Next Generation QTAIM for Scoring Molecular Wires in E-fields for Molecular Electronic Devices

Alireza Azizi¹, Roya Momen¹, Herbert Früchtl², Tanja van Mourik², Steven R. Kirk^{*1} and Samantha Jenkins^{*1}

¹Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research and Key Laboratory of Resource National and Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China

²EaStCHEM School of Chemistry, University of Saint Andrews, North Haugh, St Andrews, Fife KY16 9ST, Scotland, United Kingdom.

email: steven.kirk@cantab.net

email: samanthajsuman@gmail.com

1. Supplementary Materials S1. The variations of ellipticity ε profiles with distance along the bond-path and the values of the bond-path lengths (BPL) for external electric field, $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$.

2. Supplementary Materials S2. Two views of the QTAIM ethene molecular graph displaying the $\{p,p'\}$ and $\{q,q'\}$ paths for values of the external electric field, $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$.

3. Supplementary Materials S3. The real space trajectory $\mathbb{T}(s)$ lengths l and the variation of eigenvector following path lengths $\mathbb{H}$, $\mathbb{H}'$, $\mathbb{H}^*$ and $\mathbb{H}'^*$ for external electric field, $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$.

4. Supplementary Materials S4. The stress tensor BCP and bond-path properties.

1. Supplementary Materials S1. The variations of ellipticity ε profiles with distance (in a.u) along the bond-path for external electric field, $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$.

Figure S1(i). The variations of ellipticity ε profiles with distance (in a.u) along the bond-path for the values of the applied $\mathbf{E}$ -field (in a.u); $\mathbf{E}_x$ is presented in sub-figures (a-c) respectively. See **Figure 3** for further details.

Figure S1(ii). The variations of ellipticity ε profiles with distance (in a.u.) along the bond-path for the values of the applied E -field (in a.u.); E_y is presented in sub-figures (a-c) respectively. See **Figure 3** for further details.

Figure S1(iii). The variations of ellipticity ε profiles with distance (in a.u.) along the bond-path for the values of the applied $\mathbf{E}$ -field (in a.u.); $\mathbf{E}_z$ is presented in sub-figures (a-c) respectively. See **Figure 3** for further details.

2. Supplementary Materials S2. Two views of the QTAIM ethene molecular graph displaying the $\{p,p'\}$ and $\{q,q'\}$ paths for values of the external electric field, $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$.

Figure S2(i). Two views of the QTAIM ethene molecular graph displaying the $\{p,p'\}$ paths for values of the external electric field, $\mathbf{E}_x = -200 \times 10^{-4}$ au, $\mathbf{E}_x = 0$ and $\mathbf{E}_x = +200 \times 10^{-4}$ au are presented in sub-figures (a-c) respectively. See **Figure 1** for further details.

Figure S2(ii). The QTAIM ethene molecular graph displaying the $\{p,p'\}$ and $\{q,q'\}$ path-packets for values of the external electric field, $\mathbf{E}_{x,y,z} = -200 \times 10^{-4}$ au (pale-blue/pale-magenta), $\mathbf{E}_{x,y,z} = 0$ (blue/red) and $\mathbf{E}_{x,y,z} = +200 \times 10^{-4}$ au (dark-blue/dark-magenta), are presented in sub-figures (a-c) respectively. See **Figure 1** for further details.

Figure S2(iii). The bond-path framework set $\mathbb{B}$ displaying two views of the $\{q, q'\}$ path-packets for values of the external electric field, $\mathbf{E}_z = -200 \times 10^{-4}$ au, $\mathbf{E}_z = 0$ and $\mathbf{E}_z = +200 \times 10^{-4}$ au, are presented in sub-figures (a-c) respectively, see the middle panel of **Figure 3** for the superimposed plots of $\mathbf{E}_z$.

Figure S2(iv). Two views of the QTAIM ethene molecular graph displaying the $\{p, p'\}$ paths for values of the external electric field, $E_y = -200 \times 10^{-4}$ au, $E_y = 0$ and $E_y = +200 \times 10^{-4}$ au are presented in sub-figures (a-c) respectively. See **Figure 1** for further details.

Figure S2(v). Two views of the QTAIM ethene molecular graph displaying the $\{p,p'\}$ paths for values of the external electric field, $E_z = -200 \times 10^{-4}$ au, $E_z = 0$ and $E_z = +200 \times 10^{-4}$ au are presented in sub-figures (a-c) respectively. See **Figure 1** for further details.

Table S2(a). The values of the bond-path lengths (BPL) (in a.u) for the applied **E**-field (in a.u); E_x , E_y and E_z are presented respectively. See **Figure 4** and **Supplementary Materials S2(i), S2(ii) and S2(iii)** for further details.

E-field	E_x				
	<i>C2-BCP, BCP-C1</i>	<i>C1-BCP, BCP-H4</i>	<i>H6-BCP, BCP-C1</i>	<i>C2-BCP, BCP-H3</i>	<i>H5-BCP, BCP-C2</i>
-200	1.2807, 1.2199	1.3370, 0.6790	0.6790, 1.3370	1.2898, 0.7291	0.7291, 1.2898
-100	1.2654, 1.2352	1.3249, 0.6918	0.6918, 1.3249	1.3012, 0.7170	0.7170, 1.3012
0	1.2503, 1.2503	1.3129, 0.7045	0.7045, 1.3129	1.3129, 0.7045	0.7045, 1.3129
+100	1.2352, 1.2654	1.3012, 0.7170	0.7170, 1.3012	1.3249, 0.6918	0.6918, 1.3249
+200	1.2199, 1.2807	1.2898, 0.7291	0.7291, 1.2898	1.3370, 0.6790	0.6790, 1.3370

E-field	E_y				
	<i>C2-BCP, BCP-C1</i>	<i>C1-BCP, BCP-H4</i>	<i>H6-BCP, BCP-C1</i>	<i>C2-BCP, BCP-H3</i>	<i>H5-BCP, BCP-C2</i>
-200	1.2503, 1.2503	1.3383, 0.6776	0.7313, 1.2876	1.3383, 0.6776	0.7313, 1.2876
-100	1.2503, 1.2503	1.3256, 0.6911	0.7180, 1.3003	1.3256, 0.6911	0.7180, 1.3003
0	1.2503, 1.2503	1.3129, 0.7045	0.7045, 1.3129	1.3129, 0.7045	0.7045, 1.3129
+100	1.2503, 1.2503	1.3003, 0.7180	0.6911, 1.3256	1.3003, 0.7180	0.6911, 1.3256
+200	1.2503, 1.2503	1.2876, 0.7313	0.6776, 1.3383	1.2876, 0.7313	0.6776, 1.3383

E-field	E_z				
	<i>C2-BCP, BCP-C1</i>	<i>C1-BCP, BCP-H4</i>	<i>H6-BCP, BCP-C1</i>	<i>C2-BCP, BCP-H3</i>	<i>H5-BCP, BCP-C2</i>
-200	1.2503, 1.2503	1.3142, 0.7032	0.7032, 1.3142	1.3142, 0.7032	0.7032, 1.3142
-100	1.2503, 1.2503	1.3132, 0.7042	0.7042, 1.3132	1.3132, 0.7042	0.7042, 1.3132
0	1.2503, 1.2503	1.3129, 0.7045	0.7045, 1.3129	1.3129, 0.7045	0.7045, 1.3129
+100	1.2503, 1.2503	1.3132, 0.7042	0.7042, 1.3132	1.3132, 0.7042	0.7042, 1.3132
+200	1.2503, 1.2503	1.3142, 0.7032	0.7032, 1.3142	1.3142, 0.7032	0.7032, 1.3142

Table S2(b). The total values of the bond-path lengths (BPL) (in a.u) for the applied **E**-field (in a.u); **E_x**, **E_y** and **E_z** are presented respectively. See **Figure 4** and **Supplementary Materials S2(i), S2(ii) and S2(iii)** for further details.

E -field	E_x					E_y					E_z				
	C2-C1	C1-H4	H6-C1	C2-H3	H5-C2	C2-C1	C1-H4	H6-C1	C2-H3	H5-C2	C2-C1	C1-H4	H6-C1	C2-H3	H5-C2
-200	2.5006	2.0160	2.0160	2.0189	2.0189	2.5006	2.0159	2.0189	2.0159	2.0189	2.5006	2.0174	2.0174	2.0174	2.0174
-100	2.5006	2.0167	2.0167	2.0182	2.0182	2.5006	2.0167	2.0183	2.0167	2.0183	2.5006	2.0174	2.0174	2.0174	2.0174
0	2.5006	2.0174	2.0174	2.0174	2.0174	2.5006	2.0174	2.0174	2.0174	2.0174	2.5006	2.0174	2.0174	2.0174	2.0174
+100	2.5006	2.0182	2.0182	2.0167	2.0167	2.5006	2.0183	2.0167	2.0183	2.0167	2.5006	2.0174	2.0174	2.0174	2.0174
+200	2.5006	2.0189	2.0189	2.0160	2.0160	2.5006	2.0189	2.0159	2.0189	2.0159	2.5006	2.0174	2.0174	2.0174	2.0174

3. Supplementary Materials S3.

Table S3(a). The real space trajectory $\mathbb{T}(s)$ lengths l in atomic units (in a.u) for the values of the applied $\mathbf{E}$ -field (in a.u), $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$ are presented.

BCP	$l_{(-x), (+x)}$	$l_{(-y), (+y)}$	$l_{(-z), (+z)}$
C1-C2	0.030, 0.030	0.008, 0.008	0.004, 0.004
C1-H4	0.025, 0.024	0.025, 0.025	0.003, 0.003
C1-H6	0.025, 0.024	0.025, 0.025	0.003, 0.003
C2-H3	0.024, 0.025	0.025, 0.025	0.003, 0.003
C2-H5	0.024, 0.025	0.025, 0.025	0.003, 0.003

Table S3(b). The variation of the QTAIM eigenvector following path lengths $\mathbb{H}$, $\mathbb{H}'$, $\mathbb{H}^*$ and $\mathbb{H}'^*$ of the symmetry inequivalent values for the applied $\mathbf{E}$ -field (in a.u); $(\mathbf{E}_x, \mathbf{E}_y, \mathbf{E}_z)$ are provided respectively.

BCP	$\mathbb{H}_{(-200, 0, +200)}$	$\mathbb{H}'_{(-200, 0, +200)}$	$\mathbb{H}^*_{(-200, 0, +200)}$	$\mathbb{H}'^*_{(-200, 0, +200)}$
C1-C2	(2.733, 2.714, 2.733)	(2.733, 2.714, 2.733)	(2.733, 2.714, 2.733)	(2.733, 2.714, 2.733)
C1-H4	(2.068, 2.043, 2.027)	(2.067, 2.040, 2.026)	(2.067, 2.041, 2.026)	(2.068, 2.041, 2.026)
C1-H6	(2.068, 2.043, 2.027)	(2.067, 2.040, 2.026)	(2.067, 2.041, 2.026)	(2.068, 2.041, 2.026)
C2-H3	(2.026, 2.040, 2.067)	(2.027, 2.043, 2.068)	(2.026, 2.041, 2.068)	(2.026, 2.041, 2.067)
C2-H5	(2.026, 2.040, 2.067)	(2.027, 2.043, 2.068)	(2.026, 2.041, 2.068)	(2.026, 2.041, 2.067)

4. Supplementary Materials S4. The stress tensor BCP and bond-path properties.

Table S4. The variation of the stress tensor eigenvector following path lengths values $\mathbb{H}_\sigma$, $\mathbb{H}_\sigma'$, $\mathbb{H}_\sigma^*$ and $\mathbb{H}_\sigma^{*}$ for the applied $\mathbf{E}$ -field (in a.u); $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$ are presented respectively.

BCP	$\mathbb{H}_\sigma(-200, 0, +200)$	$\mathbb{H}_\sigma'(-200, 0, +200)$	$\mathbb{H}_\sigma^*(-200, 0, +200)$	$\mathbb{H}_\sigma^{*}(-200, 0, +200)$
C1-C2	(2.531, 2.528, 2.531)	(2.531, 2.528, 2.531)	(2.531, 2.528, 2.531)	(2.531, 2.528, 2.531)
C1-H4	(2.029, 2.024, 2.022)	(2.029, 2.024, 2.022)	(2.028, 2.023, 2.021)	(2.029, 2.025, 2.022)
C1-H6	(2.029, 2.024, 2.022)	(2.029, 2.024, 2.022)	(2.028, 2.023, 2.021)	(2.029, 2.025, 2.022)
C2-H3	(2.022, 2.024, 2.029)	(2.022, 2.024, 2.029)	(2.022, 2.025, 2.029)	(2.021, 2.023, 2.028)
C2-H5	(2.022, 2.024, 2.029)	(2.022, 2.024, 2.029)	(2.022, 2.025, 2.029)	(2.021, 2.023, 2.028)

(a)

(b)

Figure 4(i). The variations of the path-packet area the applied $\mathbf{E}$ -field (in a.u); $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$ for the stress tensor in sub-figure (a). The variations of ϵ_σ profiles with distance (in a.u) along the bond-path with applied $\mathbf{E}$ -field (in a.u); $\mathbf{E}_x$, $\mathbf{E}_y$ and $\mathbf{E}_z$ are presented in sub-figures (b-d) respectively.

Figure S4(ii). The stress tensor ethene molecular graph displaying the $\{p_{\sigma}, p_{\sigma}'\}$ (left-panel) and $\{q_{\sigma}, q_{\sigma}'\}$ (right-panel) path-packets for values of the external electric field, $\mathbf{E}_{x,y,z} = -200 \times 10^{-4}$ au (pale-blue/pale-magenta), $\mathbf{E}_{x,y,z} = 0$ (blue/red) and $\mathbf{E}_{x,y,z} = +200 \times 10^{-4}$ au (dark-blue/dark-magenta), with a magnification factor x5 are provided in sub-figures (a-c) respectively. $\mathbf{E}_{x,y,z} = 0$ ethene molecular graph have been used in all sub-figures.