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Topology of Electrostatic Potential and Electron Density Reveals Covalent to Non-Covalent Carbon-Carbon Bond Continuum

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Supporting Information

Topological concepts in MESP

The intricate topological characteristics of a scalar function f(x_1, x_2, x_3..... x_n) involving multiple variables are quantitatively defined through its first and second-order partial derivatives. These derivatives provide crucial information about the function's behavior. Specifically, the number and nature of critical points play a significant role in summarizing these features. A critical point (CP) is a point where either all the first-order partial derivatives of the function or the gradient of the field becomes zero, viz.

$$\nabla_i f(x_1, x_2, x_3, \ldots\ldots\ldots x_n)|_{CP} = 0$$

Or $$\left.\frac{\partial f}{\partial x_i}\right|_{CP} = 0 \; where \; i = 1,2,3\ldots,n$$

i.e., the CP of a scalar field can be determined by finding the points where the magnitude of the first partial derivatives with respect to the variables is minimum. Analyzing these critical points allows us to gain a deeper understanding of the function's extrema and saddle points, providing valuable insights into the function's behavior aiding in various fields. The nature of the CP can be determined by analyzing the signs of the eigenvalues of the Hessian matrix at that point. The Hessian matrix can be represented as,

$$H_{ij} = \left.\frac{\partial^2 V(r)}{\partial x_i \partial x_j}\right|_{CP}$$

The CPs are classified as non-degenerate when none of the eigenvalues of the Hessian matrix is zero. And as degenerate if at least one of the eigenvalues of the Hessian matrix is zero. A non-degenerate CP is characterized by two elements: rank (R) and signature (σ). The rank refers to the number of nonzero eigenvalues at the CP, while the signature denotes the difference between the number of positive eigenvalues and negative eigenvalues. Therefore, a CP is represented as an ordered pair of these two elements as (R, σ).

Consider a function of three variables, f(x, y, z). For non-degenerate CPs of this function, the R is 3, indicating that all three eigenvalues of the Hessian matrix are non-zero. In such cases, the σ can have four distinct values: -3, -1, +1, and +3, leading to four types of non-degenerate CPs, viz. (3, -3), (3, -1), (3, +1), and (3, +3). The (3, -3) CP is characterized by three negative eigenvalues, representing a local maximum of the function. On the other hand, the CPs of type (3, -1) and (3, +1) signify saddle points, where the eigenvalues have a mix of both positive and negative values. The CPs of type (3, -1) and (3, +1) signify saddle points, where the eigenvalues have a mix of both positive and negative values. The (3, -1) CP is the bond critical point (BCP) with two negative curvatures where function is a maximum in the plane defined by these two eigenvectors and minimum along the third axis, which is perpendicular to this plane. The (3, +1) CP, ring critical point (RCP), contain two positive eigenvalues where the function is a minimum along the plane defined by the corresponding eigenvectors and maximum along the third axis, which is perpendicular to this plane. Further, (3, +3) CP corresponds to three positive eigenvalues, indicating a local minimum in the function.

Topological concepts in MED

The value $\rho(\mathbf{r})$ can take on different characteristics in space, such as being a maximum, a minimum, or a saddle point. These specific points are commonly referred to as Critical Points (CPs). A CP can also be defined as the point on the electron density surface at which the first derivative of the function $\rho(\mathbf{r}_c)$ vanishes, $\nabla\rho(\mathbf{r}_c) = 0$.

$$\nabla\rho(r) = i\frac{d\rho}{dx} + j\frac{d\rho}{dy} + k\frac{d\rho}{dz} \rightarrow \begin{cases} = 0 \ (at\ critical\ points, r_c\ and\ at\ \infty) \\ \neq 0 (at\ all\ critical\ points) \end{cases}$$

The gradient of electron density, $\nabla\rho(\mathbf{r})$, at a specific point in space indicates the direction in which $\rho(\mathbf{r})$ experiences the maximum rate of increase, and its magnitude corresponds to the rate of increase in that particular direction. Thus, $\nabla\rho(\mathbf{r})$ is a vector quantity. A CP may correspond to maximum, minimum or a saddle point. Based on its sign, the second derivative of $\rho(\mathbf{r})$, $\nabla\nabla\rho(\mathbf{r})$ is considered for distinguishing a local minimum, a local maximum or a saddle point. The collection of nine possible second derivative electron densities at $\mathbf{r}_c$ can be expressed in the form of a matrix known as the Hessian matrix.

$$A(r_c) = \begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial y\partial x} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix}_{r=rc}$$

This matrix's diagonalization yields a collection of eigenvalues and related eigenvectors. The eigenvalues associated with each form of CP can be used to differentiate them. At a critical point, the 'Hessian matrix' is created from the nine possible second derivatives of electron density, and the Laplacian $\nabla^2\rho(\mathbf{r})$ is represented as the sum of the eigenvalues ($\lambda_{\rho1}$, $\lambda_{\rho2}$, and $\lambda_{\rho3}$) of the Hessian matrix of $\rho(\mathbf{r})$. The eigenvalues $\lambda_{\rho1}$, $\lambda_{\rho2}$, and $\lambda_{\rho3}$ represent the principal axes of curvature because the magnitudes of the three second derivatives of $\rho(\mathbf{r})$ calculated with respect to these axes are maximized or minimized.

$$\nabla^2\rho(r) = \nabla(\nabla\rho(r)) = \frac{\partial^2\rho(r)}{\partial x^2} + \frac{\partial^2\rho(r)}{\partial y^2} + \frac{\partial^2\rho(r)}{\partial z^2} = \lambda_1 + \lambda_2 + \lambda_3$$

Eigenvalues $\lambda_{\rho1}$, $\lambda_{\rho2}$, and $\lambda_{\rho3}$ are the curvatures of the density with respect to the three principal axes X,Y, and Z, respectively given as:

$$\lambda_{\rho1} = \frac{\partial^2\rho(r)}{\partial x^2}$$

$$\lambda_{\rho2} = \frac{\partial^2\rho(r)}{\partial y^2}$$

$$\lambda_{\rho3} = \frac{\partial^2\rho(r)}{\partial z^2}$$

The bond critical points represent the minimum along the bonding direction, and the maximum in all others. i.e., The electron density falls down in two perpendicular directions of space and rises in the third direction. Mathematically, this is defined by the sign of the second derivatives, $\lambda_{\rho1}$, $\lambda_{\rho2}$, and $\lambda_{\rho3}$, along the main axes of variation, i.e., At BCP, $\lambda_{\rho1}$, $\lambda_{\rho2}$ are negative whereas $\lambda_{\rho3}$ is positive.

A critical point (CP) is labeled as an ordered pair (R, σ), where ω is the rank and σ the signature. The rank (R) is the number of non-zero eigenvalues of $\rho(\mathbf{r})$ at the CPs, and the signature (σ) is the algebraic sum of the signs of eigenvalues. For energetically stable nuclear configurations ω is equal to 3, and there are four types of CPs with rank 3. The (3, -3) CP known as nuclear critical point (NCP) with three negative eigenvalues where $\rho(\mathbf{r})$ is a local maximum at $\mathbf{r}_c$. The (3, -1) CP is the bond critical point (BCP) with two negative curvatures where $\rho(\mathbf{r})$ is a maximum in the plane defined

by these two eigenvectors and minimum along the third axis, which is perpendicular to this plane. The ring critical point (RCP), (3, +1) CP contain two positive eigenvalues where $\rho(\mathbf{r})$ is a minimum along the plane defined by the corresponding eigenvectors and maximum along the third axis, which is perpendicular to this plane. The (3, +3) CP known as cage critical point (CCP) has three positive curvatures where $\rho(\mathbf{r})$ is a local minimum at $\mathbf{r}_c$.

The topology features of MESP is entirely different from that of MED. The $\lambda_{\rho 1}$, $\lambda_{\rho 2}$, and $\lambda_{\rho 3}$ are the eigenvalues corresponding to the electron density, $\rho(\mathbf{r})$ while λ_{v1}, λ_{v2}, and λ_{v3} are corresponding to the electrostatic potential, $V(\mathbf{r})$. The MED is a function of electron density only which is always positive (Eq. 3 in the MS) whereas MESP incorporates bare nuclear potential as well as potential caused by the continuous electron density (Eq. 1 in the MS) and it can assume positive, negative and zero values. At a critical point, all the first-order partial derivatives of the function become zero

$$\left.\frac{\partial V(r)}{\partial x_i}\right|_{CP} = 0 \; where \; i = 1,2,3\ldots,n$$

The nature of the CP is decided by the signs of the eigenvalues of the Hessian matrix at that point.

$$H_{ij} = \left.\frac{\partial^2 V(r)}{\partial x_i \partial x_j}\right|_{CP}$$

In the case of non-degenerate CP, none of the eigenvalues of the Hessian matrix is zero and for degenerate CP at least one of the eigenvalues of the Hessian matrix is zero. A function of three variables is always characterized by three eigenvalues. Among them, if two are negative and one is positive, then it is a (3, -1) CP. i.e., For a (3, -1) CP two of the eigenvalues must be negative and one must be positive. The eigenvalues of the MESP cannot be compared with that of MED.