Understanding the Effects of Electric Fields on Molecules through Gradient Path Curvatures

Supplementary Information

Nikodemos Hughes[1], Charles Morgenstern[2],
Amanda Morgenstern[1*]

[1]Chemistry & Biochemistry, University of Colorado Colorado Springs,
1420 Austin Bluffs Parkway, Colorado Springs, 80918, CO, USA.
[2]Colorado Springs, CO, USA.

*Corresponding author(s). E-mail(s): amorgens@uccs.edu;

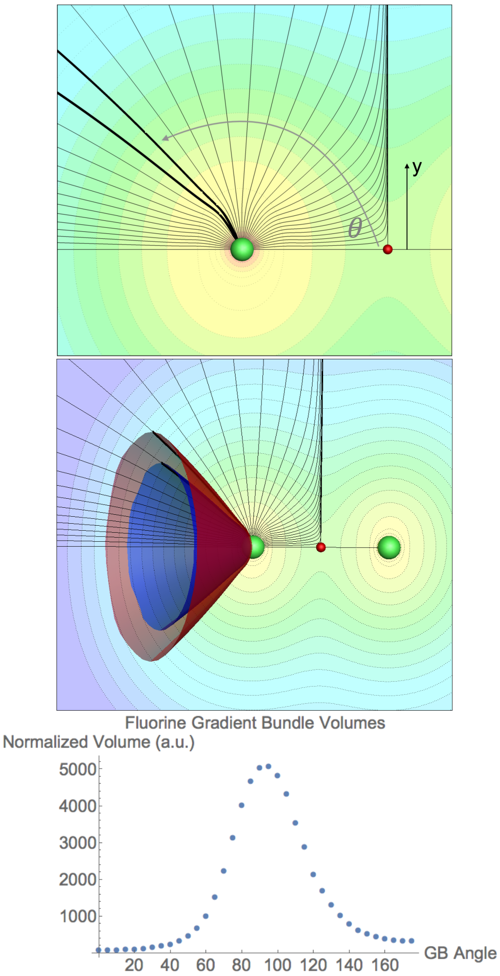

Fig. S1 Construction of a rotational gradient bundle around one fluorine nucleus in F_2. Top: Gradient paths seeded every 5° around the top half of a nucleus in the plane of the molecule as shown by the angle θ. Middle: ZFSs bounding GBs are created by rotating two neighboring GPs around the bond axis. Green sphere, nuclear CP; Red sphere, bond CP. Contours indicate values of $\rho(\boldsymbol{r})$. Bottom: Normalized volumes of GBs in one atomic basin of F_2.

Fig. S1 shows the (intensive) properties of rotational GBs are a function only of the angle, θ, generating a 1D property distribution, where θ is the angle between a GP at its initial seed point and the bond path. Numerical integrations of rotational GBs are calculated by integrating $A * 2\pi y$ where A is the property of interest ($\rho(\boldsymbol{r})$, kinetic energy, etc.) at a point in the 2D slice of the GB through the molecule and y is the distance of the point from the bond path along the y-direction. Due to the rotation around the internuclear axis, the size of GBs varies throughout each atomic basin. Normalized volumes are calculated by taking the volume of each gradient bundle and dividing by the volume the bundle would have if the charge density were spherical.

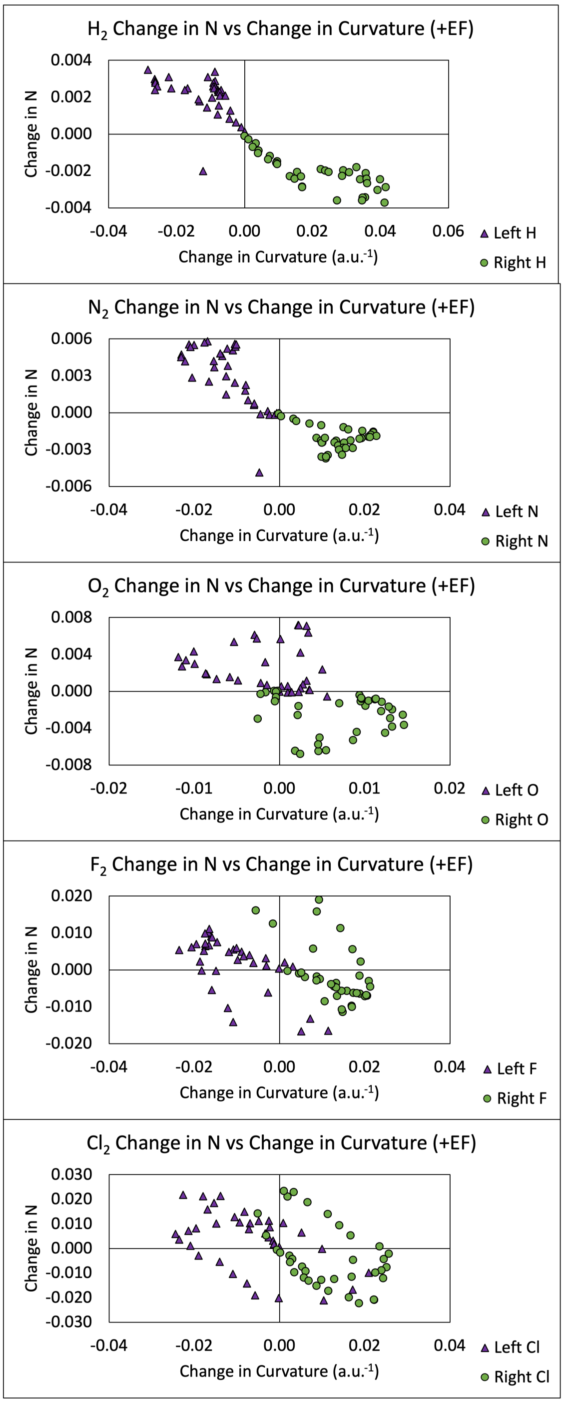

Fig. S2 Plots of ΔN vs. $\Delta\overline{\kappa}$ with a 1 V/Å EF applied along the bonds from the left to right atom in homonuclear diatomics

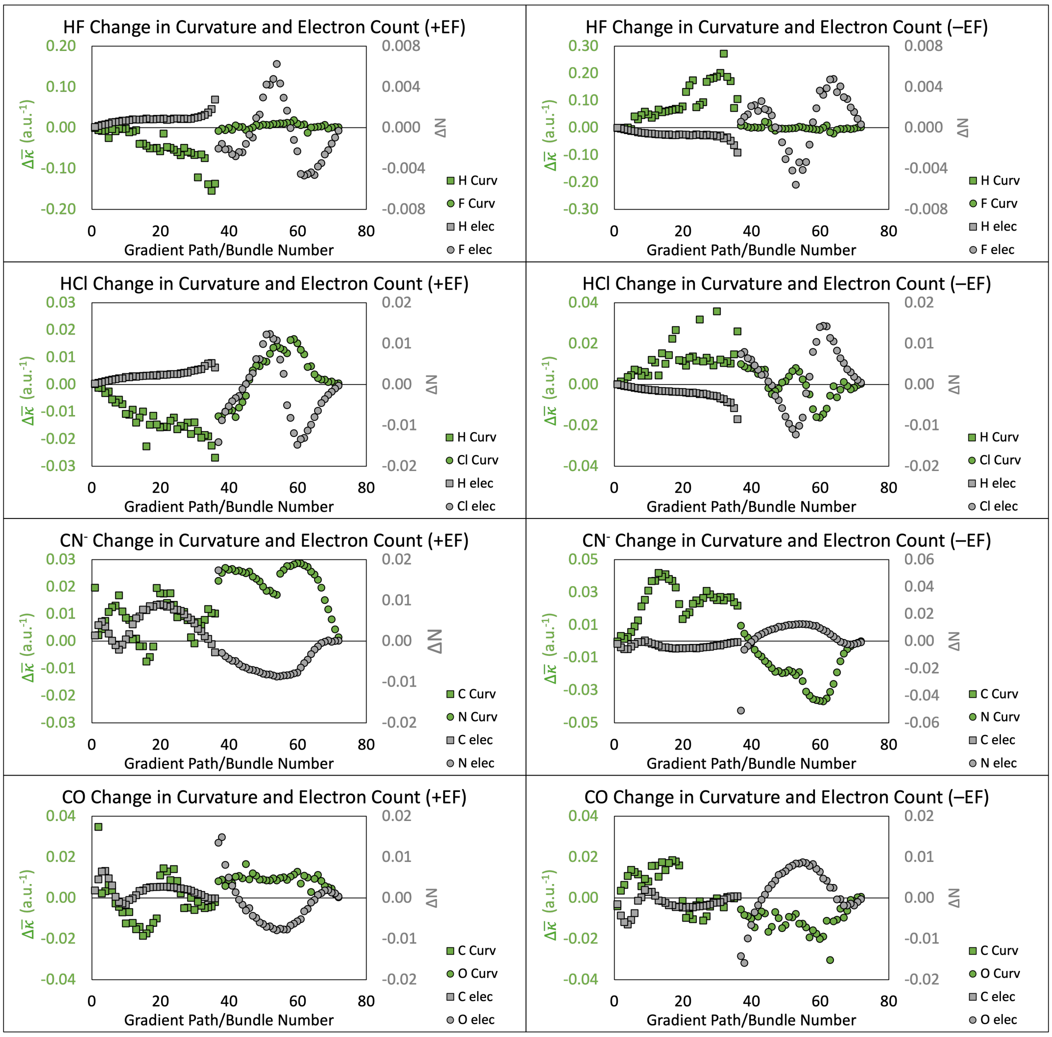

Fig. S3 Changes in gradient path $\bar{\kappa}$ and changes in GB electron counts, N, with a 1 V/Å EF applied along the bonds from the left to right atom in heteronuclear diatomic molecules

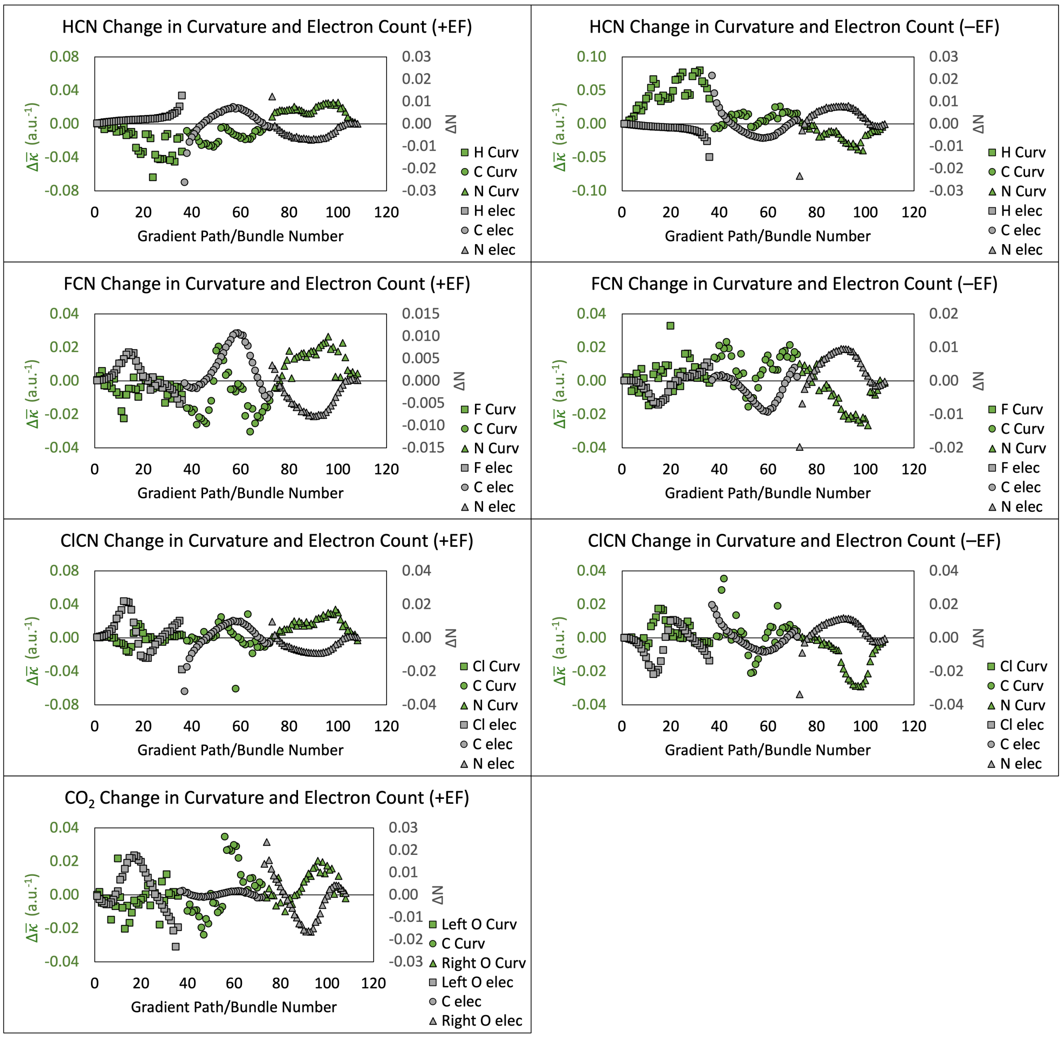

Fig. S4 Changes in gradient path $\overline{\kappa}$ and changes in GB electron counts, N, with a 1 V/Å EF applied along the bonds from the left to right atom in triatomic molecules

Table S1 Average gradient path $\Delta\overline{\kappa}$ and average changes in GB electron counts, N, with a 1 V/Å EF applied along the bonds. Data is organized by atom type.

Molecule (EF)	Atom	Average $\Delta\overline{\kappa}$ (a.u.$^{-1}$)	Average Δ N
N_2	Left N	-0.0115	0.0029
N_2	Right N	0.0135	-0.0029
HCN (+EF)	N	0.0159	-0.0036
FCN (+EF)	N	0.0122	-0.0037
ClCN (+EF)	N	0.0157	-0.0044
CN- (+EF)	N	0.0219	-0.0046
HCN (−EF)	N	-0.0151	0.0033
HCN (−EF)	N	-0.0079	0.0034
ClCN (−EF)	N	-0.0105	0.0039
ClCN (−EF)	N	-0.0162	0.0038
H_2	Left H	-0.0122	0.0021
H_2	Right H	0.0217	-0.0021
HF (+EF)	H	-0.0464	0.0008
HCl (+EF)	H	-0.0127	0.0023
HCN (+EF)	H	-0.0202	0.0024
HF (−EF)	H	0.0896	-0.0007
HCl (−EF)	H	0.0116	-0.0022
HCN (−EF)	H	0.0449	-0.0024
O_2	Left O	-0.0016	0.0025
O_2	Right O	0.0068	-0.0025
CO (+EF)	O	0.0085	-0.0017
CO_2	Left O	-0.0026	0.0015
CO_2	Right O	0.0054	-0.0017
CO (−EF)F	O	-0.0110	0.0016
F_2	Left F	-0.0104	0.0017
F_2	Right F	0.0128	-0.0017
HF (+EF)	F	0.0025	-0.0008
FCN (+EF)	F	-0.0045	0.0008
HF (−EF)	F	-0.0024	0.0007
FCN (−EF)	F	0.0029	-0.0008
Cl_2	Left Cl	-0.0074	0.0038
Cl_2	Right Cl	0.0113	-0.0038
HCl (+EF)	Cl	0.0034	-0.0023
ClCN (+EF)	Cl	-0.0005	0.0029
HCl (−EF)	Cl	-0.0006	0.0022
ClCN (−EF)	Cl	0.0024	-0.0039
CO (+EF)	C	0.0015	0.0017
HCN (+EF)	C	-0.0144	0.0012
FCN (+EF)	C	-0.0111	0.0029
ClCN (+EF)	C	-0.0014	0.0007
CN- (+EF)	C	0.0078	0.0042
CO_2	C	0.0027	0.0002
CO (−EF)	C	0.0041	-0.0016
HCN (−EF)	C	0.0082	-0.0009
HCN (−EF)	C	0.0089	-0.0026
ClCN (−EF)	C	0.0018	-0.0005
CN- (−EF)	C	0.0233	-0.0037