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Supplementary Material for "Energy decomposition analysis in an adiabatic picture"

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S1 Additional derivations of necessary equations for the implementation of adiabatic ALMO-EDA

Notations used in the equations presented in Secs. S1.1–S1.3: Greek letters μ, ν, λ, ...: AO basis indices; lowercase Romans i, j, k, ...: occupied MO indices; a, b, c, ...: virtual MO indices; p, q, r, ...: generic MO indices; uppercase Romans X, Y, Z, ...: fragment indices for ALMOs. The equations are derived with spin-orbitals (α or β) so that the resulting equations can be applied to both restricted and unrestricted calculations. Tensorial notations are used throughout, i.e., superscripts refer to contravariant indices while subscripts refer to the covariant ones. Einstein summation convention is applied to contractions between contravariant and covariant indices, except for summations over indices on different fragments, which will be shown explicitly.

S1.1 The derivation of $E_{\mathbf{frz}}^{\mathbf{S}} \cdot \mathbf{S}^x$

Based on the expression of the initial density: $P_{\text{frz}}^{A\lambda B\sigma} = (C_o)^{A\lambda}{}_{Ai}(\sigma^{-1})^{AiBj}(C_o^T)_{Bj}{}^{B\sigma}$, we have

$$\begin{align}
\sum_{YZ} \frac{\partial E_{\text{frz}}}{\partial S_{Y\mu Z\nu}} \cdot S^x_{Y\mu Z\nu} &= \sum_{ABYZ} \frac{\partial E_{\text{frz}}}{\partial P_{\text{frz}}^{A\lambda B\sigma}} \cdot \frac{\partial P_{\text{frz}}^{A\lambda B\sigma}}{\partial S_{Y\mu Z\nu}} \cdot S^x_{Y\mu Z\nu} \tag{1} \\
&= \sum_{ABYZ} F_{A\lambda B\sigma} \left[\frac{\partial (C_o)^{A\lambda}{}_{Ai}}{\partial S_{Y\mu Z\nu}} (\sigma^{-1})^{AiBj} (C_o)_{Bj}{}^{B\sigma} + (C_o)^{A\lambda}{}_{Ai} (\sigma^{-1})^{AiBj} \frac{\partial (C_o)_{Bj}{}^{B\sigma}}{\partial S_{Y\mu Z\nu}} \right. \nonumber \\
&\quad \left. + (C_o)^{A\lambda}{}_{Ai} \frac{\partial (\sigma^{-1})^{AiBj}}{\partial S_{Y\mu Z\nu}} (C_o)_{Bj}{}^{B\sigma} \right] \cdot S^x_{Y\mu Z\nu} \nonumber \\
&= \sum_{ABYZ} F_{A\lambda B\sigma} \left[\frac{\partial (C_o)^{A\lambda}{}_{Ai}}{\partial S_{Y\mu Z\nu}} (\sigma^{-1})^{AiBj} (C_o)_{Bj}{}^{B\sigma} + (C_o)^{A\lambda}{}_{Ai} (\sigma^{-1})^{AiBj} \frac{\partial (C_o)_{Bj}{}^{B\sigma}}{\partial S_{Y\mu Z\nu}} \right. \nonumber \\
&\quad \left. - (C_o)^{A\lambda}{}_{Ai} \sum_{CD} (\sigma^{-1})^{AiCk} \frac{\partial \sigma_{CkDl}}{\partial S_{Y\mu Z\nu}} (\sigma^{-1})^{DlBj} (C_o)_{Bj}{}^{B\sigma} \right] \cdot S^x_{Y\mu Z\nu} \tag{2}
\end{align}$$

$\boldsymbol{\sigma}$ is the metric of all the occupied orbitals: $\sigma_{CkDl} = (C_o)_{Ck}{}^{C\alpha} S_{C\alpha D\beta} (C_o)^{D\beta}{}_{Dl}$. Therefore,

$$\frac{\partial \sigma_{CkDl}}{\partial S_{Y\mu Z\nu}} = \frac{\partial (C_o)_{Ck}{}^{C\alpha}}{\partial S_{Y\mu Z\nu}} S_{C\alpha D\beta} (C_o)^{D\beta}{}_{Dl} + (C_o)_{Ck}{}^{C\alpha} S_{C\alpha D\beta} \frac{\partial (C_o)^{D\beta}{}_{Dl}}{\partial S_{Y\mu Z\nu}} + (C_o)_{Ck}{}^{C\alpha} \delta^{Y\mu}_{C\alpha} \delta^{Z\nu}_{D\beta} (C_o)^{D\beta}{}_{Dl} \tag{3}$$

The occupied orbitals on fragment A can be parameterized as

$$(C_o)^{A\lambda}{}_{Ai} = C^{A\lambda}{}_{Ar} (\sigma_{AA}^{-\frac{1}{2}})^{Ar}{}_{Ap} [\delta^{Ap}{}_{Ai} + \Delta^{ApAq} \sigma_{ApAi} - \Delta^{AqAp} \sigma_{AqAi}] \tag{4}$$

where the $\boldsymbol{\sigma}_{AA}^{-\frac{1}{2}}$ term enforces on-fragment orthogonality. Thus, we have

$$\begin{align}
\left. \frac{\partial (C_o)^{A\lambda}{}_{Ai}}{\partial S_{Y\mu Z\nu}} \right|_{\boldsymbol{\sigma}_{AA}=1, \boldsymbol{\Delta}^{AA}=0} &= -\frac{1}{2} C^{A\lambda}{}_{Ar} \frac{\partial (\sigma_{AA})_{ArAp}}{\partial S_{Y\mu Z\nu}} \delta^{Ap}{}_{Ai} \nonumber \\
&= -\frac{1}{2} C^{A\lambda}{}_{Ar} C_{Ar}{}^{A\pi} \delta^{Y\mu}_{A\pi} \delta^{Z\nu}{}_{A\rho} C^{A\rho}{}_{Ap} \delta^{Ap}{}_{Ai} \nonumber \\
&= -\frac{1}{2} (S_{AA}^{-1})^{A\lambda A\pi} \delta^{Y\mu}_{A\pi} \delta^{Z\nu}{}_{A\rho} (C_o)^{A\rho}{}_{Ai} \tag{5}
\end{align}$$

Substituting Eq.(3) into Eq.(2) then using Eq. (5), we get

$$
\begin{aligned}
&\sum_{YZ} \frac{\partial E_{\mathrm{frz}}}{\partial S_{Y\mu Z\nu}} \cdot S^{x}_{Y\mu Z\nu} \\
=&-\frac{1}{2}\sum_{A} (PF)^{A\rho}_{\ \ A\lambda} (S^{-1}_{AA})^{A\lambda A\pi} \cdot S^{x}_{A\pi A\rho} \\
&-\frac{1}{2}\sum_{B} (S^{-1}_{BB})^{B\pi B\sigma} (FP)_{B\sigma}^{\ \ B\rho} S^{x}_{B\rho B\pi} \\
&+\frac{1}{2}\sum_{C} (S^{-1}_{CC})^{C\pi C\alpha} (SPFP)_{C\alpha}^{\ \ C\rho} S^{x}_{C\rho C\pi} \\
&+\frac{1}{2}\sum_{D} (PFPS)^{D\rho}_{\ \ D\beta} (S^{-1}_{DD})^{D\beta D\pi} \cdot S^{x}_{D\pi D\rho} - \sum_{CD} (PFP)^{D\beta C\alpha} S^{x}_{C\alpha D\beta} \\
=&-\frac{1}{2}\sum_{A} \left\{ (\mathbf{S}^{-1}_{A})[(\mathbf{I}-\mathbf{SP})\mathbf{FP}]_{A} + [\mathbf{PF}(\mathbf{I}-\mathbf{PS})]_{A}(\mathbf{S}^{-1}_{A}) \right\} \cdot \mathbf{S}^{x}_{A} - \mathbf{W} \cdot \mathbf{S}^{x} \qquad (6)
\end{aligned}
$$

which gives Eq.(15) in the main paper.

S1.2 Evaluation of the fragment response gradient

S1.2.1 The z-vector equation

We start from the stationary condition of fragment A's SCF solution: $E_{A}^{\Delta_A} = 0$. Therefore, we have

$$\frac{\mathrm{d}}{\mathrm{d}x} E_{A}^{\Delta_A} = 0 \qquad (7)$$

which leads to

$$
\begin{aligned}
& E_{A}^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}^{x}_{A} + E_{A}^{\Delta_A \mathbf{h}_A} \cdot \mathbf{h}^{x}_{A} + E_{A}^{\Delta_A \mathrm{II}_A} \cdot \mathrm{II}^{x}_{A} + E_{\mathrm{xc},A}^{\Delta_A x} + E_{A}^{\Delta_A \Delta_A} \cdot \Delta^{x}_{A} = 0 \\
\Longrightarrow\ & E_{A}^{\Delta_A \Delta_A} \cdot \Delta^{x}_{A} = -(E_{A}^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}^{x}_{A} + E_{A}^{\Delta_A \mathbf{h}_A} \cdot \mathbf{h}^{x}_{A} + E_{A}^{\Delta_A \mathrm{II}_A} \cdot \mathrm{II}^{x}_{A} + E_{\mathrm{xc},A}^{\Delta_A x}) \qquad (8) \\
\Longrightarrow\ & E_{\mathrm{frz}}^{\Delta_A} \cdot \Delta^{x}_{A} = -(E_{\mathrm{frz}}^{\Delta_A}) \cdot (E_{A}^{\Delta_A \Delta_A})^{-1} \cdot \left(E_{A}^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}^{x}_{A} + E_{A}^{\Delta_A \mathbf{h}_A} \cdot \mathbf{h}^{x}_{A} + E_{A}^{\Delta_A \mathrm{II}_A} \cdot \mathrm{II}^{x}_{A} + E_{\mathrm{xc},A}^{\Delta_A x} \right) \\
& \qquad (9)
\end{aligned}
$$

We note that the symbol "II" refers to the two-electron AO integrals required for building $\mathbf{J}$ and $\mathbf{K}$, where the part for $\mathbf{K}$ is scaled by κ ($0 \leq \kappa \leq 1$) based on the employed density functional.

Define $\mathbf{z}_A = -(E_{\mathrm{frz}}^{\Delta_A}) \cdot (E_{A}^{\Delta_A \Delta_A})^{-1}$, we have

$$E_{\mathrm{frz}}^{\Delta_A} \cdot \Delta^{x}_{A} = -\mathbf{z}_A \cdot \left(E_{A}^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}^{x}_{A} + E_{A}^{\Delta_A \mathbf{h}_A} \cdot \mathbf{h}^{x}_{A} + E_{A}^{\Delta_A \mathrm{II}_A} \cdot \mathrm{II}^{x}_{A} + E_{\mathrm{xc},A}^{\Delta_A x} \right) \qquad (10)$$

where $\mathbf{z}_A$ can be obtained by solving the following linear equation:

$$E_{A}^{\Delta_A \Delta_A} \cdot \mathbf{z}_A = -E_{\mathrm{frz}}^{\Delta_A} \qquad (11)$$

The LHS of Eq. (11) contains the SCF Hessian of fragment A:

$$\begin{aligned} E_A^{\Delta_A \Delta_A} &= \frac{\partial^2 E}{\partial \Delta^{ai} \partial \Delta^{bj}} \\ &= 2(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 4(ia|jb) - 2\kappa(ij|ab) - 2\kappa(ib|ja) + 4(f_{\mathrm{xc}})_{ia,jb} \end{aligned} \tag{12}$$

where κ is the proportion of exact exchange in the employed density functional, $(f_{\mathrm{xc}})_{ia,jb}$ is the second functional derivative $\frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r}) \rho'(\mathbf{r})}$ expressed in the MO basis. The fragment index "A" in Eq. (12) are omitted.

The RHS of Eq. (11) is the gradient of the SCF-MI energy with respect to the orbital rotations on fragment A:

$$\begin{aligned} \frac{\partial E_{\mathrm{frz}}}{\partial \Delta^{AaAi}} &= \sum_{XY} \frac{\partial E}{\partial P^{X\mu Y\nu}} \frac{\partial P^{X\mu Y\nu}}{\partial \Delta^{AaAi}} \\ &= \sum_{XY} F_{Y\nu X\mu} \left[\frac{\partial (C_o)^{X\mu}{}_{Xj}}{\partial \Delta^{AaAi}} (\sigma^{-1})^{XjYk} (C_o)_{Y_k}{}^{Y\nu} + (C_o)^{X\mu}{}_{Xj} (\sigma^{-1})^{XjYk} \frac{\partial (C_o)_{Y_k}{}^{Y\nu}}{\partial \Delta^{AaAi}} \right. \\ &\quad \left. - (C_o)^{X\mu}{}_{Xj} (\sigma^{-1})^{XjZl} \frac{\partial \sigma_{ZlWm}}{\partial \Delta^{AaAi}} (\sigma^{-1})^{WmYk} (C_o)_{Y_k}{}^{Y\nu} \right] \end{aligned} \tag{13}$$

Using

$$\begin{aligned} \frac{\partial (C_o)^{X\mu}{}_{Xj}}{\partial \Delta^{AaAi}} &= \frac{\partial}{\partial \Delta^{AaAi}} \left[C^{X\mu}{}_{Xp} (\delta^{Xp}{}_{Xi} + \Delta^{XpXq} \sigma_{XqXj} - \Delta^{XqXp} \sigma_{XqXj}) \right] \\ &= C^{X\mu}{}_{Xp} \delta^p{}_a \delta^q{}_i \delta^X{}_A \sigma_{XqXj} \\ &= C^{X\mu}{}_{Xa} \delta^X_A \sigma_{XqXj} \end{aligned} \tag{14}$$

we can work out the SCF-MI gradient:

$$\frac{\partial E_{\mathrm{frz}}}{\partial \Delta^{AaAi}} = 2\sigma_{AiAj} \left[(\sigma^{-1}) C_o^T F (I - PS) C_v \right]^{Aj}{}_{Aa} \tag{15}$$

Substitute Eq. (12) and (15) into Eq. (11), the z-vector equation becomes

$$\begin{aligned} &\left[(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2(ia|jb) - \kappa(ij|ab) - \kappa(ib|ja) + 2(f_{\mathrm{xc}})_{ia,jb} \right] (z_A)^{bj} \\ &= -\sigma_{AiAj} \left[(\sigma^{-1}) C_o^T F (I - PS) C_v \right]^{Aj}{}_{Aa} \end{aligned} \tag{16}$$

which can be solved by iterative methods (e.g., the conjugate gradient method). Again, we note that the MOs on the LHS of Eq. (16) are on fragment A exclusively.

S1.2.2 From z-vector to fragment response gradient

Now we turn to the terms contracted with $\mathbf{z}_A$ on the RHS of Eq. (10). Since all the involved AO or MO indices are on one single fragment exclusively, we omit the fragment index "A" in the following equations.

Here we write down the Fock matrix as $\mathbf{F} = \mathbf{h} + \mathbf{II} \cdot \mathbf{P} + \mathbf{V}_{\mathrm{xc}}$, and define

$$\mathbf{P}_z = \mathbf{C}_v \mathbf{z} \mathbf{C}_o^T + \mathbf{C}_o \mathbf{z}^T \mathbf{C}_v^T \tag{17}$$

which is a symmetric, density-like matrix.

- $\mathbf{z}_A \cdot E_A^{\Delta_A \mathbf{h}_A} \cdot \mathbf{h}_A^x$:

$$\begin{aligned} z_{ai} \cdot \frac{\partial^2 E}{\partial \Delta^{ai} \partial h_{\mu\nu}} \cdot h^x_{\mu\nu} &= z_{ai} \cdot \frac{\partial}{\partial h_{\mu\nu}} \left(\frac{\partial E}{\partial P^{\lambda\sigma}} \frac{\partial P^{\lambda\sigma}}{\partial \Delta^{ai}} \right) \cdot h^x_{\mu\nu} \\ &= z_{ai} \cdot \frac{\partial}{\partial h_{\mu\nu}} \left(F_{\lambda\sigma} [C^\lambda{}_a C^\sigma{}_i + C^\lambda{}_i C^\sigma{}_a] \right) \cdot h^x_{\mu\nu} \\ &= \delta^\mu{}_\lambda \delta^\nu{}_\sigma P_z^{\lambda\sigma} h^x_{\mu\nu} = \mathrm{Tr}[\mathbf{P}_z \mathbf{h}^x] \end{aligned} \tag{18}$$

- $\mathbf{z}_A \cdot E_A^{\Delta_A \mathbf{II}_A} \cdot \mathbf{II}_A^x$:

$$\begin{aligned} z_{ai} \cdot \frac{\partial^2 E}{\partial \Delta^{ai} \partial \mathrm{II}_{\mu\nu\lambda\sigma}} \cdot \mathrm{II}^x_{\mu\nu\lambda\sigma} &= z_{ai} \cdot \frac{\partial}{\partial \mathrm{II}_{\mu\nu\lambda\sigma}} \left(F_{\pi\omega} [C^\pi{}_a C^\omega{}_i + C^\pi{}_i C^\omega{}_a] \right) \cdot \mathrm{II}^x_{\mu\nu\lambda\sigma} \\ &= P_z^{\pi\omega} \delta^\mu{}_\pi \delta^\nu{}_\omega P^{\lambda\sigma} \mathrm{II}^x_{\mu\nu\lambda\sigma} \\ &= \mathrm{Tr}[\mathbf{P}_z \mathbf{II}^x \mathbf{P}] \end{aligned} \tag{19}$$

- $\mathbf{z}_A \cdot E_{\mathrm{xc},A}^{\Delta_A x}$ (DFT only):

$$\begin{aligned} z_{ai} \cdot \frac{\partial^2 E_{\mathrm{xc}}}{\partial \Delta^{ai} \partial x} &= z_{ai} \cdot \frac{\partial}{\partial x} \left(\frac{\partial E_{\mathrm{xc}}}{\partial P^{\mu\nu}} \frac{\partial P_{\mu\nu}}{\partial \Delta^{ai}} \right) \\ &= z_{ai} \cdot \frac{\partial}{\partial x} \left((V_{\mathrm{xc}})_{\mu\nu} [C^\mu{}_a C^\nu{}_i + C^\mu{}_i C^\nu{}_a] \right) \\ &= (V^x_{\mathrm{xc}})_{\mu\nu} \cdot P_z^{\mu\nu} = \mathrm{Tr}[\mathbf{P}_z \mathbf{V}^x_{\mathrm{xc}}] \end{aligned} \tag{20}$$

- $\mathbf{z}_A \cdot E^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}_A^x$:

$$\begin{aligned} z_{ai} \cdot \frac{\partial^2 E}{\partial \Delta^{ai} \partial S_{\mu\nu}} \cdot S^x_{\mu\nu} &= z_{ai} \cdot \frac{\partial}{\partial S_{\mu\nu}} \left(\frac{\partial E}{\partial P^{\lambda\sigma}} \frac{\partial P^{\lambda\sigma}}{\partial \Delta^{ai}} \right) \\ &= z_{ai} \cdot \frac{\partial^2 E}{\partial P^{\lambda\sigma} \partial S_{\mu\nu}} \frac{\partial P^{\lambda\sigma}}{\partial \Delta^{ai}} \cdot S^x_{\mu\nu} + z_{ai} \cdot F_{\lambda\sigma} \frac{\partial^2 P^{\lambda\sigma}}{\partial \Delta^{ai} \partial S_{\mu\nu}} \cdot S^x_{\mu\nu} \end{aligned} \tag{21}$$

  The derivative of orthogonal MOs with respect to the AO overlap matrix (similar to the derivation of Eq. (5)):

$$\begin{aligned} \frac{\partial C^\pi{}_s}{\partial S_{\mu\nu}} &= -\frac{1}{2} C^\pi{}_r \frac{\partial \sigma_{rs}}{\partial S_{\mu\nu}} \\ &= -\frac{1}{2} C^\pi{}_r C^\lambda{}_r \delta^\mu{}_\lambda \delta^\nu{}_\sigma C^\sigma{}_s \\ &= -\frac{1}{2} (S^{-1})^{\pi\mu} C^\nu{}_s \end{aligned} \tag{22}$$

Based on Eq. (22), the first term in Eq. (21):

$$\begin{aligned}
z_{ai} \cdot \frac{\partial^2 E}{\partial P^{\lambda\sigma} \partial S_{\mu\nu}} \frac{\partial P^{\lambda\sigma}}{\partial \Delta^{ai}} \cdot S^x_{\mu\nu} &= z_{ai} \cdot \frac{\partial F_{\lambda\sigma}}{\partial S_{\mu\nu}} \frac{\partial P^{\lambda\sigma}}{\partial \Delta^{ai}} \cdot S^x_{\mu\nu} \\
&= P_z^{\lambda\sigma} \cdot \frac{\partial F_{\lambda\sigma}}{\partial P^{\pi\omega}} \frac{\partial P^{\pi\omega}}{\partial S_{\mu\nu}} \cdot S^x_{\mu\nu} \\
&= P_z^{\lambda\sigma} \cdot (\mathrm{II} + f_{\mathrm{xc}})_{\lambda\sigma\pi\omega} \frac{\partial P^{\pi\omega}}{\partial S_{\mu\nu}} \cdot S^x_{\mu\nu} \\
&= P_z^{\lambda\sigma} \cdot (\mathrm{II} + f_{\mathrm{xc}})_{\lambda\sigma\pi\omega} \left[-\frac{1}{2} (S^{-1})^{\pi\mu} P^{\nu\omega} - \frac{1}{2} P^{\pi\nu} (S^{-1})^{\mu\omega} \right] \cdot S^x_{\mu\nu} \\
&= -\frac{1}{2} P_z^{\lambda\sigma} (\mathrm{II} + f_{\mathrm{xc}})_{\lambda\sigma\pi\omega} \left[(S^{-1})^{\pi\mu} S^x_{\mu\nu} P^{\nu\omega} + P^{\pi\nu} S^x_{\nu\mu} (S^{-1})^{\mu\omega} \right] \\
&= -\frac{1}{2} \mathrm{Tr} \left[\mathbf{P}_z (\mathbf{II} + \boldsymbol{f}_{\mathrm{xc}}) [(\mathbf{S}^{-1}) \mathbf{S}^x \mathbf{P} + \mathbf{P} \mathbf{S}^x (\mathbf{S}^{-1})] \right] \qquad (23)
\end{aligned}$$

and the second term:

$$\begin{aligned}
z_{ai} \cdot F_{\lambda\sigma} \frac{\partial^2 P^{\lambda\sigma}}{\partial \Delta^{ai} \partial S_{\mu\nu}} \cdot S^x_{\mu\nu} &= z_{ai} F_{\lambda\sigma} \Bigg[-\frac{1}{2} (S^{-1})^{\lambda\mu} C^{\nu}{}_{a} C_{i}{}^{\sigma} - \frac{1}{2} C^{\lambda}{}_{a} C_{i}{}^{\nu} (S^{-1})^{\mu\sigma} \\
&\qquad - \frac{1}{2} (S^{-1})^{\lambda\mu} C^{\nu}{}_{i} C_{a}{}^{\sigma} - \frac{1}{2} C^{\lambda}{}_{i} C_{a}{}^{\nu} (S^{-1})^{\mu\sigma} \Bigg] \cdot S^x_{\mu\nu} \\
&= -\frac{1}{2} F_{\lambda\sigma} \cdot \left[(S^{-1})^{\lambda\mu} S^x_{\mu\nu} P_z^{\nu\sigma} + P_z^{\lambda\nu} S^x_{\nu\mu} (S^{-1})^{\mu\sigma} \right] \\
&= -\frac{1}{2} \mathrm{Tr} \left[\mathbf{F} [(\mathbf{S}^{-1}) \mathbf{S}^x \mathbf{P}_z + \mathbf{P}_z \mathbf{S}^x (\mathbf{S}^{-1})] \right] \qquad (24)
\end{aligned}$$

Up to this point, we have derived the RHS of Eq.(10). Thus, fragment A's contribution to the response gradient can be expressed as

$$\begin{aligned}
E_{\mathrm{frz}}^{\Delta_A} \cdot \Delta_A^x = &-\mathrm{Tr}[\mathbf{P}_z \mathbf{h}^x] - \mathrm{Tr}[\mathbf{P}_z \mathbf{II}^x \mathbf{P}] - \mathrm{Tr}[\mathbf{P}_z \mathbf{V}^x_{\mathrm{xc}}] \\
&+ \frac{1}{2} \mathrm{Tr} \left[\mathbf{P}_z (\mathbf{II} + \boldsymbol{f}_{\mathrm{xc}}) [(\mathbf{S}^{-1}) \mathbf{S}^x \mathbf{P} + \mathbf{P} \mathbf{S}^x (\mathbf{S}^{-1})] \right] \\
&+ \frac{1}{2} \mathrm{Tr} \left[\mathbf{F} [(\mathbf{S}^{-1}) \mathbf{S}^x \mathbf{P}_z + \mathbf{P}_z \mathbf{S}^x (\mathbf{S}^{-1})] \right] \qquad (25)
\end{aligned}$$

S1.3 Evaluation of matrix-vector products using finite difference

S1.3.1 z-vector contracted with the implicit first derivative of $\mathbf{V}_{\mathbf{xc}}$

Eq. (23) can be used to evaluate the first term of Eq. (21) when the analytical form of the second functional derivative ($\boldsymbol{f}_{\mathrm{xc}}$, also known as the implicit first derivative of $\mathbf{V}_{\mathrm{xc}}$) of the employed density functional is available. For ωB97X-V that is used in this work, we can compute the entire contribution from the XC part ($\mathbf{z}_A \cdot E_{\mathrm{xc}}^{\Delta_A \mathbf{S}_A} \cdot \mathbf{S}_A^x$) in a different way using finite difference.

$$
\begin{aligned}
z_{ai} \cdot \frac{\partial^2 E_{\text{xc}}}{\partial \Delta^{ai} \partial S_{\mu\nu}} \cdot S^x_{\mu\nu} &= z_{ai} \cdot \frac{\partial^2 E_{\text{xc}}}{\partial \Delta^{ai} \partial P^{\pi\omega}} \frac{\partial P^{\pi\omega}}{\partial S_{\mu\nu}} \cdot S^x_{\mu\nu} \\
&= \left(z_{ai} \cdot \frac{\partial (V_{\text{xc}})_{\pi\omega}}{\partial \Delta^{ai}} \right) \left(\frac{\partial P^{\pi\omega}}{\partial S_{\mu\nu}} \cdot S^x_{\mu\nu} \right)
\end{aligned} \tag{26}
$$

Using the finite-difference matrix-vector product technique,

$$
z_{ai} \cdot \frac{\partial (V_{\text{xc}})_{\pi\omega}}{\partial \Delta_{ai}} = \frac{(V_{\text{xc}})_{\pi\omega}[\mathbf{P}_{+\delta z}] - (V_{\text{xc}})_{\pi\omega}[\mathbf{P}_{-\delta z}]}{2\delta} \tag{27}
$$

where δ is the step size for finite-difference calculations (in practice we use $\delta = 10^{-4}$). $\mathbf{P}_{+\delta z}$ is the density matrix constructed upon (occupied) MOs updated as follows (a step forward of size $\delta\mathbf{z}$):

$$
\mathbf{C}' = \mathbf{C} \exp \begin{pmatrix} 0 & -\delta\mathbf{z}^T \\ \delta\mathbf{z} & 0 \end{pmatrix} \tag{28}
$$

Based on Eq. (27), the evaluation of one matrix-vector product only requires constructing the $\mathbf{V}_{\text{xc}}$ matrix twice (with $\mathbf{P}_{+\delta z}$ and $\mathbf{P}_{-\delta z}$). And the term left has been worked out before

$$
\frac{\partial P^{\pi\omega}}{\partial S_{\mu\nu}} \cdot S^x_{\mu\nu} = -\frac{1}{2} \left[(S^{-1})^{\pi\mu} S^x_{\mu\nu} P^{\nu\omega} + P^{\pi\mu} S^x_{\mu\nu} (S^{-1})^{\nu\omega} \right] \tag{29}
$$

We note that if we multiply the RHS of Eq. (27) by

$$
\frac{\partial P^{\pi\omega}}{\partial \Delta^{bj}} = C^{\pi}{}_{b} C^{\omega}{}_{j} + C^{\pi}{}_{j} C^{\omega}{}_{b} \tag{30}
$$

we can get the result for $\mathbf{z}_A \cdot E^{\Delta_A \Delta_A}$, which is necessary for iteratively solving the z-vector equation.

S1.3.2 z-vector contracted with the explicit first derivative of $\mathbf{V}_{\text{xc}}$

The use of Eq. (20) for the evaluation of $\mathbf{z}_A \cdot E^{\Delta_A x}_{\text{xc},A}$ requires the analytical form of $\mathbf{V}^x_{\text{xc}}$, which is the explicit first derivative of the XC matrix. If that is not available for the employed functional, we can also compute this quantity using finite difference. Analogous to Eq. (27), we have

$$
z_{ai} \cdot \frac{\partial^2 E_{\text{xc}}}{\partial \Delta_{ai} \partial x} = \frac{E^x_{\text{xc}}[\mathbf{P}_{+\delta z}] - E^x_{\text{xc}}[\mathbf{P}_{-\delta z}]}{2\delta} \tag{31}
$$

where $\mathbf{P}_{+\delta z}$ has the same definition as above. E^x_{xc} is the explicit first derivative of the XC energy, which is related to the change of integration quadrature with respect to the displacement of nuclei. Based on Eq. (31), it only requires computing E^x_{xc} twice to obtain $\mathbf{z}_A \cdot E^{\Delta_A x}_{\text{xc},A}$.

S2 Additional results

Table S1: Adiabatic EDA results for the water dimer in linear, bifurcated and aligned configurations computed at the B3LYP/def2-TZVPPD level of theory. Other details are the same as in Table I in the main paper.

	linear			bifurcated			aligned		
	FRZ	POL	FULL	FRZ	POL	FULL	FRZ	POL	FULL
Adiabatic ΔE	-11.18	-2.43	-5.43	-8.15	-1.19	-1.23	-5.63	-0.79	-0.64
E_{bind}	-11.18	-13.61	-19.03	-8.15	-9.34	-10.57	-5.63	-6.42	-7.06
$R(\mathrm{O}_2 \cdots \mathrm{H}_d)$	2.28	2.18	1.96	2.74	2.66	2.57	2.91	2.83	2.76
$R(\mathrm{O}_1 \cdots \mathrm{O}_2)$	3.24	3.13	2.92	3.23	3.15	3.06	3.41	3.32	3.25
$R(\mathrm{O}_1\text{–}\mathrm{H}_d)$	0.96	0.96	0.97	0.96	0.96	0.96	0.96	0.96	0.96
α angle (°)	172.66	172.76	173.04	–	–	–	–	–	–
β angle (°)	132.78	132.69	126.36	–	–	–	–	–	–
ω_1	96.86	106.13	122.51	152.26i	182.34i	231.82i	178.96i	212.76i	241.12i
ω_2	98.16	116.08	149.78	62.34	71.34	73.56	139.53i	151.04i	164.91i
ω_9	3809.58	3803.23	3692.89	3810.99	3810.55	3808.50	3811.64	3811.45	3810.56
ω_{10}	3818.05	3809.78	3804.59	3821.20	3821.71	3817.52	3821.82	3822.92	3822.14
ω_{11}	3910.15	3905.30	3885.02	3908.17	3904.93	3895.86	3910.81	3909.10	3905.88
ω_{12}	3914.97	3908.64	3904.31	3912.17	3911.47	3910.26	3911.55	3910.84	3910.17
$\omega_{10} - \omega_9$	8.47	6.55	111.70	10.21	11.16	9.02	10.18	11.47	11.58
$\omega_{12} - \omega_{11}$	4.82	3.34	19.29	4.00	6.54	14.40	0.74	1.74	4.29

Note: compared to the results in the main paper computed with the ωB97X-V functional, most of the original conclusions still hold. For instance, we still see that the linear configuration is already preferred at the FRZ level, while the red shift of ω_9 (symmetric O–H stretch of the H-donor water) turns out to be an effect of CT. Nevertheless, quantitative differences do exist between the B3LYP and ωB97X-V results. It is clear that B3LYP underbinds the water dimer relative to ωB97X-V, and the resulting intermolecular separations for bifurcated and aligned configurations are significantly larger here. This is most likely because (i) B3LYP fails to properly describe long-range dispersion and (ii) B3LYP slightly underestimates the dipole moment of water molecule compared to that given by ωB97X-V.

Table S2: Adiabatic EDA results for the water-Cl$^-$ complex computed at the B3LYP/def2-TZVPPD level of theory. Other details are the same as in Table III in the main paper.

	FRZ (C_s)	POL (C_s)	FULL (C_s)	FRZ (C_{2v})	POL (C_{2v})	FULL (C_{2v})
Adiabatic ΔE	-36.05	-9.03	-14.43	-35.97	-8.23	-7.36
E_{bind}	-36.05	-45.07	-59.50	-35.97	-44.20	-51.56
R (Cl··O)	3.47	3.38	3.13	3.43	3.33	3.17
R (Cl··H$_d$)	2.72	2.50	2.15	2.91	2.80	2.63
R (O··H$_d$)	0.96	0.97	0.99	0.96	0.96	0.97
∠Cl–H$_d$–O	134.37	151.25	168.57	115.44	115.48	115.70
∠H–O–H	100.39	100.90	101.78	99.77	98.73	96.69
ω_1	71.26	135.18	190.65	98.03i	116.43i	328.62i
ω_5	3812.42	3748.51	3311.63	3819.60	3807.36	3744.96
ω_6	3877.55	3874.99	3869.45	3871.85	3847.54	3753.34
split ($\omega_6 - \omega_5$)	65.13	126.48	557.82	52.25	40.18	8.38

Note: compared to the results by ωB97X-V, there are many similarities such as the magnitude of the split between two O–H stretches on the polarized and fully relaxed PESs. The major difference is that there appears an additional stationary point on the frozen PES wherein Cl$^-$ deviates from the bisector of ∠H–O–H. It is marginally more advantageous (by only 0.08 kJ/mol) than another stationary structure (C_{2v}) in terms of stabilization energy. Therefore, the energy minimum on the frozen PES has a broken-symmetry geometry, which might be related to the lack of long-range dispersion in B3LYP (see Table S3). Besides that, B3LYP also underbinds the water-Cl$^-$ complex for the same reasons as in the water dimer scenario.

Table S3: Adiabatic EDA results for the water-Cl$^-$ complex computed at the B3LYP-D3/def2-TZVPPD level of theory. Other details are the same as in Table III in the main paper.

	FRZ (C_{2v})	POL (C_{2v})	FULL (C_{2v})	FULL (C_s)
Adiabatic ΔE	-40.25	-8.46	-7.29	-13.63
E_{bind}	-40.25	-48.71	-56.00	-62.34
R (Cl··O)	3.39	3.31	3.20	3.13
R (Cl··H$_d$)	2.86	2.78	2.66	2.16
R (O··H$_d$)	0.96	0.96	0.97	0.99
$\angle$Cl–H$_d$–O	115.30	115.41	115.67	167.31
$\angle$H–O–H	99.61	98.71	96.99	101.51
ω_1	149.62	135.83	$284.49i$	191.94
ω_5	3821.39	3808.56	3748.17	3320.91
ω_6	3873.10	3849.40	3761.07	3868.97
split ($\omega_6 - \omega_5$)	51.71	40.84	12.90	548.06

Note: adding a D3 correction to B3LYP, the C_{2v} symmetry is restored for the energy minimum on the frozen PES. The resulting energetics is also more similar to that given by ωB97X-V. However, on the polarized PES, the minimum-energy structure retains C_{2v} symmetry (verified by frequency calculation), which is different from the previous results given by ωB97X-V or B3LYP. In our previous calculations, we have noticed that two stationary points on the polarized PES are of very close stabilization energies, and here their energetic order is overturned due to the change of functional.

Table S4: Basis set dependence of the N–B bond length (Å) and the N–B–H angle (°) at the optimized structures of NH_3-BH_3 on the frozen, polarized and fully relaxed PESs with three triple-ζ basis sets: def2-TZVPP, def2-TZVPPD, aug-cc-pVTZ. Two different models ("ALMO" and "FERF") are employed to construct the polarized surface.

Basis set	N–B distance (Å)			
	FRZ	POL (FERF)	POL (ALMO)	FULL
def2-TZVPP	2.64	2.38	2.35	1.66
def2-TZVPPD	2.76	2.36	2.10	1.66
aug-cc-pVTZ	2.80	2.41	1.77	1.66
	The N–B–H angle (°)			
	FRZ	POL (FERF)	POL (ALMO)	FULL
def2-TZVPP	92.63	94.71	95.05	104.97
def2-TZVPPD	92.08	95.08	98.38	104.97
aug-cc-pVTZ	91.95	94.60	104.17	104.97

Note: according to the results above, the optimal values for R(N–B) and ∠N–B–H on the fully relaxed PES are insensitive to the choice of basis set, while their values on the ALMO-based polarized PES vary significantly with the increase of basis size. The use of the FERF model largely reduces the basis set sensitivity of the optimal structural parameters on the polarized surface. The basis set effect on the optimal structure on the frozen PES, on the other hand, has not been discussed elsewhere. Here we see that the optimal N–B distance on the frozen PES increases with the size of the employed basis set while ∠N–B–H decreases, which might be related to the enhancement of Pauli repulsion when fragment electron density becomes more diffuse. Nevertheless, the changes are smaller than those on the original ALMO-based polarized PES, and the qualitative interpretation of the results computed on the frozen surface is *not* affected.