Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

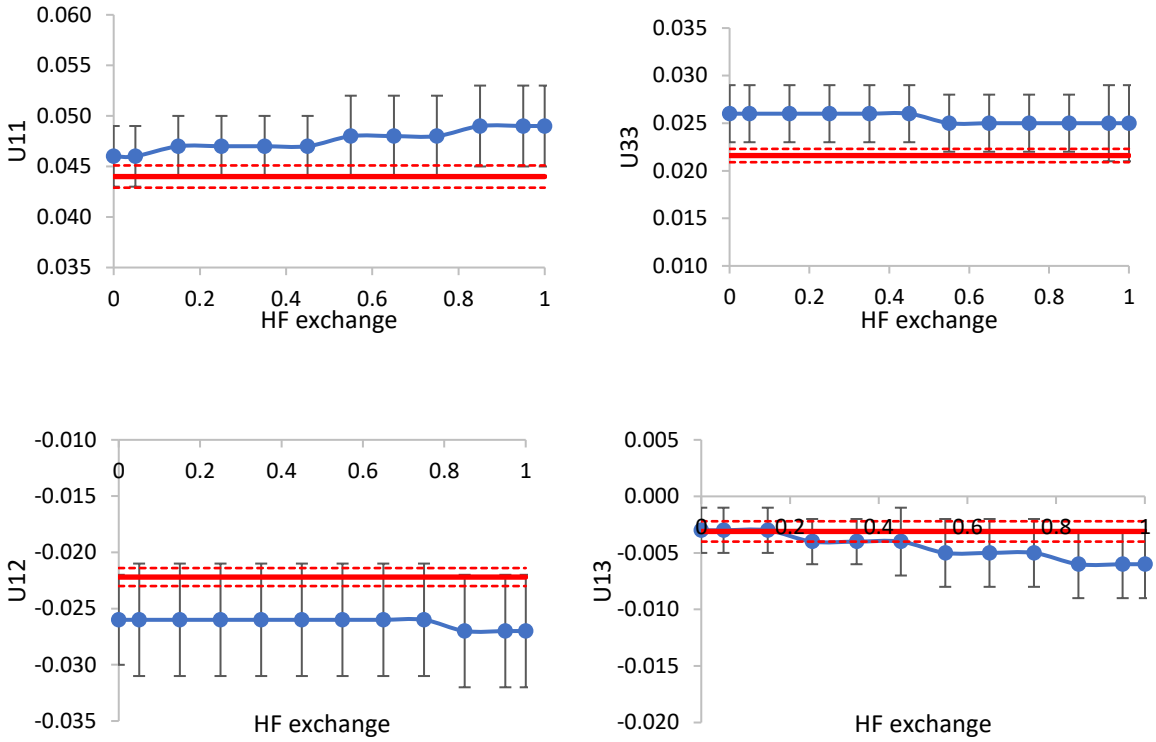


Figure S1. Unique ADPs for H1 atom of urea as a function of HF exchange, and associated std errors, refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line, and its associated std errors are shown with dashed red lines.

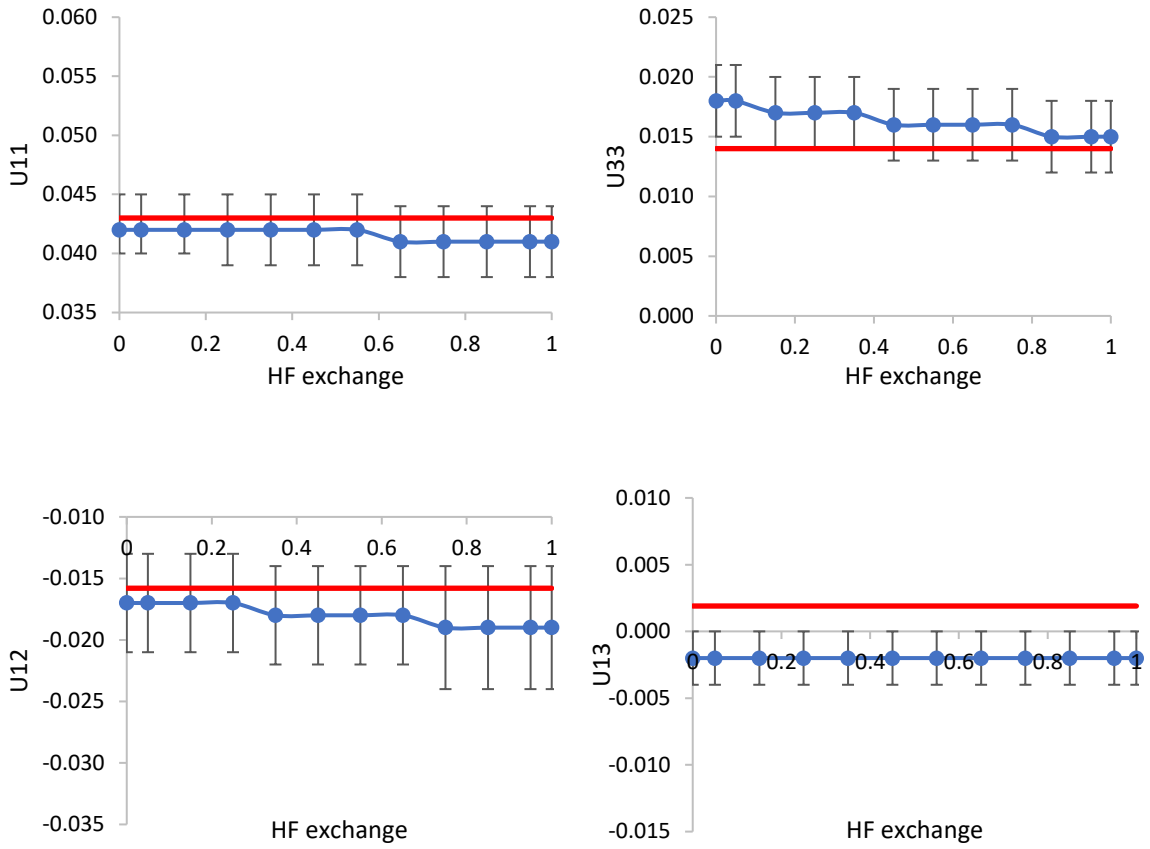


Figure S2. Unique ADPs for H2 atom of urea as a function of HF exchange, and associated std errors, refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line, and its associated std errors are shown with dashed red lines.

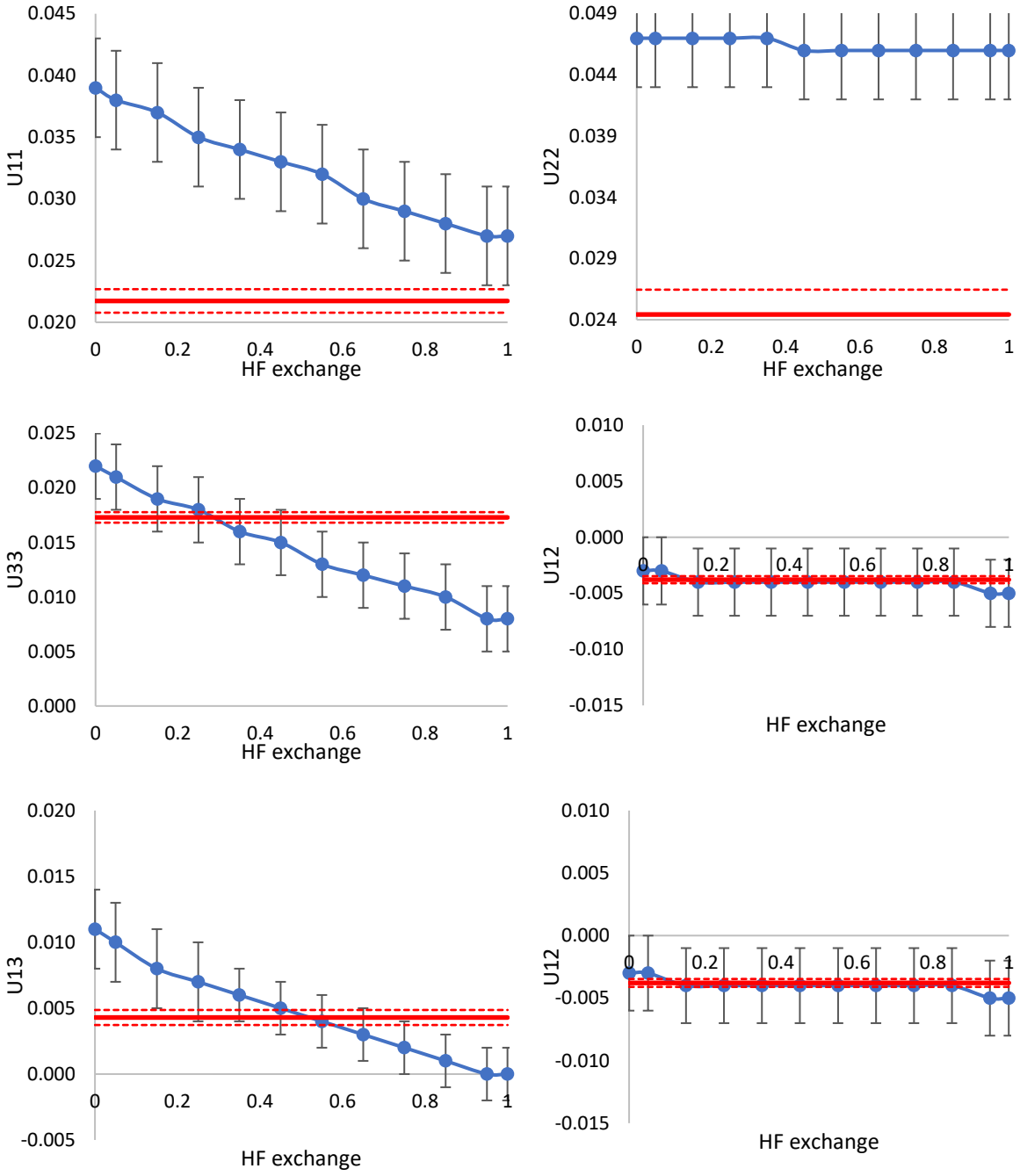


Figure S3. Unique ADPs for H1 atom of oxalic acid as a function of HF exchange, and associated std errors, refined at PBEx/def2-TVZP level of theory. The average newton diffraction value, obtained from the 14 diffraction data cited in the paper, is shown as a continuous red line, and its associated std errors are shown with dashed red lines.

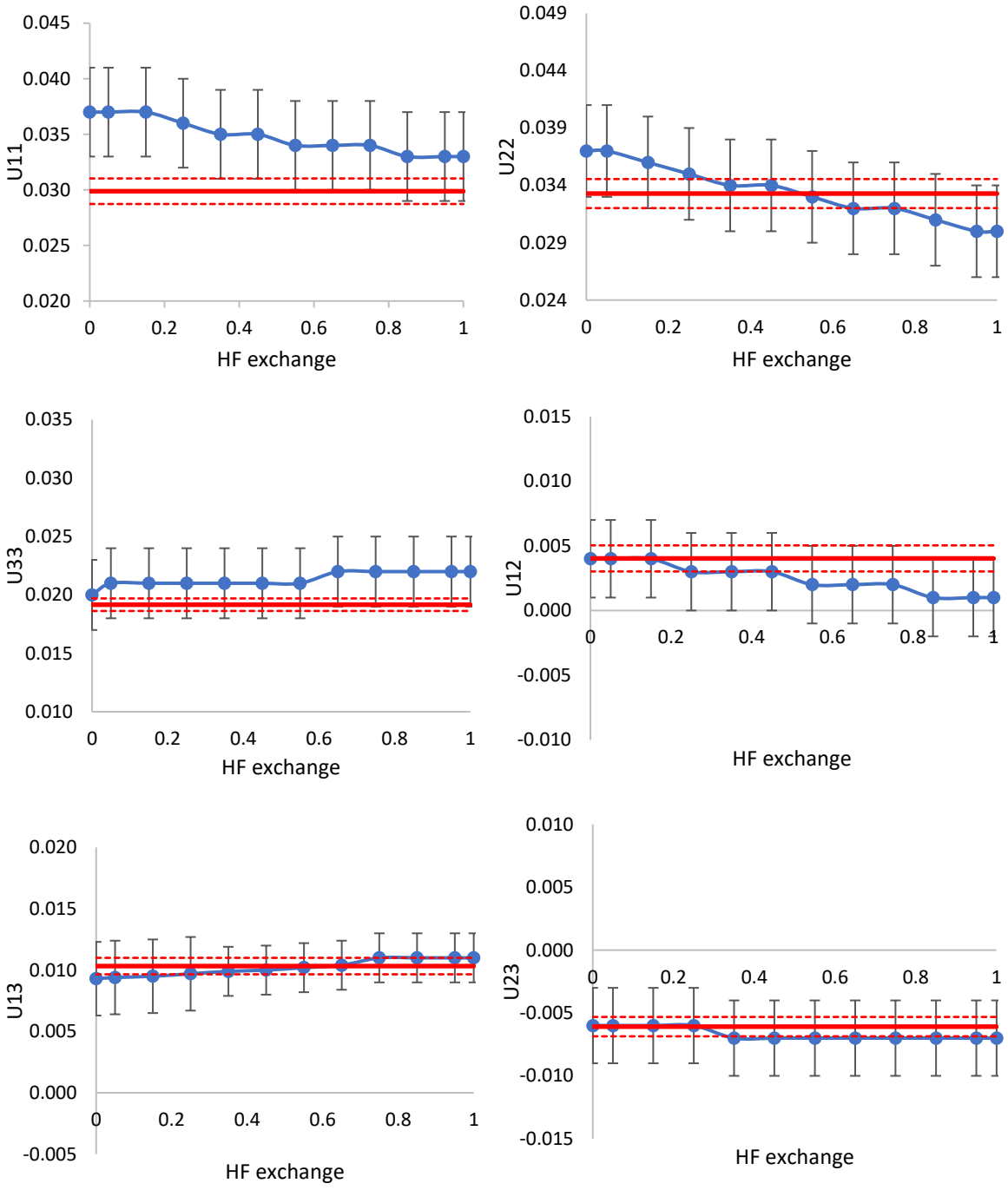


Figure S4. Unique ADPs for H2 atom of oxalic acid as a function of HF exchange, and associated std errors, refined at PBEx/def2-TVZP level of theory. The average newton diffraction value, obtained from the 14 diffraction data cited in the paper, is shown as a continuous red line, and its associated std errors are shown with dashed red lines.

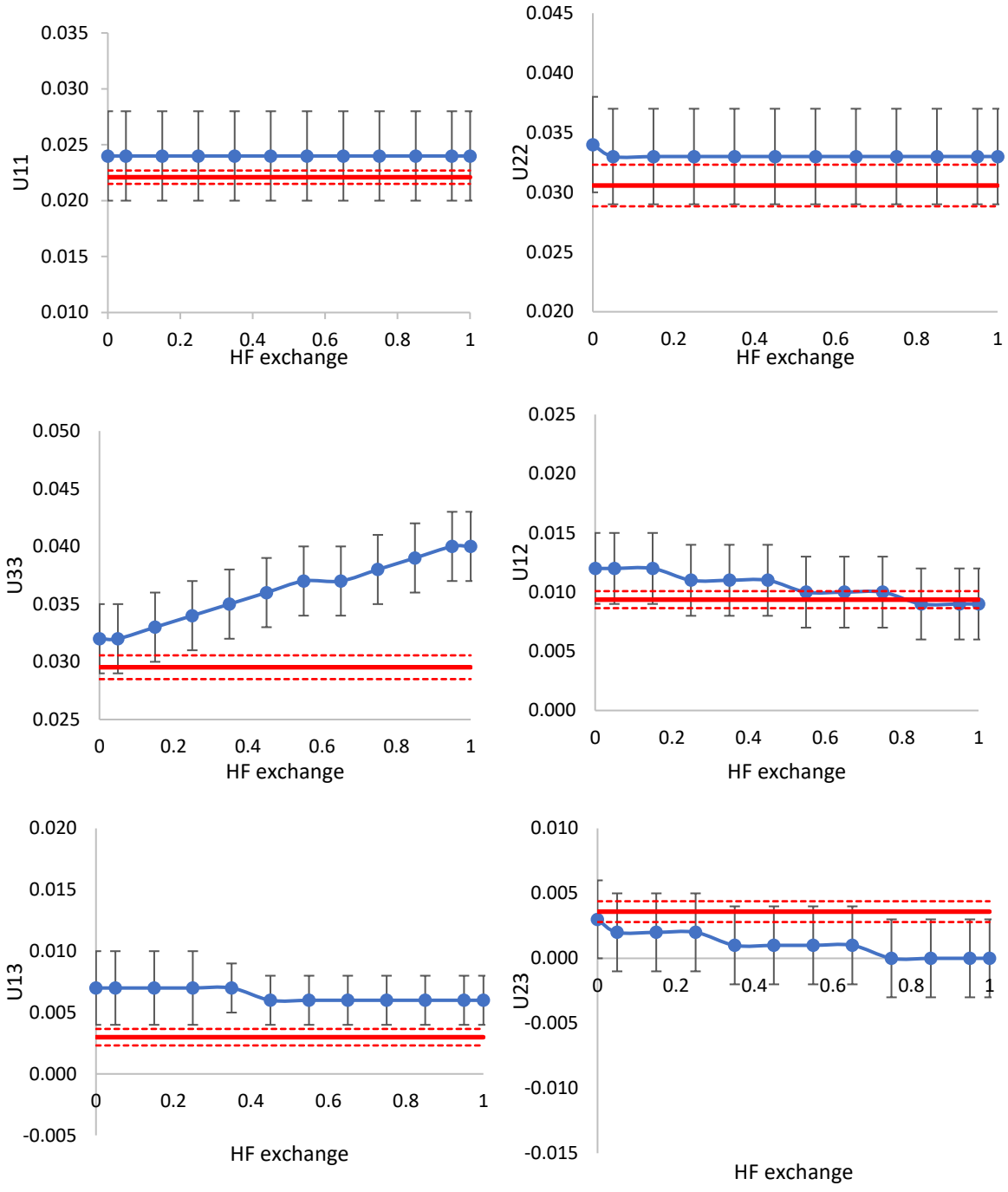


Figure S5. Unique ADPs for H3 atom of oxalic acid as a function of HF exchange, and associated std errors, refined at PBEx/def2-TVZP level of theory. The average newton diffraction value, obtained from the 14 diffraction data cited in the paper, is shown as a continuous red line, and its associated std errors are shown with dashed red lines.

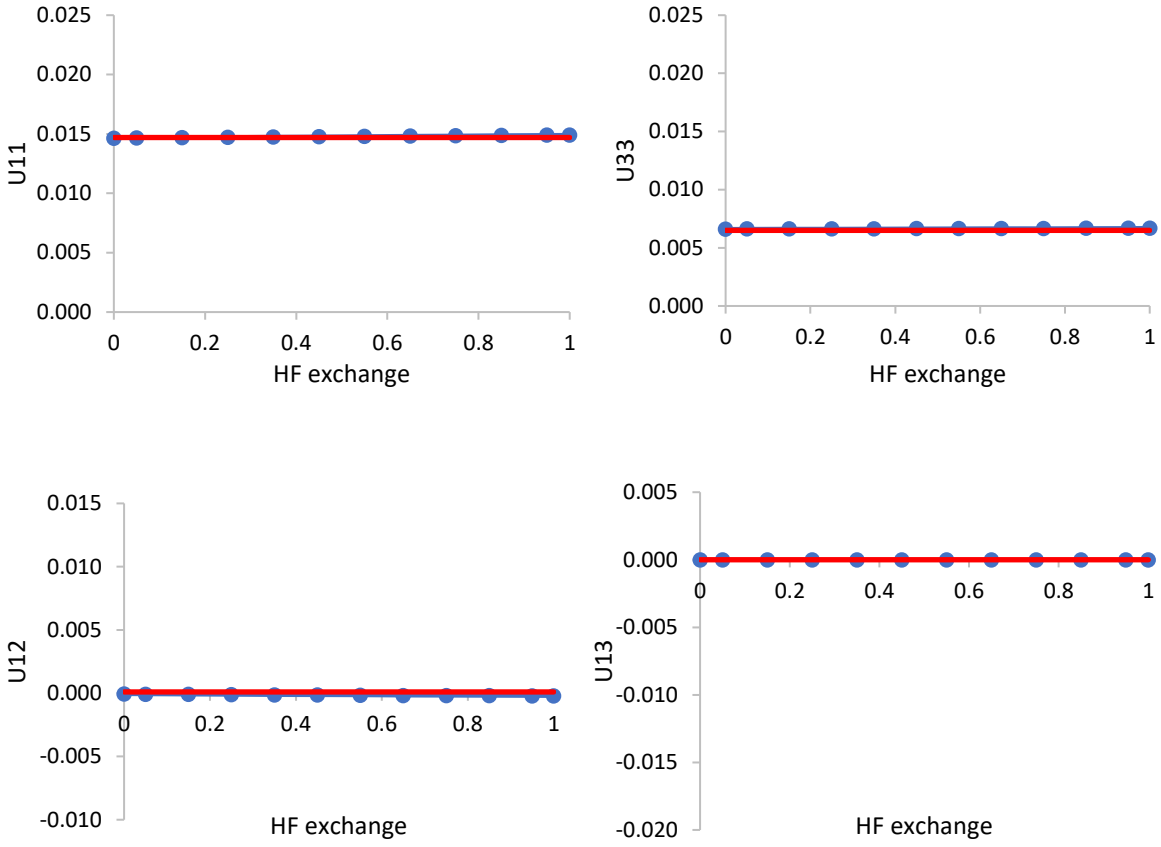


Figure S6. Unique ADPs for C atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

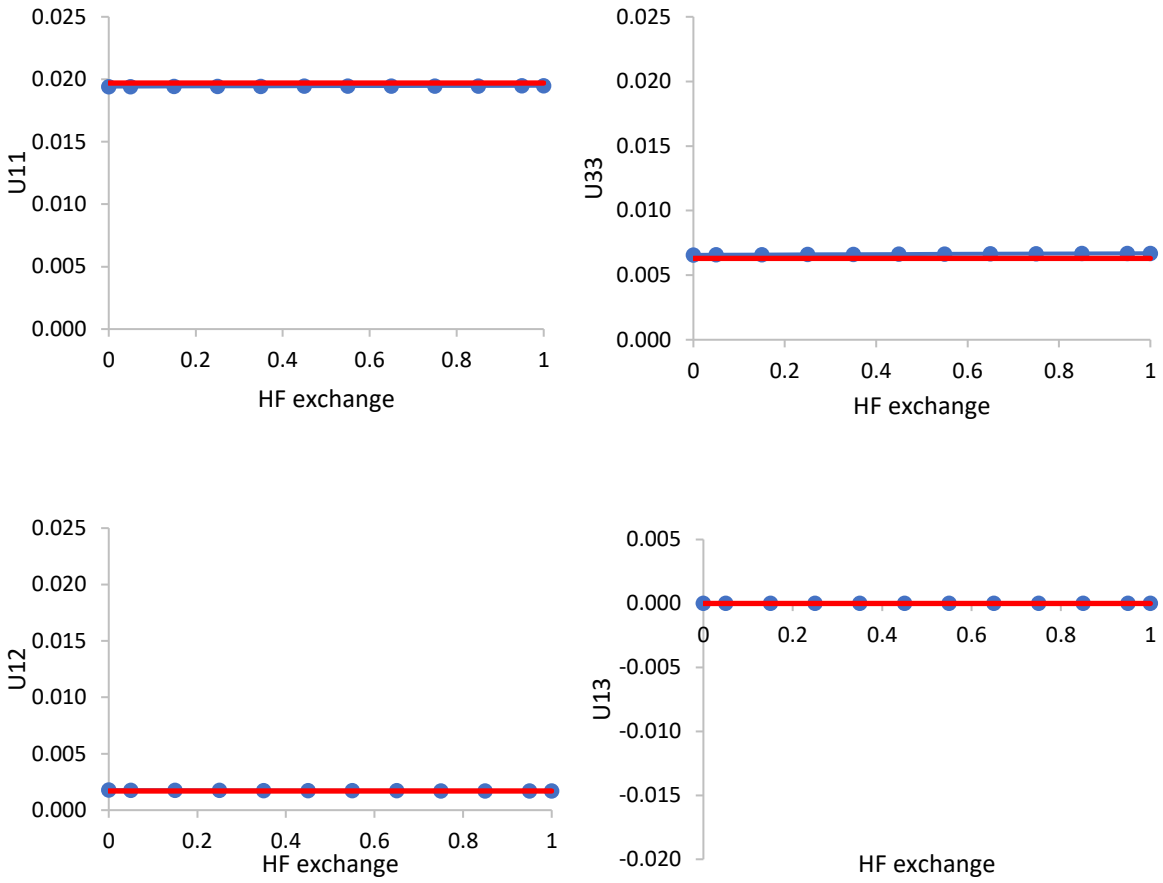


Figure S7. Unique ADPs for O atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} $Å^{-2}$, and not distinguishable at this scale.

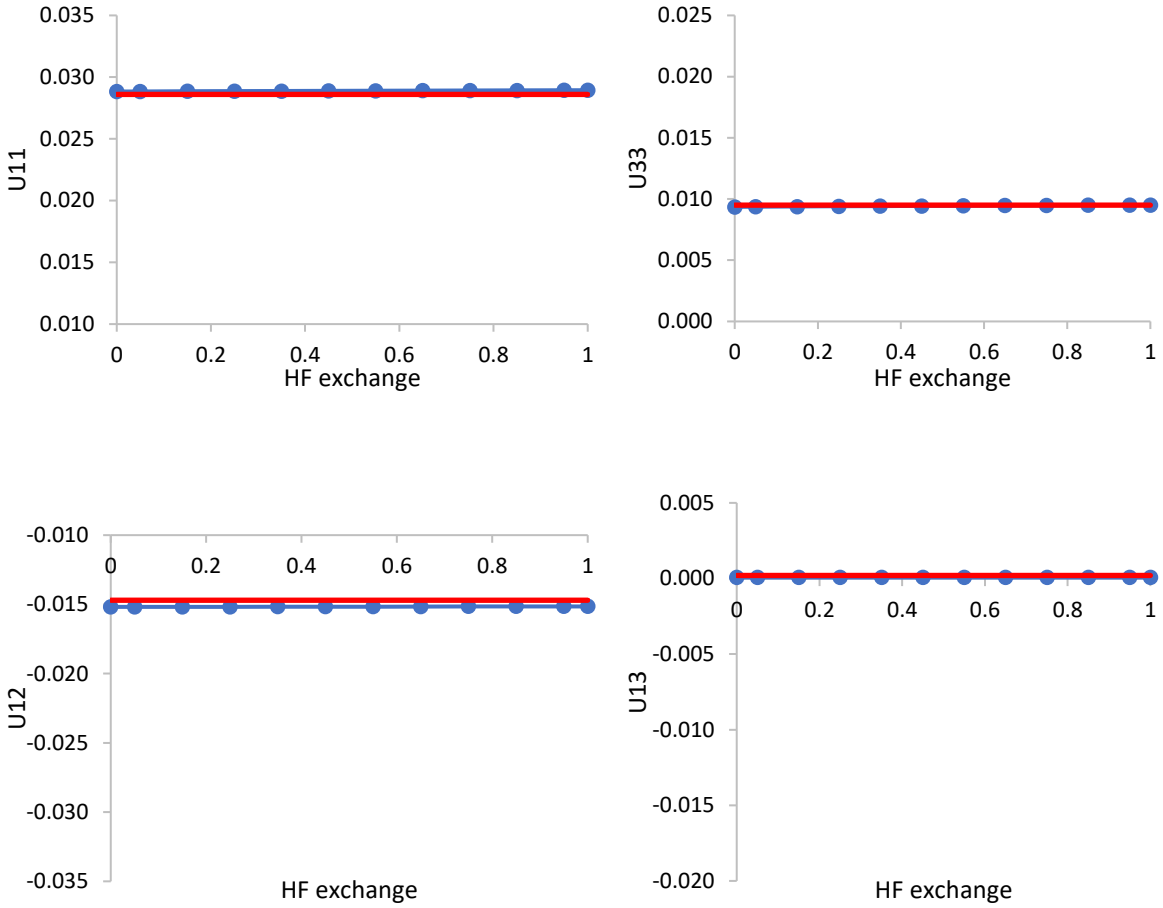


Figure S8. Unique ADPs for N atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

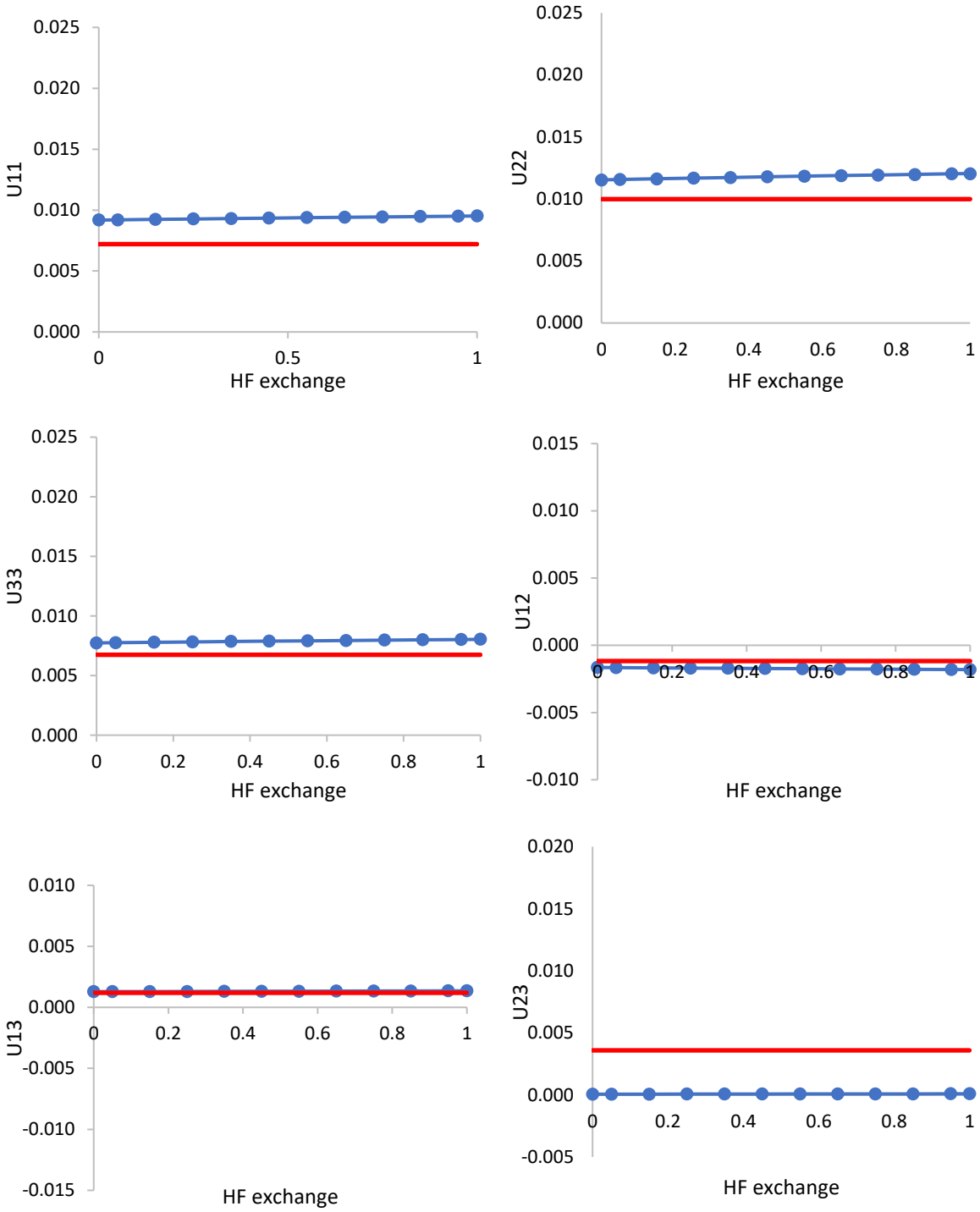


Figure S9. Unique ADPs for C1 atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

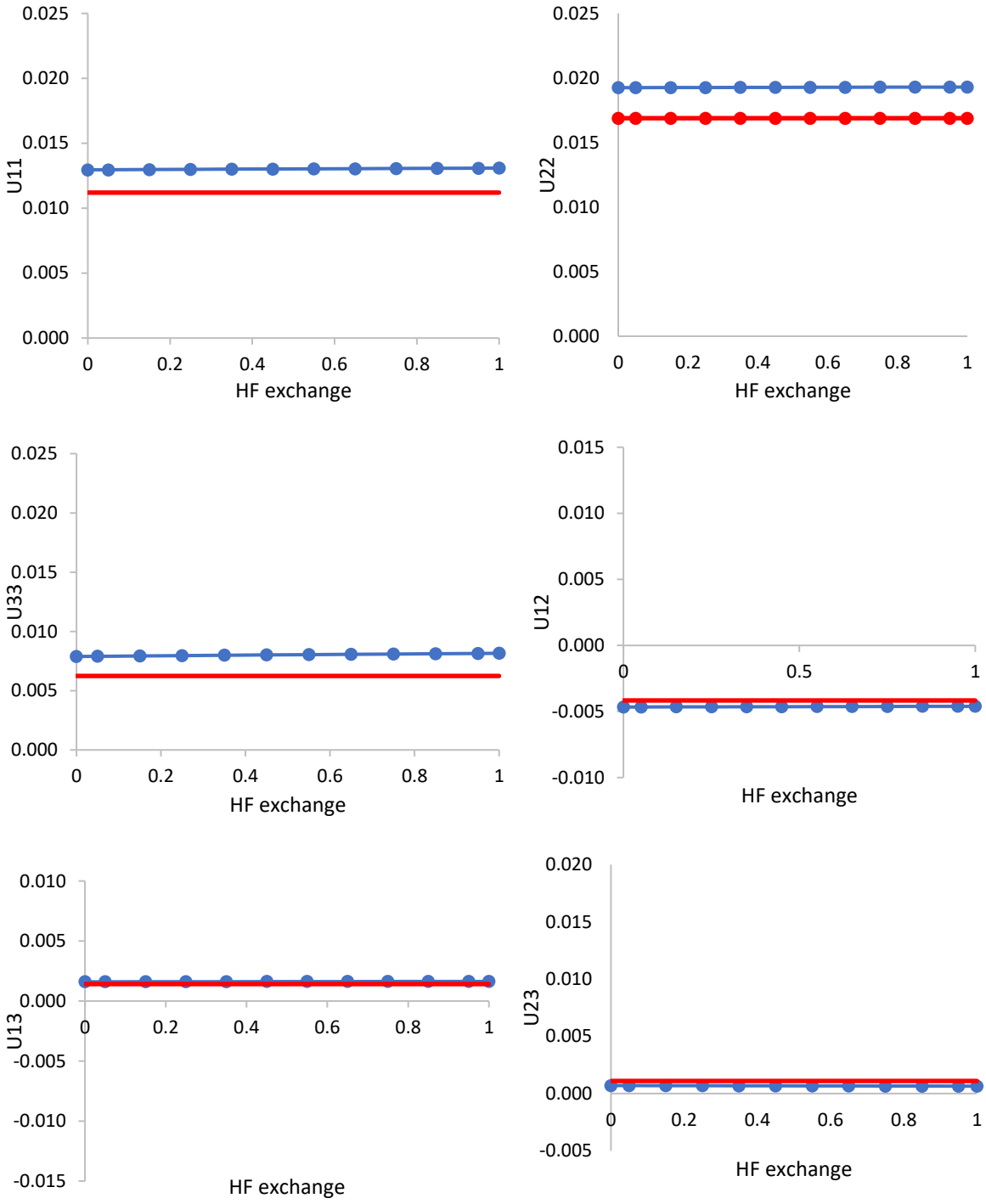


Figure S10. Unique ADPs for O1 atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

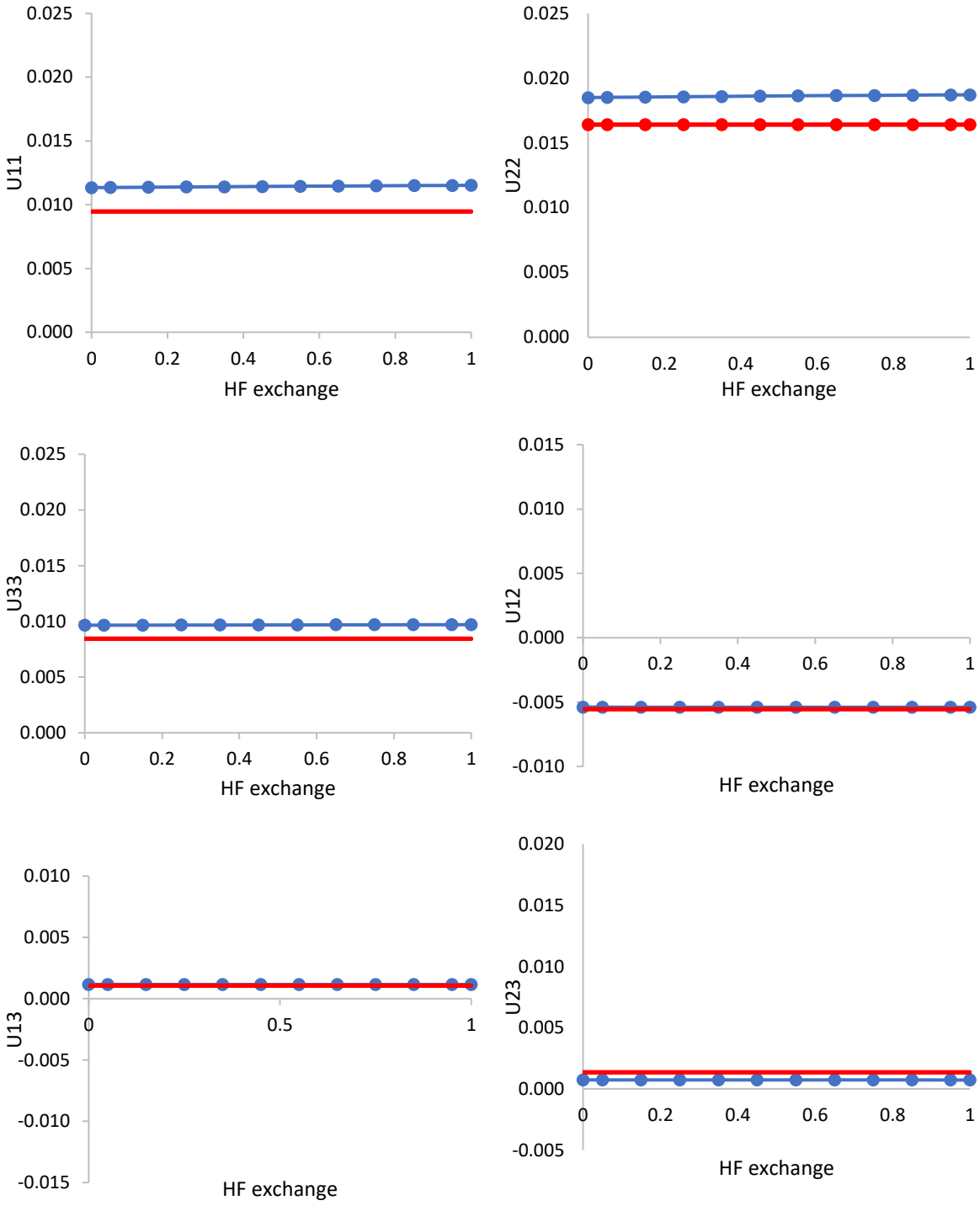


Figure S11. Unique ADPs for O2 atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

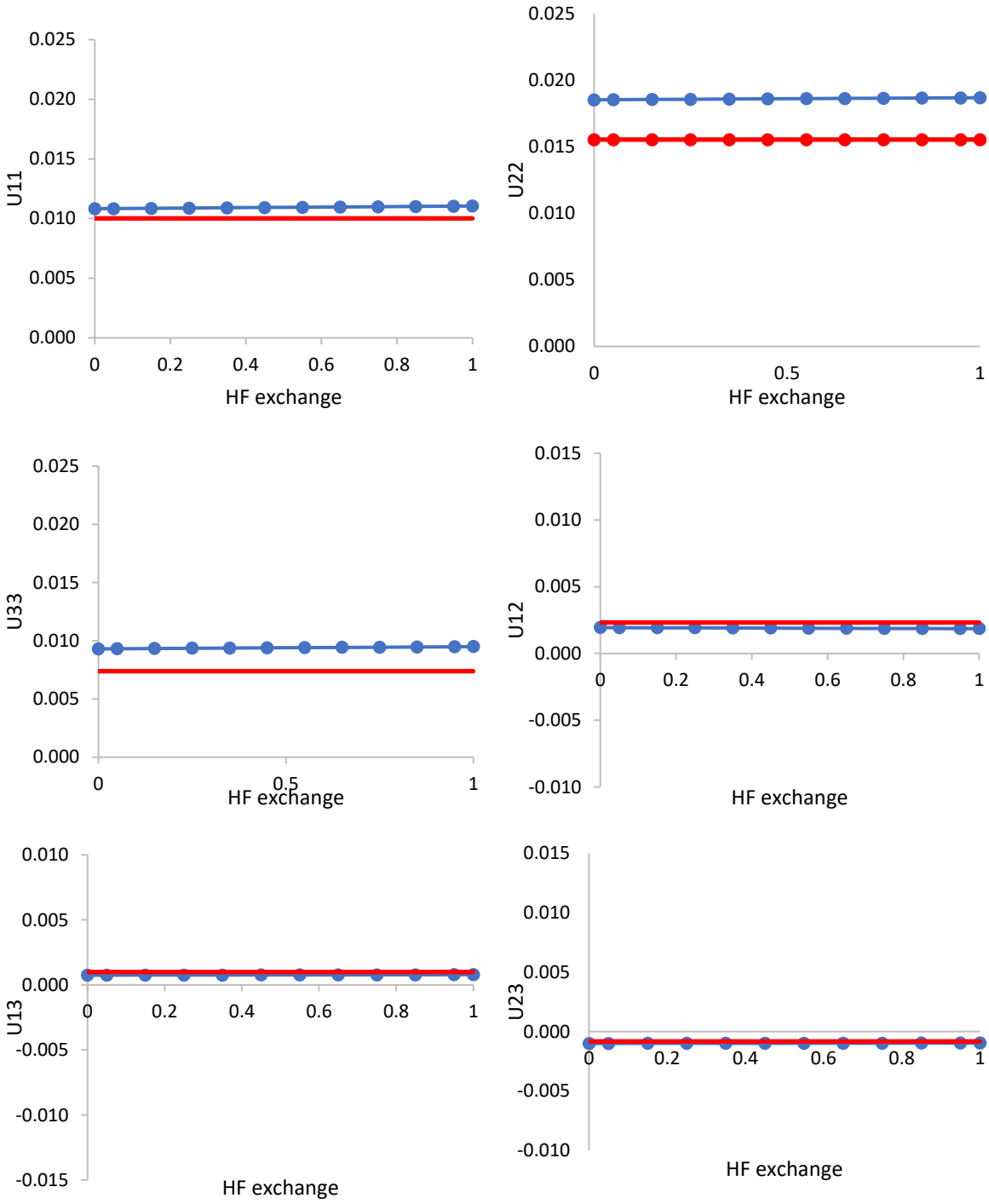


Figure S12. Unique ADPs for O3 atom of urea as a function of HF exchange refined at PBEx/def2-TVZP level of theory. Neutron diffraction value is shown as a continue red line. Std errors are of the order of magnitude of 10^{-4} - 10^{-5} Å^{-2}, and not distinguishable at this scale.

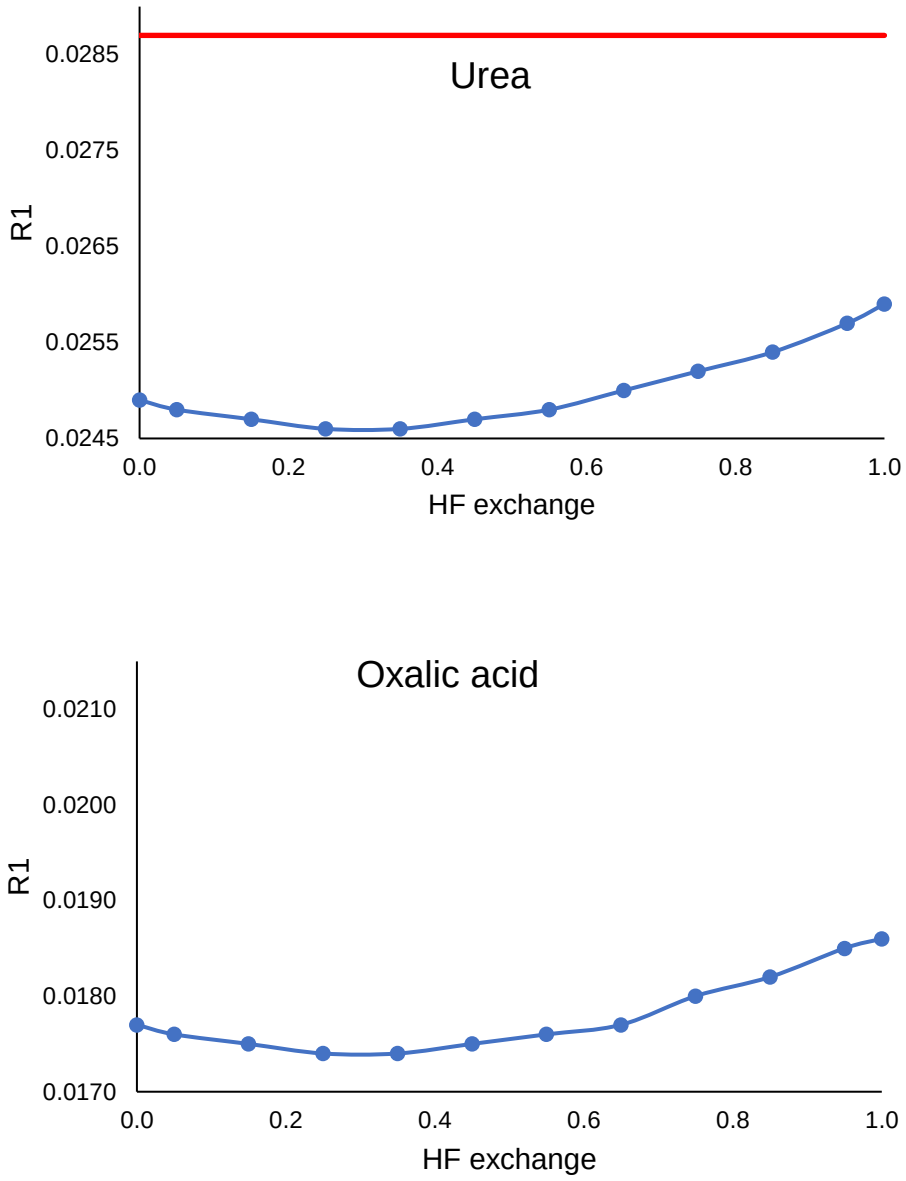
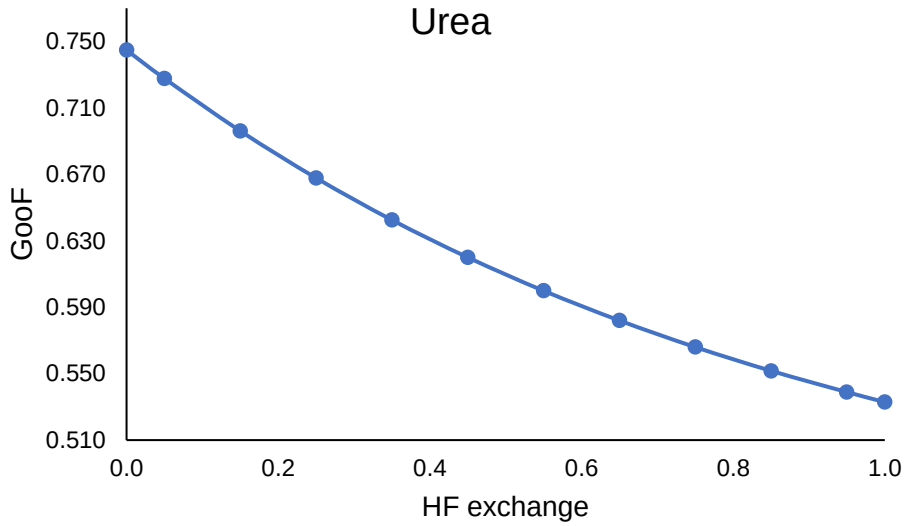


Figure S13. R_1 of urea and oxalic acid as a function of HF exchanged refined at PBEx/def2-TVZP level of theory. The value of IAM is shown as a continues red line for urea. This value, which is 0.0268 for oxalic acid, is omitted for clarity purposes.



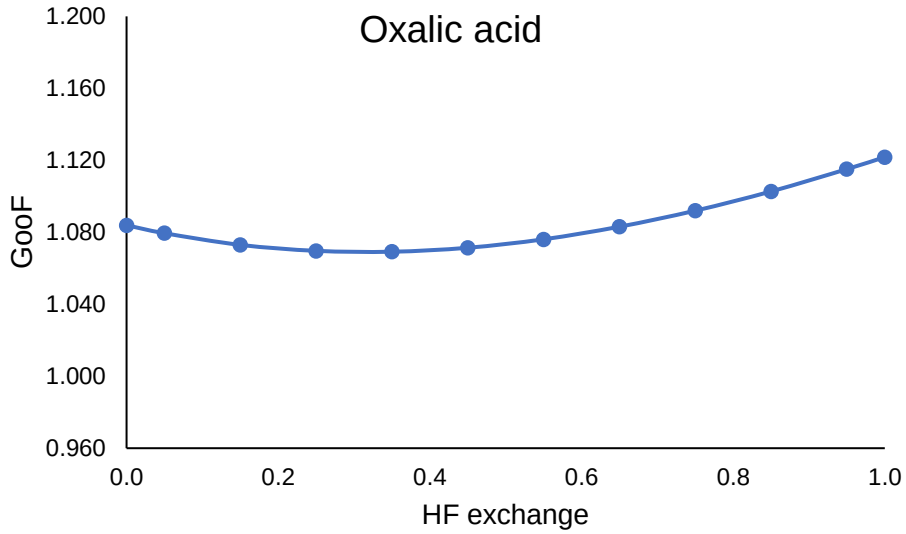


Figure S14. GooF of urea and oxalic acid as a function of HF exchanged refined at PBEx/def2-TVZP level of theory.

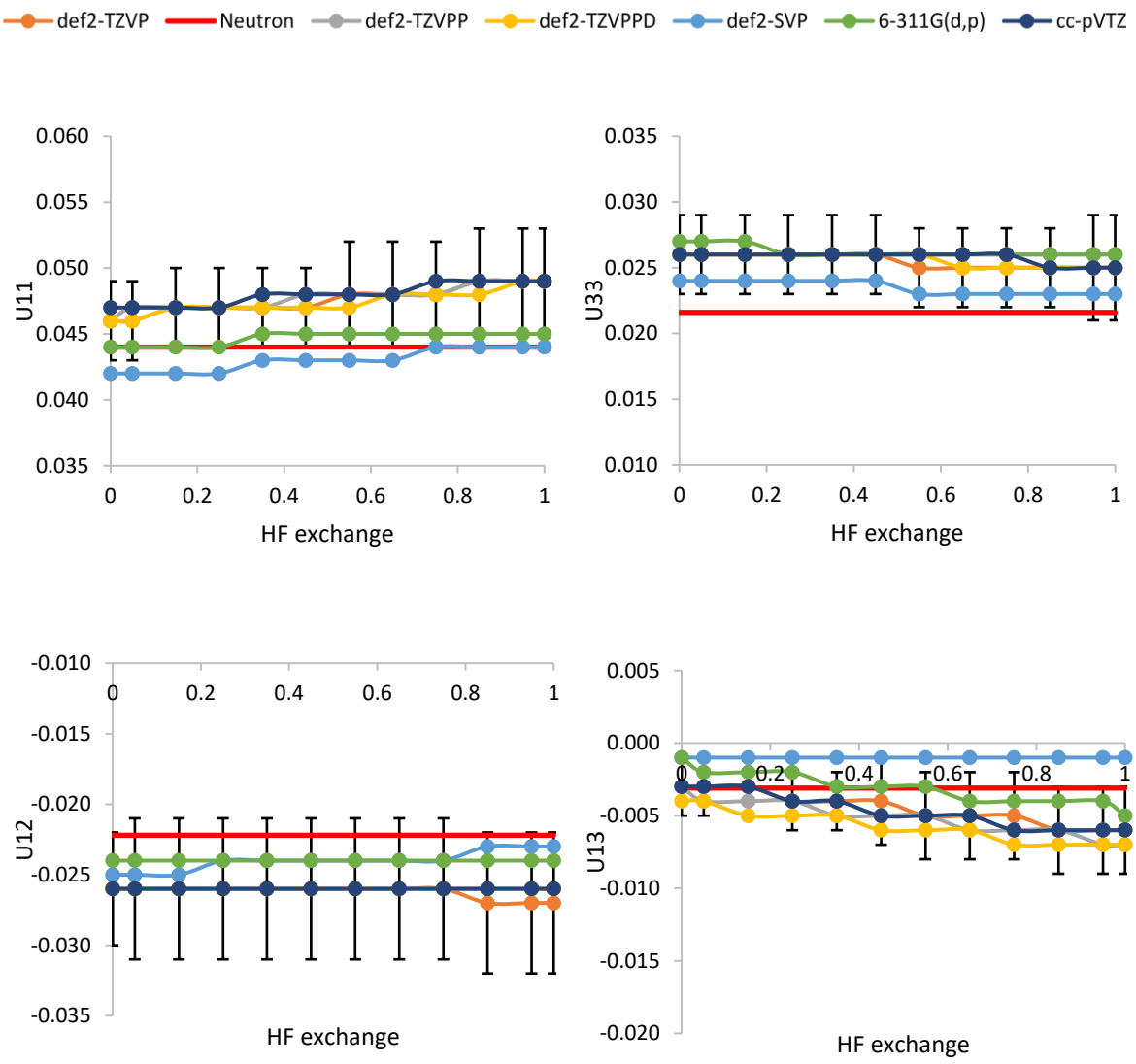


Figure S15. Unique ADPs for H1 atom of urea as a function of HF exchange refined with PBEx functional and several basis sets. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP) are shown.

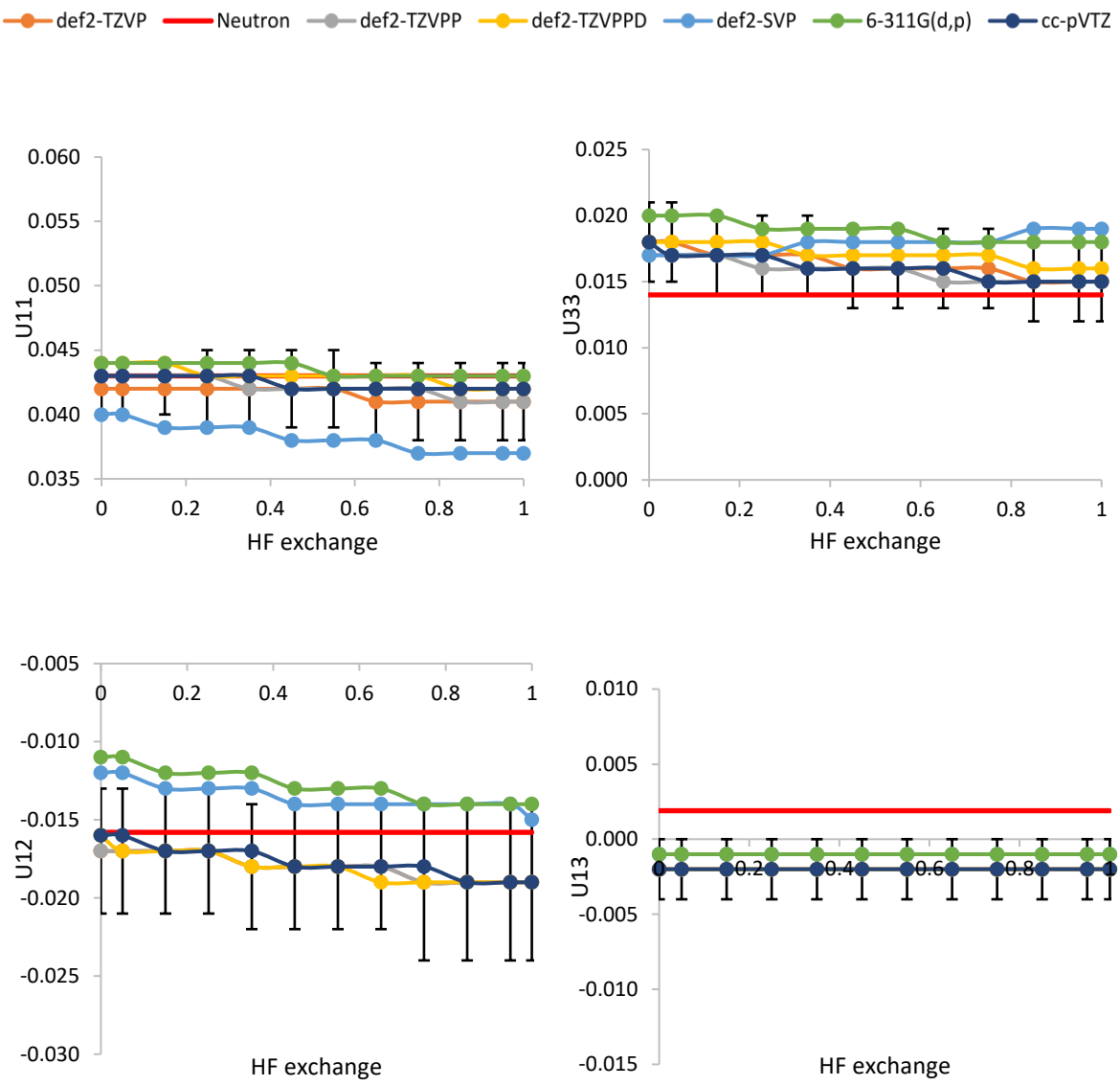


Figure S16. Unique ADPs for H2 atom of urea as a function of HF exchange refined with PBEx functional and several basis sets. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP) are shown.

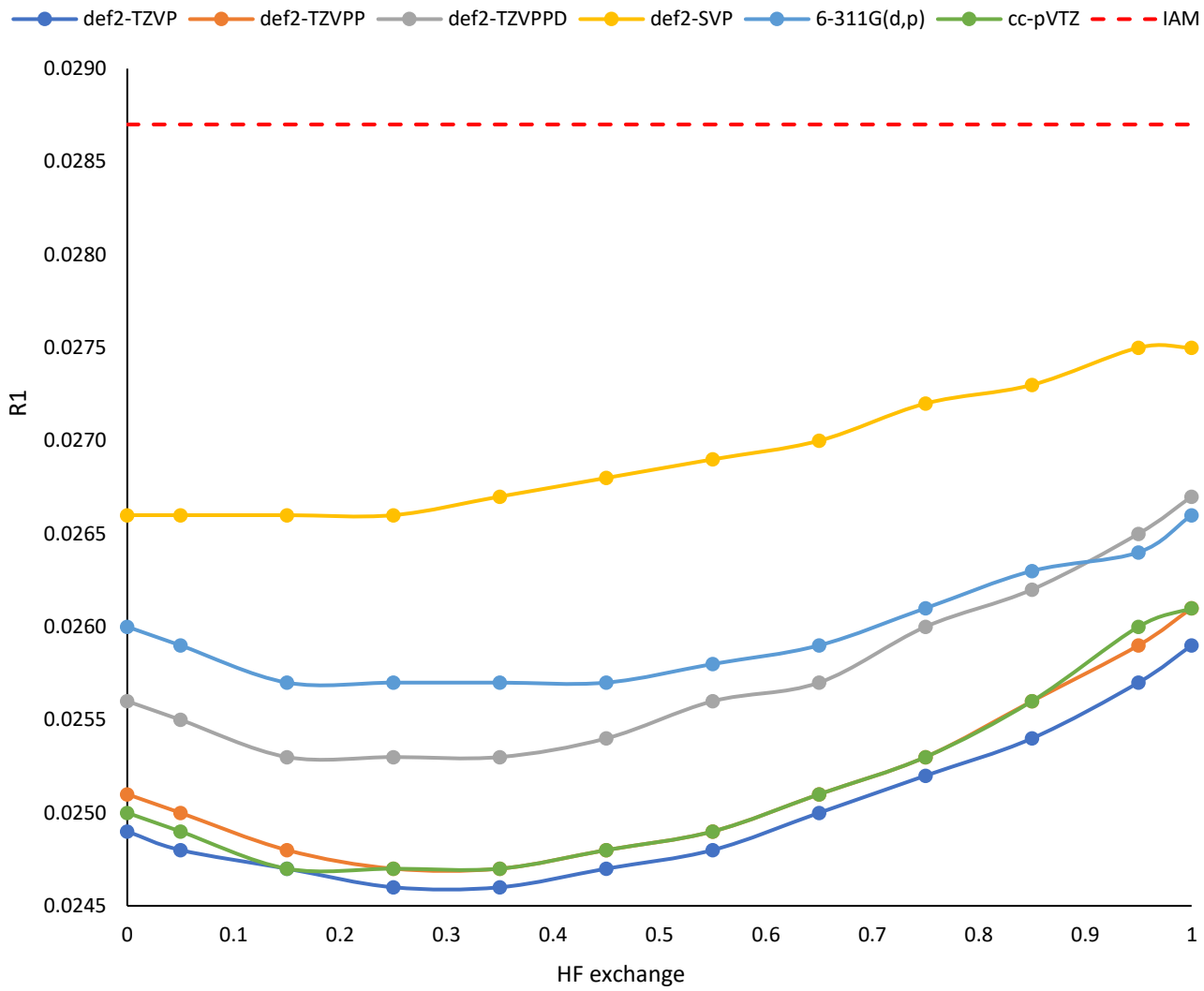


Figure S17. R1 of urea as a function of HF exchange refined with PBEx functional and several basis sets. IAM value is shown as a dashed red line.

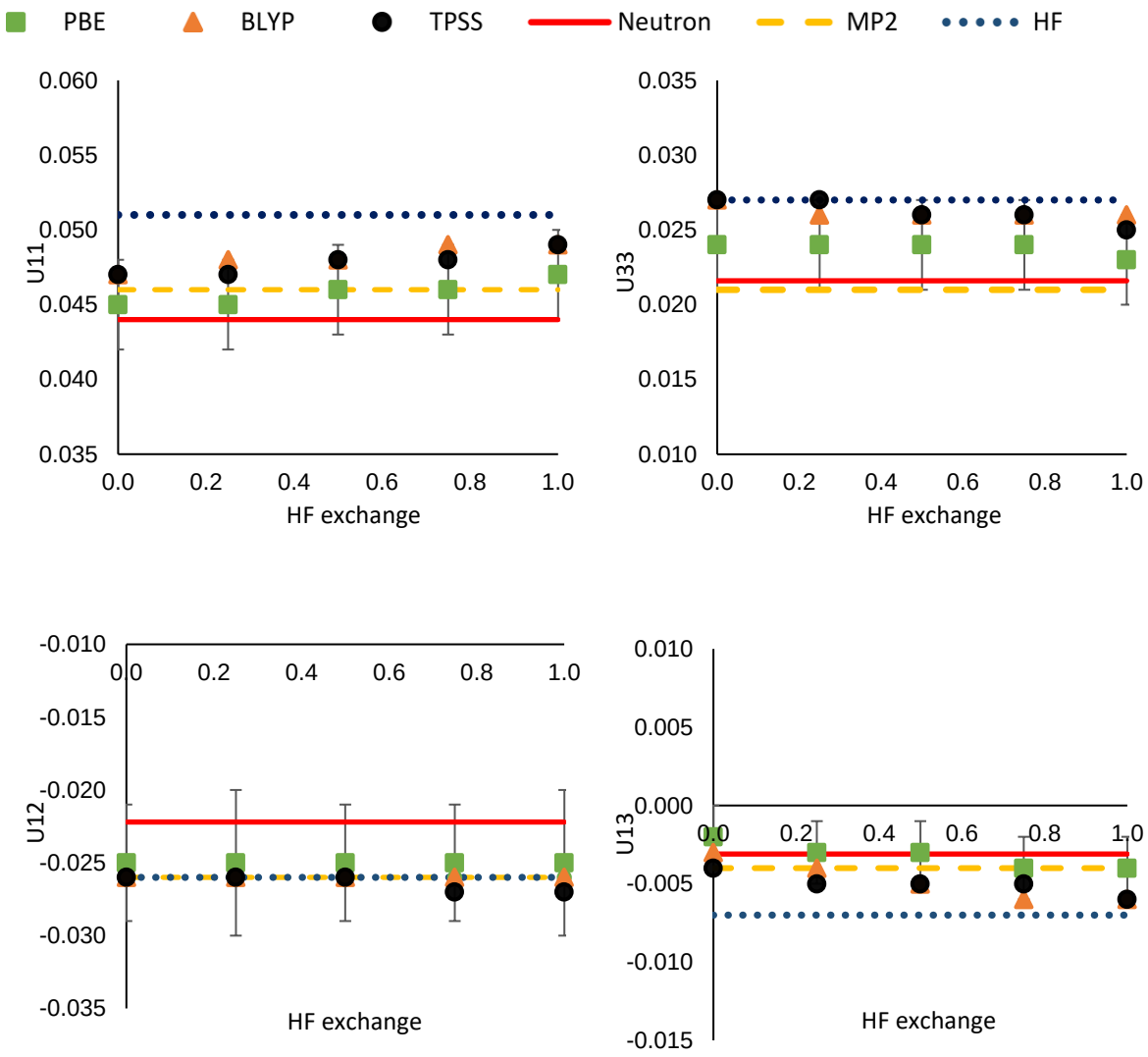


Figure S18. Unique ADPs for H1 atom of urea as a function of HF exchange refined with different levels of theory. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP) are shown.

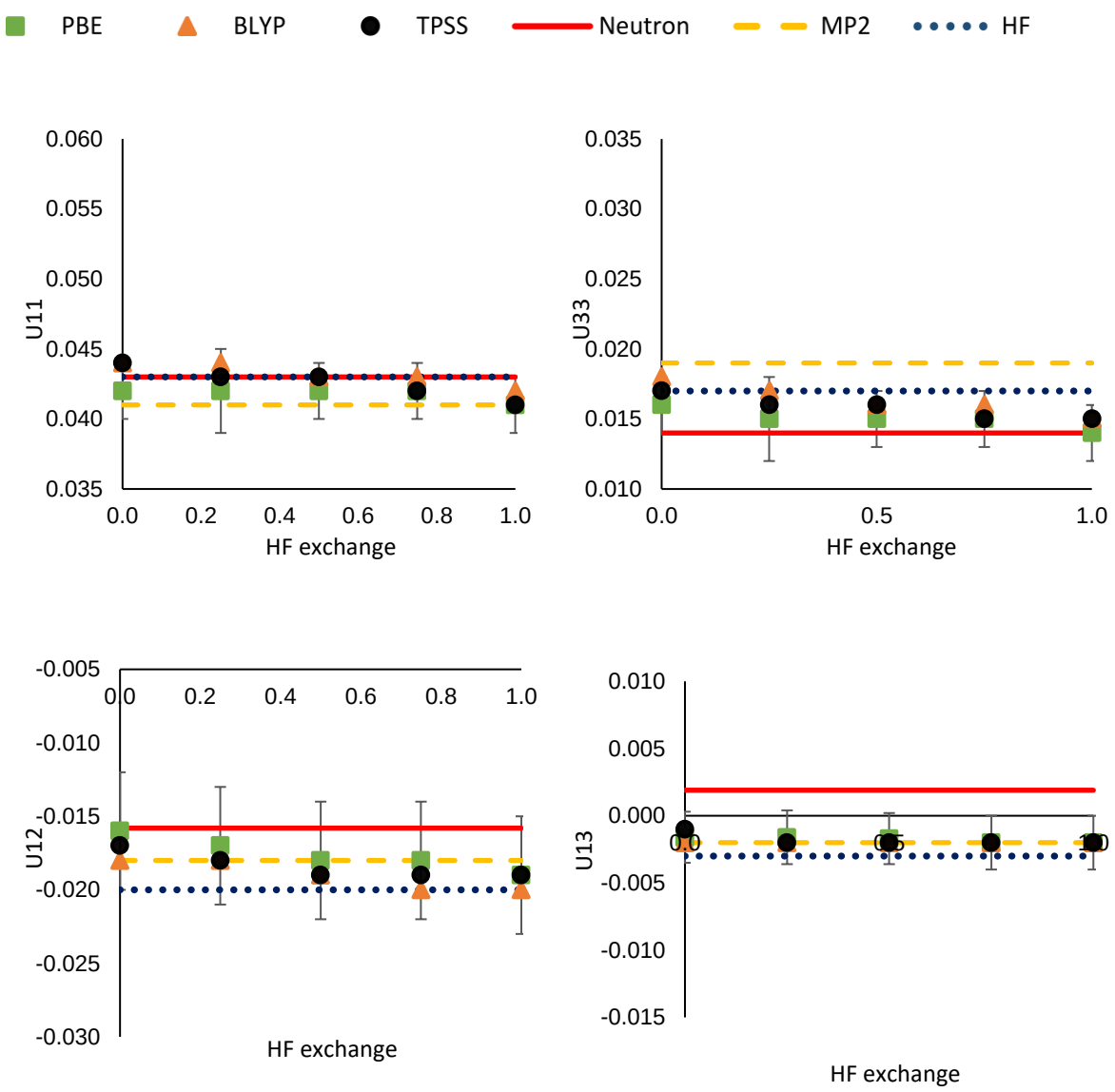


Figure S19. Unique ADPs for H2 atom of urea as a function of HF exchange refined with different levels of theory. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP) are shown.

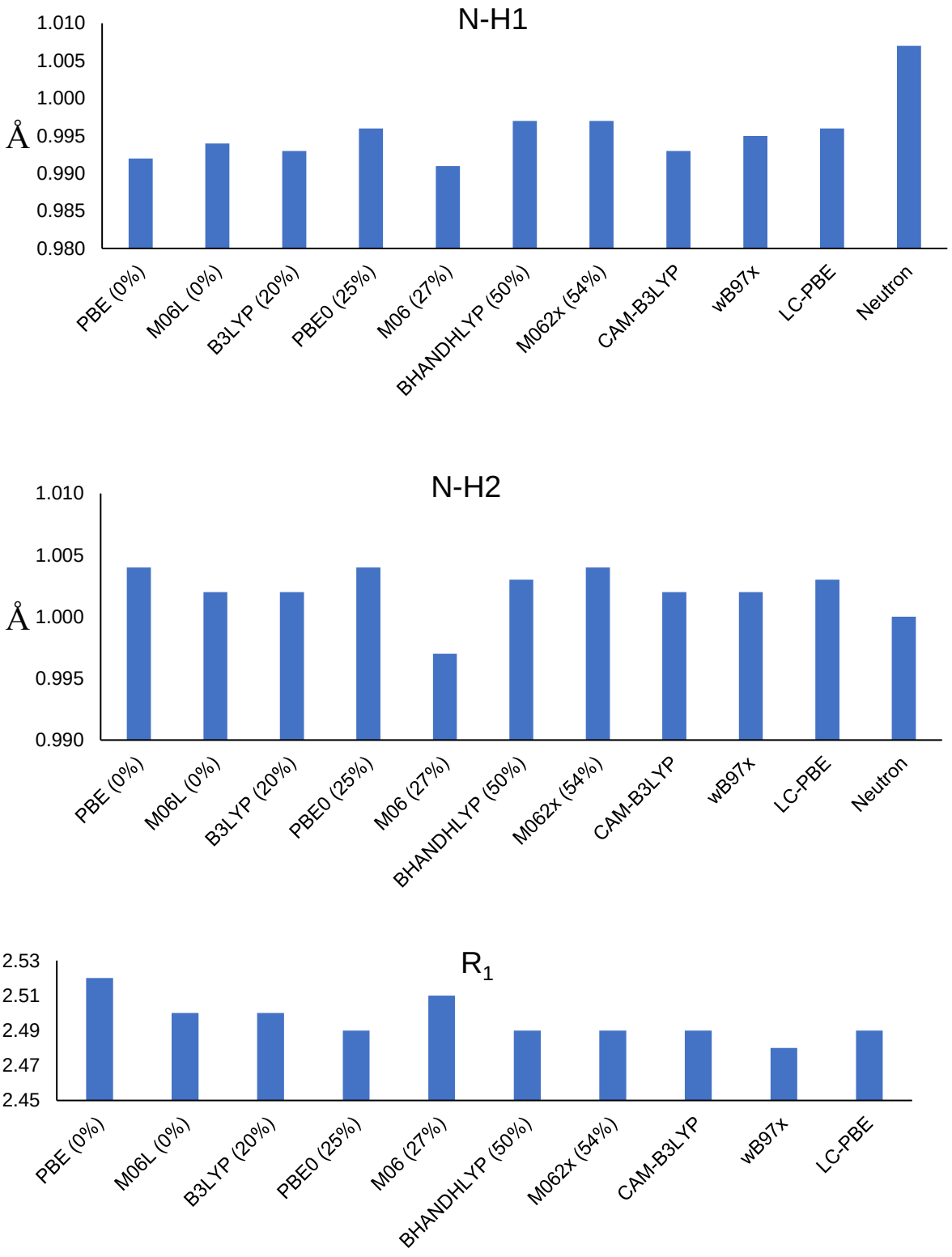


Figure S20. N-H1 (top) and N-H2 (middle) distances refined with different density functionals and the def2-TZVP basis set. The corresponding R1 values (bottom).

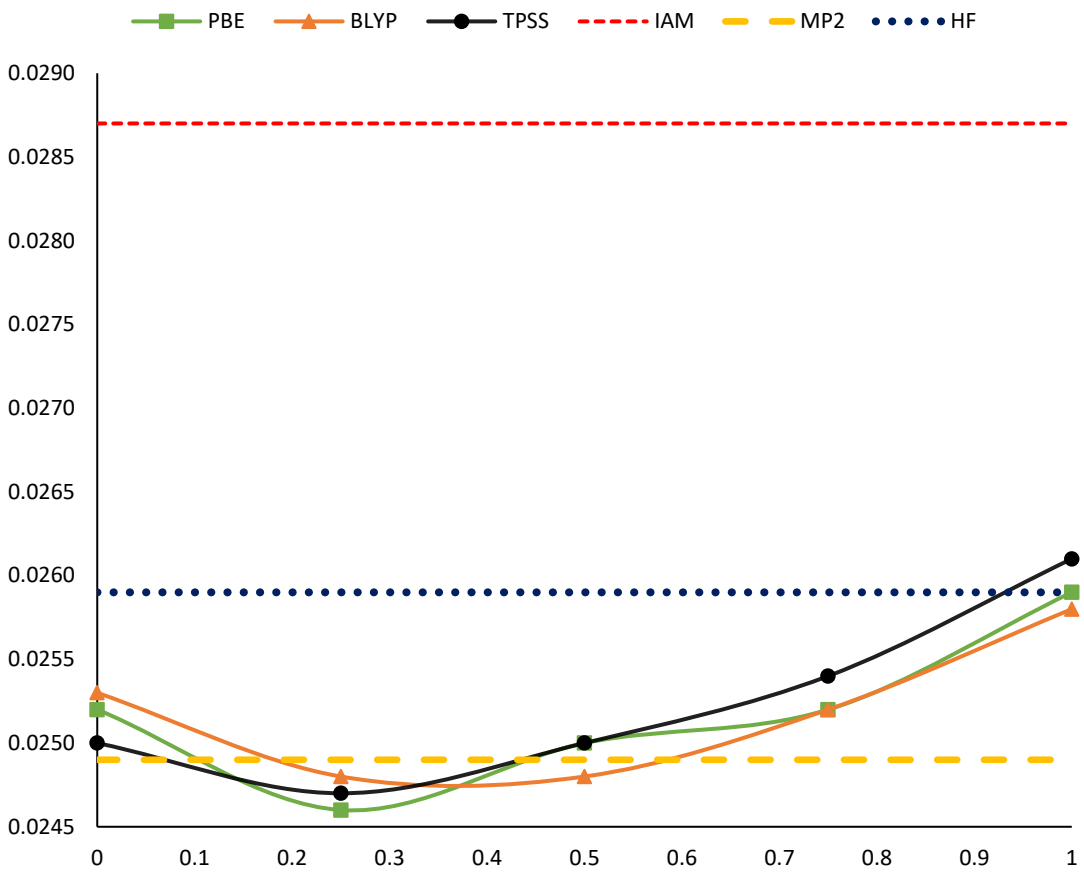


Figure S21. R1 of urea as a function of HF exchange refined with different level of theories. IAM value is shown as a dashed red line.

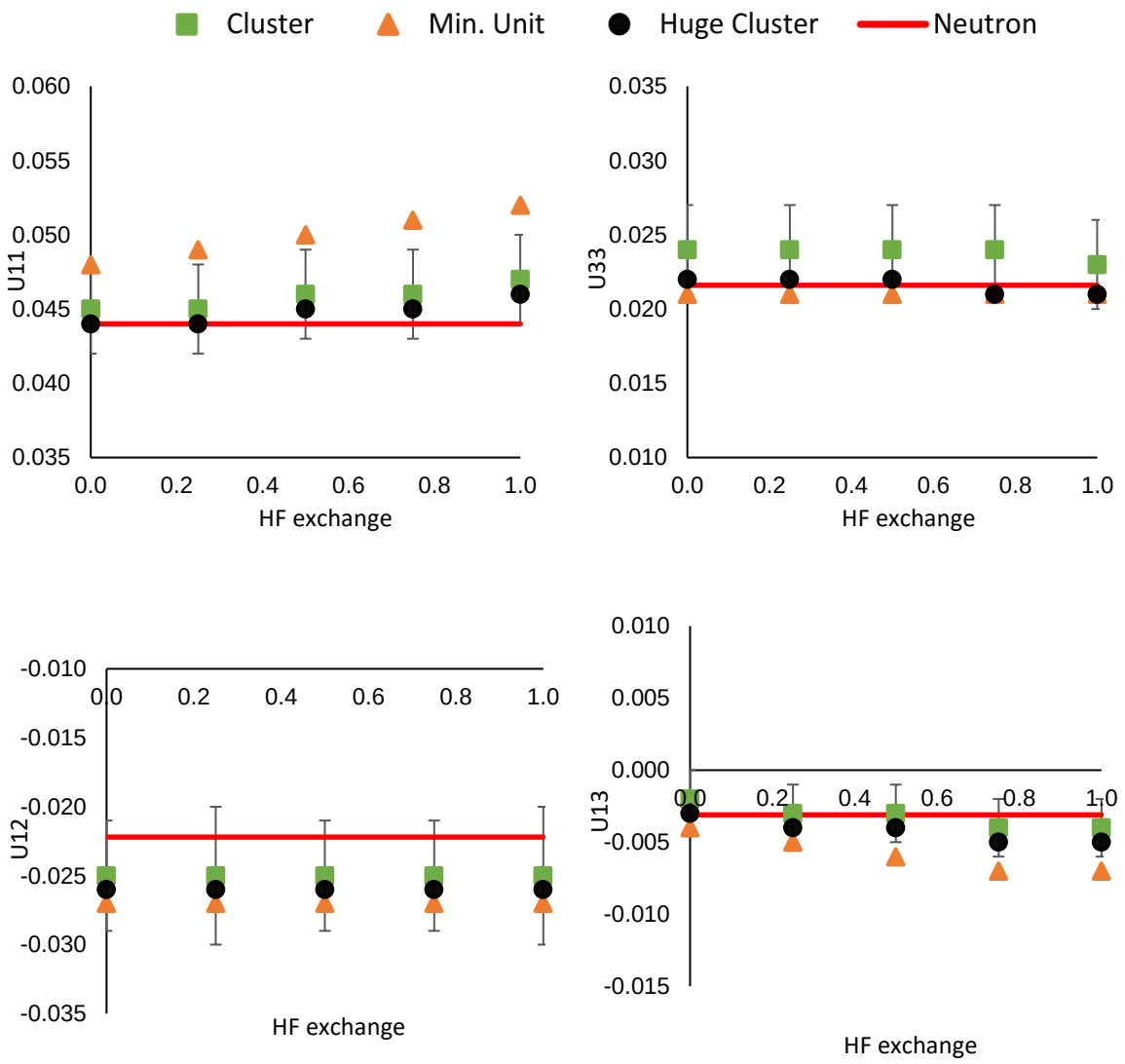


Figure S22. Unique ADPs for H1 atom of urea as a function of HF exchange refined with clusters of different sizes. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP and Figure 1 cluster) are shown.

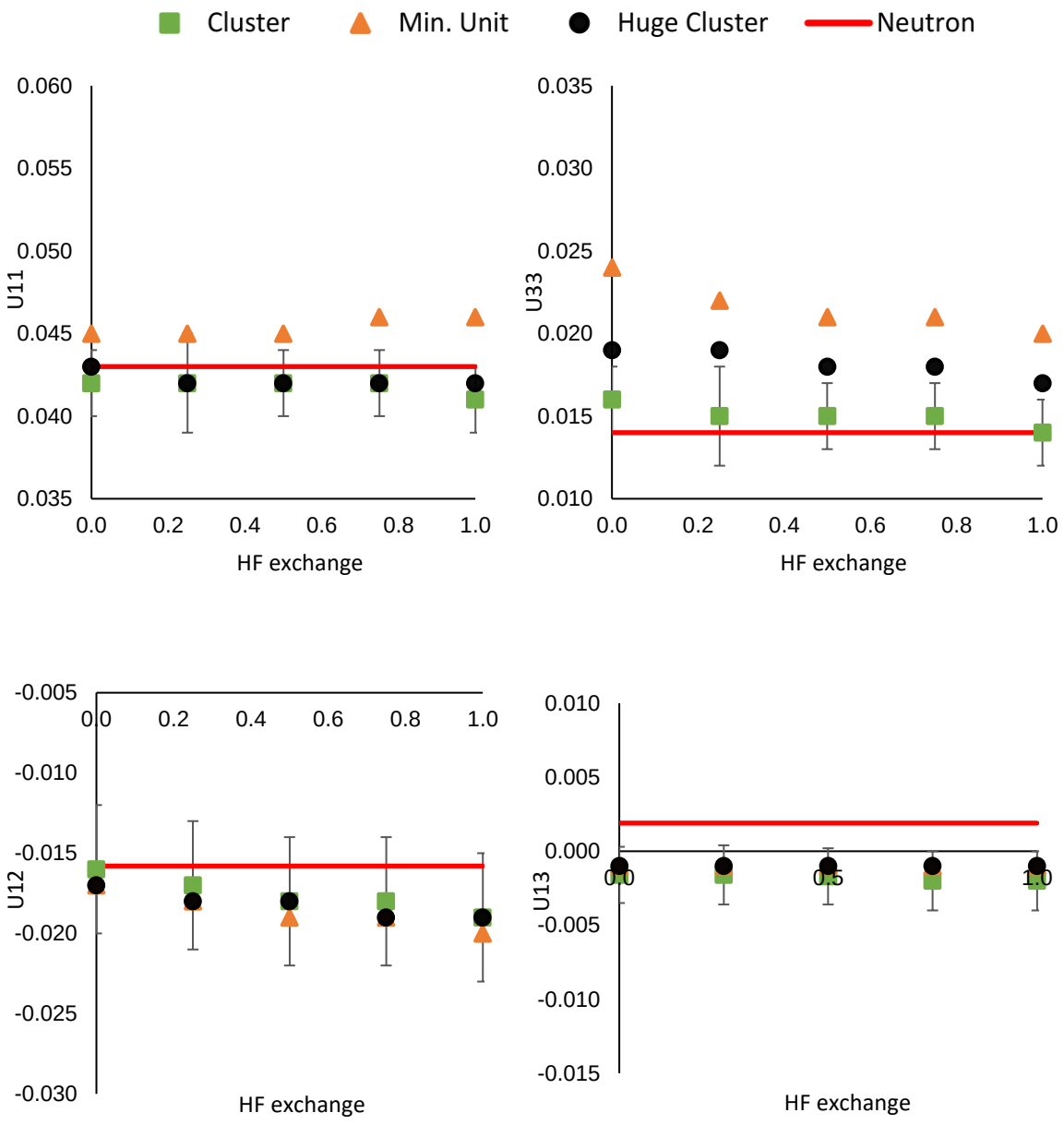


Figure S23. Unique ADPs for H2 atom of urea as a function of HF exchange refined with clusters of different sizes. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP and Figure 1 cluster) are shown.

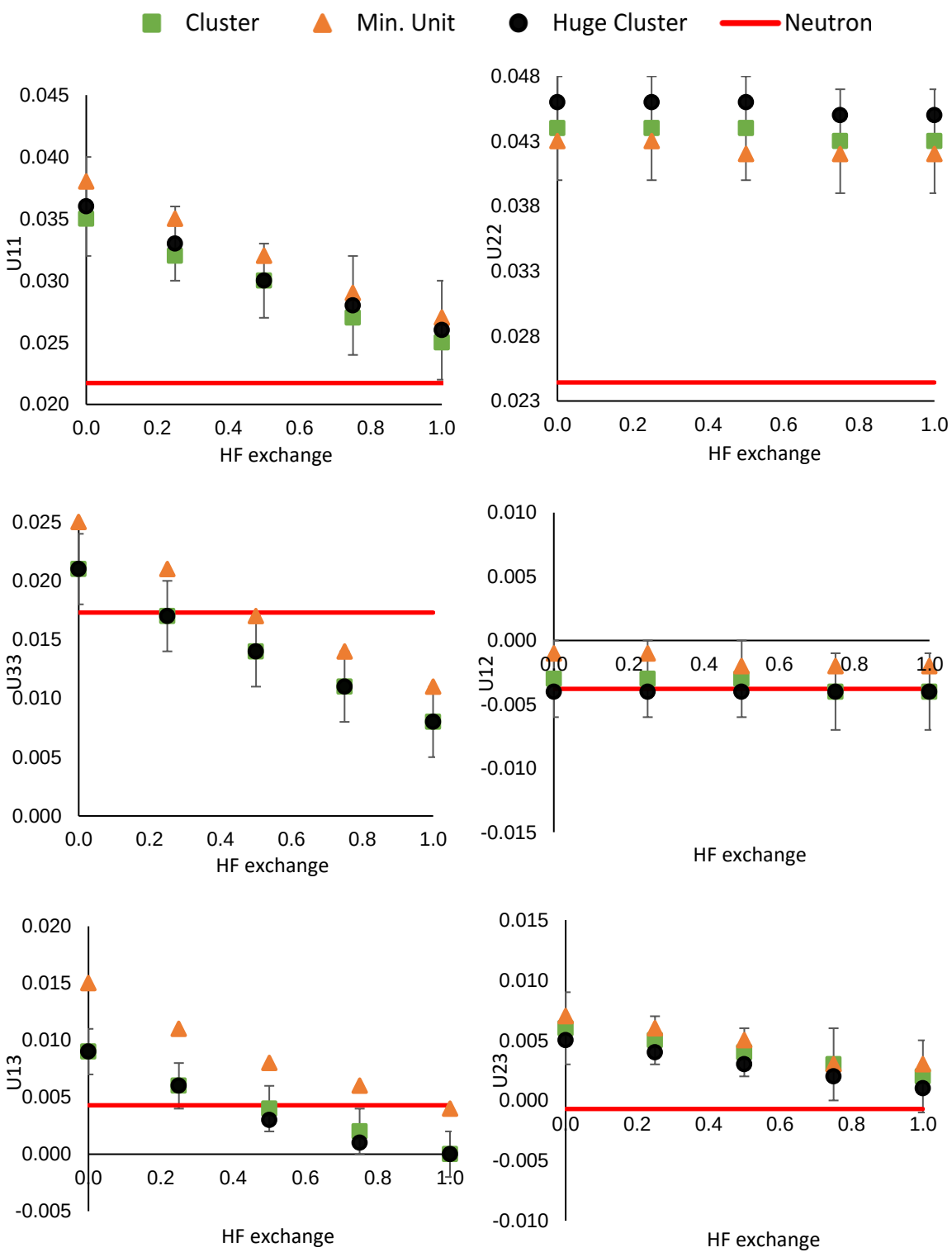


Figure S24. Unique ADPs for H1 atom of oxalic acid as a function of HF exchange refined with clusters of different sizes. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP and Figure 1 cluster) are shown.

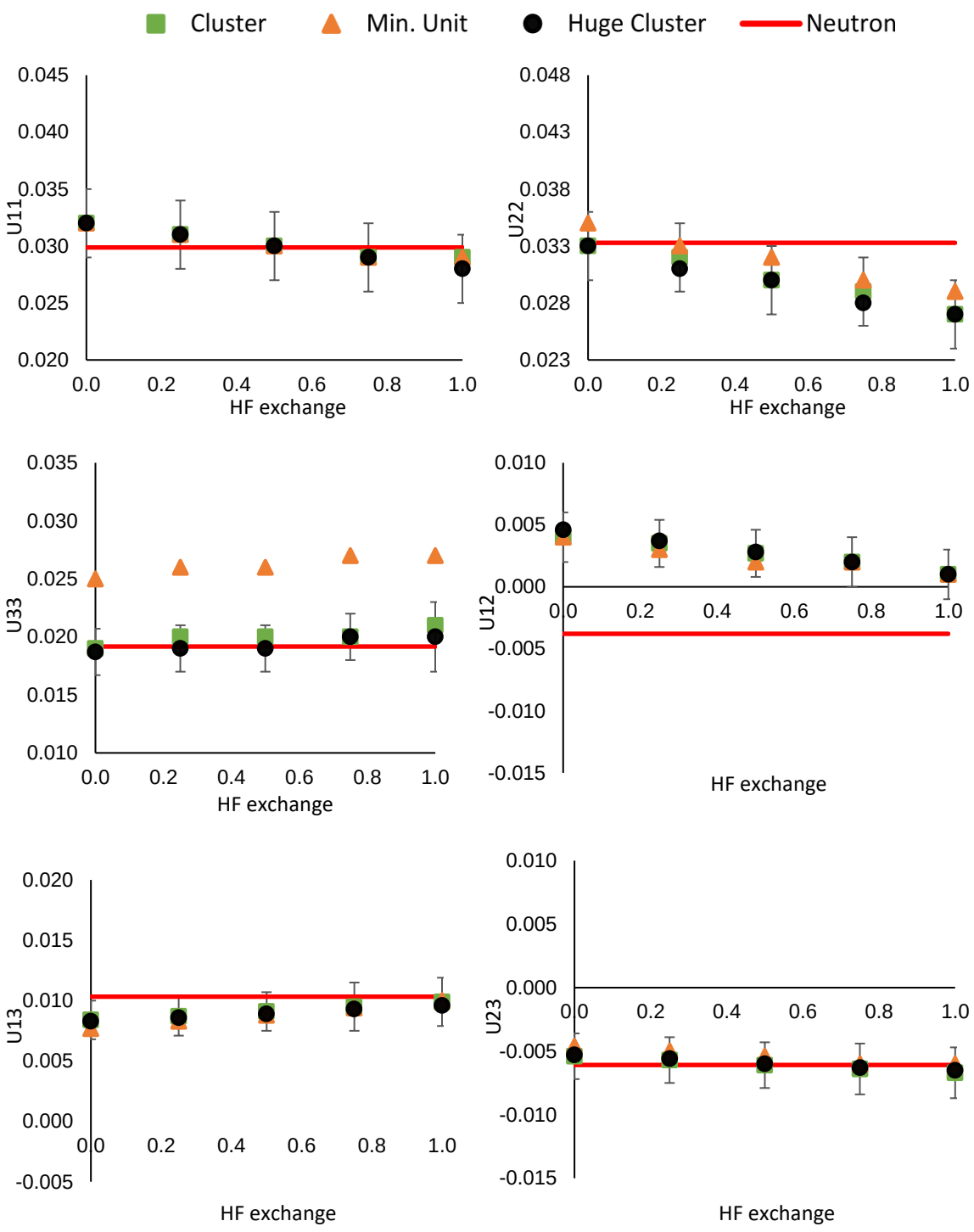


Figure S25. Unique ADPs for H2 atom of oxalic acid as a function of HF exchange refined with clusters of different sizes. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP and Figure 1 cluster) are shown.

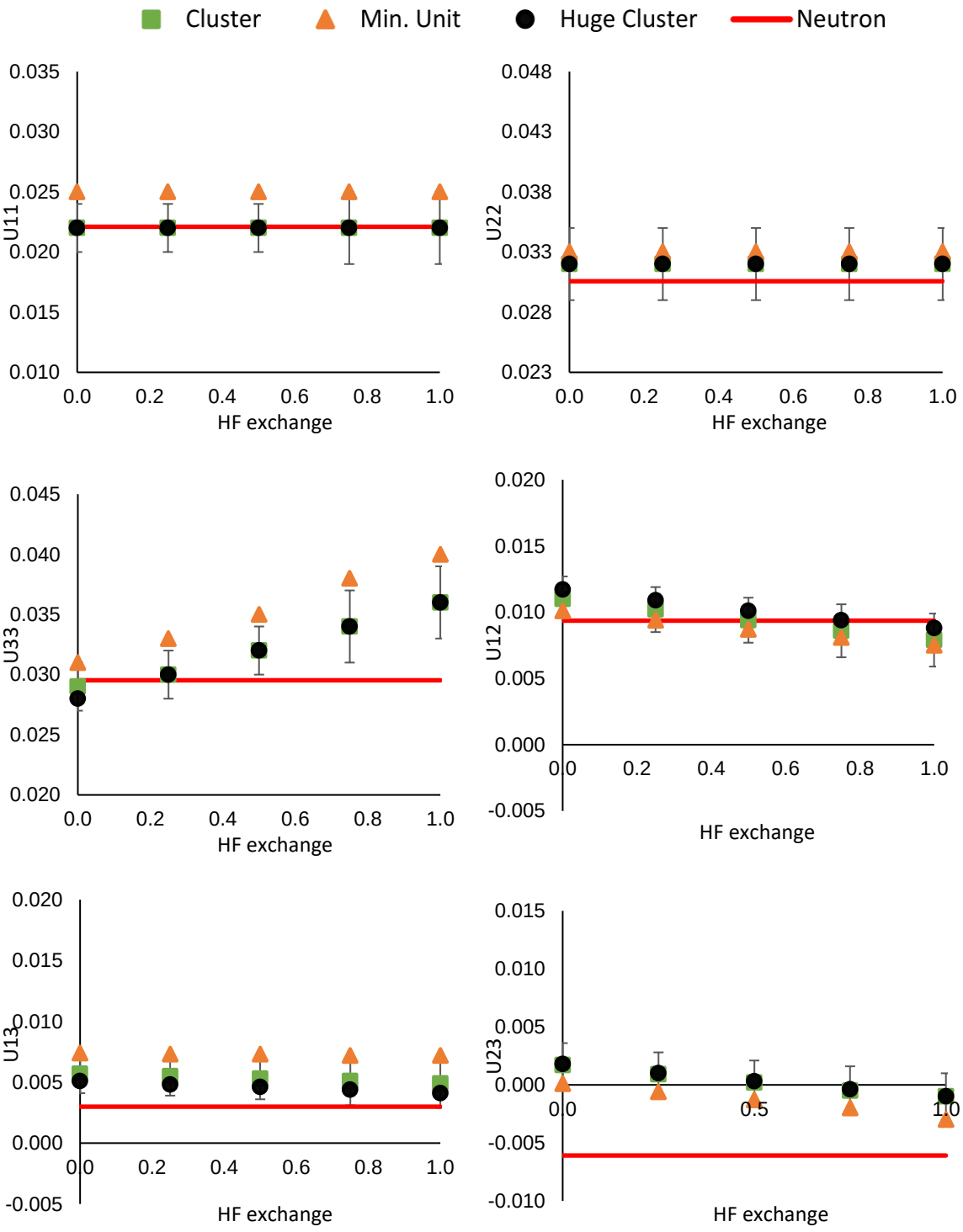


Figure S26. Unique ADPs for H3 atom of oxalic acid as a function of HF exchange refined with clusters of different sizes. Neutron diffraction value is shown as a continue red line. The std errorss of the reference refinement (PBEx/def2-TZVP and Figure 1 cluster) are shown.

Cluster Min. Unit Big Cluster IAM

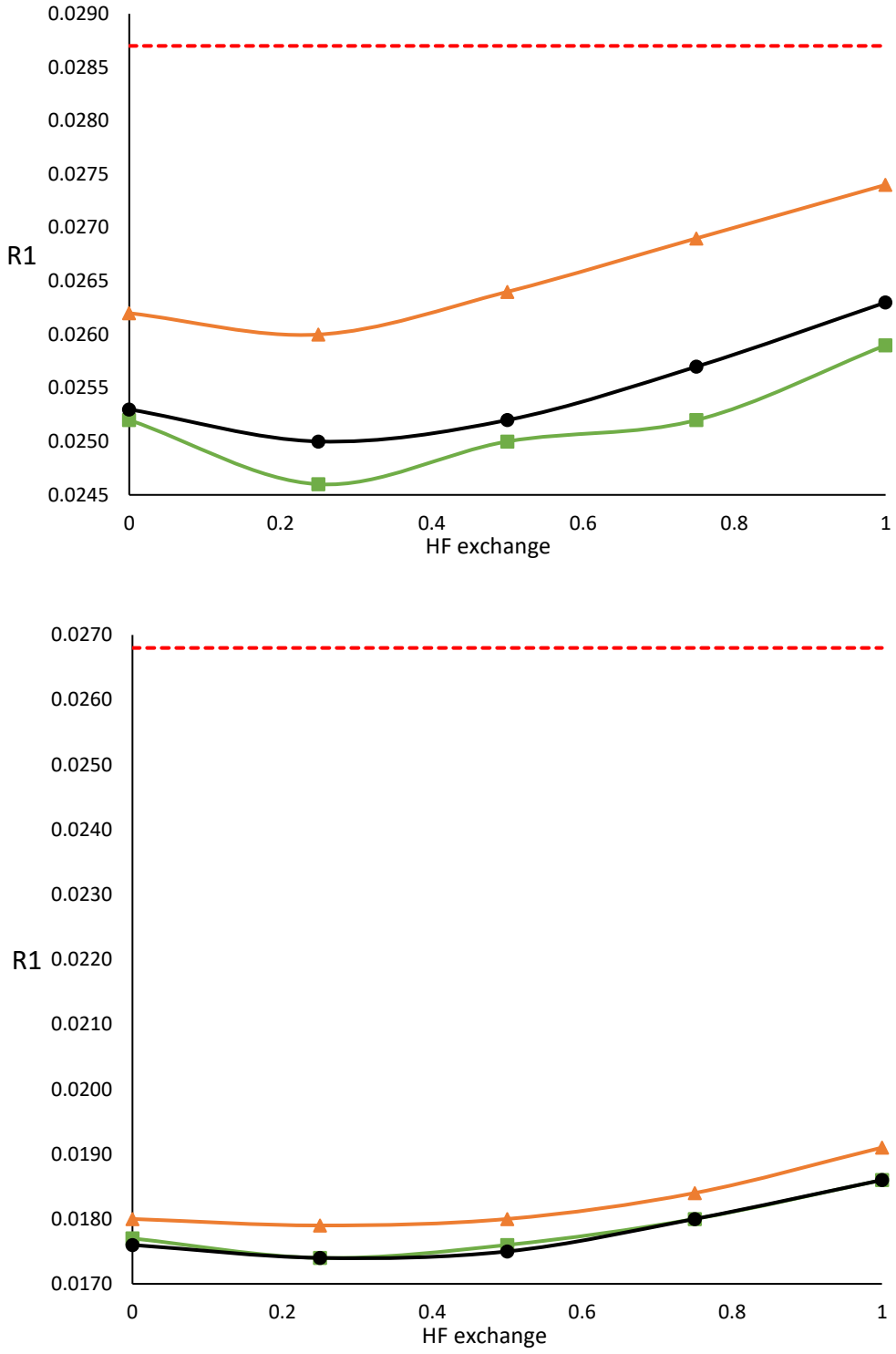


Figure S27. R1 of urea and oxalic acid as a function of HF exchange refined with clusters of different sizes at the PBEx/def2-TZVP level of theory. IAM value is shown as a dashed red line.

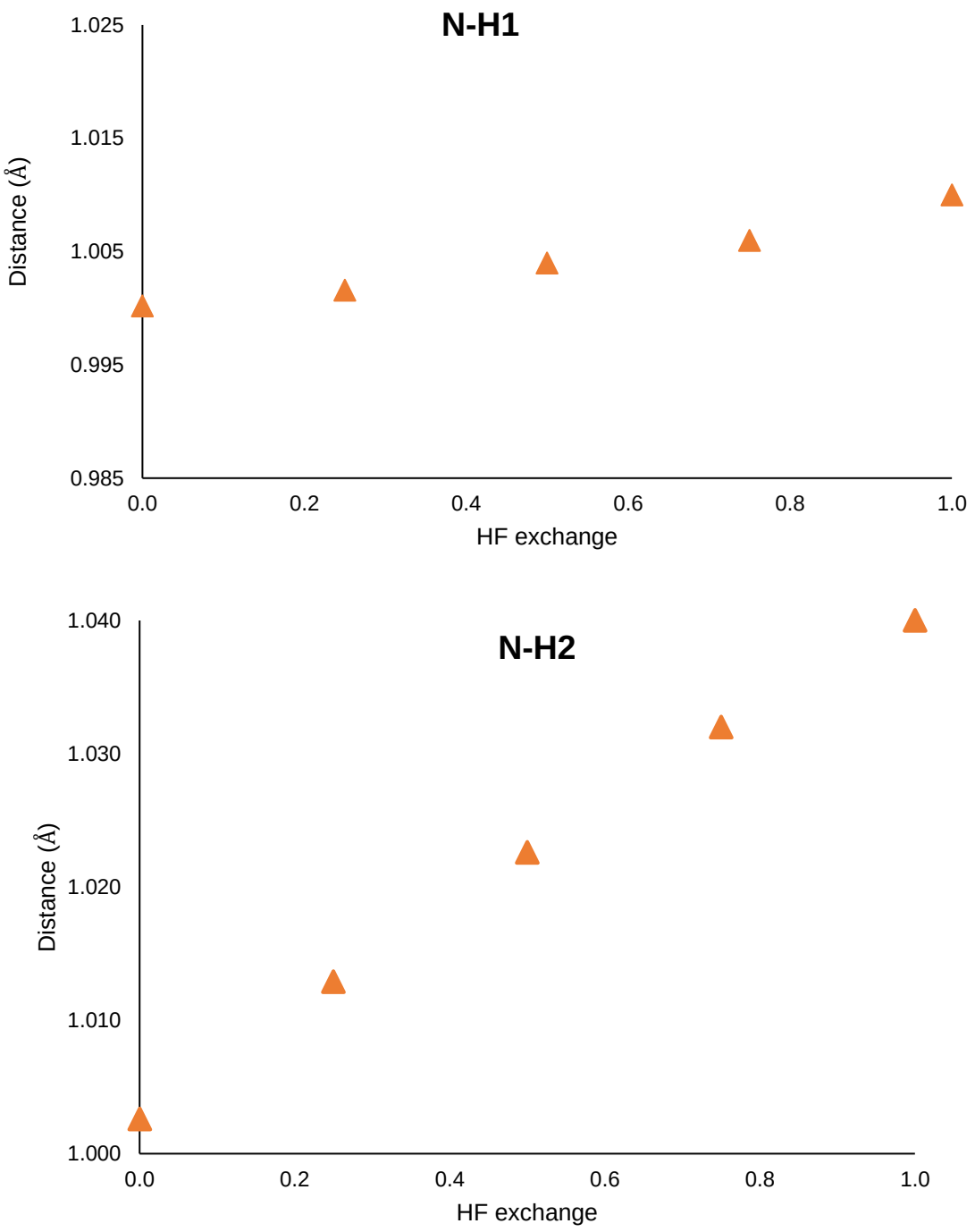


Figure S28. N-H1 and N-H2 distances obtained from HAR, using the theoretical structure factors.

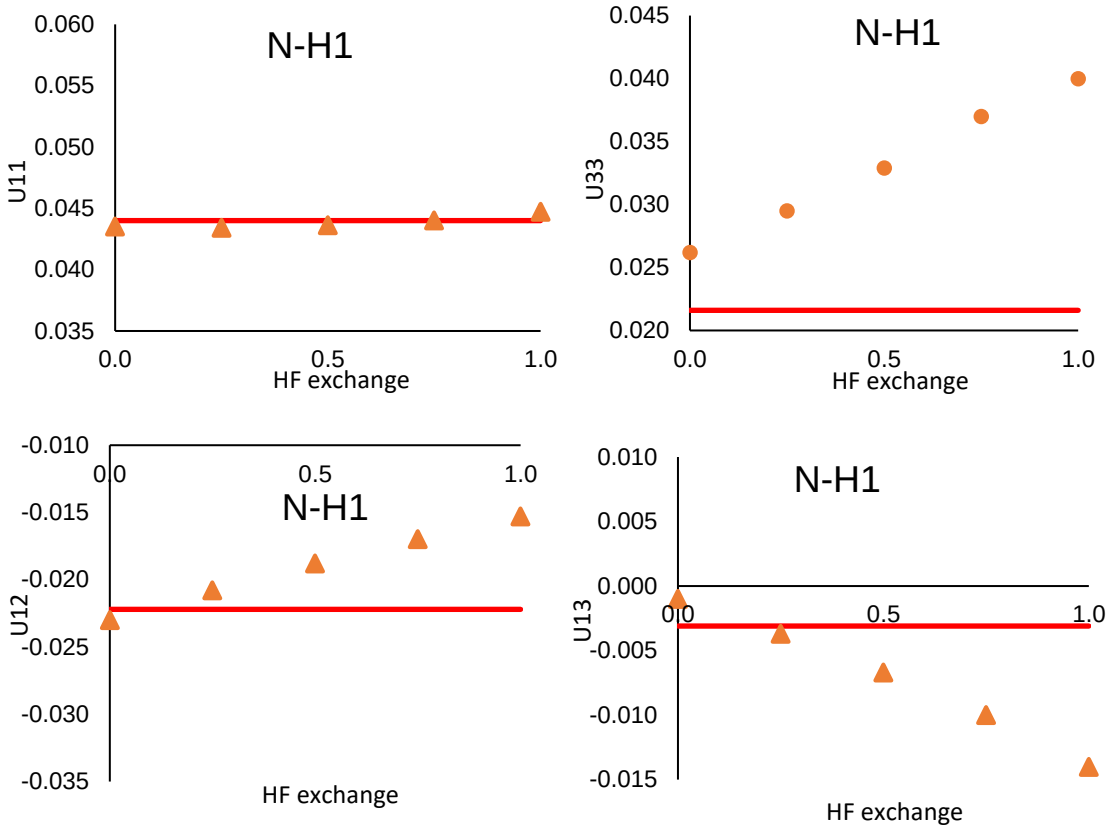


Figure S29. Unique ADPs for H1 atom of urea as a function of HF exchange, refined at PBEx/def2-TVZP level of theory, using the theoretical structure factors. Neutron diffraction value is shown as a continue red line.

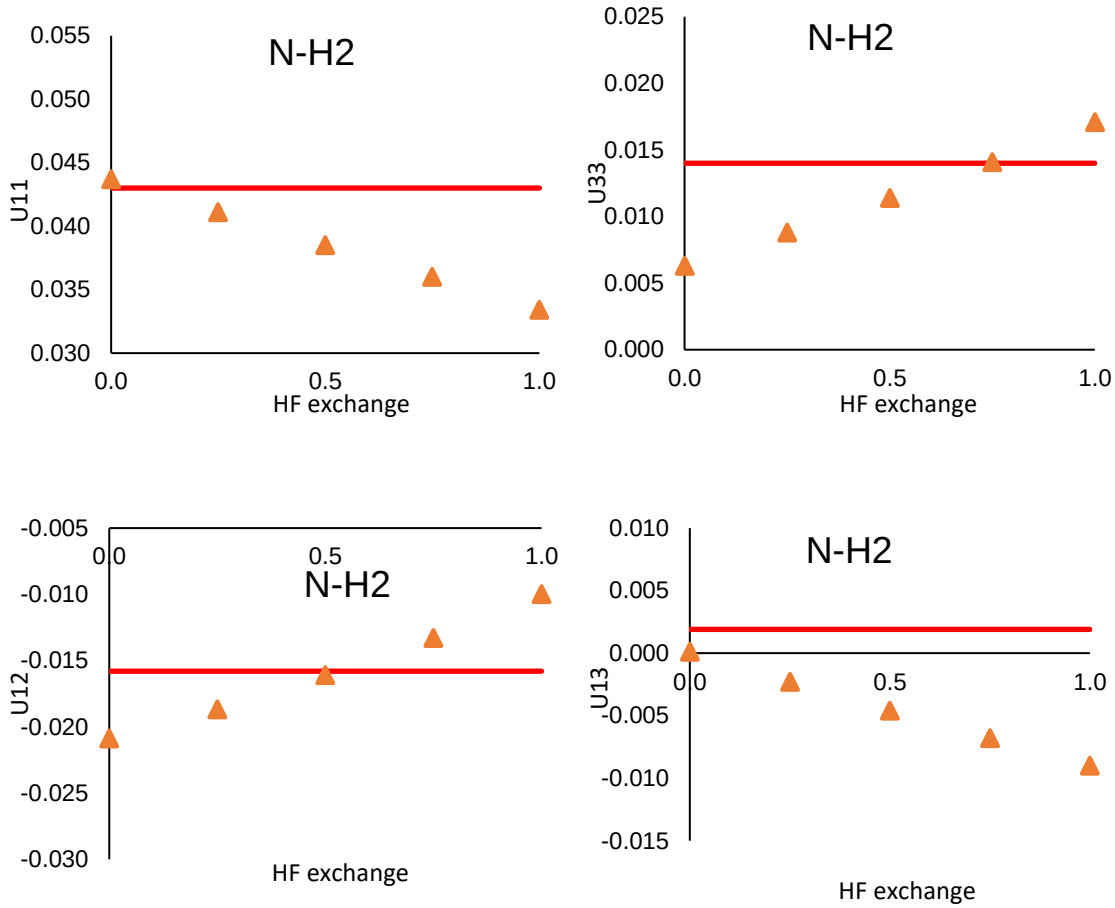


Figure S30. Unique ADPs for H2 atom of urea as a function of HF exchange, refined at PBEx/def2-TVZP level of theory, using the theoretical structure factors. Neutron diffraction value is shown as a continue red line.

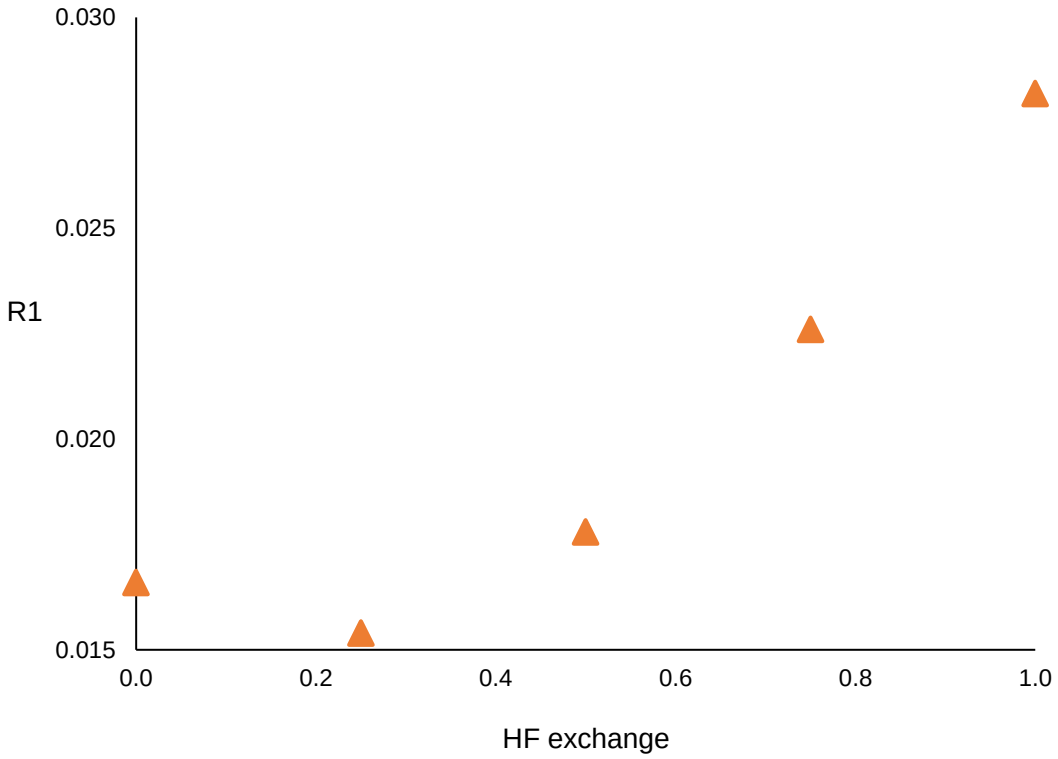


Figure S31. R1 of urea as a function of HF exchange, refined at PBEx/def2-TVZP level of theory, using the theoretical structure factors.

Table S1. QTAIM atomic charges and volumes (a. u.) of the atoms involved in the O1-H1···O3 hydrogen bond of oxalic acid for different methods and the cc-pVTZ basis set.

	Charges			Volume		
	O1	H1	O3	O1	H1	O3
PBE	-1.15	0.64	-1.20	129.45	10.05	148.02
PBE50	-1.30	0.71	-1.32	131.17	7.88	149.50
PBE100	-1.44	0.77	-1.41	132.30	5.83	150.71
HF	-1.43	0.77	-1.38	133.91	6.05	151.33
MP2	-1.18	0.72	-1.22	132.58	7.88	151.49