Mathematical derivations leading to the TPS in real space and details on its implementation in the PROMOLDEN code

SUPPLEMENTARY INFORMATION

An unexpected bridge between bonding indicators and electrical conductivity through the localization tensor

by

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Contents

1 The total position spread tensor

Let $\boldsymbol{r}_i$ the vector position of the ith electron of a N-electron molecule, Ψ the multielectron wavefunction, and

$$\boldsymbol{R} = \sum_{i}^{N} \boldsymbol{r}_i. \tag{1}$$

The total position spread (TPS) tensor is defined as [1, 2]

$$\boldsymbol{\Lambda} = \langle \Psi | \hat{\boldsymbol{R}} \otimes \hat{\boldsymbol{R}} | \Psi \rangle - \langle \Psi | \hat{\boldsymbol{R}} | \Psi \rangle \otimes \langle \Psi | \hat{\boldsymbol{R}} | \Psi \rangle \equiv \langle \hat{\boldsymbol{R}} \otimes \hat{\boldsymbol{R}} \rangle - \langle \hat{\boldsymbol{R}} \rangle \otimes \langle \hat{\boldsymbol{R}} \rangle. \tag{2}$$

Here, bold fonts are used to indicate vectors or tensors, depending on the context, and the $\otimes$ symbol stands for a tensor or cartesian product. For example, the cartesian components of the $\boldsymbol{r} \otimes \boldsymbol{r}$ tensor are $(\boldsymbol{r} \otimes \boldsymbol{r})_{ab} = x_a x_b$, and the six independent components of the symmetric $\boldsymbol{\Lambda}$ are

$$\Lambda_{ab} = \Lambda_{ba} = \langle X_a X_b \rangle - \langle X_a \rangle \langle X_b \rangle, \quad a, b = x, y, z. \tag{3}$$

$\boldsymbol{\Lambda}$ is a cumulant and size extensive.

2 The total position spread tensor from reduced density matrices

Using Eq. 1 and $\hat{\boldsymbol{R}} \otimes \hat{\boldsymbol{R}} = \sum_{i \neq j}^{N} \hat{\boldsymbol{r}}_i \otimes \hat{\boldsymbol{r}}_j + \sum_{i}^{N} \hat{\boldsymbol{r}}_i \otimes \hat{\boldsymbol{r}}_i$ in Eq. 2, and taking into account electron indistinguishability, $\boldsymbol{\Lambda}$ becomes

$$\boldsymbol{\Lambda} = N(N-1) \langle \Psi | \hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_2 | \Psi \rangle + N \langle \Psi | \hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_1 | \Psi \rangle - N \langle \Psi | \hat{\boldsymbol{r}}_1 | \Psi \rangle \otimes N \langle \Psi | \hat{\boldsymbol{r}}_2 | \Psi \rangle. \tag{4}$$

Now, we use the definition of the first order, $\rho(\boldsymbol{r}_1)$, and the second order, $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$, spinless densities, which are nothing but the electron density and the pair density, respectively:

$$\begin{aligned} \rho(\boldsymbol{r}_1) &= N \int d\sigma_1 d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_N \Psi^* \Psi, \\ \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) &= N(N-1) \int d\sigma_1 d\sigma_2 d\boldsymbol{x}_3 \cdots d\boldsymbol{x}_N \Psi^* \Psi, \end{aligned} \tag{5}$$

where $\boldsymbol{x}_i = \boldsymbol{r}_i \sigma_i$ is the space-spin coordinate of electron i. Then,

$$\begin{aligned} \boldsymbol{\Lambda} &= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 (\hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_2)\, \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) + \int d\boldsymbol{r}_1 (\hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_1) \rho(\boldsymbol{r}_1) \\ &- \int d\boldsymbol{r}_1 \hat{\boldsymbol{r}}_1\, \rho(\boldsymbol{r}_1) \otimes \int d\boldsymbol{r}_2\, \hat{\boldsymbol{r}}_2 \rho(\boldsymbol{r}_2). \end{aligned} \tag{6}$$

The above equation may be notably simplified by using $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, where ρ_{xc} is the exchange-correlation density, the part of the pair density containing all pure quantum mechanical effects. Using this expression for ρ_2 in Eq. 6, the part of $\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)$ compensates the third term, and $\boldsymbol{\Lambda}$ results

$$\boldsymbol{\Lambda} = -\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 (\hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_2)\, \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) + \int d\boldsymbol{r}_1 (\hat{\boldsymbol{r}}_1 \otimes \hat{\boldsymbol{r}}_1)\, \rho(\boldsymbol{r}_1). \tag{7}$$

If we now use the key identity $\rho(\boldsymbol{r}_1) = \int d\boldsymbol{r}_2 \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in the second integral of Eq. 7, we obtain

$$\boldsymbol{\Lambda} = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \left[\boldsymbol{r}_1 \otimes (\boldsymbol{r}_1 - \boldsymbol{r}_2)\right] \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{8}$$

$$= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \left[\boldsymbol{r}_2 \otimes (\boldsymbol{r}_2 - \boldsymbol{r}_1)\right] \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{9}$$

where the last equation arises as a consequence of the invariance of $\boldsymbol{\Lambda}$ with respect to the $\boldsymbol{r}_1 \leftrightarrow \boldsymbol{r}_2$ exchange and the equality $\rho_{xc}(\boldsymbol{r}_2, \boldsymbol{r}_1) = \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2)$. Taking the average of Eqs. 8 and 9, and defining the interparticle position vector $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$, $\boldsymbol{\Lambda}$ may be finally written in the following explicitly origin independent form

$$\boldsymbol{\Lambda} = \frac{1}{2} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \; \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) \;\; (\boldsymbol{r}_{12} \otimes \boldsymbol{r}_{12})\,. \tag{10}$$

The origin independence of $\boldsymbol{\Lambda}$ may also be explicitly proven by writing any of its six independent components, $\boldsymbol{\Lambda}_{ab}$, in a shifted frame, $\boldsymbol{r}_i' = \boldsymbol{r}_i + \boldsymbol{u}$. Using Eq. 8 one has

$$\Lambda_{ab}' = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2\, \rho_{xc}\, (x_{1a} + u_a)\, [x_{1b} - x_{2b}] \tag{11}$$

$$= \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2\, \rho_{xc}\, x_{1a}\, [x_{1b} - x_{2b}] + u_a \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2\, \rho_{xc}\, [x_{1b} - x_{2b}]\,, \tag{12}$$

where we have denoted with a prime ($'$) the position spread tensor in the displaced reference system and obviated the dependence of ρ_{xc} on $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. If the double integrals are written as $\int\int \ldots = \sum_A \sum_B \int_A \int_B \ldots$, the AA term of the second contribution of Eq. 12 becomes

$$\int_A \int_A \rho_{xc}\, [x_{1b} - x_{2b}] = \int_A d\boldsymbol{r}_1 x_{1b} \int d\boldsymbol{r}_2 \rho_{xc} - \int_A d\boldsymbol{r}_2 x_{2b} \int d\boldsymbol{r}_1 \rho_{xc} \tag{13}$$

$$= \int_A d\boldsymbol{r}_1\, x_{1b}\, G^A(\boldsymbol{r}_1) - \int_A d\boldsymbol{r}_2\, x_{2b}\, G^A(\boldsymbol{r}_2) = 0, \tag{14}$$

where

$$G^{\Omega}(\boldsymbol{r}_1) = \int_{\Omega} d\boldsymbol{r}_2\; \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{15}$$

is the domain averaged Fermi Hole (DAFH) of the Ω domain [5]. On the other hand the AB and BA terms of the second contribution of Eq. 12 become

$$\int_A \int_B \rho_{xc}\, [x_{1b} - x_{2b}] = \int_A G^B x_b - \int_B G^A x_b, , \tag{16}$$

$$\int_B \int_A \rho_{xc}\, [x_{1b} - x_{2b}] = \int_B G^A x_b - \int_A G^B x_b, \tag{17}$$

i.e the AA contribution is zero, and the AB and BA contributions are equal and of opposite sign. Consequently $\int\int \rho_{xc}\, [x_{1b} - x_{2b}] = 0$. This proves that $\Lambda_{ab} = \Lambda_{ab}'$, i.e. that Λ_{ab} is invariant with respect of a translation of the reference system.

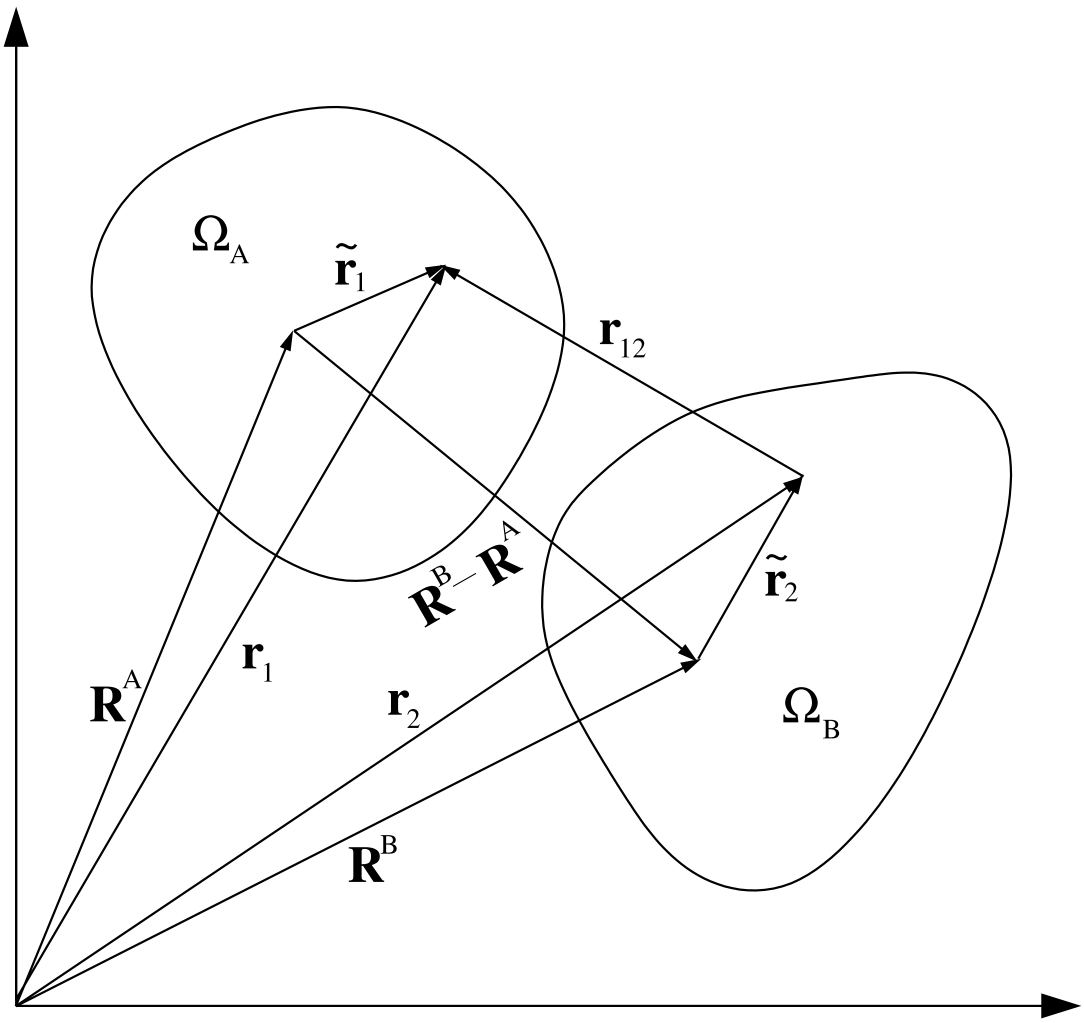

Figure 1: Coordinate System

3 Partitioning the total position spread tensor into local contributions

We partition each component Λ_{ab} into local contributions using

$$\begin{aligned}
\Lambda_{ab} &= \sum_{A\geq B} \Lambda_{ab}^{\mathrm{AB}} && (18)\\
\Lambda_{ab}^{\mathrm{AA}} &= \lambda_{ab}^{\mathrm{AA}} && (19)\\
\Lambda_{ab}^{\mathrm{AB}} &= \lambda_{ab}^{\mathrm{AB}} + \lambda_{ab}^{\mathrm{BA}} && (20)\\
\lambda_{ab}^{\mathrm{AB}} &= \int_A d\boldsymbol{r}_1 \int_B d\boldsymbol{r}_2\ \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)\ x_{1a}\ \left[x_{1b} - x_{2b}\right]. && (21)
\end{aligned}$$

To compute $\Lambda_{ab}^{\mathrm{AB}}$ it is convenient to transform the coordinates $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, which are referred to a common reference system, to their own local reference frames. Using $\boldsymbol{r}_1 = \tilde{\boldsymbol{r}}_1 + \boldsymbol{R}^A$ and $\boldsymbol{r}_2 = \tilde{\boldsymbol{r}}_2 + \boldsymbol{R}^B$ (See Fig. 1) or $x_{1a} = \tilde{x}_{1a} + R_a^A$ and $x_{2b} = \tilde{x}_{2b} + R_b^B$, we have

$$\begin{aligned}
\Lambda_{ab}^{\mathrm{AB}} &= \int_A d\boldsymbol{r}_1 \int_B d\boldsymbol{r}_2 \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)(\tilde{x}_{1a} + R_a^A)(\tilde{x}_{1b} + R_b^A) - (\tilde{x}_{1a} + R_a^A)(\tilde{x}_{2b} + R_b^B)\\
&+ \int_B d\boldsymbol{r}_1 \int_A d\boldsymbol{r}_2 \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)(\tilde{x}_{1a} + R_a^B)(\tilde{x}_{1b} + R_b^B) - (\tilde{x}_{1a} + R_a^B)(\tilde{x}_{2b} + R_b^A)\\
&= \langle \tilde{x}_{1a}\tilde{x}_{1b}\rangle_{\mathrm{AB}} + \langle \tilde{x}_{1a} R_b^A\rangle_{\mathrm{AB}} + \langle R_a^A \tilde{x}_{1b}\rangle_{\mathrm{AB}} + \langle R_a^A R_b^A\rangle_{\mathrm{AB}}\\
&- \langle \tilde{x}_{1a}\tilde{x}_{2b}\rangle_{\mathrm{AB}} - \langle \tilde{x}_{1a} R_b^B\rangle_{\mathrm{AB}} - \langle R_a^A \tilde{x}_{2b}\rangle_{\mathrm{AB}} - \langle R_a^A R_b^B\rangle_{\mathrm{AB}}\\
&+ \langle \tilde{x}_{1a}\tilde{x}_{1b}\rangle_{\mathrm{BA}} + \langle \tilde{x}_{1a} R_b^B\rangle_{\mathrm{BA}} + \langle R_a^B \tilde{x}_{1b}\rangle_{\mathrm{BA}} + \langle R_a^B R_b^B\rangle_{\mathrm{BA}}\\
&- \langle \tilde{x}_{1a}\tilde{x}_{2b}\rangle_{\mathrm{BA}} - \langle \tilde{x}_{1a} R_b^A\rangle_{\mathrm{BA}} - \langle R_a^B \tilde{x}_{2b}\rangle_{\mathrm{BA}} - \langle R_a^B R_b^A\rangle_{\mathrm{BA}}, && (22)
\end{aligned}$$

where the notation $\langle \hat{o}\rangle_{\Omega\Omega'} \equiv \int_A d\boldsymbol{r}_1 \int_B d\boldsymbol{r}_2\ \hat{o}\ \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ has been used. Simplifying Eq. 22

$$\begin{aligned}
\Lambda_{ab}^{\mathrm{AB}} &= \langle \tilde{x}_{1a}\tilde{x}_{1b}\rangle_{\mathrm{AB}} - \langle \tilde{x}_{1a}\tilde{x}_{2b}\rangle_{\mathrm{AB}} + \langle \tilde{x}_{1a}\tilde{x}_{1b}\rangle_{\mathrm{BA}} - \langle \tilde{x}_{1a}\tilde{x}_{2b}\rangle_{\mathrm{BA}}\\
&+ \left[R_b^A - R_b^B\right]\left[\langle \tilde{x}_{1a}\rangle_{\mathrm{AB}} - \langle \tilde{x}_{1a}\rangle_{\mathrm{BA}}\right] + R_a^A\left[\langle \tilde{x}_{1b}\rangle_{\mathrm{AB}} - \langle \tilde{x}_{2b}\rangle_{\mathrm{AB}}\right]\\
&- R_a^B\left[\langle \tilde{x}_{2b}\rangle_{\mathrm{BA}} - \langle \tilde{x}_{1b}\rangle_{\mathrm{BA}}\right] + \left[R_a^A - R_a^B\right]\left[R_b^A - R_b^B\right] N_{\mathrm{AB}}, && (23)
\end{aligned}$$

where $N_{\mathrm{AB}} \equiv \langle\rangle_{\mathrm{AB}} \equiv \langle\rangle_{\mathrm{BA}} \equiv N_{\mathrm{BA}} = \int_A d\boldsymbol{r}_1 \int_B d\boldsymbol{r}_2 \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ and $N_{\mathrm{AB}} + N_{\mathrm{BA}} = \delta_{\mathrm{AB}}$ is the delocalization index. Taking into account that $\langle \tilde{x}_{2b}\rangle_{\mathrm{BA}} = \langle \tilde{x}_{1b}\rangle_{\mathrm{AB}}$, $\langle \tilde{x}_{1b}\rangle_{\mathrm{BA}} = \langle \tilde{x}_{2b}\rangle_{\mathrm{AB}}$, and $\langle \tilde{x}_{1a}\rangle_{\mathrm{BA}} = \langle \tilde{x}_{2a}\rangle_{\mathrm{AB}}$ Eq. 23 may also be written in the more symmetrical form [1]

$$\begin{aligned}
\Lambda_{ab}^{\mathrm{AB}} &= \langle x_{1a}x_{1b}\rangle_{\mathrm{AB}} - \langle x_{1a}x_{2b}\rangle_{\mathrm{AB}} + \langle x_{1a}x_{1b}\rangle_{\mathrm{BA}} - \langle x_{1a}x_{2b}\rangle_{\mathrm{BA}}\\
&- R_b^{\mathrm{AB}}\left[\langle x_{1a}\rangle_{\mathrm{AB}} - \langle x_{2a}\rangle_{\mathrm{AB}}\right] - R_a^{\mathrm{AB}}\left[\langle x_{1b}\rangle_{\mathrm{AB}} - \langle x_{2b}\rangle_{\mathrm{AB}}\right]\\
&+ R_a^{\mathrm{AB}} R_b^{\mathrm{AB}} N_{\mathrm{AB}} && (24)
\end{aligned}$$

where we have defined $\boldsymbol{R}^{\mathrm{AB}} = \boldsymbol{R}^B - \boldsymbol{R}^A$.

Performing the same steps with the diagonal element, $\Lambda_{ab}^{\mathrm{AA}}$, we have

$$\Lambda_{ab}^{\mathrm{AA}} = \int_A d\boldsymbol{r}_1 \int_A d\boldsymbol{r}_2 \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)(x_{1a} + R_a^A)(x_{1b} + R_b^A) - (x_{1a} + R_a^A)(x_{2b} + R_b^A)$$

[1] In what follows the tildes (˜) will be suppressed for simplicity with the coordinates being always local, see Fig. 1

$$
\begin{aligned}
&= \langle x_{1a}x_{1b}\rangle_{\rm AA} + \langle x_{1a}R_b^A\rangle_{\rm AA} + \langle R_a^A x_{1b}\rangle_{\rm AA} + \langle R_a^A R_b^A\rangle_{\rm AA} \\
&- \langle x_{1a}x_{2b}\rangle_{\rm AA} - \langle x_{1a}R_b^A\rangle_{\rm AA} - \langle R_a^A x_{2b}\rangle_{\rm AA} - \langle R_a^A R_b^A\rangle_{\rm AA} \quad (25)\\
&= \langle x_{1a}x_{1b}\rangle_{\rm AA} - \langle x_{1a}x_{2b}\rangle_{\rm AA} + R_a^A\langle x_{1b}\rangle_{\rm AA} - R_a^A\langle x_{2b}\rangle_{\rm AA} \quad (26)
\end{aligned}
$$

The last two contributions are equal and of opposite sign, so that

$$
\Lambda_{ab}^{\rm AA} = \langle x_{1a}x_{1b}\rangle_{\rm AA} - \langle x_{1a}x_{2b}\rangle_{\rm AA} \quad (27)
$$

4 Basic Integrals in terms of monadic functions. Implementation in promolden

In this section we will evaluate the general integral

$$
\langle x_{1a}^n x_{1a'}^{n'} x_{2b}^m x_{2b'}^{m'}\rangle_{\rm AB} = \int_A d\boldsymbol{r}_1 x_{1a}^n x_{1a'}^{n'} \int_B d\boldsymbol{r}_2 x_{2b}^m x_{2b'}^{m'} \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2), \quad (28)
$$

with all possible combinations of the exponents n, n', m, and m'. For this purpose, we express $\rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ in terms of the monadic functions [3]

$$
\rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{i,j}^{M} \eta_{ij} f_{ij}(\boldsymbol{r}_1) f_{ij}(\boldsymbol{r}_2), \quad (29)
$$

where M is the number of partially of fully occupied MOs, $\eta_{ij} = \eta_{ji}$ are known coefficients, and $f_{ij} = f_{ji}$ is a known linear combination of producs of MOs φ_i. For closed-shell 1-det molecules, $\eta_{ij} = -2$, $f_{ij} = \varphi_i\varphi_j$, and $M = N/2$, where N is the number of electrons. Then

$$
\begin{aligned}
\langle x_{1a}^n x_{1a'}^{n'} x_{2b}^m x_{2b'}^{m'}\rangle_{\rm AB} &= \sum_{i,j} \eta_{ij} \int_A d\boldsymbol{r}_1 f_{ij}(\boldsymbol{r}_1) x_{1a}^n x_{1a'}^{n'} \int_B d\boldsymbol{r}_2 f_{ij}(\boldsymbol{r}_2) x_{2b}^m x_{2b'}^{m'} \quad (30)\\
&\equiv \sum_{i,j} \eta_{ij} \int_A d\boldsymbol{r} f_{ij}(\boldsymbol{r}) x_a^n x_{a'}^{n'} \int_B d\boldsymbol{r} f_{ij}(\boldsymbol{r}) x_2^m x_{b'}^{m'} \quad (31)\\
&\equiv \sum_{i,j} \eta_{ij} \langle x_a^n x_{a'}^{n'}\rangle_{ij,A} \langle x_b^m x_{b'}^{m'}\rangle_{ij,B} \quad (32)
\end{aligned}
$$

According to the expressions in Section 3 the following basic integrals over every domain Ω are necessary:

$$
\begin{aligned}
\langle\rangle_{ij,\Omega} &= \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r}) = \int r^2 dr \int_{\hat{r}} f_{ij}^{\Omega}(r,\theta,\phi) d\hat{r} \quad (33)\\
\langle x\rangle_{ij,\Omega} &= \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r}) x = \int r^2 dr \int_{\hat{r}} x f_{ij}^{\Omega}(r,\theta,\phi) d\hat{r} \quad (34)\\
\langle y\rangle_{ij,\Omega} &= \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r}) y = \int r^2 dr \int_{\hat{r}} y f_{ij}^{\Omega}(r,\theta,\phi) d\hat{r} \quad (35)\\
\langle z\rangle_{ij,\Omega} &= \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r}) z = \int r^2 dr \int_{\hat{r}} z f_{ij}^{\Omega}(r,\theta,\phi) d\hat{r} \quad (36)
\end{aligned}
$$

$$\langle x^2\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})x^2 = \int r^2 dr \int_{\hat{r}} x^2 f_{ij}^\Omega(r,\theta,\phi)d\hat{r} \tag{37}$$

$$\langle y^2\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})y^2 = \int r^2 dr \int_{\hat{r}} y^2 f_{ij}^\Omega(r,\theta,\phi)d\hat{r} \tag{38}$$

$$\langle z^2\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})z^2 = \int r^2 dr \int_{\hat{r}} z^2 f_{ij}^\Omega(r,\theta,\phi)d\hat{r} \tag{39}$$

$$\langle xy\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})xy = \int r^2 dr \int_{\hat{r}} xy f_{ij}^\Omega(r,\theta,\phi)d\hat{r} \tag{40}$$

$$\langle xz\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})xz = \int r^2 dr \int_{\hat{r}} xz f_{ij}^\Omega(r,\theta,\phi)d\hat{r} \tag{41}$$

$$\langle yz\rangle_{ij,\Omega} = \int_\Omega d\boldsymbol{r} f_{ij}(\boldsymbol{r})yz = \int r^2 dr \int_{\hat{r}} yz f_{ij}^\Omega(r,\theta,\phi)d\hat{r}, \tag{42}$$

$$\tag{43}$$

where $d\hat{r} = \sin\theta d\theta d\phi$. In case of a 1-det wavefunction, the first integral $\langle\rangle_{ij,\Omega}$ is equal to the atomic overlap matrix (AOM) element $S_{ij}^\Omega = \langle i|j\rangle_\Omega$.

We will see now how the above integrals can be obtained from the currently stored integrals in the `promolden` code. There, the following angular averaged are stored:

$$R_{lm}^\Omega(r) = \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} \int_{\hat{r}} S_{lm}(\hat{r}) f^\Omega(\boldsymbol{r})d\hat{r}, \tag{44}$$

where

$$f^\Omega(\boldsymbol{r}) = \begin{cases} f(\boldsymbol{r}) & \text{for } \boldsymbol{r}\in\Omega \\ 0 & \text{for } \boldsymbol{r}\notin\Omega. \end{cases} \tag{45}$$

and S_{lm} are the real spherical harmonics, defined according to Ref. [4]. The explicit $R_{lm}^\Omega(r)$'s for $l \le 2$ and $-l \le m \le +l$ are

$$R_{00}^\Omega(r) = \int_{\hat{r}} f^\Omega(\boldsymbol{r})d\hat{r} = \int_{\hat{r}} \frac{x^2+y^2+z^2}{r^2} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{46}$$

$$R_{1-1}^\Omega(r) = \int_{\hat{r}} \frac{y}{r} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{47}$$

$$R_{10}^\Omega(r) = \int_{\hat{r}} \frac{z}{r} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{48}$$

$$R_{11}^\Omega(r) = \int_{\hat{r}} \frac{x}{r} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{49}$$

$$R_{2-2}^\Omega(r) = \int_{\hat{r}} \frac{\sqrt{3}xy}{r^2} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{50}$$

$$R_{2-1}^\Omega(r) = \int_{\hat{r}} \frac{\sqrt{3}yz}{r^2} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{51}$$

$$R_{20}^\Omega(r) = \int_{\hat{r}} \frac{1}{2}\left[\frac{3z^2}{r^2} - 1\right] f^\Omega(\boldsymbol{r})d\hat{r} = \int_{\hat{r}} \frac{1}{2}\left[\frac{2z^2-x^2-y^2}{r^2}\right] f^\Omega(\boldsymbol{r})d\hat{r}, \tag{52}$$

$$R_{21}^\Omega(r) = \int_{\hat{r}} \frac{\sqrt{3}xz}{r^2} f^\Omega(\boldsymbol{r})d\hat{r}, \tag{53}$$

$$R_{22}^\Omega(r) = \int_{\hat{r}} \frac{\sqrt{3}}{2}\left[\frac{x^2-y^2}{r^2}\right] f^\Omega(\boldsymbol{r})d\hat{r}. \tag{54}$$

From Eqs. 46-49 and 50, 53, 51 we have, respectively

$$\langle\rangle_\Omega = \int r^2 dr \times R^\Omega_{00}(r) \quad (55)$$

$$\langle x\rangle_\Omega = \int r^2 dr \times rR^\Omega_{11}(r) \quad (56)$$

$$\langle y\rangle_\Omega = \int r^2 dr \times rR^\Omega_{1-1}(r) \quad (57)$$

$$\langle z\rangle_\Omega = \int r^2 dr \times rR^\Omega_{10}(r), \quad (58)$$

and

$$\langle xy\rangle_\Omega = \int r^2 dr \times \frac{r^2}{\sqrt{3}} R^\Omega_{2-2}(r) \quad (59)$$

$$\langle xz\rangle_\Omega = \int r^2 dr \times \frac{r^2}{\sqrt{3}} R^\Omega_{21}(r) \quad (60)$$

$$\langle yz\rangle_\Omega = \int r^2 dr \times \frac{r^2}{\sqrt{3}} R^\Omega_{2-1}(r). \quad (61)$$

$$(62)$$

From the sum $R^\Omega_{00}(r) + 2R^\Omega_{20}(r)$, we obtain

$$\int_{\hat{r}} z^2 f^\Omega(\boldsymbol{r}) d\hat{r} = \frac{r^2}{3}\left[R^\Omega_{00}(r) + 2R^\Omega_{20}(r)\right]. \quad (63)$$

On the other hand, we have

$$R^\Omega_{00}(r) + \frac{2}{\sqrt{3}} R^\Omega_{22}(r) = \int_{\hat{r}} \frac{2x^2+z^2}{r^2} f^\Omega(\boldsymbol{r}) d\hat{r} = 2\int_{\hat{r}} \frac{x^2}{r^2} f^\Omega(\boldsymbol{r}) d\hat{r} + \int_{\hat{r}} \frac{z^2}{r^2} f^\Omega(\boldsymbol{r}) d\hat{r}. \quad (64)$$

From the above equation and Eq. 63 we have

$$\int_{\hat{r}} x^2 f^\Omega(\boldsymbol{r}) d\hat{r} = \frac{r^2}{3}\left[R^\Omega_{00}(r) + \sqrt{3}R^\Omega_{22}(r) - R^\Omega_{20}(r)\right]. \quad (65)$$

Finally, from Eq. 54

$$\int_{\hat{r}} \frac{y^2}{r^2} f^\Omega(\boldsymbol{r}) d\hat{r} = \int_{\hat{r}} \frac{x^2}{r^2} f^\Omega(\boldsymbol{r}) d\hat{r} - \frac{2}{\sqrt{3}} R^\Omega_{22}(r), \quad (66)$$

and using Eq. 65 we obtain

$$\int_{\hat{r}} y^2 f^\Omega(\boldsymbol{r}) d\hat{r} = \frac{r^2}{3}\left[R^\Omega_{00}(r) - \sqrt{3}R^\Omega_{22}(r) - R^\Omega_{20}(r)\right]. \quad (67)$$

In terms of the above radial integrals the ij contribution of all the ab components of $\Lambda^{\mathrm{AB}}_{ab}$ and $\Lambda^{\mathrm{AA}}_{ab}$ are given by

$$\Lambda^{\mathrm{AB}}_{xx} = \langle x^2\rangle_A\langle\rangle_B + \langle x^2\rangle_B\langle\rangle_A - 2\langle x\rangle_A\langle x\rangle_B - 2R^{\mathrm{AB}}_x\left[\langle x\rangle_A\langle\rangle_B - \langle\rangle_A\langle x\rangle_B\right]$$

$$
\begin{aligned}
&- \quad R_x^{\mathrm{AB}} R_x^{\mathrm{AB}} N_{\mathrm{AB}} && (68)\\
\Lambda_{yy}^{\mathrm{AB}} =& \langle y^2\rangle_A \langle\rangle_B + \langle y^2\rangle_B \langle\rangle_A - 2\langle y\rangle_A \langle y\rangle_B - 2R_y^{\mathrm{AB}} \left[\langle y\rangle_A \langle\rangle_B - \langle\rangle_A \langle y\rangle_B\right] \\
&- \quad R_y^{\mathrm{AB}} R_y^{\mathrm{AB}} N_{\mathrm{AB}} && (69)\\
\Lambda_{zz}^{\mathrm{AB}} =& \langle z^2\rangle_A \langle\rangle_B + \langle z^2\rangle_B \langle\rangle_A - 2\langle z\rangle_A \langle z\rangle_B - 2R_z^{\mathrm{AB}} \left[\langle z\rangle_A \langle\rangle_B - \langle\rangle_A \langle z\rangle_B\right] \\
&- \quad R_z^{\mathrm{AB}} R_z^{\mathrm{AB}} N_{\mathrm{AB}} && (70)\\
\Lambda_{xy}^{\mathrm{AB}} =& \langle xy\rangle_A \langle\rangle_B + \langle xy\rangle_B \langle\rangle_A - \langle x\rangle_A \langle y\rangle_B - \langle x\rangle_B \langle y\rangle_A - R_y^{\mathrm{AB}} \left[\langle x\rangle_A \langle\rangle_B - \langle\rangle_A \langle x\rangle_B\right] \\
&- R_x^{\mathrm{AB}} \left[\langle y\rangle_A \langle\rangle_B - \langle\rangle_A \langle y\rangle_B\right] + R_x^{\mathrm{AB}} R_y^{\mathrm{AB}} N_{\mathrm{AB}} = \Lambda_{yx}^{\mathrm{AB}} && (71)\\
\Lambda_{xz}^{\mathrm{AB}} =& \langle xz\rangle_A \langle\rangle_B + \langle xz\rangle_B \langle\rangle_A - \langle x\rangle_A \langle z\rangle_B - \langle x\rangle_B \langle z\rangle_A - R_z^{\mathrm{AB}} \left[\langle x\rangle_A \langle\rangle_B - \langle\rangle_A \langle x\rangle_B\right] \\
&- R_x^{\mathrm{AB}} \left[\langle z\rangle_A \langle\rangle_B - \langle\rangle_A \langle z\rangle_B\right] + R_x^{\mathrm{AB}} R_z^{\mathrm{AB}} N_{\mathrm{AB}} = \Lambda_{zx}^{\mathrm{AB}} && (72)\\
\Lambda_{yz}^{\mathrm{AB}} =& \langle yz\rangle_A \langle\rangle_B + \langle yz\rangle_B \langle\rangle_A - \langle y\rangle_A \langle z\rangle_B - \langle y\rangle_B \langle z\rangle_A - R_z^{\mathrm{AB}} \left[\langle y\rangle_A \langle\rangle_B - \langle\rangle_A \langle y\rangle_B\right] \\
&- R_y^{\mathrm{AB}} \left[\langle z\rangle_A \langle\rangle_B - \langle\rangle_A \langle z\rangle_B\right] + R_y^{\mathrm{AB}} R_z^{\mathrm{AB}} N_{\mathrm{AB}} = \Lambda_{zy}^{\mathrm{AB}} && (73)
\end{aligned}
$$

$$
\begin{aligned}
\Lambda_{xx}^{\mathrm{AA}} &= \langle x^2\rangle_A \langle\rangle_A - \langle x\rangle_A^2 && (74)\\
\Lambda_{yy}^{\mathrm{AA}} &= \langle y^2\rangle_A \langle\rangle_A - \langle y\rangle_A^2 && (75)\\
\Lambda_{zz}^{\mathrm{AA}} &= \langle z^2\rangle_A \langle\rangle_A - \langle z\rangle_A^2 && (76)\\
\Lambda_{xy}^{\mathrm{AA}} &= \langle xy\rangle_A \langle\rangle_A - \langle x\rangle_A \langle y\rangle_A = \Lambda_{yx}^{\mathrm{AA}} && (77)\\
\Lambda_{xz}^{\mathrm{AA}} &= \langle xz\rangle_A \langle\rangle_A - \langle x\rangle_A \langle z\rangle_A = \Lambda_{zx}^{\mathrm{AA}} && (78)\\
\Lambda_{yz}^{\mathrm{AA}} &= \langle yz\rangle_A \langle\rangle_A - \langle y\rangle_A \langle z\rangle_A = \Lambda_{zy}^{\mathrm{AA}}. && (79)
\end{aligned}
$$

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