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GW with LAPW+HLOs: Challenges for Numerically Accurate *GW* Calculations

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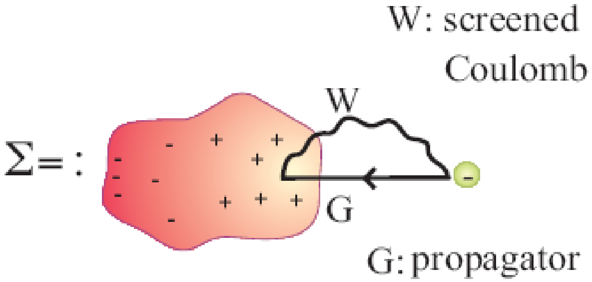
June 18, 2016

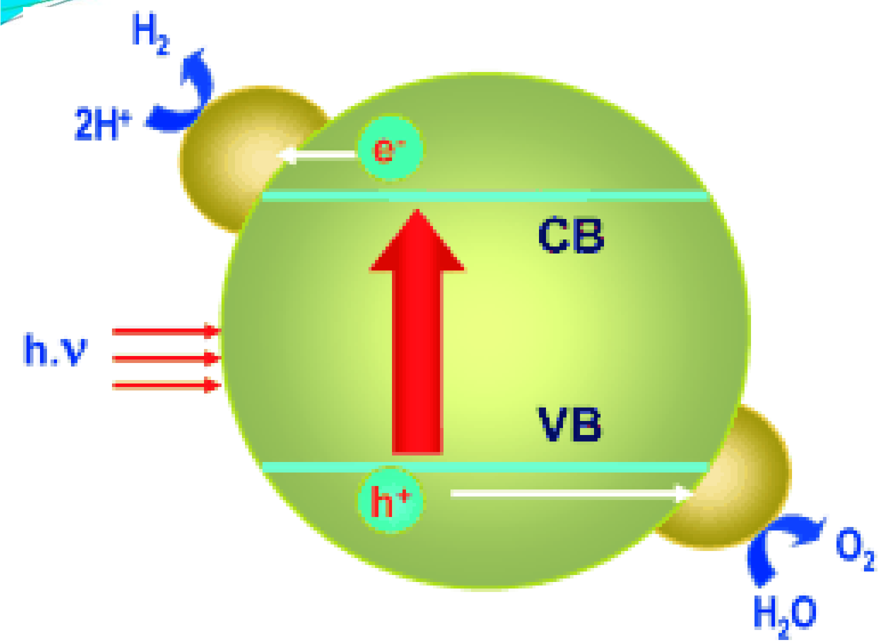
Outline

- **Introduction**
- ***GW* with LAPW+HLOs for *sp*-semiconductors**
- **GW with LAPW+HLOs for *d*- and *f*-systems**
- **Concluding remarks**

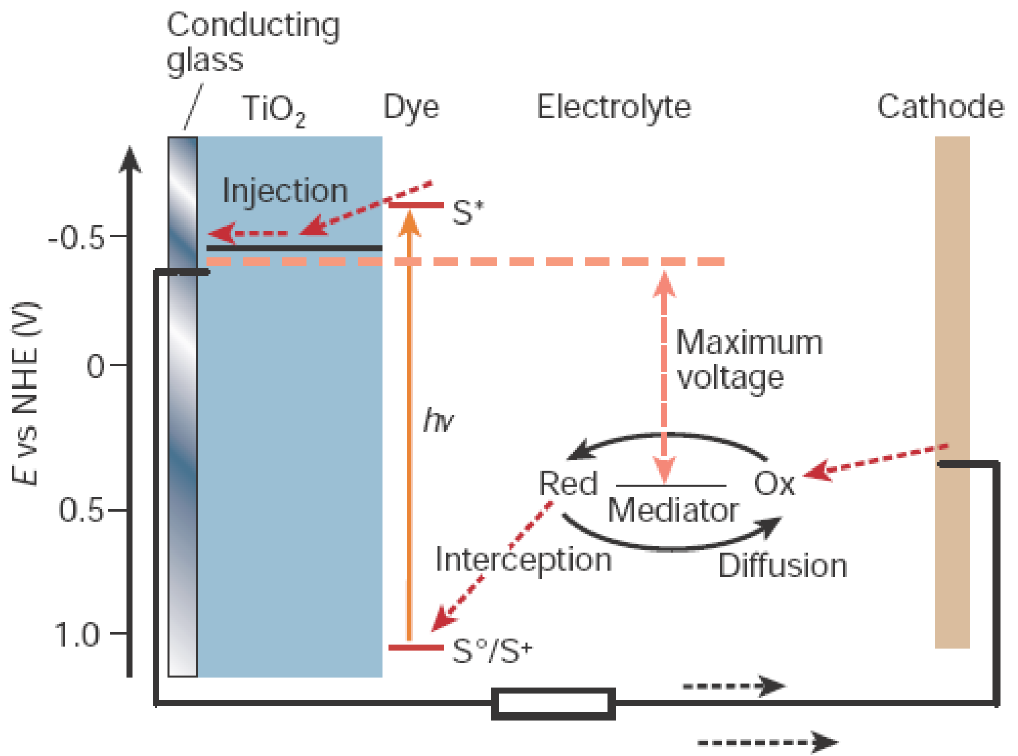
Introduction: the *GW* approach to electronic band structure of materials



Why are electronic band structure important?

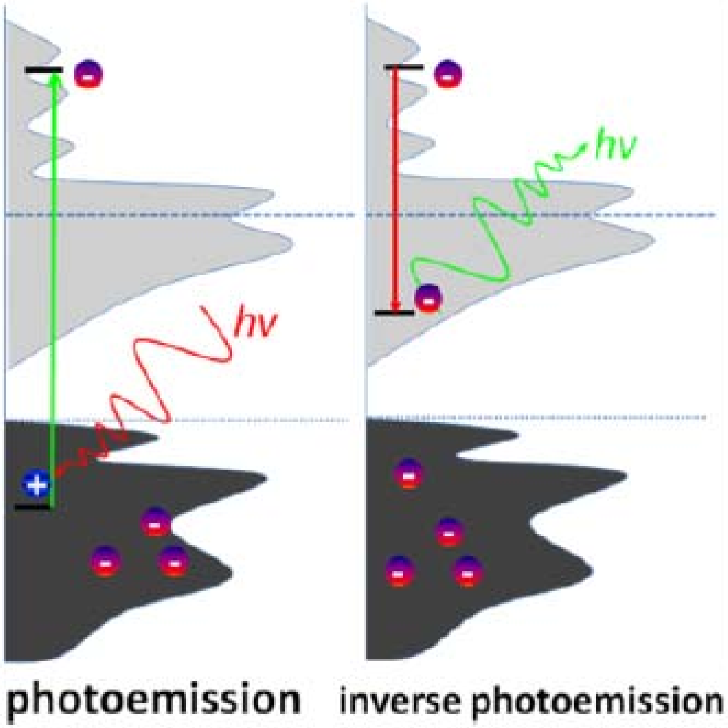


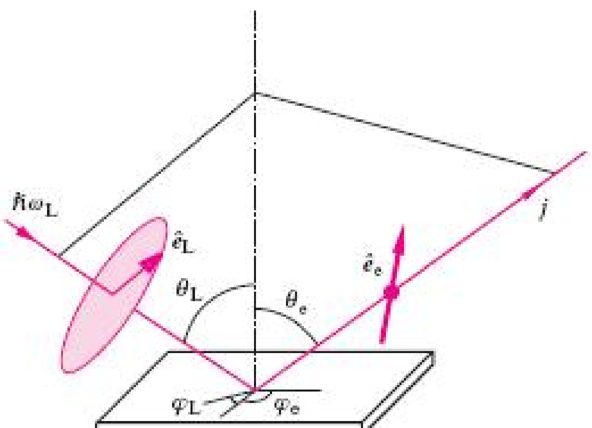
R. M. Navarro Yerga et al. (2009)

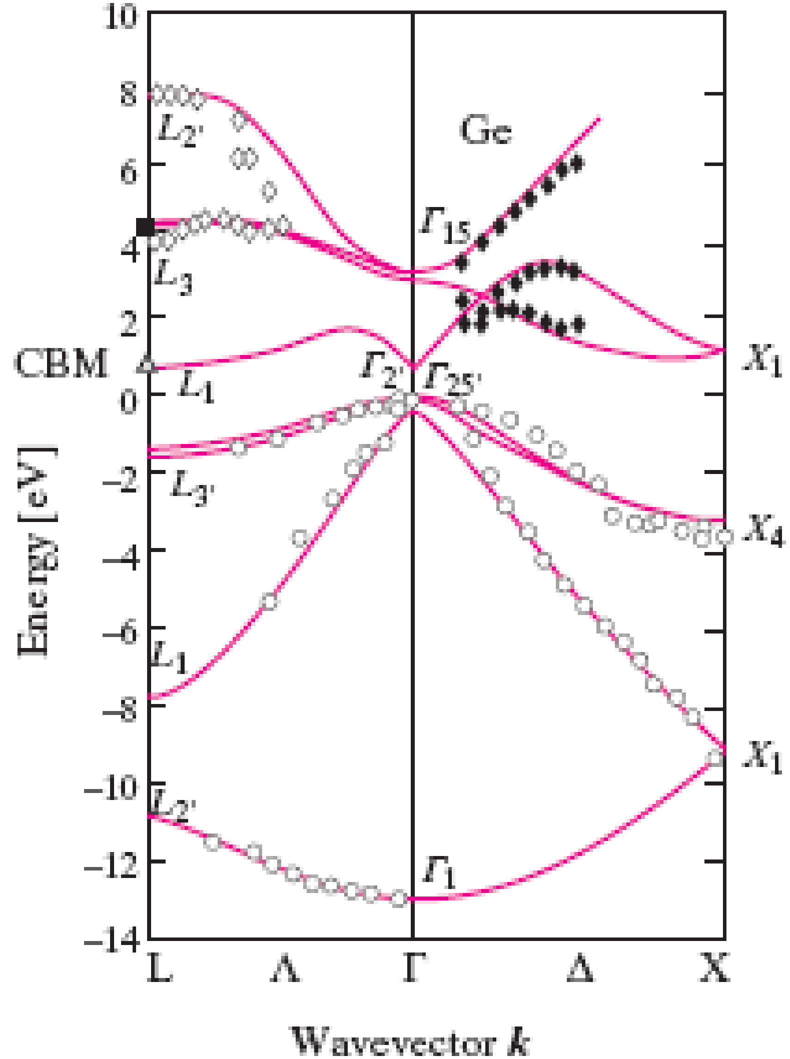


Graetzel, Nature (2001)

Electronic band structure

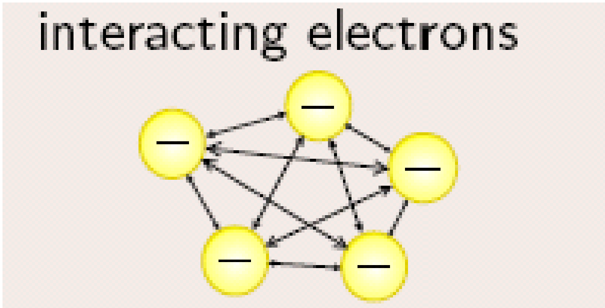


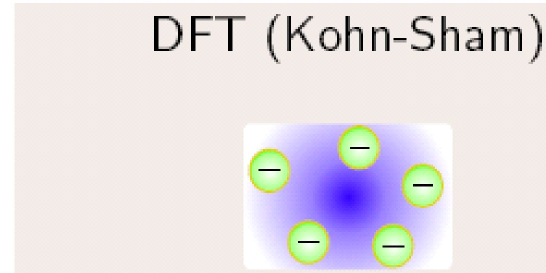




Yu and Cardona, Fundamentals of Semiconductors (2003)

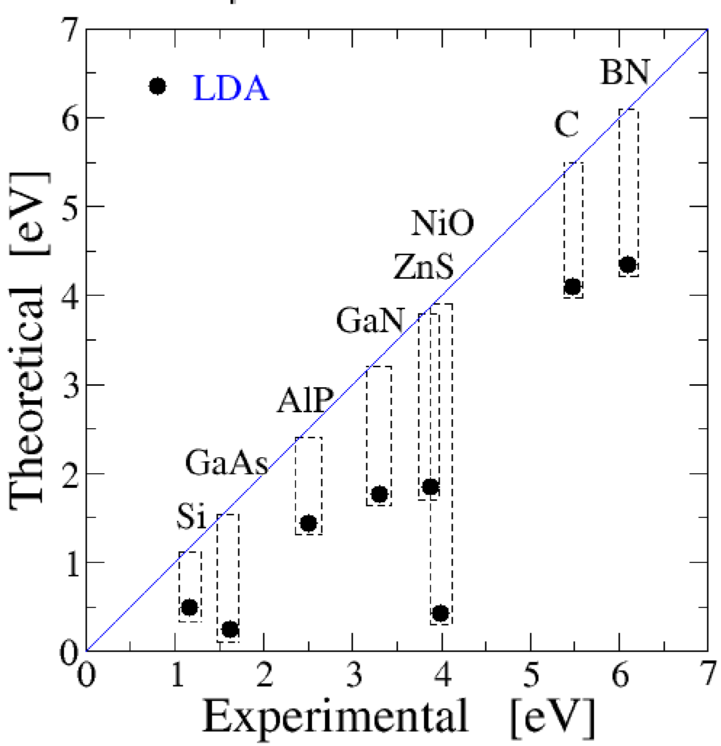
Mean field approaches

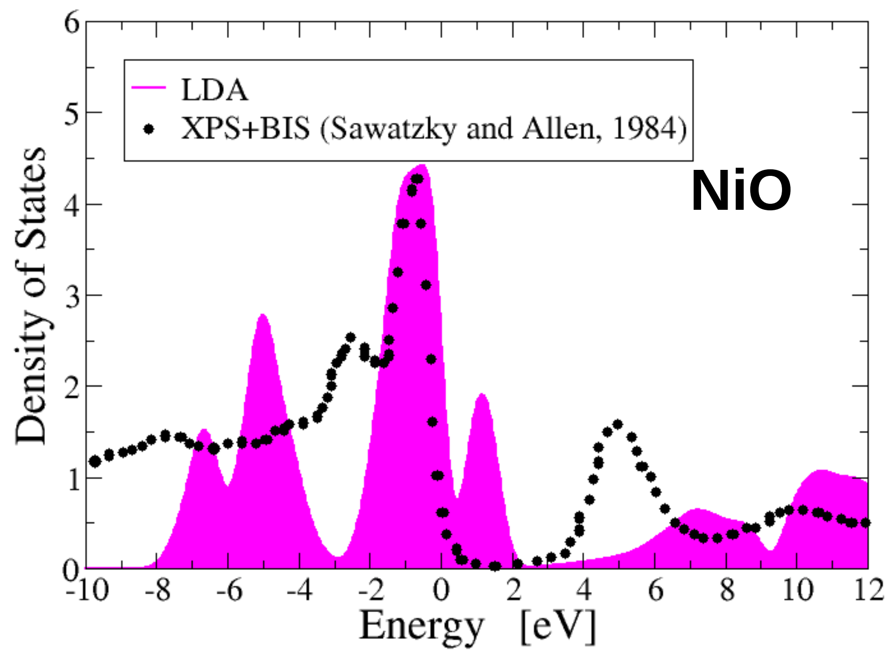




Courtesy of Dr. R. Gomez Abal

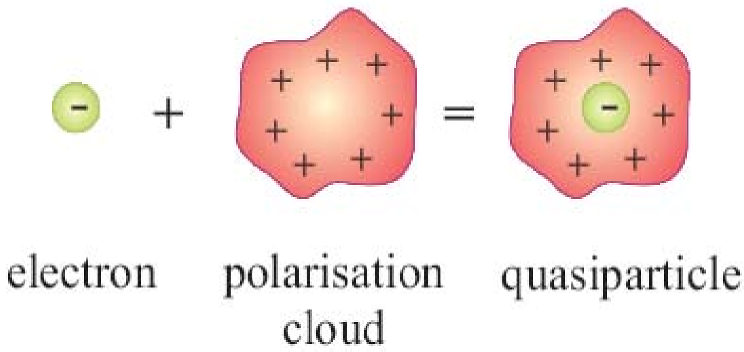
$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$





Quasi-particle theory

(courtesy of Dr. R. I. Gomez-Abal)



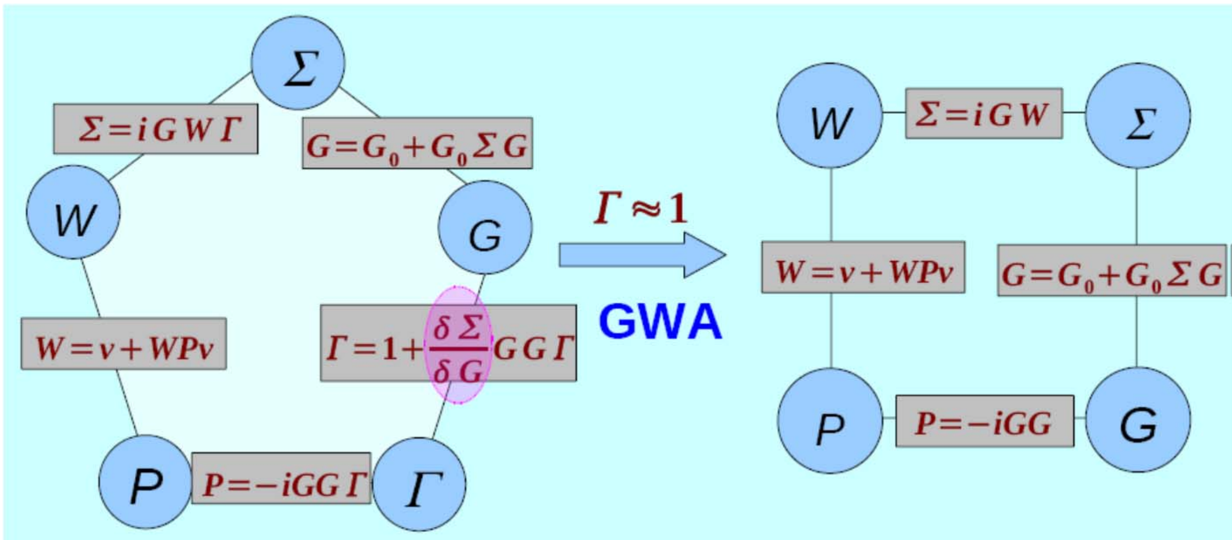
(courtesy of P. Rinke)

Quasi-particle equation

$$\left[-\frac{\nabla^2}{2}+V_{\mathrm{ext}}(\mathbf{r})+V_{\mathrm{H}}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r})+\int d^3\mathbf{r}'\Sigma_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}')=E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$

Hedin equation and *GW* approximation

$$\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}')d^3\mathbf{r}'=E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$



L. Hedin Phys. Rev. 139, A 796 (1965）; Aulbur et. al. Solid State Physics (2000)

G_0W_0 approach

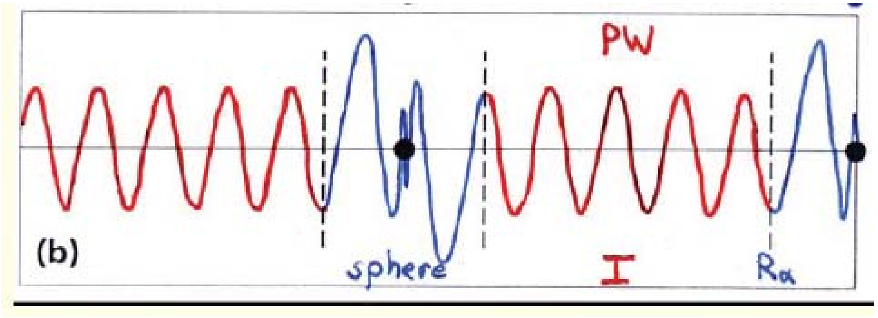
$$\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})+V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r})=\epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

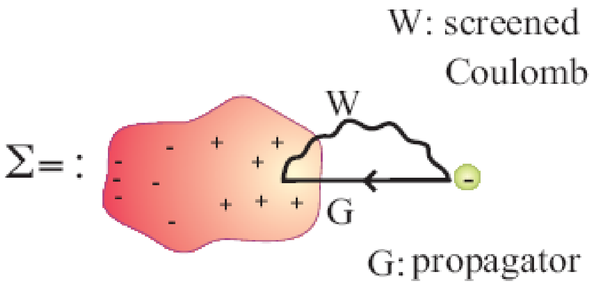
$$E_{n\mathbf{k}}=\epsilon_{n\mathbf{k}}+\Re\left[\langle\psi_{n\mathbf{k}}|\,\Sigma(E_{n\mathbf{k}})-V_{\text{xc}}^{\text{DFT}}\,|\psi_{n\mathbf{k}}\rangle\right]$$

Implementation: *GW* with Augmented Planewaves

GAP (GW with Augmented Planewaves)

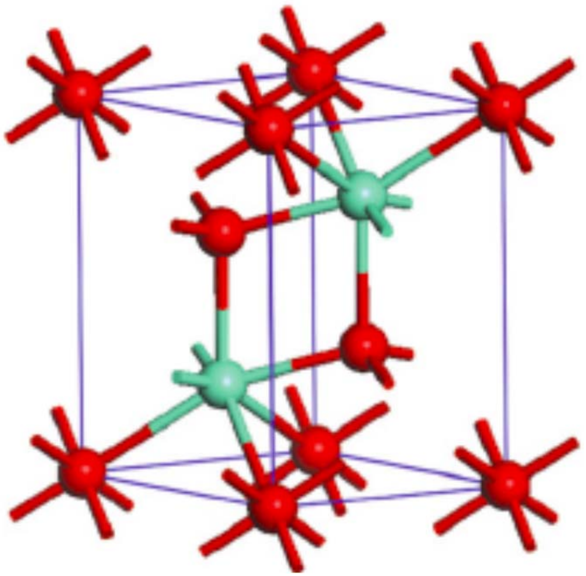
- Based on LAPW (all-electron, no pseudopotentials !)
- Interfaced with WIEN2k (P. Blaha et al. (2001))

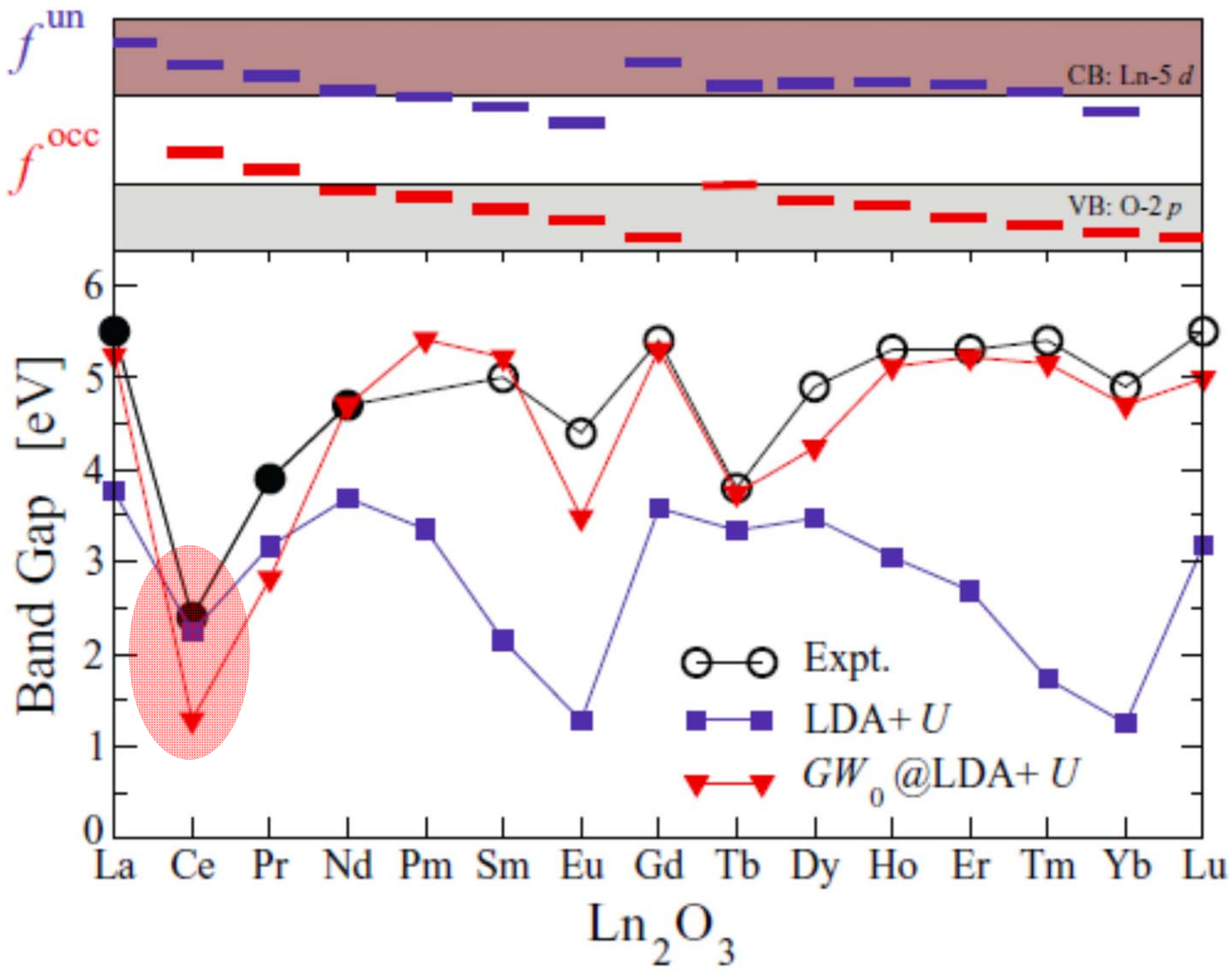




FHI-gap: H. Jiang，R. I. Gomez-Abal, X. Li, ..., M. Scheffler, *Computer Phys. Commun*., **184**, 348 (2013).

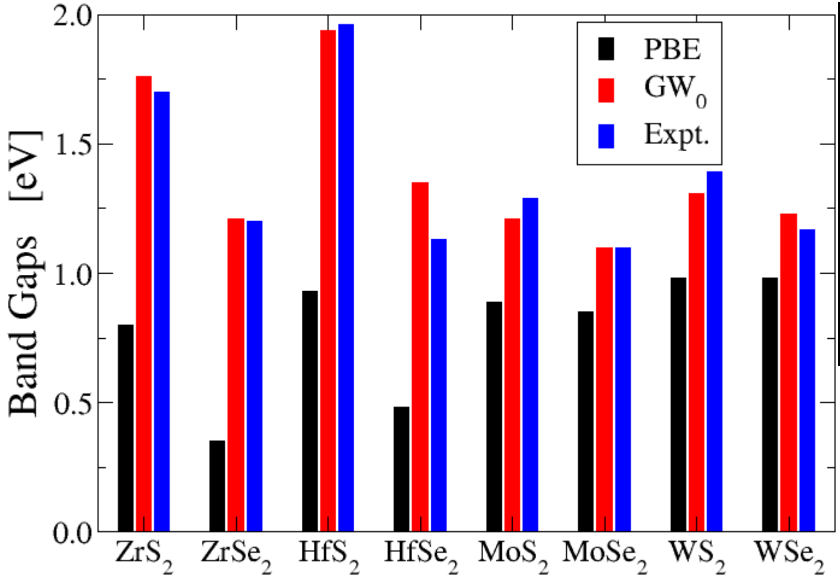
Ln_2O_3 band gaps: GW_0@LDA+U vs Expt.

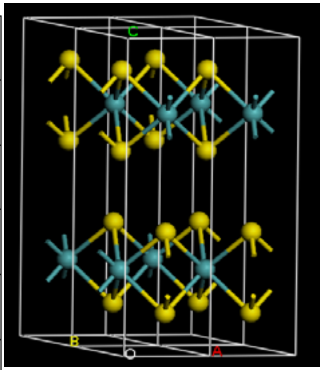




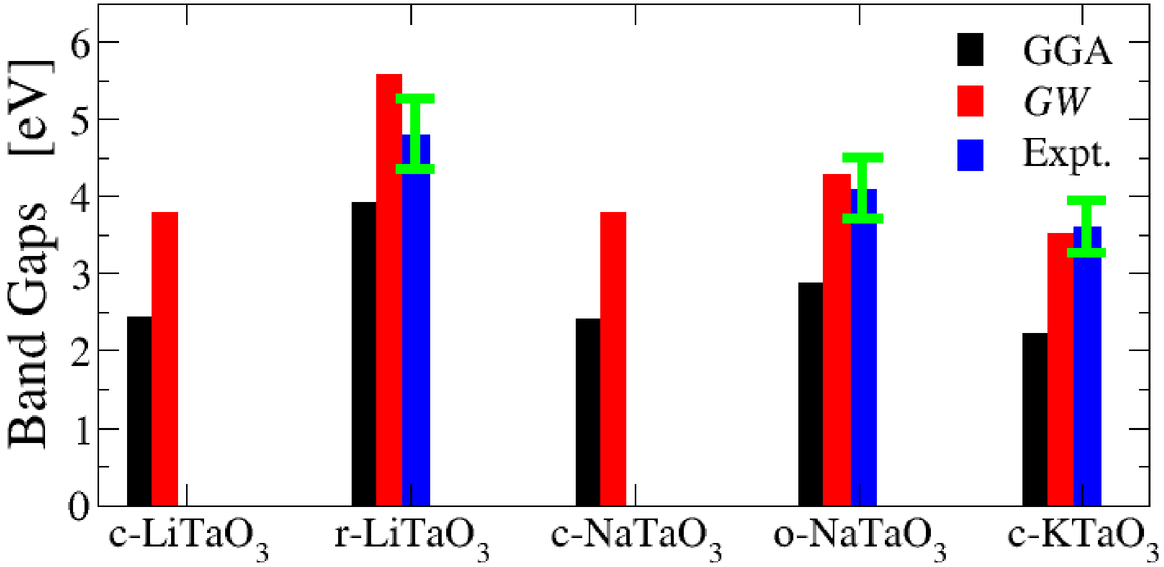
H. Jiang *et al*. **Phys. Rev. Lett. 102**, 126403(2009);
Phys. Rev. B **86**, 125115(2012).

GW for solar materials: TMDC and $ATaO_3$





Jiang, H., *J. Chem. Phys.* , **134**, 204705 (2011); Jiang, H., *J. Phys. Chem. C*, **116**,7664 (2012).

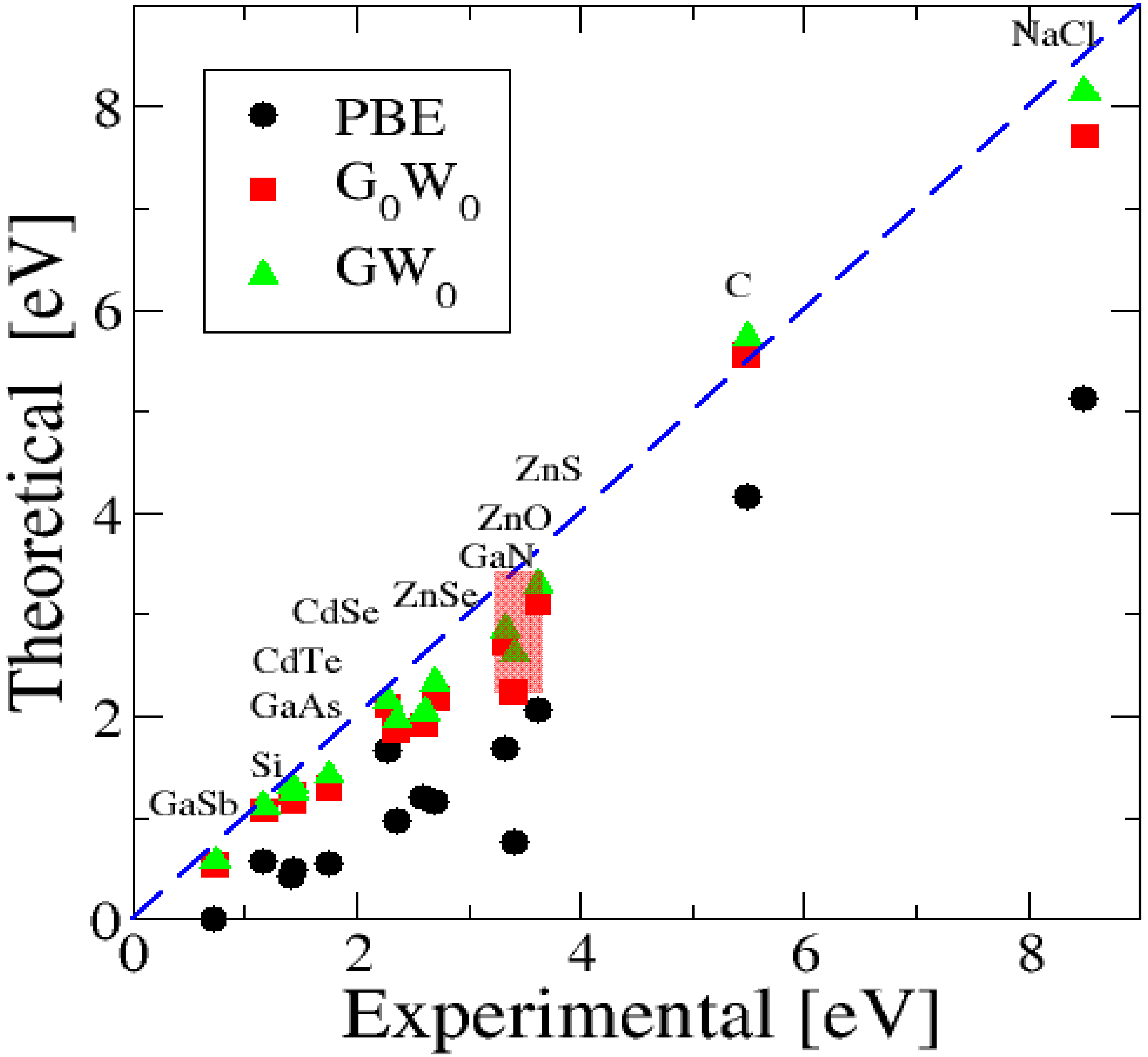


H. Wang, F. Wu & **H. Jiang***, *J. Phys. Chem. C*, **115**, 16180, (2011)

GW with LAPW+HLOs for *sp*-semiconductors

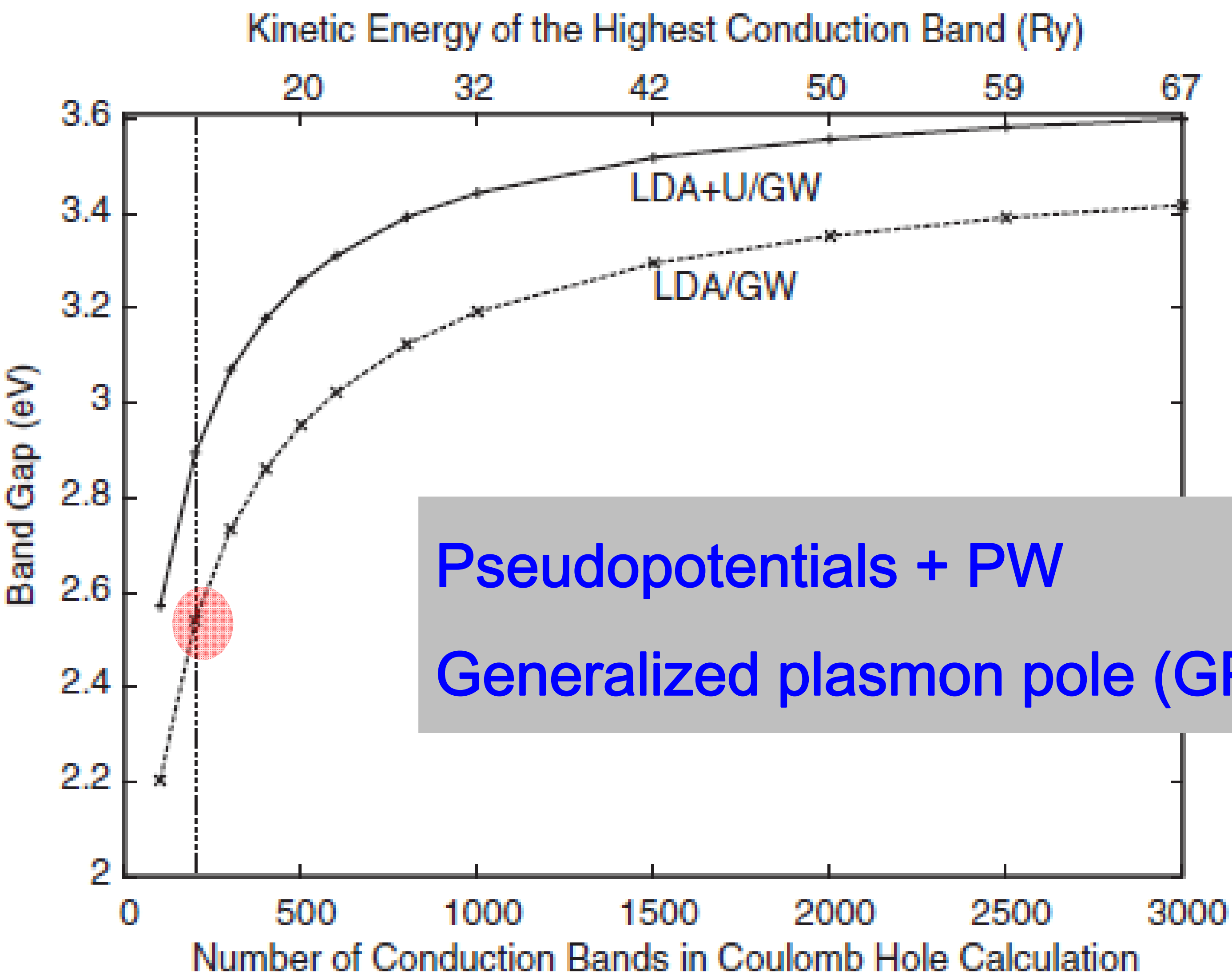
H. Jiang and P. Blaha, Phys. Rev. B, **93**,115203 (2016).

“The ZnO puzzle” (1)



H. Jiang (2009)

"The ZnO puzzle" (2)

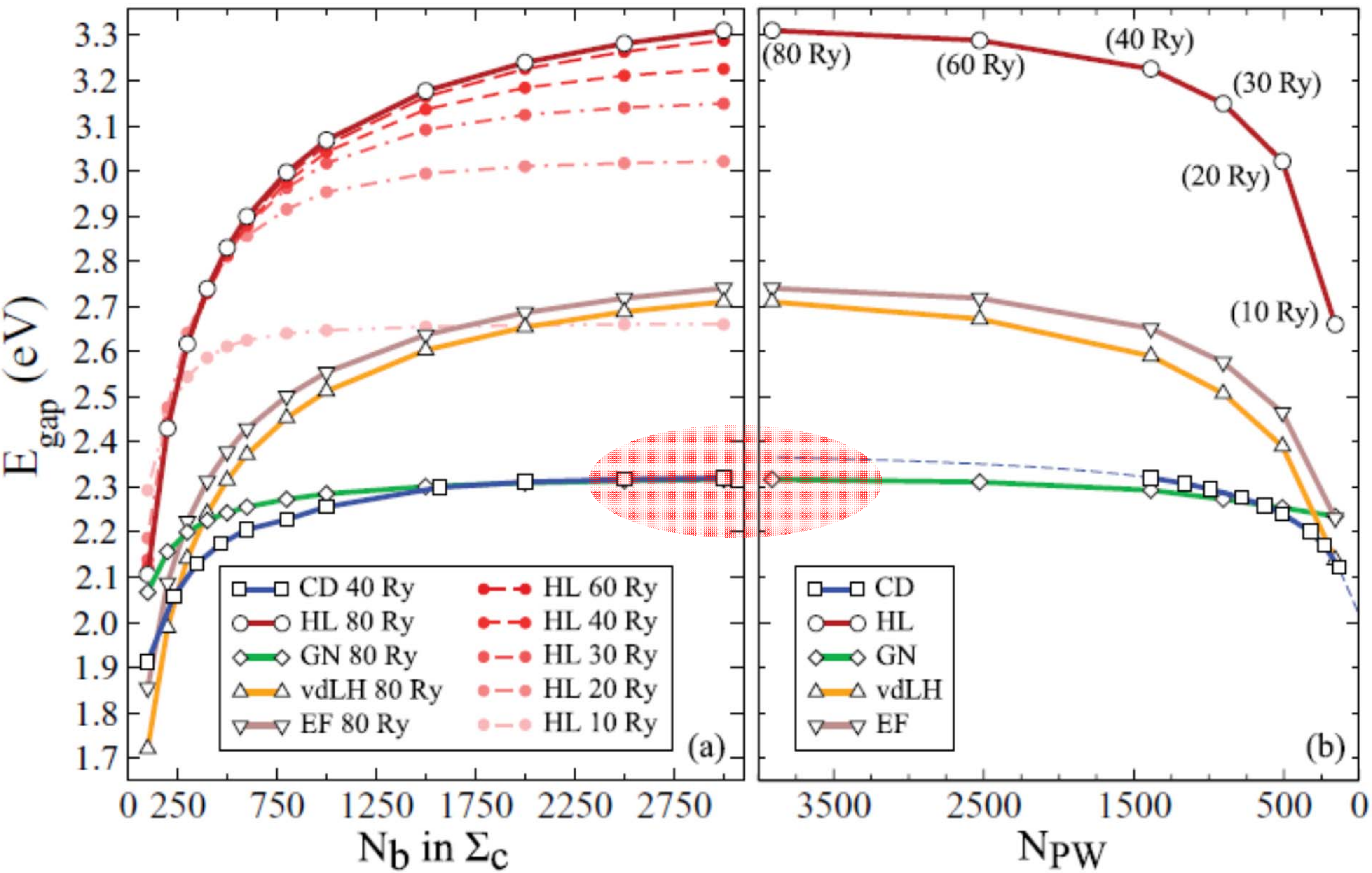


Pseudopotentials + PW

Generalized plasmon pole (GPP)

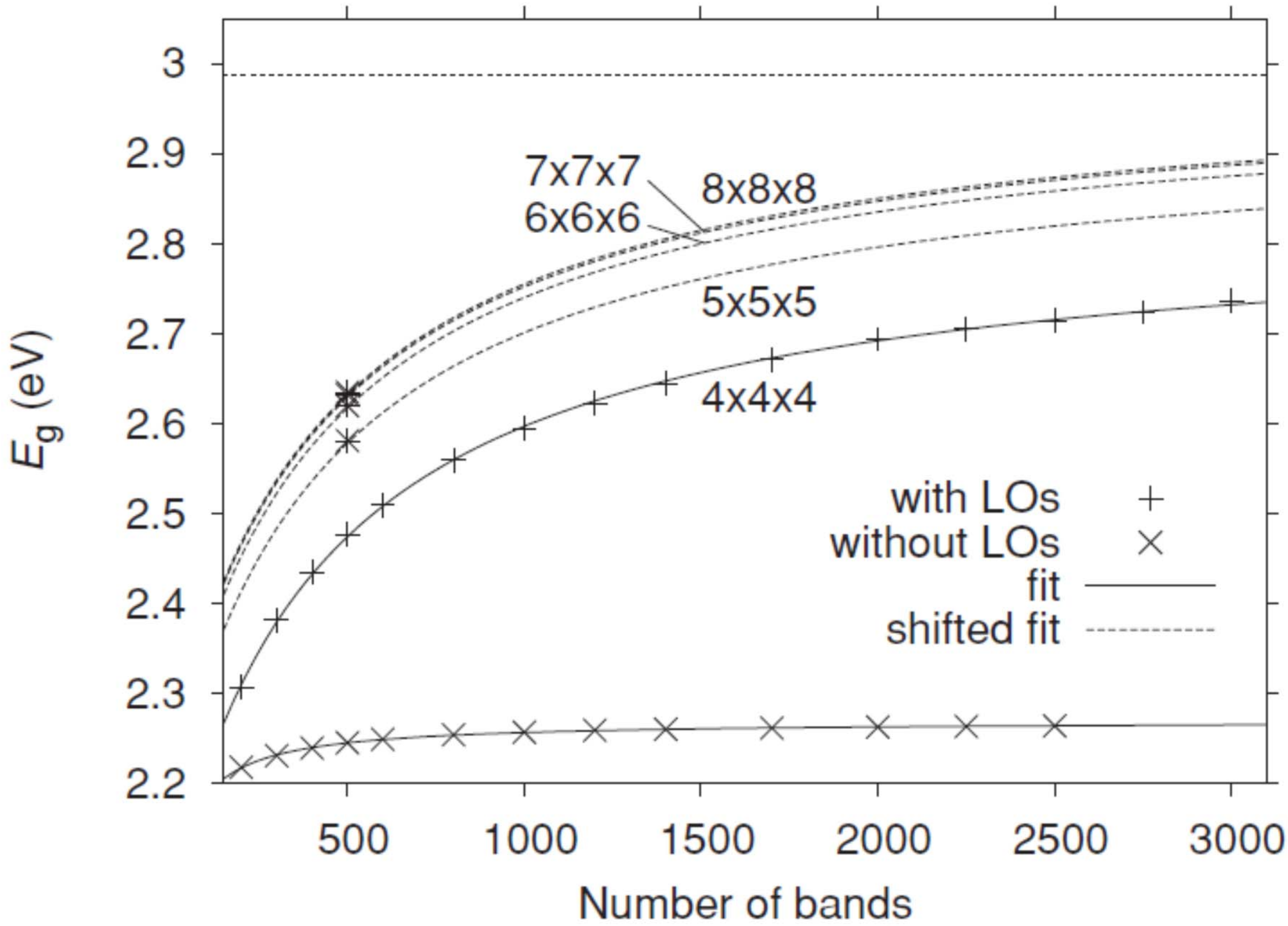
Shih, et al, PRL 105, 146401 (2010).

"The ZnO puzzle" (3)



M. Stankovski, et al, PRB **84**, 241201(R) (2011)

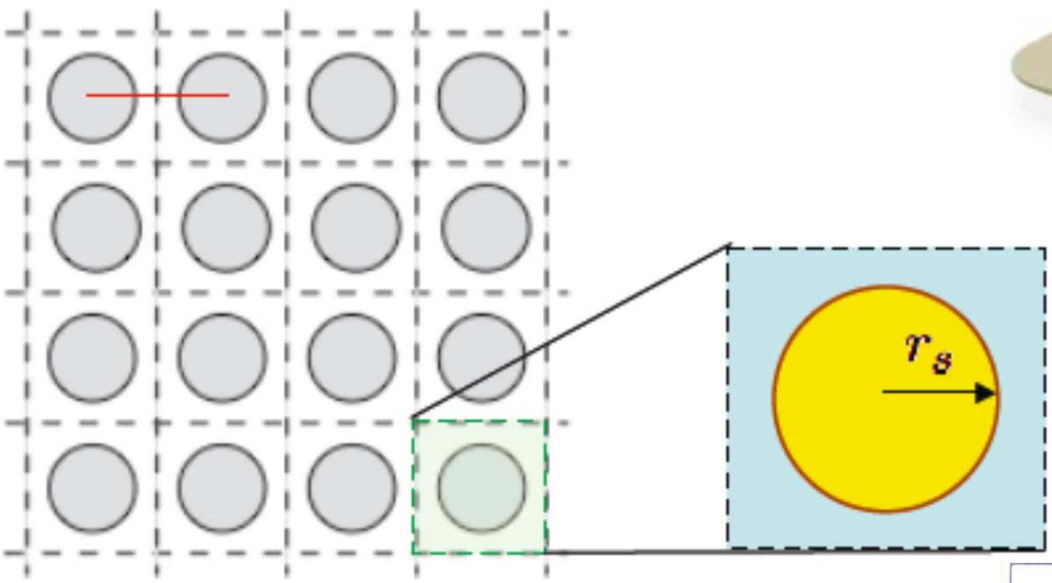
"The ZnO puzzle" (4)



C. Friedrich et al, PRB **83**, 081101(R) (2011)

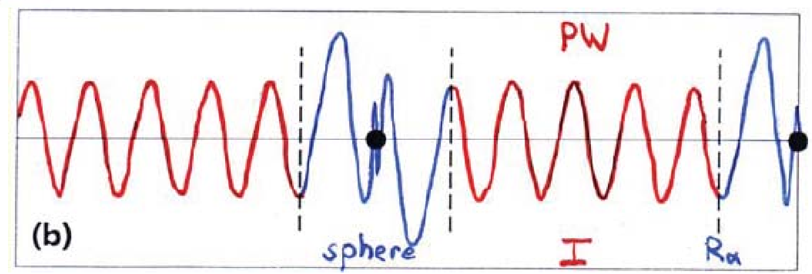
Linearized Augmented Planewaves (LAPW)

muffin tin potential



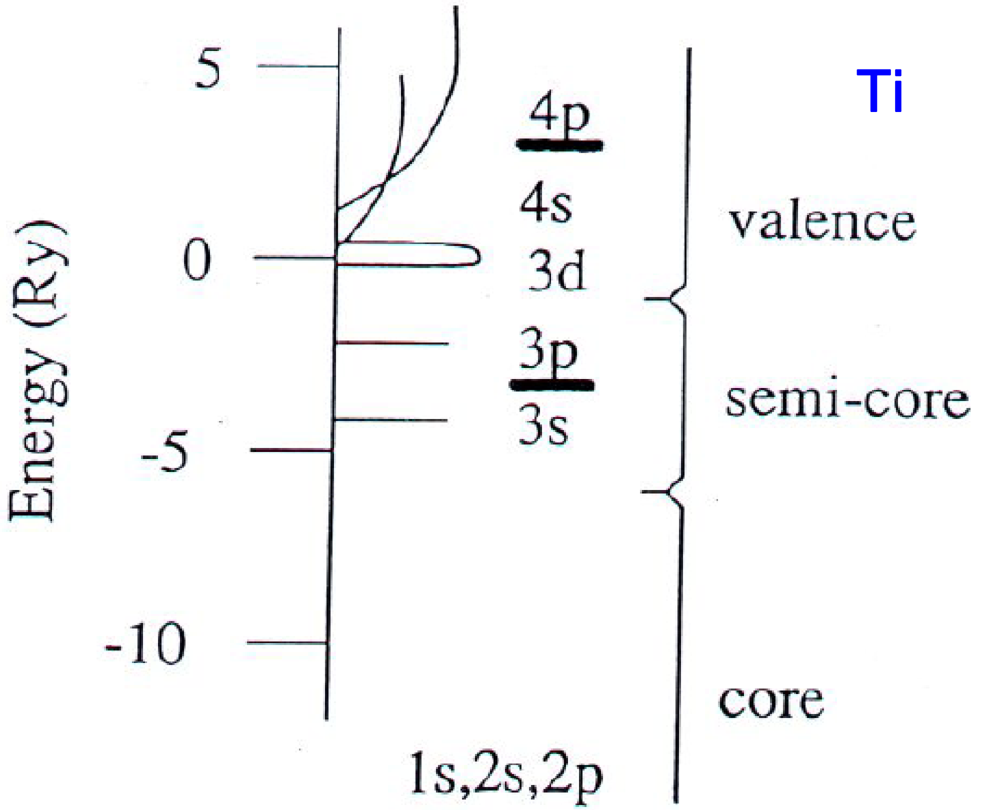
muffin tin

Wigner Seitz cell



$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & (\mathbf{r} \in I) \\ \sum_{l=0}^{l_{\max}} \sum_{m} [A_{lm}^{\alpha}(\mathbf{k}+\mathbf{G}) u_l(r^{\alpha}; E_l) + B_{lm}^{\alpha}(\mathbf{k}+\mathbf{G}) \dot{u}_l(r^{\alpha}; E_l)] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r} \in S_{\alpha}) \end{cases}$$

Local orbital (LO) basis in LAPW

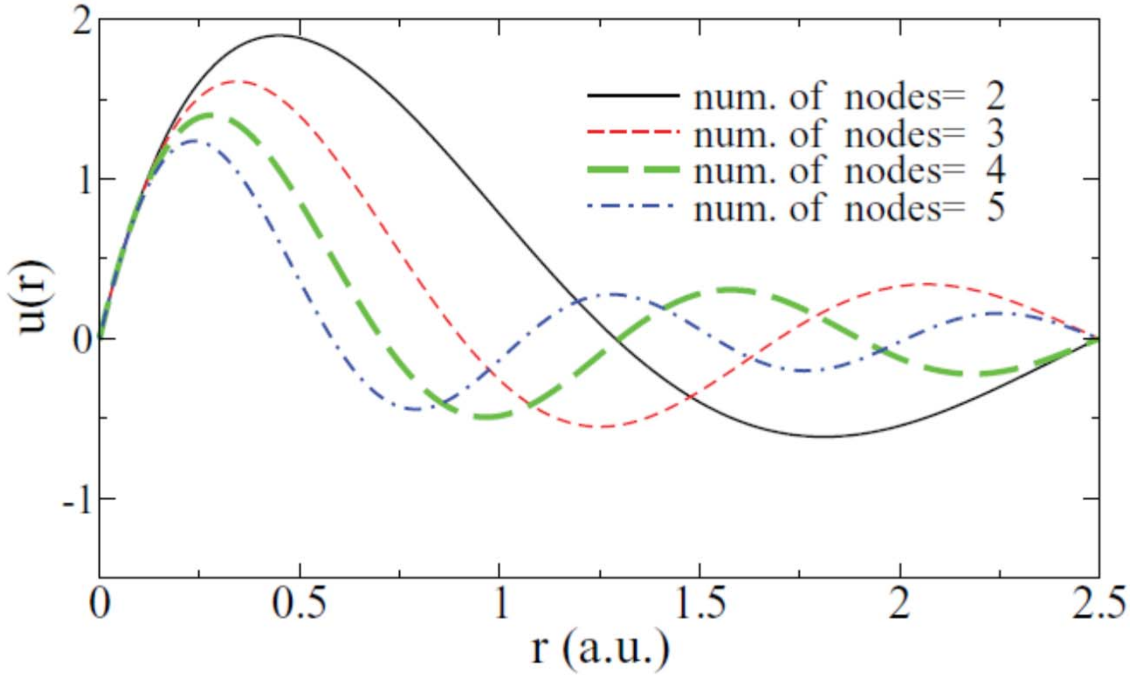


$$\phi_{\mathrm{LO}}(\mathbf{r}) = \begin{cases} 0 & (\mathbf{r} \in I) \\ [A_{lm}^{\alpha} u_l(r^{\alpha}; E_l) + B_{lm}^{\alpha} \dot{u}_l(r^{\alpha}; E_l) + C_{lm}^{\alpha} u_l(r^{\alpha}; E_l^{(2)})] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r} \in S_{\alpha}) \end{cases}$$

D. Singh, Phys. Rev. B, 43, 6388(1991)

LAPW with high-energy LOs (LAPW+HLOs)

$$\phi_{\mathrm{LO}}(\mathbf{r}) = \begin{cases} 0 & (\mathbf{r} \in I) \\ [A^{\alpha}_{lm} u_l(r^{\alpha}; E_l) + B^{\alpha}_{lm} \dot{u}_l(r^{\alpha}; E_l) + C^{\alpha}_{lm} u_l(r^{\alpha}; E_l^{(2)})] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r} \in S_{\alpha}) \end{cases}$$



R. Laskowski & P. Blaha, Phys. Rev. B, 85, 035132 (2012)

the default:

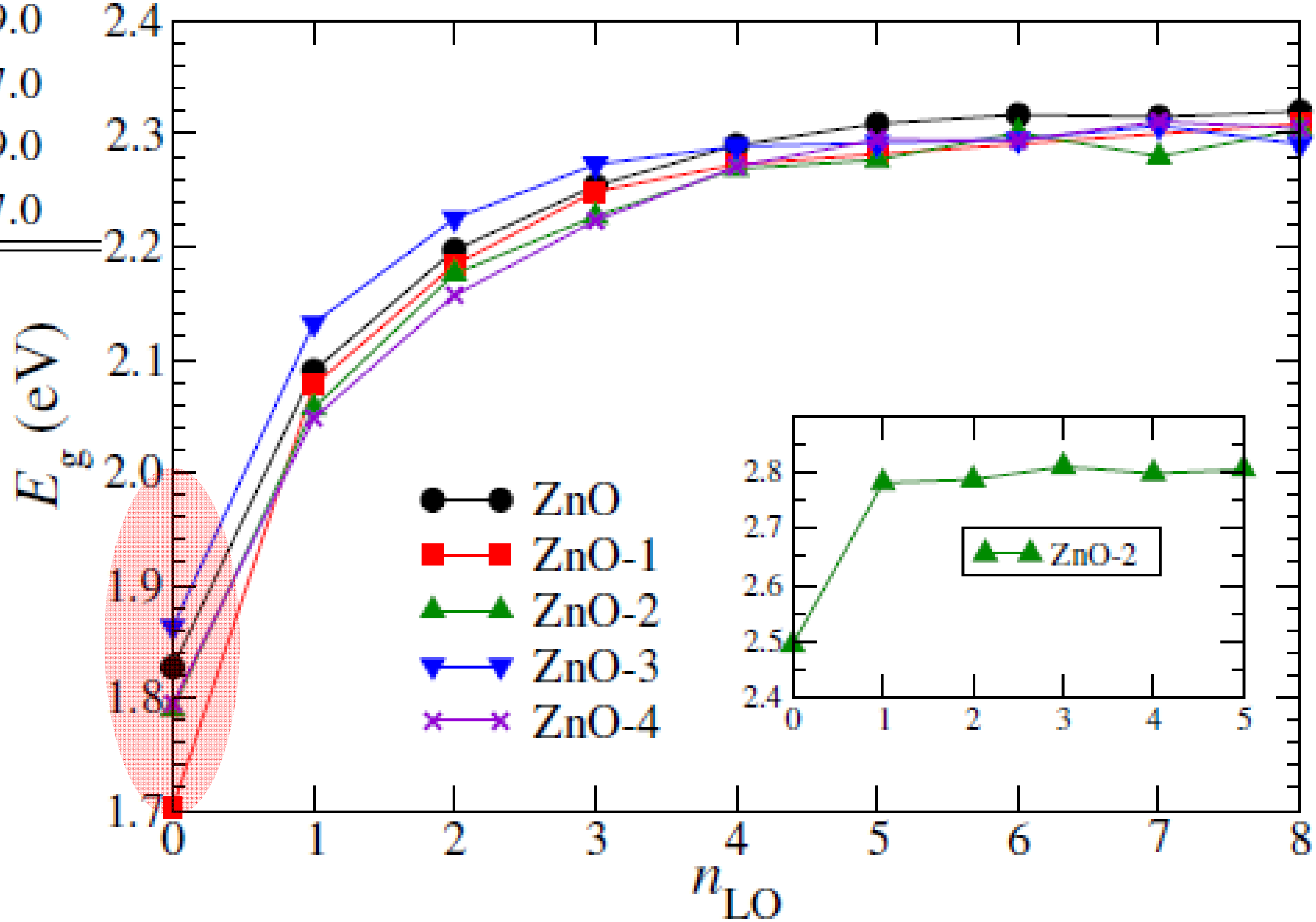
$$l_{\max}^{(\mathrm{LO})} = \min\left(3, l_{\max}^{(\mathrm{v})} + 1\right)$$

n_{LO} : additional number of radial nodes in highest-energy LO

$l_{\max}^{(\mathrm{LO})}$: maximal l of the angular channels with HLOs

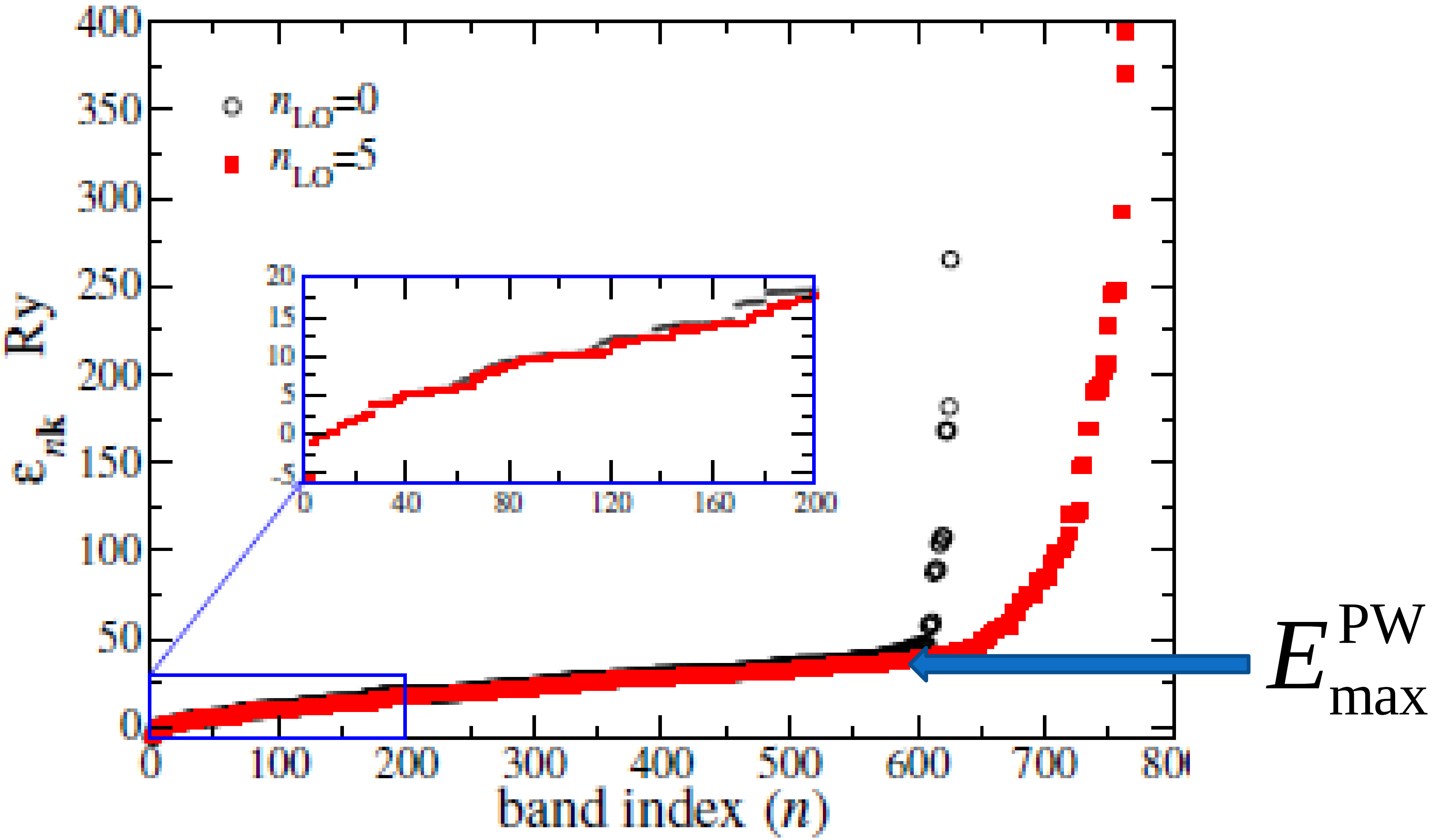
Effects of HLOs: ZnO (1)

notation	R_{MT}'s	RK_{max}
ZnO	(2.10, 1.50)	9.0
ZnO-1	(1.95, 1.70)	9.0
ZnO-2	(2.10, 1.50)	7.0
ZnO-3	(1.70, 1.20)	9.0
ZnO-4	(2.10, 1.50)	7.0

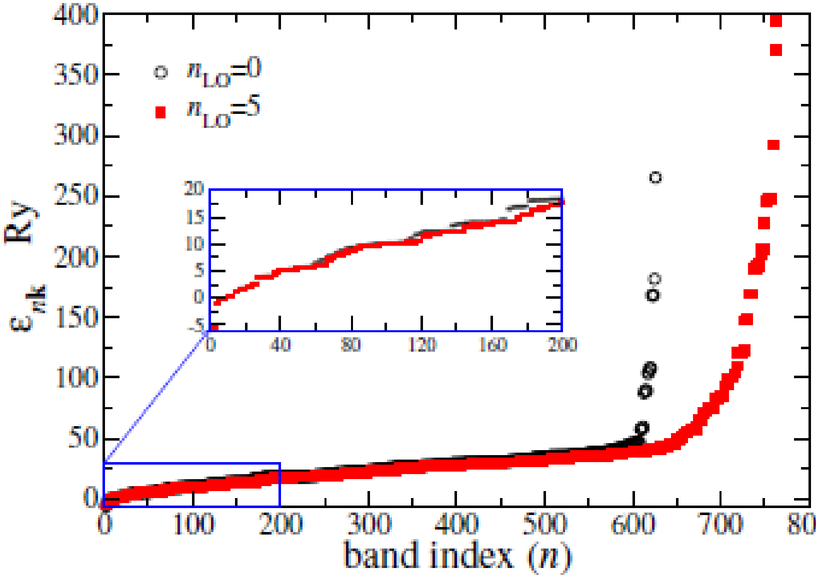


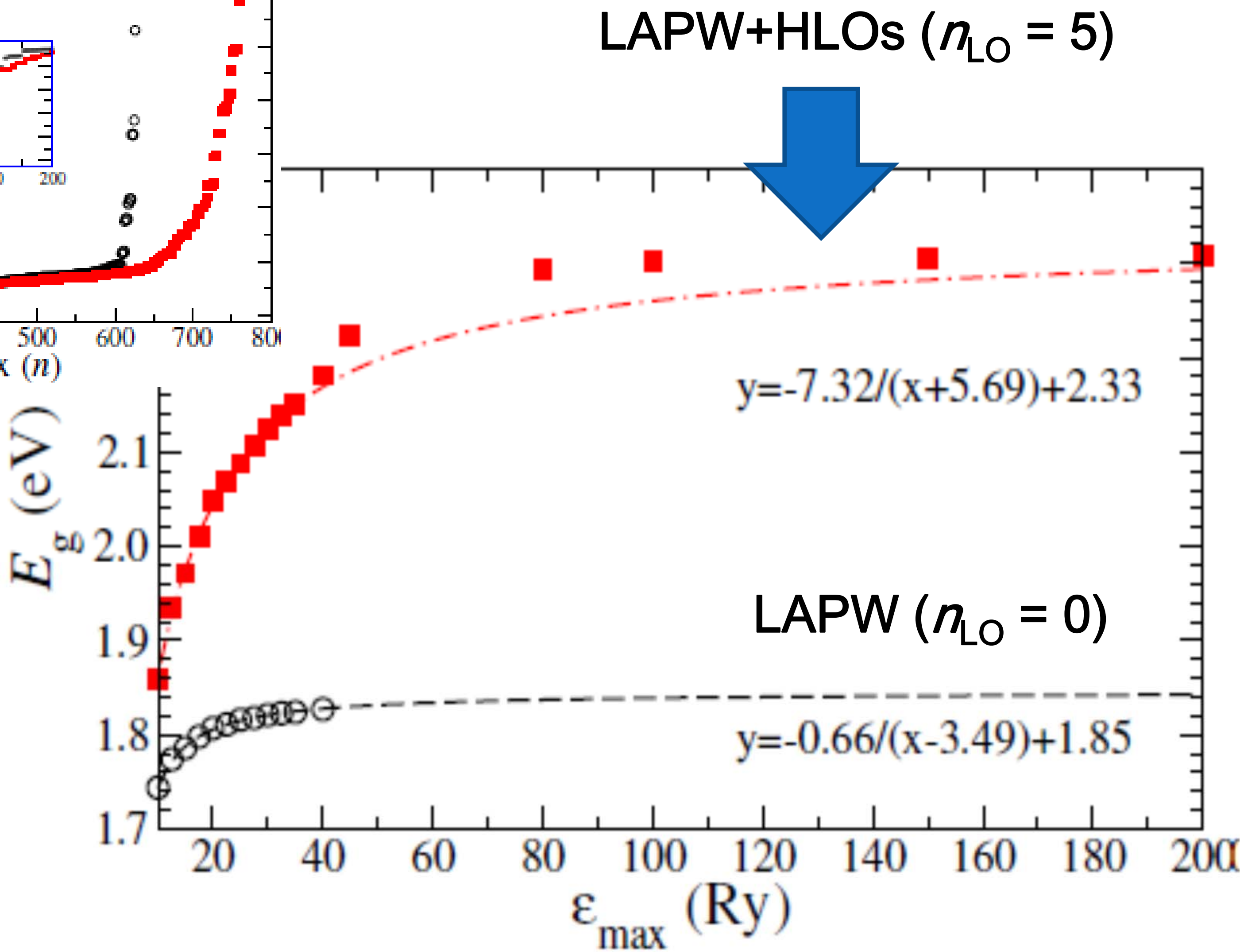
N_k=2x2x2

Effects of HLOs: ZnO (2)



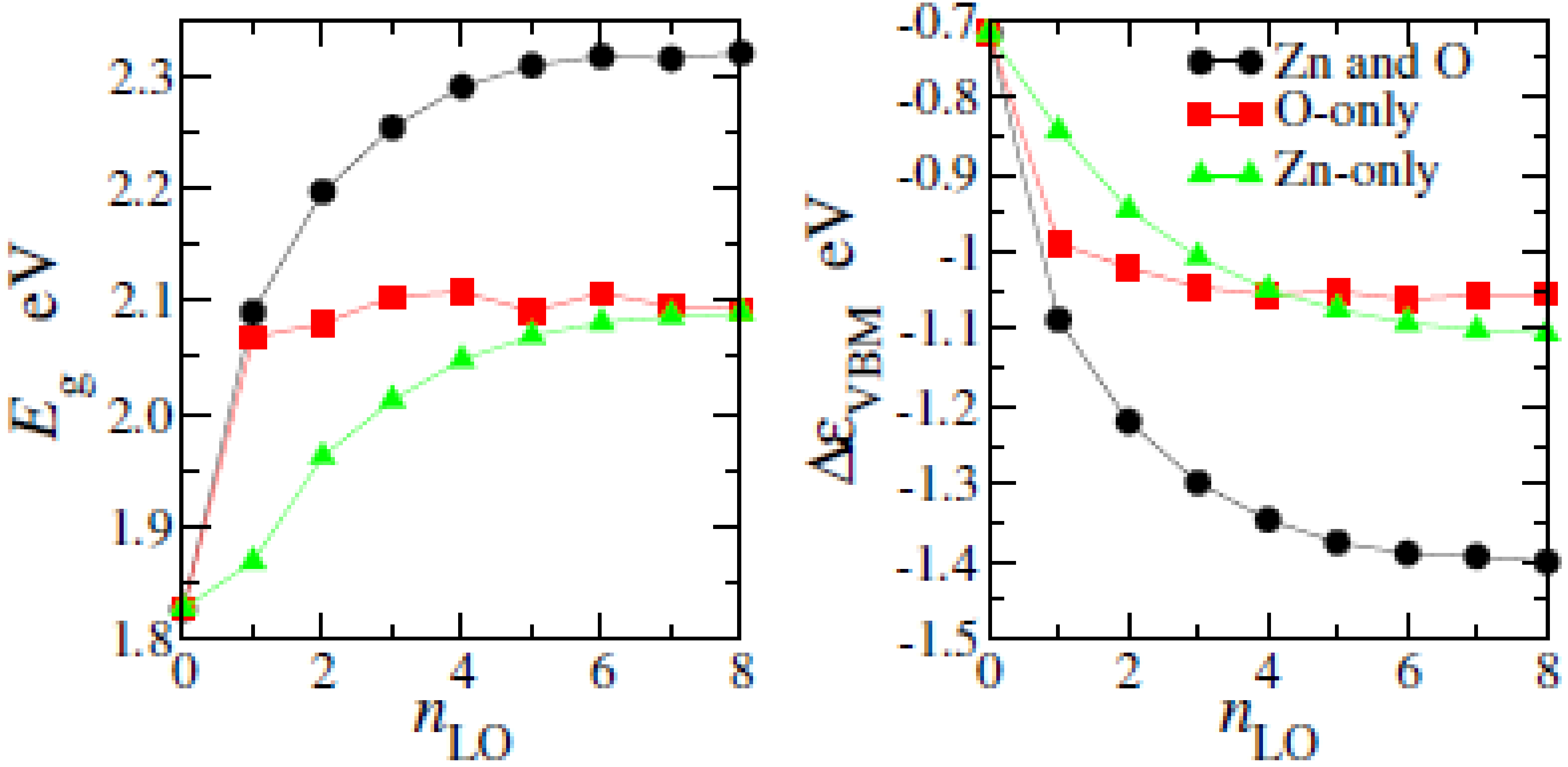
Effects of HLOs: ZnO (3)





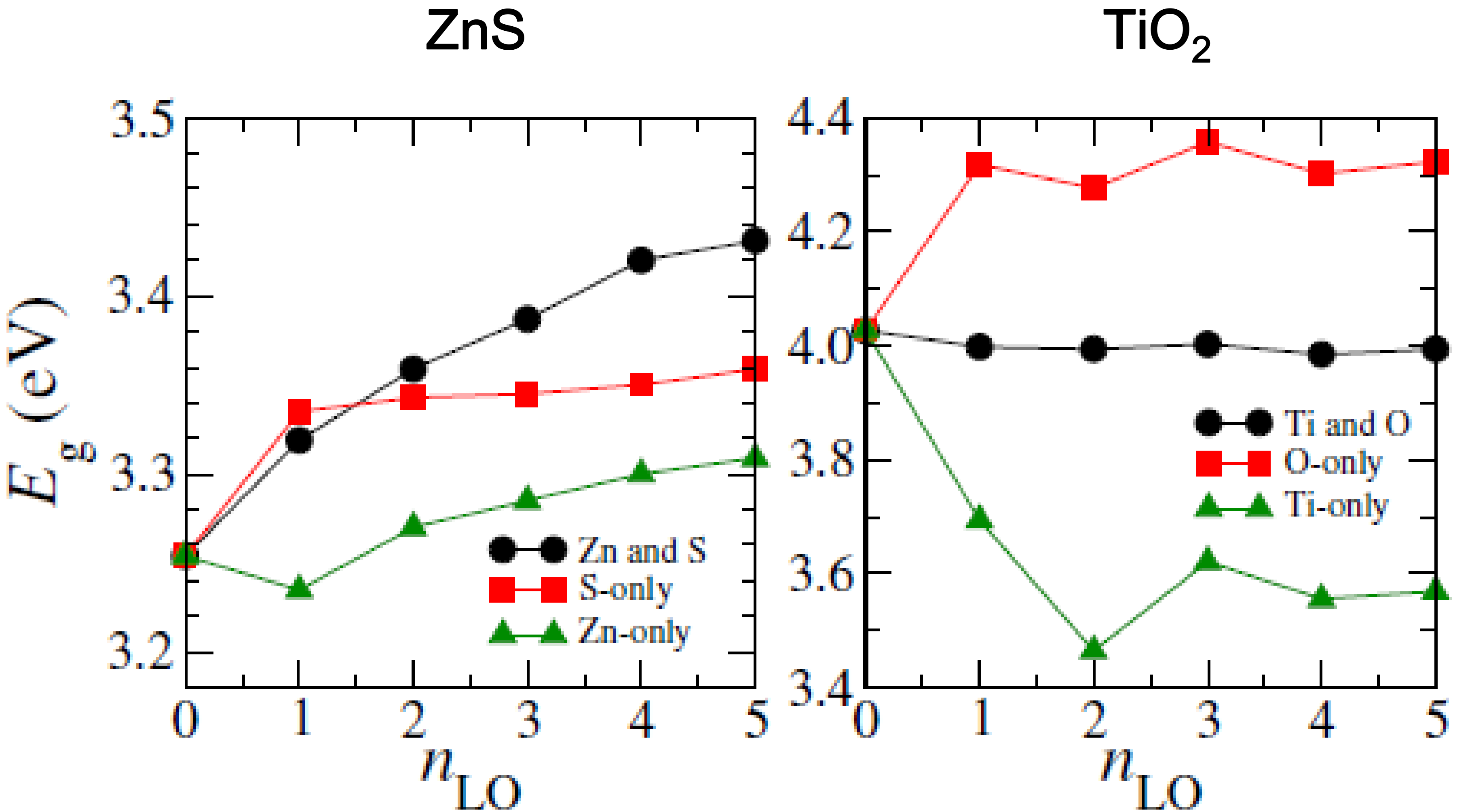
N_k=2x2x2

Effects of HLOs: ZnO(4)



N_k=2x2x2

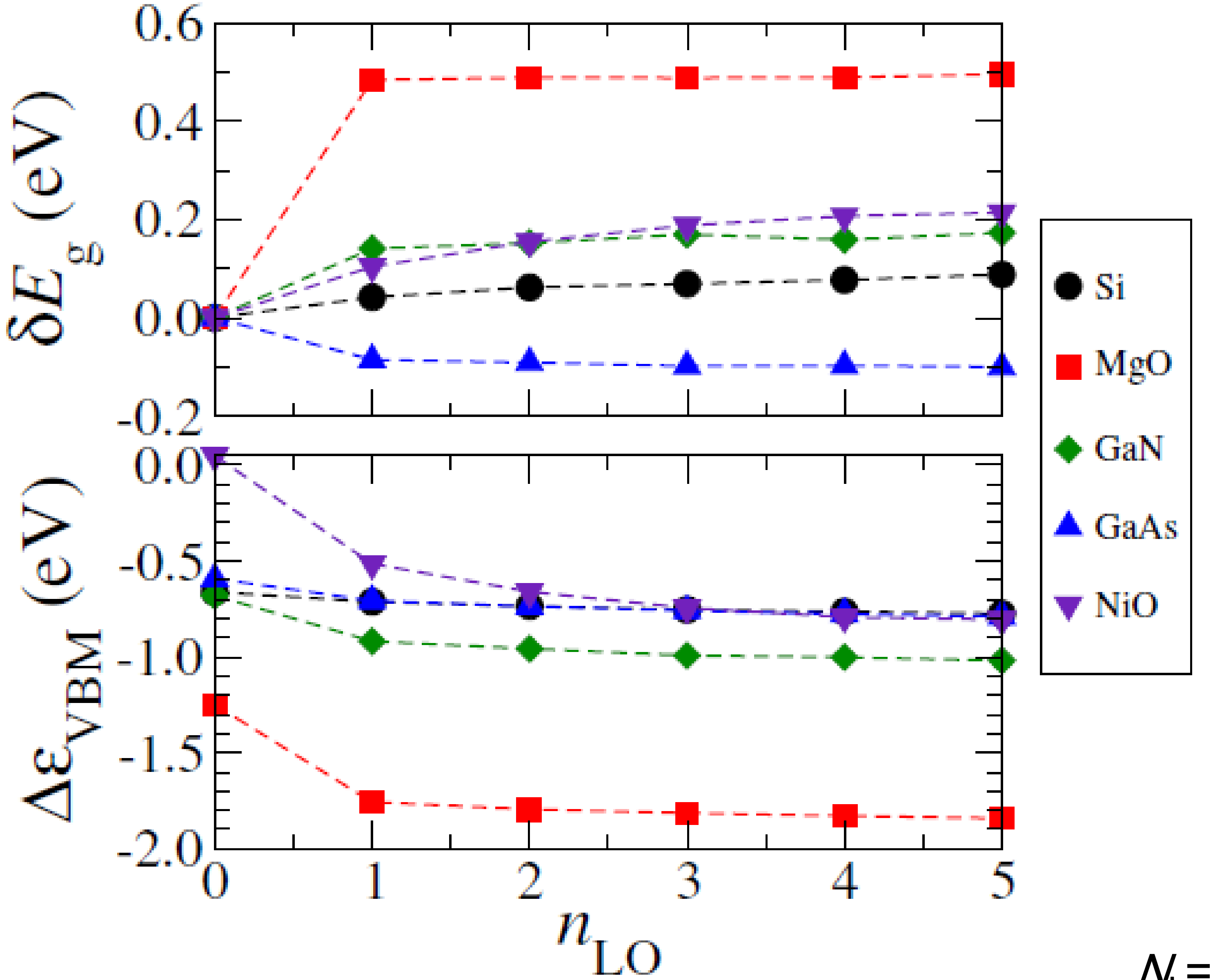
Effects of HLOs: ZnS and TiO_2



N_k=2x2x2

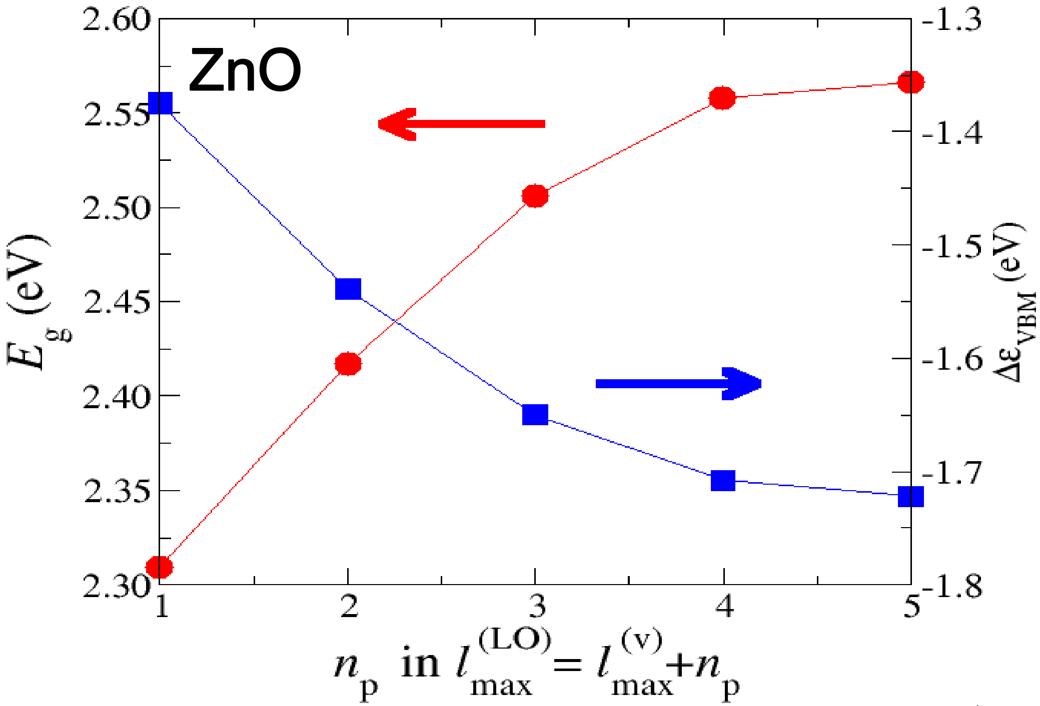
N_k=1x1x2

GW based on LAPW with HLOs: other systems

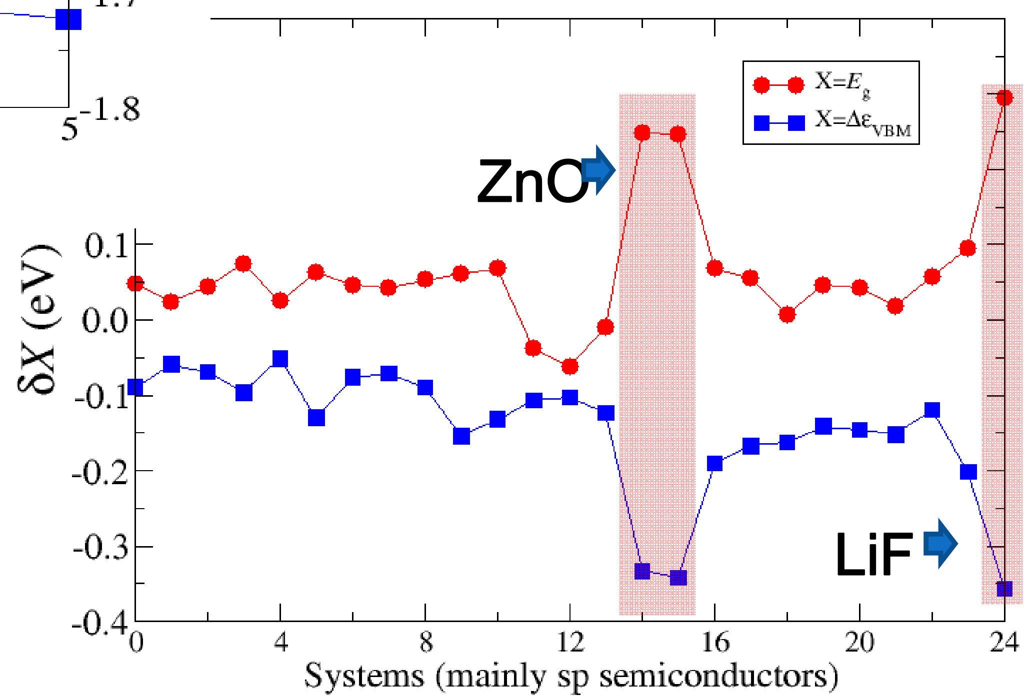


N_k=2x2x2

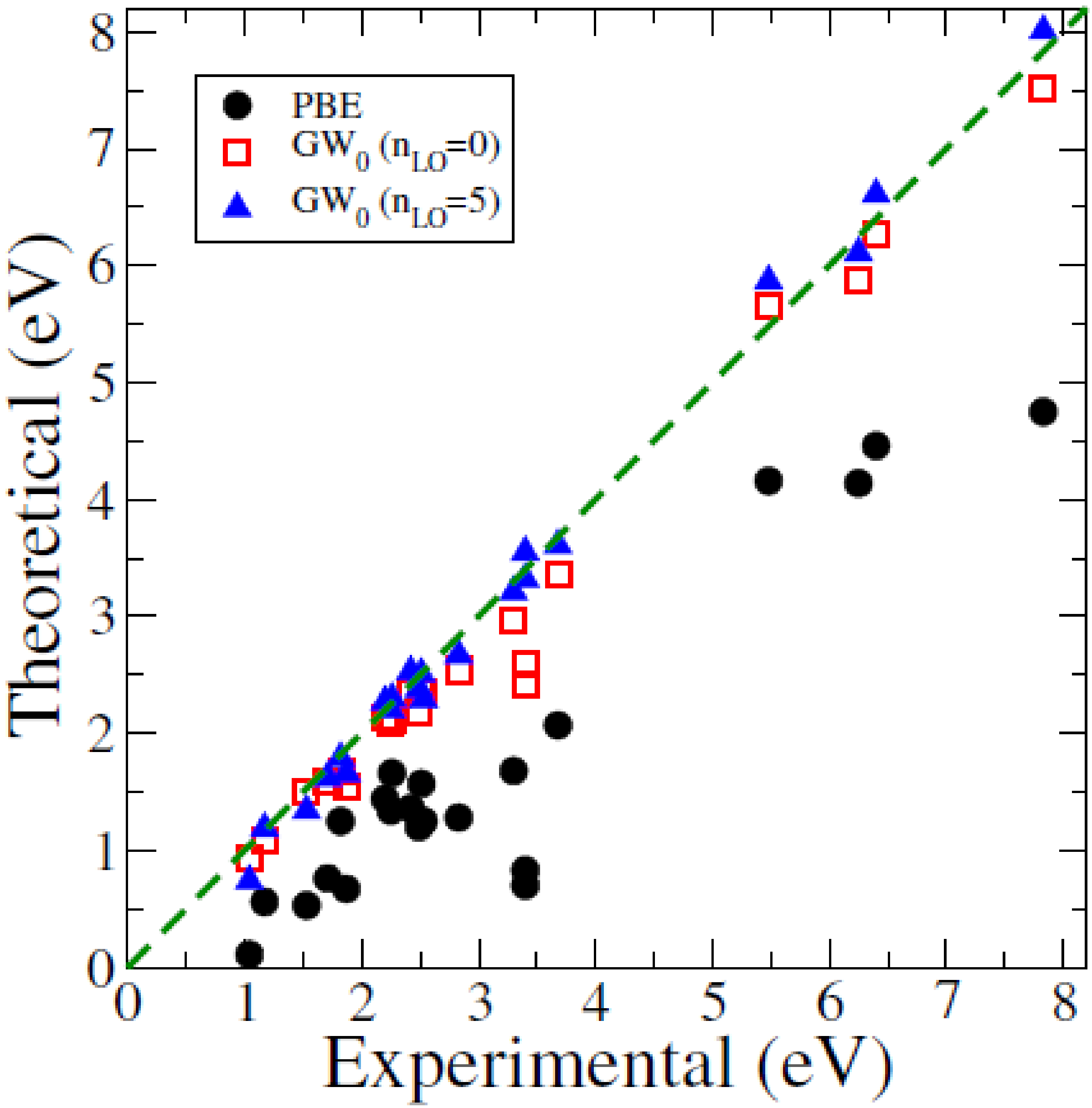
Effects of HLOs added to high-*l* channels



$$X\left(l_{max}^{(LO)} = l_{max}^{(v)} + 4\right) - X\left(l_{max}^{(LO)} = l_{max}^{(v)} + 1\right)$$



GW based on LAPW with high-energy LOs



GW based on LAPW with high-energy LOs

Systems	Expt.	PBE	G_0W_0	GW_0	G_0W_0	GW_0	δE_g	GW_0(NC-PAW)[a]
			$n_{LO}=0$		$n_{LO}=5$			
C	5.48	4.16	5.49	5.66	5.69	5.87	0.21	5.81
Si	1.17	0.56	1.03	1.09	1.12	1.19	0.10	1.21
SiC	2.42	1.36	2.23	2.36	2.38	2.53	0.17	2.60
BN	6.4	4.46	6.04	6.27	6.36	6.61	0.34	6.66
BP	2.4, 2.1	1.34	2.01	2.09	2.11	2.20	0.11	
wz-AlN	6.2-6.3	4.14	5.60	5.88	5.80	6.11	0.23	
AlP	2.51	1.57	2.25	2.36	2.37	2.51	0.15	2.62
AlAs	2.1	1.34(0.10)	1.94	2.03	2.06	2.17	0.14	2.35
AlSb	1.6	1.03(0.22)	1.40	1.45	1.50	1.57	0.12	1.76
GaN	3.30	1.68	2.78	2.96	3.00	3.21	0.25	3.48
GaP	2.26	1.66	2.05	2.12	2.21	2.30	0.18	2.40
GaAs	1.42	0.42(0.11)	1.31	1.39	1.15	1.23	-0.16	1.21
GaSb	0.81	-0.12(0.23)	0.64	0.71	0.47	0.51	-0.20	0.51
ZnO	3.4	0.70	2.05	2.41	2.78	3.32	0.91	
wz-ZnO	3.4	0.83	2.24	2.59	3.01	3.55	0.96	3.40
ZnS	3.68	2.07	3.15	3.35	3.35	3.61	0.26	3.72
ZnSe	2.7	1.15(0.13)	2.23	2.41	2.34	2.54	0.13	2.66
ZnTe	2.26	0.98(0.27)	1.95	2.08	1.89	2.02	-0.06	2.15
wz-CdS	2.49	1.20	2.02	2.18	2.19	2.38	0.20	
wz-CdSe	1.75	0.55(0.12)	1.29	1.42	1.39	1.54	0.12	1.60
CdTe	1.43	0.48(0.28)	1.20	1.30	1.23	1.34	0.04	1.44
LiF	14.20	9.28	12.36	13.98	14.27	15.13	1.15	
MgO	7.83	4.75	7.08	7.52	7.50	8.01	0.49	8.03
MAE		1.54	0.47	0.25	0.24	0.17		
MARE(%)		48	14	9	9	5		

GW based on LAPW with high-energy LOs

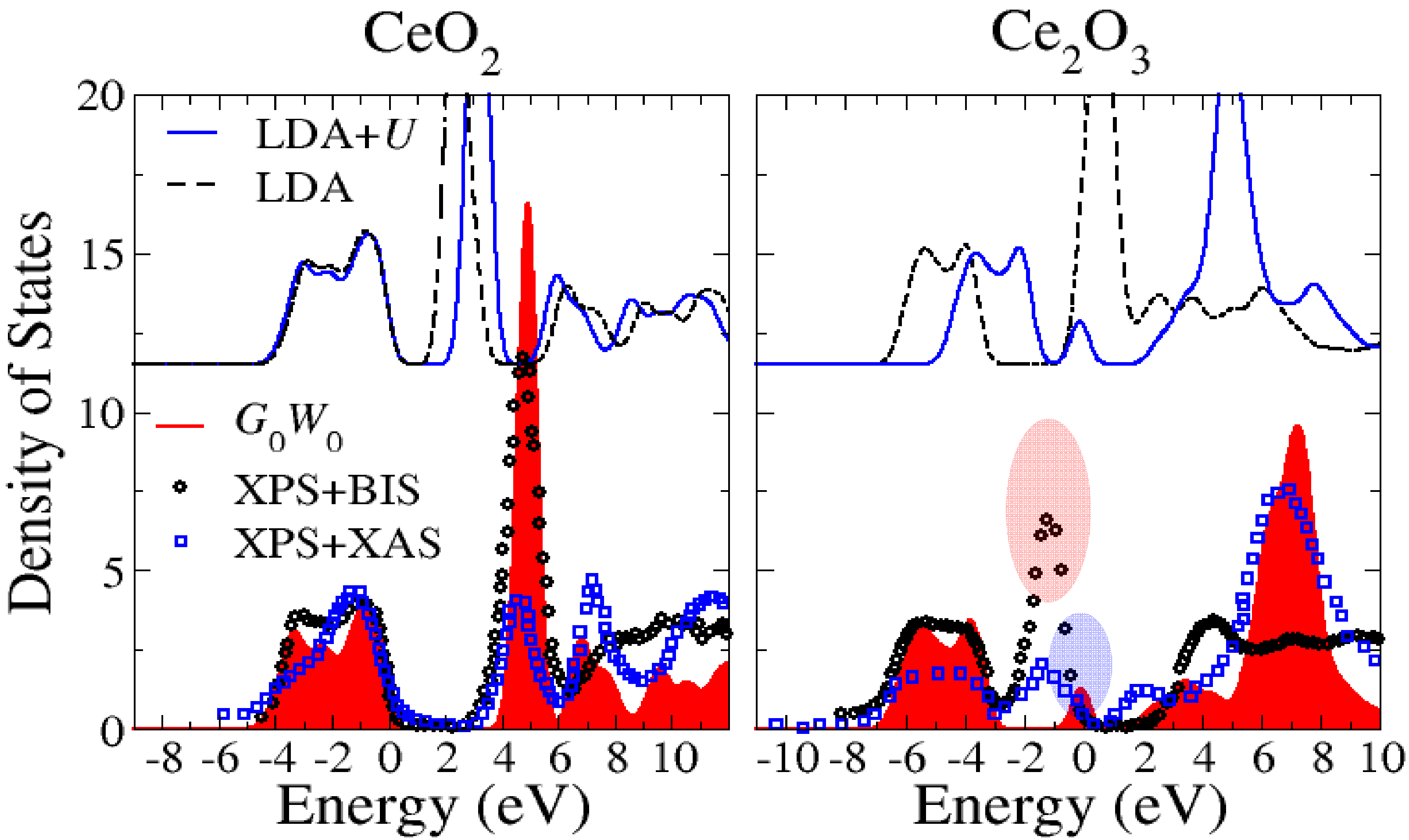
Systems	Expt.	PBE	G_0W_0	GW_0	G_0W_0	GW_0	δE_g	GW_0(NC-PAW)[a]
			$n_{LO}=0$		$n_{LO}=5$			
C	5.48	4.16	5.49	5.66	5.69	5.87	0.21	5.81
Si	1.17	0.56	1.03	1.09	1.12	1.19	0.10	1.21
SiC	2.42	1.36	2.23	2.36	2.38	2.53	0.17	2.60
BN	6.4	4.46	6.04	6.27	6.36	6.61	0.34	6.66
BP	2.4, 2.1	1.34	2.01	2.09	2.11	2.20	0.11	
wz-AlN	6.2-6.3	4.14	5.60	5.88	5.80	6.11	0.23	
AlP	2.51	1.57	2.25	2.36	2.37	2.51	0.15	2.62
AlAs	2.1	1.34(0.10)	1.94	2.03	2.06	2.17	0.14	2.35
AlSb	1.6	1.03(0.22)	1.40	1.45	1.50	1.57	0.12	1.76
GaN	3.30	1.68	2.78	2.96	3.00	3.21	0.25	3.48
GaP	2.26	1.66	2.05	2.12	2.21	2.30	0.18	2.40
GaAs	1.42	0.42(0.11)	1.31	1.39	1.15	1.23	-0.16	1.21
GaSb	0.81	-0.12(0.23)	0.64	0.71	0.47	0.51	-0.20	0.51
ZnO	3.4	0.70	2.05	2.41	2.78	3.32	0.91	
wz-ZnO	3.4	0.83	2.24	2.59	3.01	3.55	0.96	3.40
ZnS	3.68	2.07	3.15	3.35	3.35	3.61	0.26	3.72
ZnSe	2.7	1.15(0.13)	2.23	2.41	2.34	2.54	0.13	2.66
ZnTe	2.26	0.98(0.27)	1.95	2.08	1.89	2.02	-0.06	2.15
wz-CdS	2.49	1.20	2.02	2.18	2.19	2.38	0.20	
wz-CdSe	1.75	0.55(0.12)	1.29	1.42	1.39	1.54	0.12	1.60
CdTe	1.43	0.48(0.28)	1.20	1.30	1.23	1.34	0.04	1.44
LiF	14.20	9.28	12.36	13.98	14.27	15.13	1.15	
MgO	7.83	4.75	7.08	7.52	7.50	8.01	0.49	8.03
MAE		1.54	0.47	0.25	0.24	0.17		
MARE(%)		48	14	9	9	5		

GW with LAPW+HLOs

for *d*- and *f*-electron systems

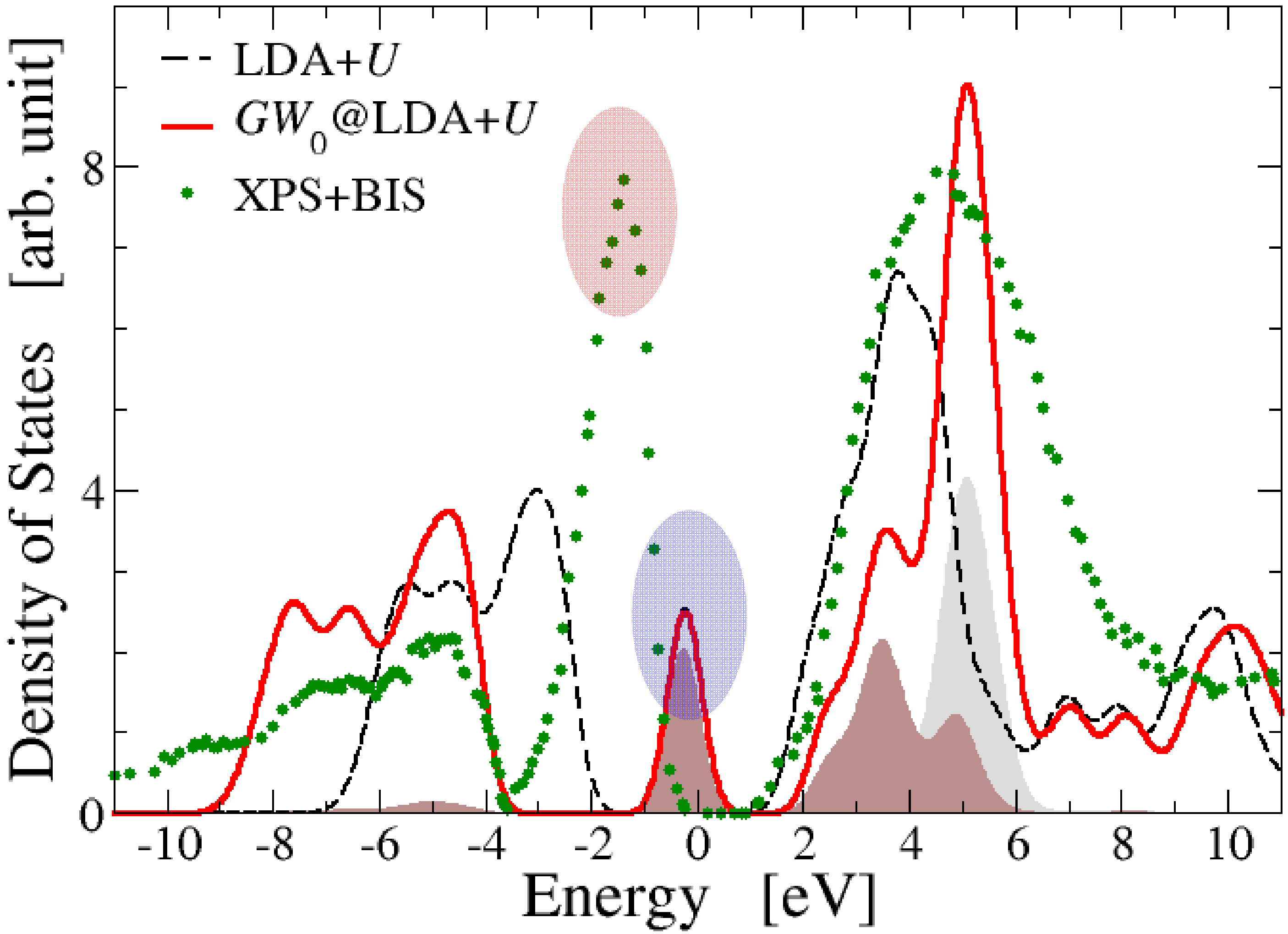
H. Jiang, in preparation (2016).

GW@LDA+U for f-electron systems: CeO_x



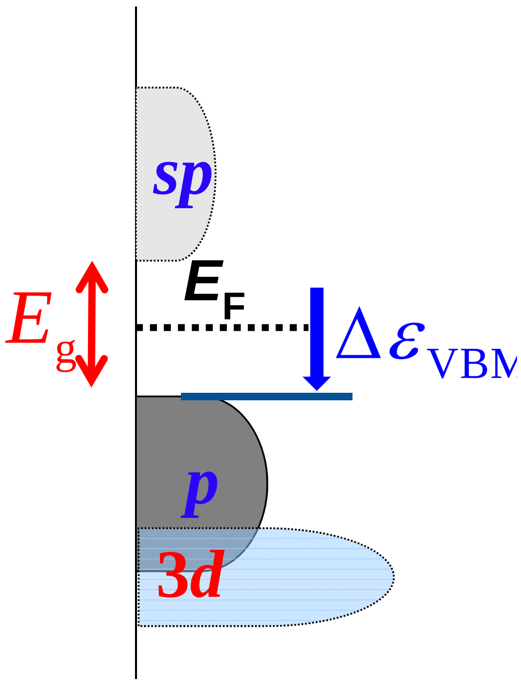
H. Jiang *et al*. **Phys. Rev. Lett. 102**, 126403(2009).

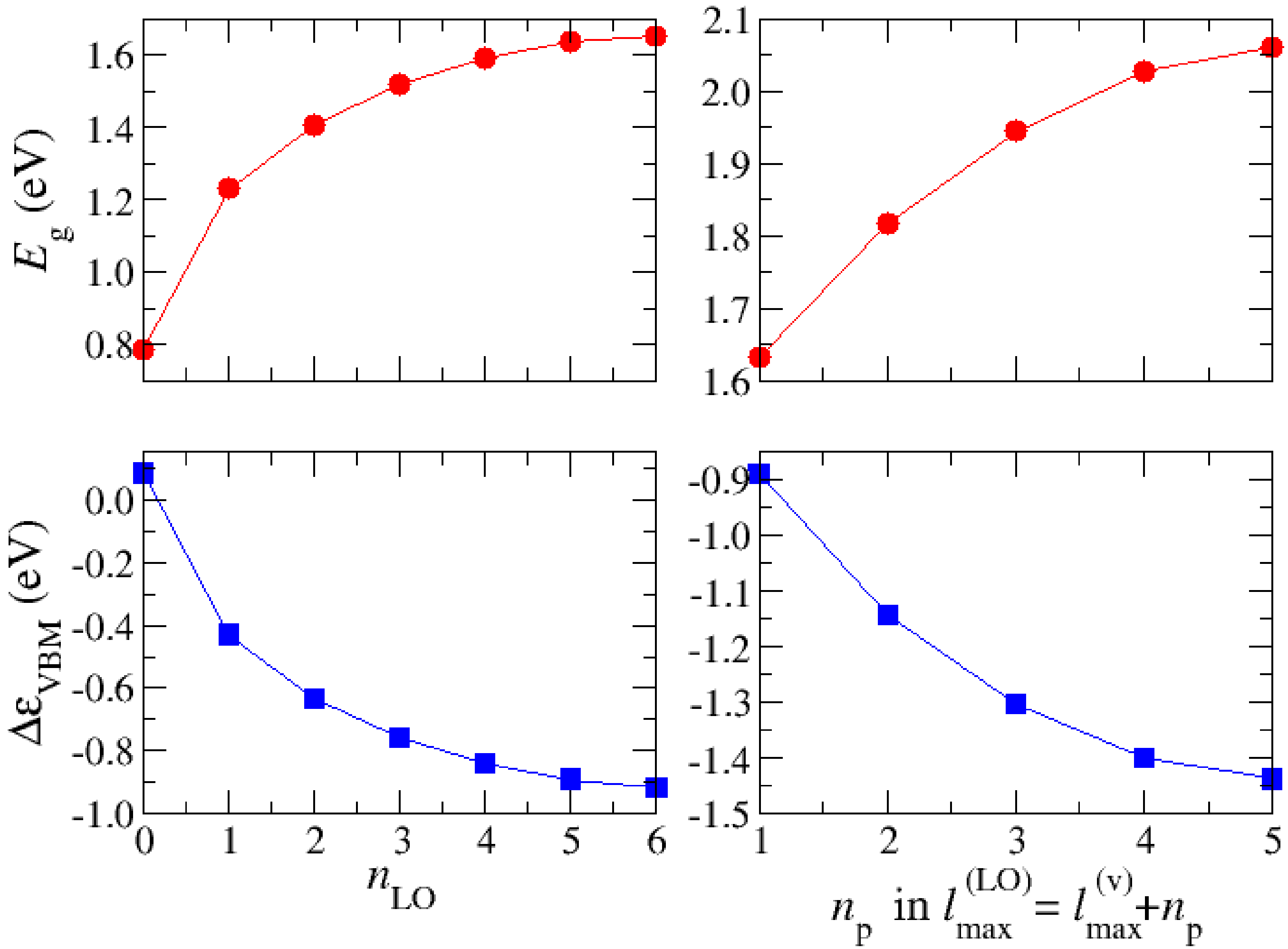
GW@LDA+*U* for *f*-electron systems: UO_2



H. Jiang (unpublished)

Effects of HLOs: CuCl



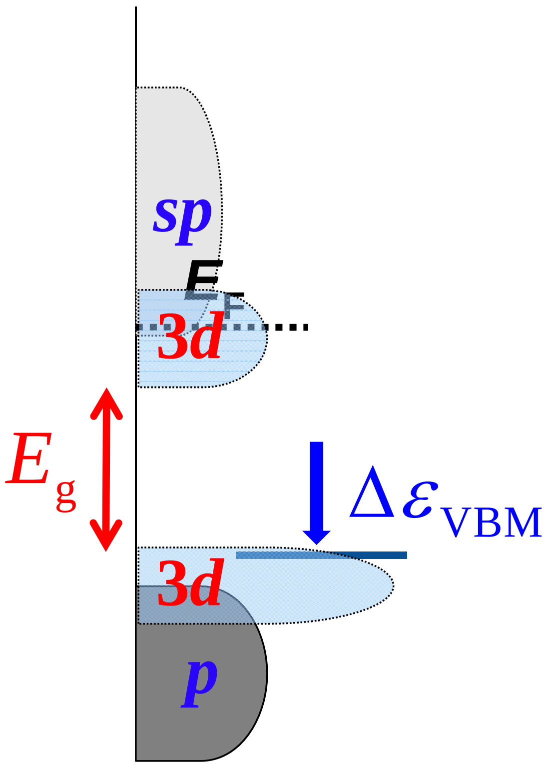


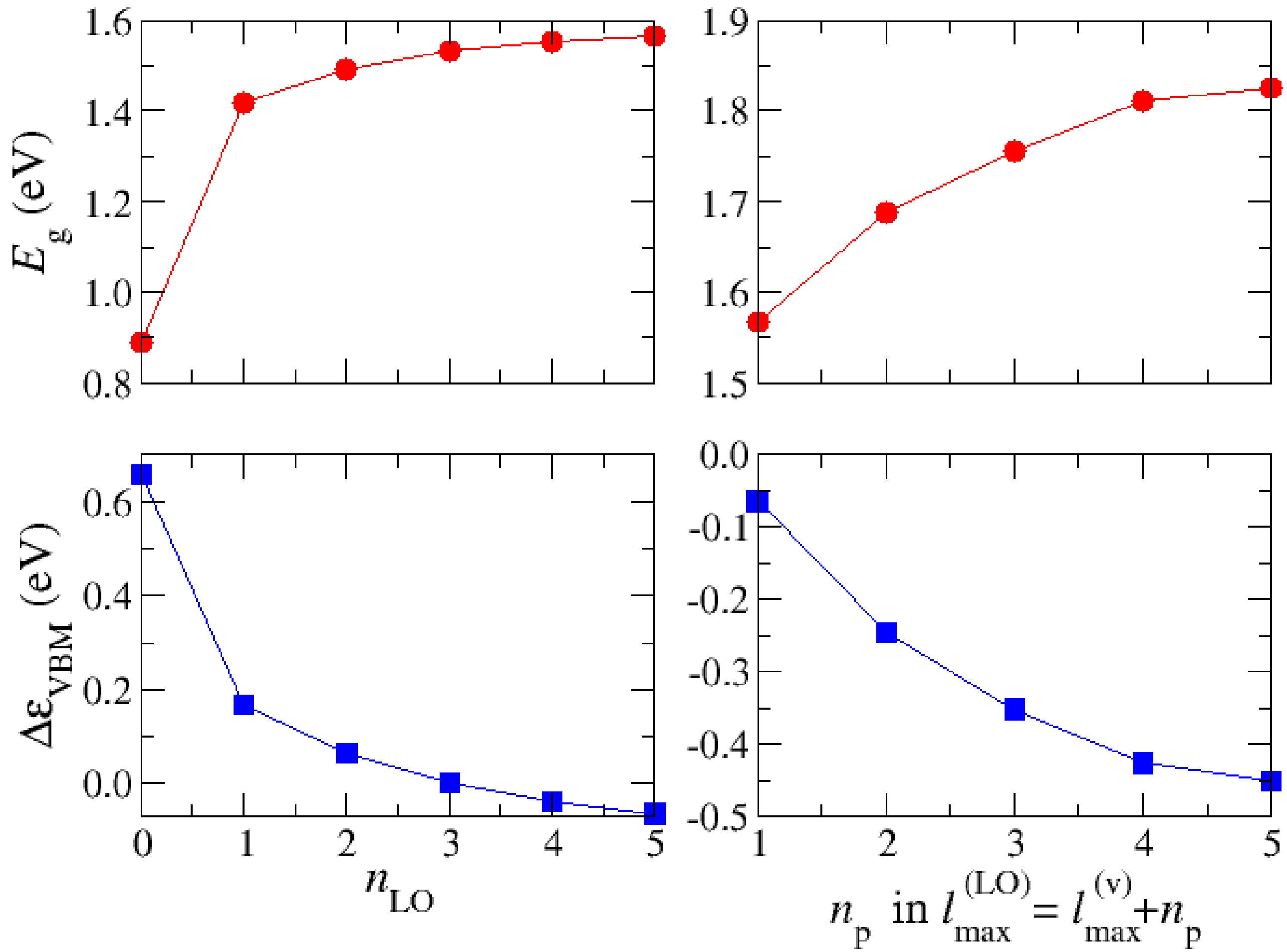
N_k=2x2x2

$l_{max}^{(LO)} = 3$

$n_{LO} = 5$

Effects of HLOs: FeS_2



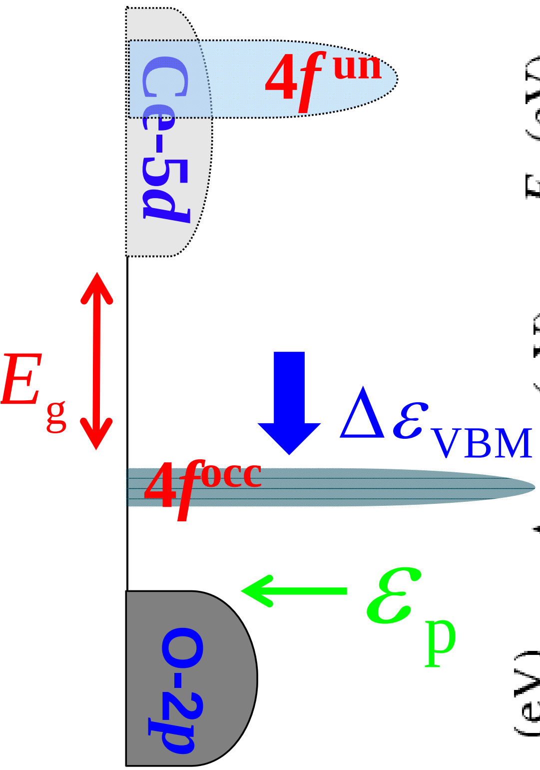


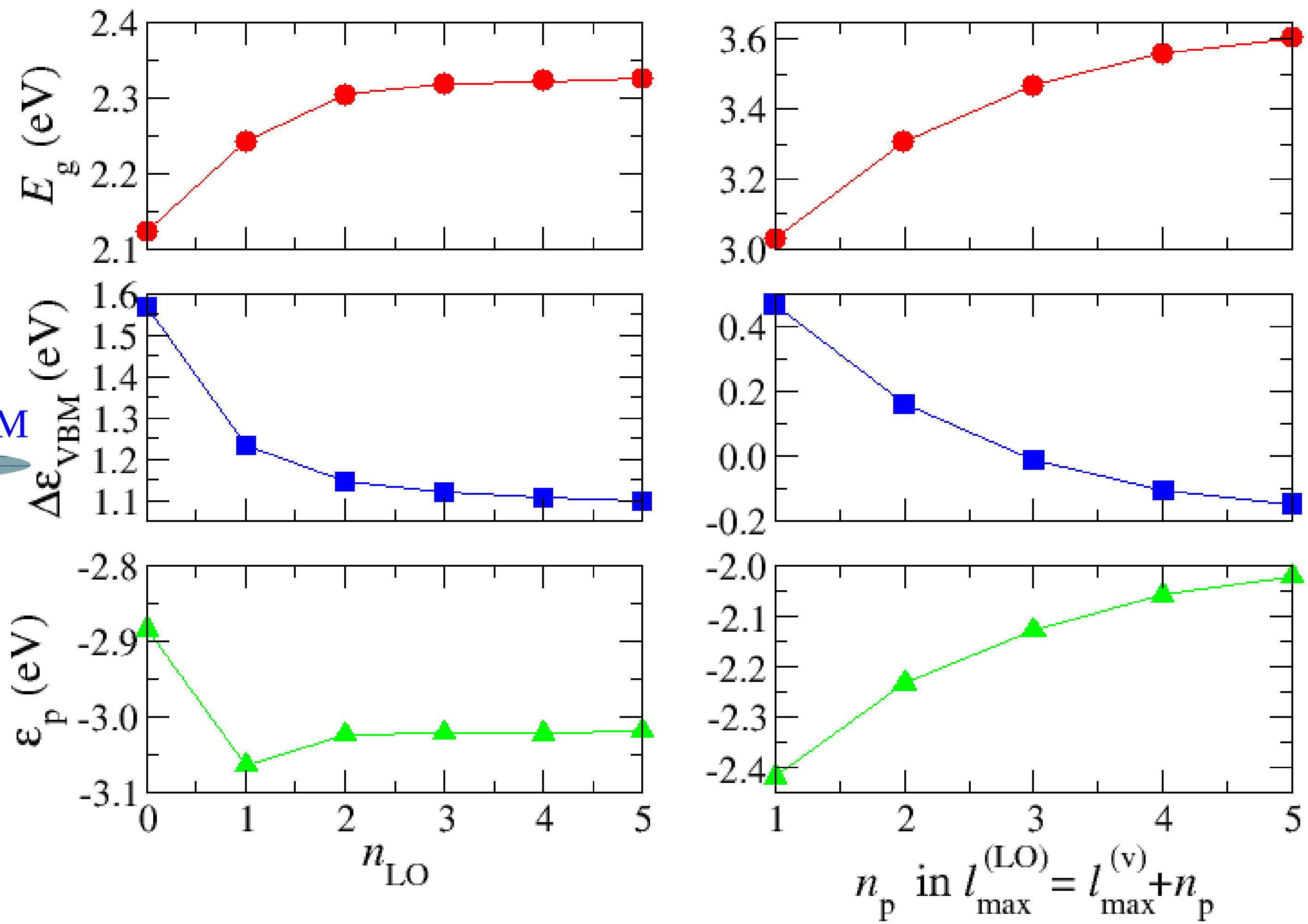
FeS_2 in the marcasite structure, N_k=2x1x2

$l_{max}^{(LO)} = 3$

$n_{LO} = 5$

Effects of HLOs: Ce_2O_3





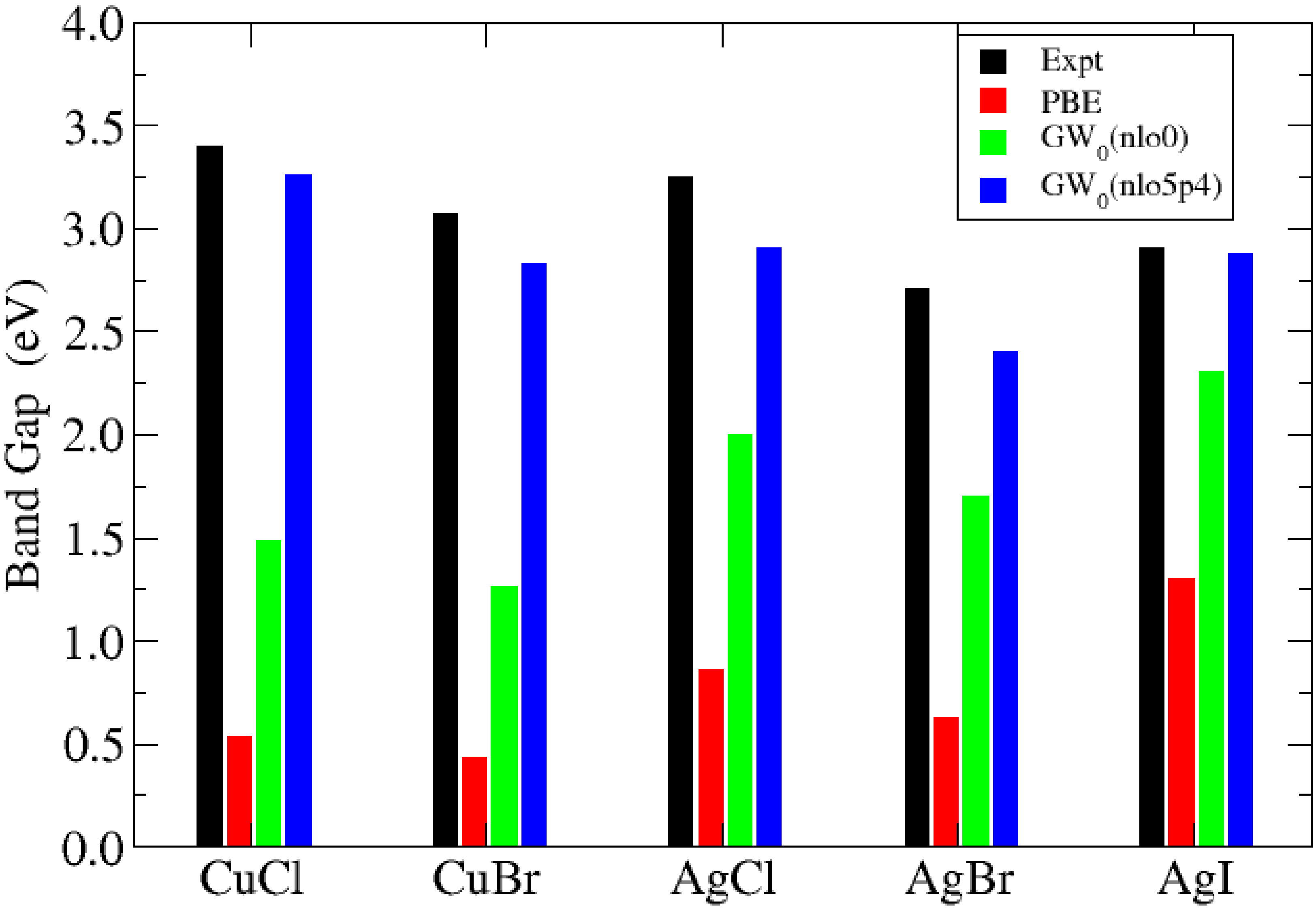
$l_{max}^{(LO)} = 3$

$n_{LO} = 5$

G_0W_0@LDA+U (6.8 eV)

N_k=2x2x1

Effects of HLOs: Ib-VII semiconductors



(N_k=4x4x4, using experimental lattice constants)

Concluding remarks

- Numerically accurate *GW* results are not easy to obtain, especially for some systems (ZnO).
- Both the accuracy and completeness of unoccupied states are important.
- The effects of including HLOs are **more dramatic** for *d*- and *f*-electron systems, and the energy position of occupied *f*-states are greatly improve.
- *GW* based on LAPW+HLOs can be used to as the benchmark

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