



NOVEL - MATERIALS  
DISCOVERY LABORATORY



FRIITZ-HABER-INSTITUT  
MAX-PLANCK-GESELLSCHAFT



# $G_0W_0$ Benchmark for Zirconium Dioxide in FHI-aims

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# Introduction

## ZrO<sub>2</sub> Applications

- Dies for hot metal extrusion
- Oxygen sensors
- Tooth crowns
- Deep well valve seats
- Marine pump seals
- Thermal-barrier coatings of turbines
- Solid oxide in fuel cells

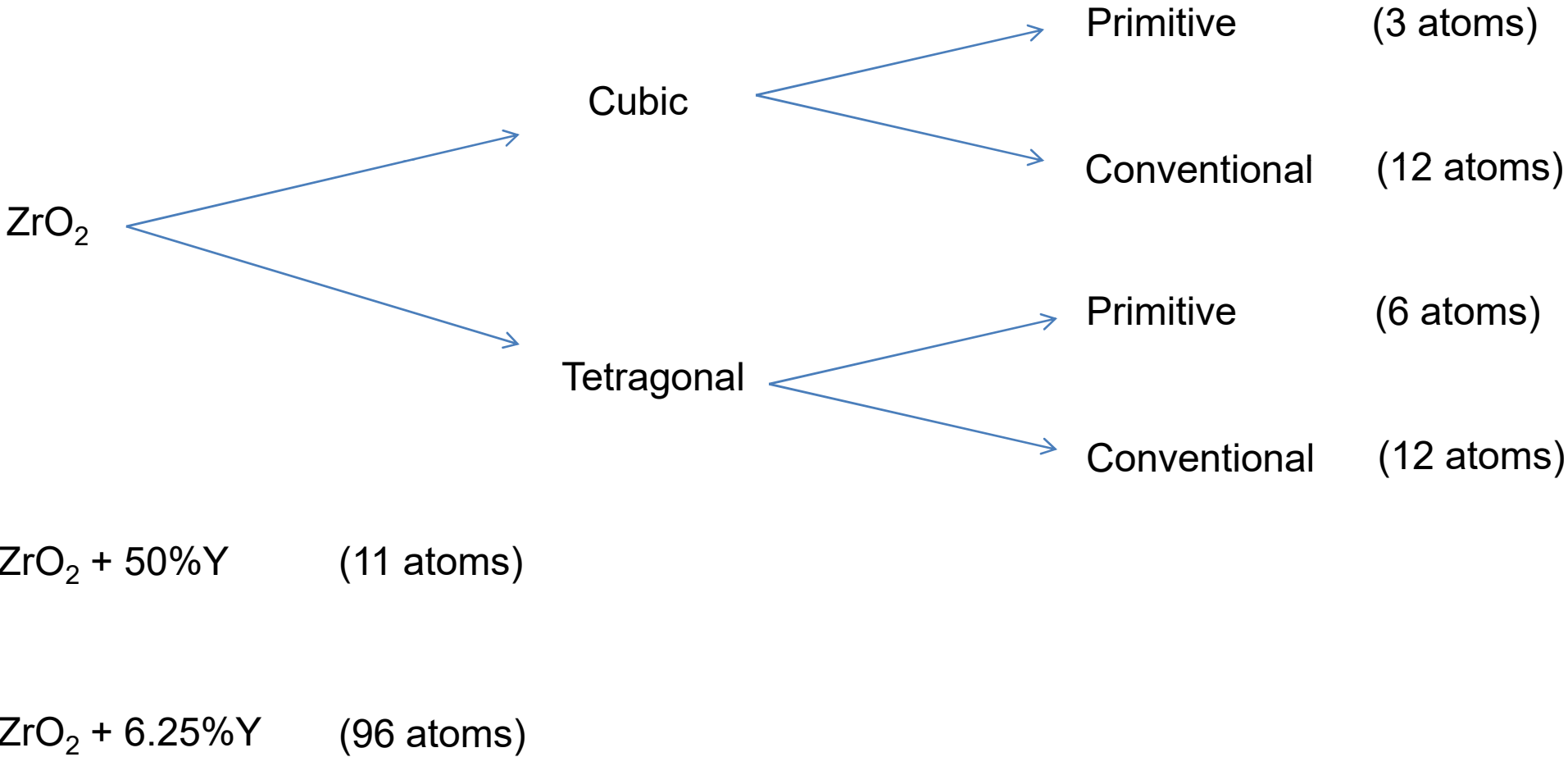
Phase transformation from monoclinic to tetragonal and then cubic

## Y-Stabilized Zirconia

- Thermal-barrier coatings of turbines (about 8% of Zr is replaced by Y)
- Solid oxide membrane in fuel cells (more than 16% of Zr is replaced by Y)

Vacancy formation and local distortion

# Structures



## $G_0W_0$ Implementation in FHI-aims

# $G_0W_0$ Implementation in Real Space

$$\Sigma_{\sigma}^{G_0W_0}(\mathbf{r}, \mathbf{r}', i\omega) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' G_{0,\sigma}(\mathbf{r}, \mathbf{r}', i\omega - i\omega') W_0(\mathbf{r}, \mathbf{r}', i\omega')$$

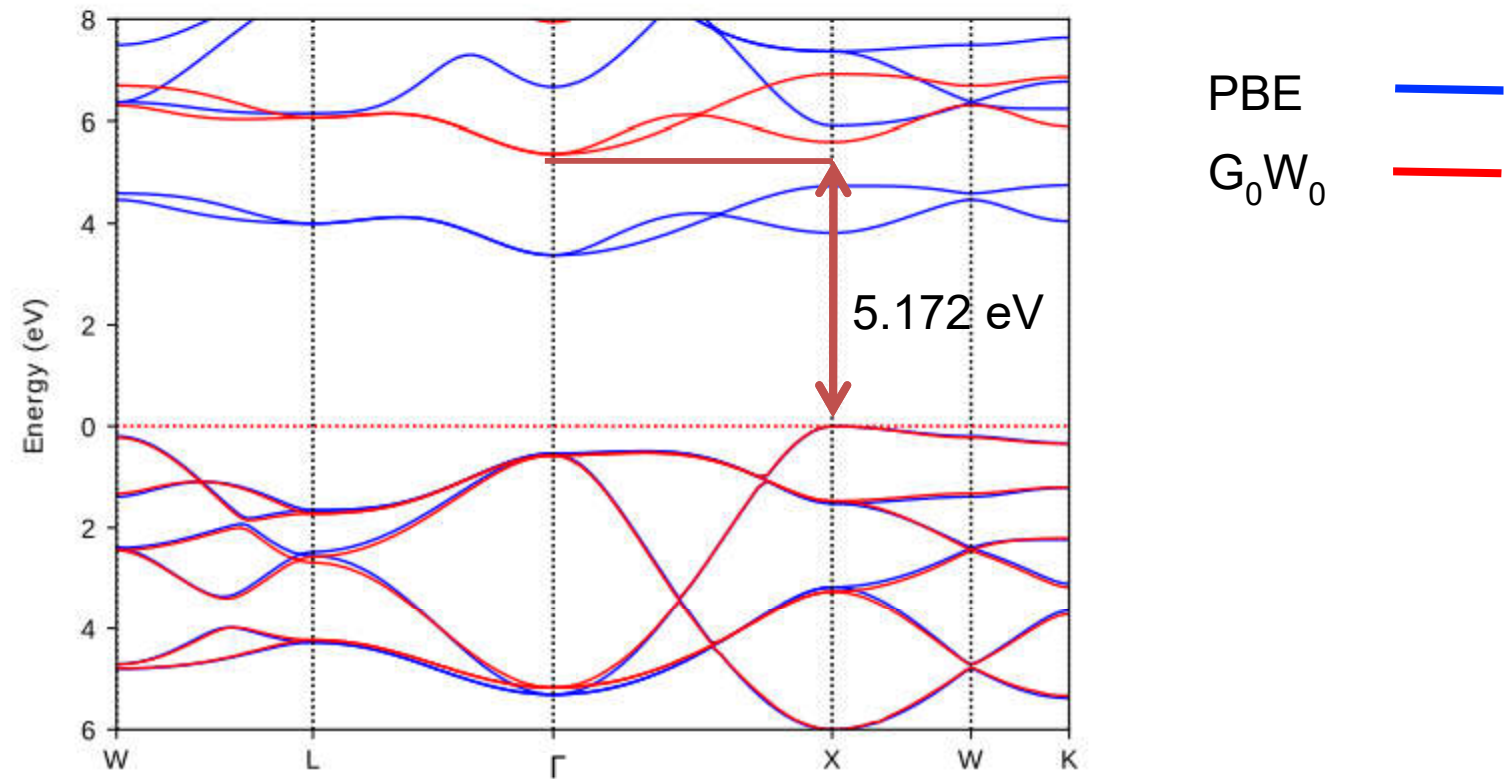
$$G_{0,\sigma}(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{n,\mathbf{k}} w_{\mathbf{k}} \frac{\psi_{n,\sigma}^{\mathbf{k}}(\mathbf{r}) \psi_{n,\sigma}^{\mathbf{k}*}(\mathbf{r}')}{i\omega + \mu - \epsilon_{n,\sigma}^{\mathbf{k}}}$$

$$W_0(\mathbf{r}, \mathbf{r}', i\omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', i\omega) v(\mathbf{r}'', \mathbf{r}')$$

$$\varepsilon(\mathbf{r}, \mathbf{r}', i\omega) = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \chi_0(\mathbf{r}'', \mathbf{r}', i\omega)$$

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{m,n,\sigma} \sum_{\mathbf{k}, \mathbf{q}}^{\text{1BZ}} w_{\mathbf{k}} w_{\mathbf{q}} \frac{(f_{m,\sigma}^{\mathbf{k}+\mathbf{q}} - f_{n,\sigma}^{\mathbf{q}}) \psi_{m,\sigma}^{\mathbf{k}+\mathbf{q}*}(\mathbf{r}) \psi_{n,\sigma}^{\mathbf{k}}(\mathbf{r}) \psi_{n,\sigma}^{\mathbf{k}*}(\mathbf{r}') \psi_{m,\sigma}^{\mathbf{k}+\mathbf{q}}(\mathbf{r}')}{\epsilon_{m,\sigma}^{\mathbf{k}+\mathbf{q}} - \epsilon_{n,\sigma}^{\mathbf{k}} - i\omega}$$

# Cubic Primitive Cell: PBE band-structure vs $G_0W_0$



How to obtain the  $G_0W_0$  band gap ...

# Convergence Test

# Convergence Test

Frequency Mesh Grid

$$\Sigma_{\sigma}^{G_0 W_0}(\mathbf{r}, \mathbf{r}', i\omega) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' G_{0,\sigma}(\mathbf{r}, \mathbf{r}', i\omega - i\omega') W_0(\mathbf{r}, \mathbf{r}', i\omega')$$

One-electron Orbital Basis Sets

Auxiliary Basis Functions

k Mesh Grid

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{m,n,\sigma} \sum_{\mathbf{k},\mathbf{q}}^{1\text{BZ}} w_{\mathbf{k}} w_{\mathbf{q}} \frac{(f_{m,\sigma}^{\mathbf{k}+\mathbf{q}} - f_{n,\sigma}^{\mathbf{q}}) \psi_{m,\sigma}^{\mathbf{k}+\mathbf{q}*}(\mathbf{r}) \psi_{n,\sigma}^{\mathbf{k}}(\mathbf{r}) \psi_{n,\sigma}^{\mathbf{k}*}(\mathbf{r}') \psi_{m,\sigma}^{\mathbf{k}+\mathbf{q}}(\mathbf{r}')}{\epsilon_{m,\sigma}^{\mathbf{k}+\mathbf{q}} - \epsilon_{n,\sigma}^{\mathbf{k}} - i\omega}$$

# Convergence test with respect to one-electron orbital basis sets

## ❖ Basis Settings defined in FHI-aims

1. Very Light (tier1, tier2, tier3)
2. Light (tier1, tier2, tier3)
3. Tight (tier1, tier2, tier3)
4. Really Tight (tier1, tier2, tier3)

➤ The list of radial functions and their angular momenta

➤ The number of points per radial shell near the nucleus

➤ The maximum number of angular grid points used outside a given radius

✓ The key physical choice to ensure converged results in FHI-aims

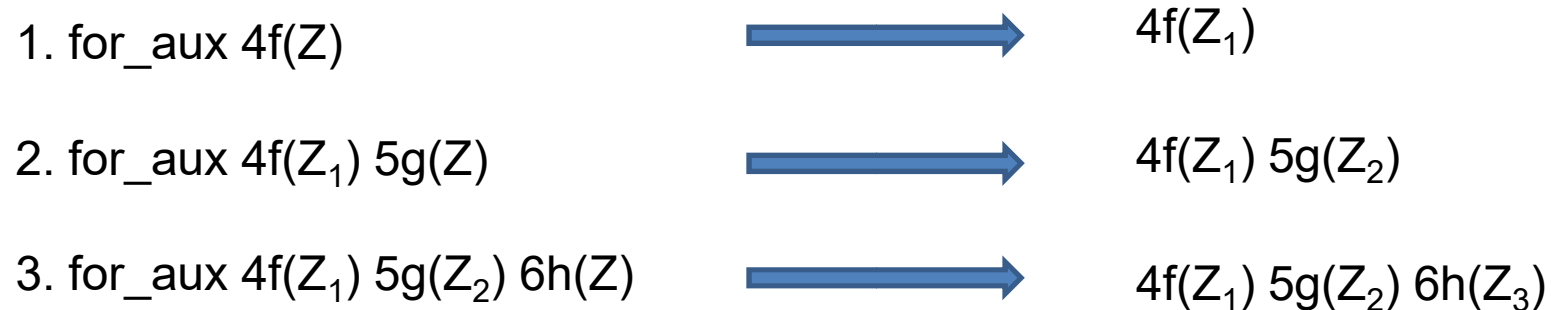
# Convergence test with respect to the auxiliary basis functions

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_i(r) + V_{\text{cut}}(r) \right] u_i(r) = \epsilon_i u_i(r)$$

❖ OBS: the standard Orbital Basis Set

❖ OBS+: an enhanced OBS with additional functions used only for auxiliary basis functions

➤ Hydrogen-like function, generated with an effective potential  $\frac{Z}{r}$



# Convergence test with respect to the number of frequency points

frequency\_points = 20, 40, ...

# Convergence test with respect to k-points

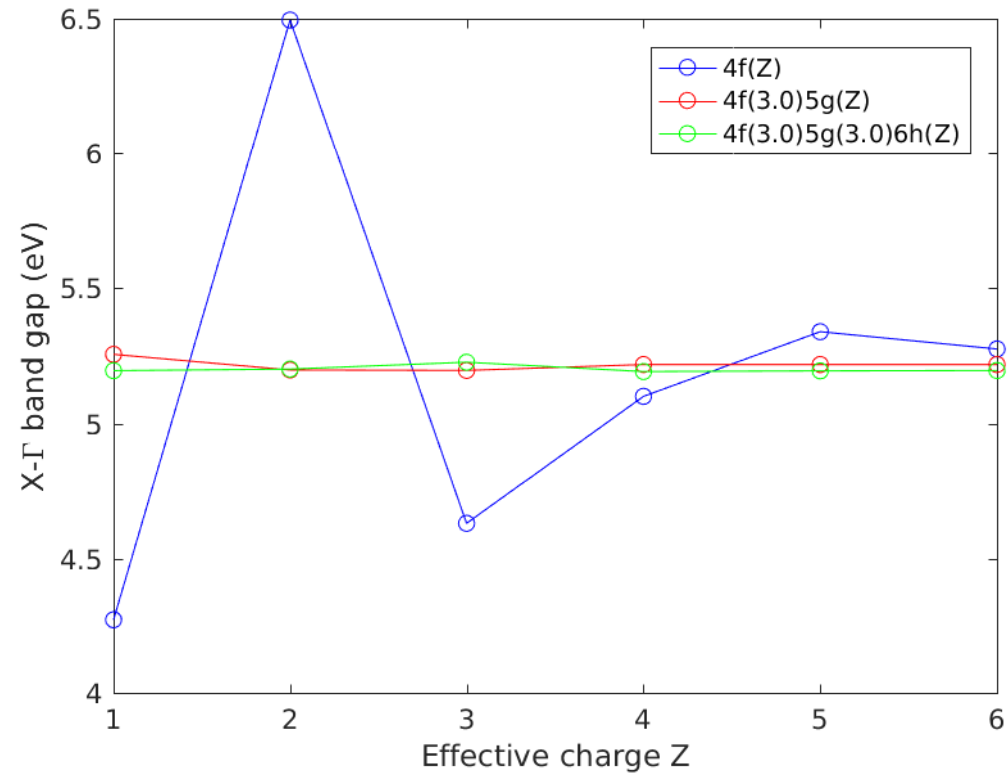
- 4x4x4
- 6x6x6
- 8x8x8



# $G_0W_0@PBEsol$ (Really-Tight)

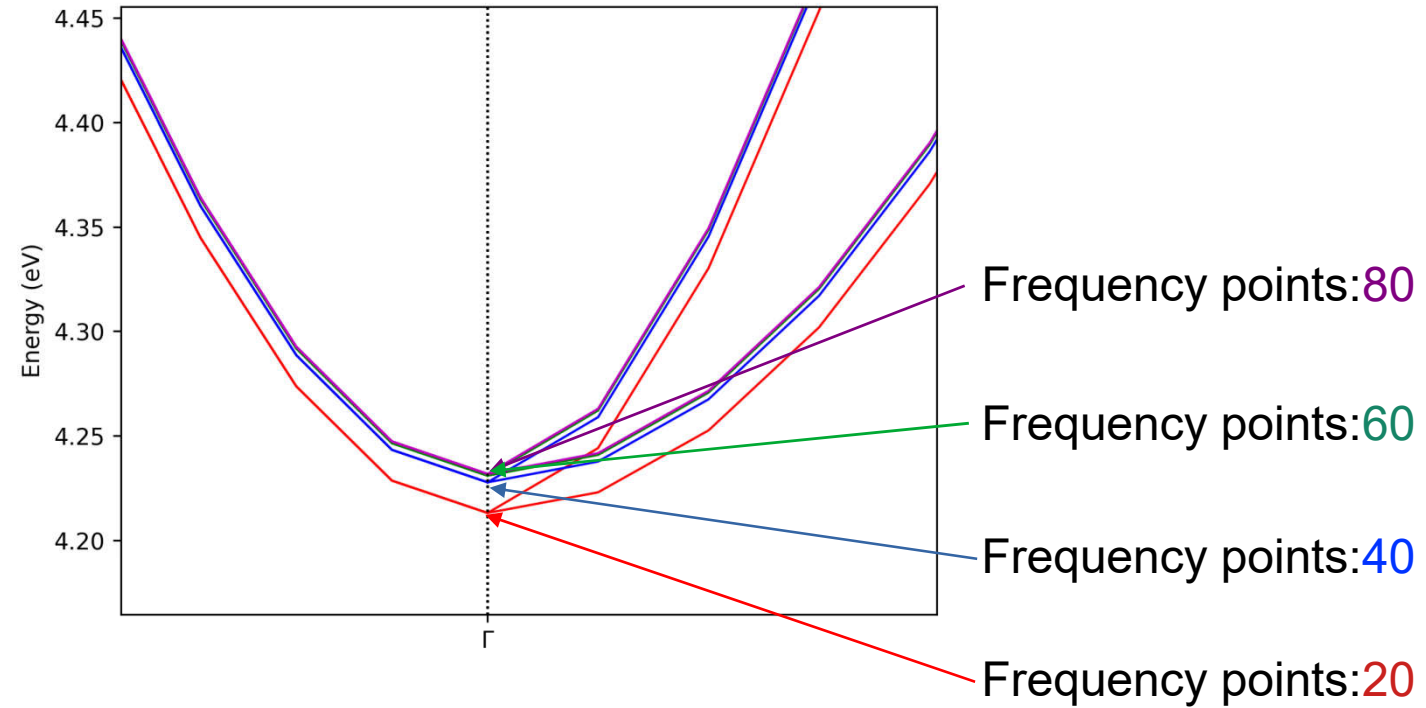
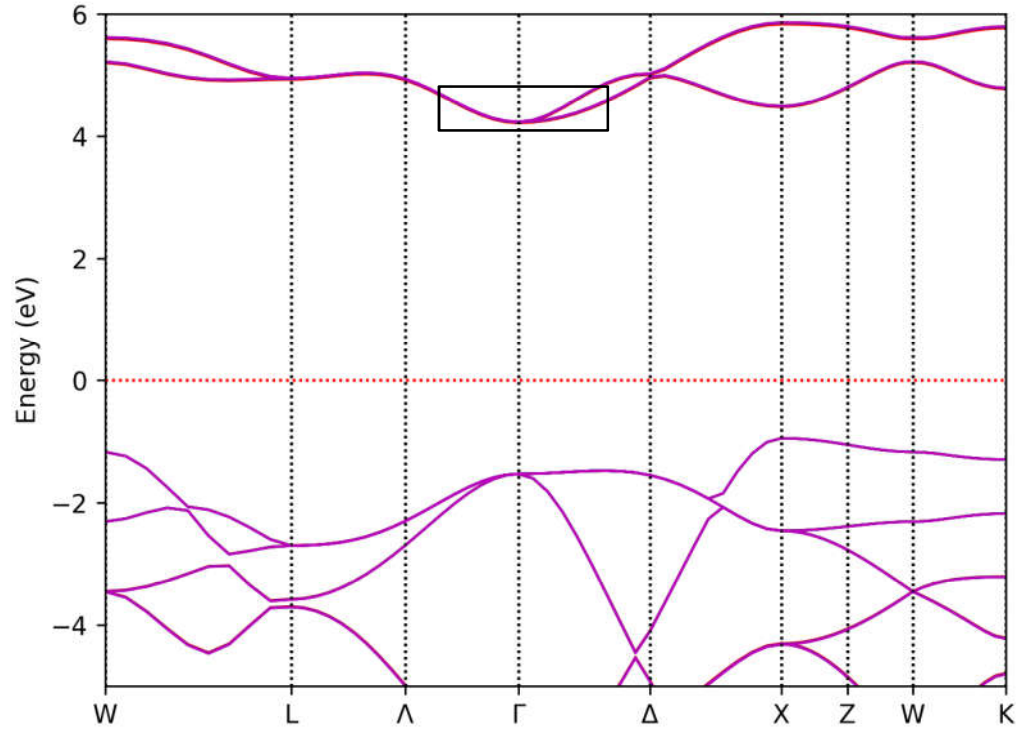
k grid	Tier	frq points	aux	$\Gamma$ -X	$\Gamma$ - $\Gamma$	X-X
4x4x4	tier1	40	f3g3	5.18369	5.77602	5.43794
4x4x4	tier1	40	noaux	5.1976	5.78617	5.44
4x4x4	tier1	60	f3g3	5.18732	5.78017	5.44209
4x4x4	tier1	60	noaux	5.20125	5.79036	5.44416
4x4x4	tier1	80	f3g3	5.1887	5.78165	5.44352
4x4x4	tier1	80	noaux	5.20265	5.79186	5.44562
6x6x6	tier1	20	f3g3	5.16427	5.74504	5.42454
6x6x6	tier1	40	f3g3	5.17678	5.75868	5.43738
6x6x6	tier1	60	f3g3	5.17967	5.76219	5.43996
6x6x6	tier1	80	f3g3	5.18044	5.76325	5.44045
6x6x6	tier2	40	f3g3	5.19464	5.76885	5.43026
6x6x6	tier2	40	noaux	5.08653	5.68558	5.11634
6x6x6	tier2	60	f3g3	5.19634	5.7711	5.43191
6x6x6	tier2	60	noaux	5.08806	5.68767	5.11777
6x6x6	tier2	80	f3g3	5.19689	5.77193	5.43224
6x6x6	tier2	80	noaux	5.0886	5.68848	5.11813
888	tier1	40	f3g3	5.15281	5.73921	5.42308

## Hydrogen-like Effective Charge

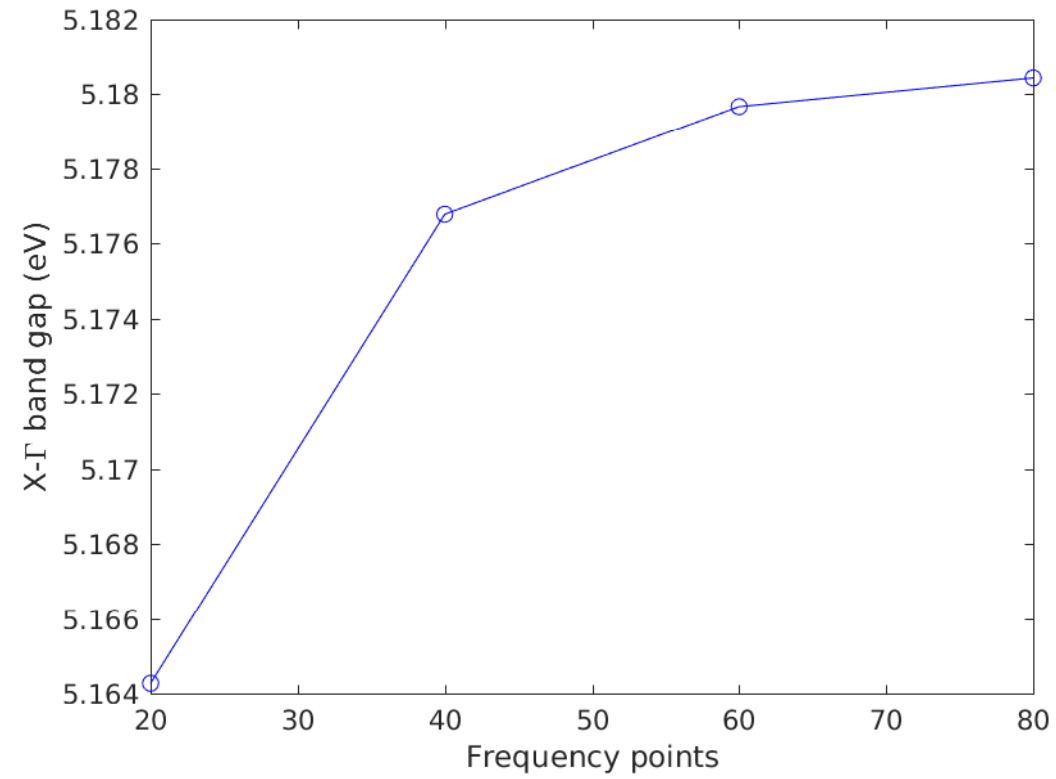


4f(3.0)5g(3.0) is selected to continue the calculations

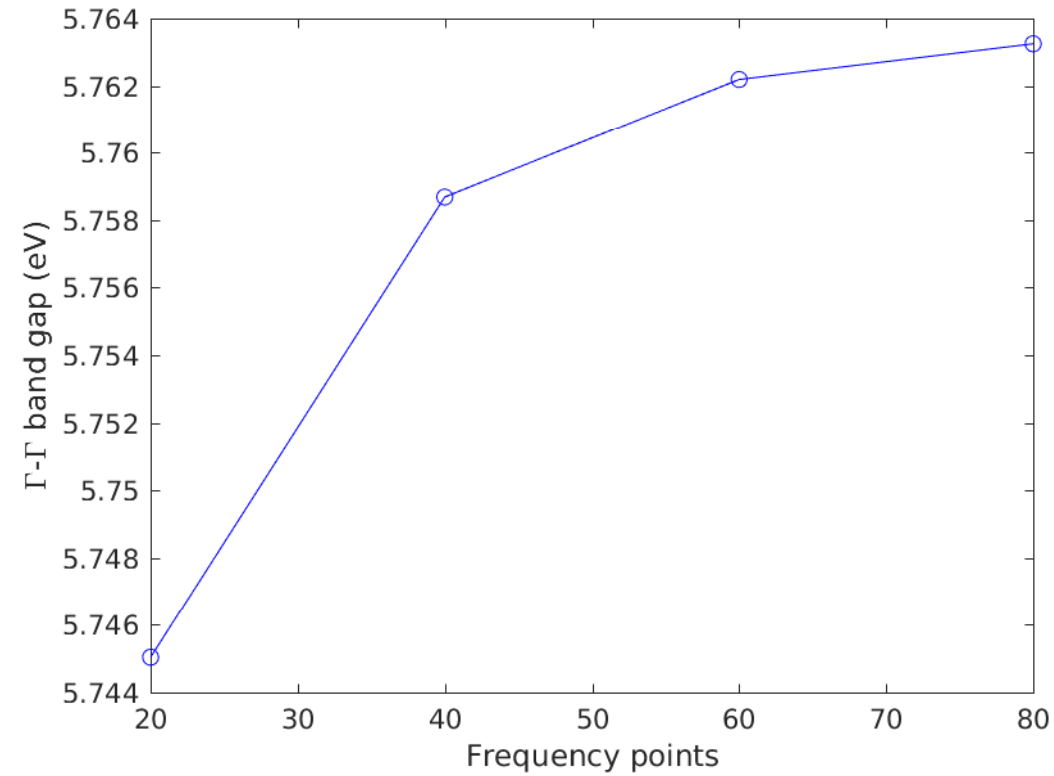
# $G_0W_0@PBEsol$ (6x6x6 Really-Tight:tier1)



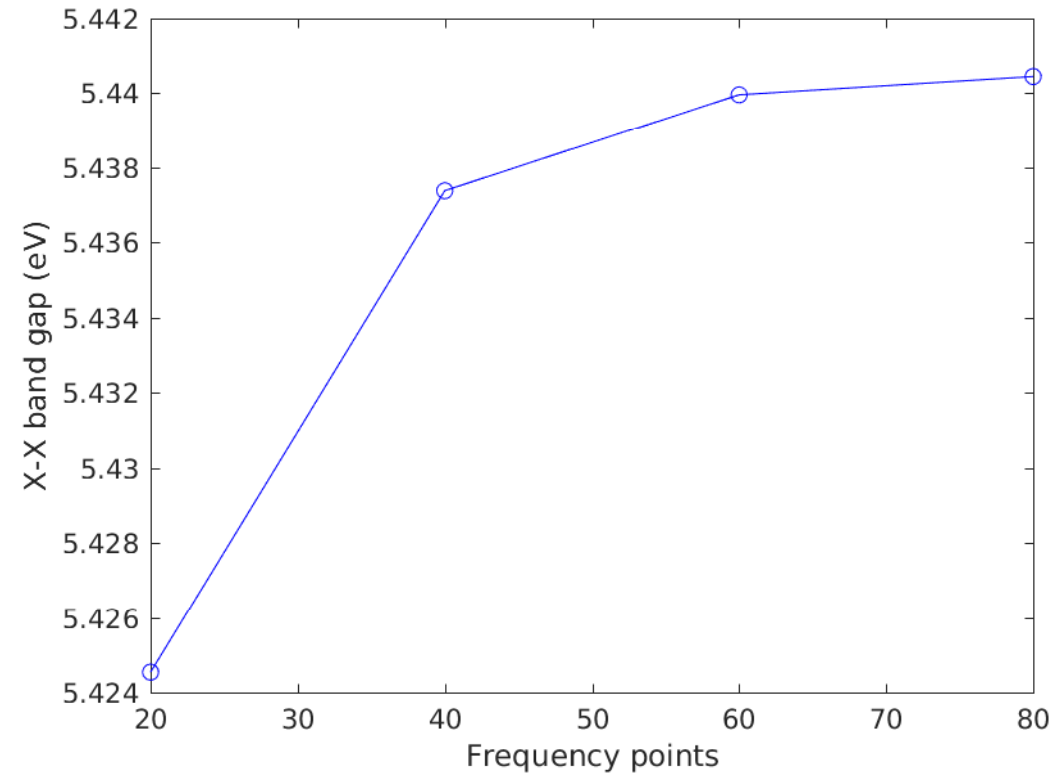
# $G_0W_0$ @PBEsol (6x6x6 Really-Tight:tier1)



# $G_0W_0$ @PBEsol (6x6x6 Really-Tight:tier1)

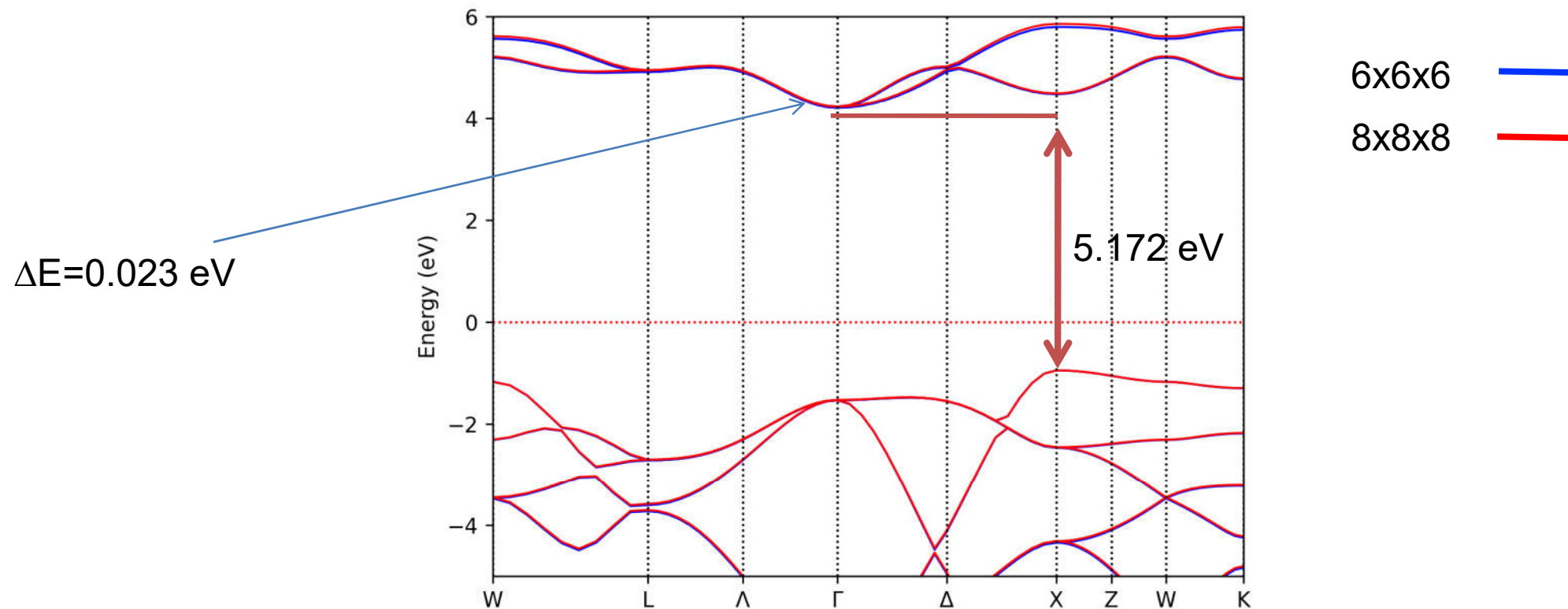


# $G_0W_0@PBEsol$ (6x6x6 Really-Tight:tier1)



# $G_0W_0@PBEsol$ (6x6x6 Really-Tight:tier2)

## 6x6x6 vs 8x8x8

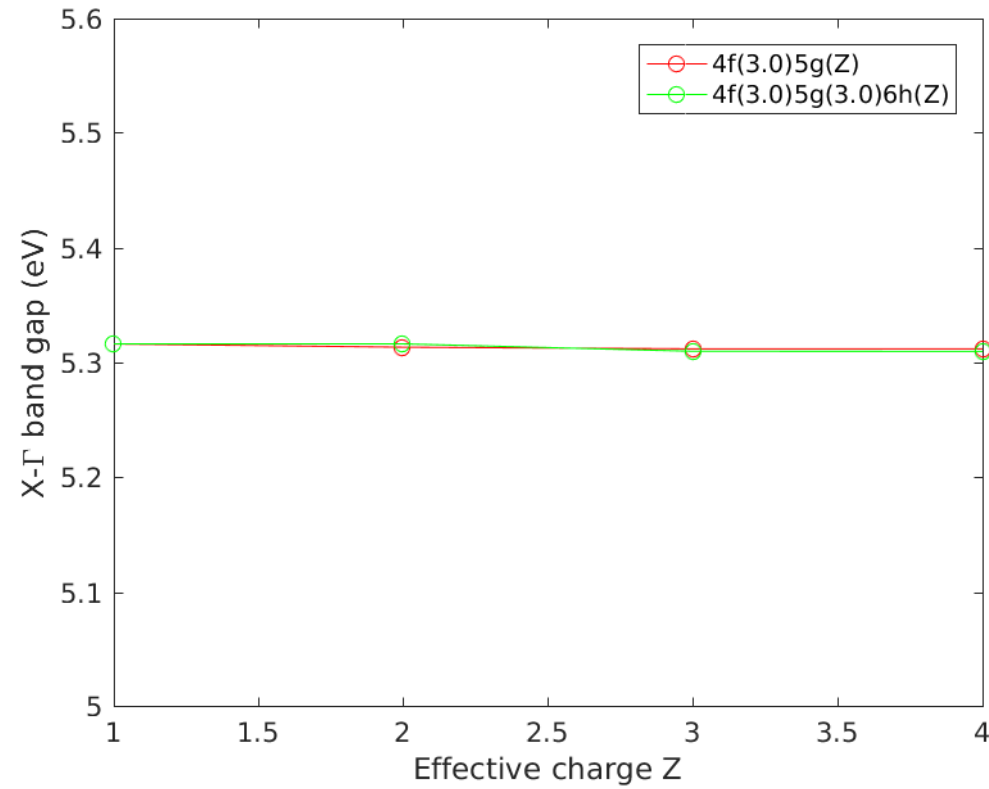


$G_0W_0@PBEsol$  (6x6x6 Tight:tier2)

Hydrogen-like Effective Charge

info	$\Gamma$ -X	$\Gamma$ - $\Gamma$	X-X
f1	5.64216	6.2376	5.84266
f3g1h0	5.31614	5.88284	5.51267
f3g2h0	5.31332	5.87983	5.50972
f3g3h0	5.31186	5.8782	5.50846
f3g3h1	5.31622	5.88298	5.51201
f3g3h3	5.30977	5.87621	5.50563
f3g3h4	5.30964	5.87599	5.50466

# $G_0W_0@PBEsol$ (Tight)

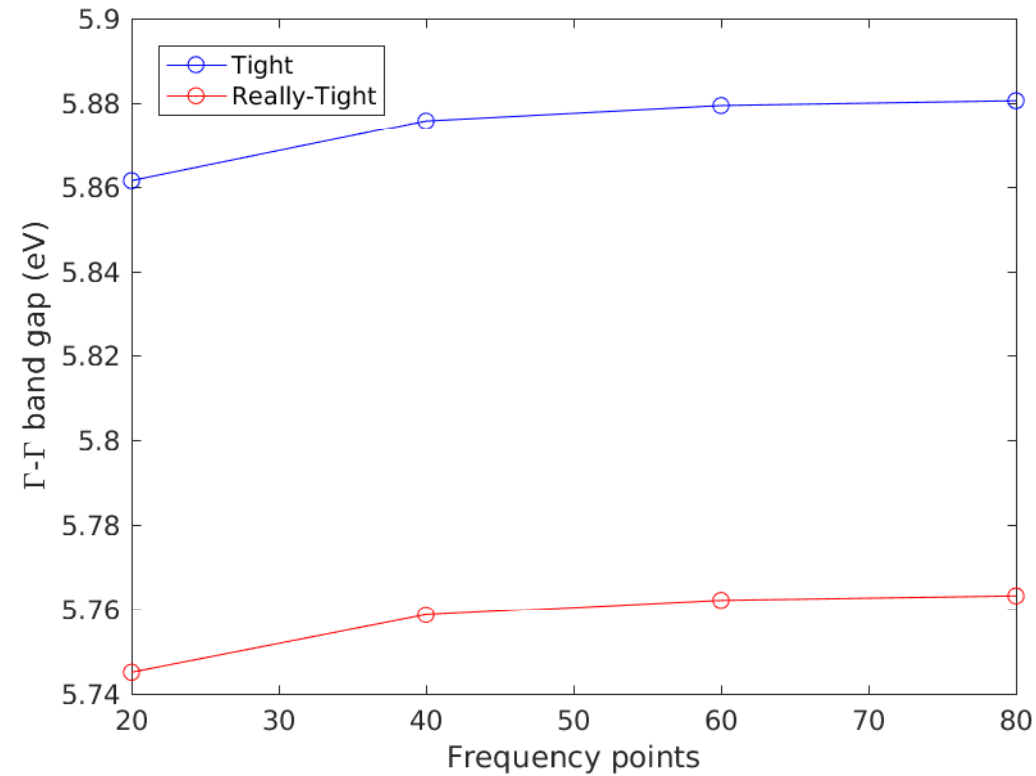


4f(3.0)5g(3.0) is selected to continue the calculations

# $G_0W_0@PBEsol$ (Tight vs. Really-Tight)

info	$\Gamma$ -X	$\Gamma$ - $\Gamma$	X-X
T1-666-f20	5.28792	5.8614	5.50718
T1-666-f40	5.30094	5.87569	5.52022
T1-666-f60	5.304	5.87939	5.5229
T1-666-f80	5.30484	5.88053	5.52343
T2-444-f60	5.53644	6.12444	5.73595
T2-666-f60	5.31372	5.88064	5.5101
T2-888-f60	5.29608	5.86441	5.50039
RT1-666-f20	5.16427	5.74504	5.42454
RT1-666-f40	5.17678	5.75868	5.43738
RT1-666-f60	5.17967	5.76219	5.43996
RT1-666-f80	5.18044	5.76325	5.44045
RT1-444-f40	5.18369	5.77602	5.43794
RT2-666-f40	5.19464	5.76885	5.43026
RT2-888-f40	5.17174	5.7451	5.411

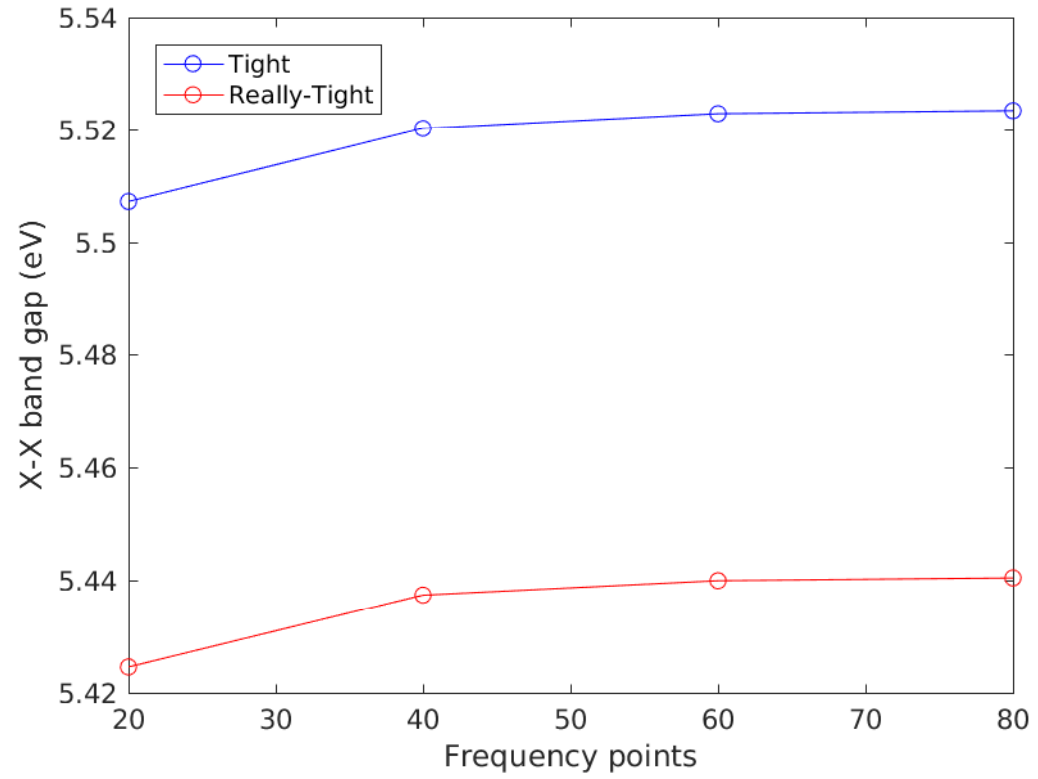
# $G_0W_0@PBEsol$ (Tight vs. Really-Tight)



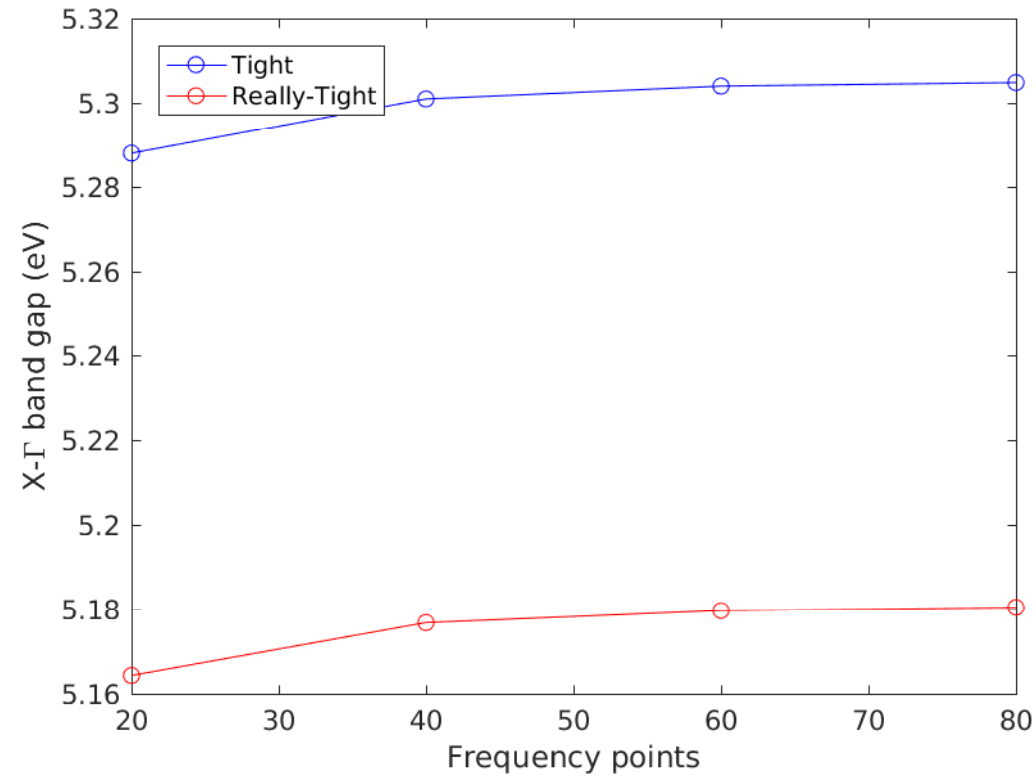
Abinit  $G_0W_0$  (plasmone pole)  $\Gamma$ - $\Gamma$  band gap = 5.461 (eV)

Abinit  $G_0W_0$  (contour deformation)  $\Gamma$ - $\Gamma$  band gap = 5.527 (eV)

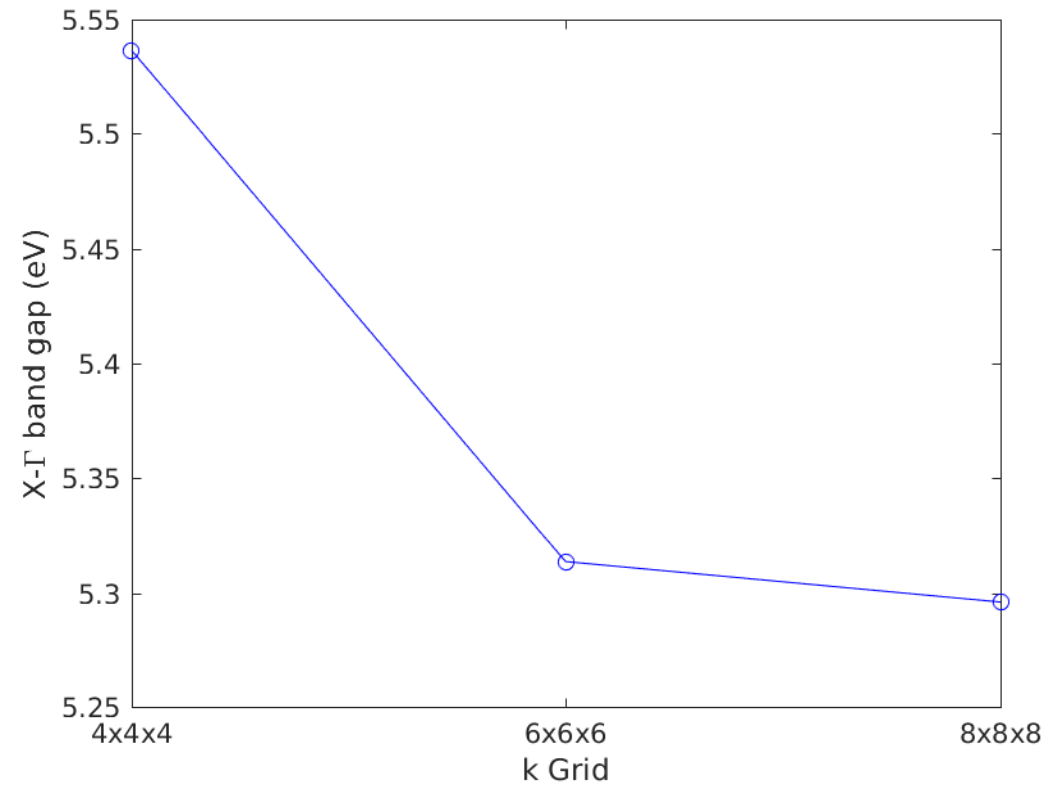
# $G_0W_0@PBEsol$ (Tight vs. Really-Tight)



# $G_0W_0@PBEsol$ (Tight vs. Really-Tight)



# $G_0W_0@PBEsol$ (Tight)

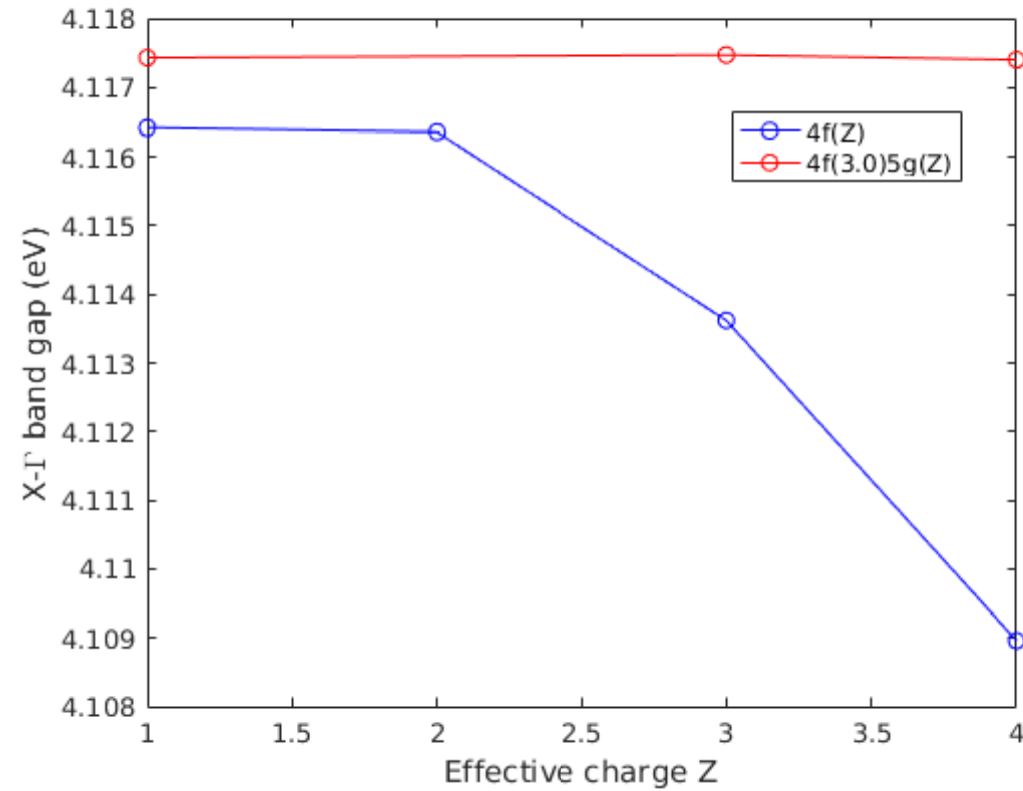




# Zr<sub>2</sub>O<sub>7</sub>Y<sub>2</sub>: G<sub>0</sub>W<sub>0</sub>@PBEsol (Hydrogen-like Effective Charge)

info	$\Gamma$ -X	$\Gamma$ - $\Gamma$	X-X
f1	4.11642	4.12516	4.74369
f2	4.11636	4.12511	4.74376
f3g1h0	4.11743	4.12616	4.7452
f3g3h0	4.11751	4.12624	4.74521
f3	4.11362	4.12244	4.74325
f4	4.10896	4.11774	4.73813

## Hydrogen-like Effective Charge

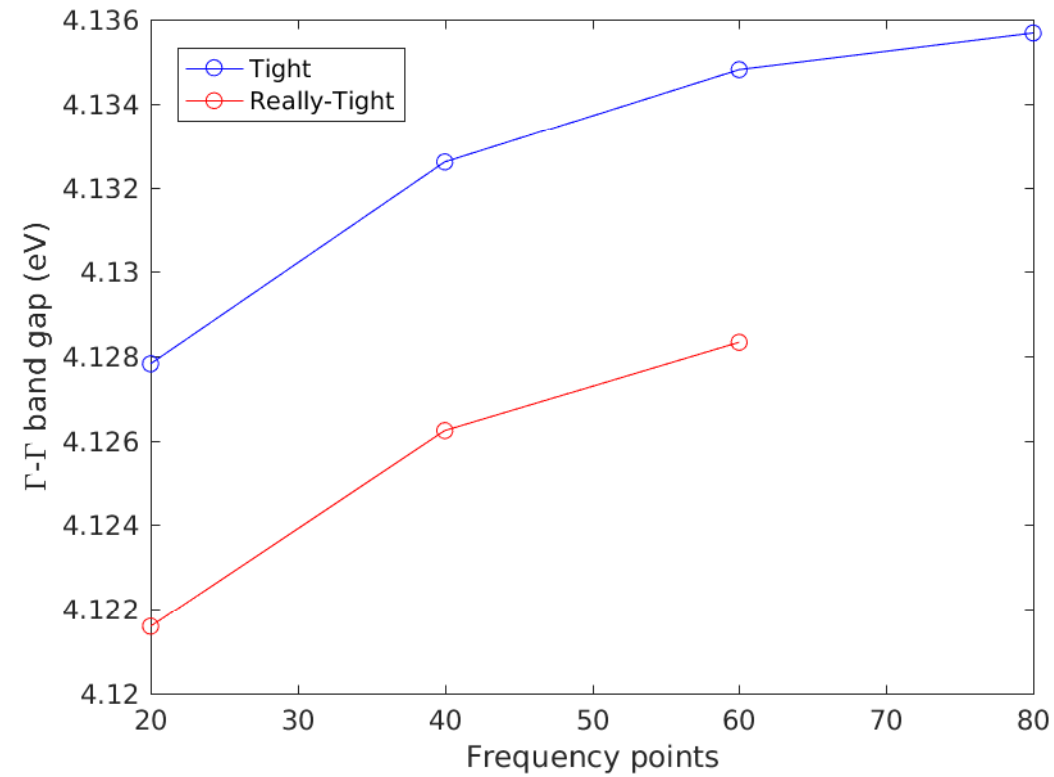


4f(3.0)5g(3.0) is selected to continue the calculations

# Zr<sub>2</sub>O<sub>7</sub>Y<sub>2</sub>: G<sub>0</sub>W<sub>0</sub>@PBEsol (Tight vs. Really-Tight)

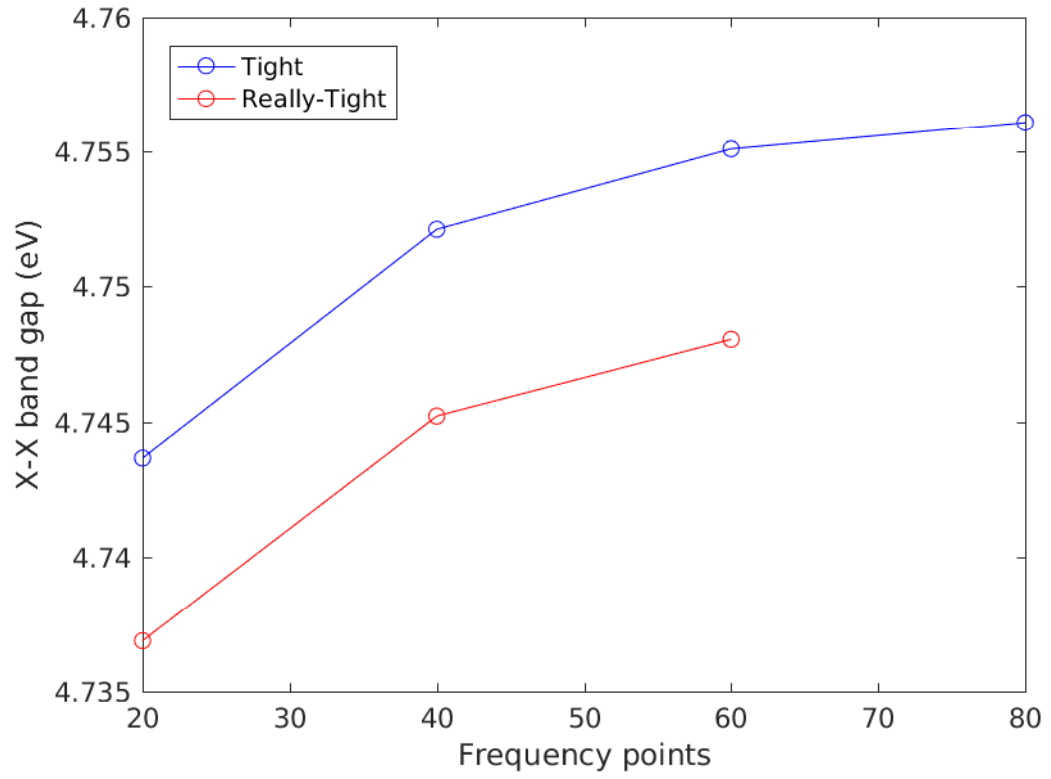
info	Γ-X	Γ-Γ	X-X
RT1-444-f20	4.11256	4.12159	4.73688
RT1-444-f40	4.11751	4.12624	4.74521
RT1-444-f60	4.11965	4.12833	4.74805
RT2-222-f60	5.09004	5.11868	5.86477
T1-444-f20	4.11954	4.12782	4.74366
T1-444-f40	4.12463	4.1326	4.75212
T1-444-f60	4.12689	4.13481	4.7551
T1-444-f80	4.12772	4.13568	4.75609

# Zr<sub>2</sub>O<sub>7</sub>Y<sub>2</sub>: G<sub>0</sub>W<sub>0</sub>@PBEsol (Tight vs. Really-Tight)

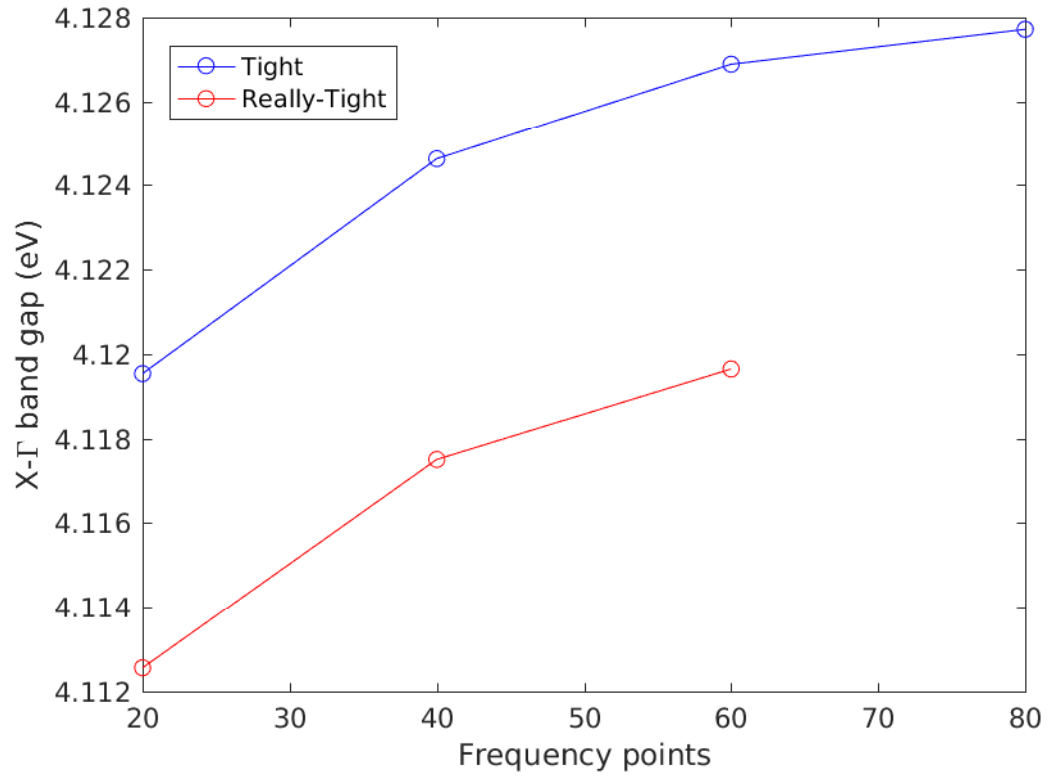


Abinit G<sub>0</sub>W<sub>0</sub> (plasmon pole)  $\Gamma$ - $\Gamma$  band gap = 4.020 (eV)

# Zr<sub>2</sub>O<sub>7</sub>Y<sub>2</sub>: G<sub>0</sub>W<sub>0</sub>@PBEsol (Tight vs. Really-Tight)



# Zr<sub>2</sub>O<sub>7</sub>Y<sub>2</sub>: G<sub>0</sub>W<sub>0</sub>@PBEsol (Tight vs. Really-Tight)



# Summary and ongoing calculations

- We could achieve  $\Delta E < 0.02$  eV according to the agreement between different groups
- We should continue our calculations for 50% Y stabilized Zirconium Oxide using Tier 2
- We are going to do scaling calculations to see the performance of the GW implementation

Thank you for your attention