Supplementary Information : Robust analytic continuation approach to many-body GW calculations

Ivan Duchemin*,† and Xavier Blase‡

†*Univ. Grenoble Alpes, CEA, IRIG-MEM-L_Sim, 38054 Grenoble, France*

‡*Univ. Grenoble Alpes, CNRS, Inst NEEL, F-38042 Grenoble, France*

E-mail: ivan.duchemin@cea.fr

We provide here below the ionization potentials (Section 1) and electronic affinities (Section 2) for the GW100 test set,[S1] comparing reference calculations (Fig. 2b scheme, $\Delta\omega = 125meV$) with data stemming from the analytic continuation of W relying on a reduced nω=14 data points sampling along the imaginary axis (Fig. 2a scheme). We consider only the 93 molecules not requiring pseudopotentials. Both def2-QZVP G_0W_0@PBE and def2-QZVP G_0W_0@PBE0 data are presented. Similarly, we list the aug-cc-pVTZ G_0W_0@PBE0 ionization potential and electronic affinities (Section 3) for the set of 24 medium size acceptor molecules from Refs. S2,S3. Finally, we reproduce Fig. 7b of the main manuscript, but over the full energy range and a lower $Z = 0.2$ cutoff value.

1 GW100 test set ionisation potentials

		GW100 IPs			
		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
1	He	23.477	23.483	23.995	23.999
2	Ne	20.376	20.376	20.879	20.879
3	Ar	15.132	15.132	15.417	15.417
4	Kr	13.571	13.571	13.781	13.781
6	H2	15.815	15.815	16.182	16.182
7	Li_2	4.992	4.992	5.247	5.247
8	Na_2	4.837	4.837	4.966	4.966
9	Na_4	4.120	4.120	4.233	4.233
10	Na_6	4.242	4.242	4.356	4.356
11	K_2	3.980	3.981	4.072	4.072
13	N_2	14.889	14.889	15.429	15.429
14	P_2	10.205	10.205	10.373	10.373
15	As_2	9.471	9.471	9.599	9.599
16	F_2	14.962	14.962	15.529	15.529
17	Cl_2	11.101	11.101	11.384	11.384
18	Br_2	10.217	10.217	10.451	10.451
20	CH_4	13.927	13.927	14.267	14.267
21	C_2H_6	12.365	12.365	12.676	12.676
22	C_3H_8	11.795	11.795	12.106	12.106
23	C_4H_{10}	11.490	11.490	11.804	11.804
24	C_2H_4	10.325	10.325	10.514	10.514
25	C_2H_2	11.020	11.020	11.271	11.271
26	C_4	10.781	10.781	11.156	11.156
27	C_3H_6	10.555	10.555	10.821	10.821
28	C_6H_6	8.985	8.985	9.196	9.196
29	C_8H_8	8.055	8.055	8.284	8.284
30	C_5H_6	8.349	8.349	8.551	8.551
31	C_2H_3F	10.197	10.197	10.441	10.441
32	C_2H_3Cl	9.761	9.761	10.008	10.008
33	C_2H_3Br	8.990	8.990	9.184	9.184
33	C_2H_3Br	9.491	9.491	9.728	9.728
35	CF_4	15.366	15.366	15.995	15.995
36	CCl_4	10.975	10.975	11.401	11.401
37	CBr_4	9.899	9.899	10.272	10.272
39	SiH_4	12.310	12.310	12.699	12.699
40	GeH_4	12.022	12.022	12.358	12.358
41	Si_2H_6	10.309	10.309	10.585	10.585
42	Si_5H_{12}	8.934	8.934	9.220	9.220
43	LiH	6.552	6.552	7.547	7.547
44	KH	4.862	4.862	5.660	5.660
45	BH_3	12.867	12.867	13.225	13.225
46	B_2H_6	11.835	11.835	12.218	12.218

Continuation of GW100 IPs

		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
47	NH_3	10.315	10.315	10.698	10.698
48	HN_3	10.395	10.395	10.686	10.686
49	PH_3	10.273	10.273	10.487	10.487
50	AsH_3	10.123	10.123	10.300	10.300
51	SH_2	10.031	10.031	10.248	10.248
52	FH	15.302	15.302	15.748	15.748
53	ClH	12.246	12.246	12.501	12.501
54	LiF	9.946	9.947	10.829	10.829
55	F_2Mg	12.323	12.323	13.188	13.188
56	TiF_4	13.896	13.896	14.868	14.868
57	AlF_3	14.252	14.252	14.950	14.950
58	BF	10.562	10.562	10.909	10.909
59	SF_4	12.117	12.117	12.558	12.558
60	BrK	7.304	7.305	7.946	7.946
61	GaCl	9.554	9.554	9.719	9.719
62	NaCl	8.098	8.099	8.835	8.835
63	$MgCl_2$	10.991	10.991	11.462	11.462
65	BN	11.010	11.010	11.543	11.543
66	NCH	13.211	13.211	13.525	13.525
67	PN	11.136	11.136	11.688	11.688
68	H_2NNH_2	9.281	9.281	9.647	9.647
69	H_2CO	10.328	10.328	10.784	10.784
70	CH_4O	10.562	10.562	10.974	10.974
71	C_2H_6O	10.157	10.157	10.604	10.604
72	C_2H_4O	9.548	9.548	10.094	10.094
73	$C_4H_{10}O$	9.319	9.319	9.777	9.777
74	CH_2O_2	10.730	10.730	11.292	11.292
75	HOOH	10.987	10.987	11.444	11.444
76	H_2O	11.973	11.973	12.387	12.387
77	CO_2	13.250	13.250	13.662	13.662
78	CS_2	9.748	9.748	9.984	9.984
79	CSO	10.906	10.906	11.170	11.170
80	CSeO	10.199	10.199	10.413	10.413
81	CO	13.571	13.571	14.120	14.120
82	O_3	11.967	11.967	12.563	12.563
83	SO_2	11.823	11.823	12.272	12.272
84	BeO	9.633	9.635	9.644	9.644
85	MgO	6.671	6.671	7.457	7.457
86	C_7H_8	8.612	8.612	8.818	8.818
87	C_8H_{10}	8.553	8.553	8.766	8.766
88	C_6F_6	9.493	9.493	9.893	9.893
89	C_6H_5OH	8.366	8.366	8.609	8.609

Continuation of GW100 IPs

		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
89	C_6H_5OH	8.263	8.263	8.502	8.502
90	$C_6H_5NH_2$	7.644	7.644	7.914	7.914
91	C_5H_5N	9.040	9.040	9.600	9.600
92	$C_5H_5N_5O$	7.691	7.691	7.976	7.976
93	$C_5H_5N_5O$	7.975	7.975	8.256	8.256
94	$C_4H_5N_3O$	8.287	8.287	8.683	8.683
95	$C_5H_6N_2O_2$	8.707	8.707	9.057	9.057
96	$C_4H_4N_2O_2$	9.223	9.223	9.457	9.457
97	CH_4N_2O	9.321	9.321	9.908	9.908
99	Cu_2	7.529	7.529	7.551	7.551
100	CuCN	9.423	9.425	10.253	10.253

Table S1: Ionization potential (defined as -E_{HOMO}) for the $GW100$ test set as obtained with the present analytic continuation scheme. Reference calculations (ref.) are associated with the fine ($\Delta\omega = 125\,meV$) Fig. 2b sampling scheme. The (P-14) calculations use only the $n\omega$=14 reference $W(i\omega)$ along the imaginary axis from Fig. 2a sampling scheme. Calculations are performed at the def2-QZVP level with Coulomb fitting resolution-of-the-identity using the corresponding def2-QZVP-RI auxiliary basis. Both PBE and PBE0 Kohn-Sham DFT starting points are presented. Digits differing between the (ref.) and (P-14) data are highlighted in red.

2 $GW100$ test set electronic affinities

GW100 EAs

		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
1	He	-11.006	-11.007	-11.019	-11.020
2	Ne	-11.643	-11.643	-11.674	-11.674
3	Ar	-8.113	-8.113	-8.166	-8.166
4	Kr	-7.635	-7.635	-7.689	-7.689
6	H2	-3.504	-3.504	-3.436	-3.436
7	Li_2	0.626	0.626	0.409	0.409
8	Na_2	0.550	0.550	0.421	0.421
9	Na_4	1.009	1.009	0.779	0.779
10	Na_6	0.971	0.971	0.762	0.762
11	K_2	0.647	0.647	0.508	0.508
13	N_2	-2.449	-2.449	-2.586	-2.586
14	P_2	0.724	0.724	0.608	0.608
15	As_2	0.847	0.847	0.753	0.753
16	F_2	0.704	0.704	0.308	0.308
17	Cl_2	0.887	0.887	0.687	0.687

Continuation of GW100 EAs

		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
18	Br_2	1.396	1.396	1.224	1.224
20	CH_4	-2.450	-2.450	-2.486	-2.486
21	C_2H_6	-2.294	-2.294	-2.357	-2.357
22	C_3H_8	-2.195	-2.195	-2.278	-2.278
23	C_4H_{10}	-2.145	-2.145	-2.244	-2.244
24	C_2H_4	-2.020	-2.020	-2.189	-2.189
25	C_2H_2	-2.863	-2.863	-2.965	-2.965
26	C_4	2.936	2.936	2.710	2.710
27	C_3H_6	-2.453	-2.453	-2.525	-2.525
28	C_6H_6	-1.087	-1.087	-1.300	-1.300
29	C_8H_8	-0.059	-0.059	-0.316	-0.316
30	C_5H_6	-1.040	-1.040	-1.274	-1.274
31	C_2H_3F	-2.146	-2.146	-2.317	-2.317
32	C_2H_3Cl	-1.425	-1.425	-1.623	-1.623
33	C_2H_3Br	-1.380	-1.380	-1.571	-1.571
33	C_2H_3Br	-1.257	-1.257	-1.472	-1.472
35	CF_4	-4.413	-4.413	-4.479	-4.479
36	CCl_4	0.008	0.008	-0.245	-0.245
37	CBr_4	1.079	1.079	0.856	0.856
39	SiH_4	-2.508	-2.508	-2.560	-2.560
40	GeH_4	-2.300	-2.300	-2.391	-2.391
41	Si_2H_6	-1.686	-1.686	-1.889	-1.889
42	Si_5H_{12}	-0.161	-0.161	-0.416	-0.416
43	LiH	0.072	0.072	0.092	0.092
44	KH	0.180	0.180	0.154	0.154
45	BH_3	-0.115	-0.115	-0.263	-0.263
46	B_2H_6	-0.838	-0.838	-1.014	-1.014
47	NH_3	-2.312	-2.312	-2.345	-2.345
48	HN_3	-1.399	-1.399	-1.549	-1.549
49	PH_3	-2.496	-2.496	-2.096	-2.096
50	AsH_3	-2.320	-2.320	-2.015	-2.015
51	SH_2	-2.557	-2.557	-2.024	-2.024
52	FH	-2.543	-2.543	-2.483	-2.483
53	ClH	-2.064	-2.064	-2.051	-2.051
54	LiF	-0.091	-0.091	0.049	0.049
55	F_2Mg	0.138	0.138	0.084	0.084
56	TiF_4	0.598	0.598	0.675	0.675
57	AlF_3	-0.157	-0.157	-0.271	-0.271
58	BF	-1.216	-1.216	-1.298	-1.298
59	SF_4	-0.377	-0.377	-0.543	-0.543
60	BrK	0.307	0.307	0.362	0.362
61	GaCl	0.020	0.020	-0.062	-0.062

Continuation of GW100 EAs

		G_0W_0@PBE		G_0W_0@PBE0	
i	Formula	ref.	P-14	ref.	P-14
62	NaCl	0.394	0.394	0.433	0.433
63	$MgCl_2$	0.430	0.430	0.333	0.333
65	BN	3.947	3.947	3.760	3.760
66	NCH	-2.577	-2.577	-2.674	-2.674
67	PN	0.202	0.202	0.084	0.084
68	H_2NNH_2	-1.993	-1.993	-2.062	-2.062
69	H_2CO	-0.959	-0.959	-1.192	-1.192
70	CH_4O	-2.247	-2.247	-2.264	-2.264
71	C_2H_6O	-2.076	-2.076	-2.130	-2.130
72	C_2H_4O	-1.050	-1.050	-1.375	-1.375
73	$C_4H_{10}O$	-2.100	-2.100	-2.199	-2.199
74	CH_2O_2	-1.910	-1.910	-2.172	-2.172
75	HOOH	-2.349	-2.349	-2.548	-2.548
76	H_2O	-2.370	-2.370	-2.377	-2.377
77	CO_2	-2.497	-2.497	-2.509	-2.509
78	CS_2	0.197	0.197	0.104	0.104
79	CSO	-1.215	-1.215	-1.360	-1.360
80	CSeO	-0.868	-0.868	-1.024	-1.024
81	CO	-0.671	-0.671	-0.797	-0.797
82	O_3	2.296	2.296	2.212	2.212
83	SO_2	1.002	1.002	0.883	0.883
84	BeO	2.493	2.493	2.161	2.161
85	MgO	1.893	1.893	1.737	1.737
86	C_7H_8	-1.016	-1.016	-1.237	-1.237
87	C_8H_{10}	-1.044	-1.044	-1.279	-1.279
88	C_6F_6	-0.657	-0.657	-0.633	-0.633
89	C_6H_5OH	-0.959	-0.959	-1.155	-1.155
89	C_6H_5OH	-1.013	-1.013	-1.211	-1.211
90	$C_6H_5NH_2$	-1.148	-1.148	-1.358	-1.358
91	C_5H_5N	-0.514	-0.514	-0.735	-0.735
92	$C_5H_5N_5O$	-0.749	-0.749	-1.008	-1.008
93	$C_5H_5N_5O$	-0.474	-0.474	-0.735	-0.735
94	$C_4H_5N_3O$	-0.263	-0.263	-0.476	-0.476
95	$C_5H_6N_2O_2$	-0.057	-0.057	-0.282	-0.282
96	$C_4H_4N_2O_2$	-0.012	-0.012	-0.229	-0.229
97	CH_4N_2O	-1.621	-1.621	-1.702	-1.702
99	Cu_2	0.756	0.756	0.595	0.595
100	CuCN	1.647	1.647	1.264	1.264

Table S2: Same as in Table S1 but for the electronic affinities (defined as -E_{LUMO}).

3 Acceptor molecular set (Ref. S2) ionization potential and electronic affinity

Table S3: Ionization potentials (IP) and electronic affinities (EA) for the 24 molecules of Refs. S2,S3. Reference CCSD(T) calculations are from Ref.[S3] All calculations are performed at the aug-cc-pVTZ level. *GW* calculations provided are based on PBE0 Kohn-Sham eigenstates, following the "reference" calculations scheme of Fig. 2B main text with $\Delta\omega$=125 meV. The eg*GW* data indicate gap-self-consistent (scissor-like) calculations. The IP and AE yielding the largest discrepancy (Max.Err.) with the CCSD(T) data are highlighted.

	CCSD(T)		G_0W_0		egGW	
	IP	EA	IP	EA	IP	EA
Anthracene	7.474	0.260	7.156	0.561	7.299	0.372
Acridine	N/A	N/A	7.637	0.897	7.811	0.715
Phenazine	8.417	1.030	8.052	1.317	8.248	1.145
Azulene	7.485	0.482	7.203	0.717	7.355	0.538
Benzoquinone	10.172	1.458	9.811	1.746	10.409	1.539
Naphthalenedione	9.791	1.388	9.405	1.681	10.007	1.445
Dichlone	9.885	1.819	**9.480**	2.117	9.724	1.896
F4-benzoquinone	11.038	2.177	10.677	2.479	10.945	2.291
Cl4-benzoquinone	10.122	2.360	9.793	2.666	10.031	2.457
Nitrobenzene	10.139	0.442	9.851	0.748	10.064	0.479
F4-benzenedicar.	10.664	1.513	10.316	1.843	10.568	1.667
Dinitrobenzoni.	11.074	1.666	10.812	2.023	11.062	1.753
Nitrobenzoni.	10.548	1.200	10.262	1.560	10.492	1.320
Benzonitrile	9.881	-0.287	9.573	-0.020	9.783	-0.237
Fumaronitrile	11.399	0.892	11.026	1.208	11.282	0.984
mDCNB	10.372	0.540	10.077	0.857	10.303	0.631
TCNE	11.898	2.944	11.518	3.344	11.774	3.173
TCNQ	9.492	3.230	9.199	**3.669**	9.345	**3.558**
Maleicanhydride	11.226	0.918	10.851	1.150	11.445	0.918
Phthalimide	10.023	0.541	9.747	0.787	**10.358**	0.562
phthalicanhydride	10.477	0.777	10.178	1.043	10.388	0.810
Cl4-isobenz.	N/A	N/A	9.651	1.843	9.868	1.614
NDCA	N/A	N/A	8.775	1.460	8.938	1.265
bodipy	N/A	N/A	7.875	1.758	7.997	1.612
MaxErr			-0.405	0.439	0.335	0.328
MAE			0.329	0.307	0.135	0.098
MSE			-0.329	0.308	-0.035	0.098

4 Analytic continuation error

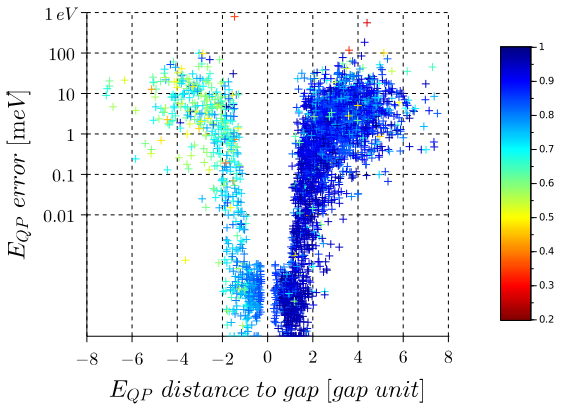

Figure S1: Same as Fig. 7b of the main manuscript, but over the full energy range and with a lower $Z = 0.2$ cutoff value. For occupied states, no new outliers are observed. In the unoccupied manifold, the main outlier corresponds to the LUMO+139 of acridine located 16eV above the LUMO G_0W_0@PBE0 value.

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[S2] Knight, J. W.; Wang, X.; Gallandi, L.; Dolgounitcheva, O.; Ren, X.; Ortiz, J. V.; Rinke, P.; Körzdörfer, T.; Marom, N. Accurate Ionization Potentials and Electron Affinities of Acceptor Molecules III: A Benchmark of GW Methods. *J. Chem. Theory Comput.* **2016**, *12*, 615–626, PMID: 26731609.

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