Supplementary Material

Multireference Calculations on Bond Dissociation and Biradical Polycyclic Aromatic Hydrocarbons as Guidance for Fractional Occupation Number Weighted Density Analysis in DFT Calculations

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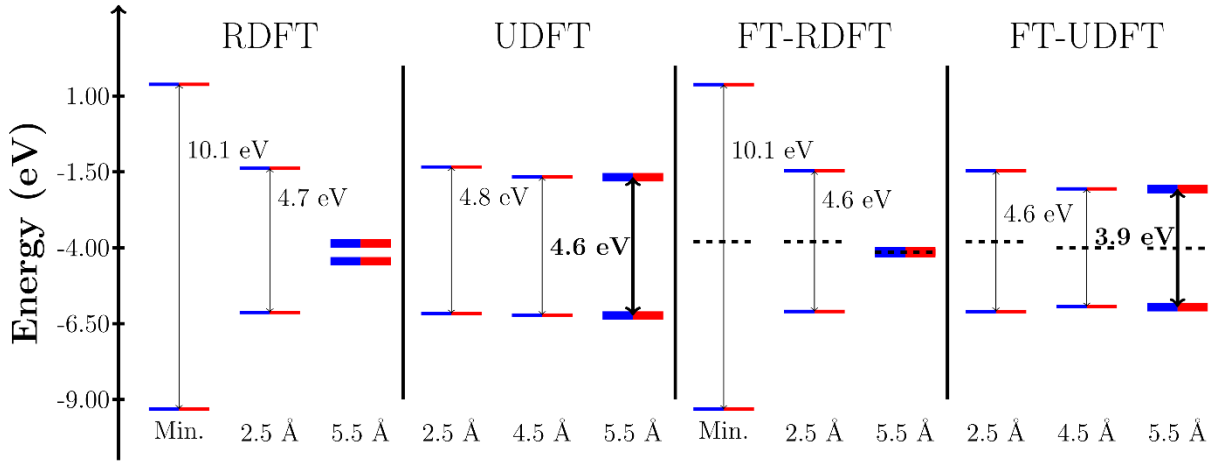

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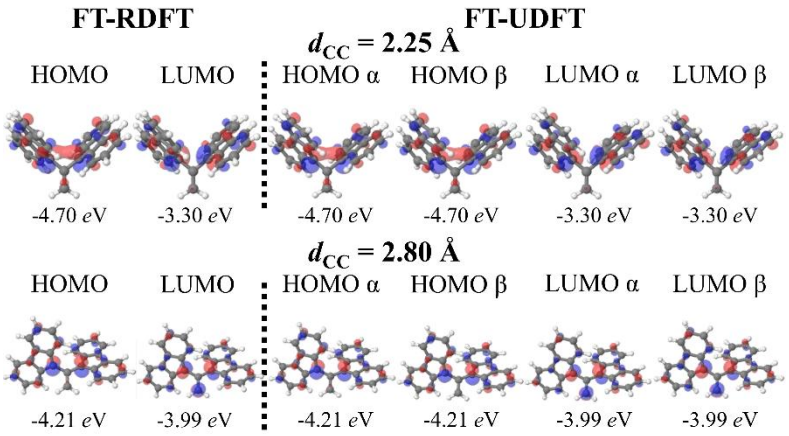
Distance	RDFT		FT-RDFT	
	$f_{i,\,HOMO}$	$f_{i,\,LUMO}$	$f_{i,\,HOMO}$	$f_{i,\,LUMO}$
Min.	2.00	0.00	2.00	0.00
2.5 Å	2.00	0.00	1.90	0.09
5.5 Å	2.00	0.00	1.02	0.98
Distance	UDFT		FT-UDFT	
	$f_{i,\,HOMO}$	$f_{i,\,LUMO}$	$f_{i,\,HOMO}$	$f_{i,\,LUMO}$
2.5 Å	1.97	0.03	1.90	0.09
4.5 Å	1.07	0.93	1.85	0.15
5.5 Å	1.01	0.99	1.85	0.15



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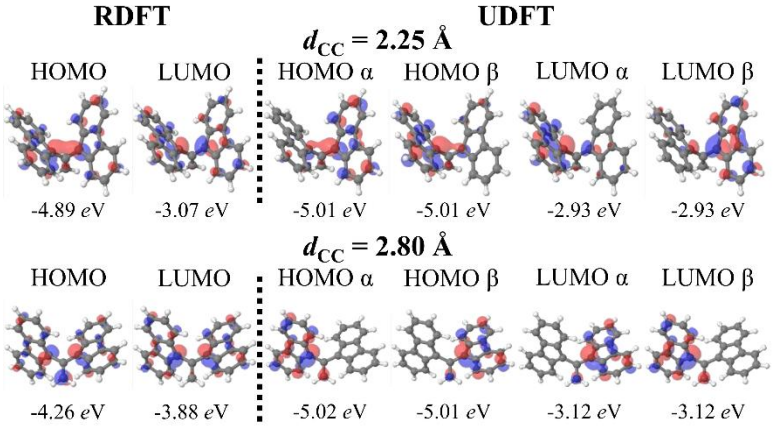

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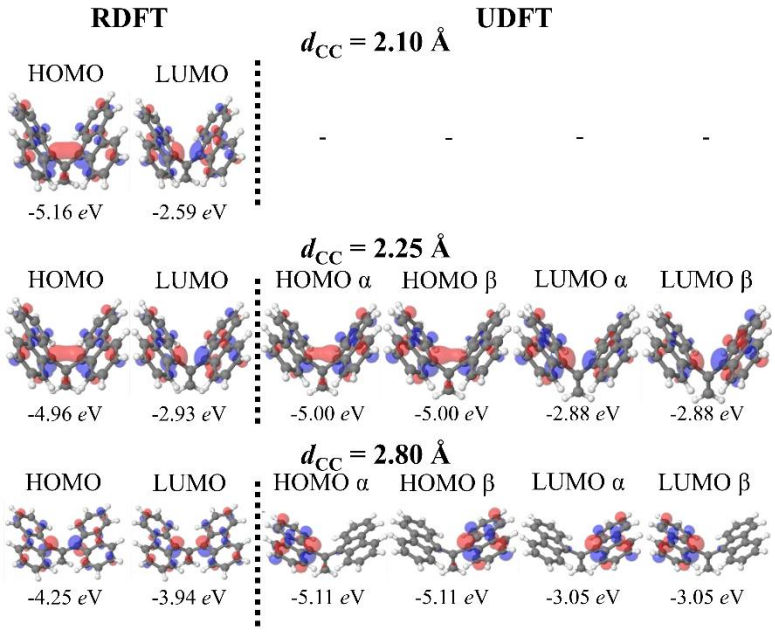

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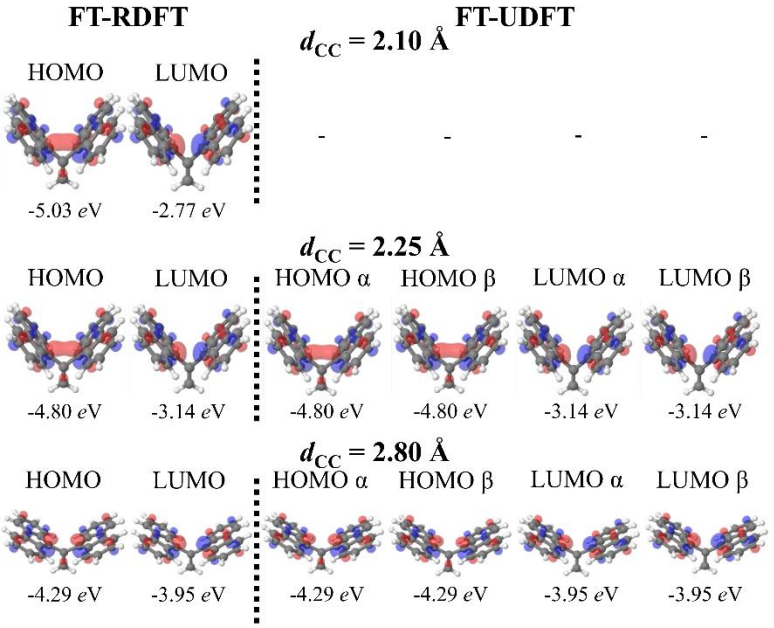

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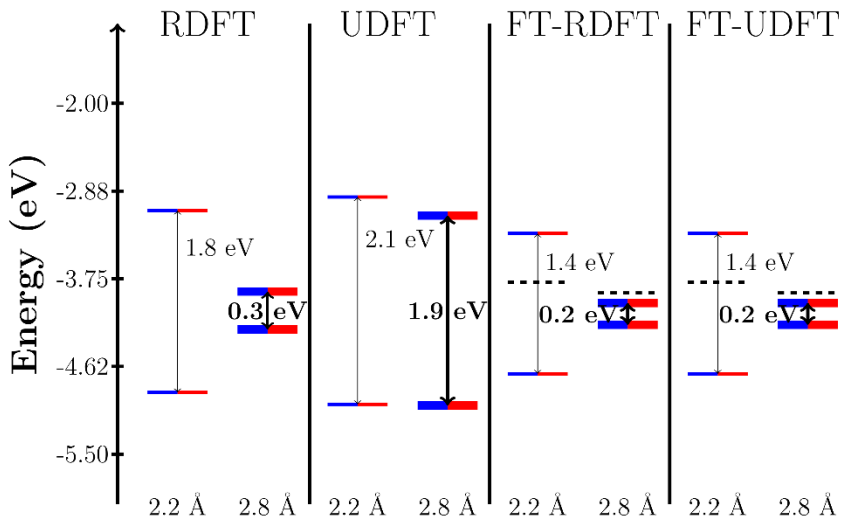

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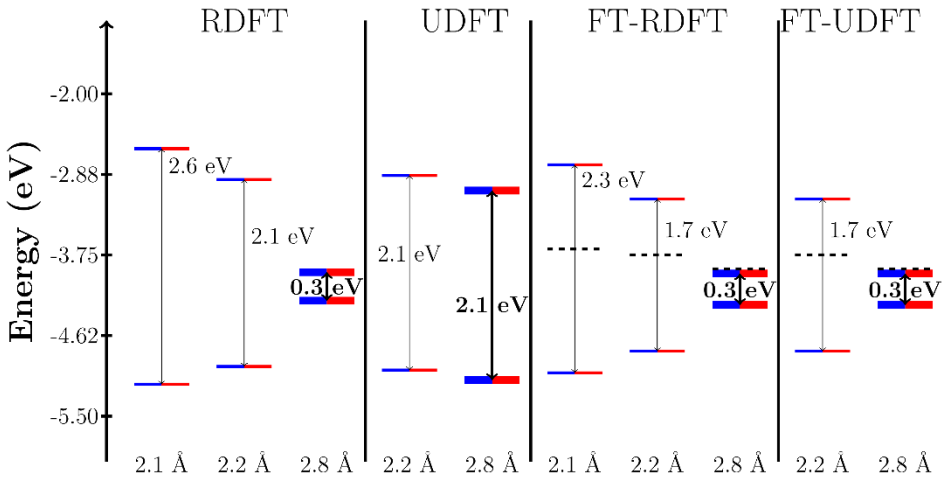

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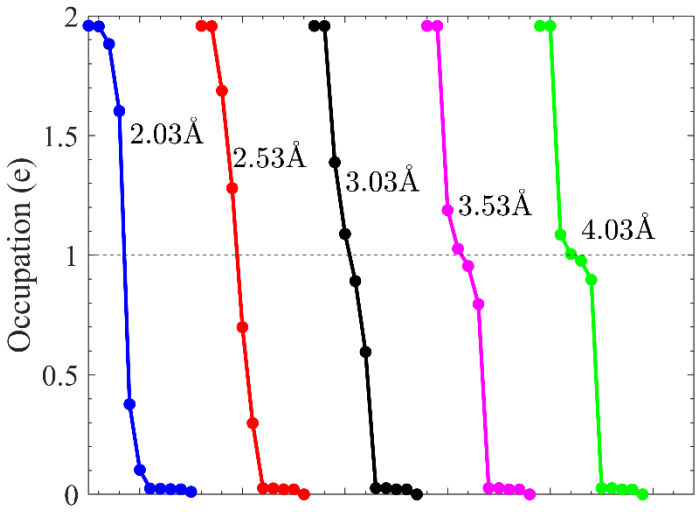

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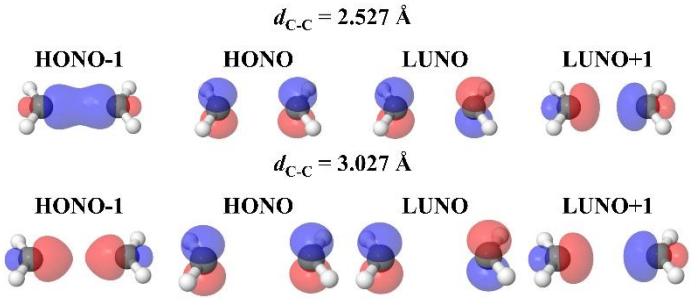
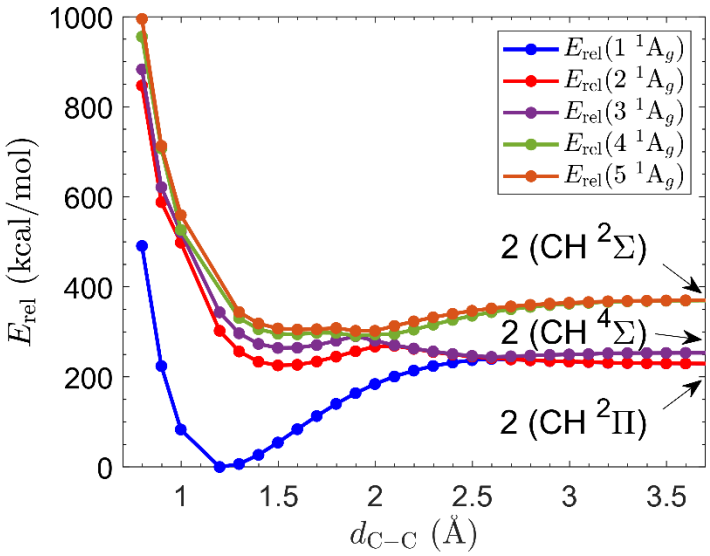


Figure S9. MR-AQCC(GVB-RCI) natural orbitals along the C-C bond in ethylene (isovalue 0.1 $e \cdot \text{Å}^{-3}$).



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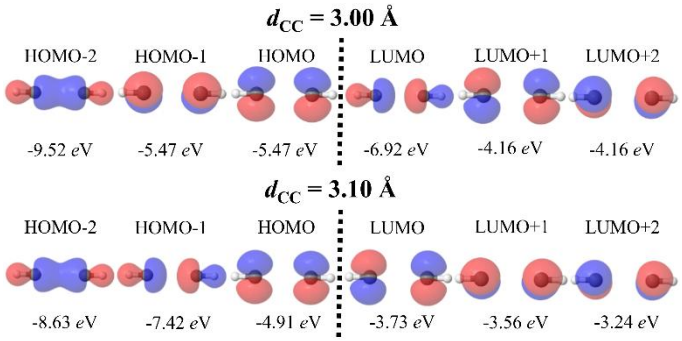

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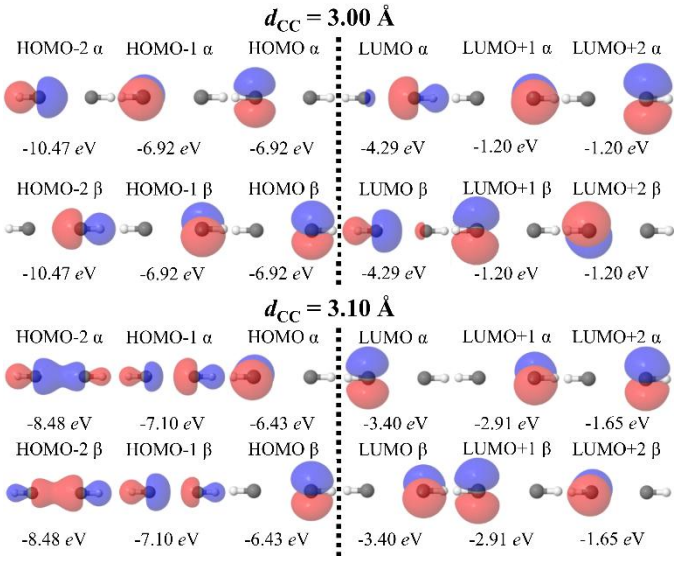

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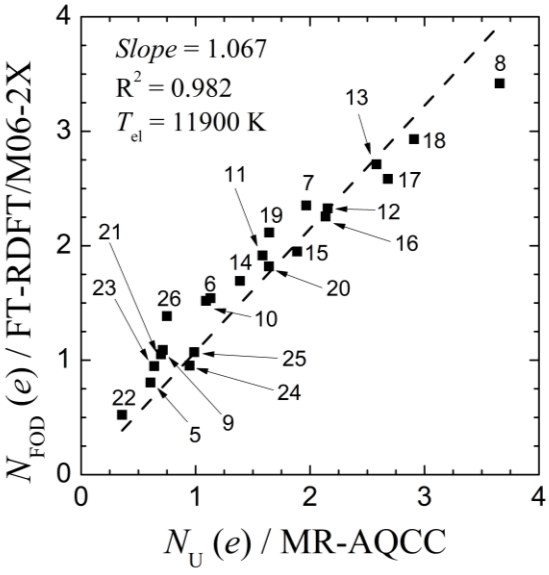
Functionals	a_x or α	β	ω
ωB97XD	0.222	0.778	0.200
ωB97M-V	0.150	0.850	0.300
CAM-B3LYP	0.190	0.460	0.330
LC-ωPBE	0.000	1.000	0.400
MN12-SX	0.250	-0.250	0.110
B2P-LYP	0.530	-	-
M06-2X	0.540	-	-



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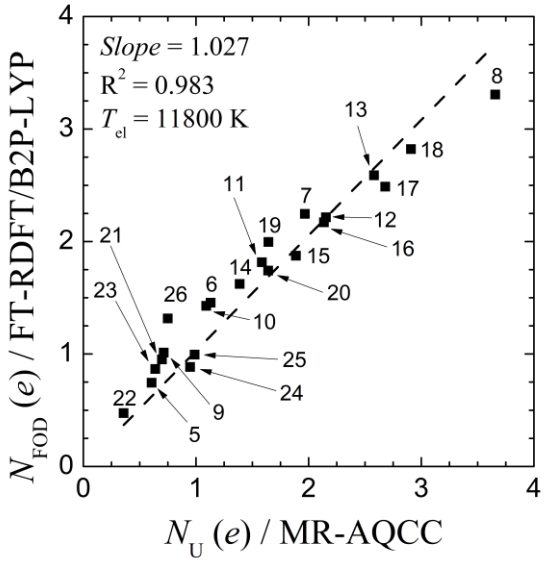

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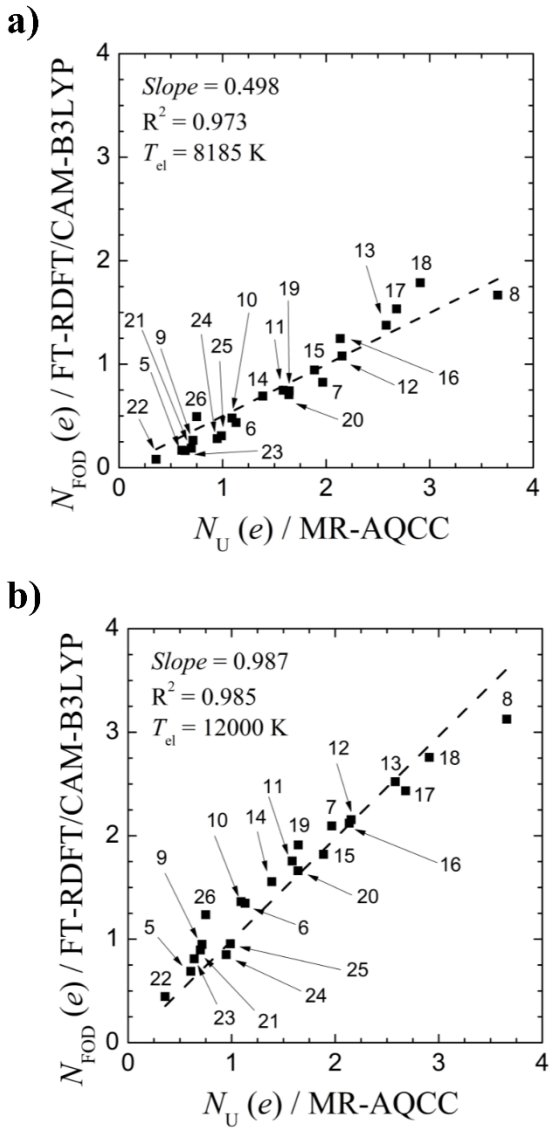

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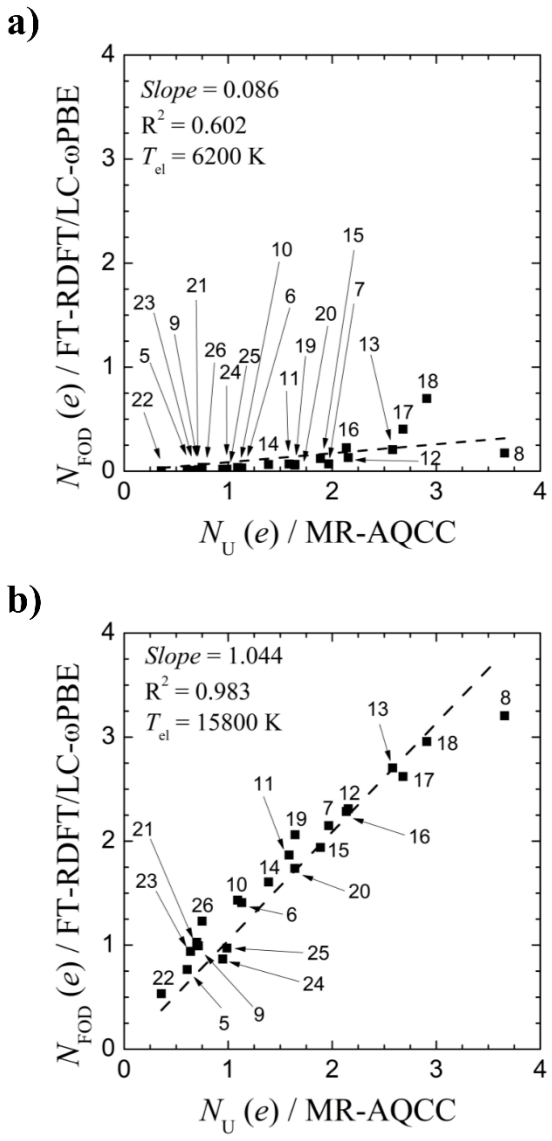

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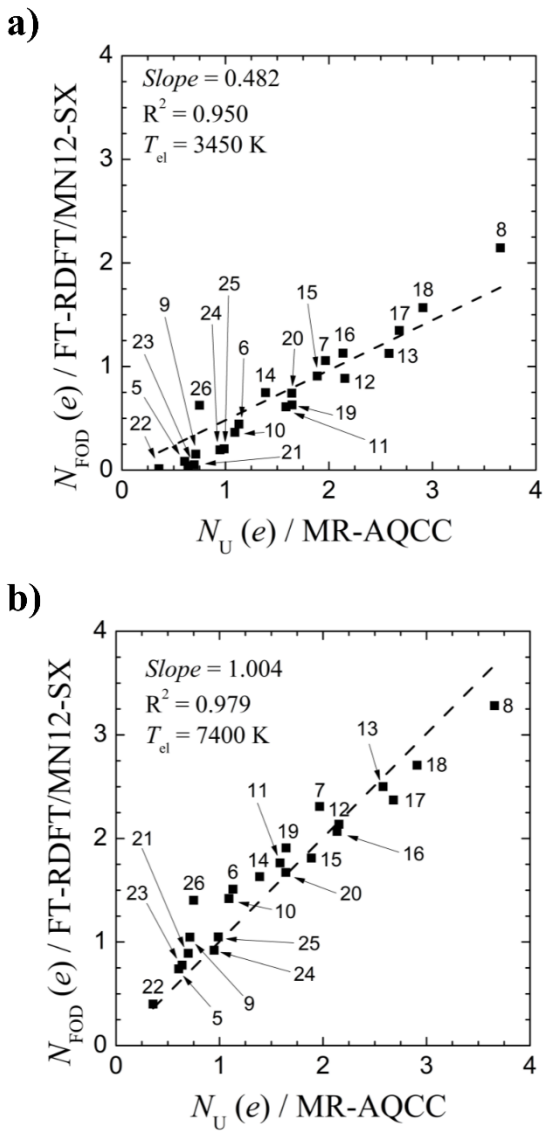

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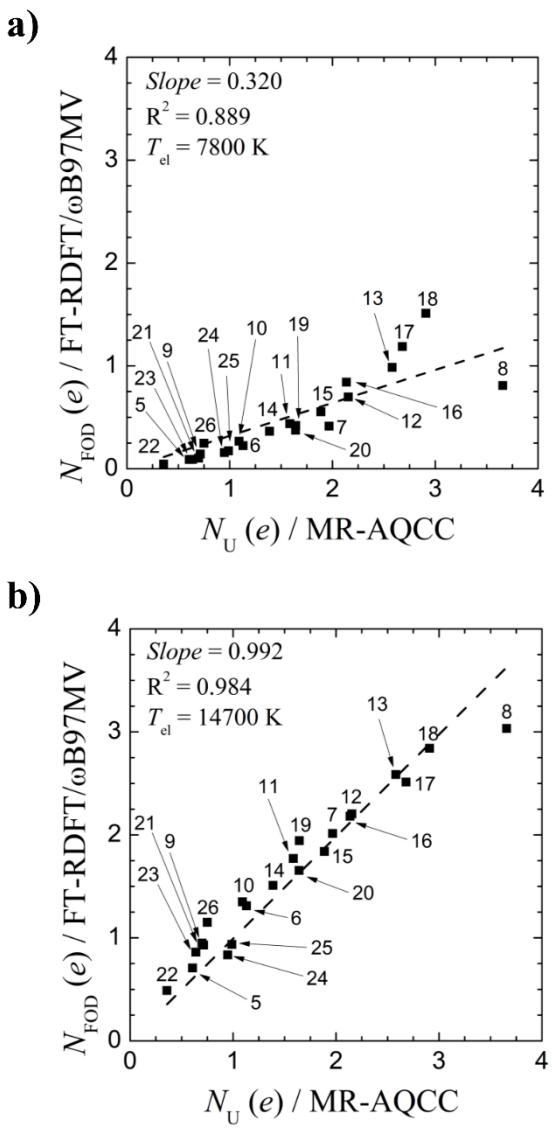

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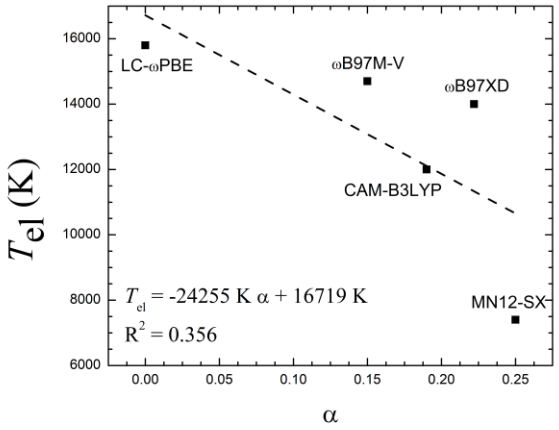

Figure S19. Linear correlation between the adjusted T_{el} (in K) and the percentage of HF exchange in the short-range limit (α) for range-separated functionals.

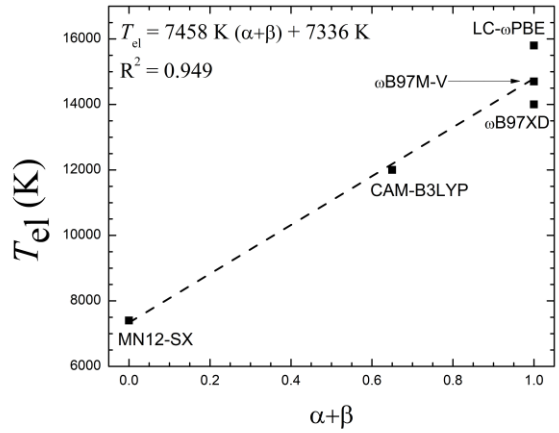

Figure S20. Linear correlation between the adjusted T_{el} (in K) and the percentage of HF exchange in the long-range limit (α+β) for range-separated functionals.

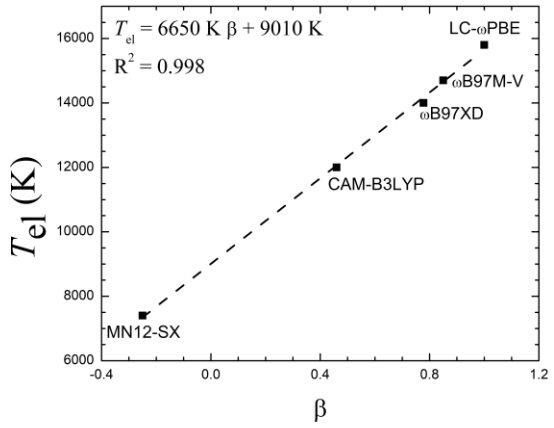

Figure S21. Linear correlation between the adjusted T_{el} (in K) and the difference between the percentage of HF exchange in the long-range limit and the corresponding percentage in the short-range (β) for range-separated functionals.

Table S3. Contribution of occupied and virtual orbitals to the N_U and N_{FOD} values in an analysis of the particle-hole symmetry of the descriptors.

Structure	Method / Orbitals	FT-RDFT/ ωB97XD (14000 K) N_{FOD}	FT-RDFT/ M06-2X (11951.5 K) N_{FOD}	FT-UDFT/ M06-2X (11951.5 K) N_{FOD}	MR-AQCC N_U
1	Occup.	0.351	0.402	-	0.316
	Virtual	0.351	0.402	-	0.291
	Total	0.702	0.804	-	0.607
3	Occup.	1.010	1.176	1.176	1.010
	Virtual	1.010	1.175	1.175	0.957
	Total	2.021	2.351	2.351	1.967
14	Occup.	1.409	1.467	1.466	1.474
	Virtual	1.410	1.465	1.464	1.435
	Total	2.819	2.931	2.931	2.909