Next Generation QTAIM for the Design of Quinone-based Switches

Tian Tian¹, Tianlv Xu¹, Lingling Wang¹, Yang Ping¹, Tanja van Mourik², Herbert Früchtl², Steven R. Kirk*¹
and Samantha Jenkins*¹

¹Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research and Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province of MOE, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China
²EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife KY16 9ST, Scotland, United Kingdom.

*email: samanthajsuman@gmail.com
*email: steven.kirk@cantab.net

1. Supplementary Materials S1. The variation of the metallicity $\xi(r_b)$ with the IRC for N10--H13 BCP and N11--H13 BCP.

2. Supplementary Materials S2. The QTAIM, bond-path framework set $B = \{p,q,r\}$.

3. Supplementary Materials S3. The complete set of $\{q,q'\}$-paths for the quinone switch.

1. Supplementary Materials S1.

Figure S1. The variation of the metallicity $\xi(r_b)$ with the IRC for N10--H13 BCP and N11--H13 BCP of the F-decorated quinone switch without and with are presented in sub-figures (a-d), respectively.
2. Supplementary Materials S2

With \( n \) scaled eigenvector \( e_2 \) tip path points on the \( q \)-path where \( \varepsilon_i = \) ellipticity at the \( i^{th} \) bond-path point \( r_i \) on the bond-path \( r \). It should be noted that the bond-path \( r \) is associated with the \( \lambda_3 \) eigenvalues of the \( e_3 \) eigenvector does not take into account differences in the \( \lambda_1 \) and \( \lambda_2 \) eigenvalues of the \( e_1 \) and \( e_2 \) eigenvectors. Analogously, for the \( e_1 \) tip path points on the \( p \)-path where \( \varepsilon_i = \) ellipticity at the \( i^{th} \) bond-path point \( r_i \) on the bond-path \( r \), where the \( p_i \) and \( q_i \) are defined by:

\[
\begin{align*}
    p_i &= r_i + \varepsilon_i e_{1,i} \\
    q_i &= r_i + \varepsilon_i e_{2,i}
\end{align*}
\]  

(3a) (3b)

We referred to the next-generation QTAIM interpretation of the chemical bond as the bond-path framework set, denoted by \( B \), where \( B = \{p,q,r\} \) with the consequence that for the ground state a bond is comprised of three ‘linkages’; \( p-, q- \) and \( r- \)paths associated with the \( e_1, e_2 \) and \( e_3 \) eigenvectors, respectively. The \( p \) and \( q \) parameters define eigenvector-following paths with lengths \( H^* \) and \( H \), see Scheme 2:

\[
\begin{align*}
    H^* &= \sum_{i=1}^{n} |p_{r_i} - p_i| \\
    H &= \sum_{i=1}^{n} |q_{r_i} - q_i|
\end{align*}
\]  

(4a) (4b)

The lengths of the eigenvector-following paths \( H^* \) or \( H \) refers to the fact that the tips of the scaled \( e_1 \) or \( e_2 \) eigenvectors sweep out along the extent of the bond-path, defined by the \( e_3 \) eigenvector, between two bonded nuclei connected by a bond-path. In the limit of vanishing ellipticity \( \varepsilon = 0 \), for all steps \( i \) along the bond-path then \( H = BPL \).

From equation (3a) and equation (3b) we see for shared-shell BCPs, in the limit of the ellipticity \( \varepsilon \approx 0 \) i.e. corresponding to single bonds, we then have \( p_i = q_i = r_i \) and therefore the value of the lengths \( H^* \) and \( H \) attain their lowest limit; the bond-path length \( (r) \) BPL. Conversely, higher values of the ellipticity \( \varepsilon \), for instance, corresponding to double bonds will always result in values of \( H^* \) and \( H \) > BPL.

Analogous to the bond-path curvature, see equation (2), we may define dimensionless, fractional versions of the eigenvector-following path with length \( H \) where several forms are possible and not limited to the following:

\[
    H_f = (H - BPL) / BPL
\]

(5)

A similar expressions to equation (5) for \( H^*_f \) can be derived using the \( e_1 \) eigenvector.
Figure S1. The pale-blue line in sub-figure (a) represents the path, referred to as the eigenvector-following path with length $H^*$, swept out by the tips of the scaled $e_1$ eigenvectors, shown in magenta, and defined by equation (4a). The red path in sub-figure (b) corresponds to $H$, constructed from the path swept out by the tips of the scaled $e_2$ eigenvectors, shown in mid-blue and is defined by equation (4b). The pale-blue and mid-blue arrows representing the $e_1$ and $e_2$ eigenvectors are scaled by the ellipticity $\varepsilon$ respectively, where the vertical scales are exaggerated for visualization purposes. The green sphere indicates the position of a given BCP.
3. Supplementary Materials S3.

(a)

(b)

(c)
Figure S3. The \( \{q,q'\} \)-paths of the quinone switch doped and undoped with Fe with F(UP) decorated is shown in sub-figures (a-b) respectively and F(DOWN) in sub-figures (c-d) respectively. The undecorated green and red spheres indicate the positions of the bond critical points (BCPs) and ring critical points (RCP), see also Scheme 1 for the atom numbering scheme.

**Figure S4.** The \( \{p, p'\} \)-paths of the quinone switch doped and undoped with Fe with F(UP) decorated is shown in sub-figures (a-b) and F(DOWN) in sub-figures (c-d). The see the captions of Figure S3 and Figure 1 for further details.