materials design

UGM 2020 Training Series

MedeA VASP 6: Random Phase Approximation, Electron-Phonon Coupling, etc.

Materials Design

October 20th, 2020

Materials Design UGM

Training & Support Team

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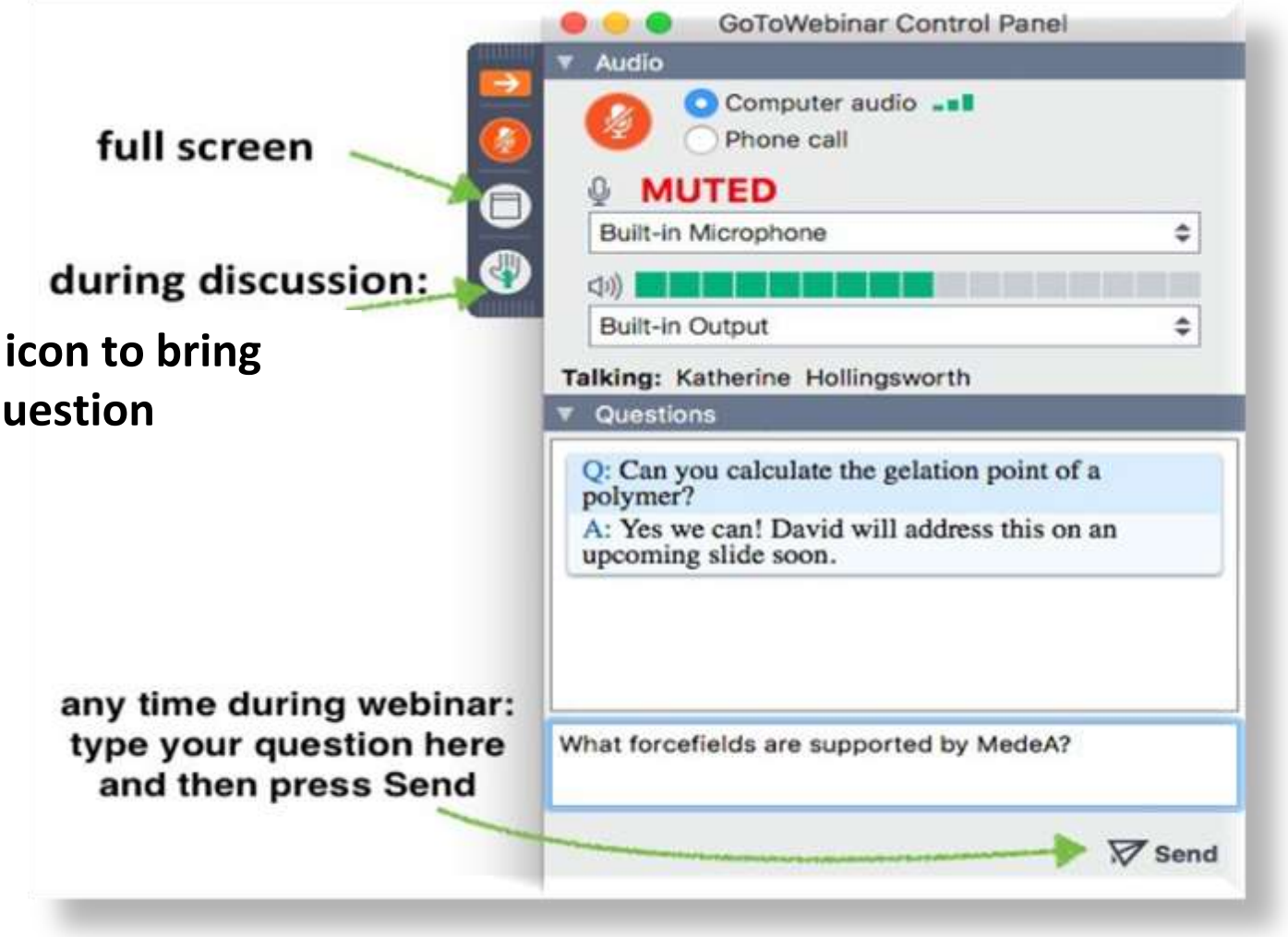
Ray Shan

Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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UGM 2020 Training Series

MedeA VASP 6: Random Phase Approximation, Electron-Phonon Coupling, etc.

Materials Design

October 20th, 2020

Outline

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- MedeA VASP: Overview and General Guidelines
- ACFDT-RPA: Heats of Formation
- Electron Phonon Coupling: Band Gap as a Function of Temperature
- Optical Properties: Color of Materials
- Conclusions

MedeA VASP 6: Overview

Methods in MedeA VASP

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- **DFT**
  - **LDA**
  - GGA-AM05
  - **GGA-PBEsol**
  - **GGA-PBE**
  - **GGA-rPBE**
  - GGA-BLYP
- **Van der Waals DFT**
  - **optB86b-vdW**
  - optB88-vdW
  - optPBE-vdW
  - BEEF-vdW
  - rev-vdW-DF2
  - rPW86-vdW2
  - revPBE-vdW
  - SCAN + rVV10
- **Meta GGA**
  - **revTPSS**
  - TPSS
  - **SCAN**
  - MS2
  - MS1
  - MS0
  - M06-L
  - **MBJLDA**
- **Hybrid Functionals**
  - **HSE06**
  - **PBE0**
  - B3LYP
  - DDH/DSH
- **Screened Exchange**
- **Hartree-Fock**
- **Time dependent DFT**
- **GW/ low scaling GW**
  - **Quasiparticle shifts**
  - Excitonic effects (Bethe-Salpeter)
  - Frequency dependent self-energy
- **MP2**
- **RPA/ low scaling RPA**

Van der Waals correction:

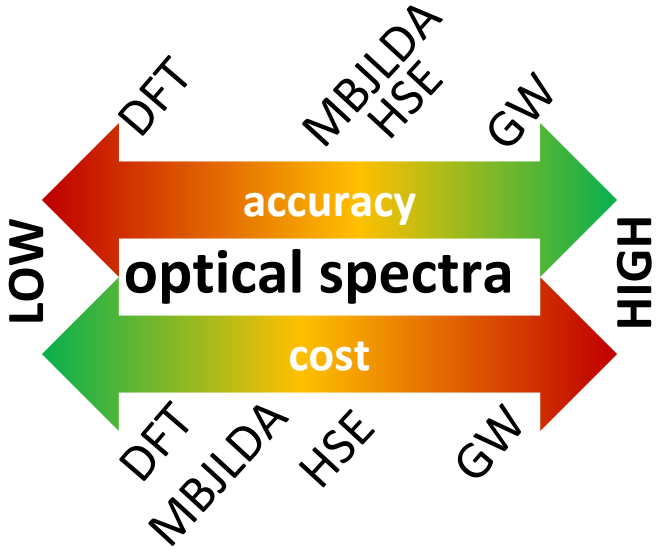
- DFT-D3 zero-damping
- DFT-D3 BJ-damping
- Tkatchenko-Scheffler
- Tkatchenko-Scheffler + SCS
- Many-body dispersion energy
- DFT-dDsC dispersion correction
- DFT-D2 forcefield (Grimme)

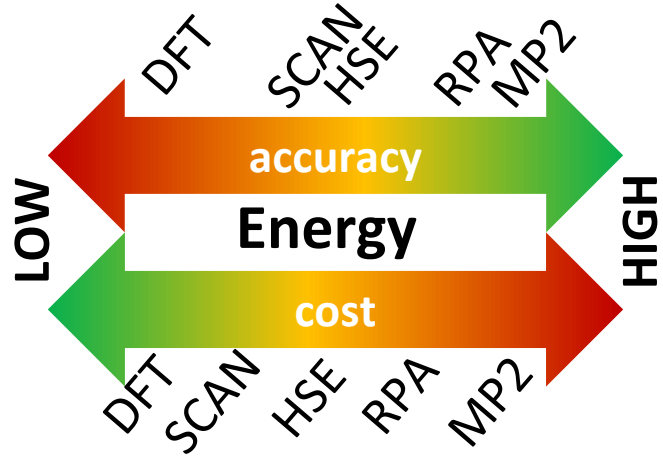
LSDA+U

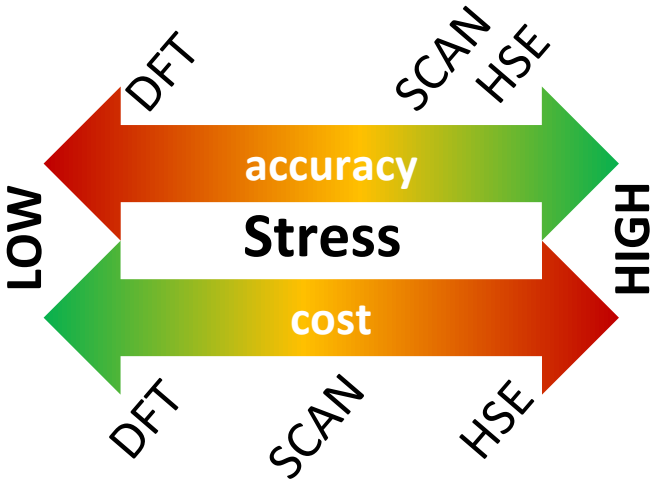
- Simplified LSDA+U
- Rotational invariant LSDA+U
- Rotational invariant LDA+U

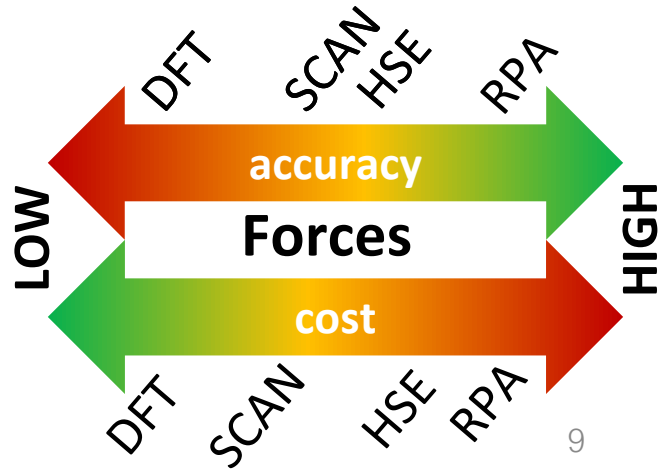
How to Choose: Optimum Method

- How accurate does the method need to be for your property?
- **Accuracy of method**
  vs.
  Applicability for many k-points/ larger systems
- Don't deviate too much from the well-trodden path
  - DFT: LDA, PBE, PBEsol
  - Hybrid: HSE06, PBE0
  - meta-GGA: SCAN, MBJLDA revTPSS
- Only electronic structure: GW, MBJLDA
- Energies: RPA, HSE, SCAN, DFT ..
- Forces: low scaling RPA, SCAN, HSE, DFT
- Stress: HSE, SCAN, DFT

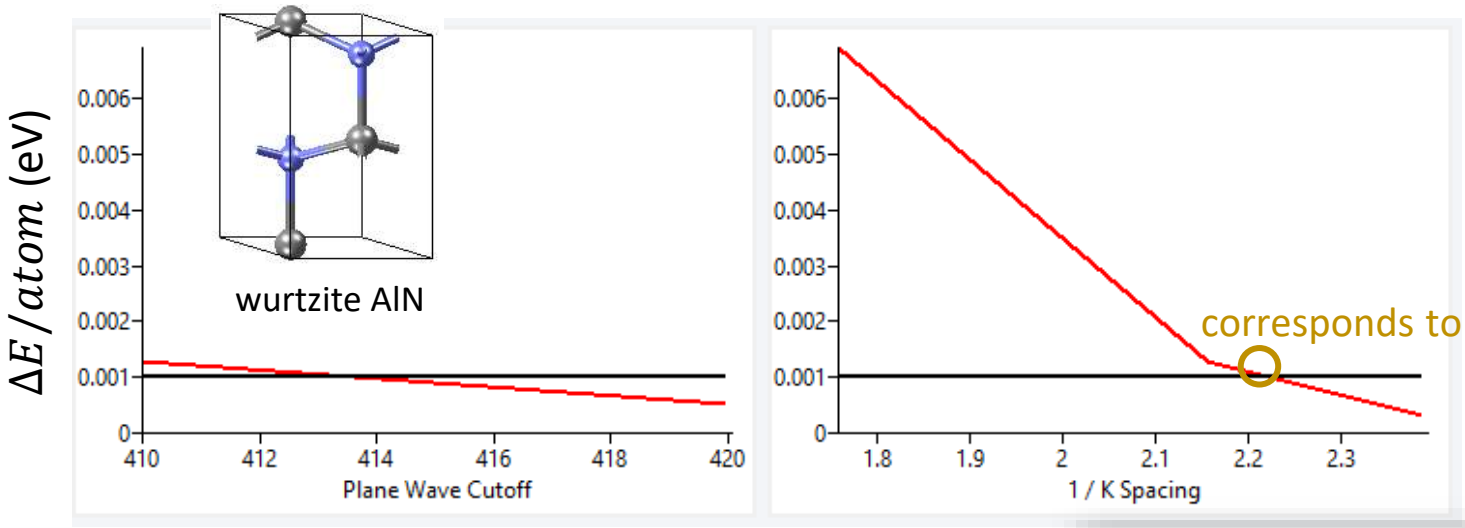








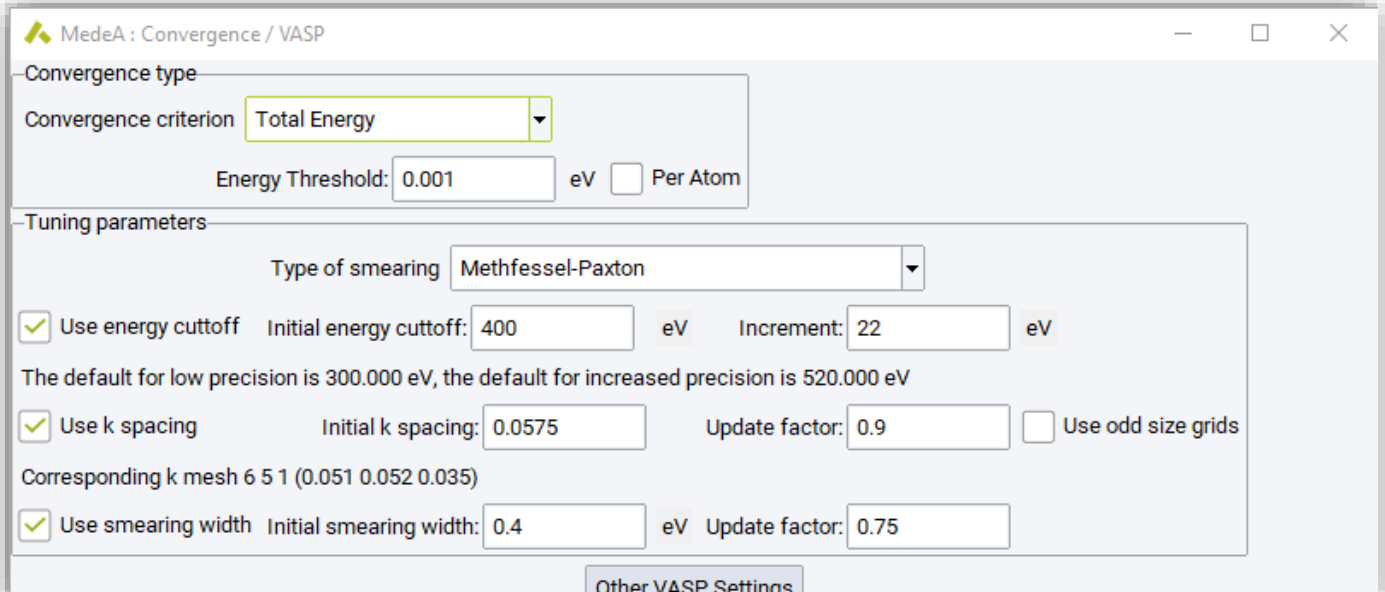
How to Choose: k-points and Planewave Cutoff Energies




```
-------------------------------------------------------
                The final, converged parameters
-------------------------------------------------------
     Smearing width:     0.225 eV
   Planewave cutoff:   420.000 eV
          k spacing:     0.418 1/Ang

-------------------------------------------------------
                Results for the converged calculation
-------------------------------------------------------
```

- Check convergence of the property that you are interested in
- Always compare like with like:
  - Same k-spacing
  - Same planewave cutoff energy
  - Same integration scheme/smearing width
  - Same method/functional/potentials



Obtain Accurate Heats of Formation for SiC with ACFDT-RPA

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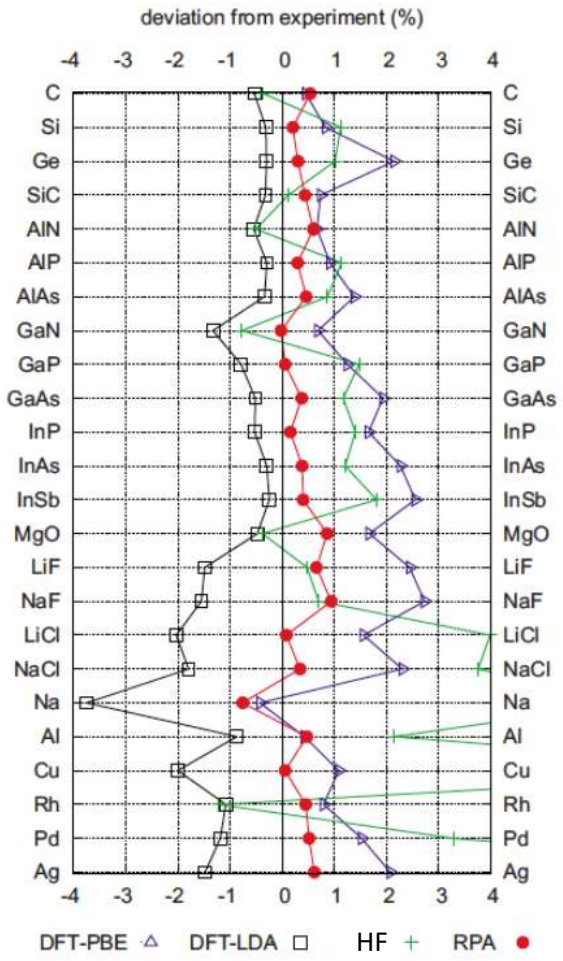
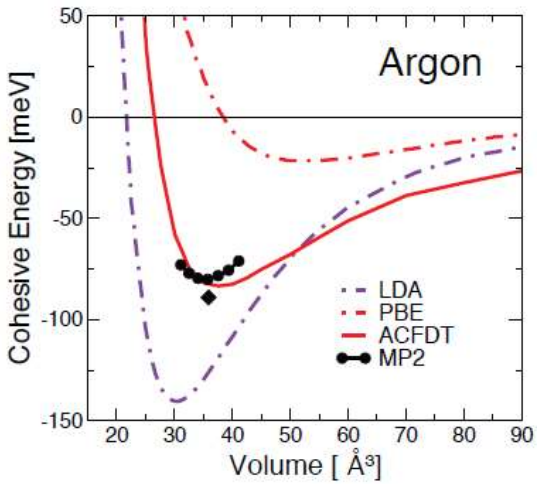
Lattice parameters

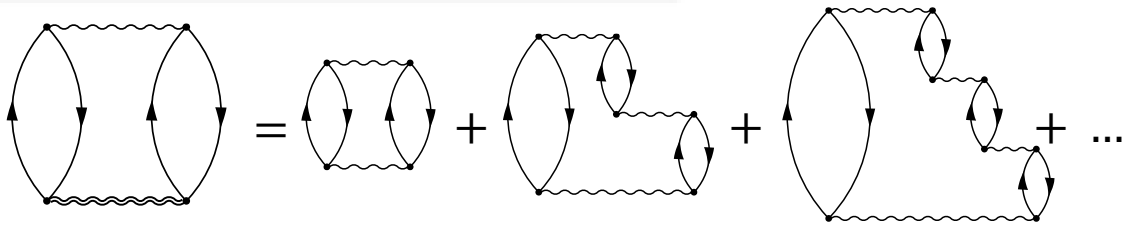


Heats of formation

	PBE	RPA	EXP
LiF	570	609	621
NaF	522	567	576
NaCl	355	405	413
MgO	516	577	603
MgH_2	52	72	78
AlN	262	291	321
SiC	51	**64**	**69**

Van der Waals interactions





2nd. order 3rd. order 4th. order

Introduction

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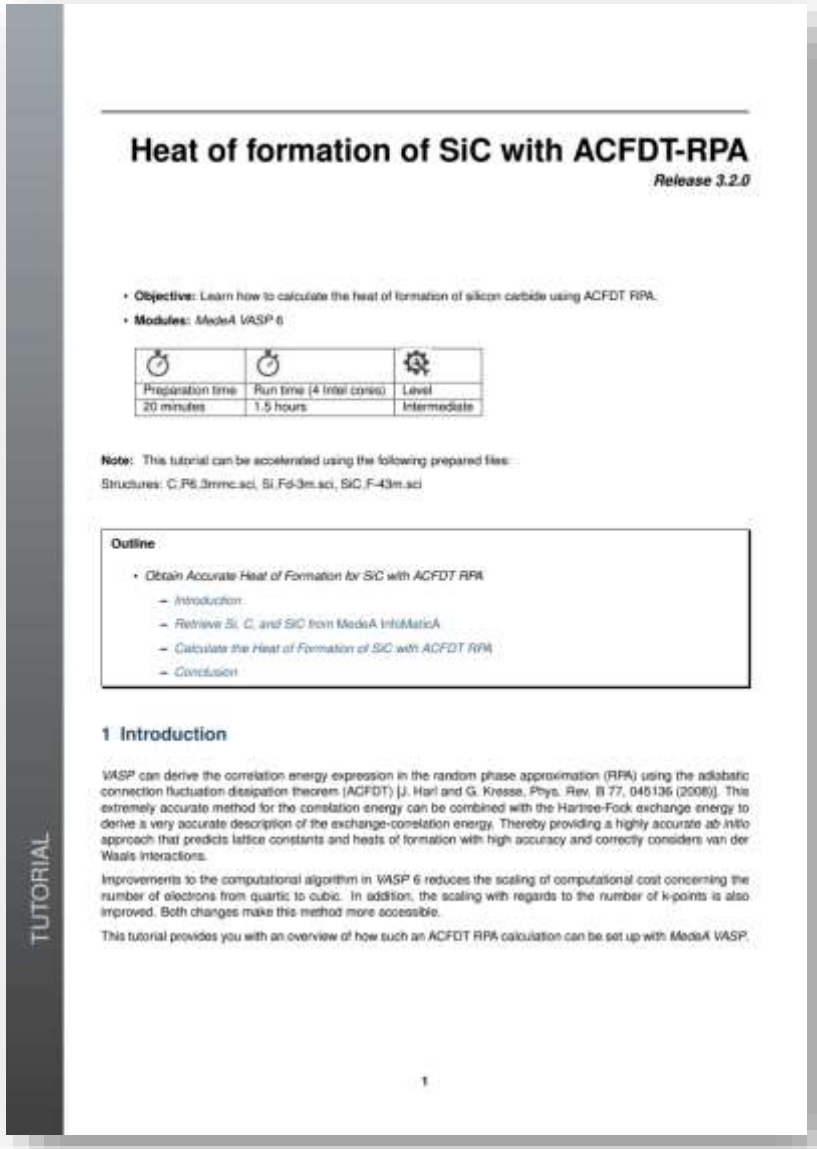
- See *MedeA* tutorial Heat of formation of SiC with ACFDT-RPA at http://my.materialsdesign.com/tutorials

- **Objective:** Learn how to calculate the heat of formation of silicon carbide using ACFDT-RPA.

- **Modules:** *MedeA VASP 6*

Preparation time	Run time (4 Intel cores)	Level
20 minutes	1.5 hours	Intermediate



TUTORIAL

Heat of formation of SiC with ACFDT-RPA

Release 3.2.0

- **Objective:** Learn how to calculate the heat of formation of silicon carbide using ACFDT RPA.
- **Modules:** *MedeA VASP 6*

Preparation time	Run time (4 Intel cores)	Level
20 minutes	1.5 hours	Intermediate

Note: This tutorial can be accelerated using the following prepared files:
Structures: C_P6_3mmc.sci, Si_Fd-3m.sci, SiC_F-43m.sci

Outline

- *Obtain Accurate Heat of Formation for SiC with ACFDT RPA*
  - *Introduction*
  - *Retrieve Si, C, and SiC from MedeA InfoMaticA*
  - *Calculate the Heat of Formation of SiC with ACFDT RPA*
  - *Conclusion*

1 Introduction

VASP can derive the correlation energy expression in the random phase approximation (RPA) using the adiabatic connection fluctuation dissipation theorem (ACFDT) [J. Harl and G. Kresse, Phys. Rev. B 77, 045136 (2008)]. This extremely accurate method for the correlation energy can be combined with the Hartree-Fock exchange energy to derive a very accurate description of the exchange-correlation energy. Thereby providing a highly accurate *ab initio* approach that predicts lattice constants and heats of formation with high accuracy and correctly considers van der Waals interactions.

Improvements to the computational algorithm in VASP 6 reduces the scaling of computational cost concerning the number of electrons from quartic to cubic. In addition, the scaling with regards to the number of k-points is also improved. Both changes make this method more accessible.

This tutorial provides you with an overview of how such an ACFDT RPA calculation can be set up with *MedeA VASP*.

1

Procedure Outline

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1. Retrieve SiC (F-43m), Si (Fd-3m) and C (P6_3/mmc)
2. Define and run the ACFDT-RPA calculation
3. Calculate the heat of formation from ACFDT-RPA total energies

Results

- Use the JobServer web-interface to open the relevant **Job.out** files

```
 ACFDT-RPA correlation energy:             -12.219715 eV for Si2
      Hartree-Fock total energy:             -18.509282 eV for Si2
Correction for partial occupancy:              -0.000000 eV for Si2
------------------------------------------------------------------
          ACFDT-RPA total energy:             -30.728997 eV for Si2

Electronic contributions:
                          Empirical Formula          Cell
                                    Si            (Si)8
                          --------------- ---------------
        ACFDT-RPA Energy       -1482.448      -11859.587 kJ/mol
```

```
 ACFDT-RPA correlation energy:             -27.349385 eV for C4
      Hartree-Fock total energy:             -61.141280 eV for C4
Correction for partial occupancy:              -0.000000 eV for C4
------------------------------------------------------------------
          ACFDT-RPA total energy:             -88.490665 eV for C4

Electronic contributions:
                          Empirical Formula          Cell
                                    C             (C)4
                          --------------- ---------------
        ACFDT-RPA Energy       -2134.512       -8538.049 kJ/mol
```

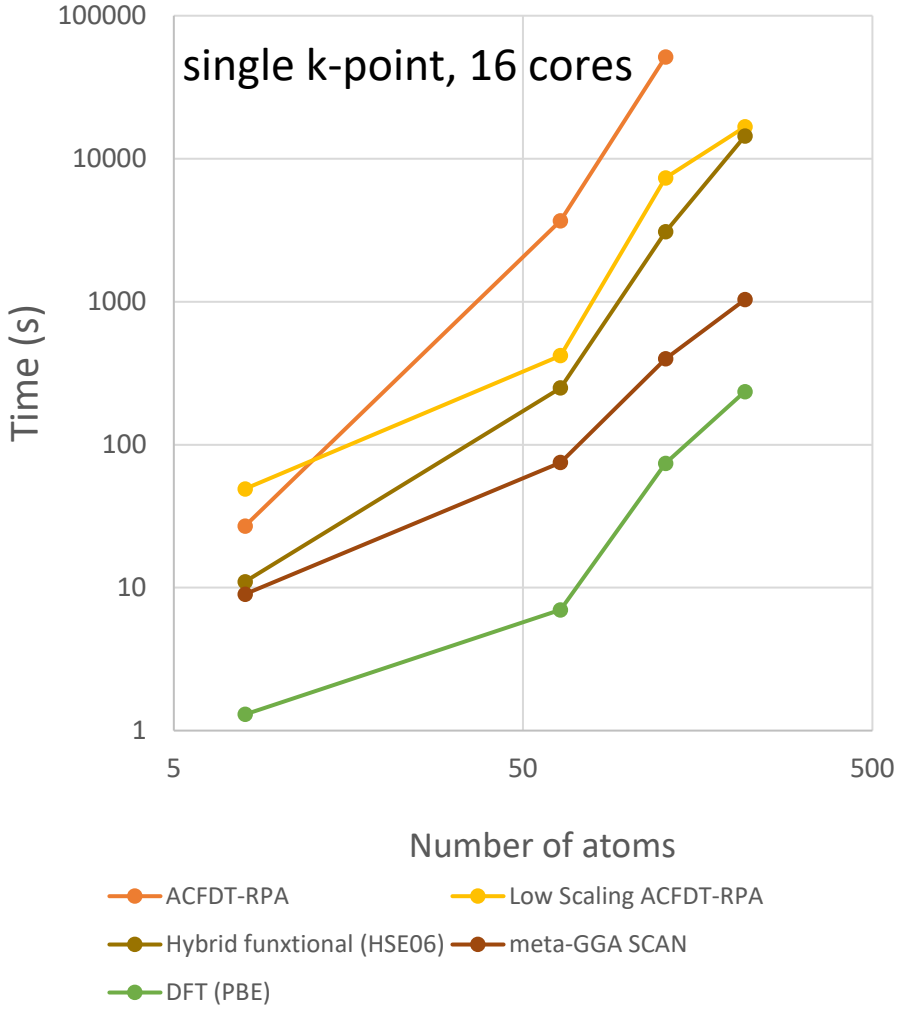
```
 ACFDT-RPA correlation energy:             -13.011143 eV for SiC
      Hartree-Fock total energy:             -25.144840 eV for SiC
Correction for partial occupancy:              -0.000000 eV for SiC
------------------------------------------------------------------
          ACFDT-RPA total energy:             -38.155983 eV for SiC

Electronic contributions:
                          Empirical Formula          Cell
                                   SiC           (SiC)4
                          --------------- ---------------
        ACFDT-RPA Energy       -3681.492      -14725.967 kJ/mol
```

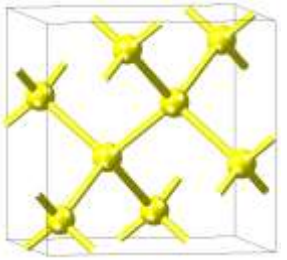
$$\Delta H_f = E_{SiC} - E_{Si} - E_C = -3681.492+1482.448+2134.512=\mathbf{-64.53}\ \text{kJ/mol}$$

	PBE	RPA	EXP
LiF	570	609	621
NaF	522	567	576
NaCl	355	405	413
MgO	516	577	603
MgH_2	52	72	78
AlN	262	291	321
SiC	51	**64**	**69**

ACFDT-RPA: Computational Cost

materials design

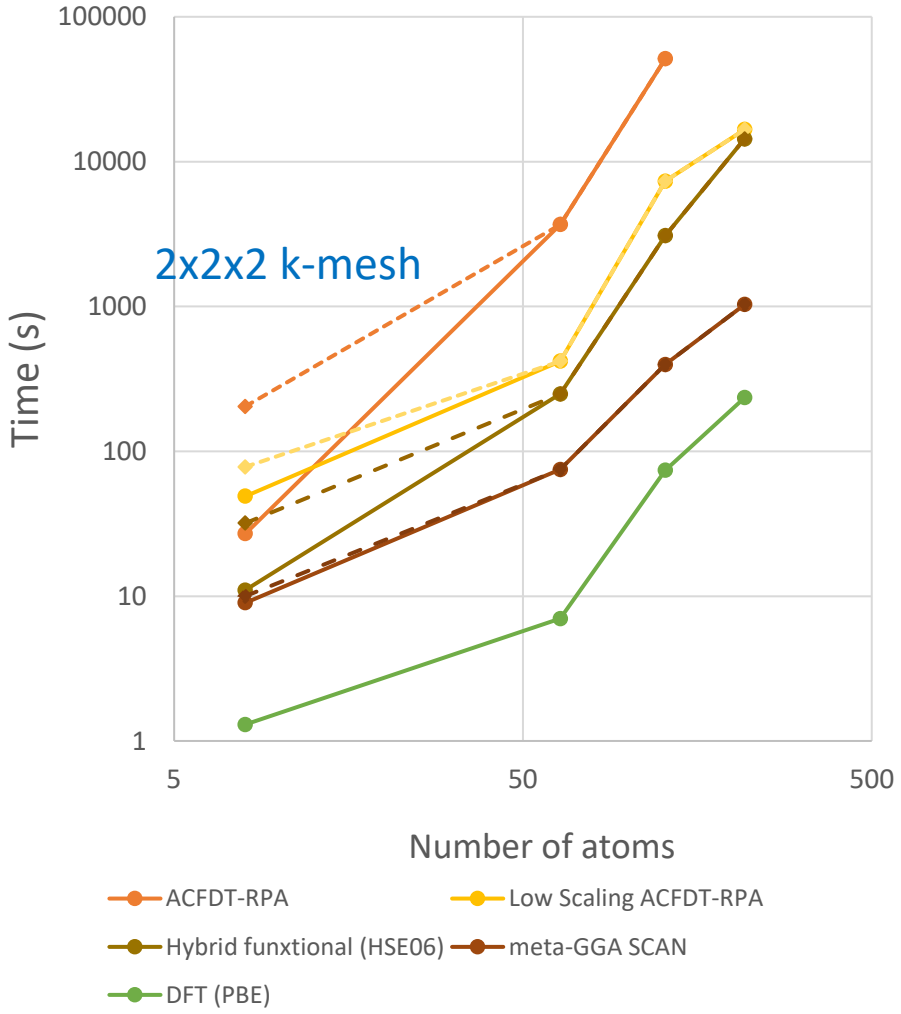




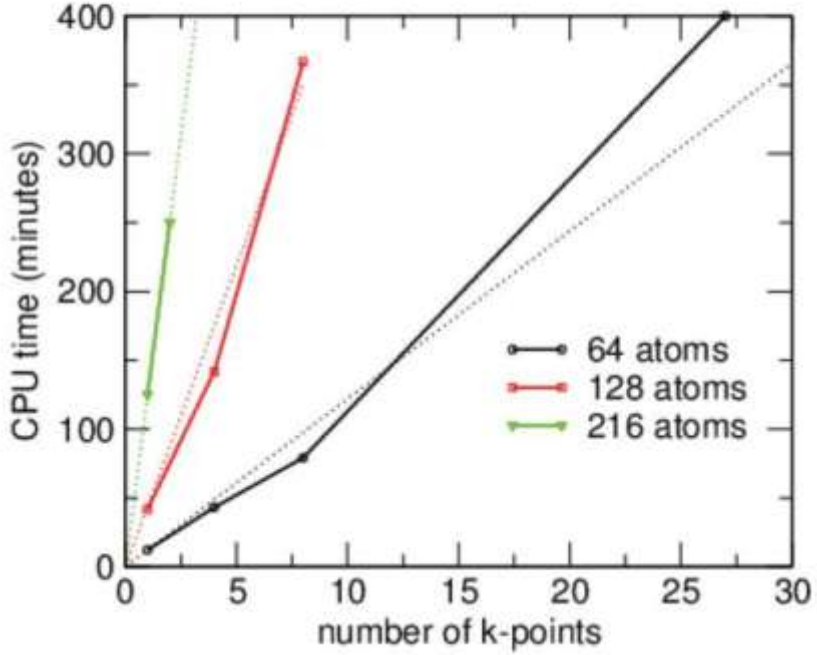
silicon

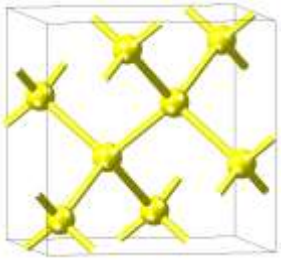
ACFDT-RPA: Computational Cost

materials design



Scaling of low scaling RPA with k-points:





silicon

Conclusion

- Tutorial showed how to use ACFDT-RPA to calculate the heat of formation
- Calculated silicon carbide HoF is 64.5 kJ/mol

- See also:

  The Random Phase Approximation: A Practical Method Beyond DFT
  https://www.materialsdesign.com/webinars/recorded/ugm-2020-plenary-kresse

  VASP 6: Total energies beyond DFT
  https://my.materialsdesign.com/webinar-35

Interlude

MedeA VASP: Handling of Symmetry in Structures

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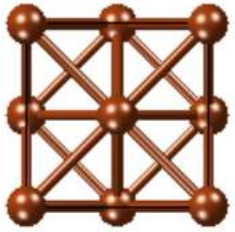
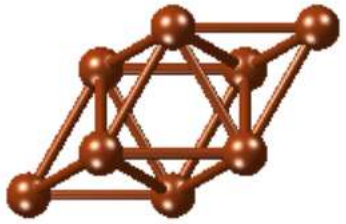
Cu (Fm-3m)





Atoms

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation
1	Cu1	Cu	29	4a	0,0,0

Structure used in VASP with full consideration of symmetry

- Definition of high symmetry points in 1st Brillouin zone for band structures
- DFT calculation structure contains a single atom instead of 4 atoms
- Use of symmetry to reduce calculation effort
- Etc.

MedeA VASP: Handling of Symmetry in Structures

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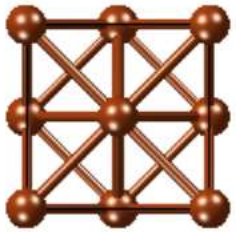
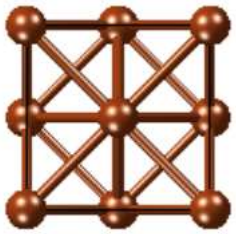
Cu (P1)



Atoms

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation
1	Cu1	Cu	29	1a	x,y,z
2	Cu2	Cu	29	1a	x,y,z
3	Cu3	Cu	29	1a	x,y,z
4	Cu4	Cu	29	1a	x,y,z



Structure used in VASP without consideration of symmetry

- Definition of high symmetry points in 1st Brillouin zone based on P1 symmetry
- Instead of 1 Cu atom structure contains 4 Cu atoms → increase in calculation effort
- In most cases no use of symmetry to reduce calculation effort (MT, Phonon, etc.) (VASP still uses symmetry – can be switched off in the Advanced/Restart tab)

MedeA VASP: Sites vs. Atom Positions

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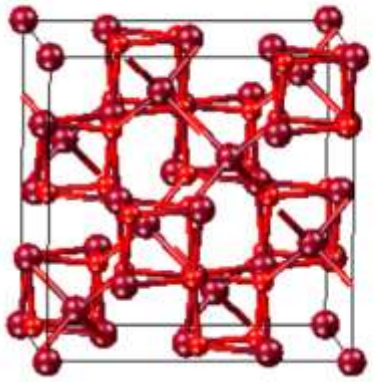
- With symmetry: **sites ≠ atom positions**



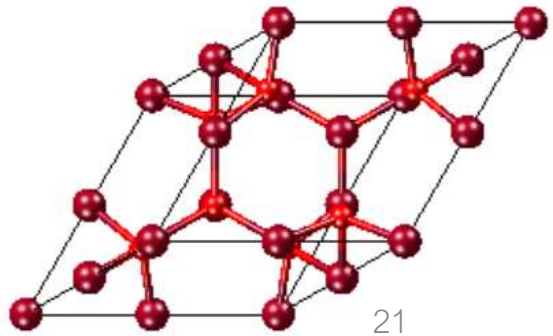
Fe_3O_4 (Fd-3m)

Atoms

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation	X
1	O	O	8	32e	x,x,x	0.2297
2	Fe1	Fe	26	16c	0,0,0	0
3	Fe2	Fe	26	8b	3/8,3/8,3/8	0.375

POSCAR:

```
(Fe3O4)8   (Fd-3m) ~ (Pearson #1221350)_1 (VASP)
    1.0
            0.00000000 4.19650000 4.19650000
            4.19650000 0.00000000 4.19650000
            4.19650000 4.19650000 0.00000000
  8 6
Direct
        0.22970000 0.22970000 0.22970000
        -0.18910000 0.22970000 0.22970000
        0.22970000 -0.18910000 0.22970000
        0.22970000 0.22970000 -0.18910000
        0.77030000 0.77030000 0.77030000
        0.18910000 0.77030000 0.77030000
        0.77030000 0.18910000 0.77030000
        0.77030000 0.77030000 0.18910000
        0.00000000 0.00000000 0.00000000
        0.50000000 0.00000000 0.00000000
        …
```



MedeA VASP: Sites vs. Atom Positions

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Fe_3O_4 (Fd-3m)

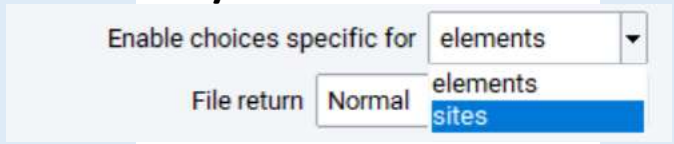
Atoms

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation	x
1	O	O	8	32e	x,x,x	0.2297
2	Fe1	Fe	26	16c	0,0,0	0
3	Fe2	Fe	26	8b	3/8,3/8,3/8	0.375

POSCAR:

```
(Fe3O4)8   (Fd-3m) ~ (Pearson #1221350)_1 (VASP)
    1.0
            0.00000000 4.19650000 4.19650000
            4.19650000 0.00000000 4.19650000
            4.19650000 4.19650000 0.00000000
  8  6
Direct
        0.22970000 0.22970000 0.22970000
        -0.18910000 0.22970000 0.22970000
        0.22970000 -0.18910000 0.22970000
        0.22970000 0.22970000 -0.18910000
        0.77030000 0.77030000 0.77030000
        0.18910000 0.77030000 0.77030000
```

Advanced/Restart tab



POSCAR:

```
(Fe3O4)8   (Fd-3m) ~ (Pearson #1221350)_1 (VASP)
    1.0
            0.00000000 4.19650000 4.19650000
            4.19650000 0.00000000 4.19650000
            4.19650000 4.19650000 0.00000000
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Direct
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        0.22970000 0.22970000 -0.18910000
        0.77030000 0.77030000 0.77030000
        0.18910000 0.77030000 0.77030000
```
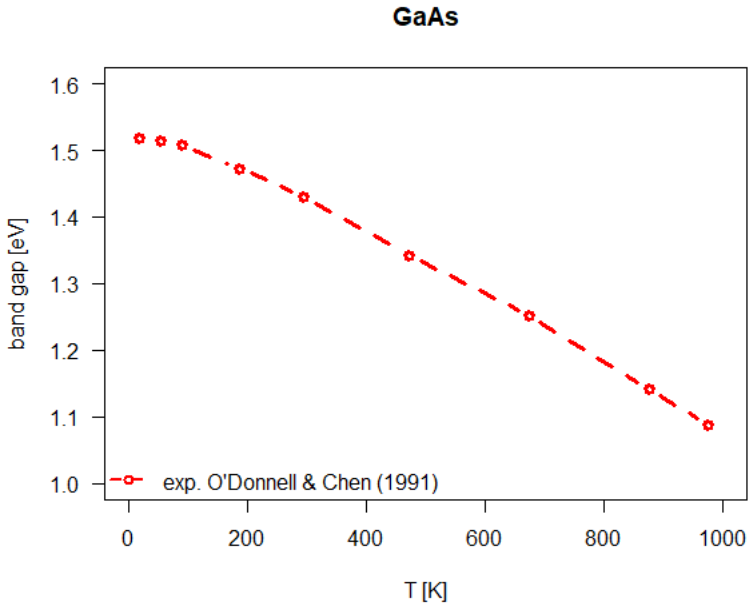
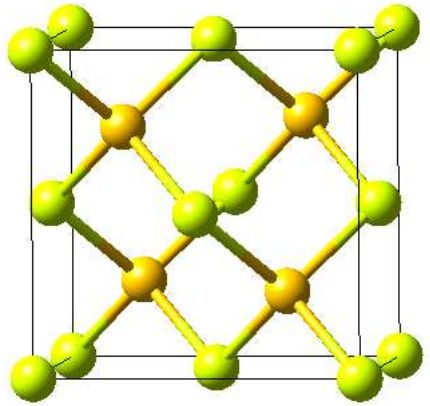
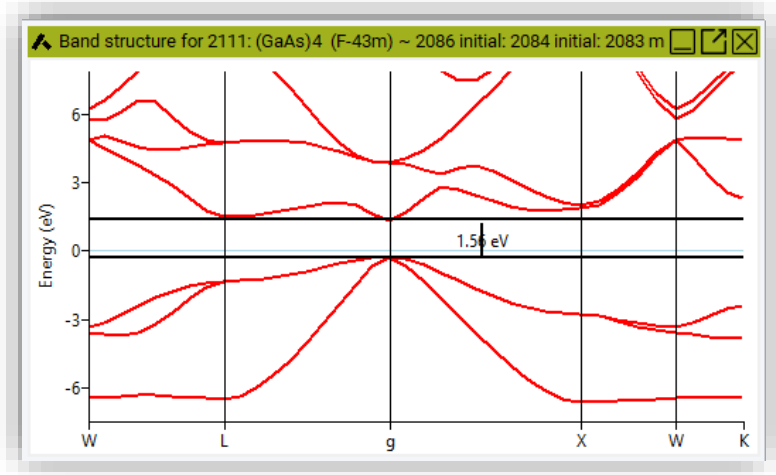

- LDA+U: apply different U(&J) values to different sites occupied by the same element
- XANES spectroscopy with MedeA VASP 6: specify a site containing a single atom position

Electron Phonon Coupling: Phonon Induced Change of Band Gap of GaAs as a Function of Temperature







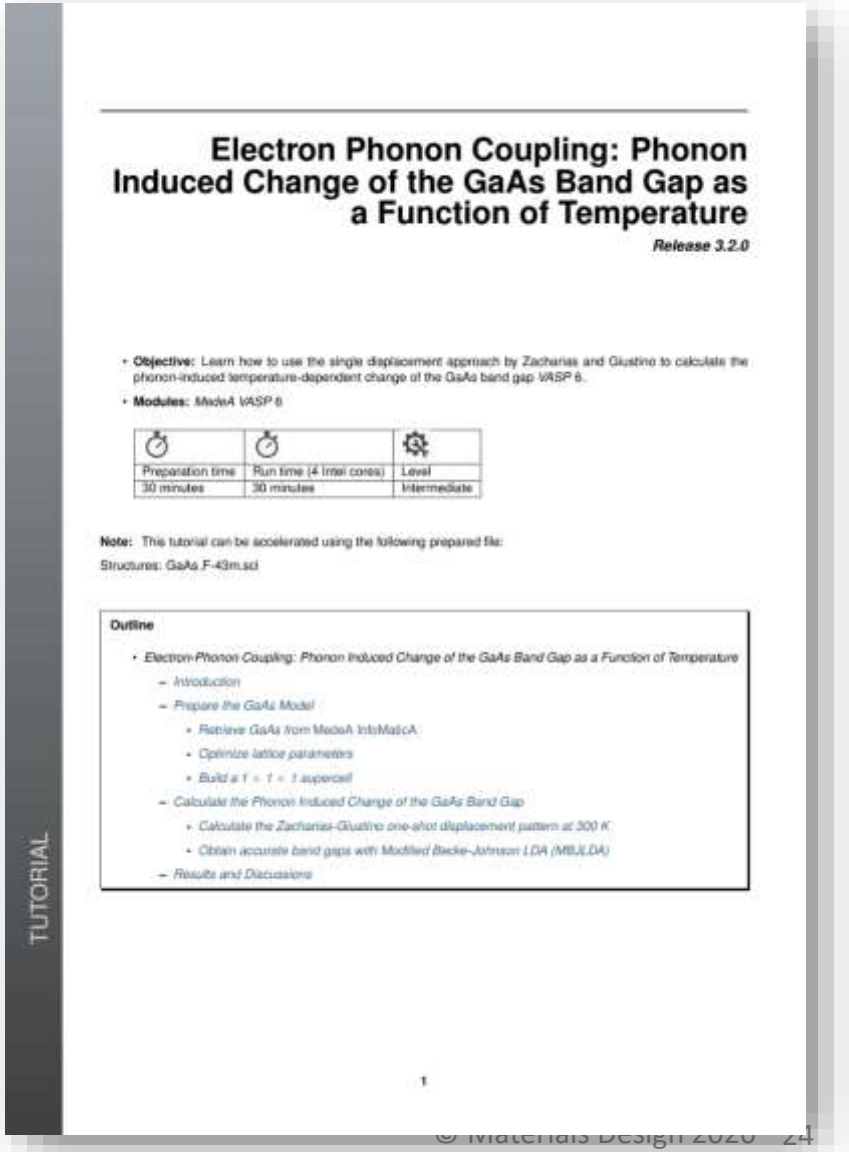
Introduction

- See *MedeA* tutorial Electron Phonon Coupling: Phonon Induced Change of the GaAs Band Gap as a Function of Temperature at http://my.materialsdesign.com/tutorials

- **Objective** Learn how to use the single displacement approach by Zacharias and Giustino to calculate the phonon-induced temperature-dependent change of the GaAs band gap by *VASP* 6.

- **Modules:** *MedeA VASP 6*

Preparation time	Run time (4 Intel cores)	Level
30 minutes	30 minutes	Intermediate


TUTORIAL

Electron Phonon Coupling: Phonon Induced Change of the GaAs Band Gap as a Function of Temperature

Release 3.2.0

- **Objective:** Learn how to use the single displacement approach by Zacharias and Giustino to calculate the phonon-induced temperature-dependent change of the GaAs band gap *VASP* 6.
- **Modules:** *MedeA VASP* 6

Preparation time	Run time (4 Intel cores)	Level
30 minutes	30 minutes	Intermediate

Note: This tutorial can be accelerated using the following prepared file:
Structures: GaAs_F-43m.sdl

Outline

1

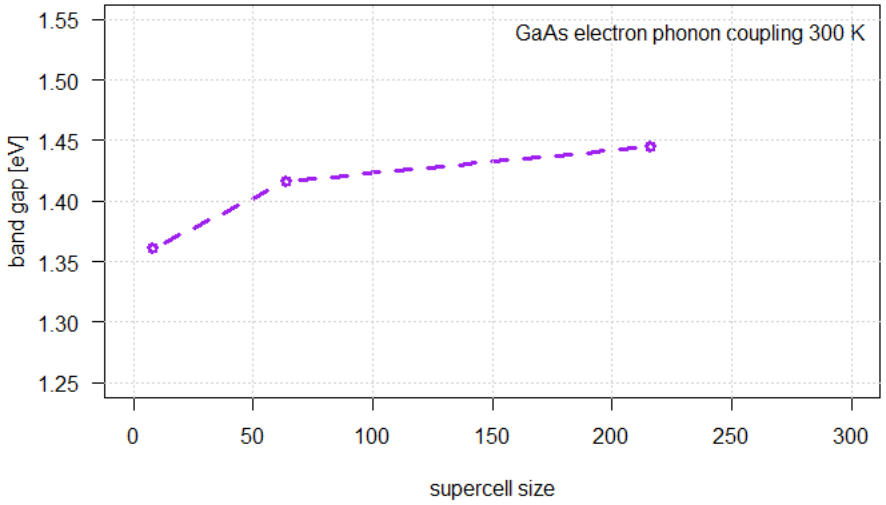
Procedure Outline

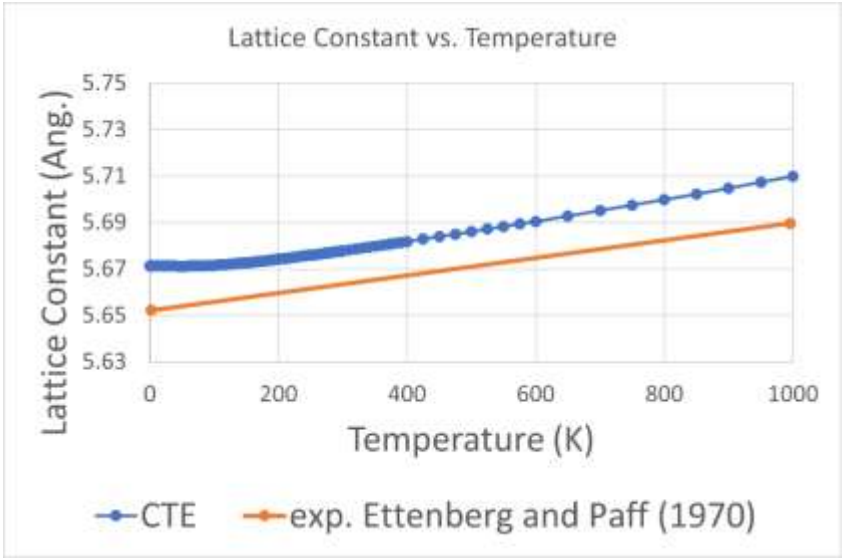
materials design

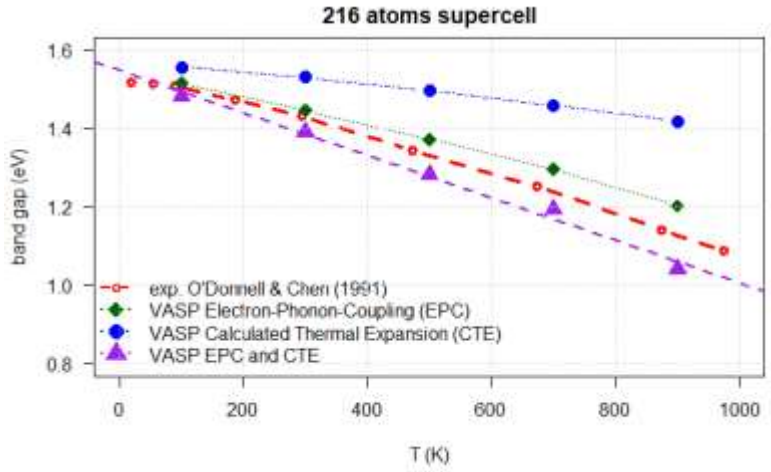
1. Retrieve crystal structures of GaAs
2. Optimize the structure with PBEsol
3. Build a 1x1x1 supercell
4. Calculate the Zacharias-Giustino one-shot displacement pattern at 300 K
5. Obtain accurate band gaps with Modified Becke-Johnson LDA

	Exp.	PBE	PBEsol	LDA
Lattice constant (Ang.)	**5.653**	5.756	**5.662**	5.610

Phonon Induced Temperature Dependent Change of the Band Gap

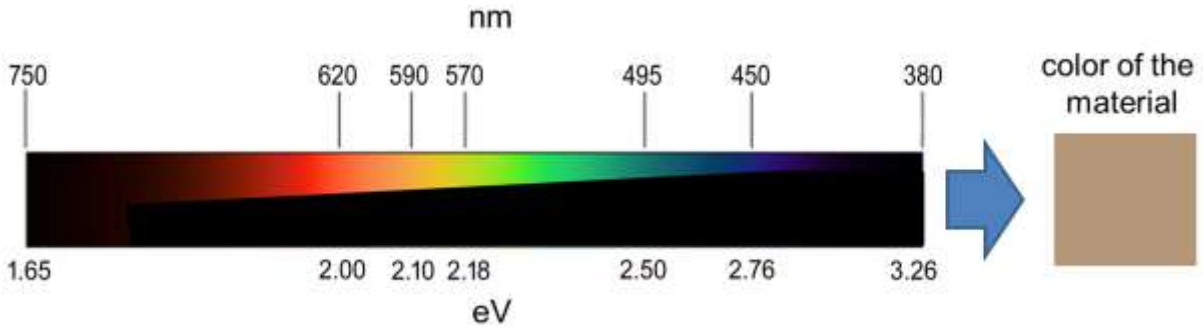


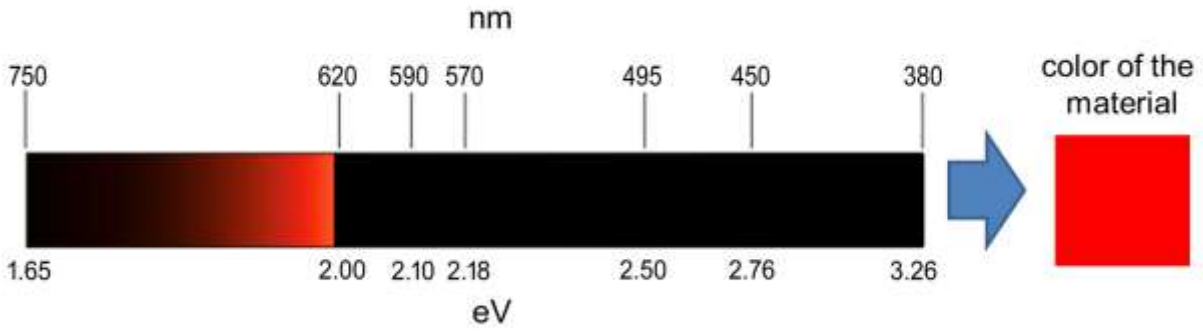


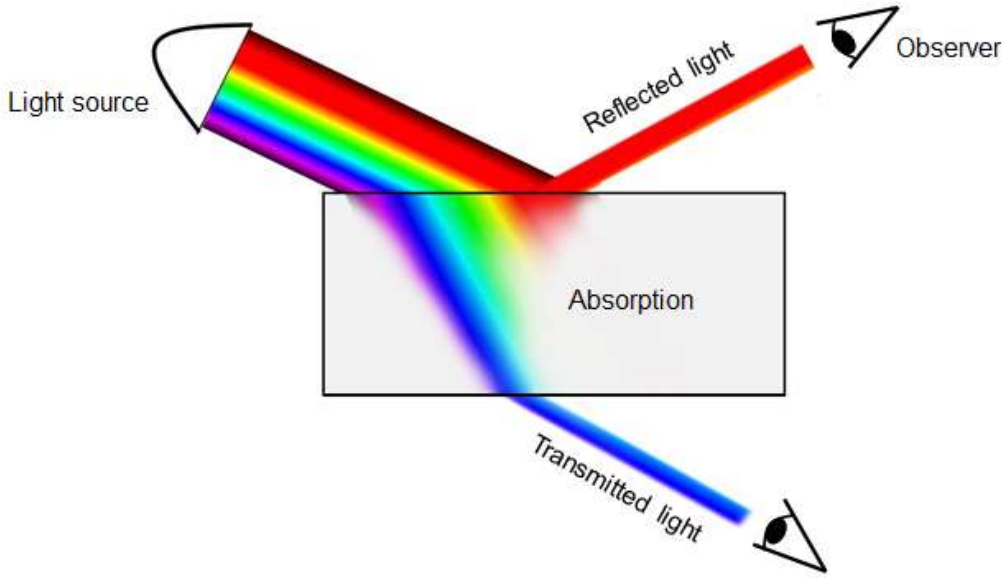


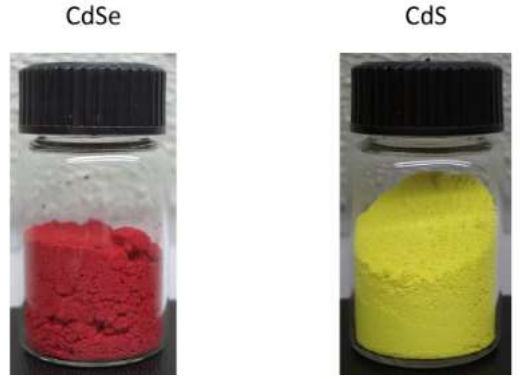
- Need large supercells
- Include thermal expansion to consider all important contributions
- Other properties can also be computed from the single displacement pattern (e.g. optical properties)
- Procedure:
  - Lattice optimization with PBEsol
  - One-shot displacement pattern (Zacharia&Giustino)
  - Band gaps with MBJLDA

Color of Cadmium Selenide and Cadmium Sulfide









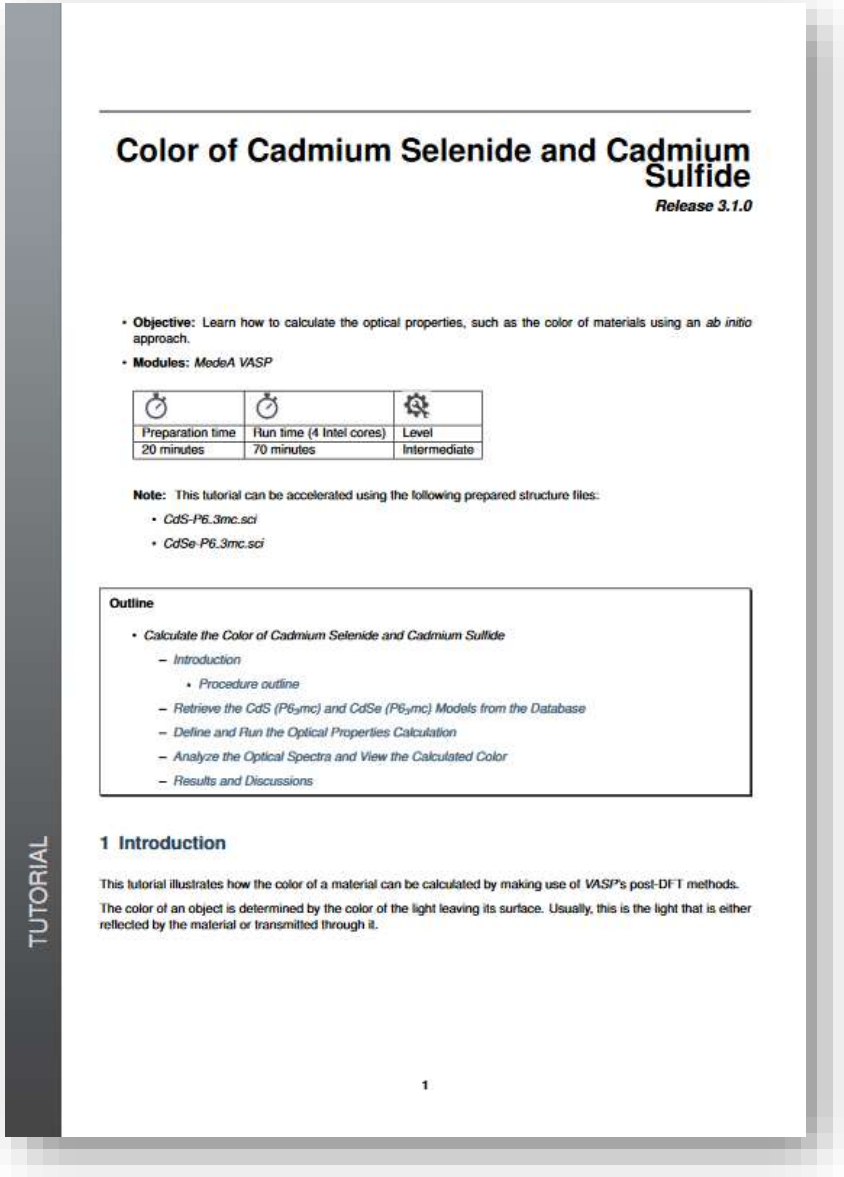
Introduction

- See *MedeA* tutorial Calculate the Color of Cadmium Selenide and Cadmium Sulfide at http://my.materialsdesign.com/tutorials

- **Objective:** Learn how to calculate the optical properties, such as the color of materials using an *ab initio* approach.

- **Modules:** *MedeA VASP*

Preparation time	Run time (4 Intel cores)	Level
20 minutes	70 minutes	Intermediate


TUTORIAL

Color of Cadmium Selenide and Cadmium Sulfide

Release 3.1.0

- **Objective:** Learn how to calculate the optical properties, such as the color of materials using an *ab initio* approach.
- **Modules:** *MedeA VASP*

Preparation time	Run time (4 Intel cores)	Level
20 minutes	70 minutes	Intermediate

Note: This tutorial can be accelerated using the following prepared structure files:

- *CdS-P6_3mc.sci*
- *CdSe-P6_3mc.sci*

Outline

- *Calculate the Color of Cadmium Selenide and Cadmium Sulfide*
  - *Introduction*
    - *Procedure outline*
  - *Retrieve the CdS ($P6_3mc$) and CdSe ($P6_3mc$) Models from the Database*
  - *Define and Run the Optical Properties Calculation*
  - *Analyze the Optical Spectra and View the Calculated Color*
  - *Results and Discussions*

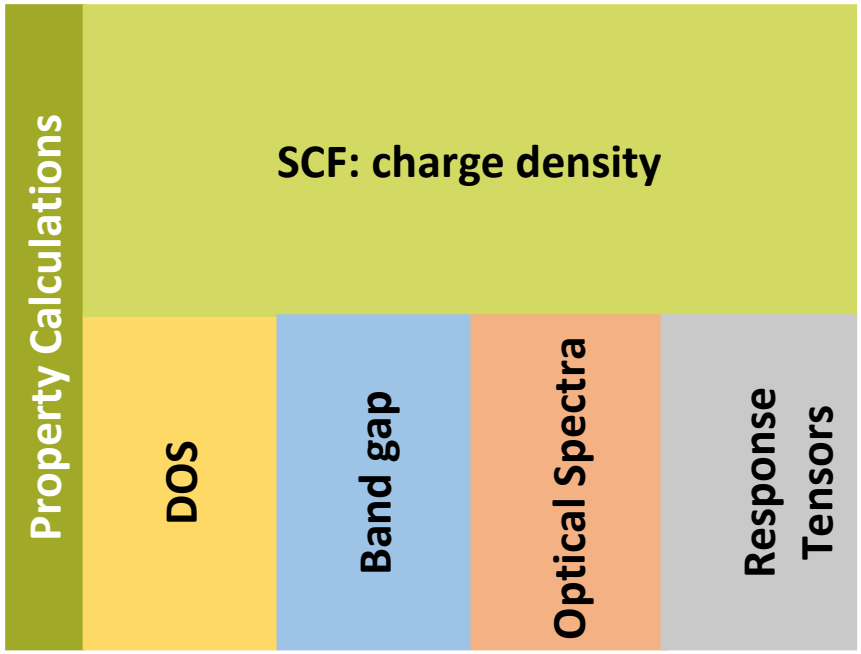
1 Introduction

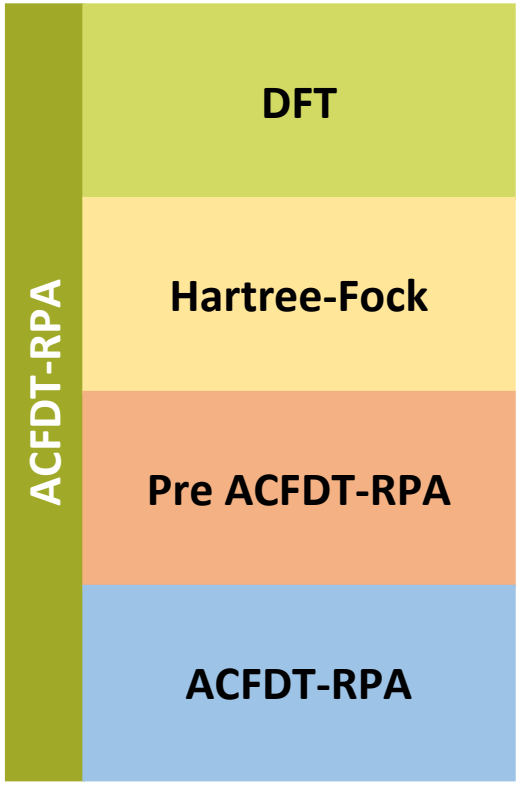
This tutorial illustrates how the color of a material can be calculated by making use of *VASP*'s post-DFT methods.

The color of an object is determined by the color of the light leaving its surface. Usually, this is the light that is either reflected by the material or transmitted through it.

1

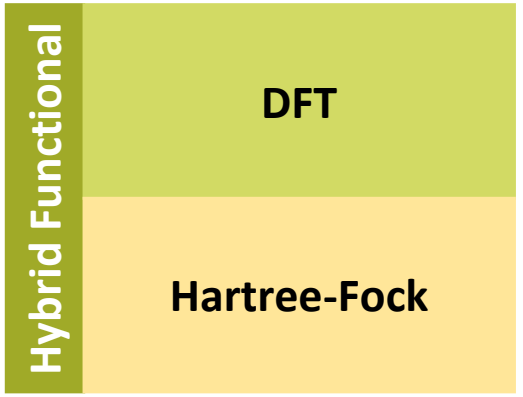
MedeA VASP: Automated Calculation Protocol





Job.out:

```
VASP 6 CALCULATION PROTOCOL:
============================
1. Single point calculation
     Saved properties in this step: wave  functions
2. Calculate Hartree-Fock energy E_EXX evaluated
   non self-consistently using orbitals from previous step
3. Prepare for ACFDT-RPA by calculation of a large
   number of accurate excited states
4. Calculate the ACFDT-RPA correlation energy
```



...

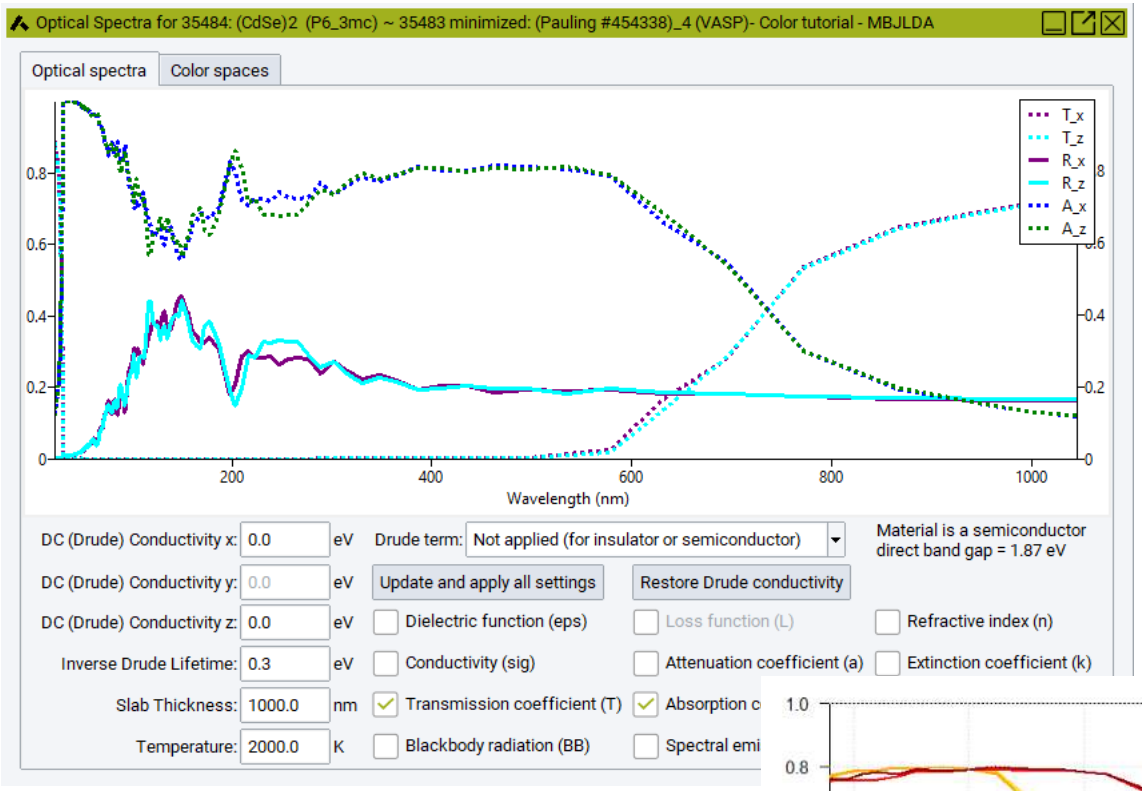
Procedure Outline

materials design

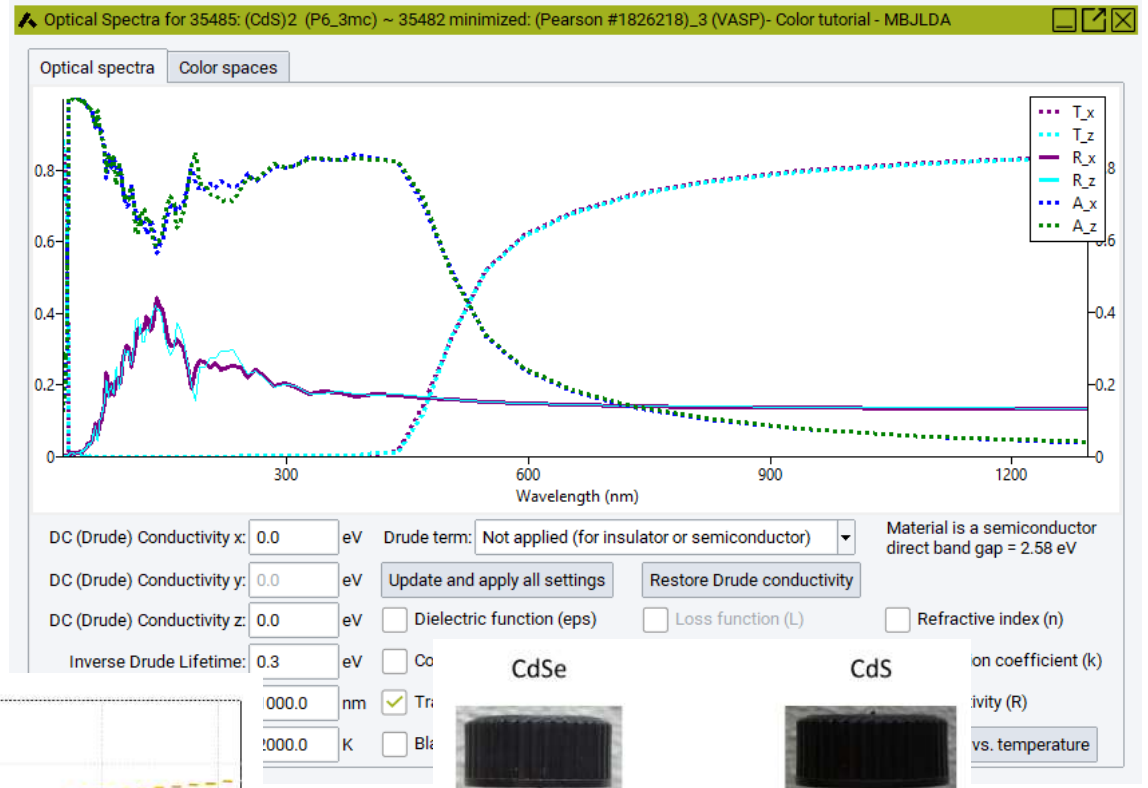
1. Retrieve crystal structures of CdSe and CdS
2. Optimize these structures with PBE
3. Define and run the optical spectra calculation using MBJLDA
4. Analyze the optical spectra and view the resulting color

Optical Spectra Analysis

- CdSe

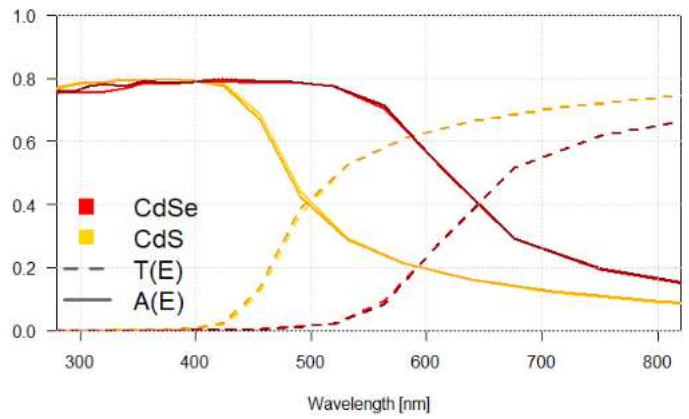


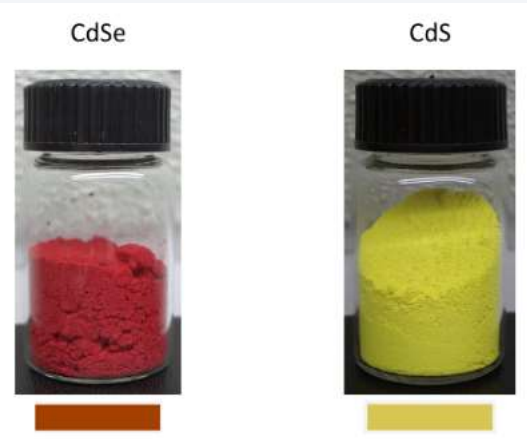
- CdS



	MBJLDA	Exp.
CdSe	1.87 eV	1.74 eV
CdS	2.58 eV	2.42 eV

band gap





Conclusion

- Tutorial showed how to predict the color of CdSe and CdS with MedeA VASP
- Good prediction of the electronic structure → good prediction of the optical spectra → good color prediction
- Modified Becke Johnson GGA predicts the electronic structure well
  - It is computationally much cheaper than other “accurate” methods
  - It yields “accurate” enough electronic structures
  - It can only be used to calculate the electronic structure
- See also:

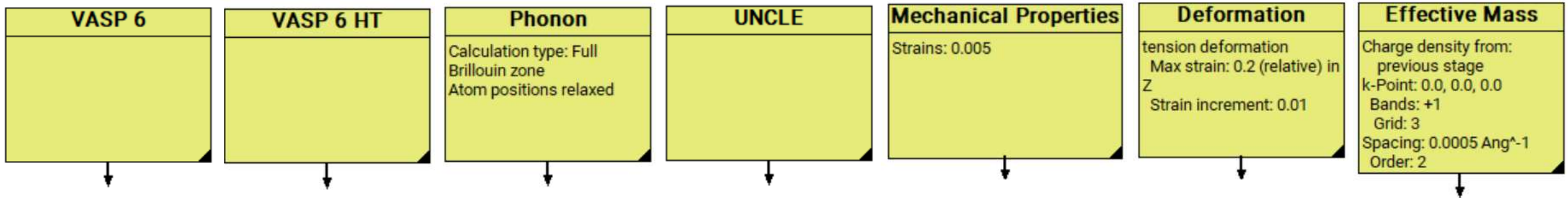
  The Color of Materials: Value from Computed Optical Properties
  http://my.materialsdesign.com/webinar-25

MedeA VASP

materials design

- Integrated with other property modules
  - **MedeA Phonon:** Phonon spectra, IR, Raman spectra, thermodynamic functions (vibrational free energy, heat capacities)
  - **MedeA MT:** Elastic, mechanical and thermodynamic properties
  - **MedeA Transition State Search:** Reaction pathways, structure and energy of transition states
  - **MedeA Electronics:** Fermi surfaces, electronic contributions to the electrical and thermal conductivity, thermoelectric power, and effective masses
  - **MedeA UNCLE:** Cluster expansion – search and identify ground states – Monte Carlo simulation to study phase stability
  - **MedeA Forcefield Optimizer:** Optimize forcefield parameters based on VASP ab initio

- MedeA Flowcharts: high throughput calculations



List of Resources

- Tutorials:
  - Introduction to MedeA VASP: Learn how to set up and run VASP first principles calculations with MedeA
  - Introduction to MedeA MT: Elastic Properties of TaN: Learn how to calculate the mechanical properties of crystals with MedeA MT and MedeA VASP
  - Introduction to MedeA Phonon: Vibrational Properties of Silicon: Learn how to calculate the vibrational spectrum of silicon using MedeA Phonon with VASP and LAMMPS
  - Introduction to MedeA UNCLE: Cluster expansion calculation of Au/Cu alloy: Learn how to set up cluster expansion calculations with MedeA UNCLE for Au/Cu alloy
  - Introduction to MedeA FFO: Optimizing Buckingham Forcefield for LiNbO3: Learn how to optimize a Buckingham forcefield for LiNbO3 with MedeA Forcefield Optimizer
  - Thermoelectrics: Seebeck Coefficient of Bismuth Chalcogenides: This tutorial describes how to calculate the Seebeck coefficient of the material Bi2Te3 with MedeA Electronics and MedeA VASP
  - Calculate the Color of Cadmium Selenide and Cadmium Sulfide: Learn how to calculate the optical properties, such as color, of materials using an ab initio approach with MedeA VASP
  - Electron-Phonon Coupling: Phonon Induced Change of the GaAs Band Gap as a Function of Temperature: Learn how to use the single displacement approach by Zacharias and Giustino to calculate the phonon-induced temperature-dependent change of the GaAs band gap with MedeA VASP 6
  - Obtain Accurate Heat of Formation for SiC with ACFDT RPA: Learn how to calculate the heat of formation of silicon carbide using ACFDT RPA with MedeA VASP 6
  - Thermal Expansion of ZnO: Learn how to calculate the thermal expansion of materials with MedeA
- Webinars:
  - VASP in MedeA: A Fast Way- From Models to Reliable Results: http://my.materialsdesign.com/webinar-31
  - The Color of Materials: Value from Computed Optical Properties: http://my.materialsdesign.com/webinar-25
  - Atomistic Simulations as a Driver of Industrial Innovation: http://my.materialsdesign.com/webinar-18
  - Predicting Elastic Properties Using Ab Initio and Forcefield Based Simulations: http://my.materialsdesign.com/webinar-15

and more..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October
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Announcements

ugm.materialsdesign.com

Professor Rutger van Santen

Eindhoven University of Technology

Next Week's Plenary Speaker

October 22nd

Dr. René Windiks

Materials Design

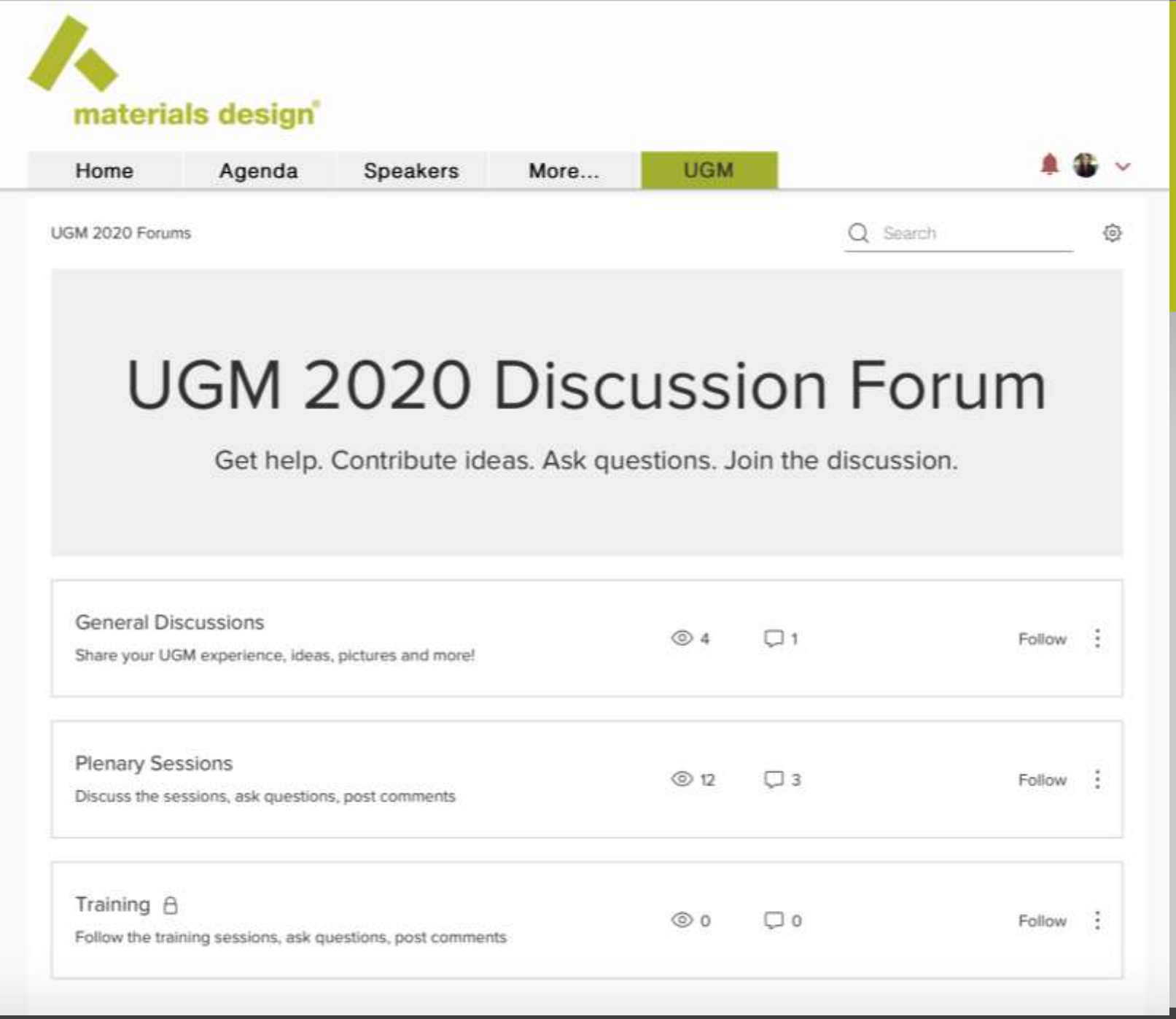
MedeA Training

October 27th

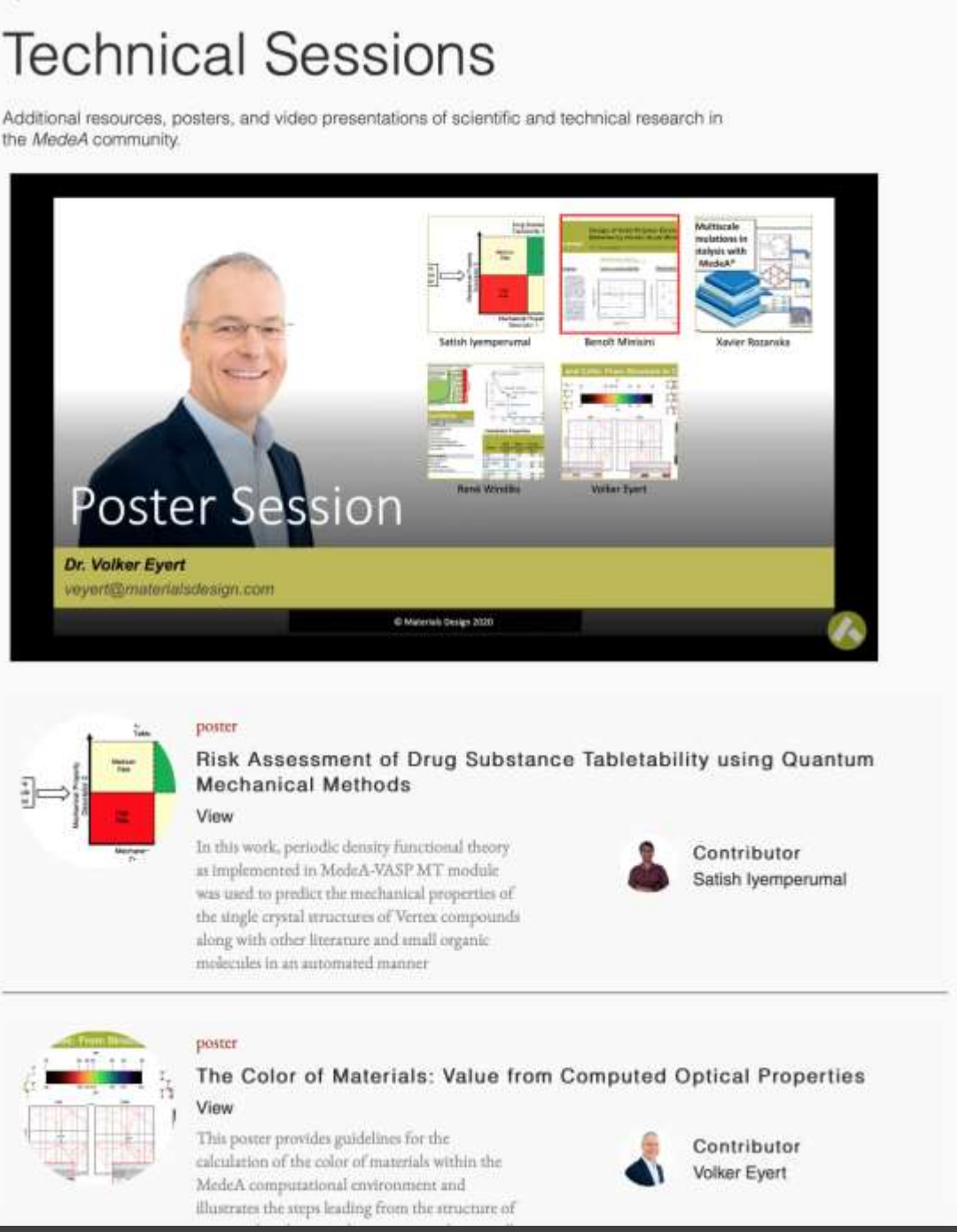
Announcements

Visit the UGM Forum page

https://www.ugm.materialsdesign.com/forum



- Get help on training
- Contribute your ideas
- Discuss the posters and plenary presentations
- Ask questions

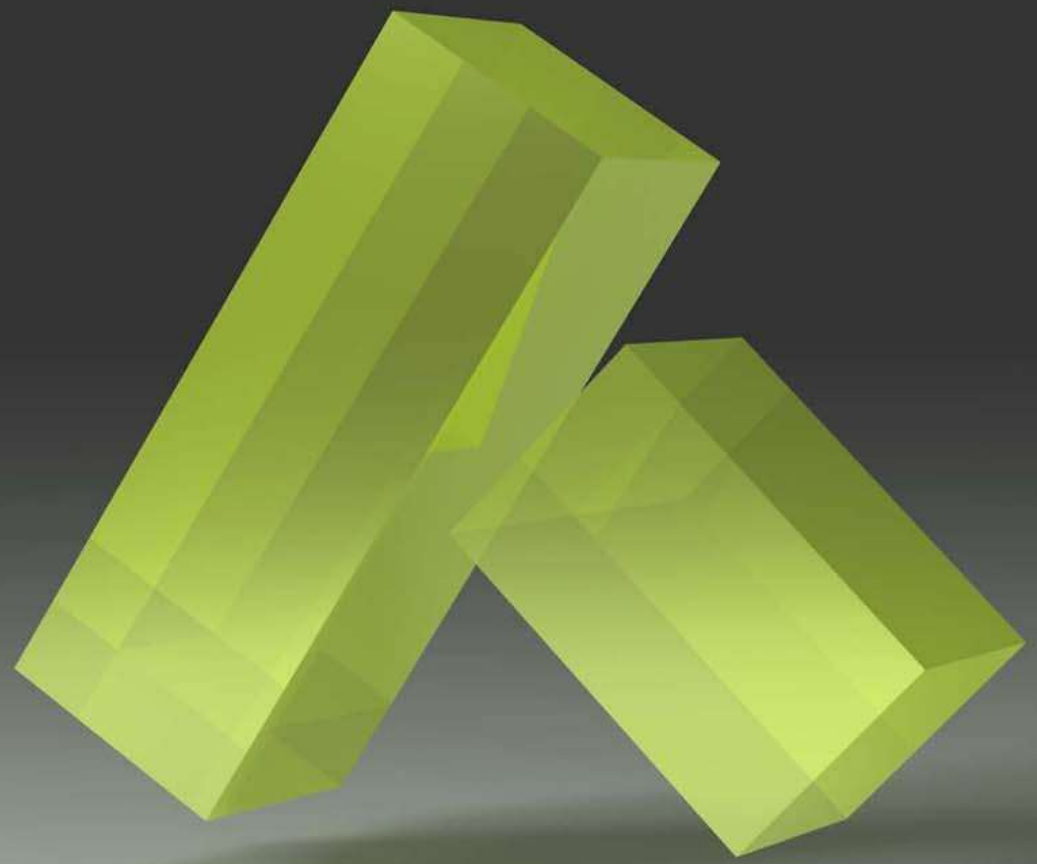


Announcements

Visit the Technical Session page Submitted Talks and Posters

https://www.ugm.materialsdesign.com/posters

- There is still time to submit
- Open to customers under maintenance
- Easily upload on the contributor's page
- Interested? Do you have questions?
  - Contact Volker Eyert
  - UGM@materialsdesign.com



MedeA

Innovation by Simulation