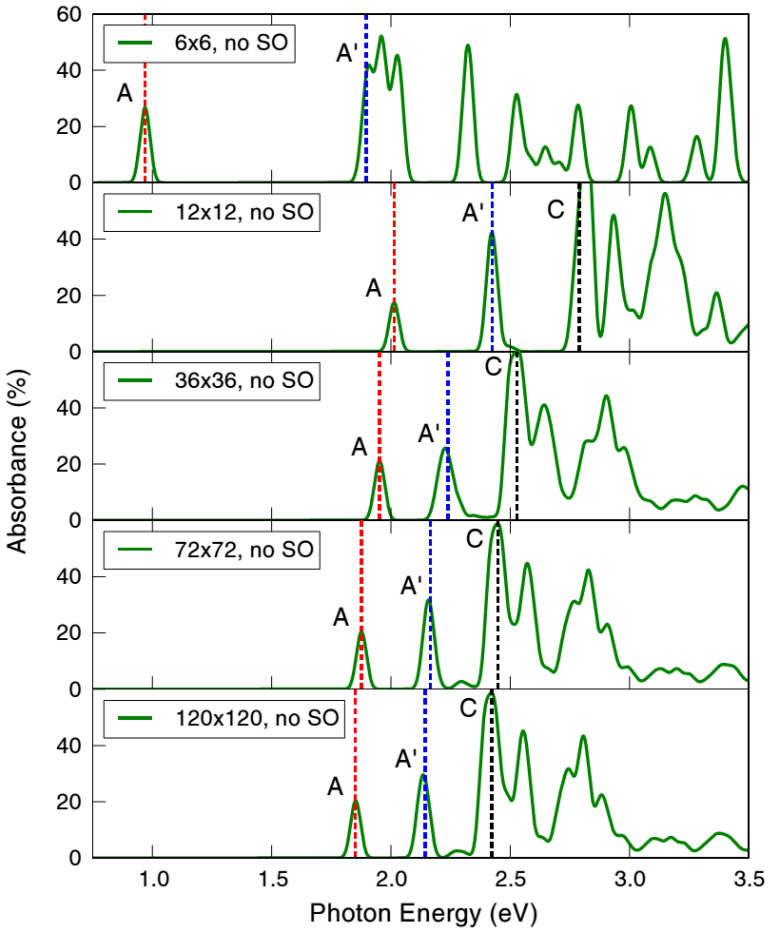
When things go wrong!



Derek Vigil-Fowler
11/23/13
BerkeleyGW Workshop 2013

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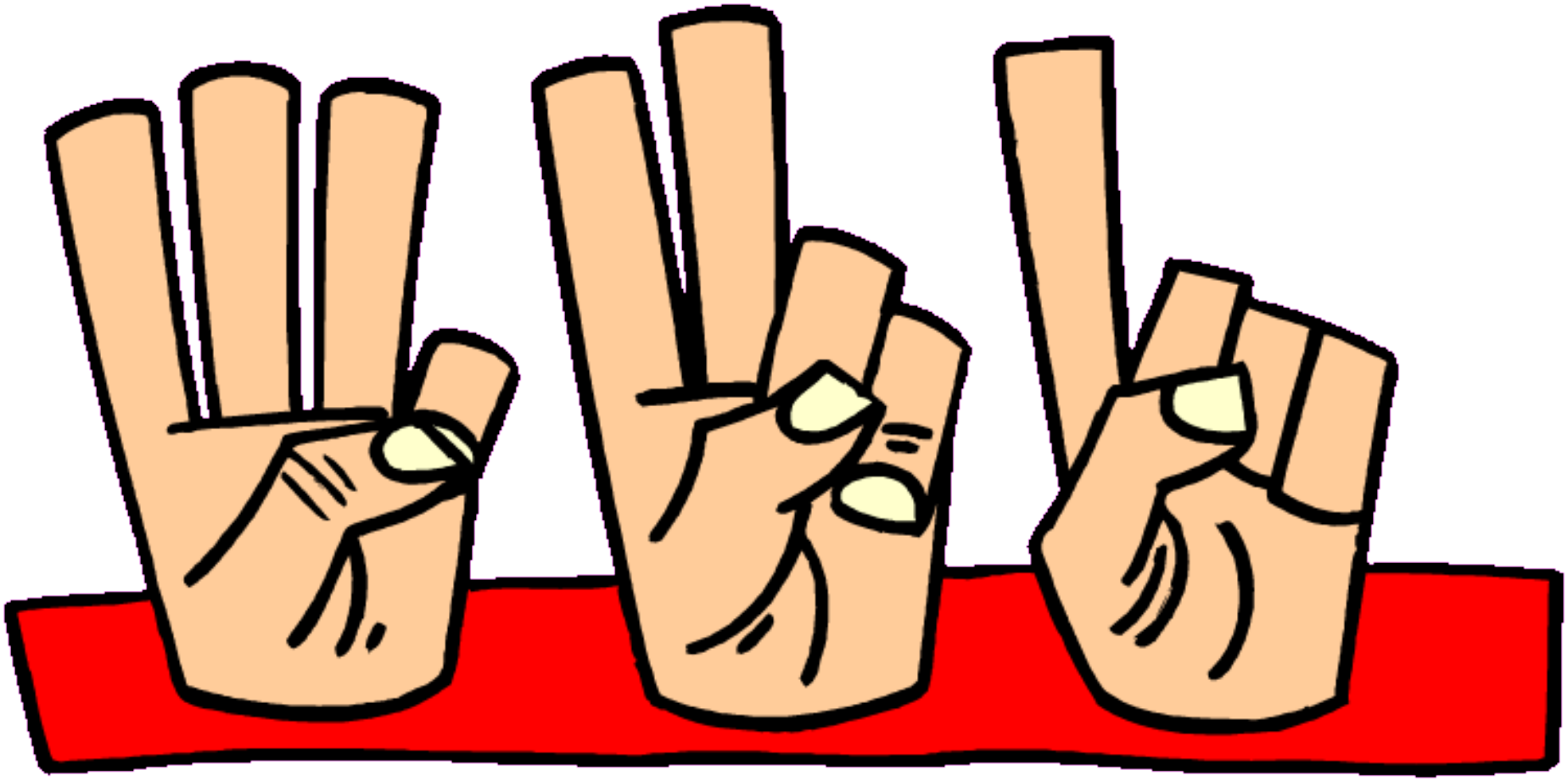

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Convergence in particular has led to many erroneous and problematic conclusions

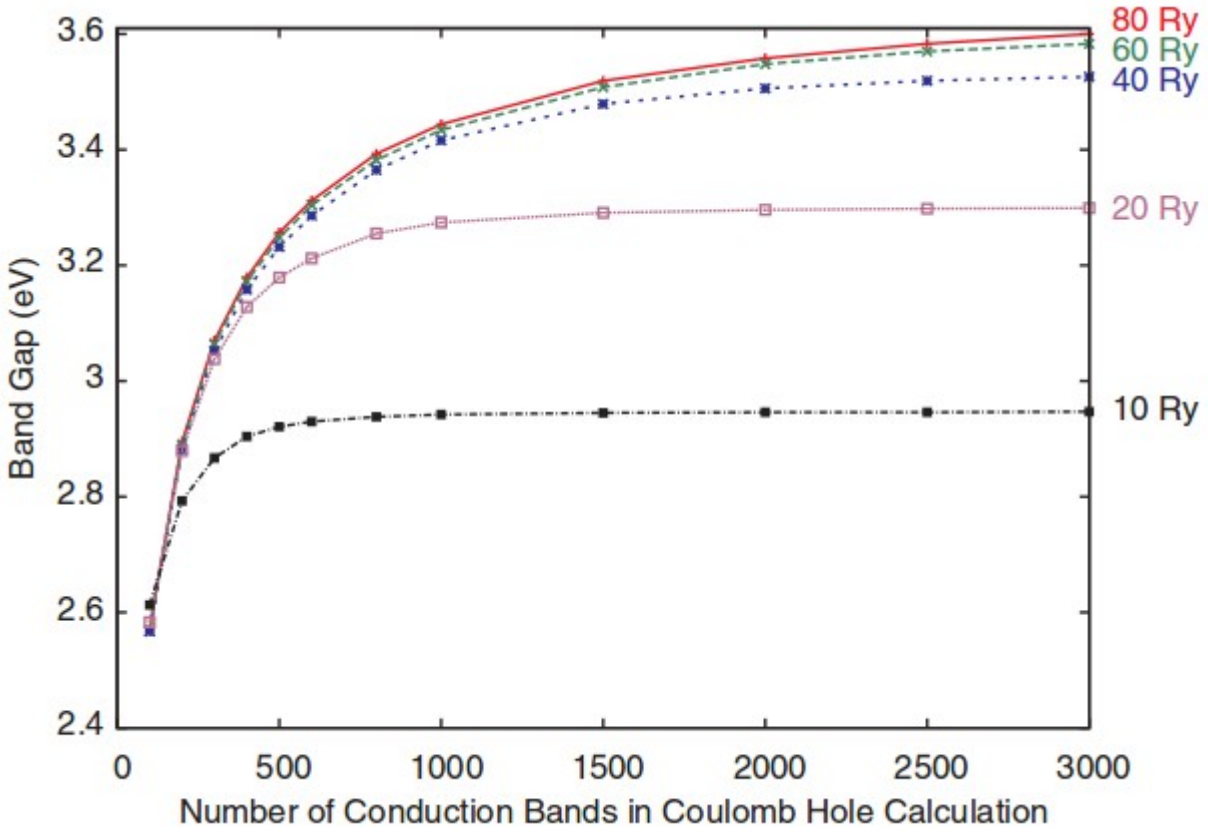
- Wrong numbers
- Incorrect understanding of the physics of system under study
- Proposals to go beyond GW formalism
  - Sometimes valid, often not

Examples

ZnO


AT&T
12:20 PM
74%
Messages
Monday
1
Calendar
Photos
Camera
Videos
280
Maps
73°
Weather
Passbook
Notes
Reminders
Clock
Stocks
Newsstand
iTunes
6
App Store
Game Center
Settings
Riptide GP
Phone
2
Mail
Safari
Music

In ZnO, using too small of a screened cutoff led to gaps that were too small and under-binding of d-electrons



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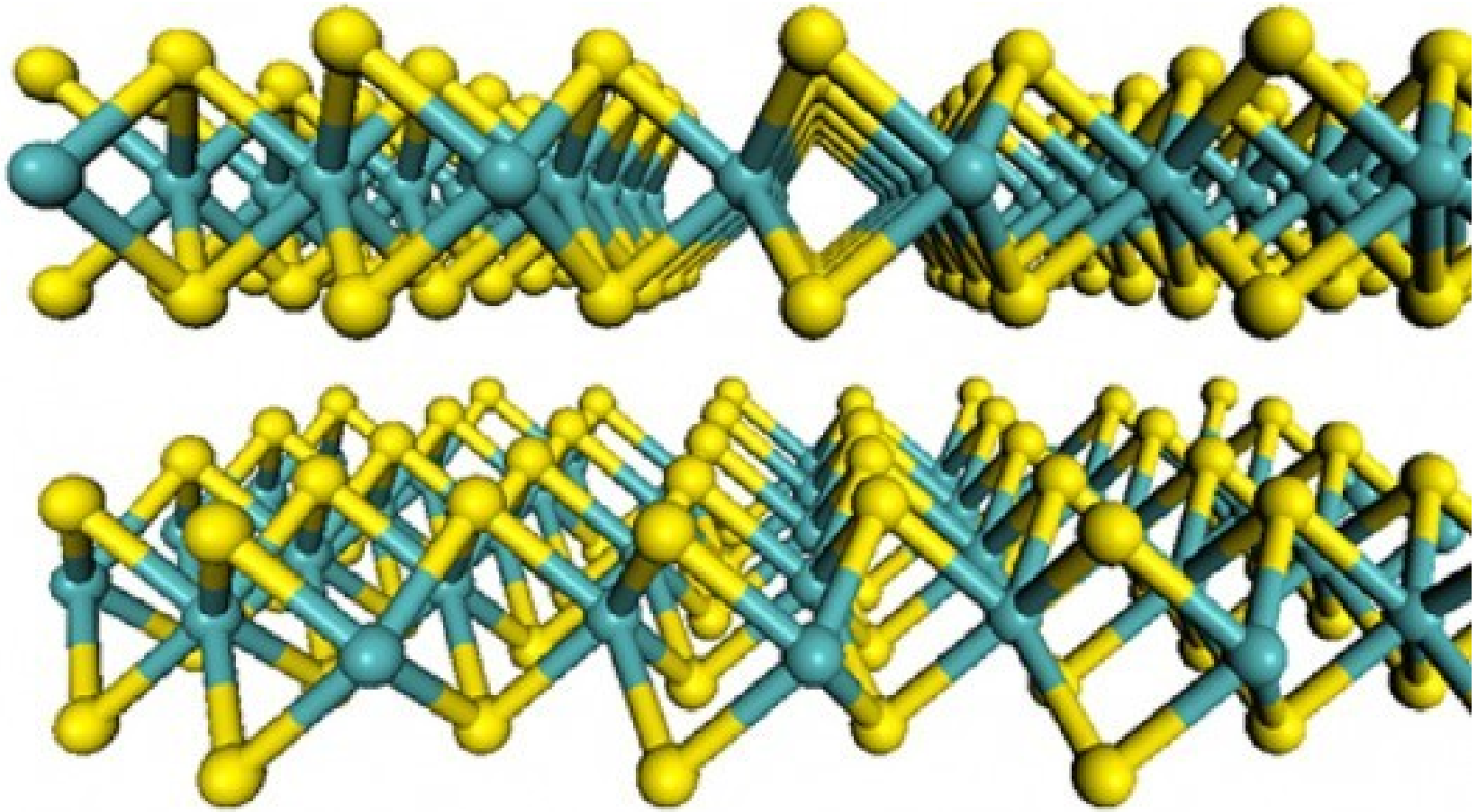
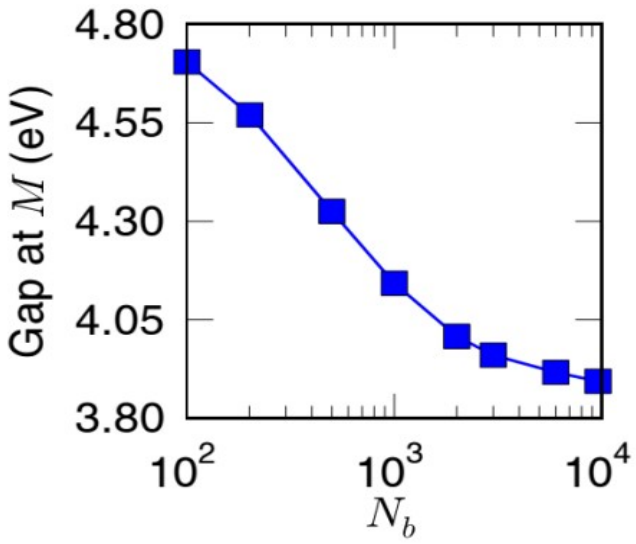
- Proposed that you need self-consistent GW to correct these failings

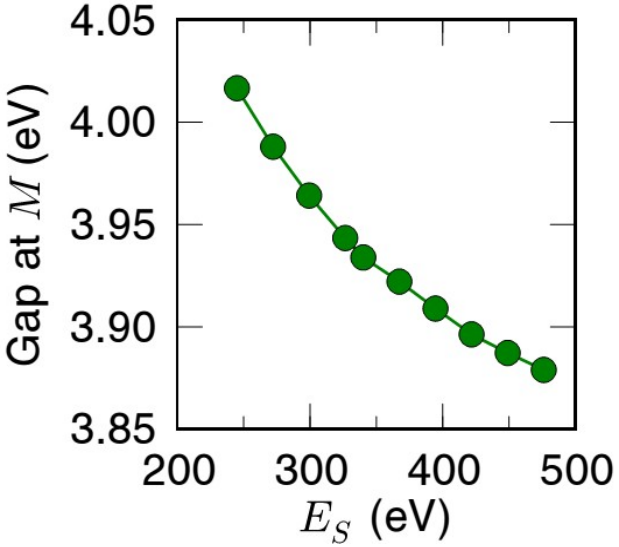
- But if you converge calculations, the underbinding of d-electrons disappears
  - We are seeing same pattern in other transition metals

MoS_2



In MoS_2 you also have very slow convergence of QP gaps with bands and screened cutoff, especially at M





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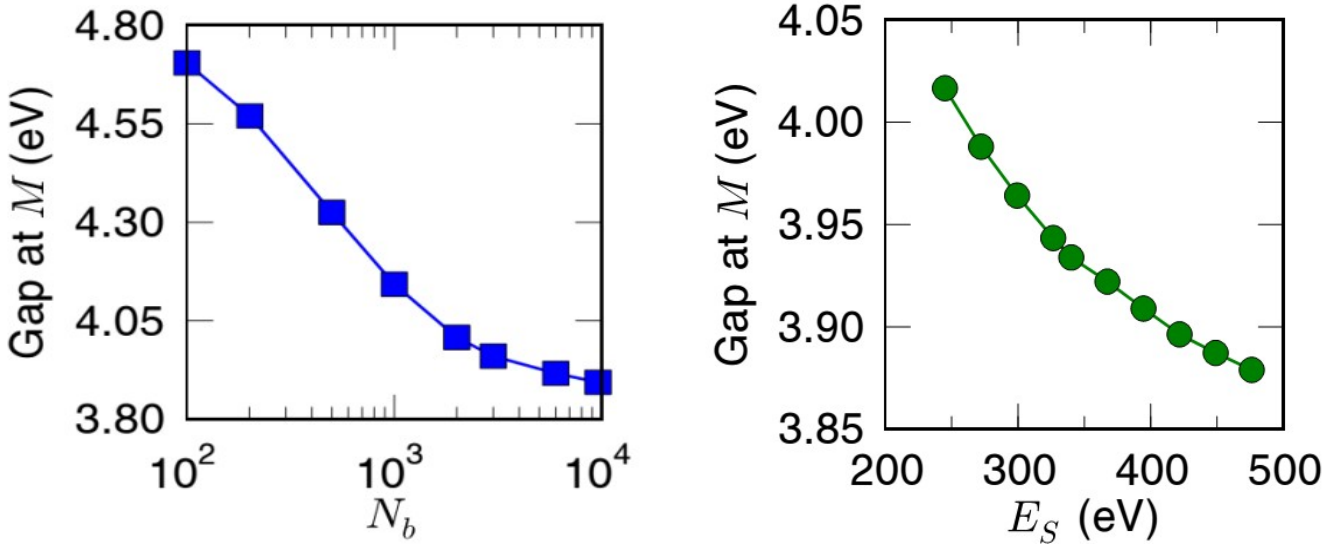
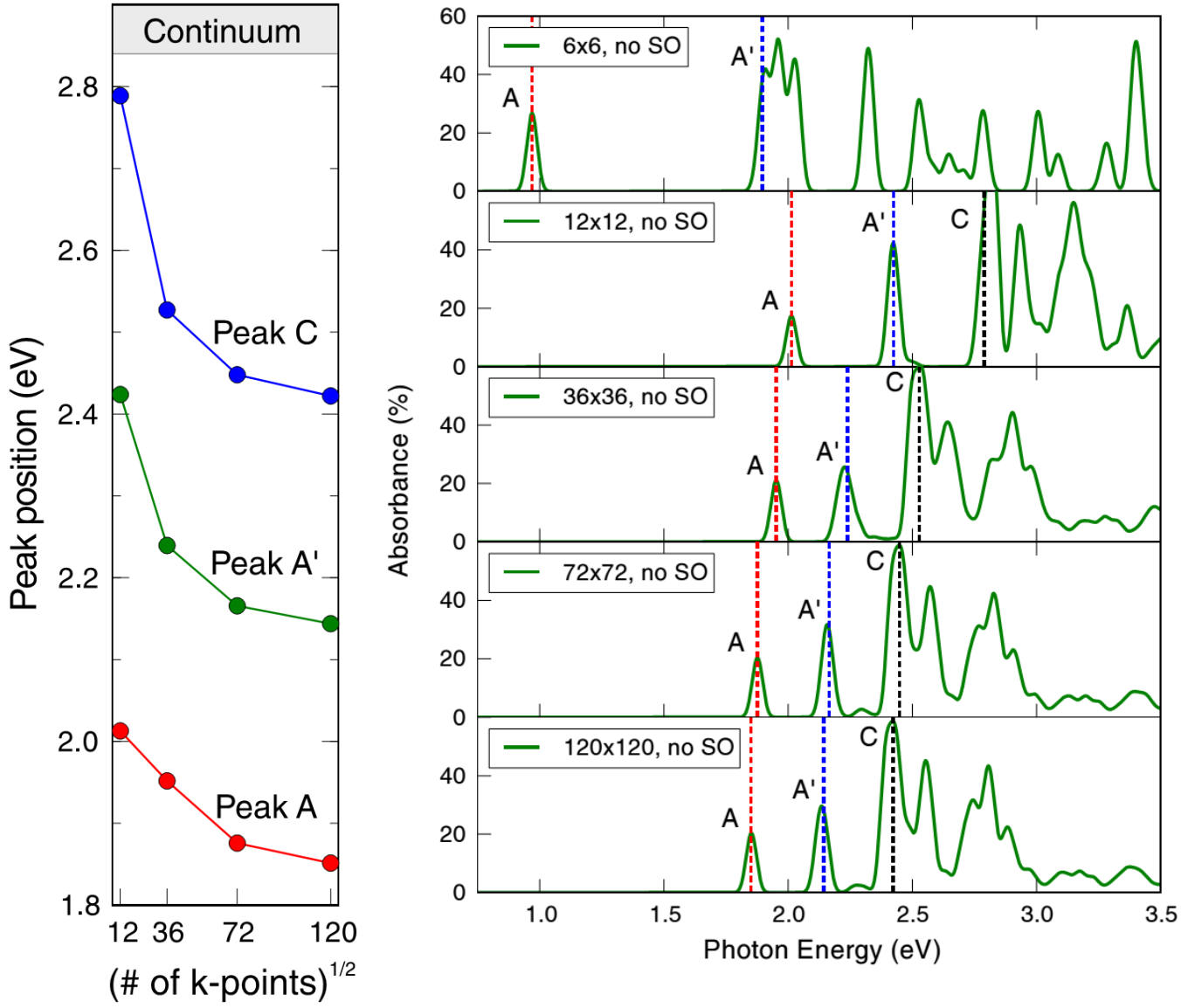


- Different k-points converge at different rates with respect to the number of bands and dielectric cutoff

- Slow and non-uniform convergence : big effect on optical properties

In MoS_2 very k-point sampling (72x72) is needed for converged absorbance spectrum



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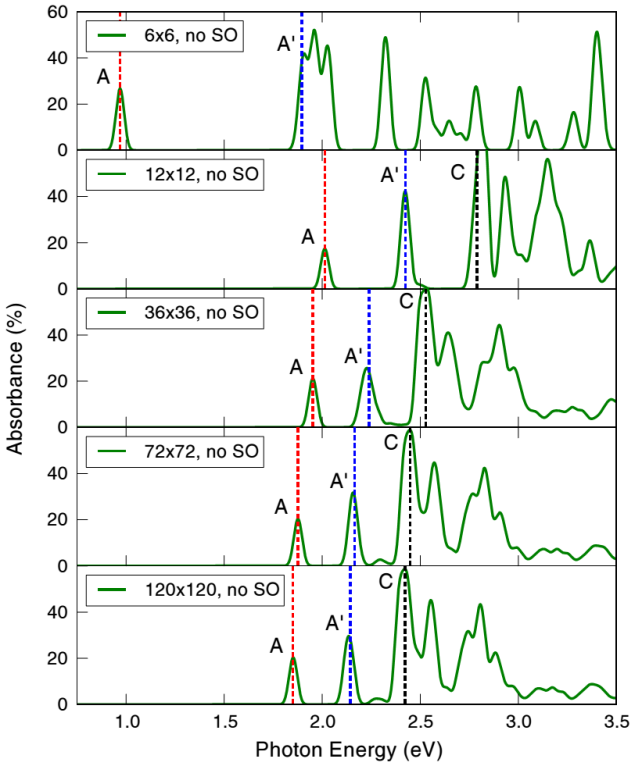

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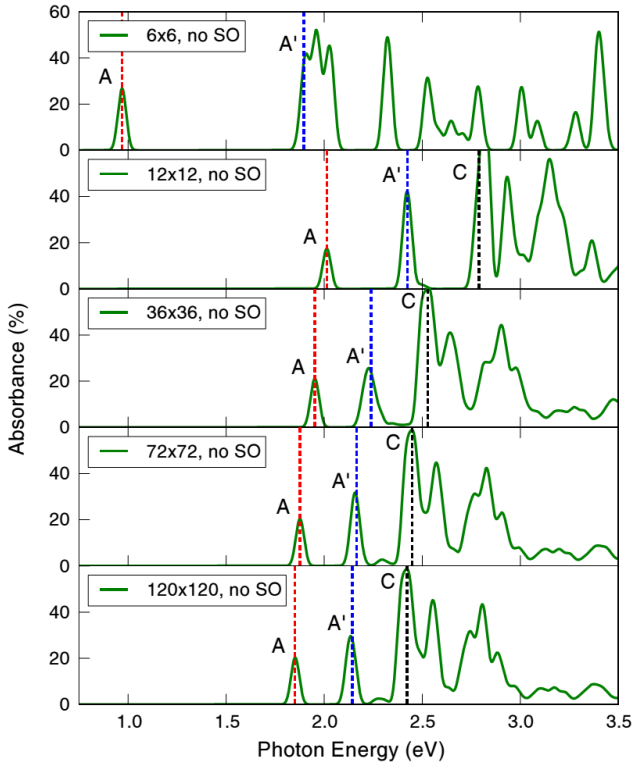

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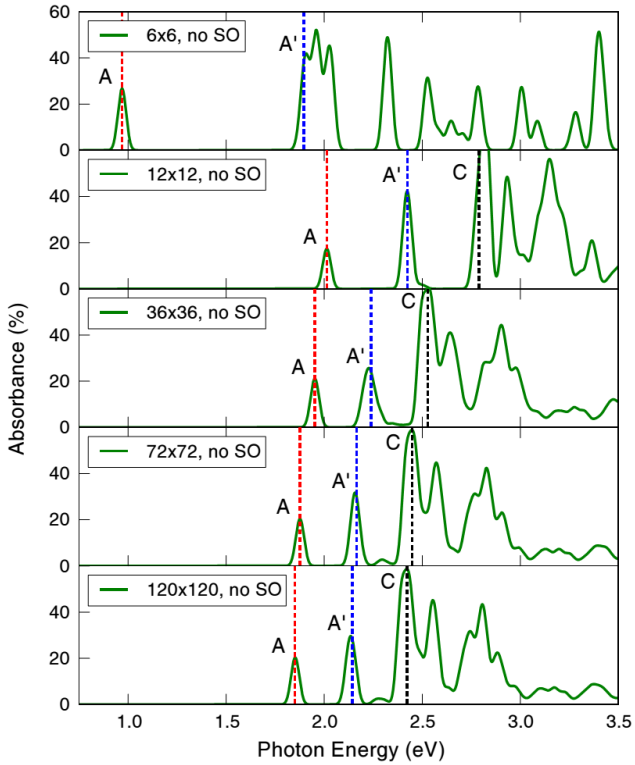

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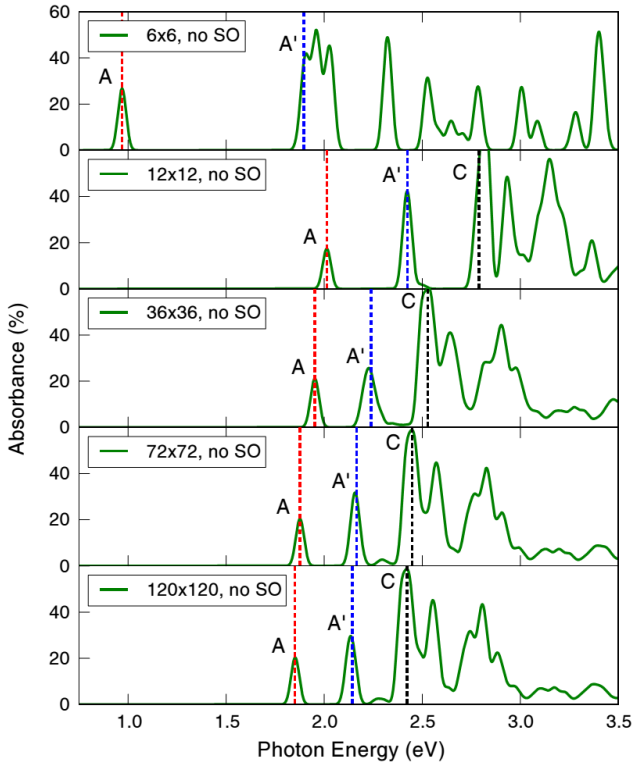
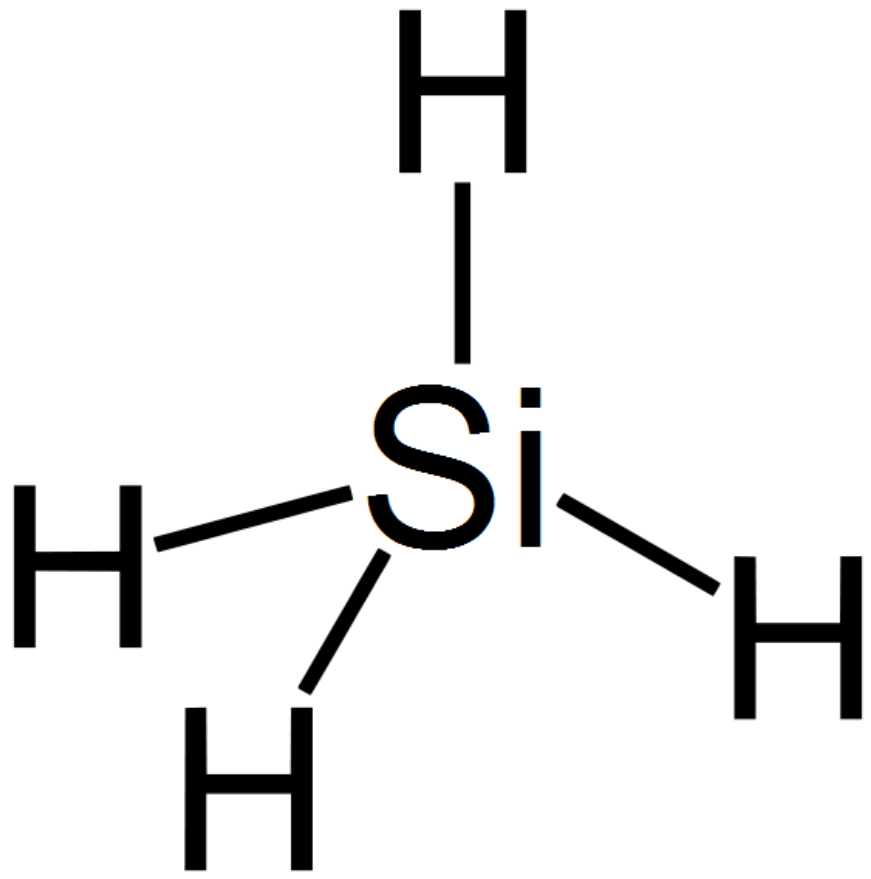


- Need detailed understanding for fundamental and applied purposes

Bad mean field



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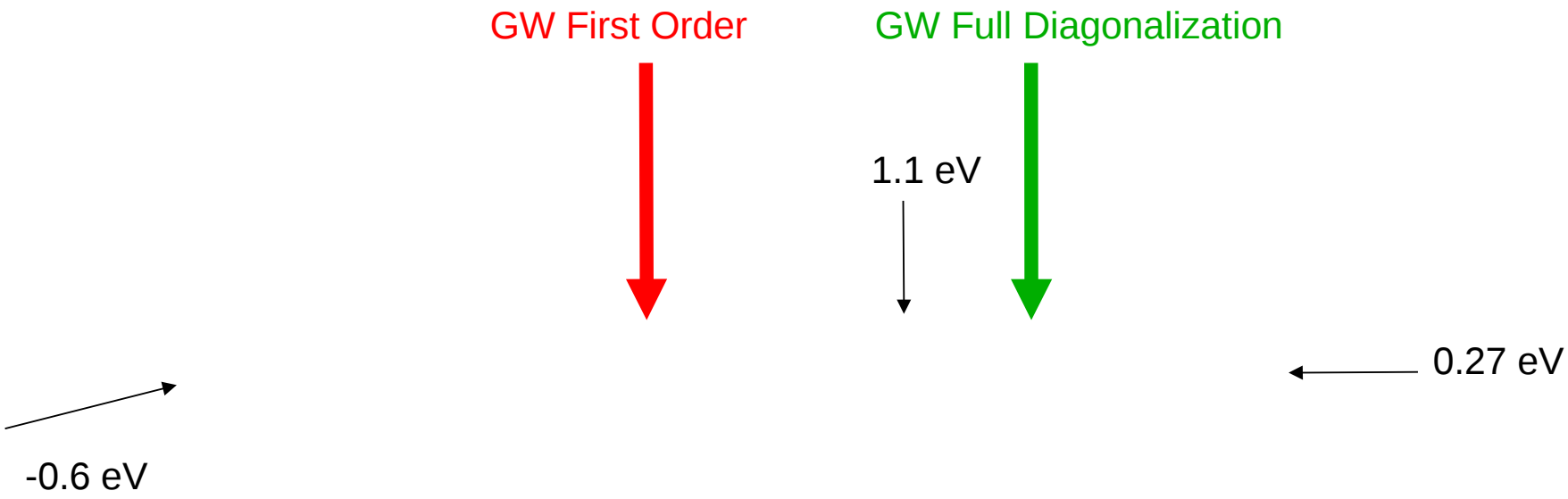
  - COHSEX
  - Hybrid functional

GW Starting Point

For a typical GW calculation, the LDA starting point is sufficient:

Notable exceptions - Silane:



M. Rohlfing and S.G. Louie Phys. Rev. B 62 4927 (2000).

GW Starting Point (silane)

	LDA	LDA+GW	COHSEX	COHSEX+GW
HOMO	-8.52	-12.80	- 13.2	-12.80
LUMO	-0.465	1.02	.1	.29
QP gap	8.06	13.82	13.3	13.10

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- Ge : cannot define occupations properly to perform GW calculations without “hack”
- LUMO : Mean-field wavefunction is poor, so matrix element of sigma not going to be good
- Solution : better mean field
  - COHSEX
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- Better mean field : GW gives semiconducting Ge, better describes silane LUMO

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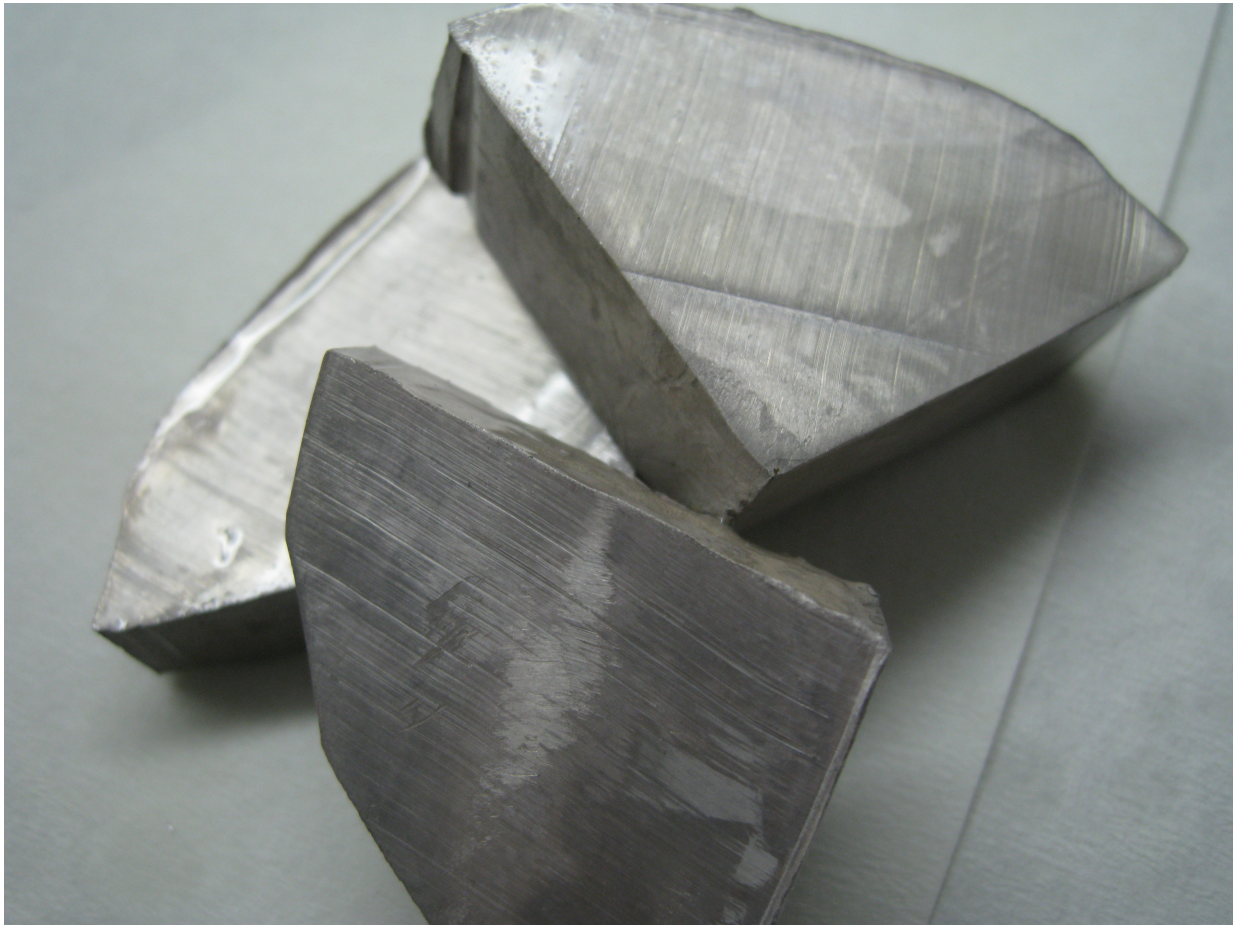
  - Hybrids
  - LDA+DMFT



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  - Generally bigger effect for alkali metals

BSE approximations

- Uncontrolled approximations:
  - Restricted interpolation (problematic for $\omega \to 0$ in metals)
  - Tamm-Dancoff approximation
  - Static screening

Si

Calculations with semicore electrons are becoming more common and important

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- Access to materials with shallow cores
  - TMDCs, TMOs, transition metals, etc.

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$$\Omega^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \omega_{\mathrm{p}}^2 \, \frac{(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2} \, \frac{\rho(\mathbf{G}-\mathbf{G}')}{\rho(\mathbf{0})}$$

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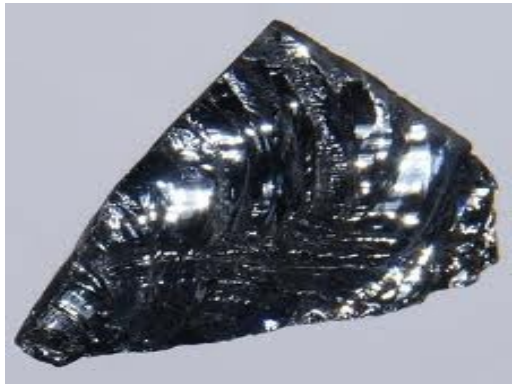

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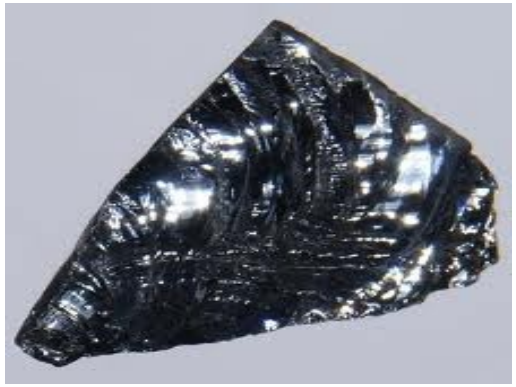

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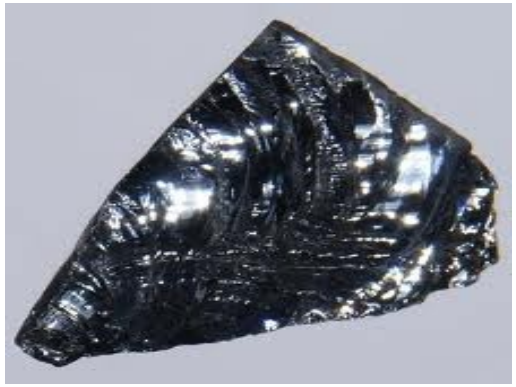

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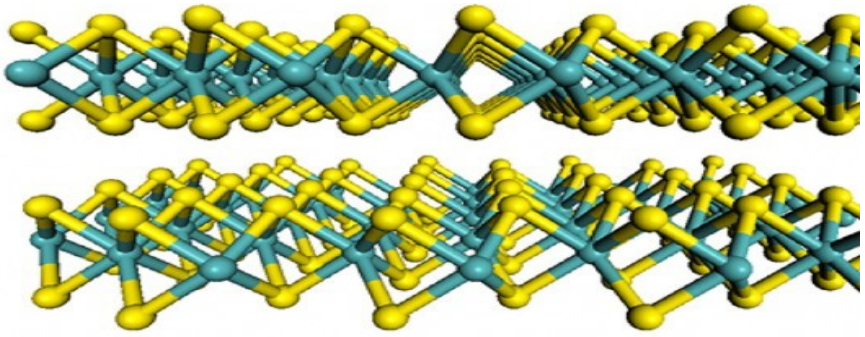

So...

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- Careful convergence with respect to all parameters crucial
  - Interdependence!
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“Problem areas” can be understood by physically analyzing underlying approximations

- Convergence : high bands have high g-vectors ↔ contribute to high energy, short wavelength screening
- Mean-field : LDA overbinds
- Semicore electrons : how to close to fermi level?

Be careful with convergence!

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1. Calculate the dielectric matrix with “infinite” number of empty states and g-vectors, test error in QP gaps as you vary number of bands used in CH summation

2. Test error as you vary the number of g-vectors in your dielectric matrix while using an infinite number of empty states and and infinite number of bands in CH summation

3. Test error as you vary the number of empty states used in dielectric matrix while using an infinite number of g-vectors and an infinite number of bands in the CH summation

Be careful with convergence!, BSE edition

- There are 4 convergence parameters in a typical BSE calculation:
  - # of k-points in the fine grid
  - # of bands in the fine grid
  - # of k-points in the coarse grid
  - # of bands in the coarse grid