

Supporting Info: Benchmarking the GW approximation and Bethe-Salpeter equation for Groups IB and IIB atoms and monoxides

Linda Hung,^{*,†} Fabien Bruneval,^{*,¶} Kopinjol Baishya,[‡] and Serdar Ögüt^{*,‡}

[†]*NIST Center for Neutron Research, National Institute of Standard and Technology,
Gaithersburg, MD, 20899, USA*

[‡]*Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60607, USA*

[¶]*CEA, DEN, Service de Recherches de Métallurgie Physique, Université Paris-Saclay,
F-91191 Gif-sur-Yvette, France*

E-mail: linda.hung@nist.gov; fabien.bruneval@cea.fr; ogut@uic.edu

1 Computational Parameters

The only computational parameter in MOLGW¹ calculations is the choice of Gaussian basis set: aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-PV5Z.

For PARSEC and RGWBS calculations,^{2,3} pseudopotentials are generated using a multi-reference fitting scheme in the Atomic Pseudopotential Engine (APE),^{4,5} with different pseudopotentials generated for LDA and GGA calculations.^{6,7} The core electrons of the O in monoxide anion calculations are represented using Troullier-Martins pseudopotentials with radial cutoff 1.45 a.u.⁸ Computational parameters for PARSEC / RGWBS, including the optimized bond lengths used for the monoxide anion calculations, are listed in Table 1.

The GW calculations and extrapolations to the complete basis set limit follow the methods outlined in the article, and the parameters for basis sets used in G_0W_0 and $evGW$ calculations are listed in Table 2. For purposes of extrapolation, perturbative GW calculations are performed on n_{calc} different basis sets by varying N , where N is the total number of states included in the sum-over-states. The cutoffs N are spaced evenly according to their DFT energies ($E_{\text{DFT}}(N)$, shown in eV), with ΔE (also in eV) indicating the increments between the basis sets. N_{max} is the total number of states in the largest perturbative GW

calculation. N_{ev} is the total number of states for eigenvalue self-consistent GW calculations. While only the QP-HOMO and QP-LUMO energies need to be computed in perturbative GW , quasiparticle energies are computed and updated for quasiparticles up to index n_{QP} at each step of a $\text{ev}GW$ calculation in RGWBS.

The TDDFT eigenvalues reported in the article are computed using the basis set corresponding to N_{max} of Table 2. For the BSE, the total number of states used in each calculation and the DFT energy of the highest included state are summarized in Table 3. Due to the high cost of GW calculations, GW energies are only computed for the lowest 65 quasiparticles for input to the BSE; the highest computed GW energy lies ~ 5 eV above the vacuum level. The remaining quasiparticle energies for the BSE calculation are set to the DFT eigenvalues. By comparison to calculations that instead apply a “scissors operator” to the remaining higher-energy states, it appears that imposing this cutoff affects computed absorption energies < 0.1 eV.

Benchmarks from RGWBS – GW energies extrapolated to the complete basis-set limit and GW -BSE and TDDFT energies from finite basis set computations – are tabulated in the following section.

Table 1: PARSEC and RGWBS computational parameters (a.u.): radial cutoff for multireference pseudopotentials, real-space grid spacing, radius of spherical domain for species of various oxidation states and the anion monoxide, and bond length of monoxide anions.

Element	r_c	h	$R(d^{10})$	$R(d^{10}s)$	$R(d^{10}s^2)$	$R(\text{XO}^-)$	$r(\text{XO}^-)$
Cu	1.50	0.22	12.	16.	20.	18.	3.189
Ag	1.60	0.25	12.	16.	20.	18.	3.646
Zn	1.30	0.20	10.	12.	16.	18.	3.212
Cd	1.55	0.25	10.	12.	16.	18.	3.752

Table 2: RGWBS calculation parameters for perturbative and self-consistent GW .

Species	n_{calc}	ΔE	N_{max}	$E_{\text{DFT}}(N_{\text{max}})$	N_{ev}	$E_{\text{DFT}}(N_{\text{ev}})$	n_{QP}
Cu^+ or Ag^+	7	20	~ 5700	180	~ 1070	60	65
Cu^0 or Ag^0	6	10	~ 4600	90	~ 1350	40	65
Cu^- or Ag^-	6	5	~ 4600	60	~ 1990	35	55
Zn^{2+} or Cd^{2+}	8	20	~ 4600	220	~ 1050	80	65
Zn^+ or Cd^+	11	10	~ 4800	160	~ 1080	60	65
Zn^0 or Cd^0	5	10	~ 4600	90	~ 1870	50	65

Table 3: Total number of states used for GW -BSE calculations in RGWBS, and DFT energy of highest included state (eV).

Element	BSE@ GW @LDA						BSE@ GW @GGA	
	$N_{d^{10}}$	$E_{\text{LDA}}(N_{d^{10}})$	$N_{d^{10}s}$	$E_{\text{LDA}}(N_{d^{10}s})$	$N_{d^{10}s^2}$	$E_{\text{LDA}}(N_{d^{10}s^2})$	$N_{d^{10}}$	$E_{\text{GGA}}(N_{d^{10}})$
Cu	1074	60.126	878	30.173	-	-	1074	60.116
Ag	1073	60.004	890	30.349	-	-	1076	60.025
Zn	1051	80.045	868	50.338	878	30.115	1051	80.034
Cd	1052	81.884	863	50.219	890	30.098	1052	81.779

2 Excitation Energies

Table 4: Negative ionization energies and GW QP-HOMO energies (eV) for atoms with d^{10} occupation.

Atom	$-\text{IE}^{9-12}$	G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0	evGW @GGA
Cu	-20.29	-20.51	-21.97	-19.75	-21.28	-19.84	-21.27
Ag	-21.48	-22.17	-22.95	-21.34	-22.15	-21.76	-22.56
Zn	-39.72	-40.34	-41.59	-39.55	-40.85	-39.61	-40.83
Cd	-37.47	-38.30	-38.98	-37.47	-38.19	-37.87	-38.55

Table 5: Negative electron affinities and GW QP-LUMO energies (eV) for atoms with d^{10} occupation.

Atom	$-\text{EA}^{11,13-15}$	G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0	evGW @GGA
Cu	-7.73	-8.08	-7.75	-7.21	-6.95	-8.18	-7.87
Ag	-7.58	-7.91	-7.65	-7.08	-6.85	-7.91	-7.67
Zn	-17.96	-18.25	-18.03	-17.42	-17.28	-18.34	-18.13
Cd	-16.91	-17.21	-16.97	-16.38	-16.20	-17.20	-16.98

Table 6: Negative ionization energies and GW QP-HOMO energies (eV) for atoms with $d^{10}s$ occupation.

Atom	$-\text{IE}^{11,13-15}$	G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0	evGW @GGA
Cu	-7.73	-8.36	-8.40	-7.43	-7.45	-8.46	-8.55
Ag	-7.58	-8.05	-8.18	-7.11	-7.25	-7.96	-8.12
Zn	-17.96	-18.74	-18.72	-17.69	-17.72	-18.71	-18.72
Cd	-16.91	-17.57	-17.54	-16.51	-16.53	-17.48	-17.47

Table 7: Negative electron affinities and GW QP-LUMO energies (eV) for atoms with $d^{10}s$ occupation.

Atom	$-EA^{11,16,17}$	G_0W_0	evGW	$G_0W_0\Gamma_{LDA}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	-1.24	-1.42	-0.82	-0.89	-0.16	-1.47	-0.90
Ag	-1.30	-1.53	-1.03	-0.95	-0.35	-1.53	-1.06
Zn	-9.39	-9.63	-9.08	-9.06	-8.43	-9.65	-9.13
Cd	-8.99	-9.28	-8.82	-8.66	-8.13	-9.26	-8.82

Table 8: Negative ionization energies and GW QP-HOMO energies (eV) for atoms with $d^{10}s^2$ occupation.

Atom	$-IE^{16-18}$	G_0W_0	evGW	$G_0W_0\Gamma_{LDA}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	-1.24	-1.46	-1.50	-0.32	-0.46	-1.64	-1.56
Ag	-1.30	-1.51	-1.50	-0.58	-0.67	-1.66	-1.52
Zn	-9.39	-9.54	-9.68	-8.59	-8.72	-9.69	-9.88
Cd	-8.99	-9.17	-9.27	-8.23	-8.32	-9.09	-9.25

Table 9: Experimental, TDDFT, and GW -BSE energies for the $d^{10} \rightarrow d^9s$ (1D) transition.

Atom	Expt. ^{9-11,19}	TDDFT @LDA	G_0W_0	evGW	BSE@ $G_0W_0\Gamma_{LDA}$ @LDA	evGW Γ_{LDA}	BSE@ G_0W_0 @GGA	evGW
Cu	3.26	2.05	2.48	3.90	3.02	4.37	1.82	3.22
Ag	5.71	4.57	5.20	5.90	5.56	6.25	4.84	5.54
Zn	10.35	8.19	9.96	11.10	10.44	11.53	9.23	10.34
Cd	11.02	9.35	10.48	11.20	10.88	11.55	10.12	10.83

Table 10: GW -BSE energies for the $d^{10} \rightarrow d^9s$ (1D) transition (diagonal approximation).

Atom	G_0W_0	evGW	BSE@ $G_0W_0\Gamma_{LDA}$ @LDA	evGW Γ_{LDA}	BSE@ G_0W_0 @GGA	evGW
Cu	2.19	3.59	2.72	4.03	1.53	2.89
Ag	4.99	5.66	5.34	6.00	4.63	5.30
Zn	9.67	10.79	10.15	11.20	8.95	10.04
Cd	10.29	11.00	10.68	11.34	9.92	10.61

Table 11: Experimental, TDDFT, and GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1F) transition.

Atom	Expt. ^{9-11,19}	TDDFT @LDA	G_0W_0	evGW	BSE@ $G_0W_0\Gamma_{LDA}$ @LDA	evGW Γ_{LDA}	BSE@ G_0W_0 @GGA	evGW
Cu	8.78	7.29	8.40	9.37	8.71	9.88	7.72	8.72
Ag	11.05	9.42	10.11	11.00	10.67	11.36	9.76	10.63
Zn	17.92	15.45	17.23	18.54	17.91	18.98	16.55	17.82
Cd	18.11	15.91	17.12	17.95	17.64	18.31	16.75	17.57

Table 12: GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1F) transition (diagonal approximation).

Atom	G_0W_0	evGW	BSE@		BSE@	
			$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	7.75	8.70	8.02	9.12	7.11	8.06
Ag	9.63	10.45	10.13	10.77	9.29	10.10
Zn	16.70	17.98	17.36	18.38	16.04	17.29
Cd	16.74	17.55	17.24	17.88	16.39	17.17

Table 13: Experimental, TDDFT, and GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1D) transition.

Atom	Expt. ^{9–11,19}	TDDFT @LDA	BSE@				BSE@	
			G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	8.86	7.40	8.59	9.65	8.93	10.14	7.91	9.00
Ag	10.77	9.49	10.26	11.22	10.86	11.60	9.91	10.86
Zn	18.01	15.57	17.60	18.92	18.27	19.35	16.92	18.21
Cd	18.41	15.97	17.37	18.24	17.93	18.63	17.00	17.86

Table 14: GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1D) transition (diagonal approximation).

Atom	G_0W_0	evGW	BSE@		BSE@	
			$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	7.97	9.02	8.29	9.44	7.32	8.38
Ag	9.79	10.70	10.35	11.05	9.46	10.35
Zn	17.12	18.41	17.77	18.81	16.45	17.71
Cd	17.01	17.86	17.55	18.23	16.66	17.48

Table 15: Experimental, TDDFT, and GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1P) transition.

Atom	Expt. ^{9–11,19}	TDDFT @LDA	BSE@				BSE@	
			G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	9.12	7.87	9.06	10.03	9.33	10.49	8.37	9.36
Ag	11.15	10.02	10.73	11.60	11.24	11.93	10.36	11.22
Zn	18.29	16.20	17.96	19.30	18.64	19.71	17.27	18.56
Cd	18.11	16.66	17.81	18.64	18.30	18.96	17.43	18.24

Table 16: GW -BSE energies for the $d^{10} \rightarrow d^9p$ (1P) transition (diagonal approximation).

Atom	G_0W_0	evGW	BSE@		BSE@	
			$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}	G_0W_0 @GGA	evGW
Cu	8.57	9.50	8.82	9.93	7.89	8.83
Ag	10.40	11.20	10.88	11.51	10.02	10.82
Zn	17.58	18.88	18.25	19.29	16.89	18.16
Cd	17.56	18.36	18.04	18.68	17.18	17.95

Table 17: Experimental, TDDFT, and GW -BSE energies for the $d^{10}s \rightarrow d^{10}p$ transition.

Atom	Expt. ^{9,11,19,20}	TDDFT @LDA	BSE@			
			G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}
Cu	3.81	4.23	3.51	3.70	3.81	3.81
Ag	3.74	4.08	3.39	3.56	3.59	3.64
Zn	6.08	6.84	6.03	6.11	6.10	6.12
Cd	5.68	6.20	5.52	5.57	5.60	5.59

Table 18: GW -BSE energies for the $d^{10}s \rightarrow d^{10}p$ transition (diagonal approximation).

Atom	BSE@			
	G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}
Cu	2.78	3.13	3.01	3.11
Ag	2.94	3.10	3.04	3.08
Zn	5.84	5.91	5.87	5.89
Cd	5.33	5.38	5.39	5.38

Table 19: Experimental, TDDFT, and GW -BSE energies for the $d^{10}s^2 \rightarrow d^{10}sp$ transition.

Atom	Expt. ^{11,21}	TDDFT @LDA	BSE@			
			G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}
Zn	5.80	5.80	5.52	5.75	5.70	5.81
Cd	5.42	5.36	5.11	5.33	5.30	5.29

Table 20: GW -BSE energies for the $d^{10}s^2 \rightarrow d^{10}sp$ transition (diagonal approximation).

Atom	BSE@			
	G_0W_0	evGW	$G_0W_0\Gamma_{\text{LDA}}$ @LDA	evGW Γ_{LDA}
Zn	5.49	5.72	5.67	5.78
Cd	5.10	5.25	5.28	5.32

References

- (1) Bruneval, F.; Rangel, T.; Hamed, S. M.; Shao, M.; Yang, C.; Neaton, J. B. *Comput. Phys. Commun.* **2016**, *208*, 149–161.
- (2) Kronik, L.; Makmal, A.; Tiago, M. L.; Alemany, M. M. G.; Jain, M.; Huang, X.; Saad, Y.; Chelikowsky, J. R. *Phys. Status Solidi B* **2006**, *243*, 1063.
- (3) Tiago, M. L.; Chelikowsky, J. R. *Phys. Rev. B* **2006**, *73*, 205334.
- (4) Oliveira, M. J. T.; Nogueira, F. *Comput. Phys. Commun.* **2008**, *178*, 524–534.
- (5) Reis, C. L.; Pacheco, J. M.; Martins, J. L. *Phys. Rev. B* **2003**, *68*, 155111.
- (6) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244–13249.
- (7) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (8) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993–2006.
- (9) Sugar, J.; Musgrove, A. *Journal of Physical and Chemical Reference Data* **1990**, *19*, 527–616.
- (10) Kramida, A. *J. Res. Natl. Inst. Stand. Technol.* **2013**, *118*, 168.
- (11) Sugar, J.; Musgrove, A. *Journal of Physical and Chemical Reference Data* **1995**, *24*, 1803–1872.
- (12) Churilov, S. S.; Joshi, Y. N.; Ryabtsev, A. N. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 5485.
- (13) MacAdam, K. B.; Dyubko, S. F.; Efremov, V. A.; Gerasimov, V. G.; Kutsenko, A. S. *J. Phys. B: At. Mol. Opt. Phys.* **2009**, *42*, 165009.
- (14) Loock, H.-P.; Beaty, L. M.; Simard, B. *Phys. Rev. A* **1999**, *59*, 873–875.
- (15) Shenstone, A. G.; Pittenger, J. T. *Journal of the Optical Society of America* **1949**, *39*, 219.
- (16) Bilodeau, R. C.; Scheer, M.; Haugen, H. K. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 3885.
- (17) Nadeem, A.; Shah, M.; Haq, S. U.; Shahzada, S.; Mumtaz, M.; Waheed, A.; Nawaz, M.; Ahmed, M.; Baig, M. A. *Eur. Phys. J. D* **2014**, *68*, 192.
- (18) Nadeem, A.; Nawaz, M.; Bhatti, S. A.; Baig, M. A. *Optics Communications* **2006**, *259*, 834–839.
- (19) Moore, C. E. *Nat. Stand. Ref. Data Ser.*; 1971; Vol. III; p 245.

- (20) Badr, T.; Plimmer, M. D.; Juncar, P.; Himbert, M. E.; Silver, J. D.; Rovera, G. D. *Eur. Phys. J. D* **2004**, *31*, 3–10.
- (21) Burns, K.; Adams, K. B. *Journal of the Optical Society of America* **1956**, *46*, 94.