Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for the Paper Entitled "On the Origin of the Steric Effect"

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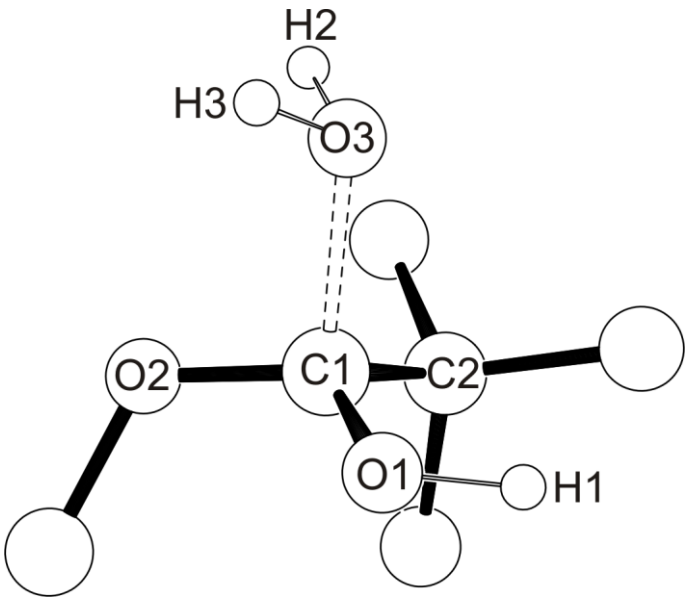

Figure S1. Transition state structure corresponding to the rate determining step of acid-catalyzed ester hydrolysis for R=*t*-butyl (**8-TS**). Methylenic hydrogens and the auxiliary water molecule [1] were omitted for clarity.

[1] Hori, K., Ikenaga, Y., Arata, K., Takahashi, T., Kasai, K., Noguchi, Y., Sumimotoa, M. & Yamamoto, H. Theoretical study on the reaction mechanism for the hydrolysis of esters and amides under acidic conditions. *Tetrahedron* **63**, 1264-1269 (2007).

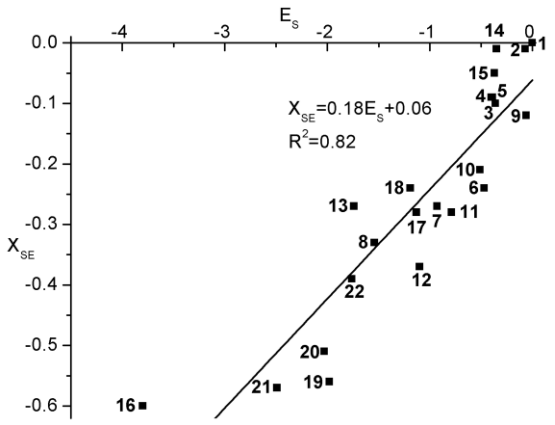

Figure S2. Correlation between calculated X_{SE} (α=0.01) values and Taft constants (E_S) for 22 alkyl substituents.

Table S1. Potentials for **1-22** determined at 2 Å from the molecule. (Values are given in kcal mol^{-1})

	1	**1**	**2**	**2**
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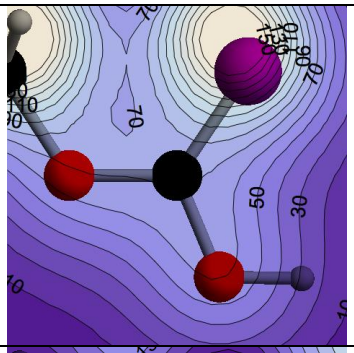
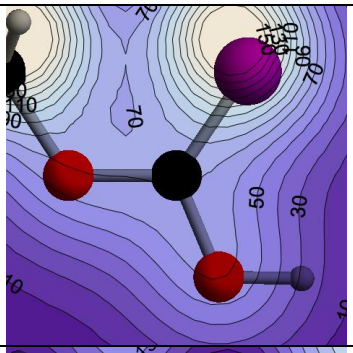
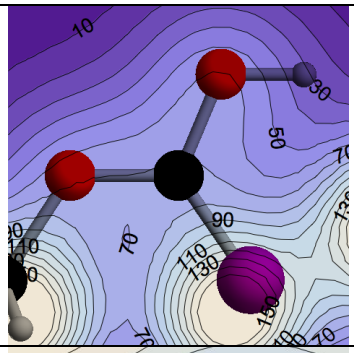
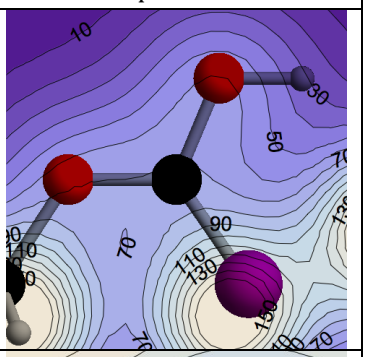
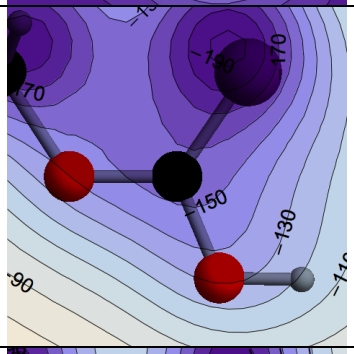
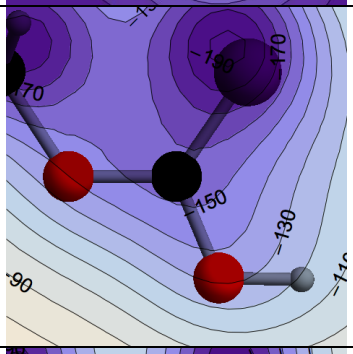
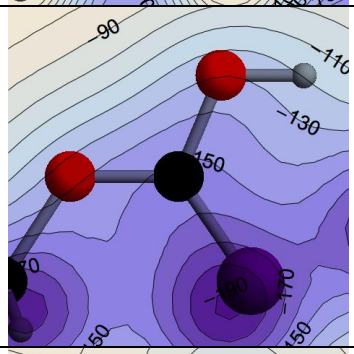
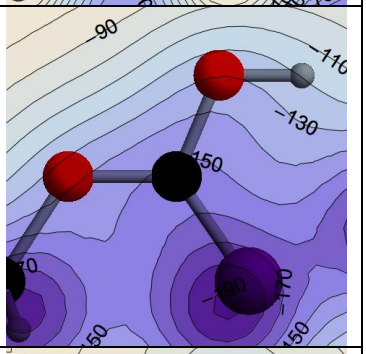
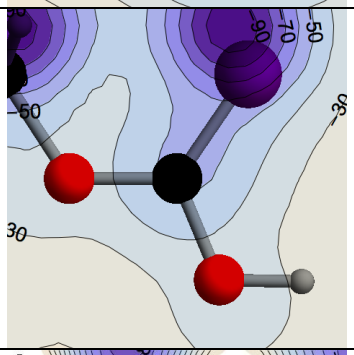
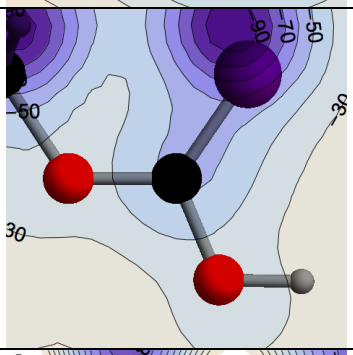
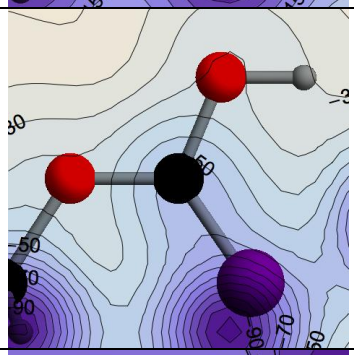
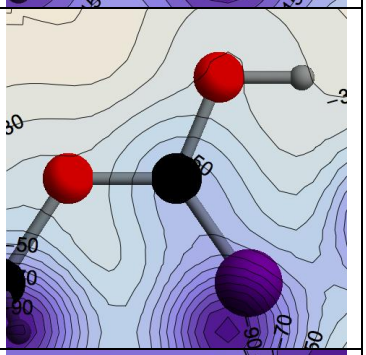
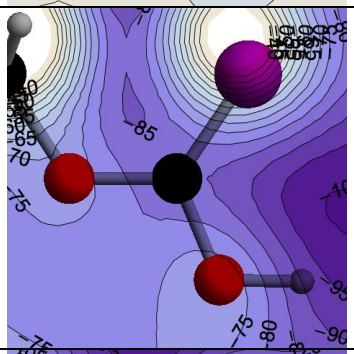
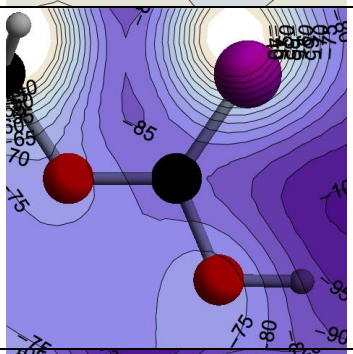
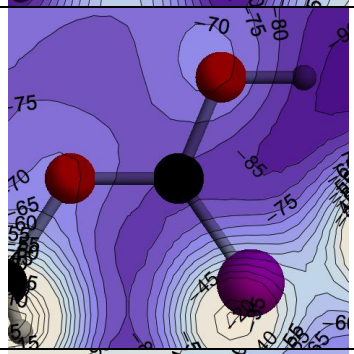
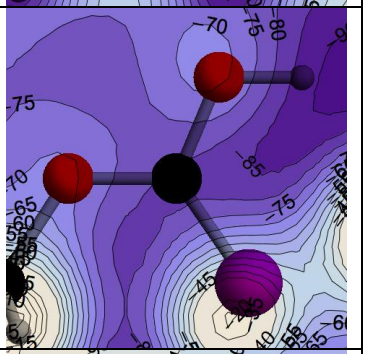
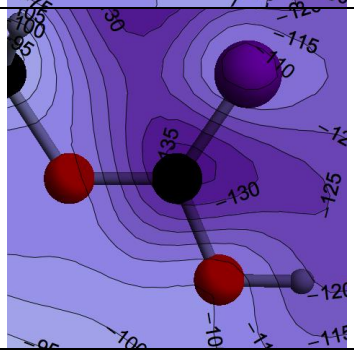
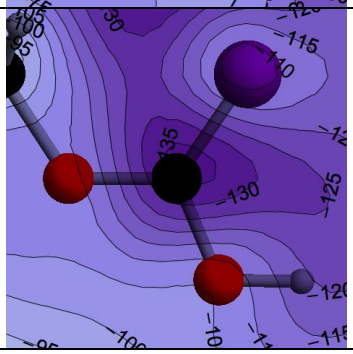
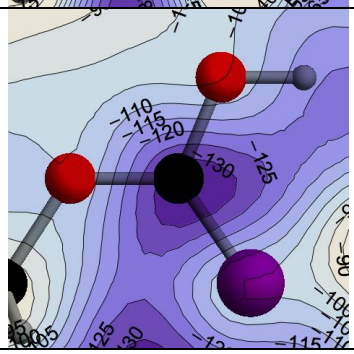
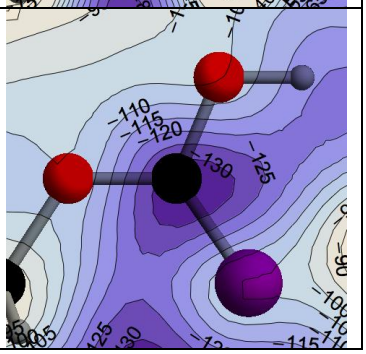
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{noi}				
ΔE_{oi}				
ΔE_{int}				

	3	**3**	**4**	**4**
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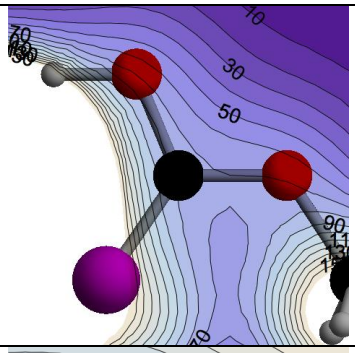
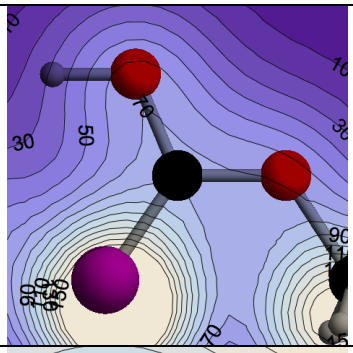
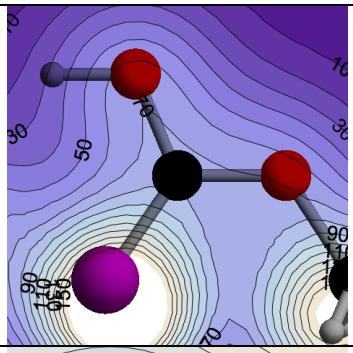
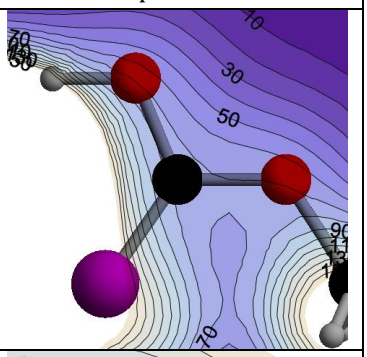
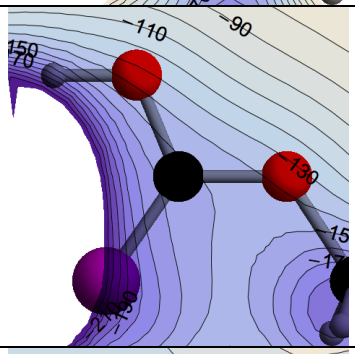
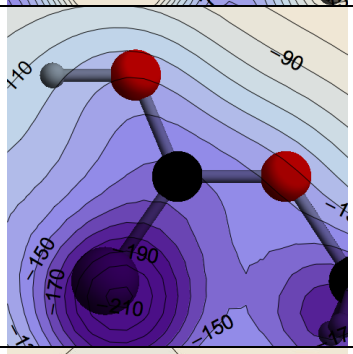
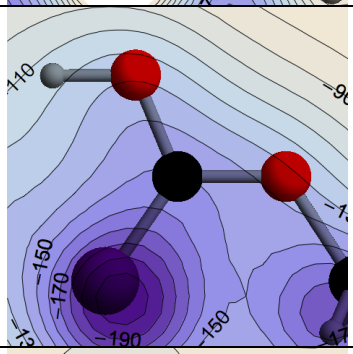
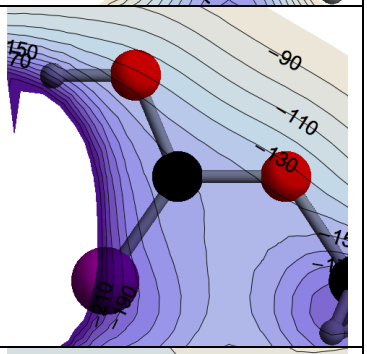
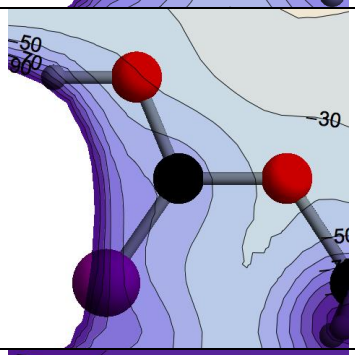
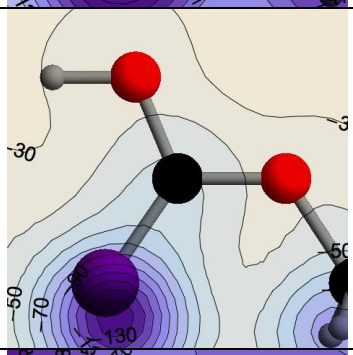
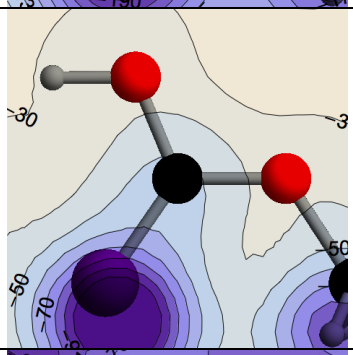
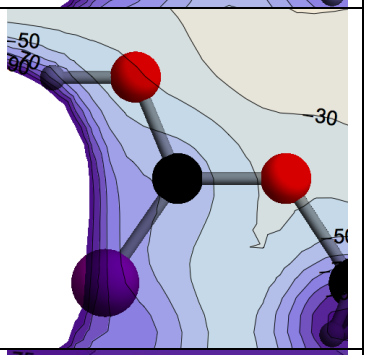
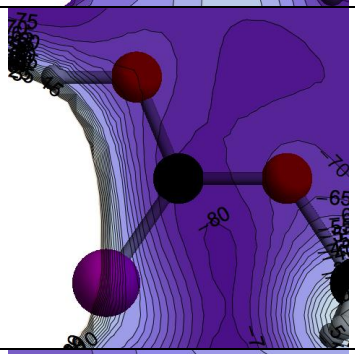
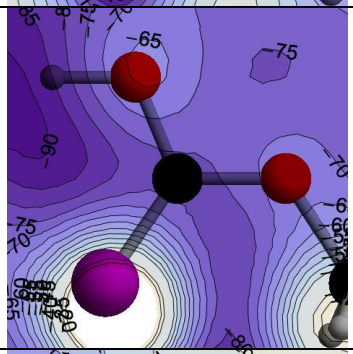
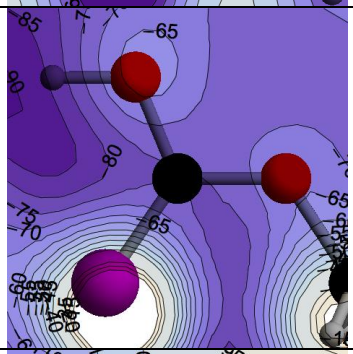
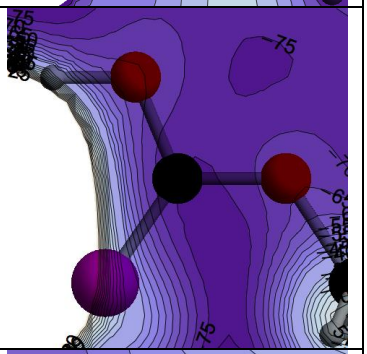
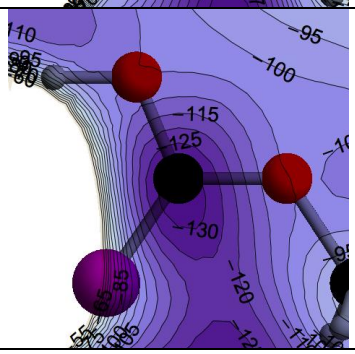
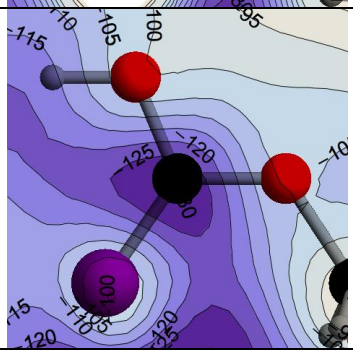
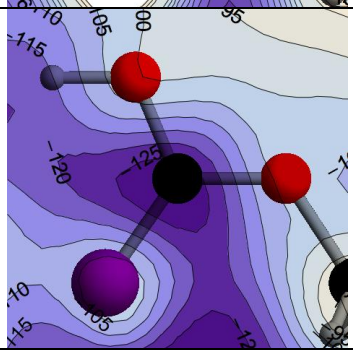
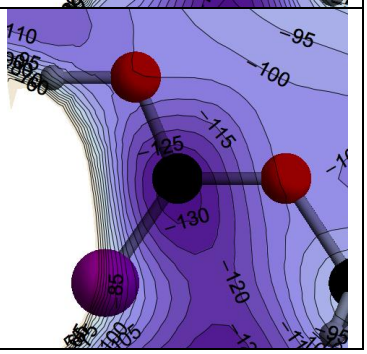
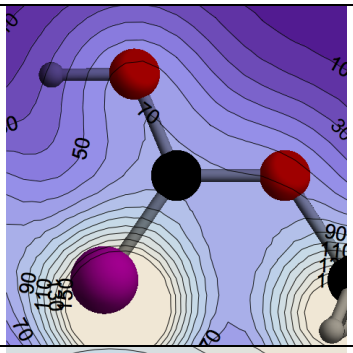
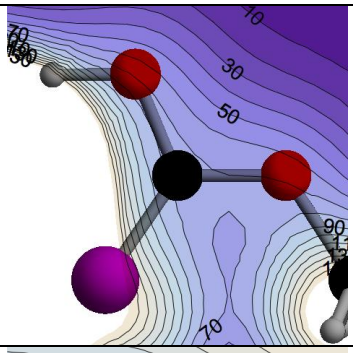
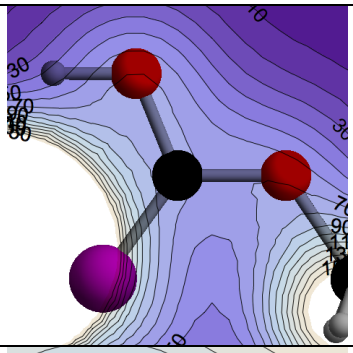
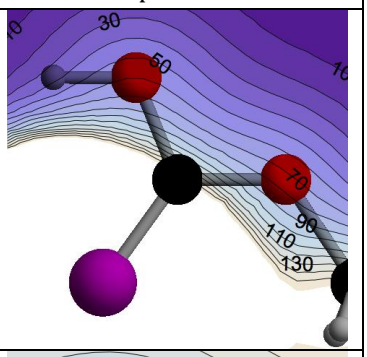
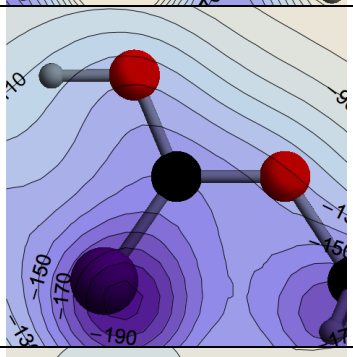
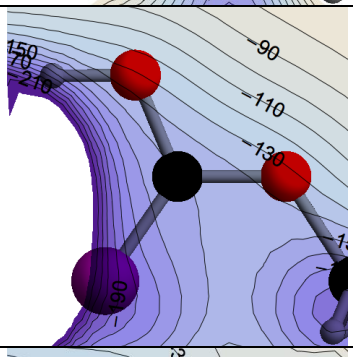
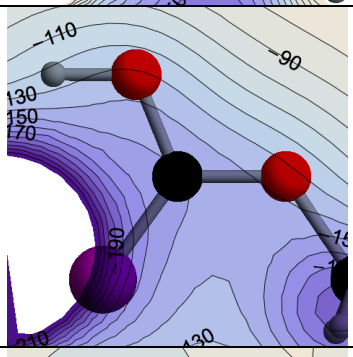
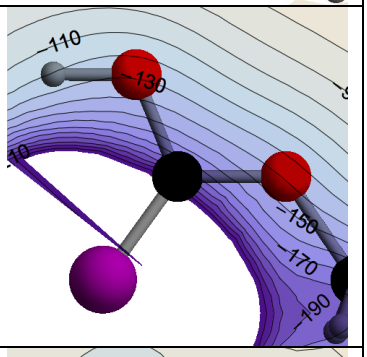
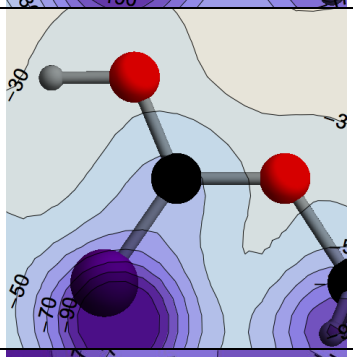
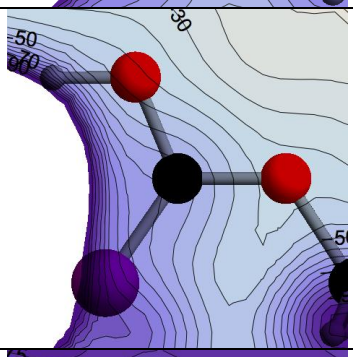
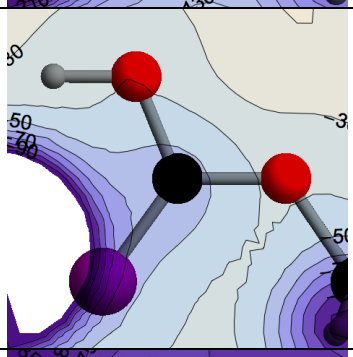
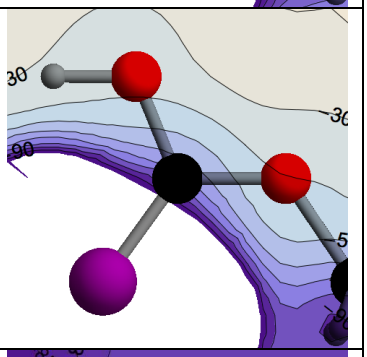
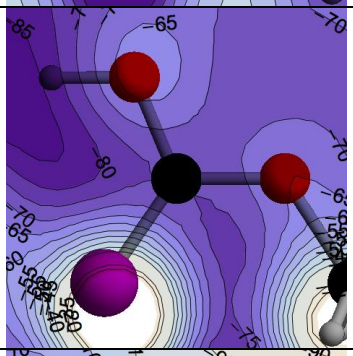
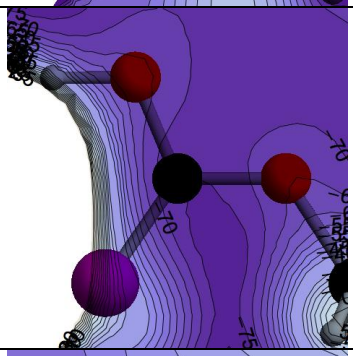
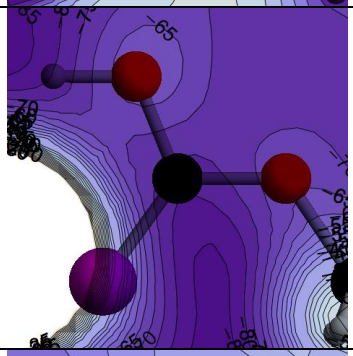
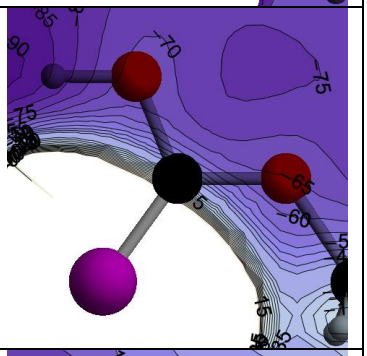
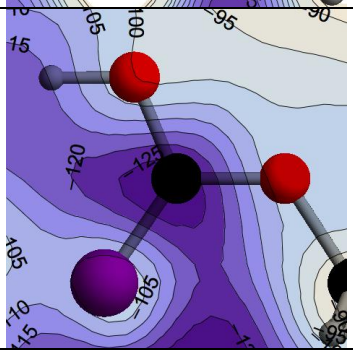
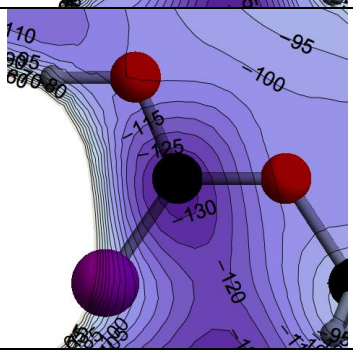
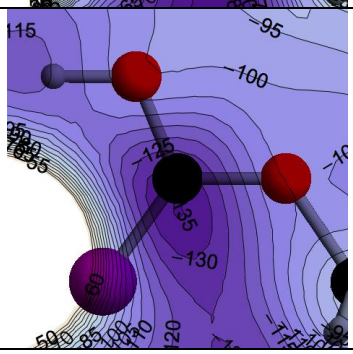
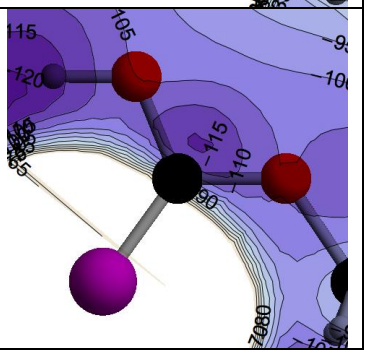
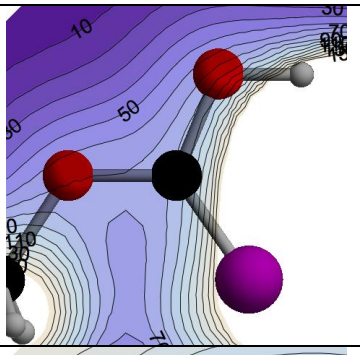
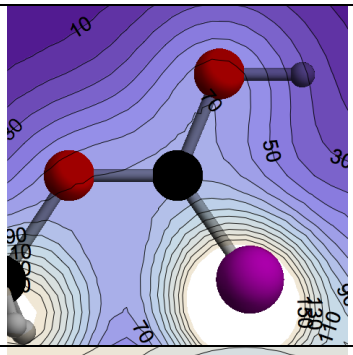
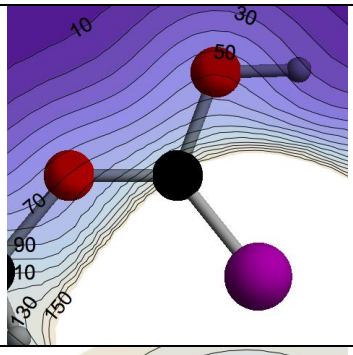
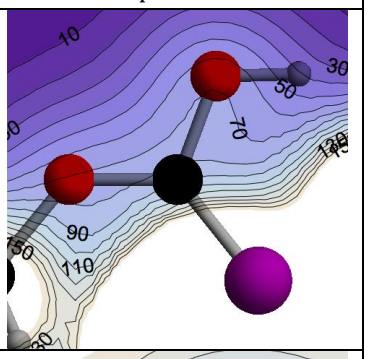
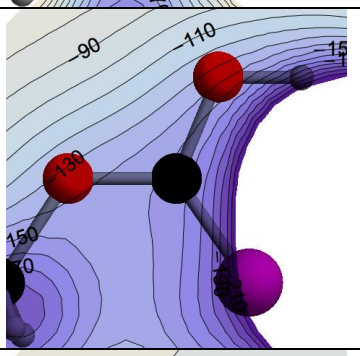
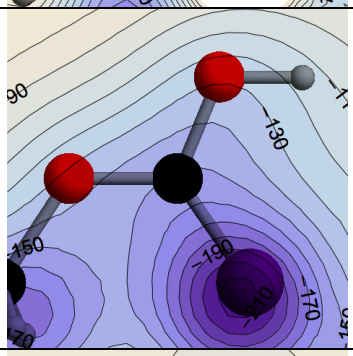
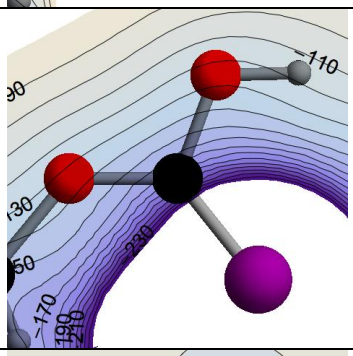
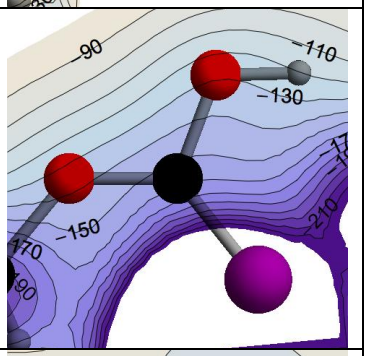
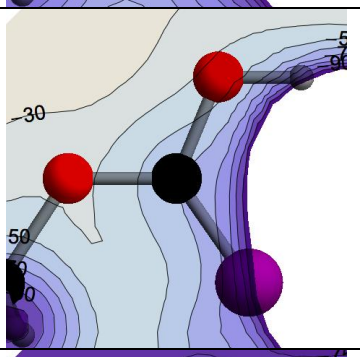
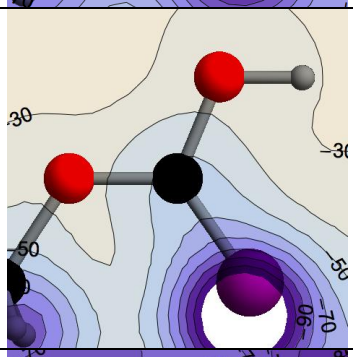
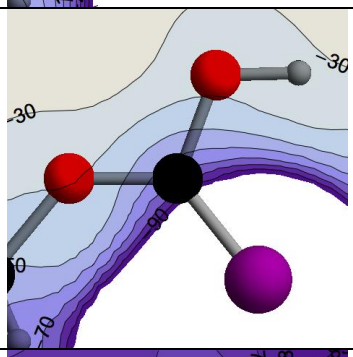
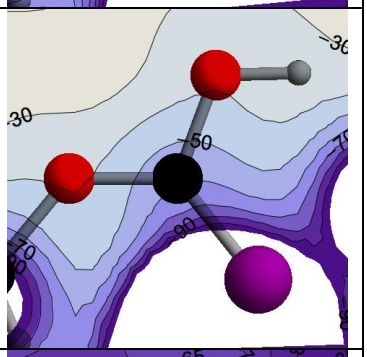
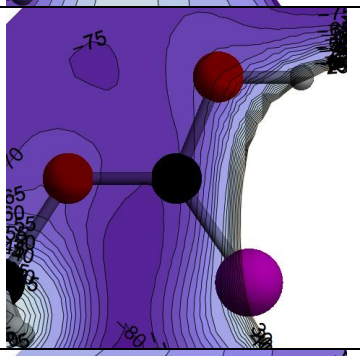
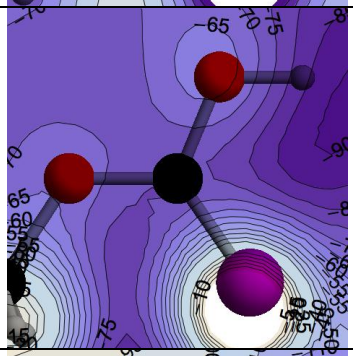
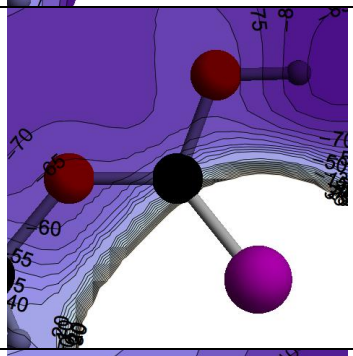
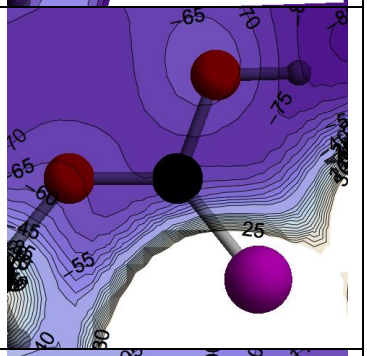
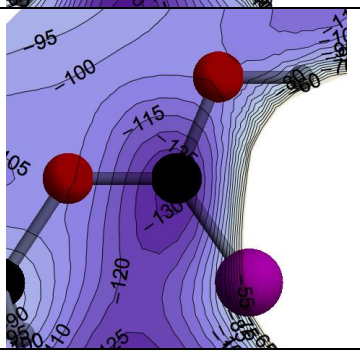
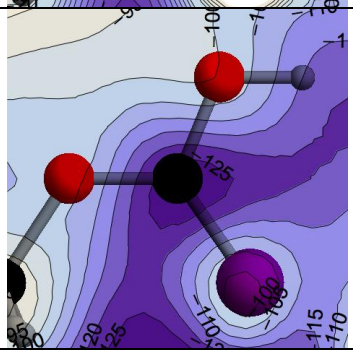
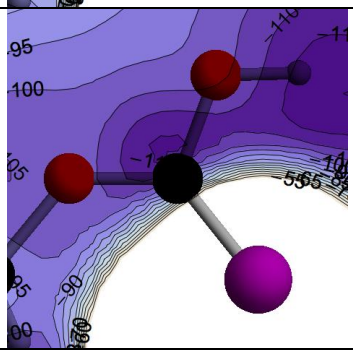
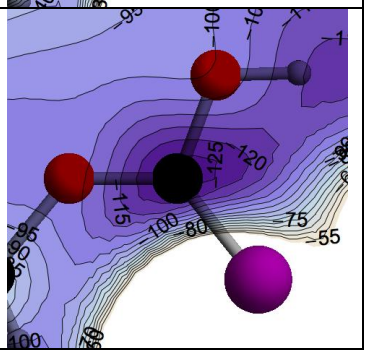
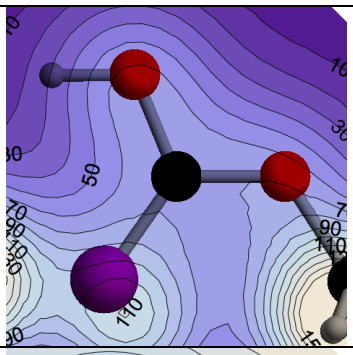
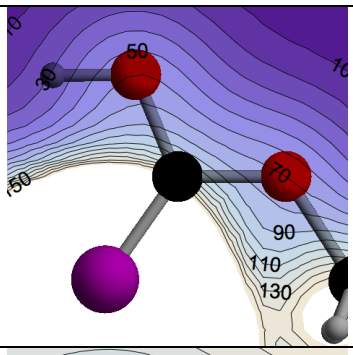
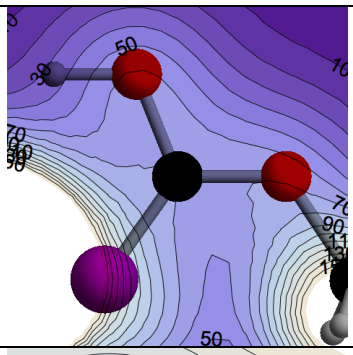
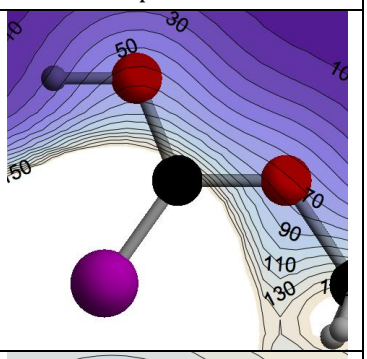
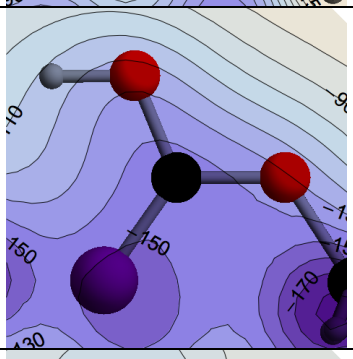
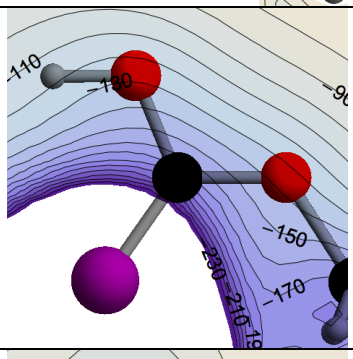
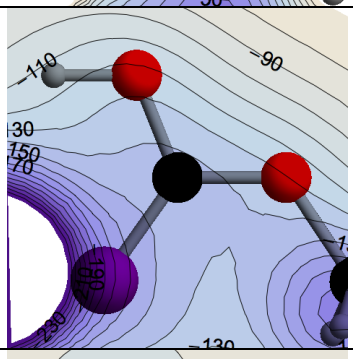
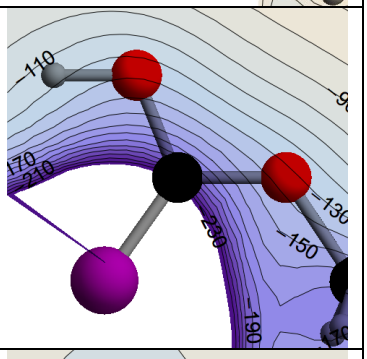
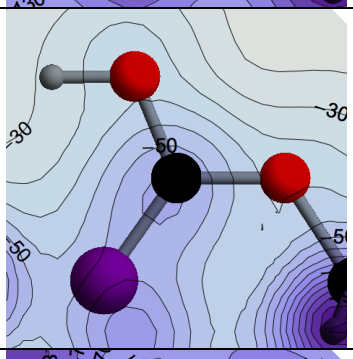
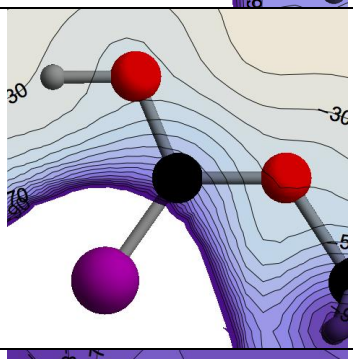
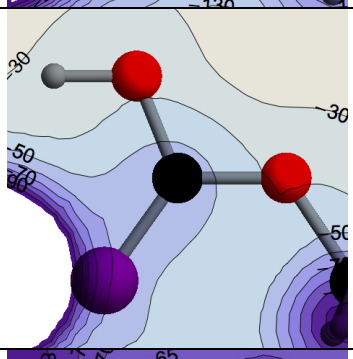
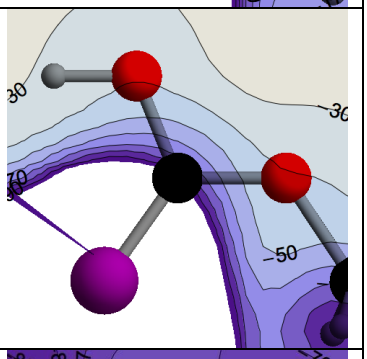
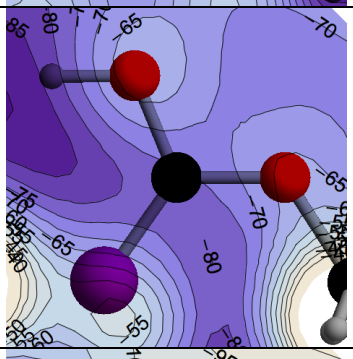
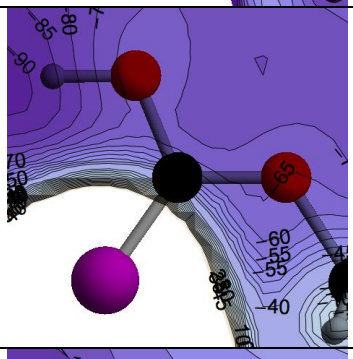
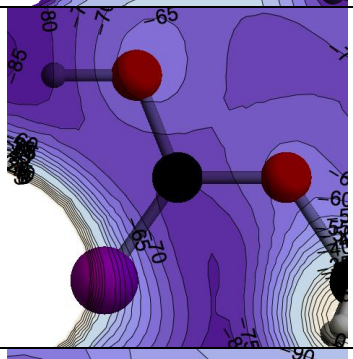
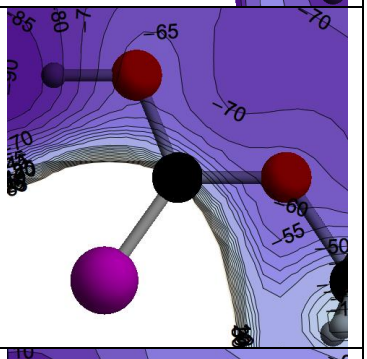
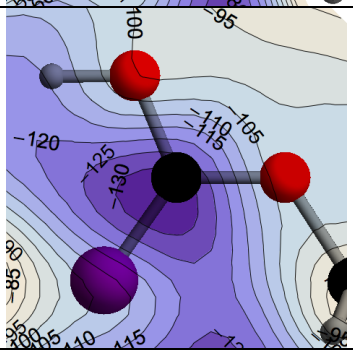
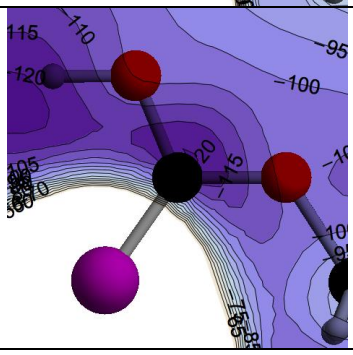
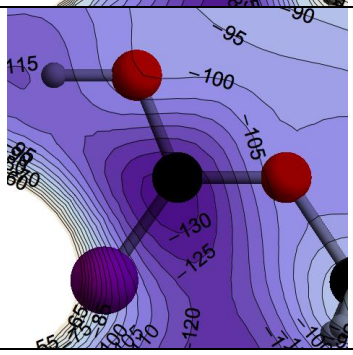
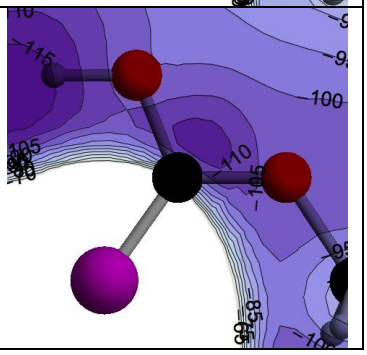
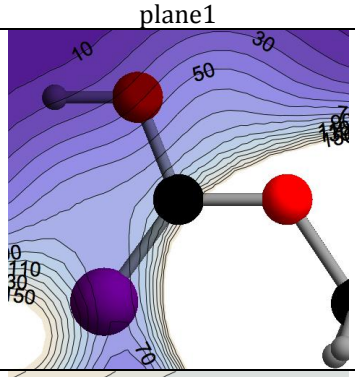
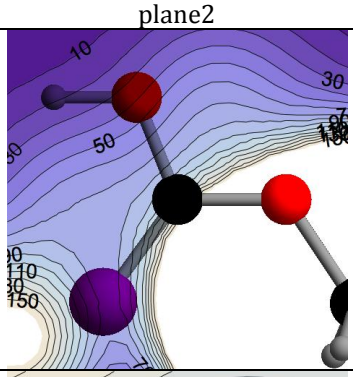
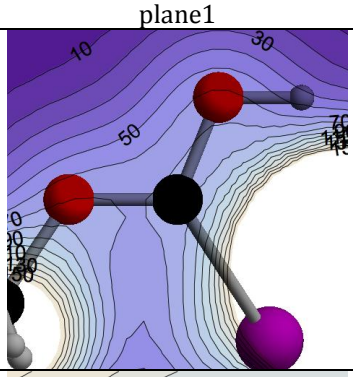
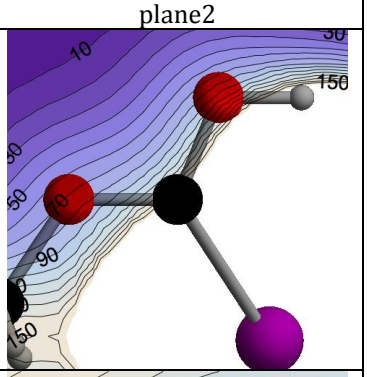
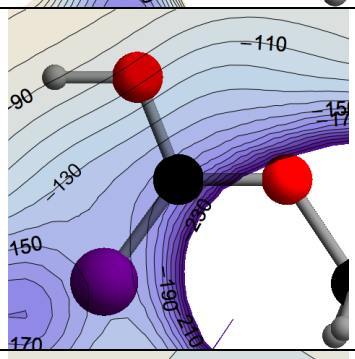
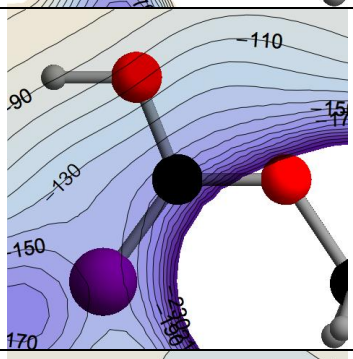
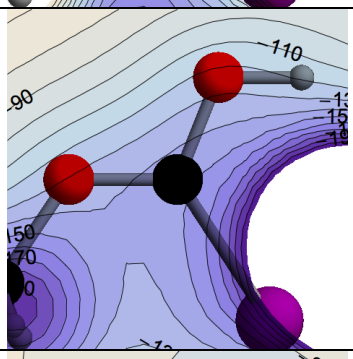
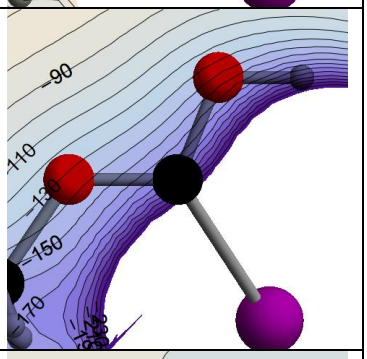
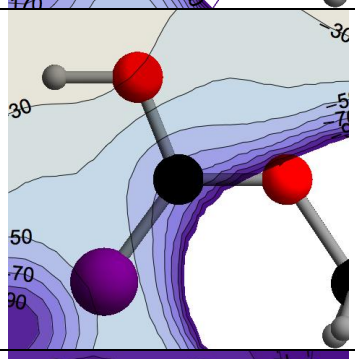
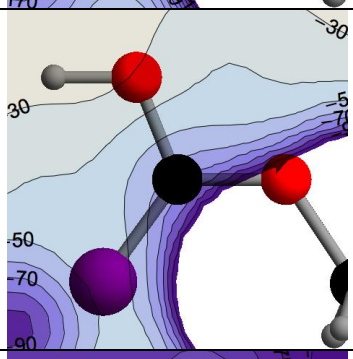
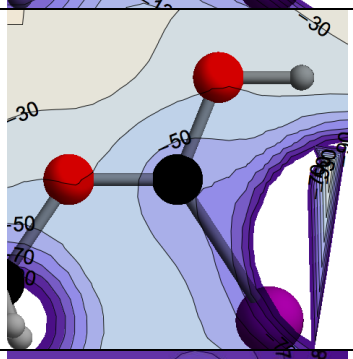
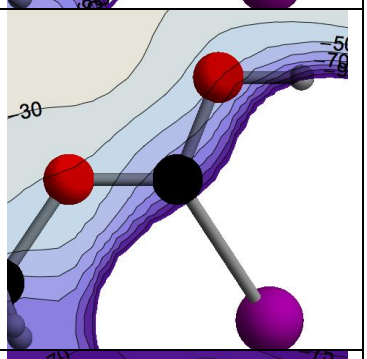
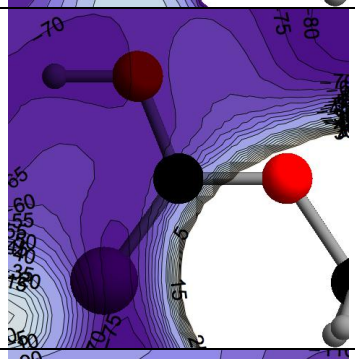
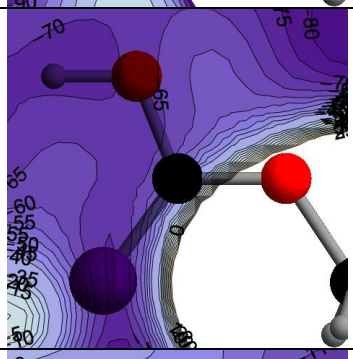
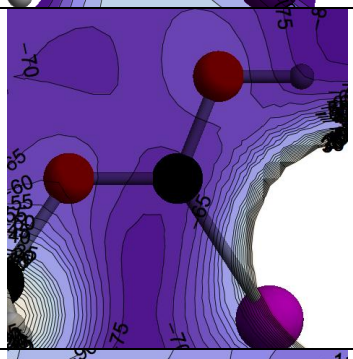
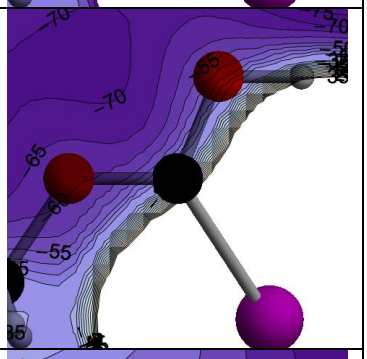
	plane1	plane2	plane1	plane2
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{oi}				
ΔE_{noi}				
ΔE_{int}				

	5	**5**	**6**	**6**
	R= n-pentyl	R= n-pentyl	R= i-propyl	R= i-propyl
	plane1	plane2	plane1	plane2
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{oi}				
ΔE_{noi}				
ΔE_{int}				

	7	**7**	**8**	**8**
	R= i-butyl	R= i-butyl	R= t-butyl	R= t-butyl
	plane1	plane2	plane1	plane2
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{oi}				
ΔE_{noi}				
ΔE_{int}				

	9	**9**	**10**	**10**
	R= c-butyl	R= c-butyl	R= c-pentyl	R= c-pentyl
	plane1	plane2	plane1	plane2
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{oi}				
ΔE_{noi}				
ΔE_{int}				

	11	**11**	**11'**	**11'**
	R= c-hexyl$_{eq}$	R= c-hexyl$_{eq}$	R= c-hexyl$_{ax}$	R= c-hexyl$_{ax}$
	plane1	plane2	plane1	plane2
ΔE_{Pauli}				
ΔE_{elst}				
ΔE_{oi}				
ΔE_{moi}				
ΔE_{int}