Numerical Precision in the LAPW Method

Sven Lubeck, HU Berlin

APW+lo: energy derivative of order 1

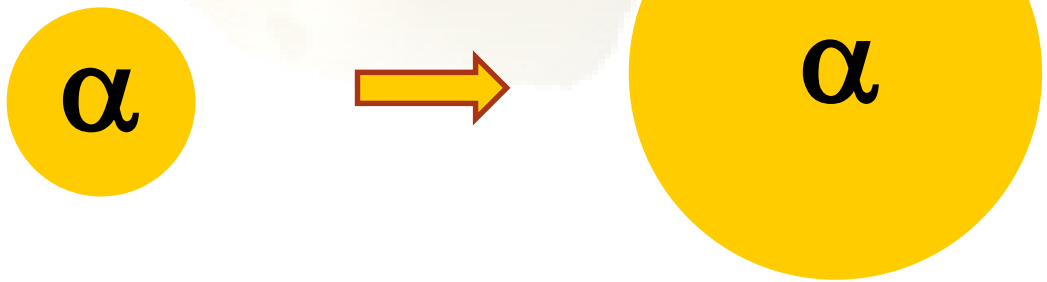
&

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} A^\alpha_{lm}(\mathbf{k}+\mathbf{G})\, u^\alpha_l(r, E_l)\, Y_{lm}(\hat{\mathbf{r}})$$

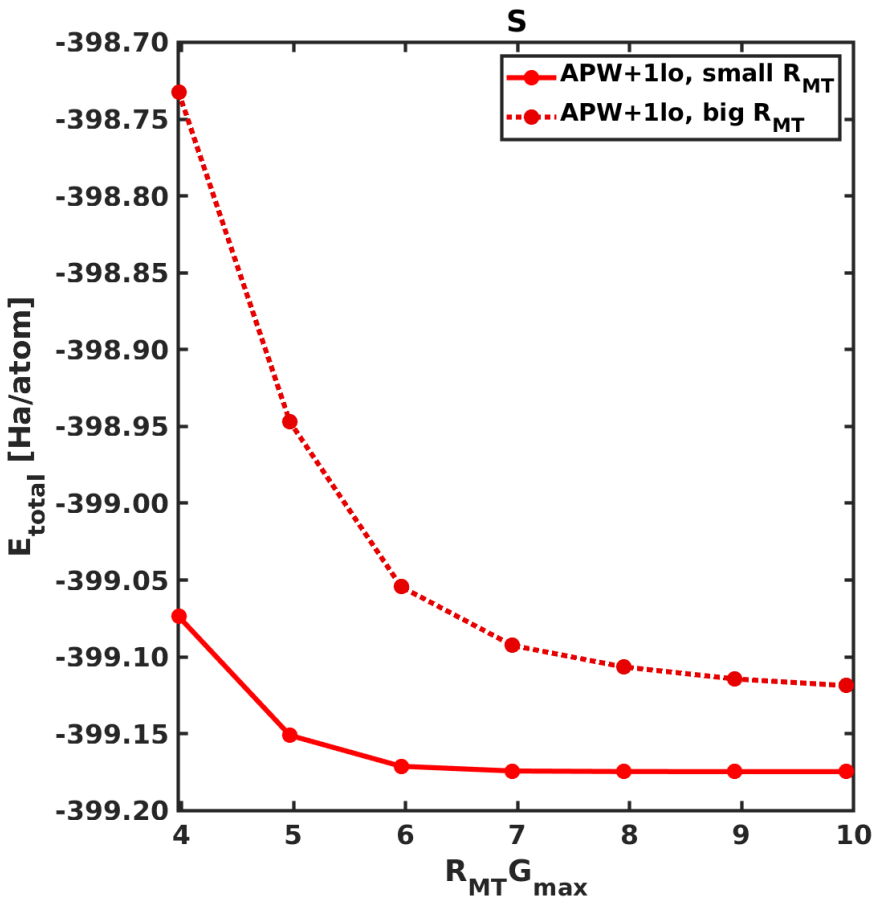
$$\phi^{lm}_{lo}(\mathbf{S}_\alpha + \mathbf{r}) = \left[\tilde{A}^\alpha_{lm} u^\alpha_l(r, E_l) + \tilde{C}^\alpha_{lm} \dot{u}^\alpha_l(r, E_l)\right] Y_{lm}(\hat{\mathbf{r}})$$

"APW+1lo"

Check quality of basis by changing muffin-tin radius

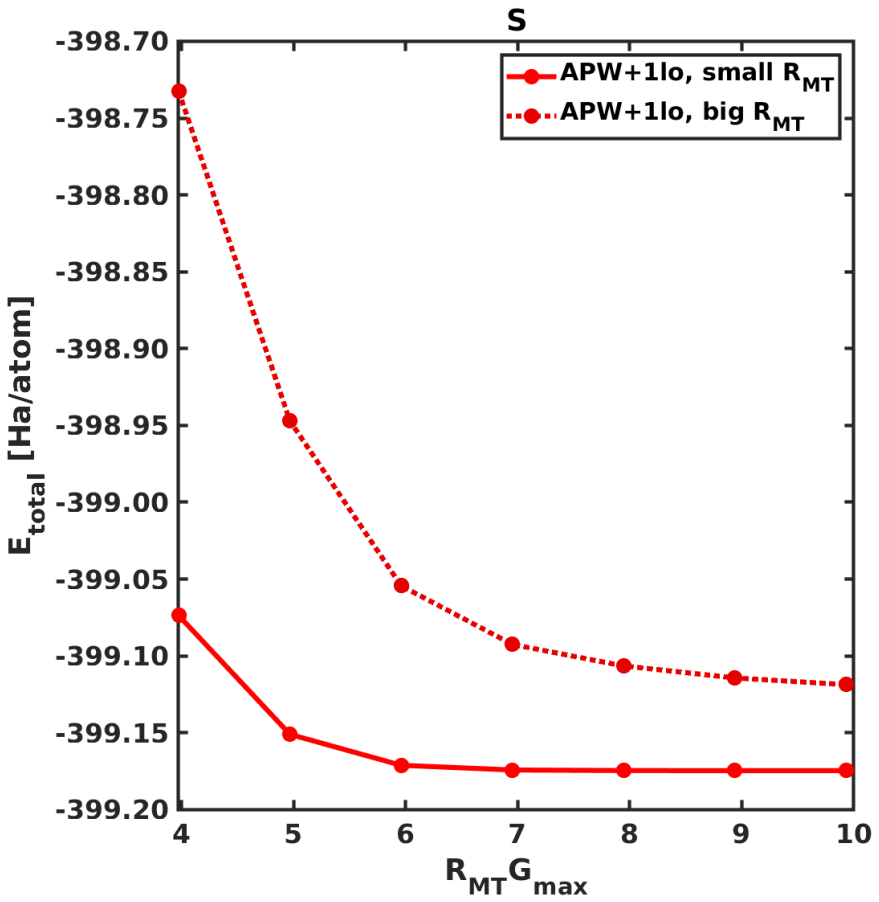


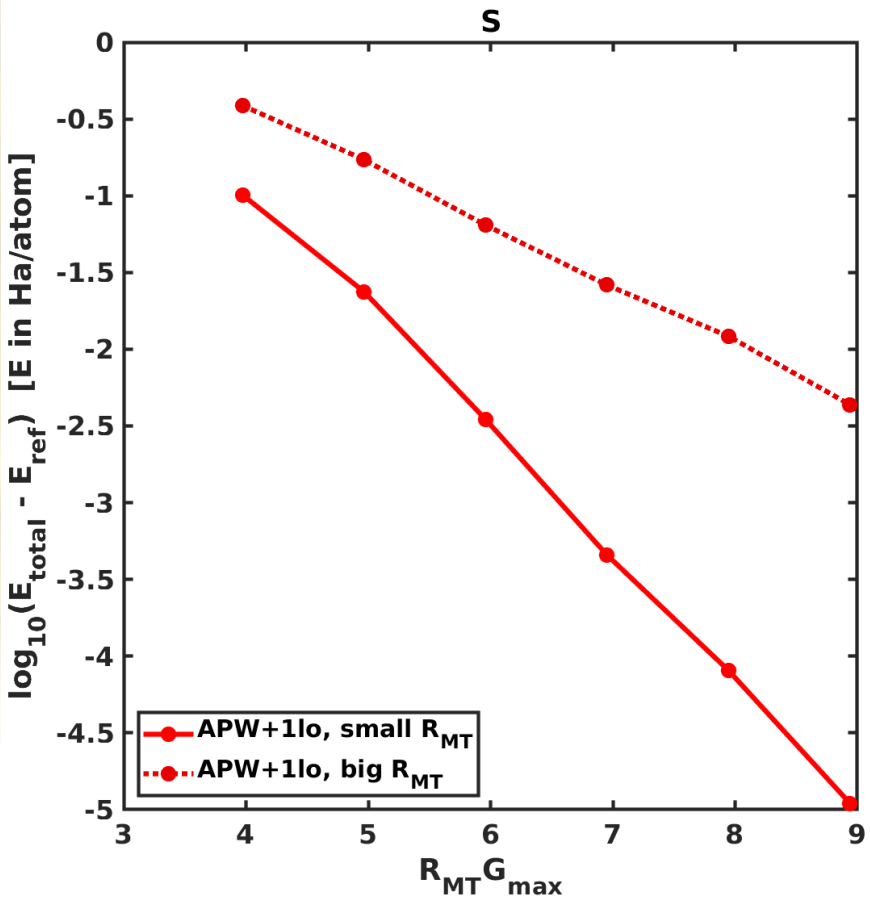
APW+lo: influence of muffin-tin radii



($R_{MT}G_{max} \equiv$ rgkmax)

APW+lo: influence of muffin-tin radii





APW+lo: energy derivative of order 1 & 2

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} A^\alpha_{lm}(\mathbf{k}+\mathbf{G})\, u^\alpha_l(r, E_l)\, Y_{lm}(\hat{\mathbf{r}})$$

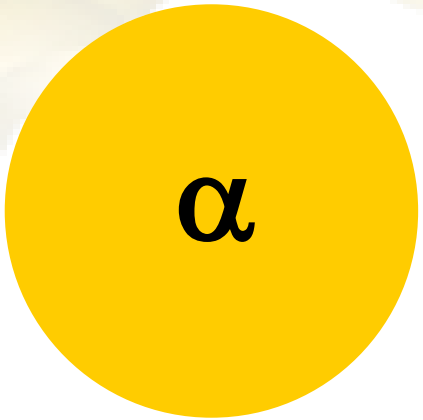
&

$$\phi^{lm}_{lo}(\mathbf{S}_\alpha + \mathbf{r}) = \left[\tilde{A}^\alpha_{lm} u^\alpha_l(r, E_l) + \tilde{C}^\alpha_{lm} \dot{u}^\alpha_l(r, E_l)\right] Y_{lm}(\hat{\mathbf{r}})$$

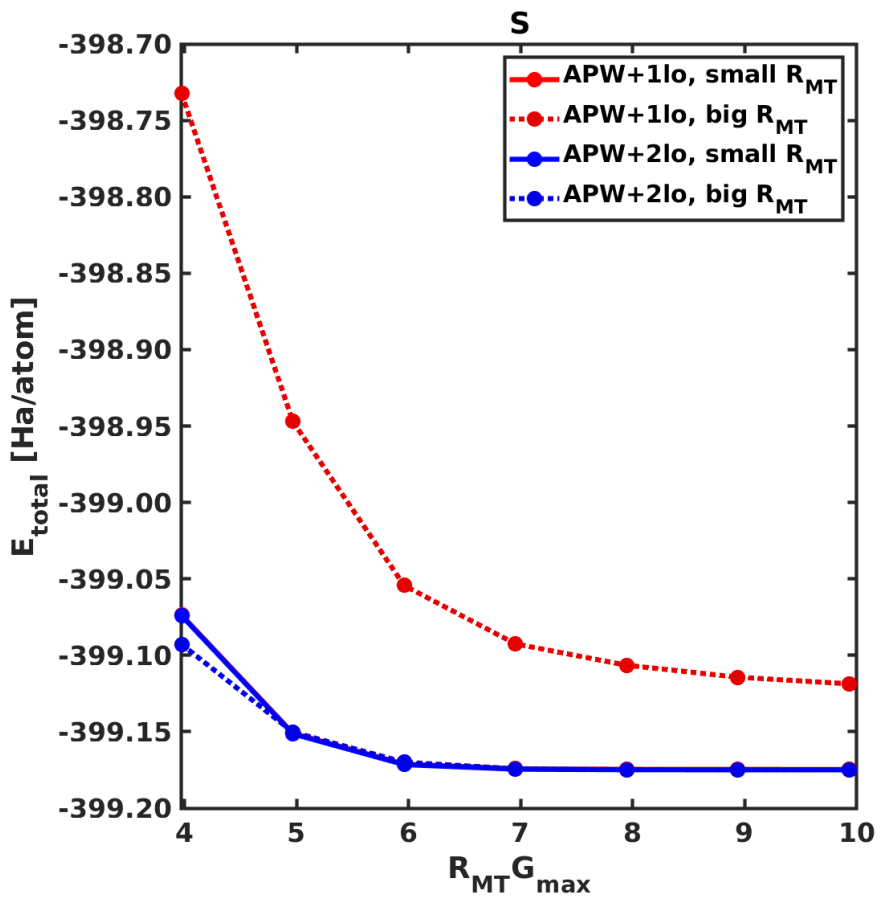
&

$$\phi^{lm}_{lo}(\mathbf{S}_\alpha + \mathbf{r}) = \left[\tilde{\tilde{A}}^\alpha_{lm} u^\alpha_l(r, E_l) + \tilde{\tilde{C}}^\alpha_{lm} \ddot{u}^\alpha_l(r, E_l)\right] Y_{lm}(\hat{\mathbf{r}})$$

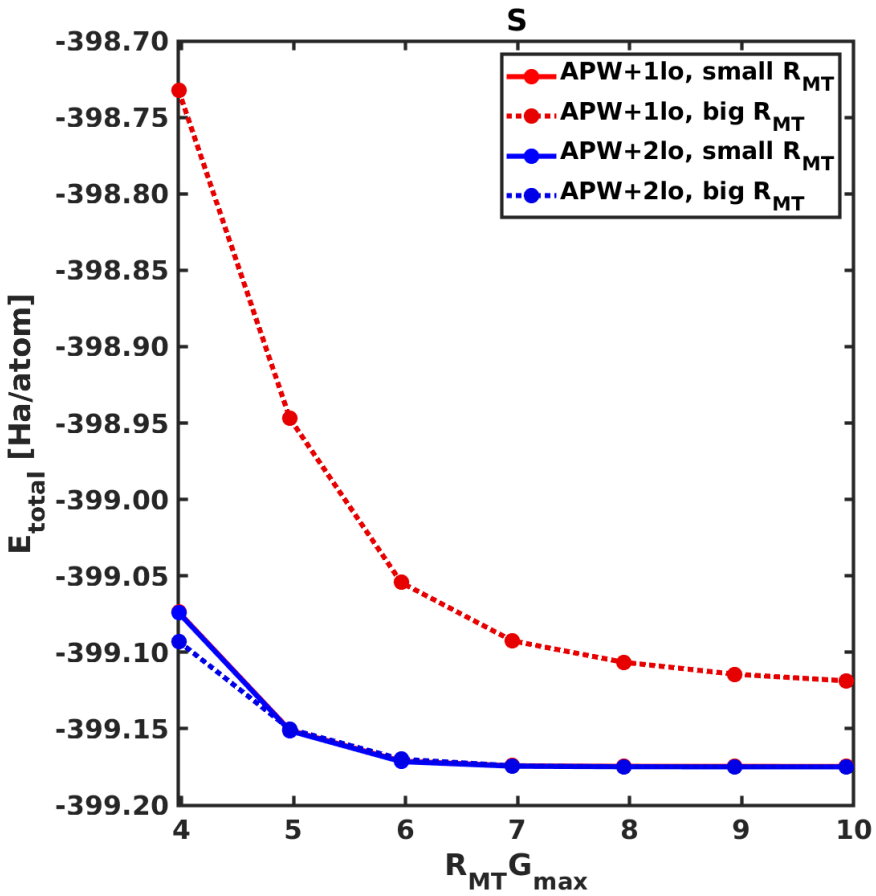
"APW+2lo"

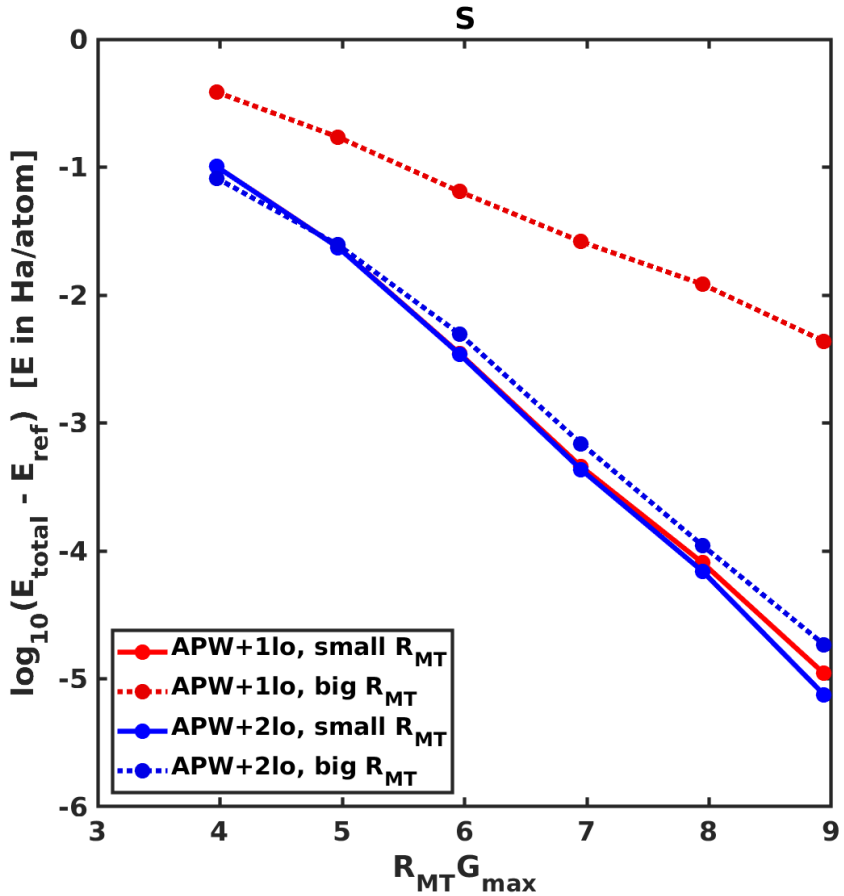


APW+lo: influence of muffin-tin radii

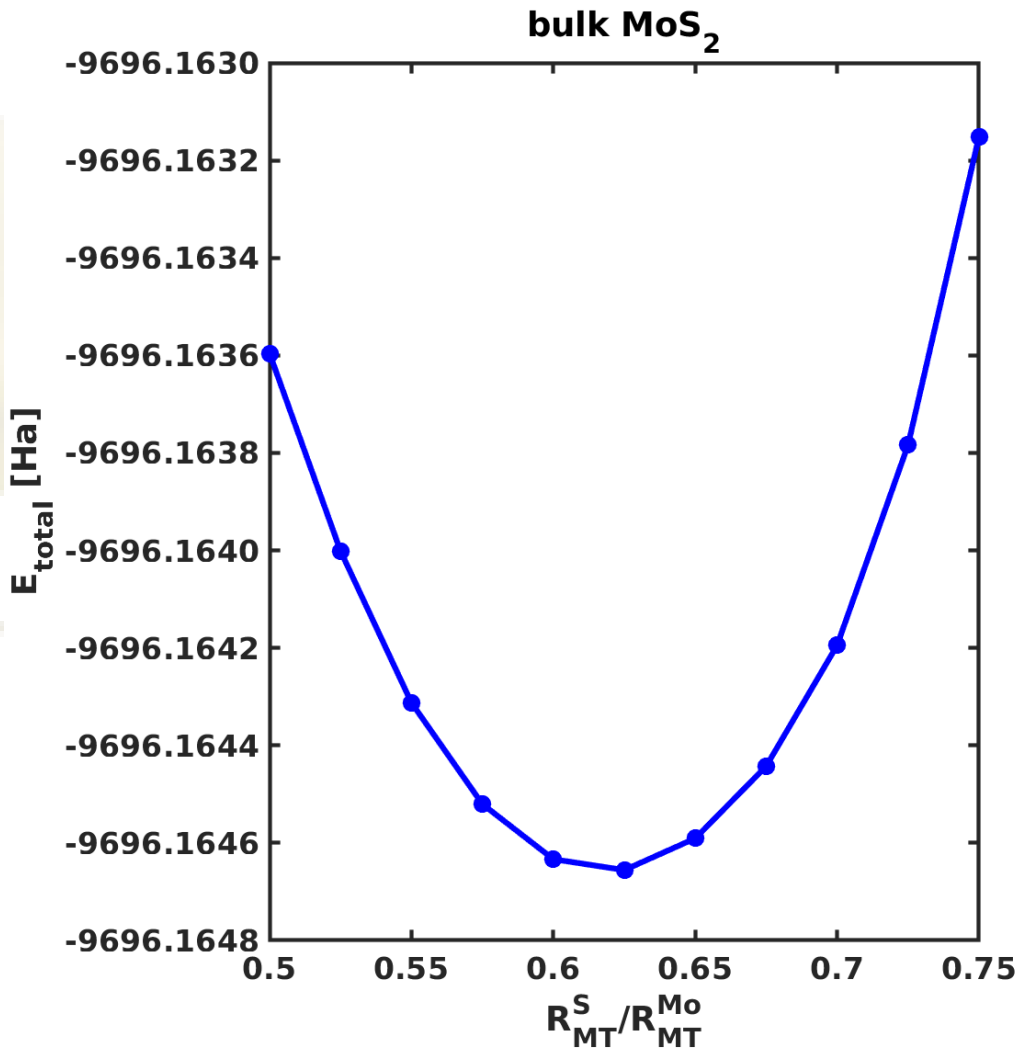


APW+lo: influence of muffin-tin radii

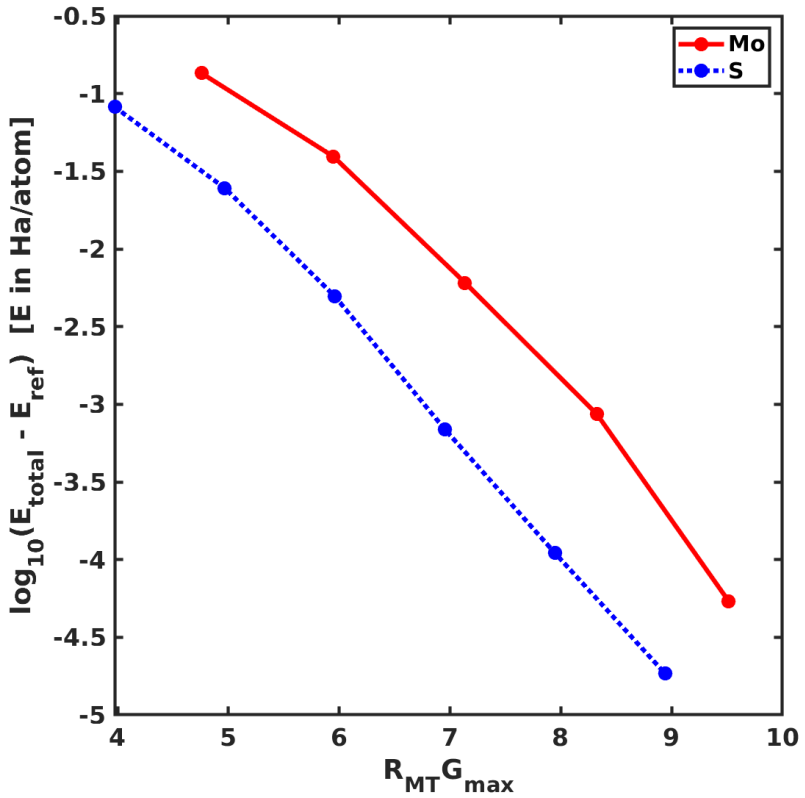




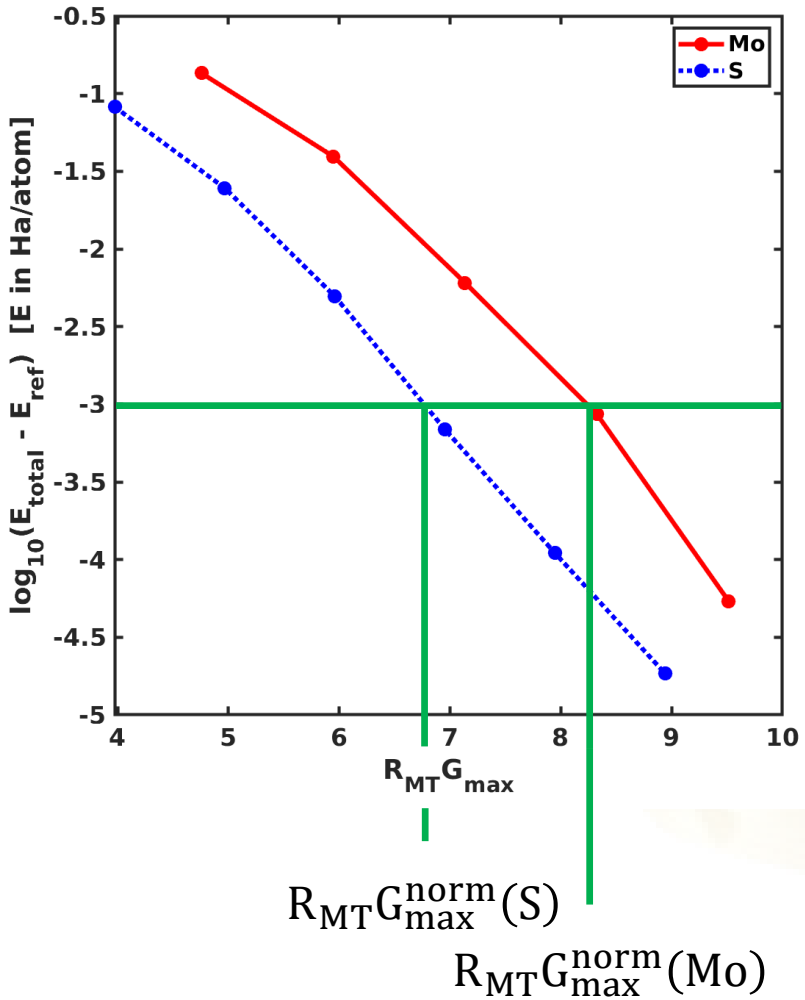
Ratios of muffin-tin radii in compound crystals



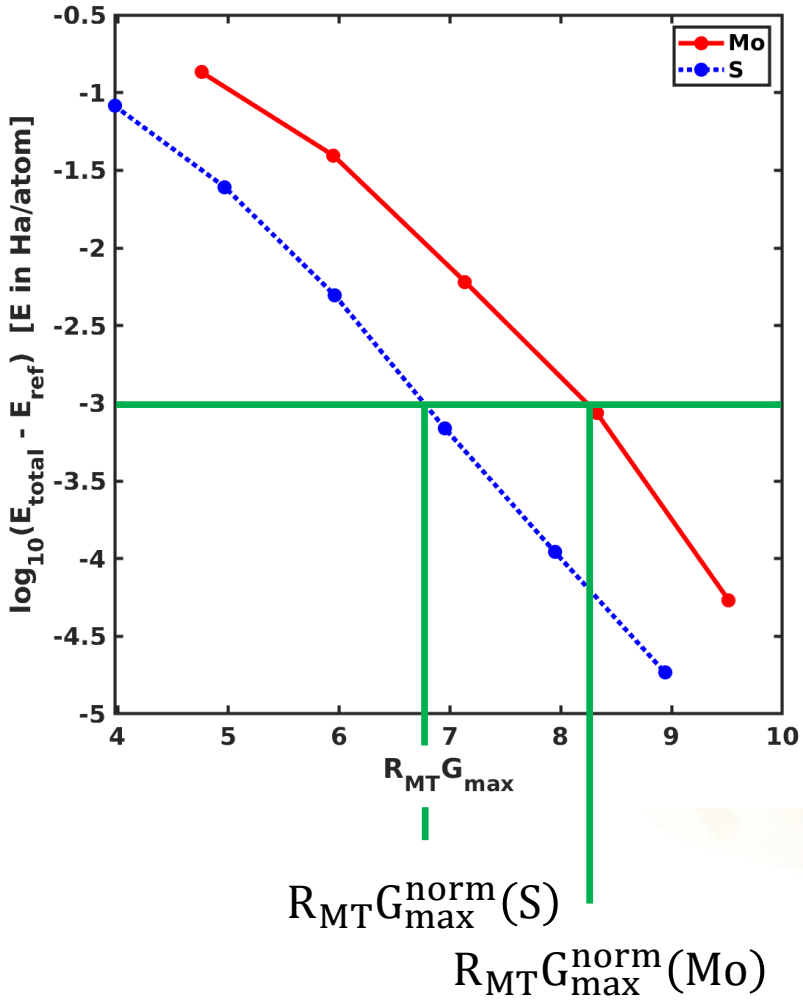
Each element has "personal" $R_{MT}G_{max}$ behavior

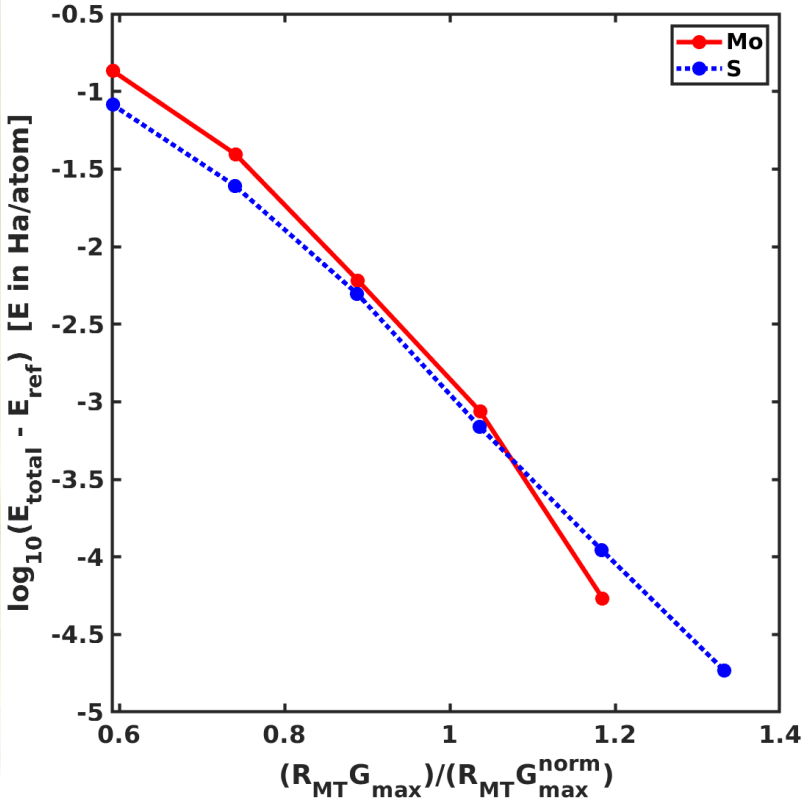


Each element has "personal" $R_{MT}G_{max}$ behavior

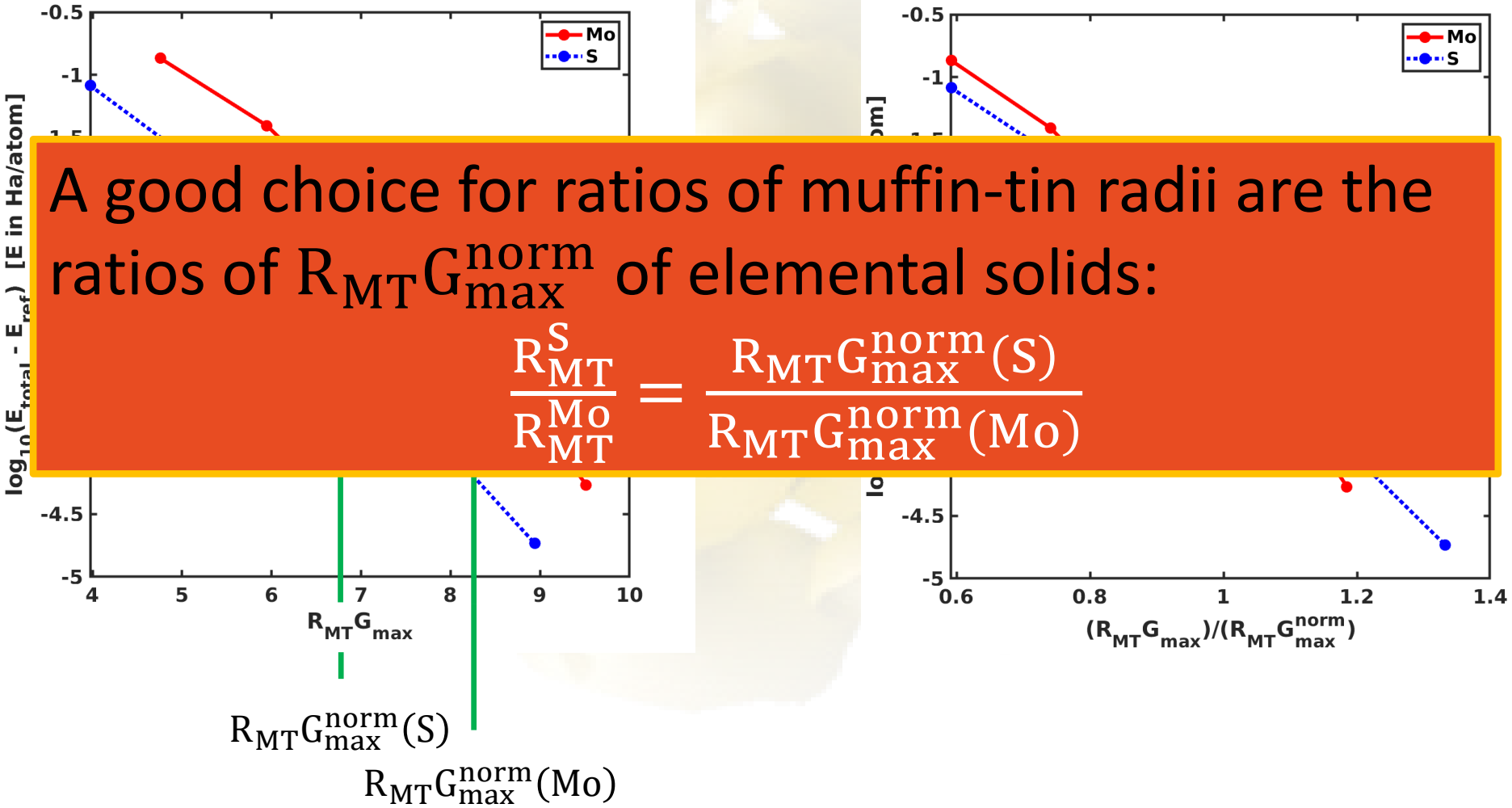


Each element has "personal" $R_{MT}G_{max}$ behavior





Each element has "personal" $R_{MT}G_{max}$ behavior



A good choice for ratios of muffin-tin radii are the ratios of $R_{MT}G_{max}^{norm}$ of elemental solids:

$$\frac{R_{MT}^{S}}{R_{MT}^{Mo}} = \frac{R_{MT}G_{max}^{norm}(S)}{R_{MT}G_{max}^{norm}(Mo)}$$

Benchmark Set: 71 Elemental Crystals

H																	He
194																	194
hP4																	hP2
nm																	nm
Li	Be											B	C	N	O	F	Ne
166	194											166	194	205	12	15	225
hR9	hP2											hR36	hP4	cP8	mS4	mS8	cF4
nm	nm											nm	nm	nm	afm	nm	nm
Na	Mg											Al	Si	P	S	Cl	Ar
166	194											225	227	64	166	64	225
hR9	hP2											cF4	cF8	oS8	hR3	oS8	cF4
nm	nm											nm	nm	nm	nm	nm	nm
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
229	225	194	194	229	229	225	229	194	225	225	194	64	227	166	152	64	225
cI2	cF4	hP2	hP2	cI2	cI2	cF4	cI2	hP2	cF4	cF4	hP2	oS8	cF8	hR6	hP3	oS8	cF4
nm	nm	nm	nm	nm	afm	afm	fm	fm	fm	nm	nm	nm	nm	nm	nm	nm	nm
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
229	225	194	194	229	229	194	194	225	225	225	194	139	227	166	152	64	225
cI2	cF4	hP2	hP2	cI2	cI2	hP2	hP2	cF4	cF4	cF4	hP2	tI2	cF8	hR6	hP3	oS8	cF4
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
229	229	194	194	229	229	194	194	225	225	225	139	194	225	166	221		225
cI2	cI2	hP2	hP2	cI2	cI2	hP2	hP2	cF4	cF4	cF4	tI2	hP2	cF4	hR6	cP1		cF4
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm

symbol

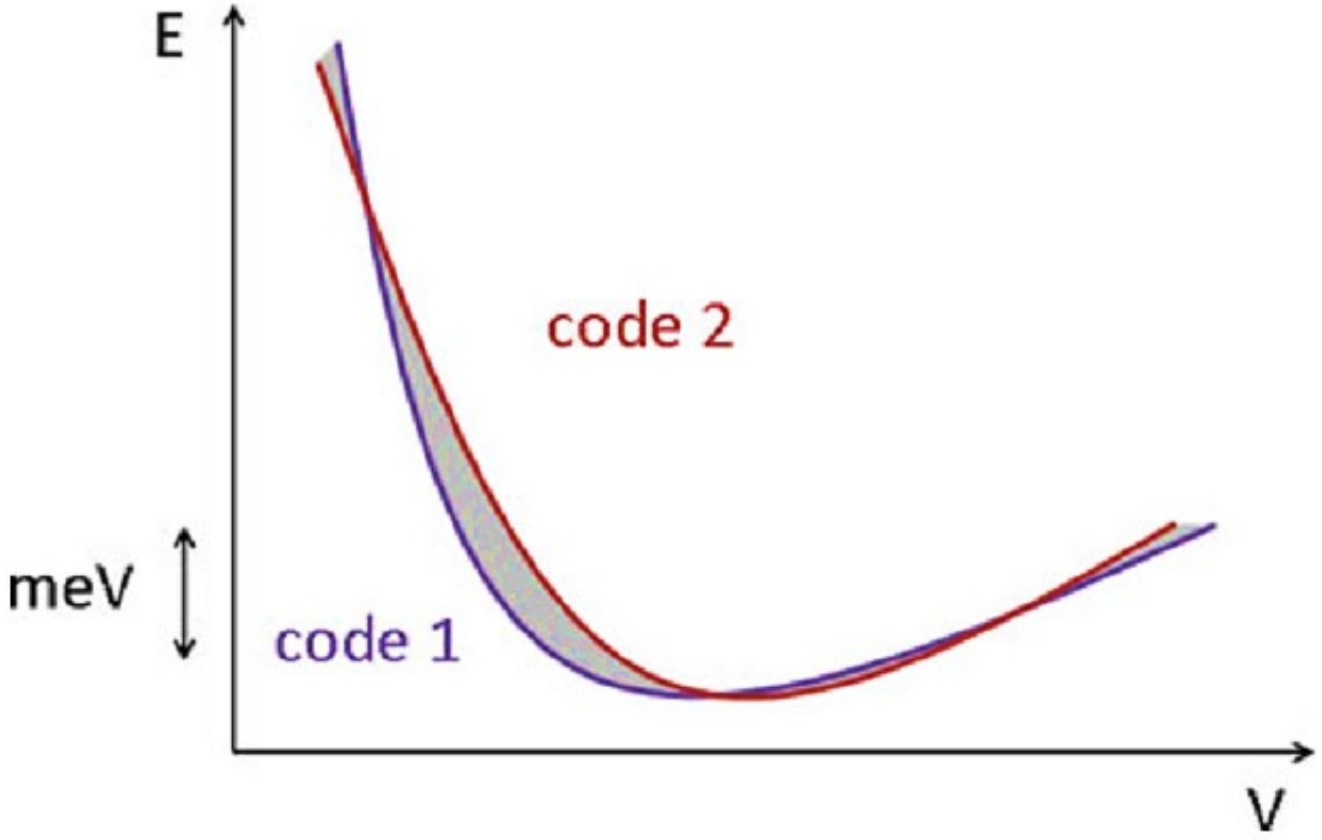
space group

Pearson

(non-)magnetic

K. Lejaeghere et al., Critical Reviews in Solid State and Materials Sciences 39, 1-24 (2014).

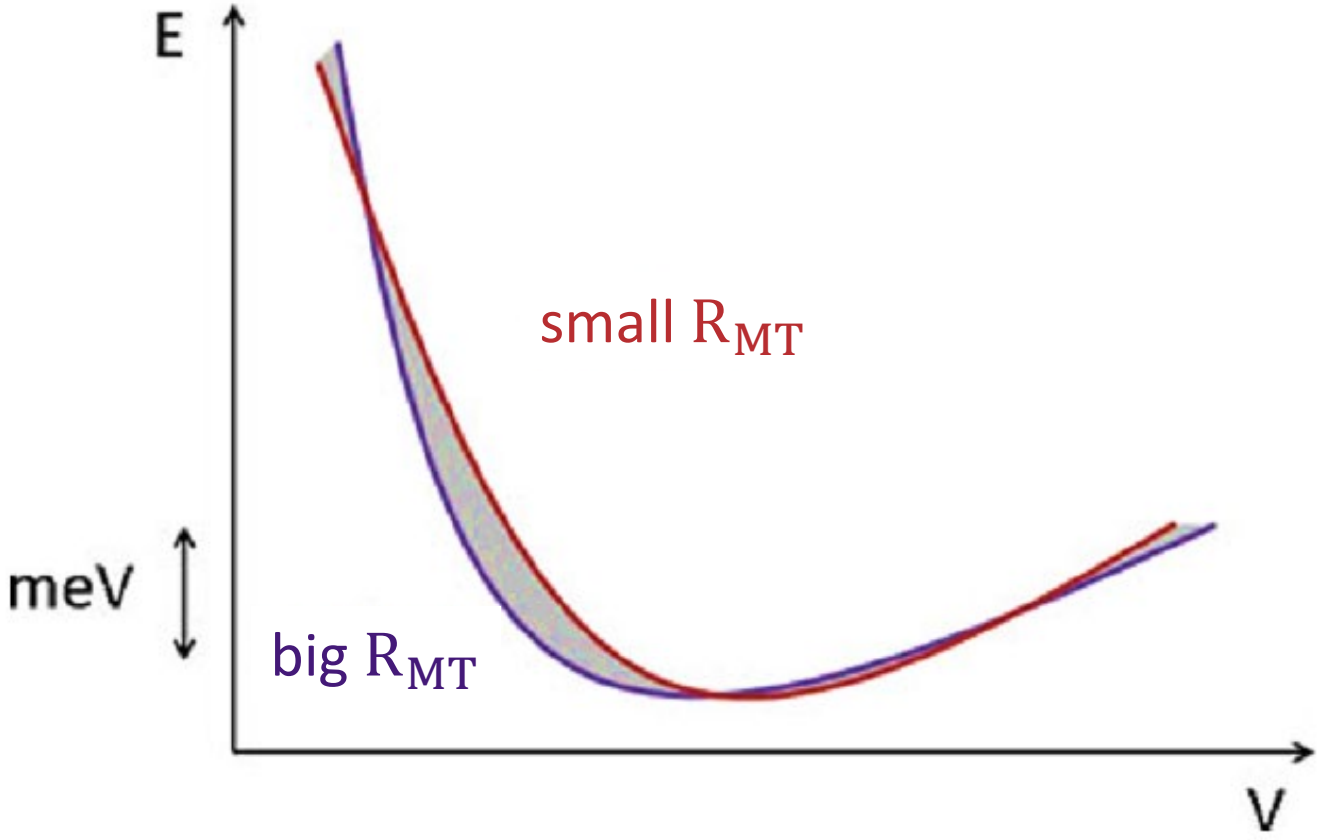
Quality factor



$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)\mathrm{d}V}{\Delta V}} \right\rangle$$

K. Lejaeghere et al., Critical Reviews in Solid State and Materials Sciences 39, 1-24 (2014).

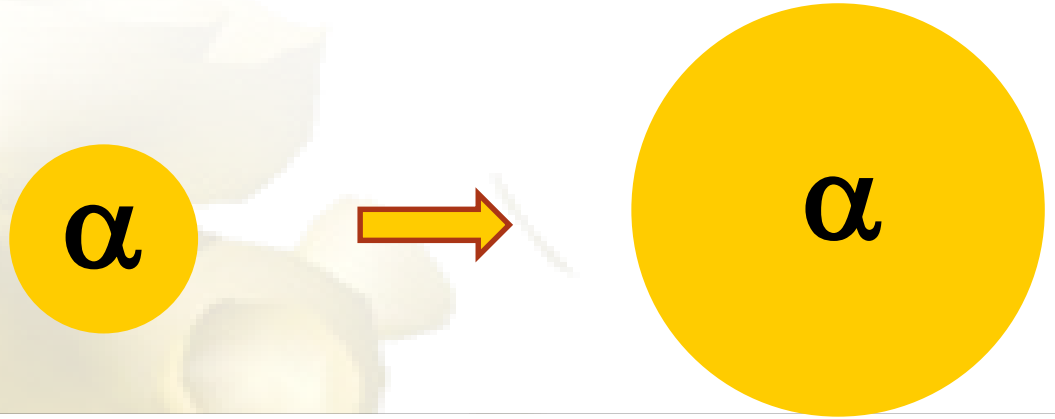
Quality factor



$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)\mathrm{d}V}{\Delta V}} \right\rangle$$

K. Lejaeghere et al., Critical Reviews in Solid State and Materials Sciences 39, 1-24 (2014).

Test Basis Completeness



Δ-factors are shown in meV/atom

Δ_{mean}= 0.008 meV/atom

Δ_{max} = 0.041 meV/atom

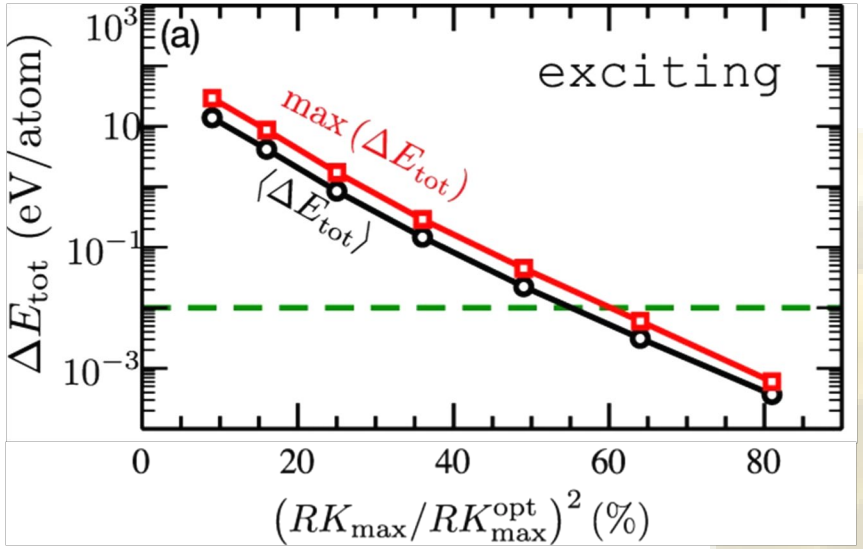
H 0.000																	He 0.000
Li 0.001	Be 0.004											B 0.003	C 0.002	N 0.001	O 0.007	F 0.015	Ne 0.004
Na 0.001	Mg 0.000											Al 0.002	Si 0.006	P 0.004	S 0.009	Cl 0.004	Ar 0.002
K 0.003	Ca 0.012	Sc 0.002	Ti 0.003	V 0.015	Cr 0.008	Mn 0.026	Fe 0.009	Co 0.011	Ni 0.016	Cu 0.018	Zn 0.009	Ga 0.004	Ge 0.002	As 0.018	Se 0.022	Br 0.004	Kr 0.002
Rb 0.003	Sr 0.001	Y 0.000	Zr 0.003	Nb 0.010	Mo 0.009	Tc 0.004	Ru 0.007	Rh 0.009	Pd 0.031	Ag 0.006	Cd 0.013	In 0.001	Sn 0.001	Sb 0.003	Te 0.005	I 0.013	Xe 0.001
Cs 0.000	Ba 0.001	Lu 0.026	Hf 0.040	Ta 0.041	W 0.009	Re 0.016	Os 0.013	Ir 0.020	Pt 0.023	Au 0.002	Hg 0.011	Tl 0.007	Pb 0.001	Bi 0.002	Po 0.001	At	Rn 0.001

Get $R_{MT}G_{max}^{norm}$ for each element

$$R_{MT}G_{max}^{norm} = R_{MT}G_{max}(\Delta E = 10^{-4}\text{eV/atom})$$

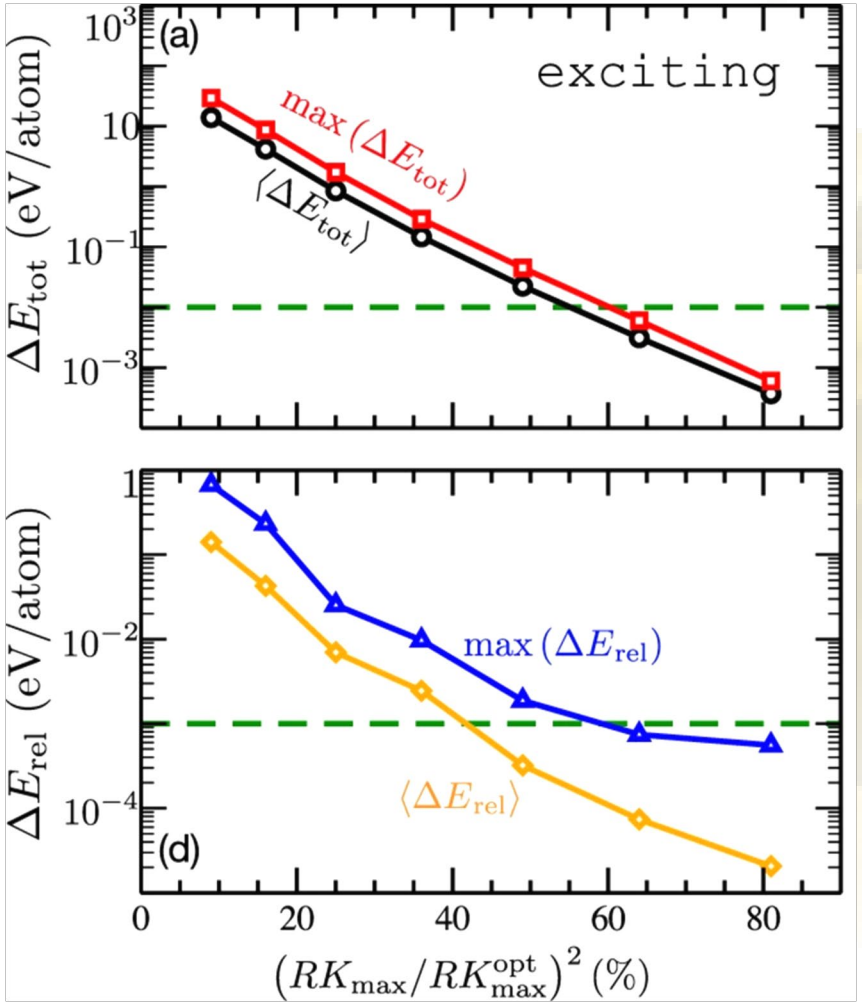
H 5.84																He 8.23
Li 8.45	Be 8.31											B 8.97	C 9.38	N 9.55	O 10.24	F 10.79	Ne 10.44
Na 10.64	Mg 10.58											Al 10.21	Si 10.61	P 10.36	S 9.93	Cl 10.22	Ar 10.47
K 10.88	Ca 10.77	Sc 11.58	Ti 11.80	V 11.92	Cr 12.26	Mn 12.42	Fe 12.57	Co 12.69	Ni 12.78	Cu 12.62	Zn 12.75	Ga 12.68	Ge 12.80	As 12.79	Se 12.90	Br 12.40	Kr 10.60
Rb 11.35	Sr 10.86	Y 11.32	Zr 11.66	Nb 11.86	Mo 11.89	Tc 12.31	Ru 12.55	Rh 12.74	Pd 12.88	Ag 13.03	Cd 13.08	In 13.23	Sn 13.45	Sb 13.50	Te 13.26	I 13.43	Xe 11.33
Cs 13.34	Ba 13.01	Lu 15.13	Hf 14.96	Ta 14.61	W 13.93	Re 13.65	Os 13.63	Ir 13.45	Pt 13.07	Au 13.23	Hg 13.26	Tl 13.37	Pb 13.56	Bi 13.57	Po 13.58	At	Rn 12.27

Energy convergence



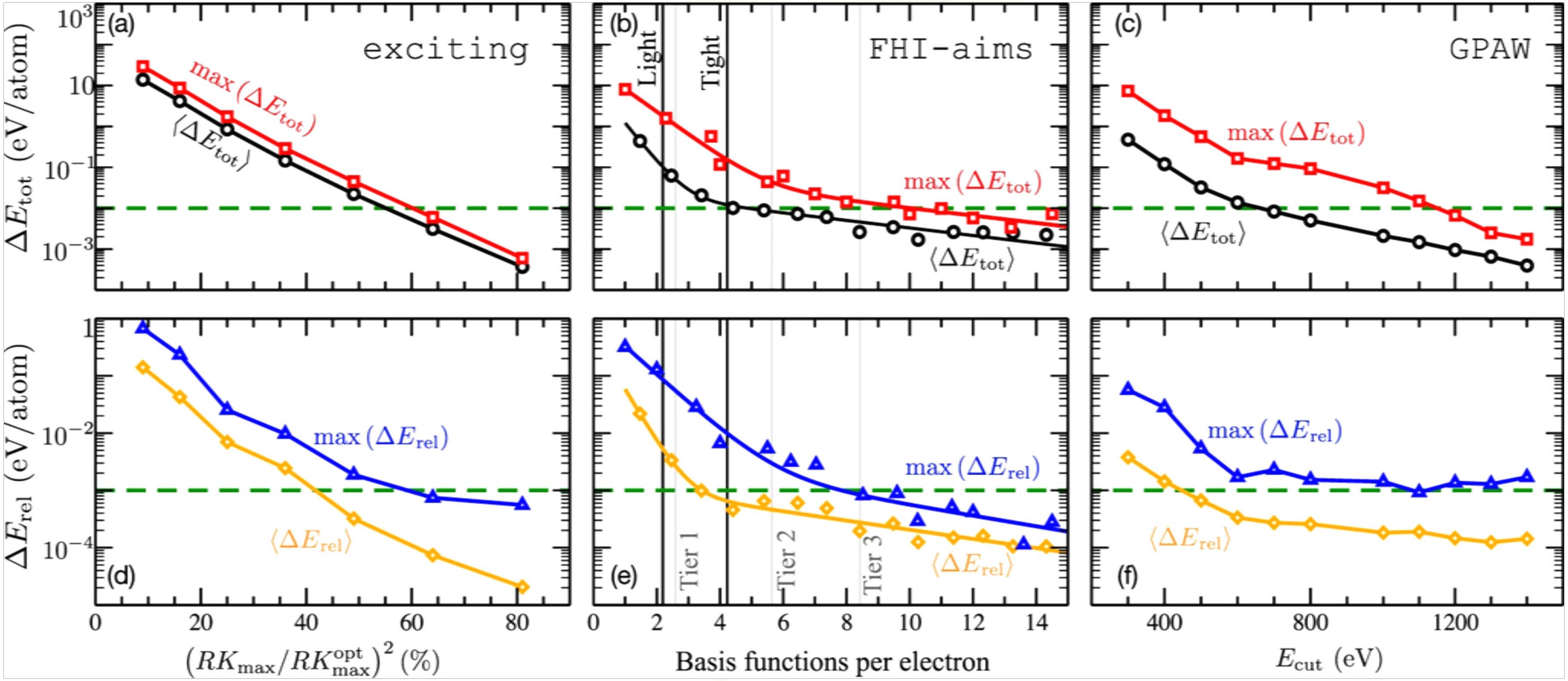
Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Energy convergence



Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Energy convergence



Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Predict Numerical Errors of Any Material Using Errors of Elemental Solids

Predicted error for a general solid

$$\widehat{\Delta E} = \frac{1}{N}\sum_{I} N_I \Delta E_I$$

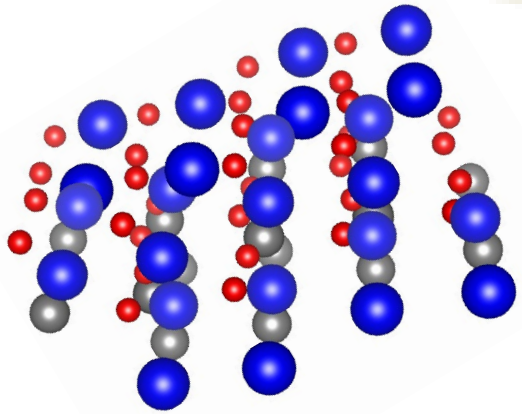
Observed error in elemental solids

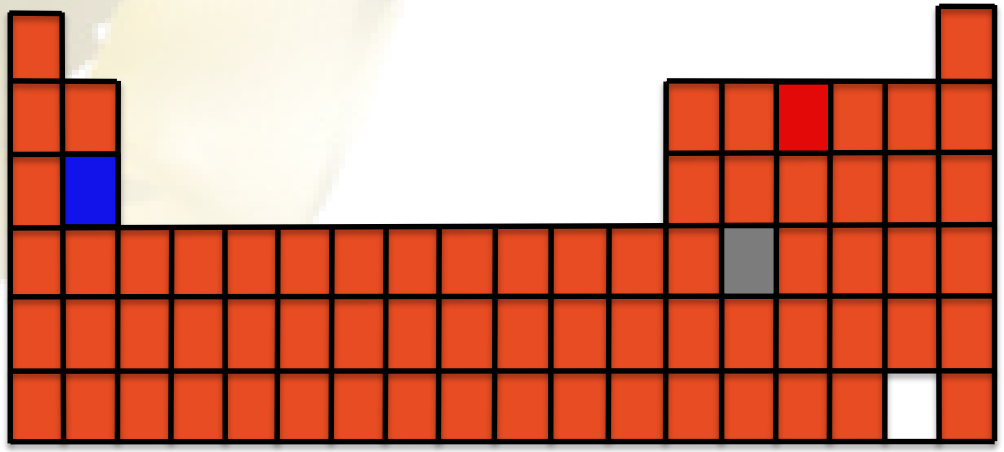
Predict Numerical Errors of Any Material Using Errors of Elemental Solids

Predicted error for a general solid

$$\widehat{\Delta E} = \frac{1}{N}\sum_I N_I \Delta E_I$$

Observed error in elemental solids

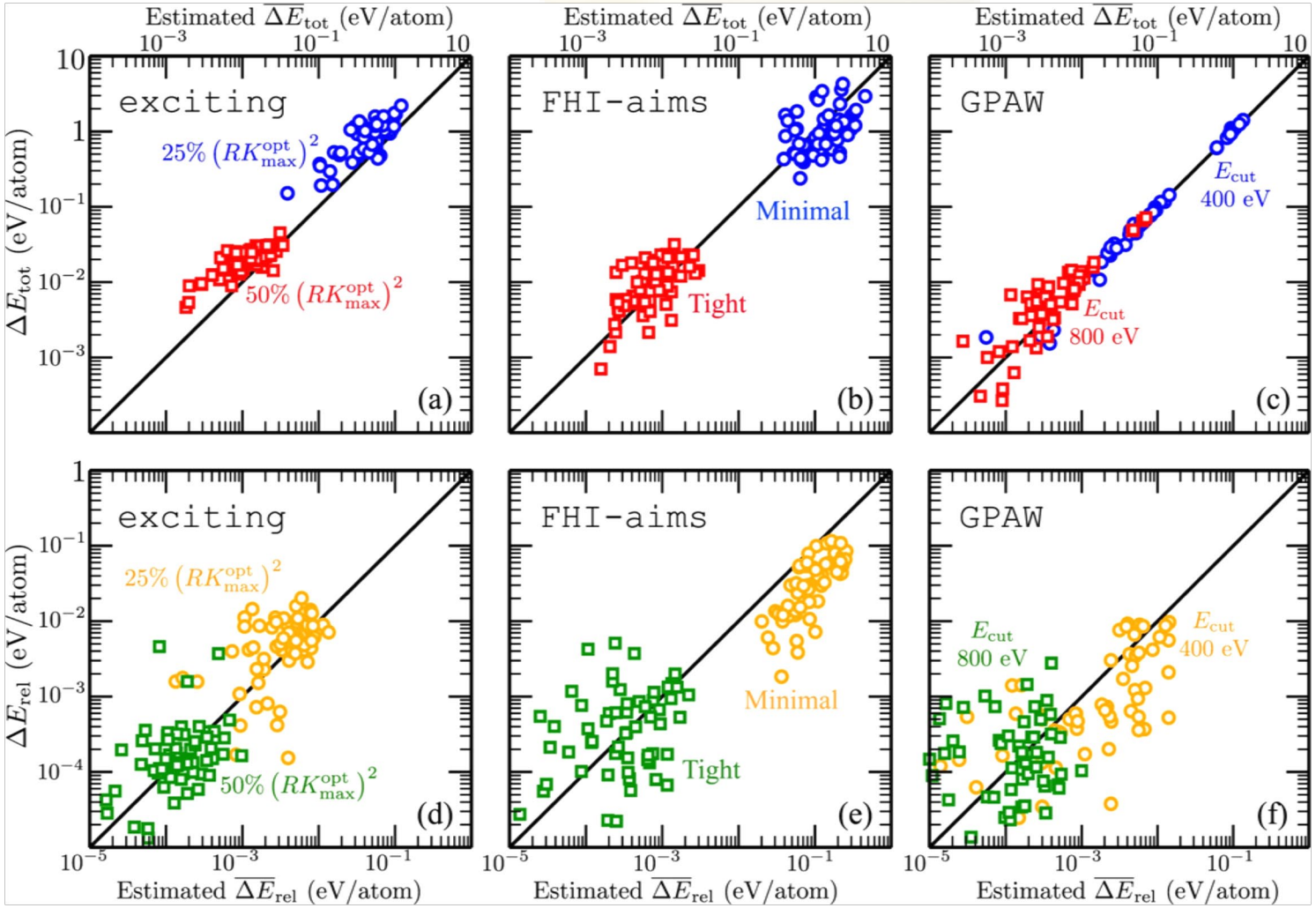




$$\widehat{\Delta E}_{\mathrm{GeMgN_2}} = \frac{1}{4}\left(\Delta E_{\mathrm{Ge}} + \Delta E_{\mathrm{Mg}} + 2\Delta E_{\mathrm{N}}\right)$$

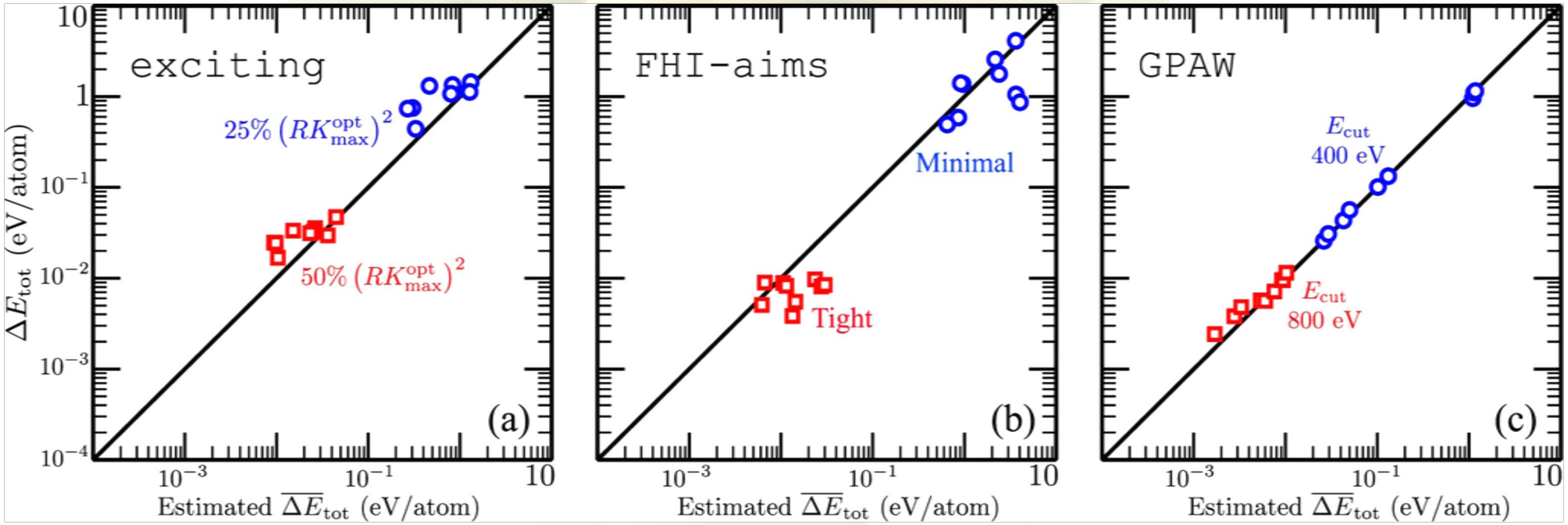
Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Numerical error prediction for 63 binary systems



Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Numerical error prediction for ternary systems



Carbogno, Christian, et al. "Numerical quality control for DFT-based materials databases." *npj Computational Materials* 8.1 (2022): 69.

Conclusion

- Second order energy derivatives in los help to make results more independent of numerical parameters like linearization energies and muffin-tin radii
- An element‘s “personal” $\mathrm{R_{MT}G_{max}}$ behavior of its error in total energy is transferable to more complex compound crystals
- Tabulated $\mathrm{R_{MT}G_{max}^{norm}}$ of elemental solids can be used to make APW input parameters more material independent
- $\widehat{\Delta E} = \frac{1}{N}\sum_I N_I \Delta E_I$ allows us to estimate numerical errors for arbitrary systems