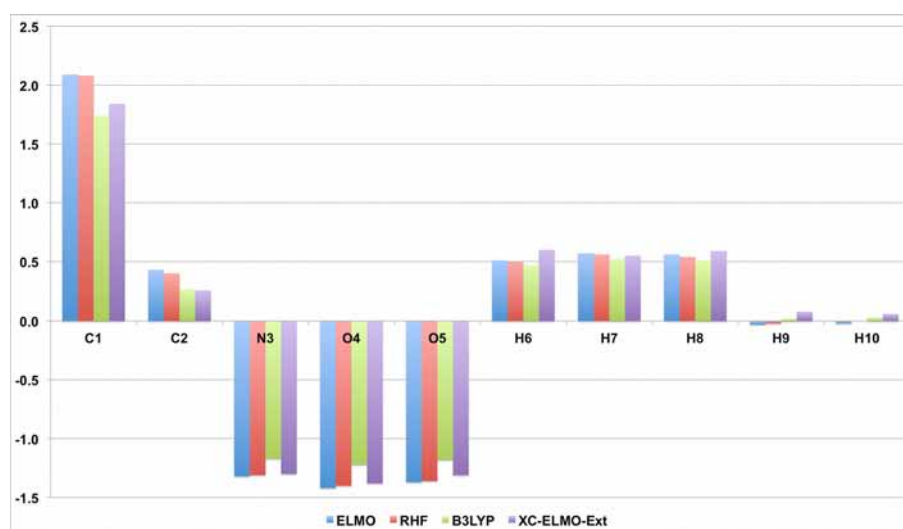**Bar-graphs of the integrated net atomic charges.**

Figure S1: Bar-graph of the integrated net atomic charges (in a.u.) associated with the ELMO, RHF, B3LYP and XC-ELMO-Ext charge distributions for the α-glycine (cc-pVDZ basis-set).
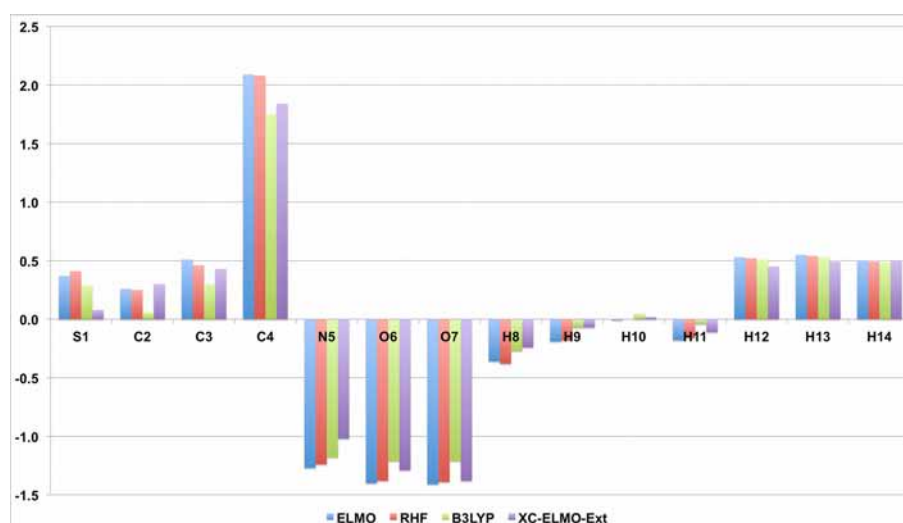

Figure S2: Bar-graph of the integrated net atomic charges (in a.u.) associated with the ELMO, RHF, B3LYP and XC-ELMO-Ext charge distributions for the L-cysteine (cc-pVDZ basis-set).
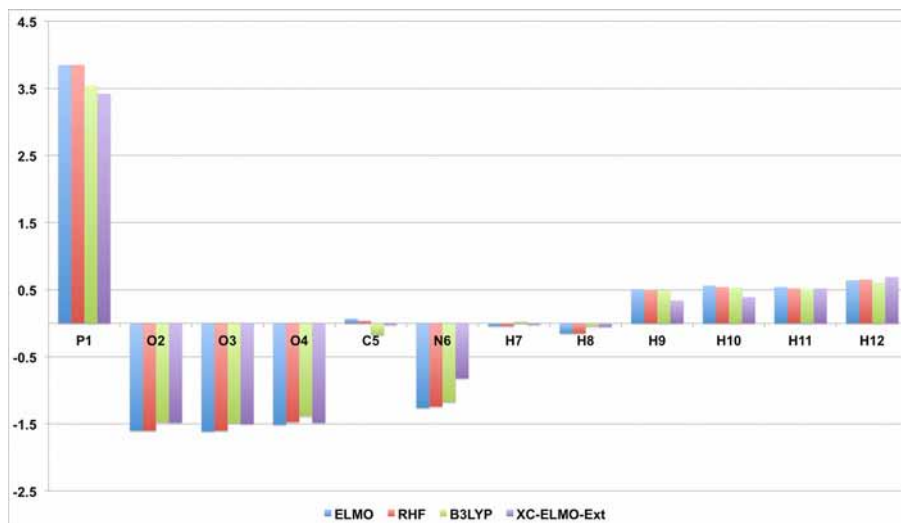
Figure S3: Bar-graph of the integrated net atomic charges (in a.u.) associated with the ELMO, RHF, B3LYP and XC-ELMO-Ext charge distributions for the (aminomethyl)phosphonic acid (cc-pVDZ basis-set).
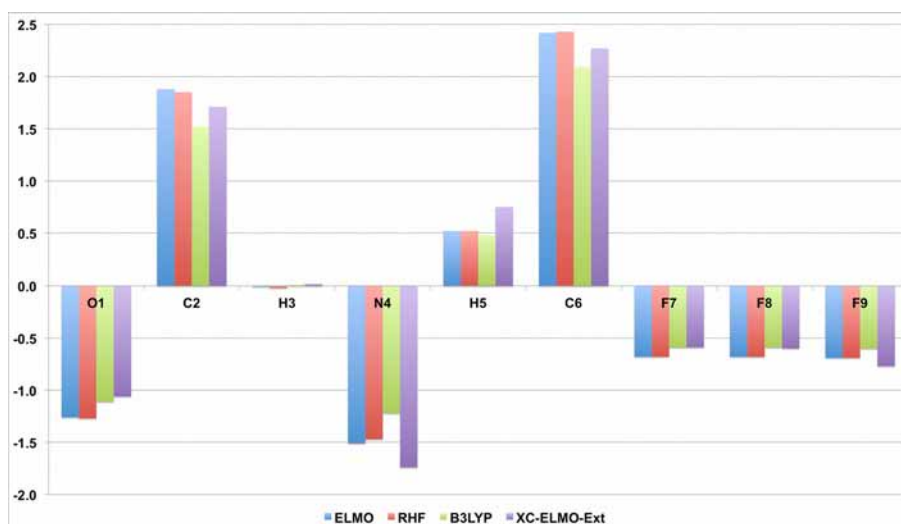

Figure S4: Bar-graph of the integrated net atomic charges (in a.u.) associated with the ELMO, RHF, B3LYP and XC-ELMO-Ext charge distributions for the N-(trifluoromethyl)formamide (cc-pVDZ basis-set).

Walker-Mezey similarity index. The Walker-Mezey similarity index[3] $L(\rho_x, \rho_y, a, a')$ compares point-by-point two electron densities ρ_x and ρ_y in a "density shell" $S(\rho_x, a, a')$ that can be considered as the space bound by the isosurfaces characterized by the values a and a' and that is defined as

$$S(\rho_x, a, a') = \left\{ \mathbf{r} : a \leq \rho_x(\mathbf{r}) \leq a' \right\} \tag{S28}$$

We have that

$$L(\rho_x, \rho_y, a, a') = 100 \ \frac{L^*(\rho_x, \rho_y, a, a') + L^*(\rho_y, \rho_x, a, a')}{2} \tag{S29}$$

where

$$L^*(\rho_x, \rho_y, a, a') = 1 - \left[\sum_{\mathbf{r} \in S(\rho_x, a, a')} \frac{\left| \rho_x(\mathbf{r}) - \rho_y(\mathbf{r}) \right|}{max\left(\rho_x(\mathbf{r}), \rho_y(\mathbf{r}) \right)} \right] \bigg/ n\left(S(\rho_x, a, a') \right) \tag{S30}$$

and

$$L^*(\rho_y, \rho_x, a, a') = 1 - \left[\sum_{\mathbf{r} \in S(\rho_y, a, a')} \frac{\left| \rho_x(\mathbf{r}) - \rho_y(\mathbf{r}) \right|}{max\left(\rho_x(\mathbf{r}), \rho_y(\mathbf{r}) \right)} \right] \bigg/ n\left(S(\rho_y, a, a') \right) \tag{S31}$$

with $n\left(S(\rho_x, a, a') \right)$ and $n\left(S(\rho_y, a, a') \right)$ as the number of grid points belonging to the "density shells" $S(\rho_x, a, a')$ and $S(\rho_y, a, a')$, respectively.

Values of the Walker-Mezey Similarity Index in Different Real-Space Regions.

Table S1: Values of the Walker-Mezey similarity index in different regions of the real-space and corresponding to the comparison of the ELMO charge distribution with the RHF, B3LYP and X-ELMO-Ext electron densities for the α-glycine (cc-pVDZ basis-set).

System	$L(0.1, 10)$	$L(0.01, 0.1)$	$L(0.001, 0.01)$
RHF	99.53	98.85	96.81
B3LYP	97.78	95.85	91.85
X-ELMO-Ext	96.80	95.03	90.24

Table S2: Values of the Walker-Mezey similarity index in different regions of the real-space and corresponding to the comparison of the ELMO charge distribution with the RHF, B3LYP and X-ELMO-Ext electron densities for the L-cysteine (cc-pVDZ basis-set).

System	$L(0.1, 10)$	$L(0.01, 0.1)$	$L(0.001, 0.01)$
RHF	99.48	98.66	96.81
B3LYP	98.06	96.56	93.12
X-ELMO-Ext	95.35	92.57	85.18

Table S3: Values of the Walker-Mezey similarity index in different regions of the real-space and corresponding to the comparison of the ELMO charge distribution with the RHF, B3LYP and X-ELMO-Ext electron densities for the (aminomethyl)phosphonic acid (cc-pVDZ basis-set).

System	$L(0.1, 10)$	$L(0.01, 0.1)$	$L(0.001, 0.01)$
RHF	99.32	97.65	95.13
B3LYP	97.97	94.74	90.34
X-ELMO-Ext	94.96	92.64	85.69

Table S4: Values of the Walker-Mezey similarity index in different regions of the real-space and corresponding to the comparison of the ELMO charge distribution with the RHF, B3LYP and X-ELMO-Ext electron densities for the N-(trifluoromethyl)formamide (cc-pVDZ basis-set).

System	$L(0.1, 10)$	$L(0.01, 0.1)$	$L(0.001, 0.01)$
RHF	99.12	97.80	96.07
B3LYP	97.66	95.38	92.30
X-ELMO-Ext	93.90	88.19	84.20

References for the Supporting Information.

(1) Obara S.; Saika A. *J. Chem. Phys.* **1986**, *84*, 3963-3974 .

(2) Head-Gordon M.; Pople J. A. *J. Chem. Phys.* **1988**, *89*, 5777-5786.

(3) Walker P. D.; Mezey P. G. *J. Am. Chem. Soc.* **1994**, *116*, 12022-12032.