Supplemental material of

Interaction region indicator (IRI): A very simple real space function clearly revealing both chemical bonds and weak interactions

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Fig. S1 Isosurface maps of DORI of diamantane–diamantane at different isovalues.
Section S1: Derivation of conditions of occurrence of IRI critical points

Gradient norm of electron density is expressed as

\[ |\nabla \rho| = \left[ \left( \frac{\partial \rho}{\partial x} \right)^2 + \left( \frac{\partial \rho}{\partial y} \right)^2 + \left( \frac{\partial \rho}{\partial z} \right)^2 \right]^{1/2} \]

Therefore

\[ \frac{\partial |\nabla \rho|}{\partial x} = \frac{1}{2} \left[ \left( \frac{\partial \rho}{\partial x} \right)^2 + \left( \frac{\partial \rho}{\partial y} \right)^2 + \left( \frac{\partial \rho}{\partial z} \right)^2 \right]^{1/2} \cdot \frac{2}{2} \left( \frac{\partial^2 \rho}{\partial x \partial x} + \frac{\partial^2 \rho}{\partial y \partial y} + \frac{\partial^2 \rho}{\partial z \partial z} \right) |\nabla \rho|^{-1} \]

IRI is defined as

\[ \text{IRI} = \frac{|\nabla \rho|}{\rho^a} \]

Derivative of IRI with respect to x coordinate is

\[ \frac{\partial \text{IRI}}{\partial x} = \frac{\partial |\nabla \rho|}{\partial x} \cdot \frac{1}{\rho^a} - \frac{1}{\rho^{a+1}} \frac{\partial^2 \rho}{\partial x \partial x} |\nabla \rho| \]

\[ = \frac{1}{\rho^a} \left( \frac{\partial \rho}{\partial x} \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial \rho}{\partial y} \frac{\partial^2 \rho}{\partial y \partial y} + \frac{\partial \rho}{\partial z} \frac{\partial^2 \rho}{\partial z \partial z} \right) |\nabla \rho|^{-1} - \frac{1}{\rho^{a+1}} \frac{\partial^2 \rho}{\partial x \partial x} |\nabla \rho| \]

Therefore,

\[ \frac{\partial \text{IRI}}{\partial x} = 0 \]

\[ \Rightarrow \frac{1}{\rho^a} \left( \frac{\partial \rho}{\partial x} \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial \rho}{\partial y} \frac{\partial^2 \rho}{\partial y \partial y} + \frac{\partial \rho}{\partial z} \frac{\partial^2 \rho}{\partial z \partial z} \right) |\nabla \rho|^{-1} = \frac{1}{\rho^{a+1}} \frac{\partial \rho}{\partial x} |\nabla \rho| \]

\[ \Rightarrow \frac{\partial^2 \rho}{\partial x \partial x} = \frac{\partial^2 \rho}{\partial y \partial y} + \frac{\partial^2 \rho}{\partial z \partial z} \]

Similarly for \( \partial \text{IRI}/\partial y \) and \( \partial \text{IRI}/\partial z \).
Section S2: Illustrating why IRI minima corresponding to intramolecular H-bond in Ni(NH₃)₂(OH)₂ can occur

For the Ni(NH₃)₂(OH)₂ discussed in Section 2.4, after rotating the Cartesian axes to (x', y', z') to eliminate coupling between different axes in Hessian of electron density, the gradient line map on x'y' plane becomes the one shown below, the green point indicates the position of IRI critical point corresponding to the intramolecular H-bond. This critical point is a minimum because all eigenvalues of Hessian of IRI at this point are found to be positive.

\[ \frac{\partial^2 \rho}{\partial x'^2} = a \frac{|\nabla \rho|^2}{\rho} \]

\[ \frac{\partial \rho}{\partial y'} = 0 \]

\[ \frac{\partial \rho}{\partial z'} = 0 \]

Note that the derivative of \( \rho \) with respect to \( z' \) axis, namely the direction perpendicular to the above map, is exactly zero in this case. Clearly, the additional condition \( \frac{\partial^2 \rho}{\partial x'^2} = a \frac{|\nabla \rho|^2}{\rho} \) allows the IRI minimum occurs where AIM CP does not occur. No AIM CP corresponding to the H-bond occurs because as can be seen from the gradient line map, there is no point in the H-bond region satisfies \( \frac{\partial \rho}{\partial x'} = 0 \) (in fact, any point in this region has a negative \( \frac{\partial \rho}{\partial x'} \)).