

Supplementary Material for:

Pauling's Conceptions of Hybridization and Resonance in Modern Quantum Chemistry

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3. Directional Hybridization

The following is a single, multi-step Gaussian-16 input file that completes frequency calculations and NBO7 analysis for each of the MP2/aug-cc-pVTZ optimized geometries of the main-group hydrides of Table 1.

```
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read
```

```
BH3...mp2/avtz
```

```
O 1
B 0.000000 0.000000 0.000000
H 0.000000 1.187202 0.000000
H 1.028147 -0.593601 0.000000
H -1.028147 -0.593601 0.000000
```

```
$nbo archive file=bh3-mp2 $end
```

```
--Link1--
```

```
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read
```

```
CH4...mp2/avtz
```

```
O 1
C 0.000000 0.000000 0.000000
H 0.627106 0.627106 0.627106
H -0.627106 -0.627106 0.627106
H -0.627106 0.627106 -0.627106
H 0.627106 -0.627106 -0.627106
```

```
$nbo archive file=ch4-mp2 $end
```

```
--Link1--
```

```
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read
```

```
NH3...mp2/avtz
```

```
O 1
N 0.000000 0.000000 0.114012
H 0.000000 0.938063 -0.266027
H 0.812387 -0.469032 -0.266027
```

H -0.812387 -0.469032 -0.266027

\$nbo archive file=nh3-mp2 \$end

--Link1--

#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

H2O...mp2/avtz

O 1

O 0.000000 0.000000 0.118232

H 0.000000 0.758133 -0.472927

H 0.000000 -0.758133 -0.472927

\$nbo archive file=h2o-mp2 \$end

--Link1--

#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

HF...mp2/avtz

O 1

F 0.000000 0.000000 0.092184

H 0.000000 0.000000 -0.829654

\$nbo archive file=hf-mp2 \$end

--Link1--

#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

AlH3...mp2/avtz

O 1

Al 0.000000 0.000000 0.000000

H 0.000000 1.579872 0.000000

H -1.368209 -0.789936 0.000000

H 1.368209 -0.789936 0.000000

\$nbo archive file=alh3-mp2 \$end

--Link1--

#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

SiH4...mp2/avtz

O 1

Si 0.000000 0.000000 0.000000

H 0.853257 0.853257 0.853257

H -0.853257 -0.853257 0.853257

H -0.853257 0.853257 -0.853257

H 0.853257 -0.853257 -0.853257

\$nbo archive file=sih4-mp2 \$end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

PH3...mp2/avtz

O	1			
P		0.000000	0.000000	0.127012
H		0.000000	1.189254	-0.635061
H		1.029924	-0.594627	-0.635061
H		-1.029924	-0.594627	-0.635061

\$nbo archive file=ph3-mp2 \$end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

H2S...mp2/avtz

O	1			
S		0.000000	0.000000	0.102929
H		0.000000	0.963093	-0.823429
H		0.000000	-0.963093	-0.823429

\$nbo archive file=h2s-mp2 \$end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

HCl...mp2/avtz

O	1			
Cl		0.000000	0.000000	0.070819
H		0.000000	0.000000	-1.203922

\$nbo archive file=hcl-mp2 \$end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

GaH3...mp2/avtz

O	1			
Ga		0.000000	0.000000	0.000000
H		0.000000	1.548180	0.000000
H		-1.340763	-0.774090	0.000000
H		1.340763	-0.774090	0.000000

\$nbo archive file=gah3-mp2 \$end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

GeH4...mp2/avtz

```

0 1
Ge 0.000000 0.000000 0.000000
H 0.872835 0.872835 0.872835
H -0.872835 -0.872835 0.872835
H -0.872835 0.872835 -0.872835
H 0.872835 -0.872835 -0.872835

$nbo archive file=geh4-mp2 $end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

AsH3...mp2/avtz

0 1
As 0.000000 0.000000 0.068882
H 0.000000 1.250750 -0.757701
H 1.083181 -0.625375 -0.757701
H -1.083181 -0.625375 -0.757701

$nbo archive file=ash3-mp2 $end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

H2Se...mp2/avtz

0 1
Se 0.000000 0.000000 0.056417
H 0.000000 1.035567 -0.959086
H 0.000000 -1.035567 -0.959086

$nbo archive file=h2se-mp2 $end

--Link1--
#mp2/aug-cc-pVTZ density=mp2 freq pop=nbo7read

HBr...mp2/avtz

0 1
Br 0.000000 0.000000 0.039072
H 0.000000 0.000000 -1.367534

$nbo archive file=hbr-mp2 $end

```

4. Resonance Delocalization

The following is a single, multi-step Gaussian-16 input file that completes frequency calculations and NBO7/NRT analysis for B3LYP/aug-cc-pVTZ optimized geometries of formamide, formimidic acid, and the transition state.

```
#b3lyp/aug-cc-pVTZ freq pop=nbo7read

Formamide...b3lyp/avtz

0 1
C 0.000000 0.418861 0.000000
O 1.196495 0.233360 0.000000
N -0.937329 -0.562322 0.000000
H -0.446298 1.428425 0.000000
H -0.646688 -1.526074 0.000000
H -1.917677 -0.346147 0.000000

$nbo nrt archive file=formamide $end

--Link1--
#b3lyp/aug-cc-pVTZ freq pop=nbo7read

Formimidic acid...b3lyp/avtz

0 1
C 0.000000 0.416598 0.000000
O -1.110473 -0.343364 0.000000
N 1.156615 -0.083827 0.000000
H -0.263395 1.473261 0.000000
H -0.825669 -1.270012 0.000000
H 1.876541 0.630866 0.000000

$nbo nrt archive file=formimidic-acid $end

--Link1--
#b3lyp/aug-cc-pVTZ freq pop=nbo7read

Formamide -> Formimidic acid TS...b3lyp/avtz

0 1
C 0.000000 0.509746 0.000000
O -1.099333 -0.147985 0.000000
N 0.988617 -0.331290 0.000000
H 0.036873 1.595627 0.000000
H -0.131137 -1.064739 0.000000
H 1.968609 -0.086449 0.000000

$nbo nrt archive file=ts $end
```

The following is a sample Gaussian-16 input file showing the set of \$NBO keylist keywords used to complete NRT analysis of the IRC geometry corresponding to the leftmost point of Figure 3. The resonance hybrid is restricted to the four bonding patterns specified in the \$NRTSTR keylist input. NRT analysis yields the weights of the leftmost points of Figure 5. See the *NBO 7.0 Program Manual* [37] for a description of NBO/NRT keywords.

```
#b3lyp/aug-cc-pVTZ pop=nbo7read

Point= -130   IRC= -2.68835   Energy=  -169.969711361 a.u. ###

0  1
C   -0.023518    0.433276    0.000000
O   -1.135351   -0.046133    0.000000
N    1.089975   -0.334942    0.000000
H    0.174323    1.518274    0.000000
H    0.960009   -1.333351    0.000000
H    2.020075    0.042092    0.000000

$nbo
  nrte2=off nrtabi=off nrtdeg=off nrtlst=0.1 thrmin=1.1 prjthr=0.1
$end
$nrtstr
  str                      ! Structure F1
    lone 2 2 3 1 end
    bond d 1 2 s 1 3 s 1 4 s 3 5 s 3 6 end
  end
  str                      ! Structure F2
    lone 2 3 end
    bond s 1 2 d 1 3 s 1 4 s 3 5 s 3 6 end
  end
  str                      ! Structure FA1
    lone 2 2 3 1 end
    bond s 1 2 d 1 3 s 1 4 s 2 5 s 3 6 end
  end
  str                      ! Structure FA2
    lone 2 1 3 2 end
    bond d 1 2 s 1 3 s 1 4 s 2 5 s 3 6 end
  end
$end
```

The following is a list (in XYZ file format) of the IRC geometries of Figure 3.

6
Point= -130 IRC= -2.68835 Energy= -169.969711361 a.u.
C -0.023518 0.433276 0.000000
O -1.135351 -0.046133 0.000000
N 1.089975 -0.334942 0.000000
H 0.174323 1.518274 0.000000
H 0.960009 -1.333351 0.000000
H 2.020075 0.042092 0.000000

6
Point= -120 IRC= -2.48155 Energy= -169.968679130 a.u.
C -0.021881 0.446923 0.000000
O -1.123689 -0.055643 0.000000
N 1.079418 -0.334643 0.000000
H 0.165598 1.533057 0.000000
H 0.907338 -1.326883 0.000000
H 2.023568 0.005124 0.000000

6
Point= -110 IRC= -2.27475 Energy= -169.967083424 a.u.
C -0.020319 0.460324 0.000000
O -1.111973 -0.065040 0.000000
N 1.069005 -0.334290 0.000000
H 0.156170 1.547557 0.000000
H 0.854496 -1.318523 0.000000
H 2.025968 -0.033075 0.000000

6
Point= -100 IRC= -2.06795 Energy= -169.964896201 a.u.
C -0.018552 0.473214 0.000000
O -1.100345 -0.074322 0.000000
N 1.058758 -0.333716 0.000000
H 0.146321 1.561465 0.000000
H 0.800039 -1.307664 0.000000
H 2.027072 -0.071973 0.000000

6
Point= -90 IRC= -1.86115 Energy= -169.962069060 a.u.
C -0.015995 0.485193 0.000000
O -1.089196 -0.083506 0.000000
N 1.048859 -0.332788 0.000000
H 0.136340 1.574340 0.000000
H 0.740736 -1.292905 0.000000
H 2.026492 -0.109381 0.000000

6
Point= -80 IRC= -1.65435 Energy= -169.958473126 a.u.
C -0.011819 0.495707 0.000000
O -1.079357 -0.092539 0.000000
N 1.039882 -0.331594 0.000000
H 0.126487 1.585558 0.000000
H 0.671984 -1.271784 0.000000
H 2.023950 -0.140133 0.000000

6
Point= -70 IRC= -1.44756 Energy= -169.953762279 a.u.
C -0.005634 0.504097 0.000000
O -1.071893 -0.101079 0.000000

N	1.032768	-0.330537	0.000000
H	0.117189	1.594279	0.000000
H	0.591990	-1.242068	0.000000
H	2.019979	-0.157622	0.000000

6

Point= -60 IRC= -1.24077 Energy= -169.947392182 a.u.

C	0.001867	0.510093	0.000000
O	-1.067066	-0.108673	0.000000
N	1.027995	-0.329924	0.000000
H	0.108940	1.600079	0.000000
H	0.504739	-1.204672	0.000000
H	2.015888	-0.160193	0.000000

6

Point= -50 IRC= -1.03397 Energy= -169.938982257 a.u.

C	0.009673	0.514032	0.000000
O	-1.064151	-0.115225	0.000000
N	1.025259	-0.329523	0.000000
H	0.101870	1.603383	0.000000
H	0.413684	-1.164628	0.000000
H	2.012828	-0.152031	0.000000

6

Point= -40 IRC= -0.82718 Energy= -169.928564937 a.u.

C	0.017120	0.516430	0.000000
O	-1.062332	-0.120860	0.000000
N	1.024205	-0.328764	0.000000
H	0.095880	1.604947	0.000000
H	0.318265	-1.129690	0.000000
H	2.011325	-0.138206	0.000000

6

Point= -30 IRC= -0.62038 Energy= -169.916808876 a.u.

C	0.023861	0.517799	0.000000
O	-1.061066	-0.125729	0.000000
N	1.024557	-0.327353	0.000000
H	0.090820	1.605494	0.000000
H	0.218418	-1.104485	0.000000
H	2.010978	-0.122573	0.000000

6

Point= -20 IRC= -0.41358 Energy= -169.905527456 a.u.

C	0.029931	0.518596	0.000000
O	-1.060046	-0.130079	0.000000
N	1.025870	-0.325488	0.000000
H	0.086418	1.605564	0.000000
H	0.116153	-1.086465	0.000000
H	2.010944	-0.107032	0.000000

6

Point= -10 IRC= -0.20678 Energy= -169.897314805 a.u.

C	0.035579	0.519117	0.000000
O	-1.059126	-0.134174	0.000000
N	1.027711	-0.323460	0.000000
H	0.082360	1.605456	0.000000
H	0.013064	-1.070864	0.000000
H	2.010670	-0.091926	0.000000

6

Point= 0 IRC= 0.00000 Energy= -169.894301419 a.u.

C	0.000000	0.509746	0.000000
O	-1.099333	-0.147985	0.000000
N	0.988617	-0.331290	0.000000
H	0.036873	1.595627	0.000000
H	-0.131137	-1.064739	0.000000
H	1.968609	-0.086449	0.000000

6

Point= 10 IRC= 0.20677 Energy= -169.897241253 a.u.

C	0.046479	0.519767	0.000000
O	-1.057582	-0.142207	0.000000
N	1.032105	-0.319403	0.000000
H	0.074703	1.605105	0.000000
H	-0.192897	-1.036675	0.000000
H	2.008950	-0.062386	0.000000

6

Point= 20 IRC= 0.41356 Energy= -169.905160260 a.u.

C	0.052176	0.519883	0.000000
O	-1.057172	-0.146183	0.000000
N	1.034527	-0.317380	0.000000
H	0.070679	1.604889	0.000000
H	-0.295411	-1.018390	0.000000
H	2.007493	-0.046849	0.000000

6

Point= 30 IRC= 0.62036 Energy= -169.915457448 a.u.

C	0.058513	0.519634	0.000000
O	-1.057471	-0.149880	0.000000
N	1.037270	-0.315198	0.000000
H	0.066060	1.604504	0.000000
H	-0.397733	-1.004356	0.000000
H	2.005601	-0.029162	0.000000

6

Point= 40 IRC= 0.82715 Energy= -169.924977573 a.u.

C	0.066021	0.518376	0.000000
O	-1.059370	-0.152570	0.000000
N	1.040845	-0.312566	0.000000
H	0.060294	1.603457	0.000000
H	-0.498488	-1.004560	0.000000
H	2.003195	-0.006808	0.000000

6

Point= 50 IRC= 1.03394 Energy= -169.932293476 a.u.

C	0.074382	0.514834	0.000000
O	-1.063734	-0.153165	0.000000
N	1.046091	-0.309306	0.000000
H	0.053295	1.600510	0.000000
H	-0.591859	-1.024177	0.000000
H	2.000391	0.022072	0.000000

6

Point= 60 IRC= 1.24073 Energy= -169.937732067 a.u.

C	0.082034	0.508051	0.000000
O	-1.070379	-0.151581	0.000000
N	1.053846	-0.305596	0.000000
H	0.046108	1.594276	0.000000
H	-0.675332	-1.048220	0.000000
H	1.997634	0.056424	0.000000

6

Point= 70 IRC= 1.44753 Energy= -169.941809727 a.u.

C	0.087697	0.498110	0.000000
O	-1.078808	-0.148199	0.000000
N	1.064481	-0.301701	0.000000
H	0.040034	1.584568	0.000000
H	-0.748361	-1.065568	0.000000
H	1.995333	0.094055	0.000000

6

Point= 80 IRC= 1.65432 Energy= -169.944928712 a.u.

C	0.091123	0.485904	0.000000
O	-1.088401	-0.143488	0.000000
N	1.077402	-0.297793	0.000000
H	0.035854	1.572440	0.000000
H	-0.810416	-1.075624	0.000000
H	1.993476	0.132516	0.000000

6

Point= 90 IRC= 1.86112 Energy= -169.947300264 a.u.

C	0.093012	0.472429	0.000000
O	-1.098598	-0.138038	0.000000
N	1.091600	-0.293868	0.000000
H	0.033499	1.559047	0.000000
H	-0.864091	-1.080736	0.000000
H	1.991573	0.170433	0.000000

6

Point= 100 IRC= 2.06792 Energy= -169.949009393 a.u.

C	0.094203	0.458350	0.000000
O	-1.109094	-0.132301	0.000000
N	1.106350	-0.289857	0.000000
H	0.032442	1.545088	0.000000
H	-0.913166	-1.082961	0.000000
H	1.989135	0.207466	0.000000

6

Point= 110 IRC= 2.27473 Energy= -169.950096381 a.u.

C	0.095224	0.444029	0.000000
O	-1.119750	-0.126530	0.000000
N	1.121308	-0.285714	0.000000
H	0.032072	1.530909	0.000000
H	-0.960500	-1.083431	0.000000
H	1.985970	0.243501	0.000000