IQA-embedded fragment attributed molecular system energy change in exploring intramolecular interactions

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Supplementary Information

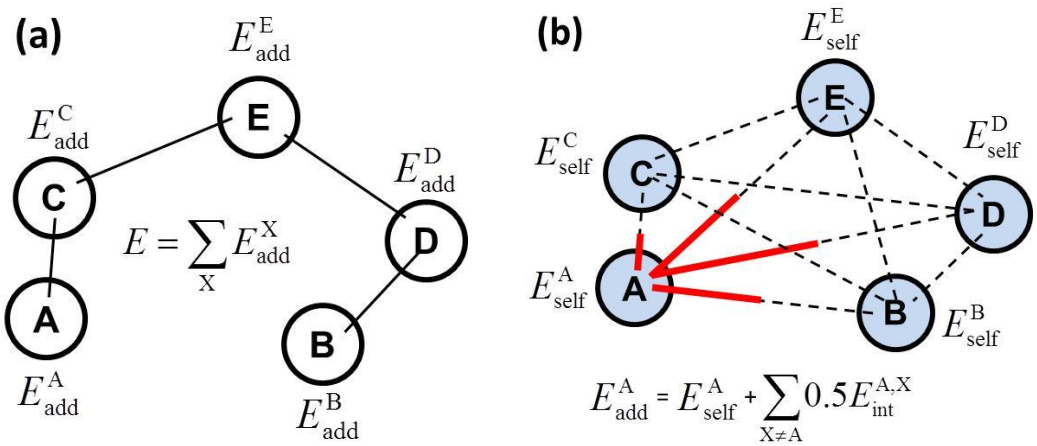


Fig. S1. Schematic illustration of a molecular energy partitioning schemes within the IQA framework (atoms, A to E, are shown as solid circles). Part (a) represents partitioning of molecular energy *E* into additive atomic energies (solid lines represent covalent bonds between atoms). Part (b) represents partitioning of a molecular energy into the self-atomic energies and diatomic interaction energies (dashed lines) also showing, as an example, partitioning of the additive atomic energy of the atom A into its self-atomic energy and halved interaction energies (shown as solid red lines) with remaining atoms of a molecule.

Part 1

Symbols and equations used

General comments

We have fully utilized notation used in the IQA method. However, it was also necessary to expand the IQA notation for the purpose of this work and any attempt was made to make it as consistent with the IQA notation and as intuitive and self-explanatory as possible for a chemist to follow. The energy terms used in this work were also designed such it is easy to retrieve them from commonly used AIMAll software which is dedicated to the QTAIM and IQA methods.

Either a single molecule or a molecular system composed of few molecules can be investigated by use of FAMSEC protocol and, for clarity and convenience, A and B notation is reserved here for atoms involved in an interaction of interest whereas X and XY is used for any atom and any pair of atoms, respectively, of a molecular system. Hence, a molecular system is divided here into two fragments, the one of interest $\mathcal{G}$ ={A,B} which is made of A and B atoms involved in the interaction under investigation, whereas the remaining atoms constitute a second fragment $\mathcal{H}$.

The FAMEC concept is based on monitoring changes in any property of an atom or molecular fragment in a final form of a molecular system, *fin* (here, *fin* states for a conformer of a molecule where an intramolecular interaction takes place between A and B) relative to a reference state of a molecular system, *ref* (in this work, a conformer of a molecule was used where atoms A and B are not involved in a classical interaction implying that d(A,B) >> sum of the van der Waals radii). However, the FAMSEC concept can be applied to monitor changes of properties of any two atoms (*e.g.* covalently bonded) or *n*-atom functional group when a molecular system changes from the *ref* state to its *fin* structural form.

IQA-defined energy terms making use of primary energy terms, also showing symbols used for the FAMSEC purpose to clearly distinguish energy contributions related to atoms A and B of a selected molecular fragment $\mathcal{G}$ and remaining atoms X of the fragment $\mathcal{H}$.

$E_{\mathrm{add}}^{\mathrm{A}}$ An additive energy of an atom A of a molecular fragment $\mathcal{G}$ (a 'total' atom's energy).

${}^{\mathrm{ref}}E_{\mathrm{add}}^{\mathrm{A}}$ and ${}^{\mathrm{fin}}E_{\mathrm{add}}^{\mathrm{A}}$ applies to a reference (*ref*) and final (*fin*) structural form of a molecular system, respectively. The same notation (*ref* and *fin*) is applicable to all other energy terms.

$E_{\mathrm{add}}^{\mathrm{X}}$ An additive energy of any atom X of a molecular system.

$E = \sum_{\mathrm{X}} E_{\mathrm{add}}^{\mathrm{X}}$ IQA-defined energy of a molecule.

$E_{\mathrm{int}}^{\mathrm{AB}}$ Diatomic interaction energy between atoms A and B of the fragment $\mathcal{G}$.

$E_{\mathrm{int}}^{\mathrm{XY}}$ Applies to any two atoms X and Y of a molecular system.

$E_{\mathrm{int}}^{\mathrm{AX}}$ Applies to diatomic interaction energy between atom A of the fragment $\mathcal{G}$ and any other atom X of a molecular system.

$E_{\mathrm{self}}^{\mathrm{A}}$ A self-atomic energy of an atom A of the molecular fragment $\mathcal{G}$.

$E_{\mathrm{self}}^{\mathrm{X}}$ Applies to any atom X of the molecular system.

$\sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}}$ Sum of all halved unique diatomic interaction energies between atom A of the fragment $\mathcal{G}$ and all remaining atoms of the molecular system.

$\sum_{\mathrm{X}\neq\mathrm{Y}} 0.5E_{\mathrm{int}}^{\mathrm{XY}}$ Applies to any atom X of a molecular system.

$E_{\mathrm{add}}^{\mathrm{A}} = E_{\mathrm{self}}^{\mathrm{A}} + \sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}}$ IQA-defined additive energy of an atom A of the fragment $\mathcal{G}$.

$E_{\mathrm{add}}^{\mathrm{X}} = E_{\mathrm{self}}^{\mathrm{X}} + \sum_{\mathrm{X}\neq\mathrm{Y}} 0.5E_{\mathrm{int}}^{\mathrm{XY}}$ As above, but applies to any atom X of a molecular system.

$\sum_{\mathrm{X}\neq\mathrm{A}} E_{\mathrm{int}}^{\mathrm{AX}}$ An energy contribution attributed to all unique diatomic interactions atom A of the molecular fragment $\mathcal{G}$ is involved in with all remaining atoms of the molecular system.

$E_{\mathrm{eff}}^{\mathrm{A}} = E_{\mathrm{self}}^{\mathrm{A}} + \sum_{\mathrm{X}\neq\mathrm{A}} E_{\mathrm{int}}^{\mathrm{AX}}$ IQA-defined effective energy of an atom A of the fragment $\mathcal{G}$.

$E_{\mathrm{eff}}^{\mathrm{X}} = E_{\mathrm{self}}^{\mathrm{X}} + \sum_{\mathrm{Y}\neq\mathrm{X}} E_{\mathrm{int}}^{\mathrm{XY}}$ As above, but applies to any atom X of a molecular system.

$0.5\sum_{\mathrm{X}}\sum_{\mathrm{Y}\neq\mathrm{X}} E_{\mathrm{int}}^{\mathrm{XY}}$ An energy contribution coming from all unique diatomic interactions involving all atoms of a molecular system.

$E = \sum_{\mathrm{X}} E_{\mathrm{self}}^{\mathrm{X}} + 0.5\sum_{\mathrm{X}}\sum_{\mathrm{Y}\neq\mathrm{X}} E_{\mathrm{int}}^{\mathrm{XY}}$ Electronic energy of a molecule as defined in the IQA framework.

Energy terms expressed in the molecular fragment notation

$E_{\mathrm{int}}^{\mathcal{G}}$ Intra-fragment interaction energy between atoms A and B of a molecular fragment $\mathcal{G}$.

$E_{\mathrm{int}}^{\mathcal{G}} = E_{\mathrm{int}}^{\mathrm{AB}}$ as the molecular fragment $\mathcal{G}$ is made just of atoms A and B.

$E_{\mathrm{int}}^{\mathcal{M}} = 0.5\sum_{\mathrm{X}\in\mathcal{M}}\sum_{\substack{\mathrm{Y}\neq\mathrm{X}\\ \mathrm{Y}\in\mathcal{M}}} E_{\mathrm{int}}^{\mathrm{XY}}$ A general expression for an intra-fragment interaction energy term; it accounts for all unique diatomic interaction energies between atoms constituting a polyatomic molecular fragment $\mathcal{M}$.

$E_{\mathrm{self}}^{\mathcal{G}}$ Self-energy of a molecular fragment $\mathcal{G}$ made of atoms A and B, hence

$E_{\mathrm{self}}^{\mathcal{G}} = E_{\mathrm{self}}^{\mathrm{A}} + E_{\mathrm{self}}^{\mathrm{B}}$.

$E_{\mathrm{self}}^{\mathcal{M}} = \sum_{\mathrm{X}\in\mathcal{M}} E_{\mathrm{self}}^{\mathrm{X}}$ A general expression for self-energy of a polyatomic molecular fragment $\mathcal{M}$.

$E_{\mathrm{net}}^{\mathcal{G}} = E_{\mathrm{self}}^{\mathcal{G}} + E_{\mathrm{int}}^{\mathcal{G}}$ IQA-defined net energy of a molecular fragment $\mathcal{G}$.

$E_{\mathrm{net}}^{\mathcal{G}} = E_{\mathrm{self}}^{\mathrm{A}} + E_{\mathrm{self}}^{\mathrm{B}} + E_{\mathrm{int}}^{\mathrm{AB}}$.

$E_{\text{net}}^{\mathcal{M}} = \sum_{\text{X}\in\mathcal{M}} E_{\text{self}}^{\text{X}} + 0.5 \sum_{\text{X}\in\mathcal{M}} \sum_{\substack{\text{Y}\neq\text{X} \\ \text{Y}\in\mathcal{M}}} E_{\text{int}}^{\text{XY}}$ or $E_{\text{net}}^{\mathcal{M}} = E_{\text{self}}^{\mathcal{M}} + E_{\text{int}}^{\mathcal{M}}$ A general expression for the IQA-defined net energy of a polyatomic molecular fragment $\mathcal{M}$.

$E_{\text{net}}^{\mathcal{H}} = \sum_{\text{X}\in\mathcal{H}} E_{\text{self}}^{\text{X}} + 0.5 \sum_{\text{X}\in\mathcal{H}} \sum_{\substack{\text{X}\neq\text{Y} \\ \text{Y}\in\mathcal{H}}} E_{\text{int}}^{\text{XY}}$ or $E_{\text{net}}^{\mathcal{H}} = E_{\text{self}}^{\mathcal{H}} + E_{\text{int}}^{\mathcal{H}}$ As above, but written for the molecular fragment $\mathcal{H}$ considered in this work.

$E_{\text{int}}^{\mathcal{G}\mathcal{H}} = \sum_{\text{X}\in\mathcal{G}} \sum_{\text{Y}\in\mathcal{H}} E_{\text{int}}^{\text{XY}}$ IQA-defined the inter-fragment, here between the fragments $\mathcal{G}$ and $\mathcal{H}$, interaction energy; the sum of all unique diatomic interactions between atoms of the fragment $\mathcal{G}$ and atoms of the fragment $\mathcal{H}$.

$E = \sum_{\mathcal{M}} E_{\text{net}}^{\mathcal{M}} + 0.5 \sum_{\mathcal{M}} \sum_{\mathcal{N}\neq\mathcal{M}} E_{\text{int}}^{\mathcal{M}\mathcal{N}}$ IQA-defined a molecular energy which is recovered from any number of molecular fragments $\mathcal{M}$, $\mathcal{N}$, $\mathcal{O}$, … a molecule was divided into; E is made of net energies of all molecular fragments and all inter-fragment interaction energies.

$E_{\text{eff}}^{\mathcal{G}} = E_{\text{net}}^{\mathcal{G}} + \sum_{\text{X}\notin\mathcal{G}} E_{\text{int}}^{\mathcal{G}\text{X}}$ IQA-defined effective energy of a molecular fragment $\mathcal{G}$.

$E_{\text{eff}}^{\mathcal{G}} = E_{\text{net}}^{\mathcal{G}} + E_{\text{int}}^{\mathcal{G}\mathcal{H}}$ As above, but expressed fully in the fragment notation when a molecular system is made of two fragments, $\mathcal{G}$ and $\mathcal{H}$.

Energy terms used in computing the fragment attributed molecular system energy change, the FAMSEC term:

$\Delta E_{\text{add}}^{\text{A}}$ A change in the additive atomic energy of an atom A of the molecular fragment $\mathcal{G}$ when a molecular system changes from the *ref* to *fin* state;

$\Delta E_{\text{add}}^{\text{A}} = {}^{\text{fin}}E_{\text{add}}^{\text{A}} - {}^{\text{ref}}E_{\text{add}}^{\text{A}}$.

$\Delta E_{\text{self}}^{\text{A}}$ As above, but applies to the self-atomic energy of an atom A;

$$\Delta E^{\mathrm{A}}_{\mathrm{self}} = {}^{\mathrm{fin}}E^{\mathrm{A}}_{\mathrm{self}} - {}^{\mathrm{ref}}E^{\mathrm{A}}_{\mathrm{self}}\,.$$

$\Delta E^{\mathcal{G}}_{\mathrm{add}}$ A change in the additive energy of a molecular fragment $\mathcal{G}$ when a molecular system changes from the *ref* to *fin* state;

$$\Delta E^{\mathcal{G}}_{\mathrm{add}} = \Delta E^{\mathrm{A}}_{\mathrm{add}} + \Delta E^{\mathrm{B}}_{\mathrm{add}} = ({}^{\mathrm{fin}}E^{\mathrm{A}}_{\mathrm{add}} - {}^{\mathrm{ref}}E^{\mathrm{A}}_{\mathrm{add}}) + ({}^{\mathrm{fin}}E^{\mathrm{B}}_{\mathrm{add}} - {}^{\mathrm{ref}}E^{\mathrm{B}}_{\mathrm{add}})$$

$$\Delta E^{\mathcal{G}}_{\mathrm{add}} = \Delta E^{\mathcal{G}}_{\mathrm{self}} + \Delta E^{\mathrm{AB}}_{\mathrm{int}} + 0.5\Delta \sum_{\mathrm{X}\in\mathcal{H}} E^{\mathcal{G}\mathrm{X}}_{\mathrm{int}}$$ (the last term is explained below).

$\Delta E^{\mathcal{G}}_{\mathrm{self}}$ A change in the self-energy of a molecular fragment $\mathcal{G}$ when a molecular system changes from the *ref* to *fin* state;

$$\Delta E^{\mathcal{G}}_{\mathrm{self}} = \Delta E^{\mathrm{A}}_{\mathrm{self}} + \Delta E^{\mathrm{B}}_{\mathrm{self}} = ({}^{\mathrm{fin}}E^{\mathrm{A}}_{\mathrm{self}} - {}^{\mathrm{ref}}E^{\mathrm{A}}_{\mathrm{self}}) + ({}^{\mathrm{fin}}E^{\mathrm{B}}_{\mathrm{self}} - {}^{\mathrm{ref}}E^{\mathrm{B}}_{\mathrm{self}}).$$

$\Delta E^{\mathrm{AB}}_{\mathrm{int}}$ A change in the diatomic interaction energy between atoms A and B of a selected molecular fragment $\mathcal{G}$ when a molecule changes from the *ref* to *fin* state;

$$\Delta E^{\mathrm{AB}}_{\mathrm{int}} = {}^{\mathrm{fin}}E^{\mathrm{AB}}_{\mathrm{int}} - {}^{\mathrm{ref}}E^{\mathrm{AB}}_{\mathrm{int}}\,.$$

$\Delta E^{\mathcal{G}}_{\mathrm{int}}$ A change in the intra-fragment interaction energy of a molecular fragment $\mathcal{G}$ (composed of two atoms A and B) when a molecular system changes from the *ref* to *fin* state;

$$\Delta E^{\mathcal{G}}_{\mathrm{int}} = \Delta E^{\mathrm{AB}}_{\mathrm{int}}\,.$$

$\sum_{\mathrm{X}\in\mathcal{H}} 0.5E^{\mathrm{AX}}_{\mathrm{int}}$ Sum of all halved diatomic interaction energies between an atom A of a molecular fragment $\mathcal{G}$ and all atoms of a molecular fragment $\mathcal{H}$.

$0.5E^{\mathrm{A}\mathcal{H}}_{\mathrm{int}}$ As above, but written in a molecular fragment notation.

$\sum_{\mathrm{X}\in\mathcal{H}} E^{\mathrm{AX}}_{\mathrm{int}}$ Sum of all unique diatomic interaction energies between an atom A of a molecular fragment $\mathcal{G}$ and all atoms of a molecular fragment $\mathcal{H}$.

$E_{\text{int}}^{\text{A}\mathcal{H}}$ As above, but written in a molecular fragment notation.

$\Delta \sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\text{AX}}$ A change in the total interaction energy between an atom A of a selected fragment $\mathcal{G}$ and all atoms of molecular fragment $\mathcal{H}$ when a molecular system changes from the *ref* to *fin* state;

$$\Delta \sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\text{AX}} = {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\text{AX}} - {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\text{AX}} .$$

$\Delta E_{\text{int}}^{\text{A}\mathcal{H}}$ As above, but written in the fragment notation

$\sum_{\text{X}\neq\text{A}} 0.5 E_{\text{int}}^{\text{AX}}$ Sum of all halved diatomic interaction energies between a selected atom A (of a molecular fragment $\mathcal{G}$) and all remaining atoms of a molecular system (this also includes an atom B of the fragment $\mathcal{G}$).

$\sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}}$ Sum of all unique diatomic interaction energies between a selected atom A (of a molecular fragment $\mathcal{G}$) and all remaining atoms of a molecular system (this also includes atom B of the fragment $\mathcal{G}$).

$\Delta \sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}}$ A change in the total diatomic interaction energy between an atom A of a selected fragment $\mathcal{G}$ and all remaining atoms in a molecular system (this also includes an atom B of the fragment $\mathcal{G}$) when it changes from the *ref* to *fin* structure or state;

$$\Delta \sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}} = {}^{\text{fin}}\sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}} - {}^{\text{ref}}\sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}} .$$

$\sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\mathcal{G}\text{X}}$ Energy attributed to all interactions atoms A and B of the molecular fragment $\mathcal{G}$ are involved in with remaining atoms of the molecular system, *i.e.* atoms of the molecular fragment $\mathcal{H}$.

$E_{\text{int}}^{\mathcal{G}\mathcal{H}}$ As above, but written in the molecular fragment notation and it represents the inter-fragment interaction energy term.

$\Delta \sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X}$ A change in the energy attributed to all diatomic interactions of atoms of the molecular fragment $\mathcal{G}$ with remaining atoms of the molecular system (*i.e.* atoms of molecular fragment $\mathcal{H}$) when a molecular system changes from the *ref* to *fin* state;

$$\Delta \sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X} = {}^{fin}\sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X} - {}^{ref}\sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X} = {}^{fin}\left(\sum_{X \in \mathcal{H}} E_{int}^{AX} + \sum_{X \in \mathcal{H}} E_{int}^{BX}\right) - {}^{ref}\left(\sum_{X \in \mathcal{H}} E_{int}^{AX} + \sum_{X \in \mathcal{H}} E_{int}^{BX}\right)$$

$$\Delta \sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X} = \Delta \sum_{X \neq A} E_{int}^{AX} + \Delta \sum_{X \neq B} E_{int}^{BX} - 2\,\Delta E_{int}^{AB}$$

$\Delta E_{int}^{\mathcal{G}\mathcal{H}}$ As above, but written in the fragment notation and it represents the change in the inter-fragment interaction energy when a molecular system made of two fragments $\mathcal{G}$ and $\mathcal{H}$ changes from the *ref* to *fin* state.

$0.5 \sum_{X \neq A} \sum_{Y \neq B} E_{int}^{XY}$ An energy contribution coming from all, except the interaction between atoms A and B of the fragment $\mathcal{G}$, unique diatomic interactions involving all atoms in a molecular system.

$$0.5 \sum_{X \neq A} \sum_{Y \neq B} E_{int}^{XY} = 0.5 \sum_{X} \sum_{Y \neq X} E_{int}^{XY} - E_{int}^{AB}$$

FAMSEC related energy terms

$E_{attr\text{-}mol}^{\mathcal{G}}$ An energy contribution to the entire molecular system which is attributed to a molecular fragment $\mathcal{G}$ (it contains atoms A and B involved in the interaction of interest) when a molecular system changes from the *ref* to *fin* state:

$$E_{attr\text{-}mol}^{\mathcal{G}} = \Delta E_{self}^{\mathcal{G}} + \Delta E_{int}^{AB} + \Delta \sum_{X \in \mathcal{H}} E_{int}^{\mathcal{G}X},$$

$E_{attr\text{-}mol}^{\mathcal{M}} = \Delta E_{self}^{\mathcal{M}} + \Delta E_{int}^{\mathcal{M}} + \Delta E_{int}^{\mathcal{M}\mathcal{N}}$ A general form of the above equation written for a molecular fragment $\mathcal{M}$ in the fragment notation.

$$E^{\mathcal{G}}_{\text{attr-mol}} = 2\,\Delta E^{\mathcal{G}}_{\text{add}} - \Delta E^{\mathcal{G}}_{\text{self}} - \Delta E^{\text{AB}}_{\text{int}}\,,$$

$$E^{\mathcal{G}}_{\text{attr-mol}} = 2\,\Delta E^{\mathcal{G}}_{\text{add}} - E^{\mathcal{G}}_{\text{attr-loc}} = 2\,\Delta E^{\mathcal{G}}_{\text{add}} - \Delta E^{\mathcal{G}}_{\text{net}}\,,$$

$$E^{\mathcal{G}}_{\text{attr-mol}} = \Delta E^{\mathcal{G}}_{\text{self}} - \Delta E^{\text{AB}}_{\text{int}} + \Delta \sum_{\text{X}\neq\text{A}} E^{\text{AX}}_{\text{int}} + \Delta \sum_{\text{X}\neq\text{B}} E^{\text{BX}}_{\text{int}}\,,$$

$$E^{\mathcal{G}}_{\text{attr-mol}} = E^{\mathcal{G}}_{\text{attr-loc}} + \Delta \sum_{\text{X}\in\mathcal{H}} E^{\mathcal{G}\text{X}}_{\text{int}} = E^{\mathcal{M}}_{\text{attr-loc}} + \Delta E^{\mathcal{M}\mathcal{N}}_{\text{int}} = \Delta E^{\mathcal{G}}_{\text{net}} + \Delta E^{\mathcal{G}\mathcal{H}}_{\text{int}}\,,$$

$$E^{\mathcal{G}}_{\text{attr-mol}} = \Delta E^{\mathcal{G}}_{\text{eff}}\,.$$

$E^{\mathcal{G}}_{\text{attr-loc}}$ An energy contribution localized to the atomic basins of atoms A and B constituting the molecular fragment $\mathcal{G}$ and interatomic region between A and B when a molecular system changes from the *ref* to *fin* state:

$$E^{\mathcal{G}}_{\text{attr-loc}} = \Delta E^{\mathcal{G}}_{\text{self}} + \Delta E^{\text{AB}}_{\text{int}}\,,$$

$$E^{\mathcal{G}}_{\text{attr-loc}} = \Delta E^{\mathcal{G}}_{\text{net}}\,.$$

Part 2

Expressing *local*-FAMSEC and *mol*-FAMSEC in molecular fragment notation.

An energy of a molecule can also be recovered by the use of energy terms defined for molecular fragments constituting a molecule, namely as

$$E = \sum_{\mathcal{M}} E_{\text{net}}^{\mathcal{M}} + 0.5 \sum_{\mathcal{M}} \sum_{\mathcal{N} \neq \mathcal{M}} E_{\text{int}}^{\mathcal{M}\mathcal{N}} \tag{S1}$$

where

$$E_{\text{net}}^{\mathcal{M}} = \sum_{\text{X} \in \mathcal{M}} E_{\text{self}}^{\text{X}} + 0.5 \sum_{\text{X} \in \mathcal{M}} \sum_{\substack{\text{Y} \neq \text{X} \\ \text{Y} \in \mathcal{M}}} E_{\text{int}}^{\text{XY}} \tag{S2}$$

stands for the *net* energy of a fragment $\mathcal{M}$ (also named a fragment self-energy [36]) and it is made of the sum of self-atomic energies of atoms constituting the fragment $\mathcal{M}$ and *intra*-fragment diatomic interaction energies (note that for diatomic fragment made of atoms A and B, the $0.5 \sum_{\text{X} \in \mathcal{M}} \sum_{\substack{\text{Y} \neq \text{X} \\ \text{Y} \in \mathcal{M}}} E_{\text{int}}^{\text{XY}}$ term becomes $E_{\text{int}}^{\text{AB}}$), whereas the $0.5 \sum_{\mathcal{M}} \sum_{\mathcal{N} \neq \mathcal{M}} E_{\text{int}}^{\mathcal{M}\mathcal{N}}$ term in Eq. S1 accounts for the *inter*-fragment interaction energies, *i.e.* all unique diatomic interactions between atoms of $\mathcal{M}$ and atoms of $\mathcal{N}$. It is now obvious that the FAMSEC term can be immediately expressed in terms of fragments' energy terms reported in the original paper on IQA [32], namely the *net* energy of a selected fragment (here containing atoms A and B involved in an interaction under investigation) and *inter*-fragment energy term as

$$E_{\text{attr-mol}}^{\mathcal{G}} = \Delta E_{\text{net}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}} \tag{S3}$$

where $\Delta E_{\text{net}}^{\mathcal{G}} = E_{\text{attr-loc}}^{\mathcal{G}}$. As a matter of fact, the FAMSEC term is directly linked with the concept of *effective* energy of a molecular group $\mathcal{G}$. Recall that the *effective* energy of a given atom was defined [32] as

$$E_{\text{eff}}^{\text{A}} = E_{\text{self}}^{\text{A}} + \sum_{\text{X}\neq\text{A}} E_{\text{int}}^{\text{AX}} \tag{S4}$$

where $E_{\text{self}}^{\text{A}}$ is the same as $E_{\text{net}}^{\text{A}}$ (the latter notation was used in ref. 32) and the second term represents full interactions of selected atom A with all the remaining atoms in a molecule. By analogy, the *effective* energy of a molecular fragment $\mathcal{G}$ can be written as [36]

$$E_{\text{eff}}^{\mathcal{G}} = E_{\text{net}}^{\mathcal{G}} + \sum_{\text{X}\notin\mathcal{G}} E_{\text{int}}^{\mathcal{G}\text{X}} . \tag{S5}$$

which, in our case, where two molecular fragments are considered, can be written as $E_{\text{eff}}^{\mathcal{G}} = E_{\text{net}}^{\mathcal{G}} + E_{\text{int}}^{\mathcal{G}\mathcal{H}}$. Hence, the FAMSEC term represents the change in the effective energy of a fragment when a molecular system goes from the *ref* to *fin* state,

$$E_{\text{attr-mol}}^{\mathcal{G}} = \Delta E_{\text{eff}}^{\mathcal{G}} . \tag{S6}$$

Part 3

It is demonstrated here that $E^{\mathcal{G}}_{\text{attr-mol}}$ can be obtained from just three and 'quick' to compute energy terms, namely the additive and self-atomic energies of just two atoms A and B of the $\mathcal{G}$ fragment plus a single interaction energy between these two atoms.

Molecules considered in this work can be seen as made of two molecular fragments, $\mathcal{G}$ (made of atoms A and B involved in an interaction in the *fin* state of a molecular system) and $\mathcal{H}$ (containing all other atoms X). Considering the $\mathcal{G}$ fragment, we can express the change in its additive energy as

$$\Delta E^{\mathcal{G}}_{\text{add}} = \Delta E^{\text{A}}_{\text{add}} + \Delta E^{\text{B}}_{\text{add}} = ({}^{\text{fin}}E^{\text{A}}_{\text{add}} - {}^{\text{ref}}E^{\text{A}}_{\text{add}}) + ({}^{\text{fin}}E^{\text{B}}_{\text{add}} - {}^{\text{ref}}E^{\text{B}}_{\text{add}}). \tag{S7}$$

Using the IQA definition, we can express the additive energy of atom A in the *fin* structure as

$${}^{\text{fin}}E^{\text{A}}_{\text{add}} = {}^{\text{fin}}E^{\text{A}}_{\text{self}} + {}^{\text{fin}}\sum_{\text{X}\neq\text{A}} 0.5E^{\text{AX}}_{\text{int}} = {}^{\text{fin}}E^{\text{A}}_{\text{self}} + {}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}} 0.5E^{\text{AX}}_{\text{int}} \tag{S8}$$

where the term ${}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}}$ stands for the halved interaction energy between atoms A and B and ${}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}} 0.5E^{\text{AX}}_{\text{int}}$ represents a sum of halved diatomic interaction energies between atom A and all remaining atoms in a molecule except atom B, *i.e.*, interactions between atom A and atoms of a molecular fragment $\mathcal{H}$. Hence, for atom A in *ref* we can write an analogues expression

$${}^{\text{ref}}E^{\text{A}}_{\text{add}} = {}^{\text{ref}}E^{\text{A}}_{\text{self}} + {}^{\text{ref}}\sum_{\text{X}\neq\text{A}} 0.5E^{\text{AX}}_{\text{int}} = {}^{\text{ref}}E^{\text{A}}_{\text{self}} + {}^{\text{ref}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}} 0.5E^{\text{AX}}_{\text{int}} \ . \tag{S9}$$

Similarly, we can express the additive atomic energy of atom B in the *fin* structure as

$${}^{\text{fin}}E^{\text{B}}_{\text{add}} = {}^{\text{fin}}E^{\text{B}}_{\text{self}} + {}^{\text{fin}}\sum_{\text{X}\neq\text{B}} 0.5E^{\text{BX}}_{\text{int}} = {}^{\text{fin}}E^{\text{B}}_{\text{self}} + {}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}} 0.5E^{\text{BX}}_{\text{int}} \tag{S10}$$

and for the same atom B in *ref* the following applies

$${}^{\text{ref}}E^{\text{B}}_{\text{add}} = {}^{\text{ref}}E^{\text{B}}_{\text{self}} + {}^{\text{ref}}\sum_{\text{X}\neq\text{B}} 0.5E^{\text{BX}}_{\text{int}} = {}^{\text{ref}}E^{\text{B}}_{\text{self}} + {}^{\text{ref}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}} 0.5E^{\text{BX}}_{\text{int}} \tag{S11}$$

Substituting ${}^{\text{fin}}E^{\text{A}}_{\text{add}}$, ${}^{\text{ref}}E^{\text{A}}_{\text{add}}$, ${}^{\text{fin}}E^{\text{B}}_{\text{add}}$ and ${}^{\text{ref}}E^{\text{B}}_{\text{add}}$ in Eq. S7 by expressions from Eqs. S8–S11 we obtain

$$\Delta E^{\mathcal{G}}_{\text{add}} = {}^{\text{fin}}E^{\text{A}}_{\text{self}} + {}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{AX}}_{\text{int}} - {}^{\text{ref}}E^{\text{A}}_{\text{self}} - {}^{\text{ref}}0.5E^{\text{AB}}_{\text{int}} - {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{AX}}_{\text{int}}$$

$$+ {}^{\text{fin}}E^{\text{B}}_{\text{self}} + {}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}} + {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{BX}}_{\text{int}} - {}^{\text{ref}}E^{\text{B}}_{\text{self}} - {}^{\text{ref}}0.5E^{\text{AB}}_{\text{int}} - {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{BX}}_{\text{int}} \tag{S12}$$

For convenience, let us combine terms in Eq. S12 as

$$\Delta E^{\text{A}}_{\text{self}} = {}^{\text{fin}}E^{\text{A}}_{\text{self}} - {}^{\text{ref}}E^{\text{A}}_{\text{self}} \tag{S13}$$

$$\Delta E^{\text{B}}_{\text{self}} = {}^{\text{fin}}E^{\text{B}}_{\text{self}} - {}^{\text{ref}}E^{\text{B}}_{\text{self}} \tag{S14}$$

$$\Delta 0.5E^{\text{AB}}_{\text{int}} = {}^{\text{fin}}0.5E^{\text{AB}}_{\text{int}} - {}^{\text{ref}}0.5E^{\text{AB}}_{\text{int}} \tag{S15}$$

$$0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{AX}}_{\text{int}} = {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{AX}}_{\text{int}} - {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{AX}}_{\text{int}} \tag{S16}$$

$$0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{BX}}_{\text{int}} = {}^{\text{fin}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{BX}}_{\text{int}} - {}^{\text{ref}}\sum_{\text{X}\in\mathcal{H}}0.5E^{\text{BX}}_{\text{int}} \tag{S17}$$

and by substituting these terms in Eq. 12 we obtain

$$\Delta E^{\mathcal{G}}_{\text{add}} = \Delta E^{\text{A}}_{\text{self}} + \Delta 0.5E^{\text{AB}}_{\text{int}} + 0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{AX}}_{\text{int}} + \Delta E^{\text{B}}_{\text{self}} + \Delta 0.5E^{\text{AB}}_{\text{int}} + 0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{BX}}_{\text{int}} \tag{S18}$$

To express changes in terms of the $\mathcal{G}$ fragment containing atoms A and B, we can combine terms in Eqs. S13 and S14 as

$$\Delta E^{\mathcal{G}}_{\text{self}} = \Delta E^{\text{A}}_{\text{self}} + \Delta E^{\text{B}}_{\text{self}} \tag{S19}$$

and also we can combine terms in Eqs. S16 and S17 as

$$0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\mathcal{G}\text{X}}_{\text{int}} = 0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{AX}}_{\text{int}} + 0.5\Delta\sum_{\text{X}\in\mathcal{H}}E^{\text{BX}}_{\text{int}} \tag{S20}$$

Substituting terms in Eq. S18 by Eqs. S19 and S20 results in the final expression for the change in the total atomic energies of atoms of the $\mathcal{G}$ fragment as

$$\Delta E_{\text{add}}^{\mathcal{G}} = \Delta E_{\text{self}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\text{AB}} + 0.5\Delta \sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\mathcal{G}\text{X}} \quad . \tag{S21}$$

Now, by substituting the term $0.5\Delta \sum_{\text{X}\in\mathcal{H}} E_{\text{int}}^{\mathcal{G}\text{X}}$ from Eq. S21 to Eq. 7 in the main body of the text, we obtain

$$E_{\text{attr-mol}}^{\mathcal{G}} = \Delta E_{\text{self}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\text{AB}} + 2(\Delta E_{\text{add}}^{\mathcal{G}} - \Delta E_{\text{self}}^{\mathcal{G}} - \Delta E_{\text{int}}^{\text{AB}}) \tag{S22}$$

which simplifies to a convenient for calculations form which involves only selected two atoms

$$E_{\text{attr-mol}}^{\mathcal{G}} = 2\,\Delta E_{\text{add}}^{\mathcal{G}} - \Delta E_{\text{self}}^{\mathcal{G}} - \Delta E_{\text{int}}^{\text{AB}} = \Delta\, E_{\text{eff}}^{\mathcal{G}} \,. \tag{S23}$$

Eq. S23 can also be written as

$$E_{\text{attr-mol}}^{\mathcal{G}} = 2\,\Delta E_{\text{add}}^{\mathcal{G}} - E_{\text{attr-loc}}^{\mathcal{G}} = 2\,\Delta E_{\text{add}}^{\mathcal{G}} - \Delta E_{\text{net}}^{\mathcal{G}} \tag{S24}$$

to show that it also contains a localized to a fragment energy change, as defined in Eq. 9 in the main body of the text.

Part 4

Although computationally very convenient, Eq. 11 in the main body of the text (or Eq S23) is somewhat counter-intuitive as it does not provide any direct information on the diatomic interactions of the $\mathcal{G}$ fragment with remaining atoms in a molecule; clearly, this can also be seen as a drawback because important information is missing. Fortunately, a detailed inspection of the output file generated from the IQA calculations revealed that it is possible to economically compute the $\Delta\sum_{\mathrm{X}\in\mathcal{F}f} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}}$ term using a convenient feature of Keith's AIMAll software. It provides, for each atom selected for the IQA calculation (say atoms A and B), the sum of halved interaction energies with all remaining atoms in a molecule, $\sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}}$ and $\sum_{\mathrm{X}\neq\mathrm{B}} 0.5E_{\mathrm{int}}^{\mathrm{BX}}$. For clarity, the protocol used is schematically presented in Fig. S2

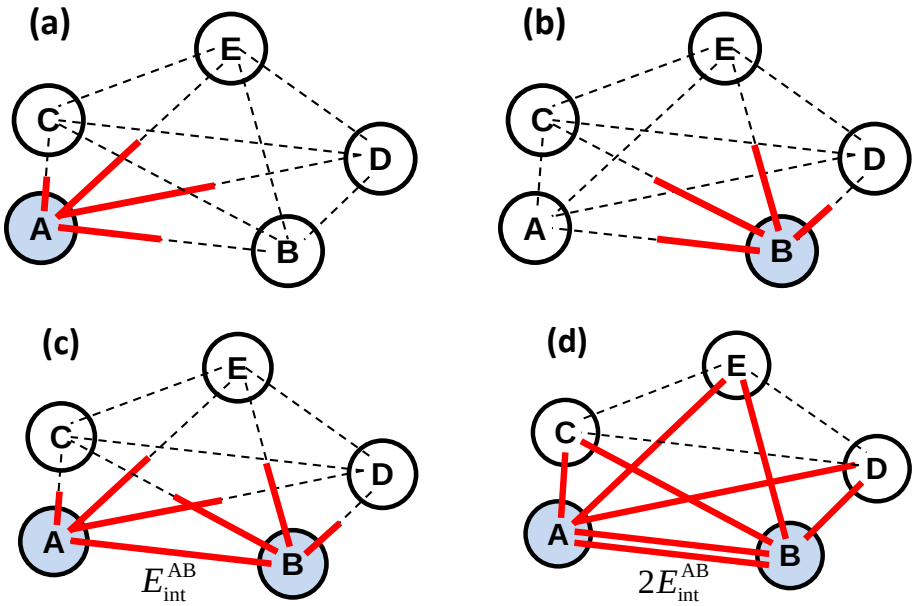


Fig. S2. A schematic representation showing how third term in Eq. 7 of the main body of the text can be obtained from halved interaction energies (solid thick red lines) between atom A (part a) and atom B (part b) and remaining atoms in a molecule. A molecule is made of atoms A to E shown as circles. All unique diatomic interactions are shown as dashed lines. For further details, see the text above.

where (i) halved interaction energies between atom A (part a) and atom B (part b) with remaining atoms are schematically shown as solid thick lines whereas (ii) the dashed lines represent all possible interactions between atoms (shown as circles) in a molecule. The addition $\sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}}$ + $\sum_{\mathrm{X}\neq\mathrm{B}} 0.5E_{\mathrm{int}}^{\mathrm{BX}}$ generates a full interaction energy between atoms A and B, $E_{\mathrm{int}}^{\mathrm{AB}}$, of the selected $\mathcal{G}$ fragment and this is represented as superimposed parts (a) and (b) in Fig. S2(c) and it can be written as

$$\sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}} + \sum_{\mathrm{X}\neq\mathrm{B}} 0.5E_{\mathrm{int}}^{\mathrm{BX}} = 0.5\sum_{\mathrm{X}\in\mathcal{H}} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}} + E_{\mathrm{int}}^{\mathrm{AB}} \tag{S25}$$

where the energy term related to the interaction of interest is expressed separately ($E_{\mathrm{int}}^{\mathrm{AB}}$) and the $0.5\sum_{\mathrm{X}\in\mathcal{H}} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}}$ represents halved sum of all unique diatomic interaction energies the two atoms of molecular fragment $\mathcal{G}$ are involved in with all the remaining atoms which constitute a molecular fragment $\mathcal{H}$ of the system. Multiplying Eq. S25 by 2 one obtains, as shown in Fig. S2(d), a full set of diatomic interaction energies between A and B with remaining atoms plus doubled interaction energy between A and B, Eq. S26

$$2\sum_{\mathrm{X}\neq\mathrm{A}} 0.5E_{\mathrm{int}}^{\mathrm{AX}} + 2\sum_{\mathrm{X}\neq\mathrm{B}} 0.5E_{\mathrm{int}}^{\mathrm{BX}} = 2\times\left(0.5\sum_{\mathrm{X}\in\mathcal{H}} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}} + E_{\mathrm{int}}^{\mathrm{AB}}\right) = \sum_{\mathrm{X}\in\mathcal{H}} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}} + 2\,E_{\mathrm{int}}^{\mathrm{AB}}. \tag{S26}$$

One can rearrange Eq. S26 to obtain an alternative expression for the sum of all diatomic interactions the molecular fragment is involved in with the remaining atoms of the system

$$\sum_{\mathrm{X}\in\mathcal{H}} E_{\mathrm{int}}^{\mathcal{G}\mathrm{X}} = \sum_{\mathrm{X}\neq\mathrm{A}} E_{\mathrm{int}}^{\mathrm{AX}} + \sum_{\mathrm{X}\neq\mathrm{B}} E_{\mathrm{int}}^{\mathrm{BX}} - 2\,E_{\mathrm{int}}^{\mathrm{AB}}. \tag{S27}$$

A change in the energy attributed to the interactions of the molecular fragment $\mathcal{G}$ with remaining atoms in a system when a molecule changes from the *ref* to *fin* state is

$$\Delta \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X} = {}^{\text{fin}} \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X} - {}^{\text{ref}} \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X} \tag{S28}$$

and by making use of Eq. S27 we obtain

$$\Delta \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X} = {}^{\text{fin}} \sum_{X \neq A} E_{\text{int}}^{AX} + {}^{\text{fin}} \sum_{X \neq B} E_{\text{int}}^{BX} - {}^{\text{fin}} 2E_{\text{int}}^{AB} - {}^{\text{ref}} \sum_{X \neq A} E_{\text{int}}^{AX} - {}^{\text{ref}} \sum_{X \neq B} E_{\text{int}}^{BX} + {}^{\text{ref}} 2E_{\text{int}}^{AB} \tag{S29}$$

By combining some terms as shown below

$${}^{\text{fin}} \sum_{X \neq A} E_{\text{int}}^{AX} - {}^{\text{ref}} \sum_{X \neq A} E_{\text{int}}^{AX} = \Delta \sum_{X \neq A} E_{\text{int}}^{AX} \tag{S30}$$

$${}^{\text{fin}} \sum_{X \neq B} E_{\text{int}}^{BX} - {}^{\text{ref}} \sum_{X \neq B} E_{\text{int}}^{BX} = \Delta \sum_{X \neq B} E_{\text{int}}^{BX} \tag{S31}$$

$${}^{\text{fin}} 2E_{\text{int}}^{AB} - {}^{\text{ref}} 2E_{\text{int}}^{AB} = 2\,\Delta E_{\text{int}}^{AB} \tag{S32}$$

one can express Eq. S29 as

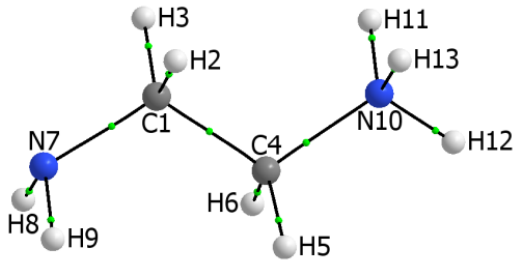
$$\Delta \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X} = \Delta \sum_{X \neq A} E_{\text{int}}^{AX} + \Delta \sum_{X \neq B} E_{\text{int}}^{BX} - 2\,\Delta E_{\text{int}}^{AB} \tag{S33}$$

By substituting the term $\Delta \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X}$ in Eq. 7 in the main body of the text by expression obtained in Eq. S33 one obtains another expression for the *mol*-FAMSEC term

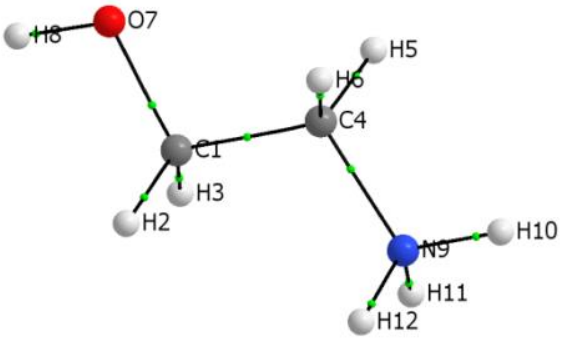
$$E_{\text{attr-mol}}^{\mathcal{G}} = \Delta E_{\text{self}}^{\mathcal{G}} - \Delta E_{\text{int}}^{AB} + \Delta \sum_{X \neq A} E_{\text{int}}^{AX} + \Delta \sum_{X \neq B} E_{\text{int}}^{BX} \tag{S34}$$

which can be economically computed because the expensive $\Delta \sum_{X \in \mathcal{H}} E_{\text{int}}^{\mathcal{G}X}$ term has been replaced by the equivalent but computationally much cheaper expression (Eq. S33).

(a)



(b)



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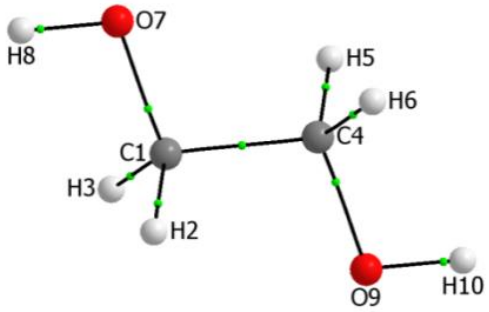

(d)

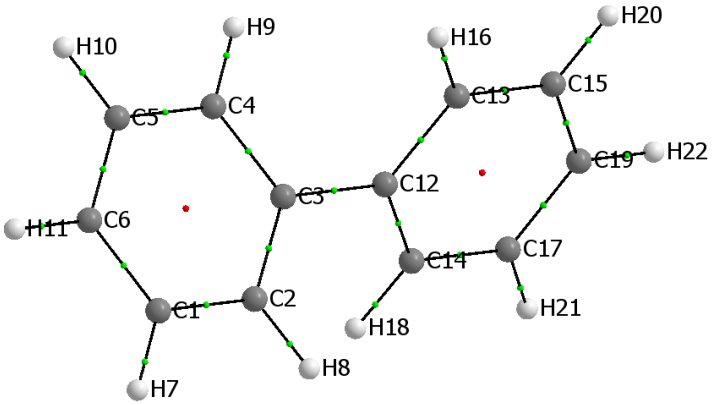

Fig. S3. *Ref* structures of molecules discussed in this work: (a) – protonated ethylenediamine (**Hen**), (b) – protonated ethanolamine (**Hea**), (c) – 1,2-ethanediol (ethylene glycol, **gc**) and (d) – biphenyl (**bph**).

Table S1. IQA-defined additive and self-atomic energies (in a.u.) at MP2/6–311++G(d,p) in solvent = water (PCM/UFF) of all atoms X in the *ref* and *fin* structures of the protonated form of ethylenediamine, **Hen**–*ref* and **Hen**–*fin*, respectively.

Atom X	**Hen–*ref***		**Hen–*fin***	
	E^{X}_{add}	E^{X}_{self}	E^{X}_{add}	E^{X}_{self}
C1	–38.0027	–37.5106	–38.0041	–37.5181
H2	–0.5838	–0.4688	–0.5823	–0.4685
H3	–0.5838	–0.4688	–0.5813	–0.4684
C4	–38.0007	–37.5236	–38.0028	–37.5242
H5	–0.5726	–0.4652	–0.5740	–0.4657
H6	–0.5726	–0.4652	–0.5726	–0.4659
N7	–54.9627	–54.2530	–54.9933	–54.2318
H8	–0.5066	–0.3935	–0.4982	–0.3888
H9	–0.5066	–0.3935	–0.4990	–0.3910
N10	–55.1008	–54.1713	–55.0877	–54.1567
H11	–0.4387	–0.3580	–0.4429	–0.3443
H12	–0.4360	–0.3556	–0.4454	–0.3590
H13	–0.4387	–0.3580	–0.4468	–0.3609

Table S2. IQA-defined additive and self-atomic energies (in a.u.) at MP2/6–311++G(d,p) in solvent = water (PCM/UFF) of all atoms X in the *ref* and *fin* structures of the protonated form of ethanolamine, **Hea**–*ref* and **Hea**–*fin*, respectively.

Atom X	**Hea–*ref***		**Hea–*fin***	
	E^{X}_{add}	E^{X}_{self}	E^{X}_{add}	E^{X}_{self}
C1	–37.9522	–37.4270	–37.9534	–37.4366
H2	–0.5827	–0.4686	–0.5810	–0.4683
H3	–0.5827	–0.4686	–0.5783	–0.4677
C4	–37.9957	–37.5206	–38.0008	–37.5240
H5	–0.5702	–0.4641	–0.5696	–0.4647
H6	–0.5702	–0.4641	–0.5706	–0.4644
O7	–75.4447	–74.7828	–75.4644	–74.7732
H8	–0.4410	–0.2913	–0.4328	–0.2888
N9	–55.1047	–54.1681	–55.0937	–54.1644
H10	–0.4348	–0.3542	–0.4402	–0.3564
H11	–0.4368	–0.3568	–0.4415	–0.3585
H12	–0.4368	–0.3568	–0.4413	–0.3509

Table S3. IQA-defined additive and self-atomic energies (in a.u.) at MP2/6–311++G(d,p) in solvent = water (PCM/UFF) of all atoms X in the staggered and eclipsed forms of ethylene glycol, **gc**–*ref* and **gc**–*fin*, respectively.

Atom X	**gc–*ref***		**gc–*fin***	
	E^{X}_{add}	E^{X}_{self}	E^{X}_{add}	E^{X}_{self}
C1	–37.9966	–37.4292	–37.9988	–37.4333
H2	–0.5885	–0.4704	–0.5887	–0.4696
H3	–0.5885	–0.4704	–0.5887	–0.4696
C4	–37.9966	–37.4292	–37.9987	–37.4331
H5	–0.5885	–0.4704	–0.5887	–0.4696
H6	–0.5885	–0.4704	–0.5887	–0.4696
O7	–75.3658	–74.7813	–75.3504	–74.7816
H8	–0.4819	–0.2959	–0.4866	–0.2990
O9	–75.3658	–74.7813	–75.3506	–74.7817
H10	–0.4819	–0.2959	–0.4866	–0.2990

Table S4. IQA-defined additive and self-atomic energies (in a.u.) at MP2/6–311++G(d,p) in the gas phase of selected atoms X in the twisted and planar forms of biphenyl, **bph**–*ref* and **bph**–*fin*, respectively.

Atom X	**bph–*ref***		**bph–*fin***	
	E^{X}_{add}	E^{X}_{self}	E^{X}_{add}	E^{X}_{self}
C3	–38.0948	–37.6173	–38.0960	–37.6230
C4	–38.0919	–37.6376	–38.0902	–37.6362
H9	–0.5881	–0.4698	–0.5885	–0.4671
C12	–38.0949	–37.6175	–38.0960	–37.6230
C13	–38.0919	–37.6377	–38.0901	–37.6361
H16	–0.5881	–0.4697	–0.5885	–0.4671

Table S5. Relative to the lowest energy conformer (a twisted form of **bph**) changes in the additive, $\Delta E_{\mathrm{add}}^{\mathrm{X}}$, and self-atomic, $\Delta E_{\mathrm{self}}^{\mathrm{X}}$, energies (in kcal mol^{-1}) obtained for the planar form of **bph** from a SPC at the B3LYP/6–311++G(d,p) level of theory on the MP2-optimized structures in the gas phase.

Atom X	$\Delta E_{\mathrm{add}}^{\mathrm{X}}$	Atom X	$\Delta E_{\mathrm{self}}^{\mathrm{X}}$
C12	–1.82	C12	–4.06
C3	–1.77	C3	–3.87
H7	–0.09	H11	–0.02
H21	–0.09	H22	–0.02
H10	–0.08	H20	–0.02
H20	–0.08	H10	–0.02
H9	–0.05	H7	–0.02
H18	–0.05	H21	–0.01
H16	–0.03	C19	0.17
H8	–0.03	C6	0.28
H11	0.06	C1	0.42
H22	0.06	C17	0.42
C1	0.24	C15	0.50
C17	0.25	C5	0.51
C15	0.26	C4	1.22
C5	0.26	C13	1.25
C6	0.48	C14	1.27
C19	0.48	C2	1.38
C4	1.31	H9	1.72
C14	1.31	H18	1.72
C13	1.33	H16	1.74
C2	1.38	H8	1.74

Table S6. Relative to *ref* structures, changes in the selected QTAIM- and IQA-defined energy terms and additional atomic properties of atoms constituting functional groups in **Hen** and **Hea**.[a]

functional group	atom X	ΔE^{X}_{self}	ΔT^{X}	ΔV^{XX}_{ne}	ΔV^{XX}_{ee}	ΔE^{X}	ΔN^{X}	ΔVol^{X}	ΔA^{X}	Δd^{X}_{e}
					Hen					
$-NH_2$	**N7**	13.30	16.01	–84.89	82.18	–12.83	0.021	–7.81	–7.79	0.0048
	H8	2.98	–4.81	10.31	–2.53	4.84	–0.017	–1.24	–1.70	0.0002
	H9	1.57	–2.95	6.08	–1.56	2.98	–0.010	–0.66	–0.44	0.0001
$-NH_3^+$	N10	9.16	17.50	–63.34	55.00	–14.32	0.019	–0.58	–9.88	0.0008
	H11	8.56	–9.28	18.24	–0.41	9.32	–0.017	–4.15	2.64	0.0030
	H12	–2.14	2.99	–6.17	1.03	–2.97	0.008	0.39	0.89	0.0000
	H13	–1.84	2.69	–5.38	0.85	–2.67	0.007	0.25	0.23	0.0001
					Hea					
–OH	**O7**	6.06	6.54	–45.32	44.84	–4.57	0.012	–3.809	–1.675	0.0024
	H8	1.55	–2.51	4.60	–0.54	2.52	–0.006	–0.338	–0.343	0.0000
$-NH_3^+$	N9	2.31	6.30	–12.18	8.20	–4.86	0.001	–1.154	10.486	0.0012
	H10	–1.36	1.60	–3.55	0.60	–1.59	0.005	0.301	0.544	0.0000
	H11	–1.08	1.42	–2.95	0.46	–1.41	0.004	0.117	0.201	0.0001
	H12	3.71	–3.14	7.05	–0.20	3.15	–0.009	–2.444	–1.975	0.0017

[a] Energies are in kcal mol^{-1} and all values at MP2; $E^{X}_{self} = T^{X} + V^{XX}_{ne} + V^{XX}_{ee}$, by definition; T^{X} - the electronic kinetic energy of an atom (a Hamiltonian form); V^{XX}_{ne} - attraction energy between electron density distribution of atom X and nucleus of Atom X; V^{XX}_{ee} - two-electron interaction energy of atom X with itself; E^{X} - approximation to a virial-based total energy of atom X; N^{X} - average No of electrons in atom X (atomic electron population); Vol^{X} – atomic volume in bohr^3 (volume bounded by interatomic surfaces of atom X and by isosurface of the electron density distribution (0.001a.u. isodensity surface was used); A^{X} – atomic surface area in bohr^2 for 0.001 a.u. isodensity surface; $d_e^{X} = N(Vol^{X})/Vol^{X}$ - average electron density in Vol^{X} where $N(Vol^{X})$ is an average number of electrons in Vol^{X}.

From the analysis of data in Table S6 we found:

Trend-1 – when $\Delta Vol^{X} < 0$ and $\Delta N^{X} < 0$ then $\Delta E^{X}_{self} > 0$, $\Delta E^{X} > 0$ and $\Delta V^{XX}_{ne} > 0$,

Trend-2 – when $\Delta Vol^{X} > 0$ and $\Delta N^{X} > 0$ then $\Delta E^{X}_{self} < 0$, $\Delta E^{X} < 0$ and $\Delta V^{XX}_{ne} < 0$,

Trend-3 – always $|\Delta V^{XX}_{ne}| > |\Delta V^{XX}_{ee}|$.

Trend-4 – unidirectional variations are observed for the following paired physical properties: ΔV^{XX}_{ne} and ΔE^{X}, ΔV^{XX}_{ee} and ΔT^{X} as well as ΔN^{X} and ΔV^{XX}_{ee}, *e.g.*, when $\Delta N^{X} < 0$ then $\Delta V^{XX}_{ee} < 0$,

Trend-5 – opposite variation in the paired physical properties was found for ΔN^{X} and ΔE^{X}, ΔN^{X} and ΔV_{ne}^{XX} as well as ΔV_{ne}^{XX} and ΔV_{ee}^{XX}, *e.g.*, when $\Delta N^{X} < 0$ then $\Delta E^{X} > 0$.

At the same time it appeared obvious that there is no correlation between the change in the average electron density and any other property shown in Table 3; $\Delta d_{e}^{X} > 0$ is observed for all atoms of the functional groups.

Furthermore, it is apparent that hetero- and H-atoms directly involved in the interactions are characterized by a number of different in sign changes in these atoms properties, namely, $\Delta T^{X} > 0$, $\Delta V_{ne}^{XX} < 0$, $\Delta V_{ee}^{XX} > 0$, $\Delta N^{X} > 0$ applies to heteroatoms and an opposite trends are observed for H11 in **Hen** and H12 in **Hea**.

Remarkably, not only the trends in the ΔE_{self}^{X} and ΔE_{add}^{X} values for relevant atoms of functional groups in both molecules are exactly the same (as illustrated in Fig. 3 in the manuscript) but also the ΔT^{X}, ΔV_{ne}^{XX}, ΔV_{ee}^{XX}, ΔN^{X} and ΔVol^{X} values change in the same direction. Combining all these descriptors we found the following sets of indices:

Set-(A) – $\Delta E_{self}^{X} > 0$, $\Delta E_{add}^{X} < 0$, $\Delta T^{X} > 0$, $\Delta V_{ne}^{XX} < 0$, $\Delta V_{ee}^{XX} > 0$, $\Delta N^{X} > 0$ and $\Delta Vol^{X} < 0$ for heteroatoms which are directly involved in the interactions in **Hen** and **Hea**.

Set-(B) – $\Delta E_{self}^{X} > 0$, $\Delta E_{add}^{X} < 0$, $\Delta T^{X} < 0$, $\Delta V_{ne}^{XX} > 0$, $\Delta V_{ee}^{XX} < 0$, $\Delta N^{X} < 0$ and $\Delta Vol^{X} < 0$ for H11 and H12 which are directly involved in the interactions in **Hen** and **Hea**, respectively.

Set-(C) – $\Delta E_{self}^{X} < 0$, $\Delta E_{add}^{X} < 0$, $\Delta T^{X} > 0$, $\Delta V_{ne}^{XX} < 0$, $\Delta V_{ee}^{XX} > 0$, $\Delta N^{X} > 0$ and $\Delta Vol^{X} > 0$ for H12 and H13 in **Hen** as well as H10 and H11 in **Hen**, all of them belonging to the $-NH_3^{+}$ functional groups of both molecules.

Set-(D) – $\Delta E_{self}^{X} > 0$, $\Delta E_{add}^{X} > 0$, $\Delta T^{X} < 0$, $\Delta V_{ne}^{XX} > 0$, $\Delta V_{ee}^{XX} < 0$, $\Delta N^{X} < 0$ and $\Delta Vol^{X} < 0$ for H8 and H9 in **Hen** as well as H8 in **Hea** even though they belong to different functional groups.

Clearly, it would be of interest and importance to study more interactions of this kind to find out whether these observations and trends are of a general nature and, importantly, how they depend on the molecular environment.

Table S7. Relative to *ref* structure, changes in the selected QTAIM- and IQA-defined energy terms and additional atomic properties of atoms in **gc**.[a]

atom X	ΔE^{X}_{self}	ΔT^{X}	ΔV^{XX}_{ne}	ΔV^{XX}_{ee}	ΔE^{X}	ΔN^{X}	ΔVol^{X}	ΔA^{X}	Δd^{X}_{e}
C1	–2.6	–13.1	24.1	–13.6	13.0	0.0009	1.821	4.10	–0.0037
H2	0.5	3.9	–5.0	1.6	–4.0	0.0055	–0.308	–0.65	0.0002
H3	0.5	4.0	–5.0	1.6	–4.0	0.0055	–0.207	0.08	0.0002
O9	–0.3	–1.8	44.3	–42.8	1.6	–0.0187	–3.462	–0.90	0.0018
H10	–1.9	2.8	–5.4	0.6	–2.8	0.0073	0.499	0.61	–0.0001

[a] Energies are in kcal mol^{-1} and all values at MP2. For details, see a footnote of Table S6. Due to molecular symmetry, only data for representative atoms are included.

Table S8. Relative to *ref* structure, changes in the selected QTAIM- and IQA-defined energy terms and additional atomic properties for atoms in **bph**.[a]

atom X	ΔE^{X}_{self}	ΔT^{X}	ΔV^{XX}_{ne}	ΔV^{XX}_{ee}	ΔE^{X}	ΔN^{X}	ΔVol^{X}	ΔA^{X}	Δd^{X}_{e}
B3LYP (SPC on MP2-optimized structures)									
C3	–3.9	–20.6	44.3	–27.6	21.0	–0.0026	2.623	–49.67	–0.0032
C4	1.2	0.6	6.9	–6.3	–0.3	–0.0055	–0.266	–19.73	0.0002
C5	0.5	1.2	2.3	–3.0	–1.0	–0.0032	–0.305	0.15	0.0002
C6	0.3	3.1	–6.0	3.2	–2.8	0.0002	0.200	0.81	–0.0002
H9	1.7	6.9	–10.0	4.8	–7.0	0.0098	–3.177	1.11	0.0016
H10	0.0	0.5	–0.8	0.3	–0.5	0.0009	–0.052	0.01	0.0000
H11	0.0	–0.4	0.6	–0.3	0.4	–0.0011	–0.060	–0.20	0.0000
MP2									
C3	–3.5	–20.6	45.8	–28.7	21.6	–0.0044	2.417	–50.13	–0.0029
C4	0.9	0.8	6.2	–6.1	0.1	–0.0060	–0.410	–19.99	0.0003
H9	1.7	7.8	–10.8	4.7	–7.8	0.0107	–3.290	1.25	0.0017

[a] Energies are in kcal mol^{-1}. For details, see a footnote of Table S6. Due to molecular symmetry, only data for representative atoms are included.

Note that properties of H9 follow exactly the Trend-3, Trend-4 and Trend-5 found for atoms directly involved in the intramolecular interactions in **Hen** and **Hea** (similar observation also applies to O-atoms of **gc**); it suggests that these trends do not depend on the kind of the interaction.

Table S9. Relative to the *ref* structure, values of $\Delta E_{\text{int}}^{\text{XY}}$, $\Delta V_{\text{cl}}^{\text{XY}}$ and $\Delta V_{\text{XC}}^{\text{XY}}$ (in kcal mol^{-1}) computed for all diatomic interactions in the *fin* structure of **Hen** at MP2/PCM.

Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$	Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$
N7	**H11**	–54.7	–45.2	–9.5	H3	H6	0.2	0.1	0.1
C4	N7	–15.0	–15.5	0.5	H5	N10	0.2	0.3	–0.1
N7	H13	–14.0	–13.9	–0.1	H3	H5	0.3	0.1	0.1
N7	H12	–13.6	–13.6	0.0	H2	H3	0.3	0.2	0.1
H9	N10	–10.6	–10.5	0.0	H2	H6	0.3	0.2	0.1
H8	N10	–9.2	–9.2	–0.1	H3	H13	0.4	0.4	0.0
C1	N10	–8.3	–8.2	–0.2	H2	H12	0.4	0.4	0.0
C4	N10	–6.8	–5.0	–1.7	H3	H12	0.4	0.5	0.0
N7	H8	–5.9	–7.6	1.6	H3	C4	0.5	0.6	–0.1
N10	H11	–4.8	–14.7	9.9	H3	H8	0.5	0.4	0.1
N7	H9	–4.7	–5.8	1.1	H6	N7	0.5	0.0	0.5
H12	H13	–1.6	–1.6	0.0	C4	H6	0.5	1.2	–0.6
H2	N10	–1.3	–1.3	0.1	C4	H12	0.6	0.6	0.0
H2	N7	–1.2	–1.3	0.2	H11	H13	0.6	0.5	0.1
C1	H9	–1.1	–1.2	0.0	H2	H13	0.7	0.5	0.2
H3	N7	–1.1	–1.5	0.4	H2	H8	0.8	0.7	0.1
H5	H13	–1.1	–0.9	–0.2	H3	H9	0.8	0.6	0.1
C1	H8	–1.0	–1.1	0.1	H2	C4	0.8	0.7	0.1
H3	N10	–1.0	–1.4	0.4	H5	H11	0.9	0.7	0.2
H6	N10	–0.8	–1.1	0.3	H2	H11	1.0	1.0	0.0
C1	H5	–0.6	–0.5	–0.1	C4	H13	1.0	1.0	0.0
H5	H8	–0.6	–0.5	0.0	H6	H13	1.1	1.0	0.1
C1	H6	–0.5	–0.5	0.0	C1	H13	1.3	1.2	0.1
N10	H13	–0.5	0.9	–1.4	C1	H12	1.4	1.4	0.0
H5	H12	–0.4	–0.3	–0.1	H3	H11	1.5	1.3	0.3
H6	H8	–0.3	–0.6	0.3	H9	H13	2.0	2.0	0.0
H2	H5	–0.2	0.0	–0.2	H8	H12	2.2	2.2	0.0
C1	H3	–0.2	0.2	–0.3	H8	H9	2.2	2.1	0.1
N10	H12	–0.2	1.4	–1.6	C4	H8	3.2	3.1	0.1
H6	H11	–0.1	0.0	–0.1	H9	H12	3.3	3.3	0.0
H6	H9	–0.1	–0.1	0.0	C1	N7	3.4	–0.1	3.5
H11	H12	–0.1	–0.2	0.1	H8	H13	3.5	3.5	0.0
C1	H2	–0.1	0.2	–0.3	C4	H9	3.9	3.7	0.2
H5	H9	0.0	–0.2	0.2	C4	H11	4.2	4.1	0.0
H2	H9	0.0	0.2	–0.2	C1	C4	4.8	5.0	–0.2
H5	H6	0.1	0.0	0.0	C1	H11	9.0	9.2	–0.1
H5	N7	0.1	0.0	0.1	H8	H11	9.4	9.5	–0.1
C4	H5	0.1	0.2	–0.1	H9	H11	10.7	10.8	–0.1
H6	H12	0.1	0.1	0.1	N7	N10	41.2	46.8	–5.6

Table S10. Relative to the *ref* structure, values of $\Delta E_{\text{int}}^{\text{XY}}$, $\Delta V_{\text{cl}}^{\text{XY}}$ and $\Delta V_{\text{XC}}^{\text{XY}}$ (in kcal mol^{-1}) computed for all diatomic interaction in the *fin* structure of **Hea** at MP2/PCM.

Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$	Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$
O7	**H12**	–37.8	–33.8	–4.0	H6	O7	0.3	0.2	0.0
H8	N9	–12.8	–12.8	0.0	H3	H5	0.3	0.3	0.1
O7	H11	–12.5	–12.5	0.0	H2	H5	0.3	0.2	0.1
O7	H10	–10.0	–10.0	0.0	H5	H12	0.4	0.4	0.0
C1	N9	–9.5	–9.9	0.4	H11	H12	0.4	0.4	0.0
C4	O7	–8.7	–9.7	1.0	H2	H10	0.4	0.4	0.0
O7	H8	–3.1	–4.3	1.2	H2	C4	0.4	0.5	0.0
H3	O7	–3.0	–3.3	0.2	H3	H6	0.5	0.3	0.1
C1	H8	–2.3	–2.3	0.1	H3	C4	0.5	0.8	–0.3
H3	N9	–1.9	–2.3	0.4	H2	H3	0.5	0.4	0.1
N9	H12	–1.7	–5.2	3.5	C1	H2	0.6	0.6	–0.1
H2	O7	–1.4	–1.4	0.0	H2	H8	0.6	0.7	0.0
H2	N9	–1.2	–1.3	0.1	N9	H11	0.8	1.5	–0.7
C1	H5	–1.2	–1.0	–0.2	H3	H10	0.9	0.9	0.0
H10	H11	–1.0	–1.0	0.0	C4	H12	1.0	1.0	0.1
C4	H10	–1.0	–1.0	0.0	C1	C4	1.1	3.1	–2.0
C4	H11	–0.7	–0.7	0.0	N9	H10	1.2	2.0	–0.9
C1	H6	–0.5	–0.5	–0.1	H3	H12	1.2	1.2	0.0
H5	N9	–0.3	–0.6	0.2	H2	H12	1.4	1.1	0.3
H5	H8	–0.3	–0.2	0.0	H3	H11	1.5	1.2	0.3
C4	H6	–0.2	–0.3	0.1	H3	H8	1.6	1.5	0.0
H6	H10	–0.2	–0.1	0.0	H5	O7	1.8	1.1	0.7
H2	H6	–0.1	0.0	–0.1	C1	H10	1.9	1.9	0.0
H10	H12	–0.1	–0.2	0.0	C1	H3	2.4	2.3	0.1
H6	H11	–0.1	–0.1	0.0	C1	H11	2.6	2.6	0.0
H6	H8	–0.1	–0.1	0.0	C4	N9	2.6	2.3	0.3
C4	H5	0.0	0.4	–0.4	C4	H8	3.1	3.1	0.0
H5	H6	0.1	0.0	0.0	H8	H10	3.7	3.7	0.0
H2	H11	0.1	0.3	–0.2	H8	H11	4.9	4.9	0.0
H6	H12	0.1	0.1	0.0	C1	O7	5.6	3.6	2.0
H5	H10	0.1	0.1	0.0	C1	H12	10.0	10.0	0.1
H6	N9	0.2	0.2	0.0	H8	H12	11.9	12.0	0.0
H5	H11	0.2	0.3	0.0	O7	N9	31.9	36.2	–4.3

Table S11. Relative to the *ref* structure, values of $\Delta E_{\text{int}}^{\text{XY}}$, $\Delta V_{\text{cl}}^{\text{XY}}$ and $\Delta V_{\text{XC}}^{\text{XY}}$ (in kcal mol^{-1}) computed for all diatomic interaction in the eclipsed form of **gc** at MP2/PCM.

Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$	Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$
C1	O9	–283.2	–132.7	–150.6	H2	H5	–0.4	0.1	–0.5
C4	O7	–283.2	–132.6	–150.6	H5	H6	–0.2	–0.1	–0.1
C4	H10	–41.4	–42.3	0.8	H2	H3	–0.2	–0.1	–0.1
C1	H8	–41.4	–42.3	0.8	H2	H6	0.0	–0.1	0.1
O7	H10	–9.9	–9.8	–0.1	H3	H5	0.0	–0.1	0.1
H8	O9	–9.9	–9.8	–0.1	H3	H10	1.2	1.3	–0.1
H2	O9	–8.2	–3.6	–4.6	H6	H8	1.2	1.3	–0.1
H3	O9	–8.2	–3.6	–4.6	H2	H10	1.2	1.3	–0.1
H5	O7	–8.2	–3.6	–4.6	H5	H8	1.2	1.3	–0.1
H6	O7	–8.2	–3.6	–4.6	H8	H10	3.0	3.0	0.0
H3	H8	–1.8	–1.9	0.1	O9	H10	3.4	4.6	–1.2
H6	H10	–1.8	–1.9	0.1	O7	H8	3.5	4.6	–1.2
H2	H8	–1.8	–1.9	0.1	C1	C4	7.6	2.2	5.4
H5	H10	–1.8	–1.9	0.1	H2	O7	10.3	4.8	5.4
C1	H2	–1.5	–0.7	–0.8	H5	O9	10.3	4.8	5.4
C4	H6	–1.5	–0.7	–0.8	H6	O9	10.3	4.8	5.4
C1	H3	–1.5	–0.7	–0.8	H3	O7	10.3	4.8	5.4
C4	H5	–1.5	–0.7	–0.8	**O7**	**O9**	25.8	34.0	–8.2
H2	C4	–0.7	–0.6	–0.2	C4	H8	43.9	44.9	–0.9
C1	H5	–0.7	–0.6	–0.2	C1	H10	43.9	44.8	–0.9
H3	C4	–0.7	–0.6	–0.2	C4	O9	279.5	126.8	152.8
C1	H6	–0.7	–0.6	–0.2	C1	O7	279.5	126.7	152.8
H3	H6	–0.4	0.1	–0.5					

Table S12. Relative to the *ref* structure, values of $\Delta E_{\text{int}}^{\text{XY}}$, $\Delta V_{\text{cl}}^{\text{XY}}$ and $\Delta V_{\text{XC}}^{\text{XY}}$ (in kcal mol^{-1}) computed for selected diatomic interactions in the planar conformer of biphenyl at MP2/gas.

Atoms X	Atoms Y	$\Delta E_{\text{int}}^{\text{XY}}$	$\Delta V_{\text{cl}}^{\text{XY}}$	$\Delta V_{\text{XC}}^{\text{XY}}$
H9	**H16**	–3.79	0.00	–3.79
C4	H16	–0.24	0.02	–0.26
H9	C13	–0.23	0.02	–0.25
C13	H16	0.04	0.14	–0.10
C4	H9	0.05	0.14	–0.09
C4	C13	0.07	0.26	–0.19
C3	H9	0.10	–0.03	0.13
C12	H16	0.12	–0.03	0.15
C3	H16	0.49	–0.04	0.53
H9	C12	0.50	–0.04	0.53
C3	C13	0.51	0.00	0.51
C4	C12	0.53	0.00	0.53
C3	C4	0.72	–0.23	0.96
C12	C13	0.74	–0.24	0.98
C3	C12	1.08	–0.10	1.19

Table S13. Interaction energy (between an indicated atom and remaining atoms in a molecule) and its components obtained for all atoms of the *ref* and *fin* states of **bph** from the SPC at the B3LYP/6-311++G(d,p) level on the MP2/6-311++G(d,p)-optimized structures.

Atom X	$\sum_{Y\neq X} 0.5E_{int}^{XY}$ [a]		$\Delta\sum_{Y\neq X} 0.5E_{int}^{XY}$ [b]	$\Delta\sum_{Y\neq X} 0.5V_{cl}^{XY}$ [b]	$\Delta\sum_{Y\neq X} 0.5V_{XC}^{XY}$ [b]
	ref	***fin***			
C1	–0.5038	–0.5041	–0.18	0.28	–0.45
C2	–0.5039	–0.5039	0.00	0.01	–0.01
C3	–0.5288	–0.5255	2.10	–0.28	2.39
C4	–0.5040	–0.5038	0.09	0.15	–0.05
C5	–0.5038	–0.5042	–0.25	0.19	–0.44
C6	–0.5028	–0.5024	0.20	0.17	0.03
H7	–0.1277	–0.1278	–0.07	–0.02	–0.05
H8	–0.1288	–0.1317	–1.77	–0.16	–1.61
H9	–0.1288	–0.1317	–1.77	–0.15	–1.62
H10	–0.1277	–0.1278	–0.07	–0.02	–0.04
H11	–0.1278	–0.1277	0.09	0.04	0.04
C12	–0.5290	–0.5255	2.24	–0.13	2.37
C13	–0.5040	–0.5039	0.08	0.14	–0.06
C14	–0.5039	–0.5038	0.04	0.08	–0.04
C15	–0.5037	–0.5041	–0.24	0.20	–0.44
H16	–0.1288	–0.1317	–1.77	–0.17	–1.61
C17	–0.5039	–0.5042	–0.17	0.28	–0.45
H18	–0.1288	–0.1317	–1.77	–0.15	–1.62
C19	–0.5029	–0.5024	0.31	0.29	0.02
H20	–0.1277	–0.1278	–0.07	–0.03	–0.04
H21	–0.1277	–0.1278	–0.07	–0.03	–0.04
H22	–0.1278	–0.1277	0.09	0.04	0.04

[a] Values in a.u.
[b] Values in kcal mol^{-1}