Defects in Materials

Manish Jain

Department of Physics,
Indian Institute of Science,
Bangalore

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May 2016.

Outline of the talk

- Introduction.
  - Motivation.
  - Methods for calculating material properties.
- Defects in materials.
  - Why are defects challenging?
  - Oxygen vacancies in α-Alumina.
- Conclusions.

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- High-temperature structural ceramics

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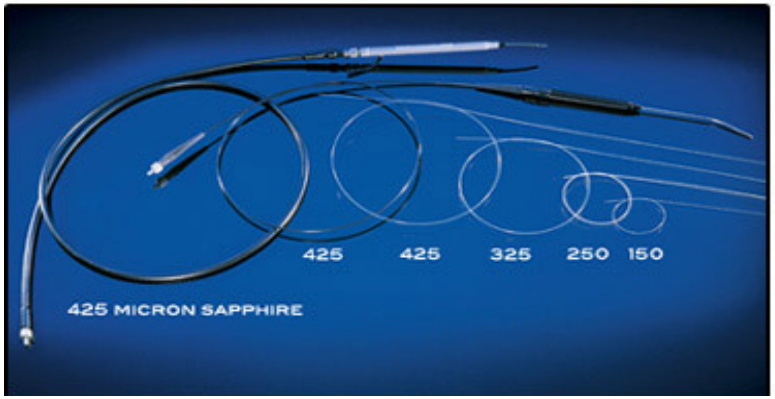

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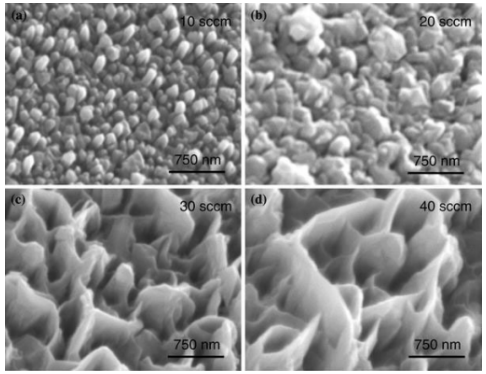

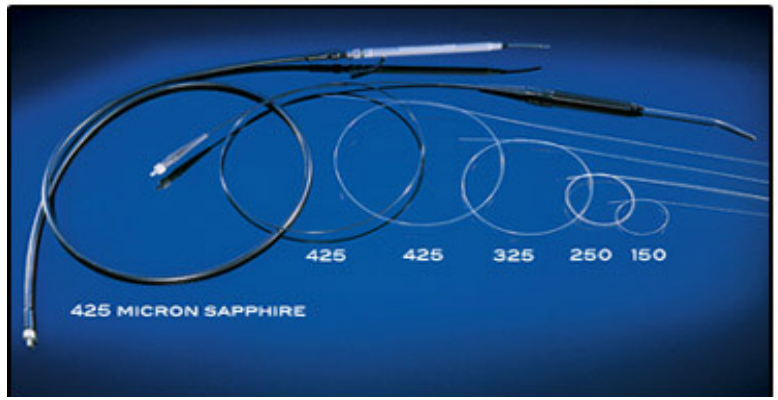

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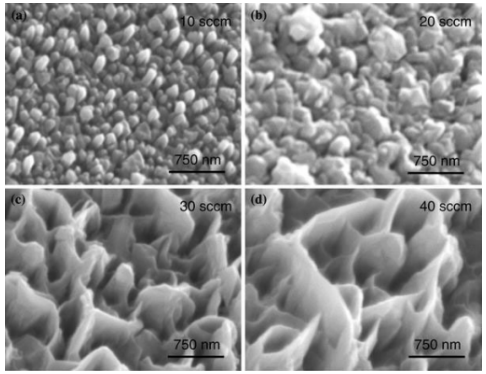

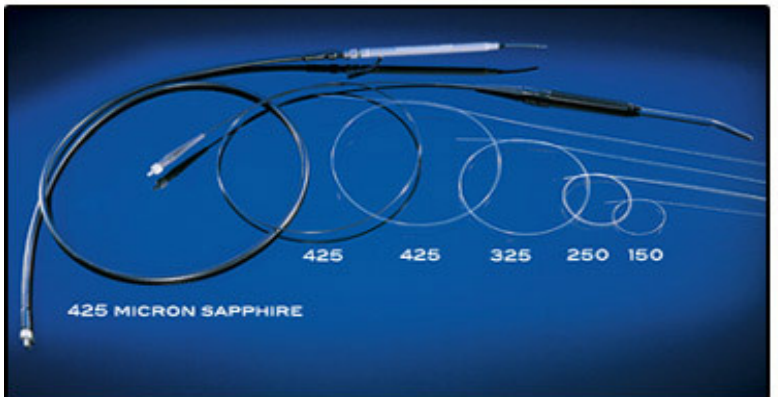

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- Optical devices
- Semiconductor manufacturing
- Mechanical usage

Importance of studying defects

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- Strongly dominate a wide variety of material properties i.e, optical, mechanical, electrical, and other transport properties.
- The performance and long-term stability of devices is often governed by the creation, transport and annihilation of point defects.
- Product manufacturing process can be improved by studying the defect formation at different environmental conditions.

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- Density functional theory is the "standard model" for understanding ground-state properties.
- Total energy is a functional of the charge density.
- Kohn-Sham formulation: Map the interacting many-electron problem to non-interacting electrons moving in a self-consistent field.

$$\Big(-\frac{\nabla^2}{2} + \mathrm{V_{ionic}}(\mathbf{r}) + \mathrm{V_{Hartree}}(\mathbf{r}) + \mathrm{V_{xc}}(\mathbf{r}) \Big)\psi(\mathbf{r}) = \epsilon\,\psi(\mathbf{r})$$

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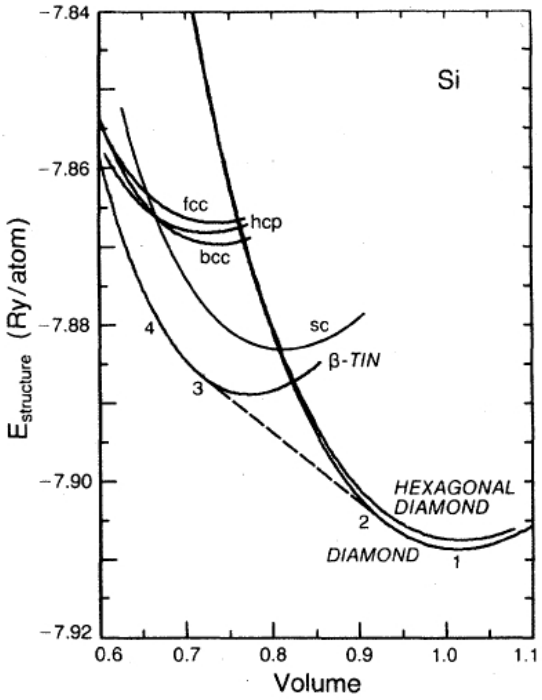
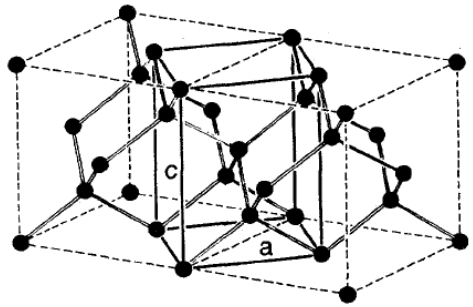
Local density approximation
Generalized gradient approximation

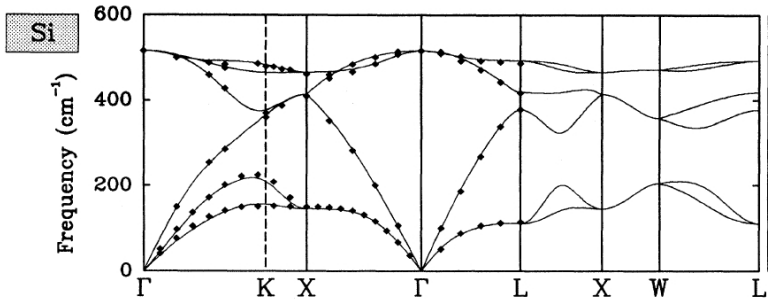
Methods – Ground-state properties



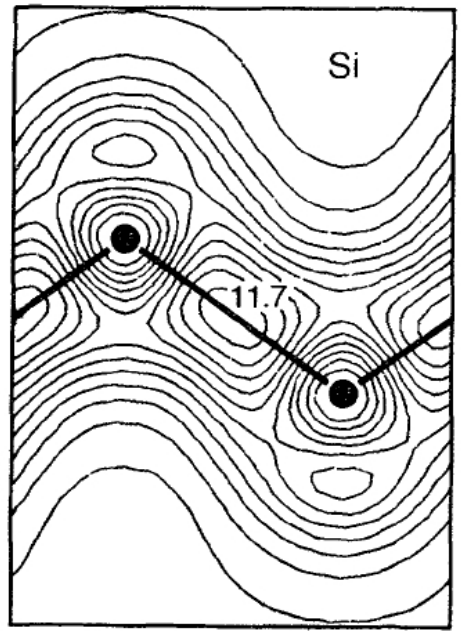
Phase transitions[1]



Crystal Structure[1]



Phonons[2]



Charge density[1]

[1] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).
[2] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

Methods – Excited-state properties

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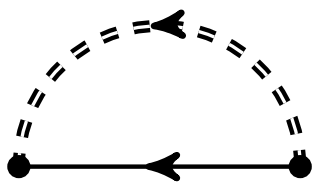
- Concept and formalism of interacting particle Green's function (G).
- Many-body perturbation theory is the "standard model" for understanding excited-state properties.

$$\mathrm{G}^{-1} = \mathrm{G}_{\mathrm{DFT}}^{-1} + \Sigma - \mathrm{V}_{\mathrm{xc}}$$

- GW approximation to the self-energy (Σ).

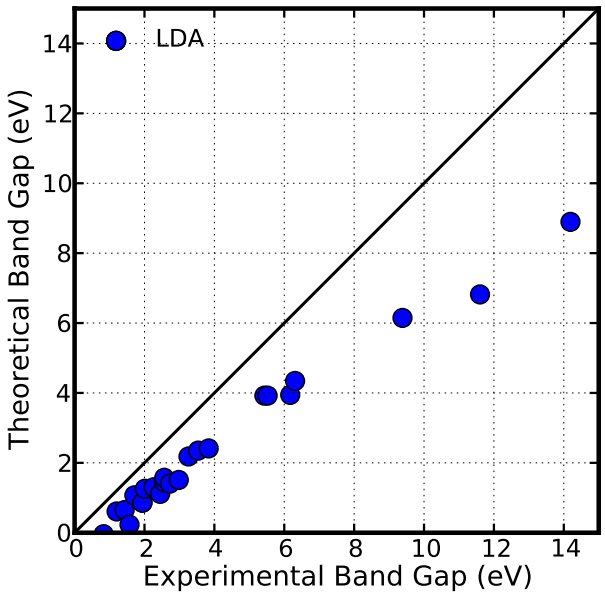
$$\Sigma = \quad = i\mathrm{GW}$$



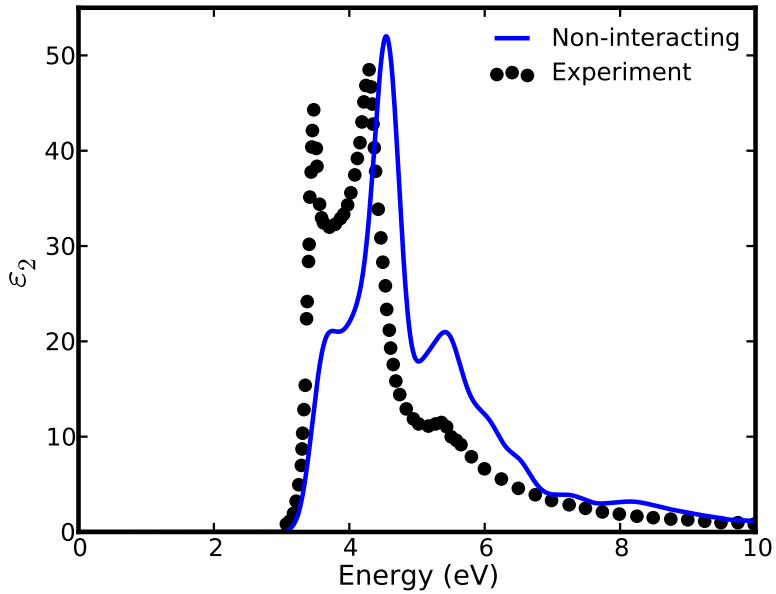
$$\mathrm{W} = \varepsilon^{-1}\, v$$

Methods – Excited-state properties

Materials: InSb, InAs, Ge, GaSb, Si, InP, GaAs, CdS, AlSb, AlAs, CdSe, CdTe, BP, SiC, C_{60}, GaP, AlP, ZnTe, ZnSe, c-GaN, w-GaN, InS, w-BN, c-BN, diamond, w-AlN, LiCl, Fluorite, LiF



Quasiparticle Gap[1]



Optical absorption[2]

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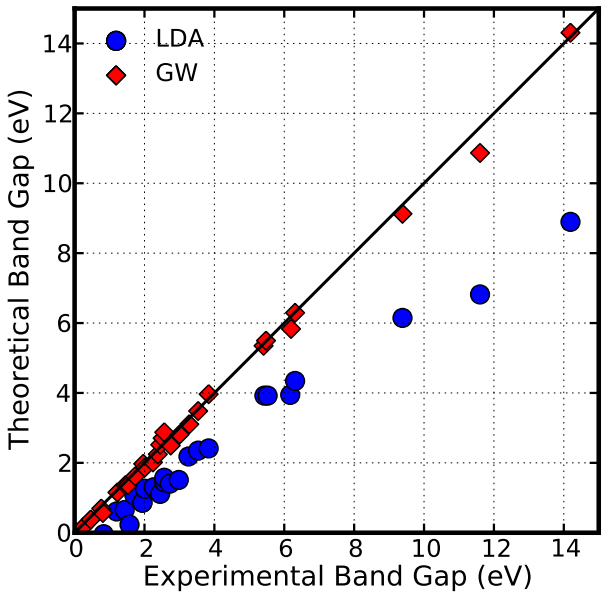

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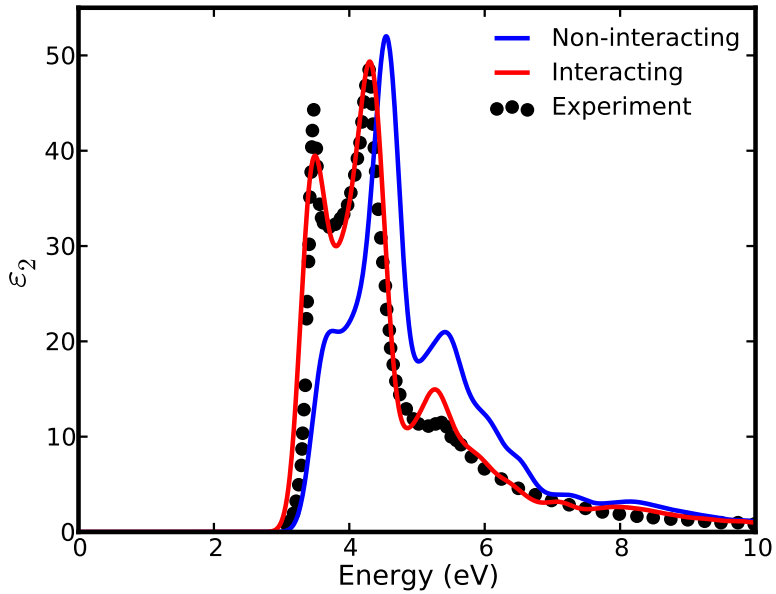

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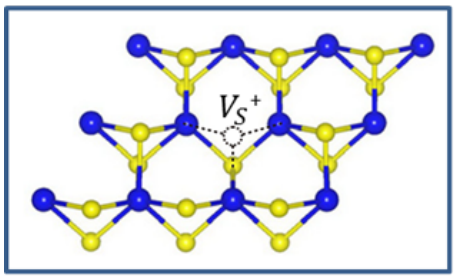
Formation energy and charge transition level

$$\mathrm{E}_{\mathrm{q}}^{f}[\vec{\mathrm{R}}_{\mathrm{q}}](\mathrm{E}_{\mathrm{F}}) = \mathrm{E}_{\mathrm{q}}[\vec{\mathrm{R}}_{\mathrm{q}}] - \mathrm{E}_{\mathrm{ref}} + \mu_S + \mathrm{q}(\mathrm{E}_{\mathrm{F}} + \mathrm{E}_{\mathrm{v}})$$



MoS_2 with mono-vacancy of sulfur, V_S^+

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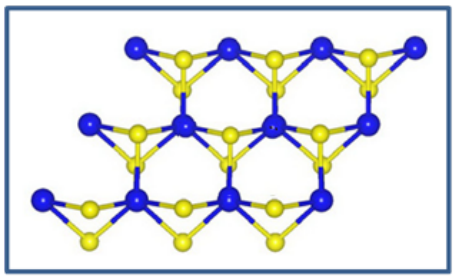
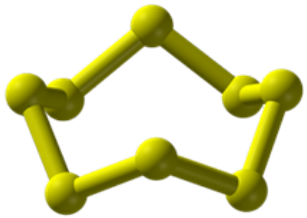


Pristine MoS_2

$+ \frac{1}{8}$



Orthorhombic sulfur, S_8

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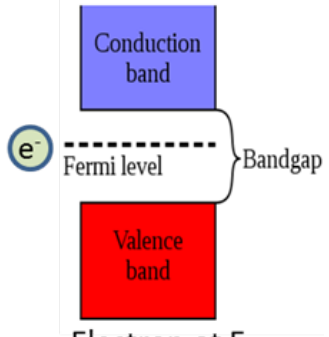

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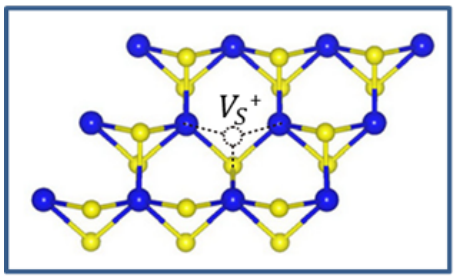

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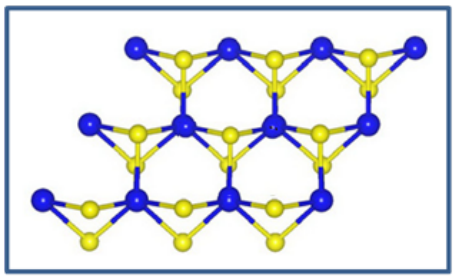

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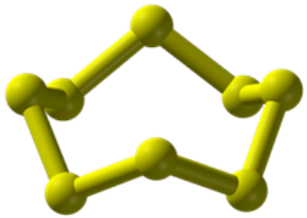

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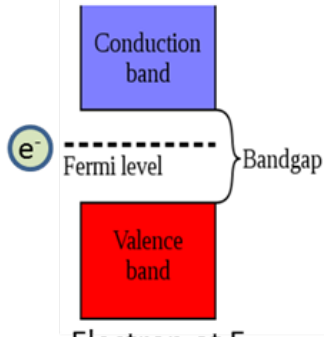

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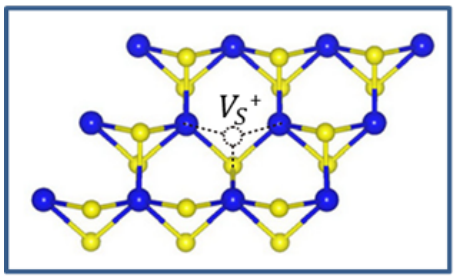

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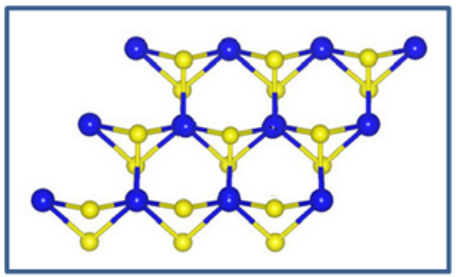

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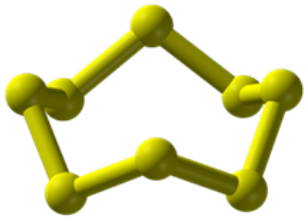

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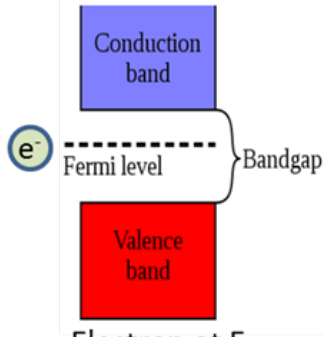

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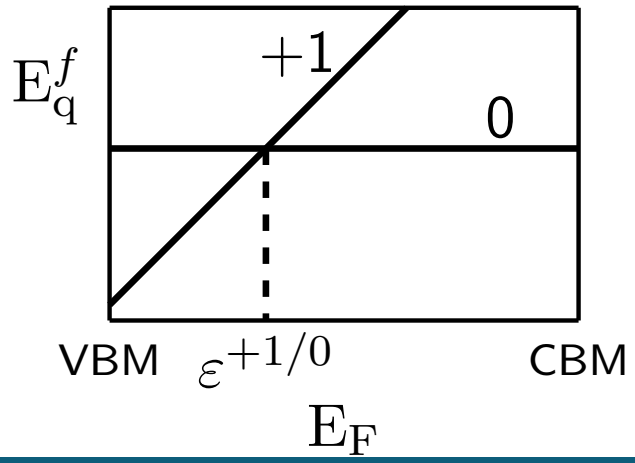

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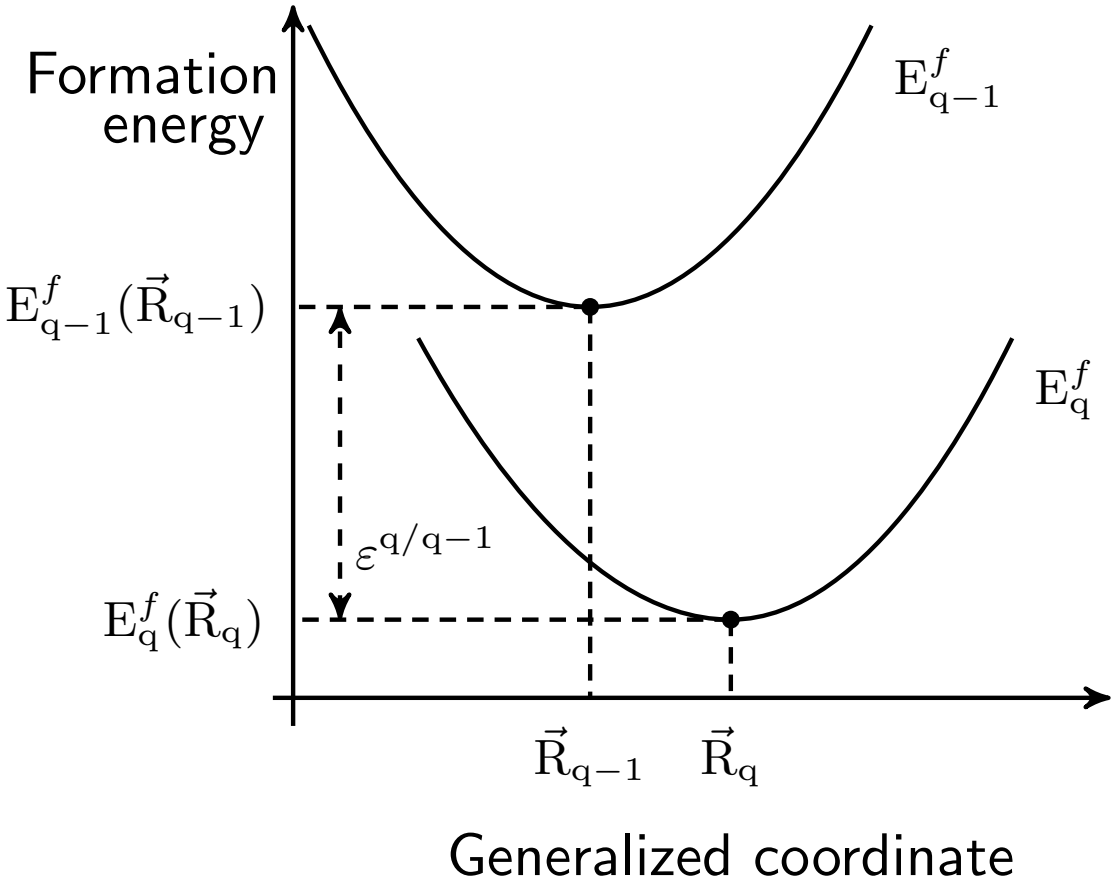
DFT + GW methodology.



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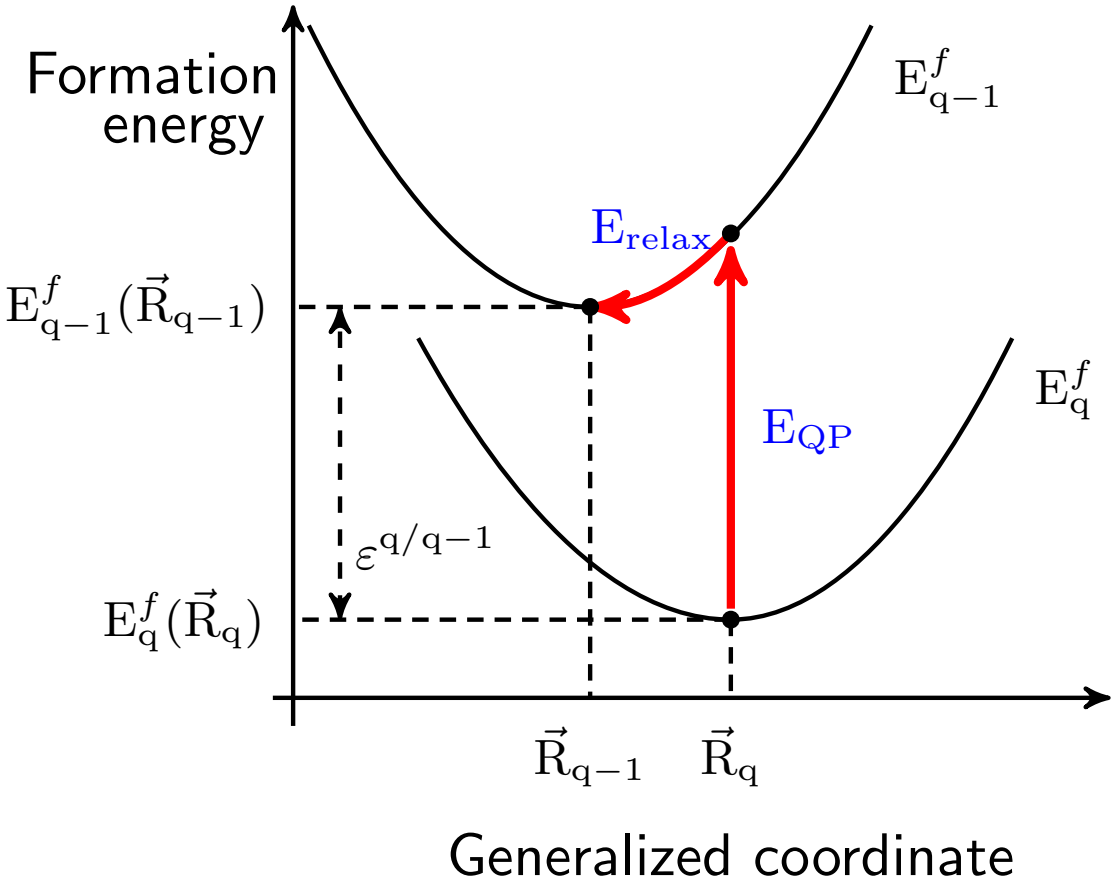

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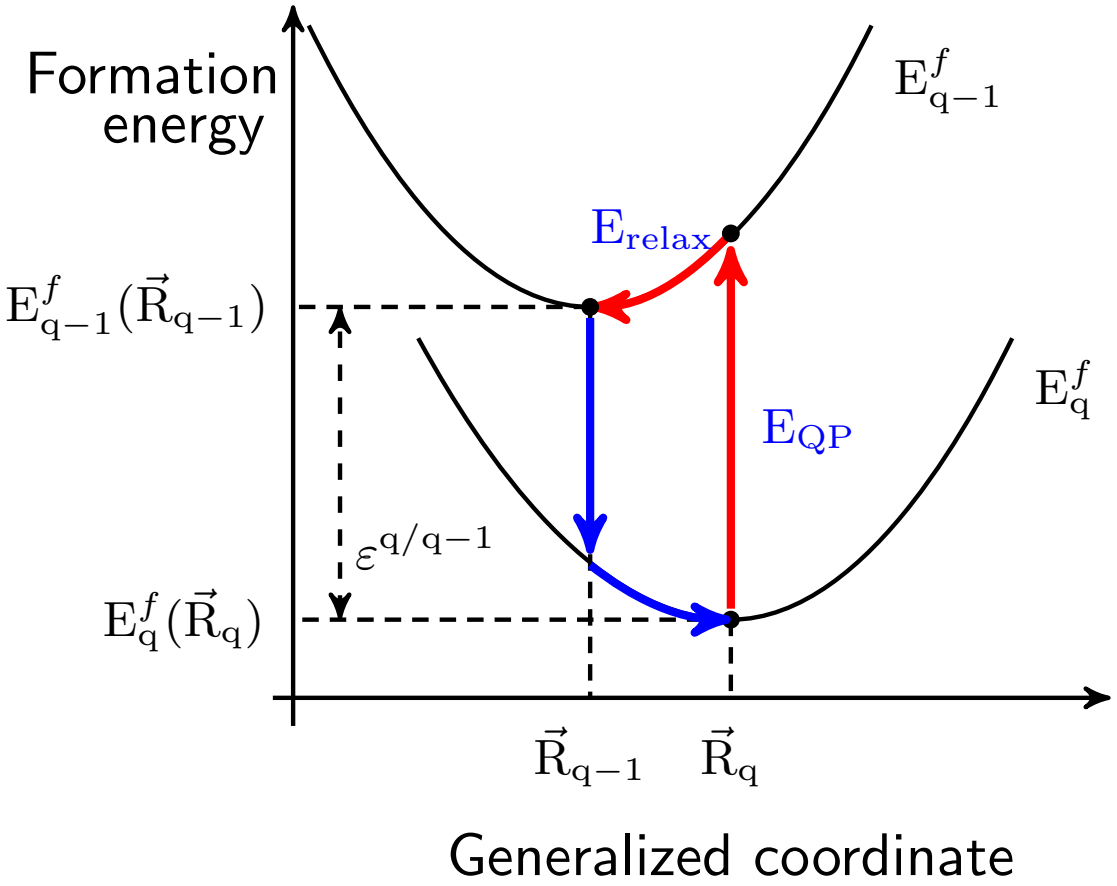

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Why are defects challenging?

- Potentially strong electron-electron correlations.
  - Can be open-shell systems.
  - Multiple localized, interacting electrons.
- Lattice relaxation effects.
- Screening from the host.
  - Mimicking the system by isolated cluster may be incorrect.
- Experiments often involve excited-state properties (deep level transient spectroscopy or optical absorption etc.)
- Computational difficulty – isolated defect.

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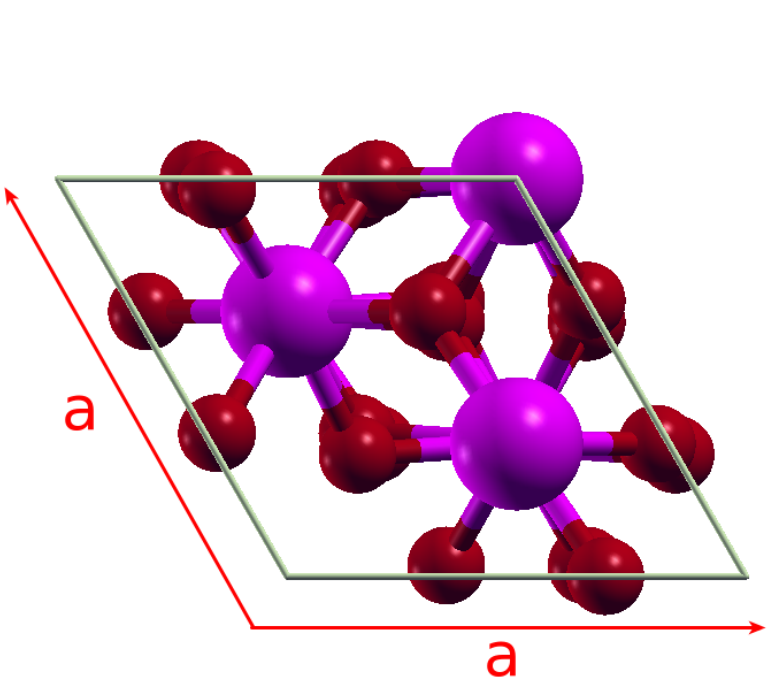
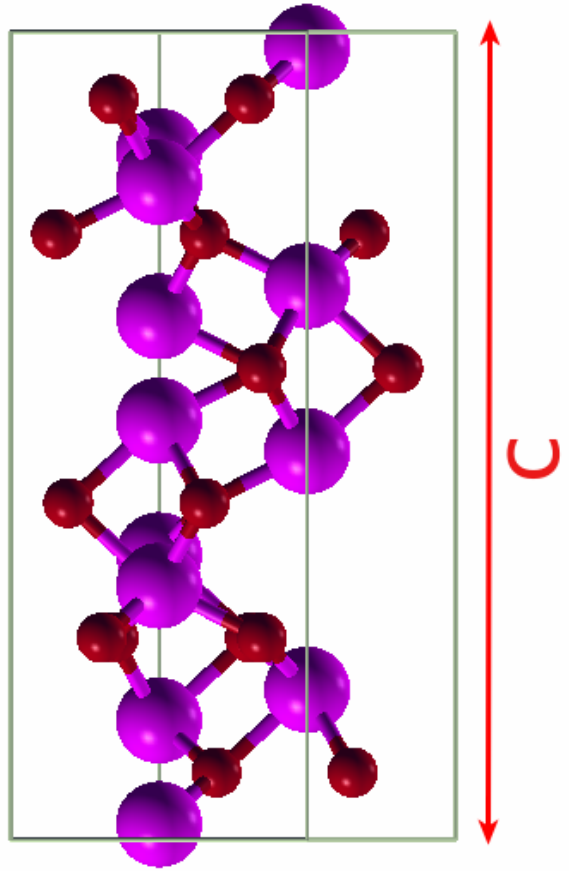
Structure of α-alumina





Hexagonal unit cell (space group $R\bar{3}C$) contains 30 atoms

Details of our calculation: α-alumina

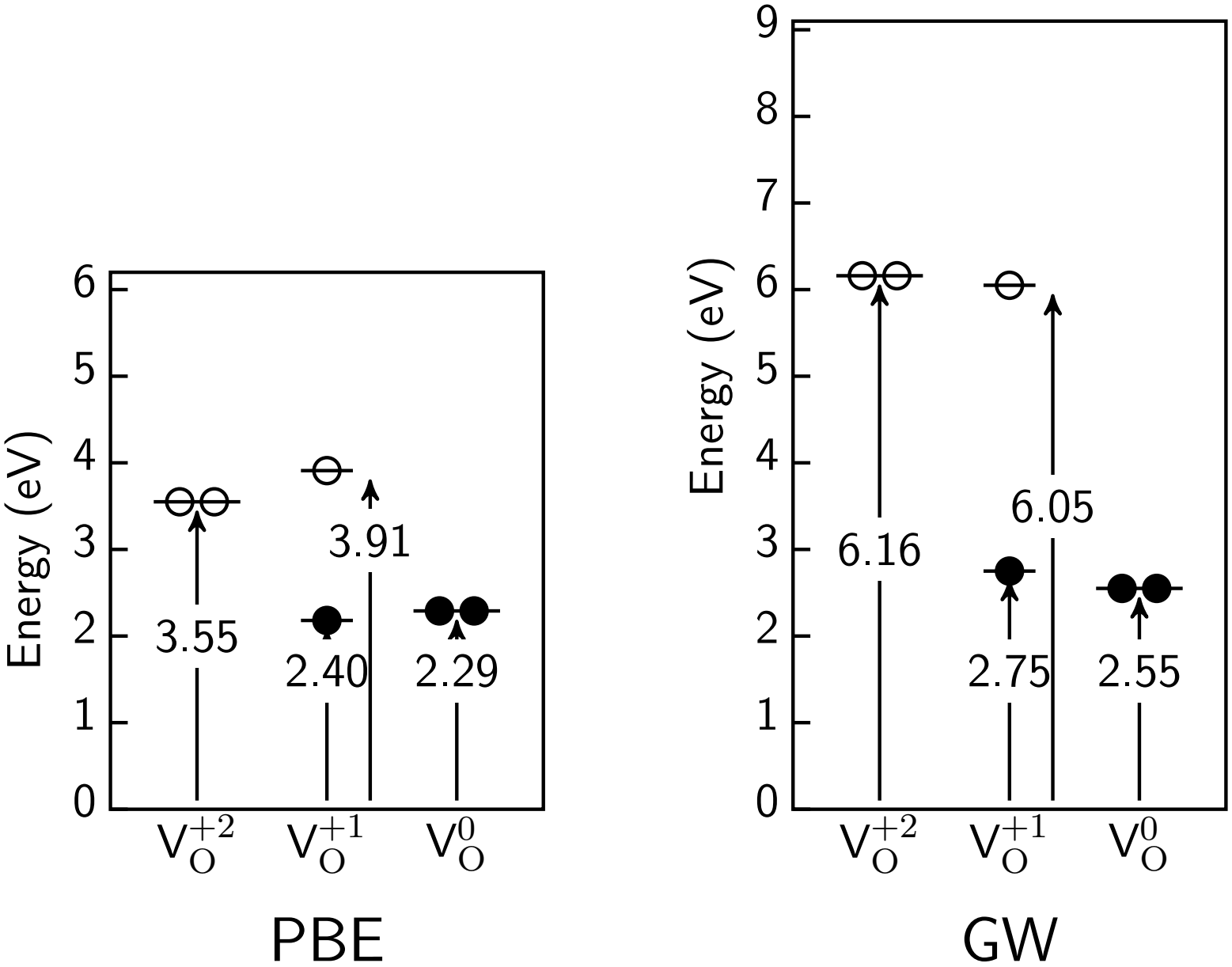
DFT calculation

- Quantum Espresso package
- Norm-conserving Pseudopotentials
- PBE exchange correlation
- Wavefunction cutoff: 75 Ry
- 2x2x2 kgrid for 120 atom supercell (2x2x1)
- Only Γ point for 270 atom supercell (3x3x1)

GW calculation

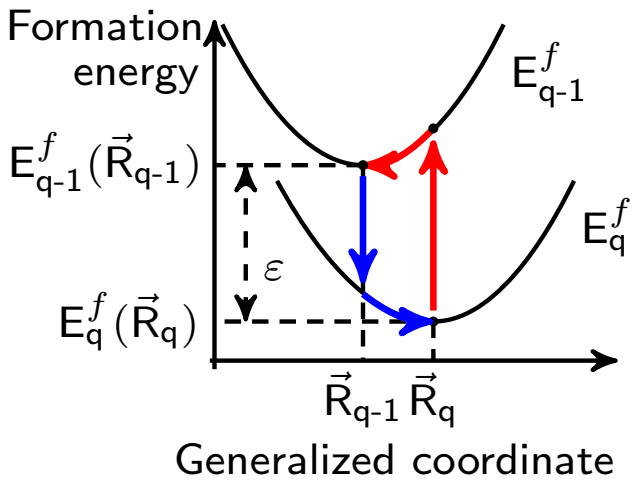
- BerkeleyGW package
- 25 Ry cutoff for static dielectric matrix
- For finite frequency used GPP (Generalized Plasmon Pole)
- 4000 bands for 120 atom supercell
- 9000 bands for 270 atom supercell

PBE and quasiparticle level diagram - V_O



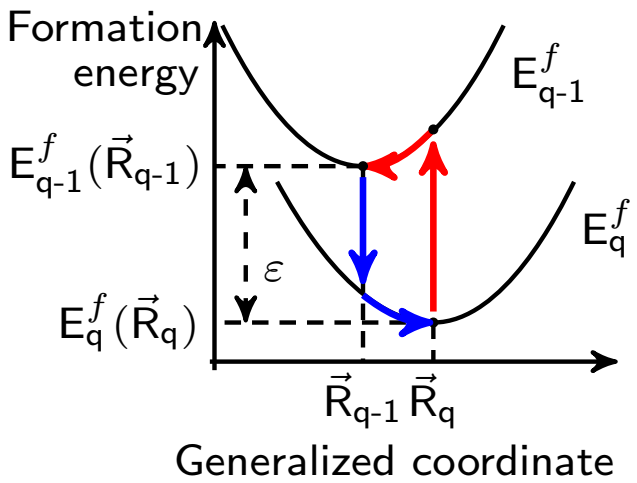
Results:Charge transition levels

CT levels	P1	P2	Δ
$\epsilon_{120}^{+1/0}$	4.95	3.65	1.30
$\epsilon_{270}^{+1/0}$	4.87	3.79	1.08
$\epsilon_{120}^{+2/+1}$	5.21	3.79	1.42
$\epsilon_{270}^{+2/+1}$	5.05	3.85	1.20



Results:Charge transition levels

	without correction			with correction			
CT levels	P1	P2	Δ	P1	P2	Δ	Mean
$\epsilon_{120}^{+1/0}$	4.95	3.65	1.30	3.77	3.65	0.12	3.71
$\epsilon_{270}^{+1/0}$	4.87	3.79	1.08	3.93	3.79	0.14	3.86
$\epsilon_{120}^{+2/+1}$	5.21	3.79	1.42	2.86	2.62	0.24	2.74
$\epsilon_{270}^{+2/+1}$	5.05	3.85	1.20	3.17	2.91	0.26	3.04



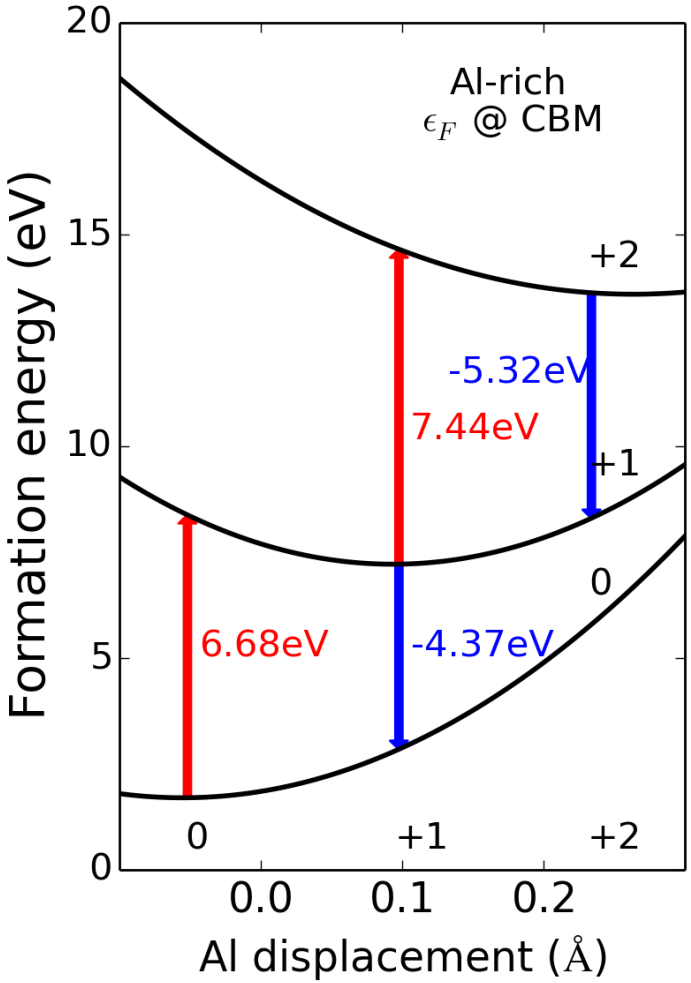
Results:Comparison with literature

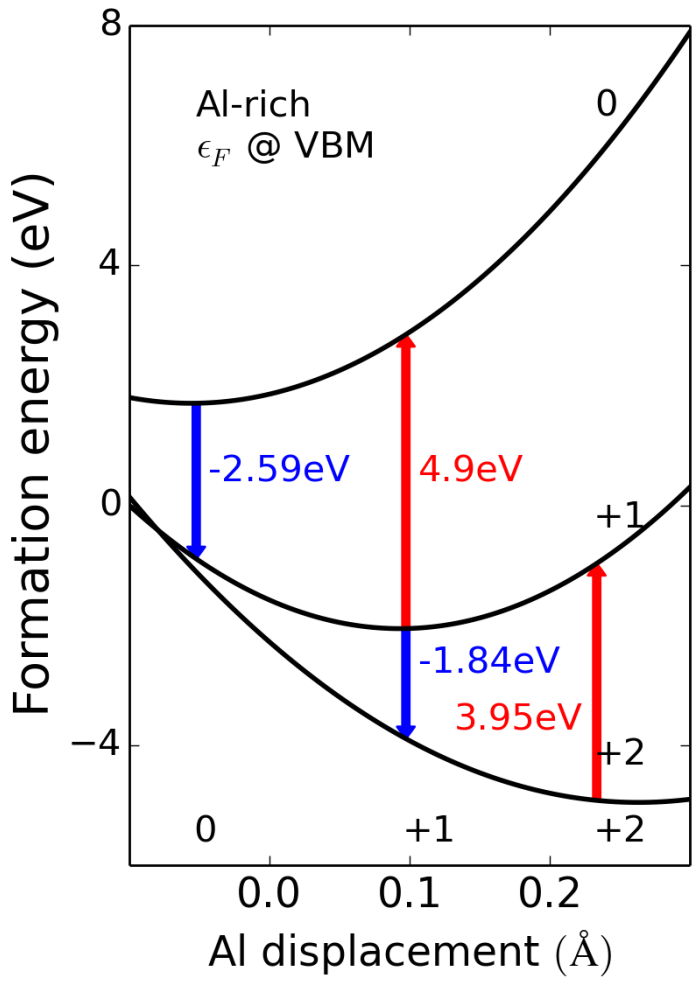
CT levels	DFT+GW	HSE[1]	GGA[2]	GGA
$\epsilon^{+1/0}$	3.8 $\pm$ 0.1	4.1	5.2	5.65
$\epsilon^{+2/+1}$	2.9 $\pm$ 0.1	3.2	5.0	4.35

- Ref. [1] HSE calculation with a band gap of 9.2 eV.
- Ref. [2] GGA with a scissors shift.

[1] M. Choi, A. Janotti and C. G. van de Walle, J. Appl. Phys. **113**, 44501 (2013).
[2] K. Matsunaga et al, Phys. Rev. B **68**, 85110 (2003).

Configuration coordinate diagram





	V_O^0	V_O^{+1}	V_O^{+2}
Al (Nearest Neighbors)	-0.052	0.098	0.234
O (Next Nearest Neighbors)	-0.011	-0.034	-0.067

Comparison to experiments

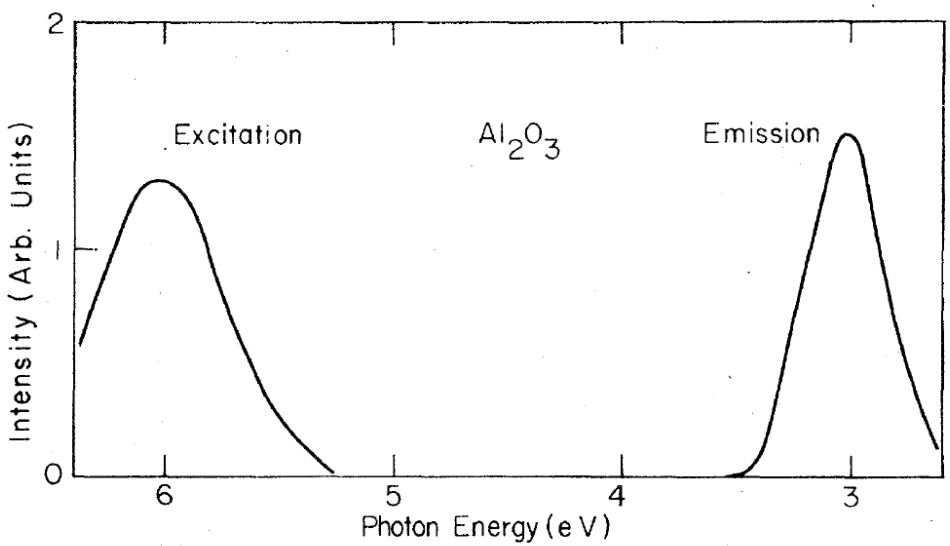
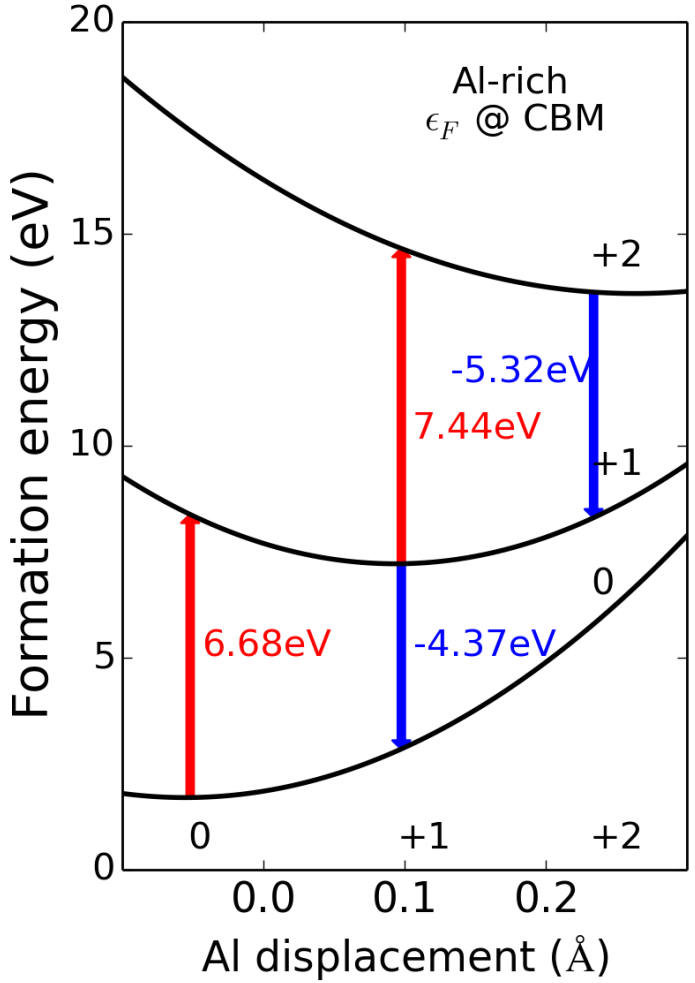


FIG. 2. Excitation and emission spectra of the F center from subtractively colored Al_2O_3 measured at 300 K.



K. H. Lee and J. H. Crawford, Phys. Rev. B **19**, 3217 (1979).

Outline of the talk

- Introduction.
  - Motivation.
  - Methods for calculating material properties.
- Defects in materials.
  - Why are defects challenging?
  - Oxygen vacancies in α-Alumina.
- Conclusions.

Conclusions

- DFT and GW are powerful techniques to calculate ground-state and excited-state properties of materials from first principles.
- DFT+GW method combines these to calculate properties of defects from first principles.
- Used DFT+GW to understand and charaterize F centers in α-alumina.

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Tathagata Biswas

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