Erratum to "Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems"

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Abstract: This erratum corrects independent gradient model based on Hirshfeld partition of molecular density (IGMH) proposed in our previous paper (*J. Comput. Chem.* 2022, **43**, 539–555), and a brief analysis shows why IGMH based on incorrect implementation (inversed sign) of gradient of free-state atomic densities works surprisingly better for graphically representing interaction regions of chemical systems than based on mathematically correct implementation.

Recently we notice a bug of our code in realizing the IGM based on Hirshfeld partition of molecular density (IGMH) proposed in our previous paper (*J. Comput. Chem.* 2022, **43**, 539–555), that is, the sign of gradient of free-state atomic density calculated by our code is incorrectly inverted. Correspondingly, the equation of calculating the gradient of Hirshfeld atomic density ρ_i^{Hirsh} involved in g^{IGMH} and δg in our previous study, in fact is not the following one (Eq. 7 of previous paper)

$$\frac{\partial \rho_i^{\mathrm{Hirsh}}}{\partial \mu} = w_i \frac{\partial \rho}{\partial \mu} + \rho \frac{\partial w_i}{\partial \mu} \quad (\mu = x, y, z) \tag{1}$$

but corresponds to the following one

$$\frac{\partial \rho_i^{\mathrm{Hirsh}}}{\partial \mu} = w_i \frac{\partial \rho}{\partial \mu} - \rho \frac{\partial w_i}{\partial \mu} \quad (\mu = x, y, z) \tag{2}$$

Although Eq. 2 is mathematically incorrect, as extensively illustrated in our previous paper, the IGMH based on Eq. 2 exhibits a quite satisfactory capability in revealing interactions in chemical systems. In contrast, we found the IGMH based on the mathematically correct Eq. 1 results in even worse graphical representation of interactions compared to its predecessor IGM. In our previous paper adenine-thymine base pair was investigated, the corresponding map of IGMH (Eq. 1) with defining the two monomers as two fragments is shown in Fig. 1. It can be seen that the isosurfaces corresponding to hydrogen bonds are extremely bulgy and greatly intrude into the regions very close to nuclei, this graphical representation is evidently undesirable.
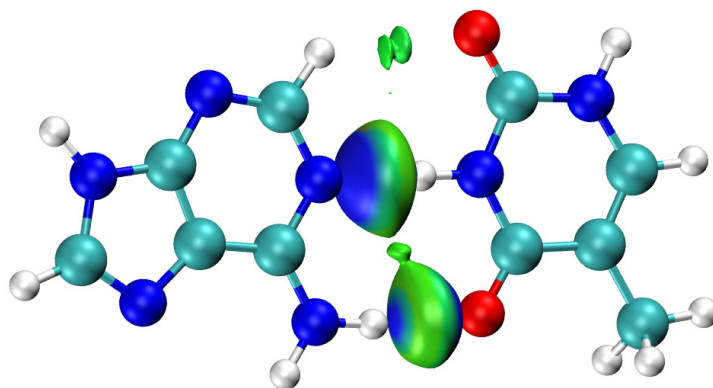

Fig. 1 $sign(\lambda_2)\rho$ colored IGMH map calculated based on Eq. 1 for adenine-thymine base pair. Isovalue of δg is chosen as 0.005 a.u. Adenine and thymine are defined as the two fragments for IGMH analysis.

Note that the C-H...O interaction can hardly be recognized if larger isovalue is adopted.

It is worth to explore the reason why the δg of IGMH calculated based on the incorrect Eq. 2 surprisingly works well in revealing interaction regions. For simplicity, we consider a diatomic molecule aligning along X axis, for which the following relations exist. Note that the derivatives of ρ and w with respect to Y and Z directions are vanished, and the second equal sign of Eq. 5 follows Eq. 2.

$$\delta g = g^{\text{IGMH}} - g \tag{3}$$

$$g = \left| \frac{\partial \rho}{\partial x} \right| \tag{4}$$

$$g^{\text{IGMH}} = \left| \frac{\partial \rho_1^{\text{Hirsh}}}{\partial x} \right| + \left| \frac{\partial \rho_2^{\text{Hirsh}}}{\partial x} \right| = \left| \underbrace{w_1 \frac{\partial \rho}{\partial x}}_{a_1} - \underbrace{\rho \frac{\partial w_1}{\partial x}}_{b_1} \right| + \left| \underbrace{w_2 \frac{\partial \rho}{\partial x}}_{a_2} - \underbrace{\rho \frac{\partial w_2}{\partial x}}_{b_2} \right| \tag{5}$$

Given that $\rho \frac{\partial w_2}{\partial x} = \rho \frac{\partial (1 - w_1)}{\partial x} = -\rho \frac{\partial w_1}{\partial x}$ and $w_1 \frac{\partial \rho}{\partial x} + w_2 \frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial x}$, g^{IGMH} can be further expressed as

$$g^{\text{IGMH}} = \begin{cases} \partial \rho / \partial x & \text{case 1}: a_1 > b_1, a_2 > b_2 \\ -\partial \rho / \partial x & \text{case 2}: a_1 < b_1, a_2 < b_2 \\ (w_1 - w_2) \partial \rho / \partial x - 2\rho \, \partial w_1 / \partial x & \text{case 3}: a_1 > b_1, a_2 < b_2 \\ (w_2 - w_1) \partial \rho / \partial x + 2\rho \, \partial w_1 / \partial x & \text{case 4}: a_1 < b_1, a_2 > b_2 \end{cases} \tag{6}$$

In practice we find $\partial \rho / \partial x > 0$ and $\partial \rho / \partial x < 0$ are satisfied in the regions corresponding to case 1 and case 2, respectively, so in these cases $g^{\text{IGMH}} = g = |\partial \rho / \partial x|$ and hence $\delta g = 0$, clearly no isosurface of δg will occur. By contrast, g^{IGMH} differs from g in cases 3 and 4, which generally correspond to the most representative interaction regions, enabling δg of IGMH based on Eq. 2 to clearly reveal the interactions of interest. To better illustrate this point, we plotted δg, g, g^{IGMH} as well as various terms labelled in Eq. 5 for CO molecule along its bond axis. From Fig. 2(a), it is seen that δg is non-vanished only in bonding region between C and O, where case 3 or 4 is satisfied; while in other regions, g^{IGMH} is exactly identical to g and thus $\delta g = 0$. The reason of the

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featured distribution of g^{IGMH} can be understood in more depth by inspecting variation of the a_1, b_1, a_2, b_2 from Fig. 3 and comparing them with conditions given in Eq. 6. We found the δg of IGMH calculated based on Eq. 1 does not show such an appealing distribution character. From Fig. 2(b) it is clear that the non-vanished δg (Eq. 1) spans the entire region between nuclei of C and O, which does not well correspond to the main bonding region. This observation is also in line with the quite bulgy and thus undesirable isosurfaces shown in Fig. 1.
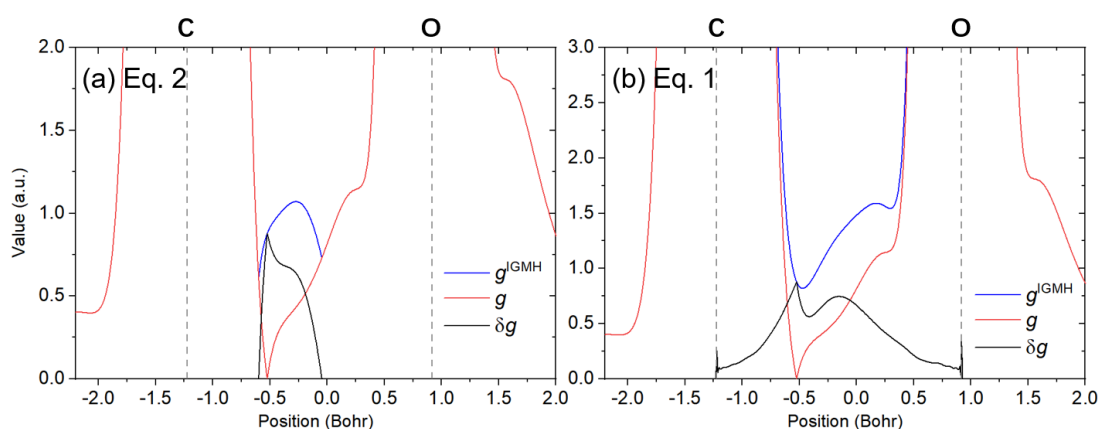

Fig. 2 g, g^{IGMH} and δg along bond axis of CO molecule using gradients of Hirshfeld atomic densities respectively calculated via Eq. 2 and Eq. 1 with B3LYP/cc-pVDZ wavefunction. Positions of nuclei of C and O are highlighted by dashed lines.
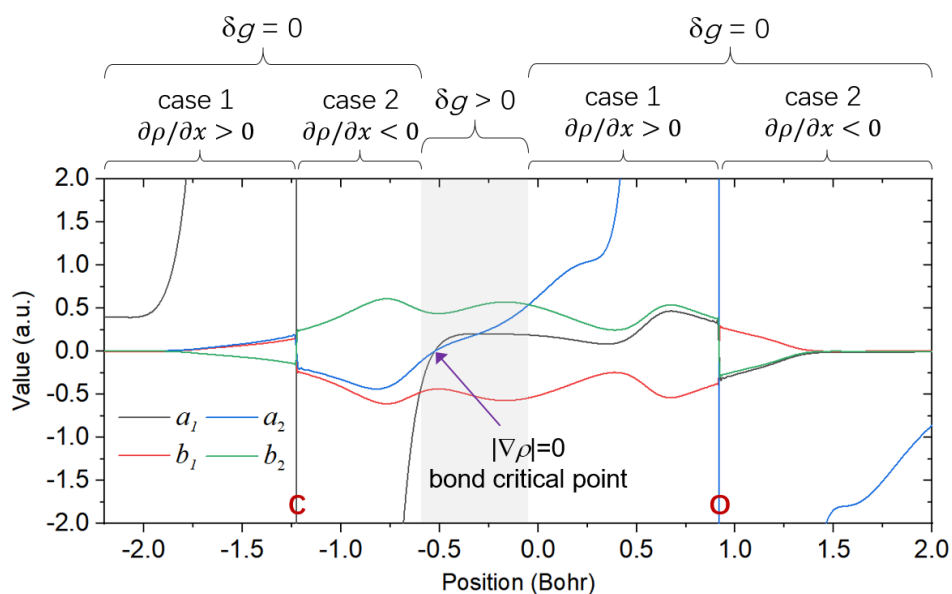
Fig. 3 Variation of various terms labelled in Eq. 5 along bond axis of CO. The regions satisfying cases 1 and 2 in Eq. 6 are indicated.

In summary, in our previous paper what we employed for calculating gradient of Hirshfeld atomic densities actually is Eq. 2, which is mathematically incorrect, but making IGMH performs significantly better in revealing interaction regions than using the correct Eq. 1. So, Eq. 2 should be regarded as the key ingredient of the definition of our IGMH method. We thank Prof. Eric Hénon for bringing the error in our code to our attention.