Supplementary-Information materials for: Nature of frontier quasi-particle states in nitrogen-base systems

Raul Quintero-Monsebaiz, Per Hyldgaard, and Elsebeth Schröder

Department of Microtechnology and Nanoscience – MC2, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

(Dated: December 21, 2025)

We here document accuracy of the AHBR-mRSH* generalized-Kohn-Sham functional [J. Phys.:Condens. Matter **32**, 211501 (2025)] as a predictor of frontier-level quasiparticles (QPs) in nitrogen-base system. To that end we supplement (and slightly correct) the originally reported comparison of AHBR-mRSH* frontier level QP energies against more litterature theory values and against here-presented results on the preformance of HSE06 [J. Chem. Phys. **124**, 219906 (2006)] as an approximate QP-energy predictor.

This supplementary-information (SI) document contains Tables S.I and S.II substantiating our accuracy for predicting quasiparticle (QP) levels of nitrogen-base system by use of our optimally tuned AHBR-mRSH* functional [2] for generalized Kohn-Sham (gKS) density functional theory (DFT) calculations.

In practice, we compare our AHBR-mRSH* predictions with litterature theory and experimental results that

TABLE S I. Documentation of accuracy for frontier-quasi-particle energies (or 'levels'): individual T and A nitrogen bases. We take the atomic configuration as set by the positions that are defined by the TpC step in a benchmark [1]; See also zipped collection of coordinate files. All quasiparticle levels in eV.

		HOMO-1	HOMO	LUMO	LUMO+1
Thymine	AHBR-mRSH*[a]	-9.778	-8.910	-0.070	-0.008
	HSE06	-7.365	-6.705	-0.687	-1.681
	G_0W_0[b]	-8.94	-8.63	0.26	-0.24
	GW[c]	-10.41	-9.05	0.67	
	LC-BLYP[d]	-9.71	-8.90	0.59	
	Exper.[e]	-10.14	-9.2	-0.06	∼0.4
	KIPZ[f]	-9.77	-9.02	-0.06	0.32
Adenine	AHBR-mRSH*	-9.236	-8.214	0.007	0.121
	HSE06	-6.848	-6.067	-0.460	-1.081
	G_0W_0[b]	-8.80	-7.99	0.31	0.25
	GW[c]	-9.47	-8.22	1.14	
	LC-BLYP[d]	-9.21	-8.21	1.13	
	Exper.[e]	-9.45	-8.47	0.012	∼0.5
	KIPZ[f]	-9.01	-8.41	0.02	0.47

[a] Minute adjustment of Thymine HOMO-1 level energy compared to original characterization [2].

[b] Ref. 3.

[c] Ref. 4.

[d] Ref. 5.

[c] Ref. 3.

[e] Collected in Ref. 6.

[f] Ref. 6.

TABLE S II. Documentation of accuracy for frontier-quasi-particle energies (or 'levels'): individual C and G nitrogen bases.

		HOMO-1	HOMO	LUMO	LUMO+1
Cytosine	AHBR-mRSH*[a]	-9.174	-8.565	-0.110	0.072
	HSE06	-6.777	-6.344	-0.718	-1.488
	$G_0W_0^b$	-8.5	-8.18	0.23	0.02
	GW[c]	-9.52	-8.73	0.91	
	LC-BLYP[d]	-9.37	-8.73	0.93	
	Exper.[e]	-9.55	-8.89	-0.23	∼0.4
	KIPZ[f]	-9.12	-8.70	-0.11	0.41
Guanine	AHBR-mRSH*[a]	-9.350	-7.816	-0.165	0.050
	HSE06	-6.929	-5.679	-0.942	-0.639
	$G_0W_0^b$	-8.67	-7.64	-	0.43
	GW[c]	-9.82	-7.81	1.58	
	LC-BLYP[d]	-9.29	-7.78	1.69	
	Exper.[e]	-9.90	-8.30	-	-
	KIPZ[f]	-9.25	-8.07	-0.08	0.36

[a] Results for cytosine, guanine (and adenine) are unchanges from Ref. 2.

[b] Ref. 3.

[c] Ref. 4.

[d] Ref. 5.

[c] Ref. 3.

[e] Collected in Ref. 6.

[f] Ref. 6.

exist for the individual nitrogen bases and we document that AHBR-mRSH* provides significant accuracy gains for predictions of nitrogen-base QP levels, compared with, for example, HSE06 [7, 8] and optimally-tuned long-range-corrected BLYP [5] gKS DFT studies. Our performance-comparison work amounts to an extension of the accuracy documentation that we originally provided in Ref. [2], finding only a minute adjustment ($-9.776 \rightarrow -9.778$ eV) of one thymine QP level.

We note that the measured lowest-unoccupied molecular orbitals (LUMOs) are dipole-trapped statess (or charge-transfer states), something that is also corrected predicted in so-called KIPZ studies [6]. Following Ref. 6, we therefore list as the LUMO energy in any given theory study, the energy of the first orbital has this dipole-trapped nature (when known).

We finally note, as also observed in the main text, that Fig. 5 of Ref. [2] contains documentation that use of AHBR-mRSH* as a traditional total-energy predictor simultaneously gives about an order-of magnitude accuracy improvements over HSE06 and over dispersion-corrected HSE06.

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