Supplementary Information for "Mapping spin contamination-free potential energy surfaces using restricted open-shell methods with Grassmannians"

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A. Cartesian Coordinates and Definition of Dihedral Angle in Benzyl Radical Scan

TABLE S1: Cartesian coordinates for the RO-B3LYP/def2-TZVP optimized structure for benzyl radical.

Charge	Spin Multiplicity		
0	2		
Atom	X	Y	Z
H	0.0000000000	0.0000000000	0.0000000000
C	0.0000000000	0.0000000000	1.0830930900
C	1.2072711987	0.0000000000	1.7808534192
C	-1.2072711987	0.0000000000	1.7808534192
H	2.1457560422	0.0000000000	1.2401715902
H	-2.1457560422	0.0000000000	1.2401715902
C	1.2232122670	0.0000000000	3.1751701359
C	-1.2232122670	0.0000000000	3.1751701359
H	2.1670834399	0.0000000000	3.7063931122
H	-2.1670834399	0.0000000000	3.7063931122
C	0.0322093818	0.0000000000	3.9003496666
C	0.0658219443	0.0000000000	5.3046694038
H	0.7336620086	-0.6546770416	5.8467815877
H	-0.5753171777	0.6546770416	5.8781121626

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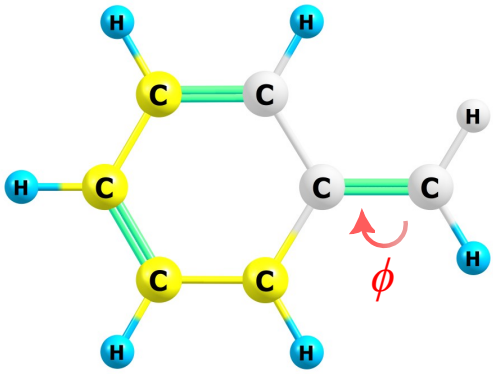

FIG. S1: The gray atoms are used to define the dihedral angle potential energy scan for benzyl radical.

B. The Interpolated Density Matrix for Benzyl Radical

From the optimized geometry, the dihedral angle between the benzyl and $-CH_2$ moieties were sampled in the range $-90.00^\circ \leq \phi \leq 90.00^\circ$ with a step size of $\phi = 10.00^\circ$. This grid corresponds to a total of 19 points. The information at $\phi = 0.00^\circ$ from the sampled points was used as the reference in defining the tangent space. From these sampled points, G-Int was conducted to interpolate points in the range $-85.00^\circ \leq \phi \leq 85.00^\circ$ with a step size of $\phi = 10.00^\circ$. The interpolation was conducted using an 18^{th}-order Lagrange interpolation.

TABLE S2: Quality of the interpolated density matrices for benzyl radical in the range $-90.00^\circ \leq \phi \leq 90.00^\circ$ with $d\phi = 10.00^\circ$. The corresponding RMS error for the GDM algorithm, initial SCF energy, and SCF energy error are also shown.

$\phi(^\circ)$	$\|\|\Delta\mathbf{P}^\alpha\|\|_\mathbf{F}$	$\|\|\Delta\mathbf{P}^\beta\|\|_\mathbf{F}$	RMS Gradient	$E^{\text{SCF}}_{\text{initial}}(E_\text{h})$	$E^{\text{SCF}}_{\text{initial}} - E^{\text{SCF}}_{\text{conv}}(E_\text{h})$
-85	2.47×10^{-1}	1.75×10^{-1}	1.22×10^{-2}	-270.9877625991	9.04×10^{-4}
-75	2.41×10^{-2}	1.69×10^{-2}	9.09×10^{-4}	-270.9900053968	8.10×10^{-6}
-65	4.35×10^{-3}	2.99×10^{-3}	1.50×10^{-4}	-270.9925794710	2.27×10^{-7}
-55	1.07×10^{-3}	7.86×10^{-4}	3.37×10^{-5}	-270.9961026156	1.47×10^{-8}
-45	3.49×10^{-4}	2.76×10^{-4}	1.60×10^{-5}	-271.0002579089	2.00×10^{-9}
-35	2.86×10^{-4}	1.28×10^{-4}	1.01×10^{-5}	-271.0045120012	6.00×10^{-10}
-25	3.38×10^{-4}	9.52×10^{-5}	5.53×10^{-6}	-271.0083237229	2.00×10^{-10}
-15	3.45×10^{-4}	1.01×10^{-4}	3.24×10^{-6}	-271.0111940995	1.00×10^{-10}
-5	3.14×10^{-4}	1.06×10^{-4}	2.18×10^{-6}	-271.0127178032	1.00×10^{-10}
5	3.14×10^{-4}	1.06×10^{-4}	2.18×10^{-6}	-271.0127178032	1.00×10^{-10}
15	3.45×10^{-4}	1.01×10^{-4}	3.24×10^{-6}	-271.0111940995	1.00×10^{-10}
25	3.38×10^{-4}	9.52×10^{-5}	5.54×10^{-6}	-271.0083237229	2.00×10^{-10}
35	2.86×10^{-4}	1.28×10^{-4}	1.01×10^{-5}	-271.0045120012	6.00×10^{-10}
45	3.49×10^{-4}	2.76×10^{-4}	1.60×10^{-5}	-271.0002579089	2.00×10^{-9}
55	1.07×10^{-3}	7.86×10^{-4}	3.37×10^{-5}	-270.9961026156	1.47×10^{-8}
65	4.35×10^{-3}	2.99×10^{-3}	1.50×10^{-4}	-270.9925794710	2.27×10^{-7}
75	2.41×10^{-2}	1.69×10^{-2}	9.09×10^{-4}	-270.9900053967	8.10×10^{-6}
85	2.47×10^{-2}	1.75×10^{-1}	1.22×10^{-2}	-270.9877625998	9.04×10^{-4}

C. The Interpolated Density Matrix for $CH_3SCl^{\bullet+}$ using an equally-spaced grid

From the optimized geometry, the dihedral angle H-C-S-Cl dihedral angle were sampled in the range $-64.00^\circ \leq \phi \leq 64.00^\circ$ using an equally-spaced grid, $d\phi = 8.00^\circ$. This grid corresponds to a total of 17 points. The information at $\phi = 0.00^\circ$ from the sampled points was used as the reference in defining the tangent space. From these sampled points, G-Int was conducted to interpolate selected points as provided in the table below. The interpolation was conducted using an 16^{th}-order Lagrange interpolation.

TABLE S3: Performance of G-Int in predicting the restricted open-shell (RO) density matrices using an equally-spaced grid for $CH_3SCl^{\bullet+}$ for both α and β spins along the H-C-S-Cl dihedral angle (ϕ) at the level of RO-revPBE0/def2-TZVP. The corresponding SCF energy and SCF error are also shown.

$\phi(^\circ)$	$\|\|\Delta\mathbf{P}^{\alpha}\|\|_{\mathbf{F}}$	$\|\|\Delta\mathbf{P}^{\beta}\|\|_{\mathbf{F}}$	$E^{\text{SCF}}_{\text{initial}}(E_{\text{h}})$	$E^{\text{SCF}}_{\text{initial}} - E^{\text{SCF}}_{\text{conv}}(E_{\text{h}})$
5.00	5.07×10^{-5}	4.54×10^{-5}	-897.8546831466	1.00×10^{-9}
10.00	4.03×10^{-5}	3.65×10^{-5}	-897.8547752340	7.00×10^{-9}
15.00	2.27×10^{-5}	2.05×10^{-5}	-897.8549169126	2.00×10^{-9}
31.00	5.55×10^{-5}	4.95×10^{-5}	-897.8556851472	1.60×10^{-9}
38.00	2.00×10^{-4}	1.82×10^{-4}	-897.8560571596	2.00×10^{-8}
45.00	6.96×10^{-4}	6.61×10^{-4}	-897.8563720178	2.46×10^{-7}
58.00	2.66×10^{1}	2.52×10^{1}	-896.6827160911	1.17
60.00	2.45×10^{1}	2.33×10^{1}	-896.7067530319	1.15
62.00	2.25×10^{1}	2.14×10^{1}	-896.7303517837	1.13

D. Quality of the Interpolated Density Matrix in Relation to Different Reference Points Defining the Tangent Space

To test how sensitive is an interpolated density matrix with respect to the choice of reference point (ϕ_{ref}) used in defining the tangent space, we interpolated the restricted open-shell (RO) α and β density matrices for $CH_3SCl^{\bullet+}$ at $\phi = 58.00^\circ$ at the level of RO-revPBE0/def2-TZVP. The reference points use in defining the tangent space are at $\phi_{\text{ref}} \in \{0.00^\circ, 40.00^\circ, \text{ and } 64.00^\circ\}$. The corresponding G-Int energy and SCF error are also shown. The sampling used for the G-Int method is an equally-spaced grid in the range $-64.00^\circ \leq \phi \leq 64.00^\circ$ with $d\phi = 8.00^\circ$.

TABLE S4: Quality of the interpolated density matrix for $CH_3SCl^{\bullet+}$ at $\phi = 58.00^\circ$ using different reference points (ϕ_{ref}) for the G-Int tangent space.

$\phi_{\text{ref}}(^\circ)$	$\|\|\Delta\mathbf{P}^{\alpha}\|\|_{\mathbf{F}}$	$\|\|\Delta\mathbf{P}^{\beta}\|\|_{\mathbf{F}}$	$E_{\text{G-Int}}(E_{\text{h}})$	$E_{\text{G-Int}} - E^{\text{SCF}}_{\text{conv}}(E_{\text{h}})$
0.00	26.6	25.2	-896.6827160911	1.17
40.00	26.6	25.2	-896.5309443223	1.33
64.00	22.1	25.4	-896.7282084923	1.13

We note that errors, regardless of the reference point defining the tangent space, exhibit the same order of magnitude. Consequently, we conclude that large end-point errors stem from the interpolation method employed rather than the choice of the reference point defining the tangent space.