

10月28日上机实习安排

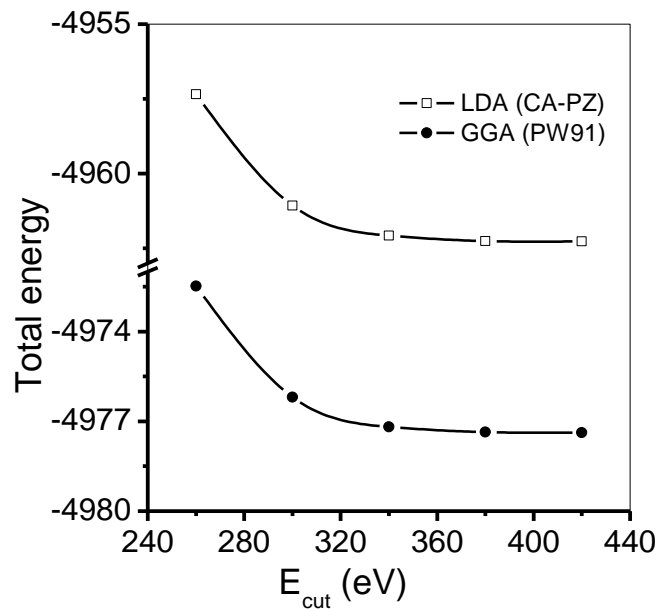
使用MS软件CASTEP模块完成：

Graphene的第一性原理(DFT)计算

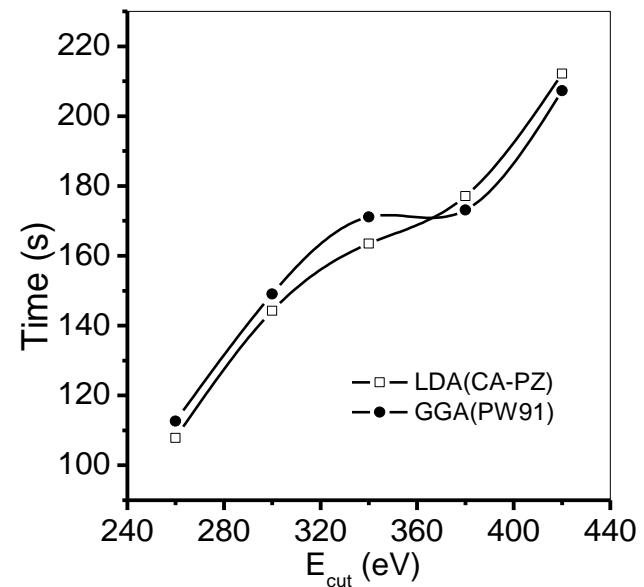
1. 建模→
2. 结构优化→
3. 电荷密度计算（高精度单点能）→
4. 能带结构计算（FBZ高对称 K 点）→
5. 态密度计算(DOS & PDOS)

Graphene DFT计算的结果可靠性测试

1. 截断能(cutoff energy)



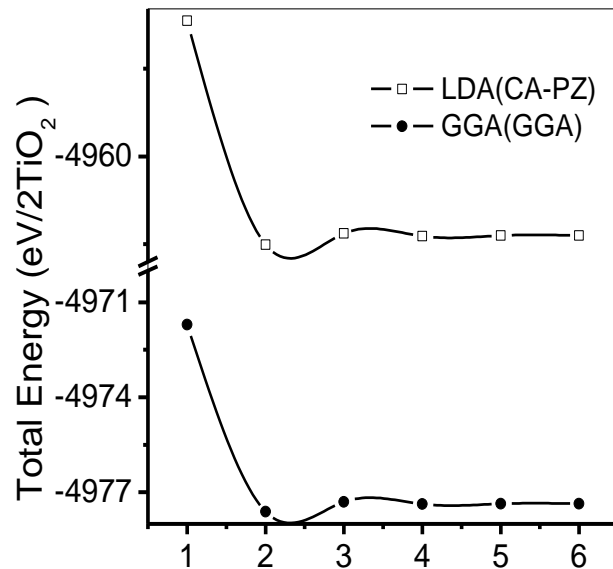
截断能与总能量的关系



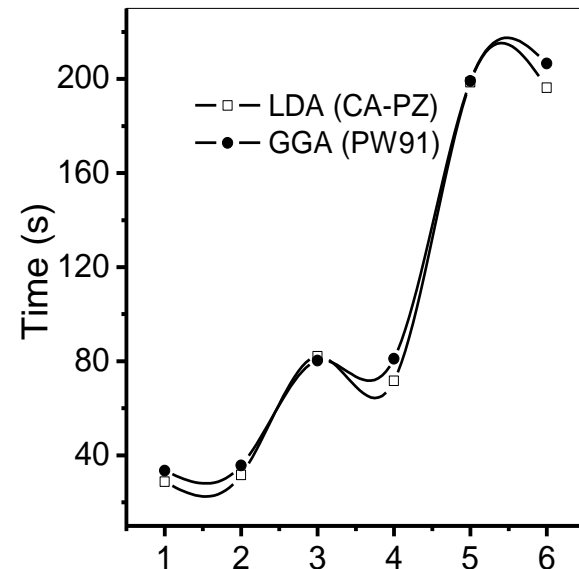
截断能与计算时间的关系

Graphene DFT计算的结果可靠性测试

2. K points



K 点设置与总能量的关系



K 点设置与计算时间的关系

Graphene DFT计算的参考文献

1. A. G. Marinopoulos et al. Ab Initio Study of the Optical Absorption and Wave-Vector-Dependent Dielectric Response of Graphite. *Phys. Rev. B* **2004**, 69, 245419.
2. N. Ooi, A. Rairkar, and J. B. Adams. Density Functional Study of Graphite Bulk and Surface Properties. *Carbon* **2006**, 44, 231-242.

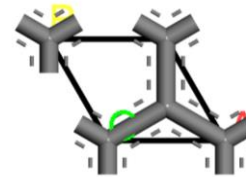
1. Slab Model Building

(1) Import crystal structure of graphite in MS

(2) Make “P1” to delete a layer graphene

(3) “Rebuild Crystal” to change the lattice parameter c into 20 \AA

Top View

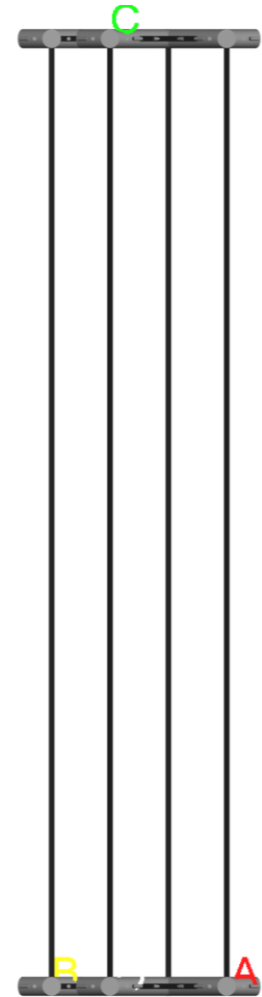


$$a = b = 2.460 \text{ \AA}$$

$$c = 20.0 \text{ \AA}$$

$$\alpha = \beta = 90.0^\circ$$

$$\gamma = 120.0^\circ$$



Side View

2. Geometry Optimization

Top View

Before

$$a = b = 2.460 \text{ \AA}$$

$$c = 20.0 \text{ \AA}$$

$$\alpha = \beta = 90.0^\circ$$

$$\gamma = 120.0^\circ$$

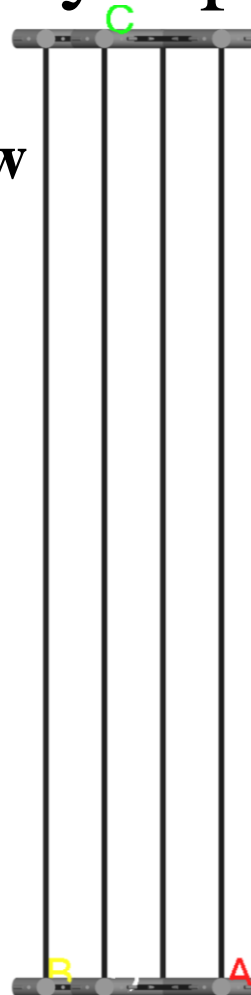
After

$$a = b = 2.460 \text{ \AA}$$

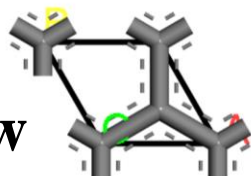
$$c = 20.0 \text{ \AA}$$

$$\alpha = \beta = 90.0^\circ$$

$$\gamma = 120.0^\circ$$



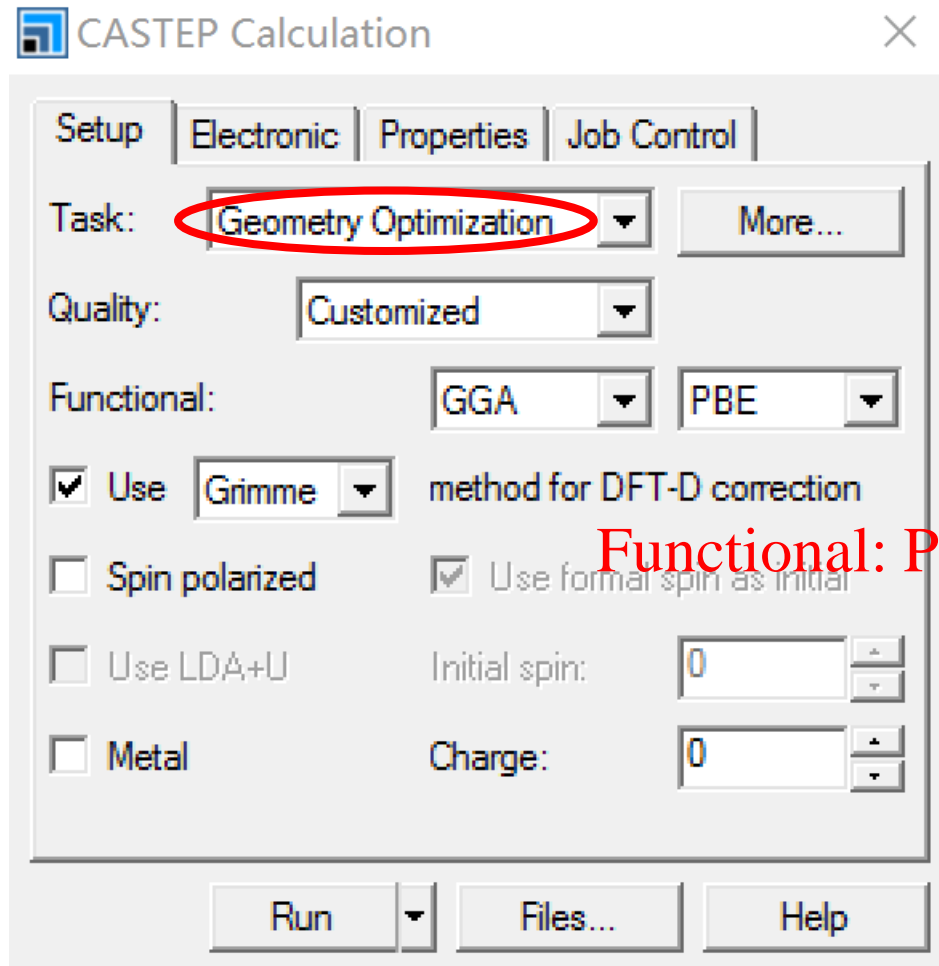
Side View



2. Geometry Optimization

CASTEP Calculation

Setup



The image shows the 'CASTEP Calculation' dialog box with the 'Setup' tab selected. The 'Task' dropdown is set to 'Geometry Optimization' and is circled in red. The 'Quality' dropdown is set to 'Customized'. The 'Functional' dropdown is set to 'GGA', and the 'PBE' dropdown is also visible. The 'Use Grimme' checkbox is checked, and the 'method for DFT-D correction' is set to 'Grimme'. The 'Spin polarized' checkbox is unchecked. The 'Use LDA+U' checkbox is unchecked. The 'Metal' checkbox is unchecked. The 'Initial spin' is set to 0. The 'Charge' is set to 0. The 'Use formal spin as initial' checkbox is checked. The 'Run' button is highlighted.

CASTEP Calculation

Setup | Electronic | Properties | Job Control

Task: **Geometry Optimization** More...

Quality: Customized

Functional: GGA PBE

☒ Use Grimme method for DFT-D correction

☐ Spin polarized ☒ Use formal spin as initial

☐ Use LDA+U Initial spin: 0

☐ Metal Charge: 0

Run Files... Help

Functional: PBE-D2

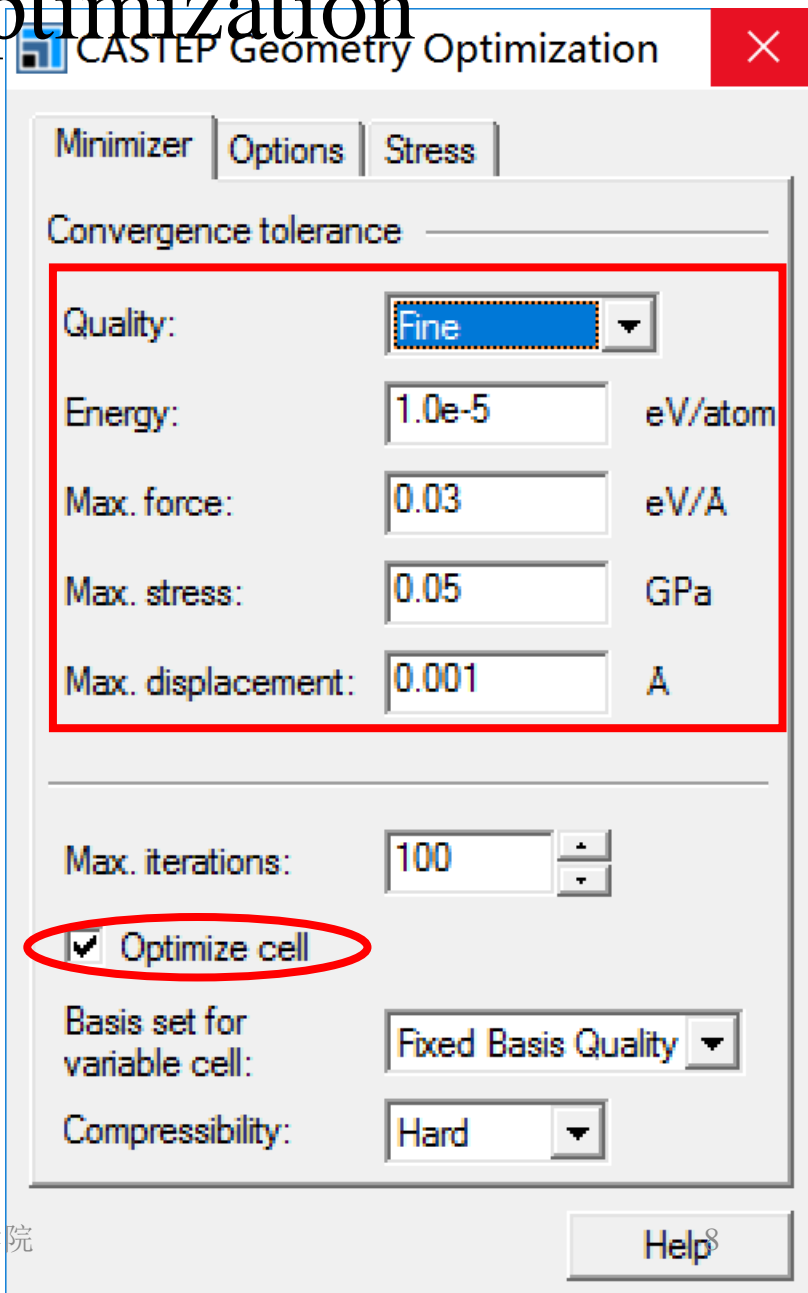
2. Geometry Optimization

CASTEP Calculation

Setup → More... for **Minimizer**

优化结束的判据:

- 能量判据: 相继两次结构对应能量差足够小
- 力判据: 单个原子受力小于设定的最大值
- 应力判据: 保证结构模型单元中的应力足够小
- 位移判据: 相继两次结构变化引起的原子位移足够小



The image shows the 'CASTEP Geometry Optimization' dialog box. It has three tabs: 'Minimizer', 'Options', and 'Stress'. The 'Minimizer' tab is selected. The 'Convergence tolerance' section is highlighted with a red box and contains the following settings:

Parameter	Value	Unit
Quality:	Fine	
Energy:	1.0e-5	eV/atom
Max. force:	0.03	eV/A
Max. stress:	0.05	GPa
Max. displacement:	0.001	A

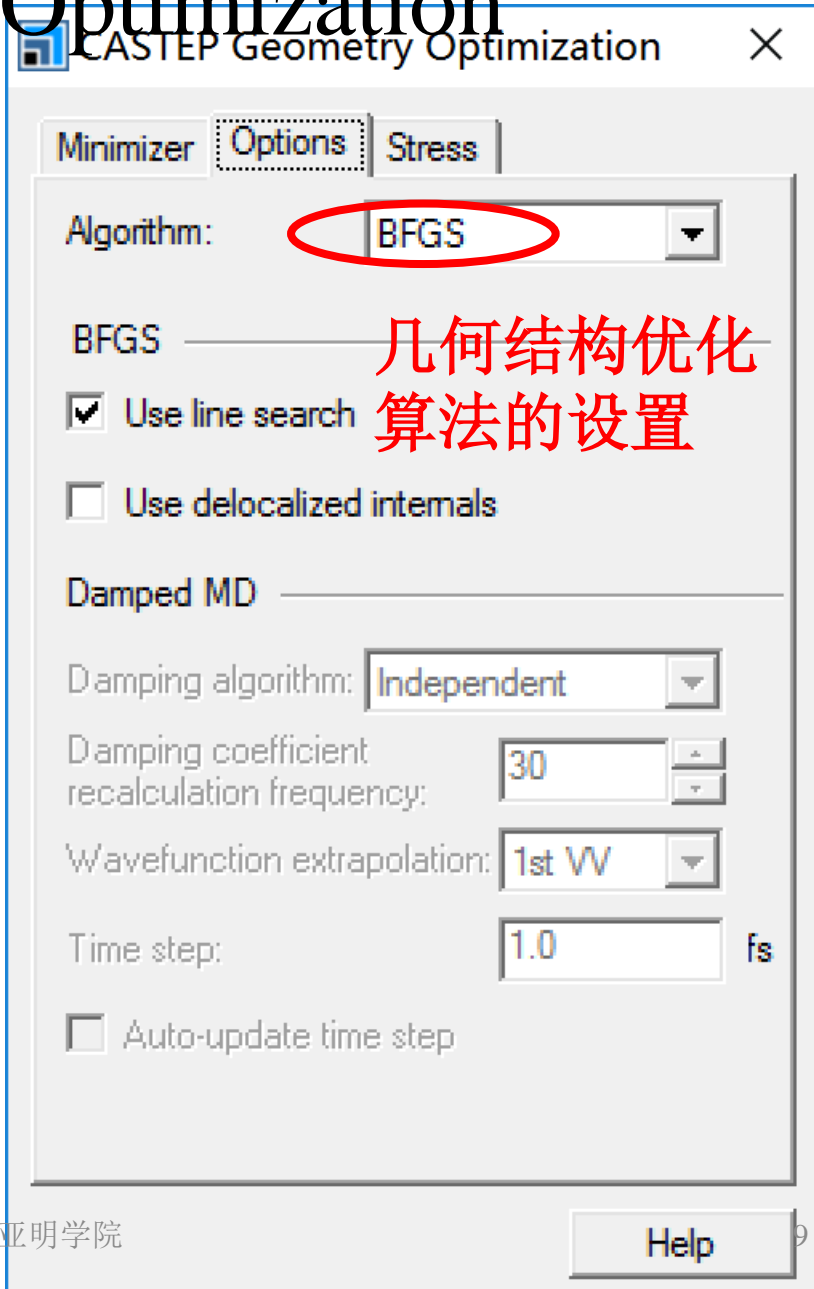
Below this section, the 'Max. iterations' is set to 100. The 'Optimize cell' checkbox is checked and circled in red. The 'Basis set for variable cell' is set to 'Fixed Basis Quality', and the 'Compressibility' is set to 'Hard'. A 'Help' button is located at the bottom right.

2. Geometry Optimization

CASTEP Calculation

Setup

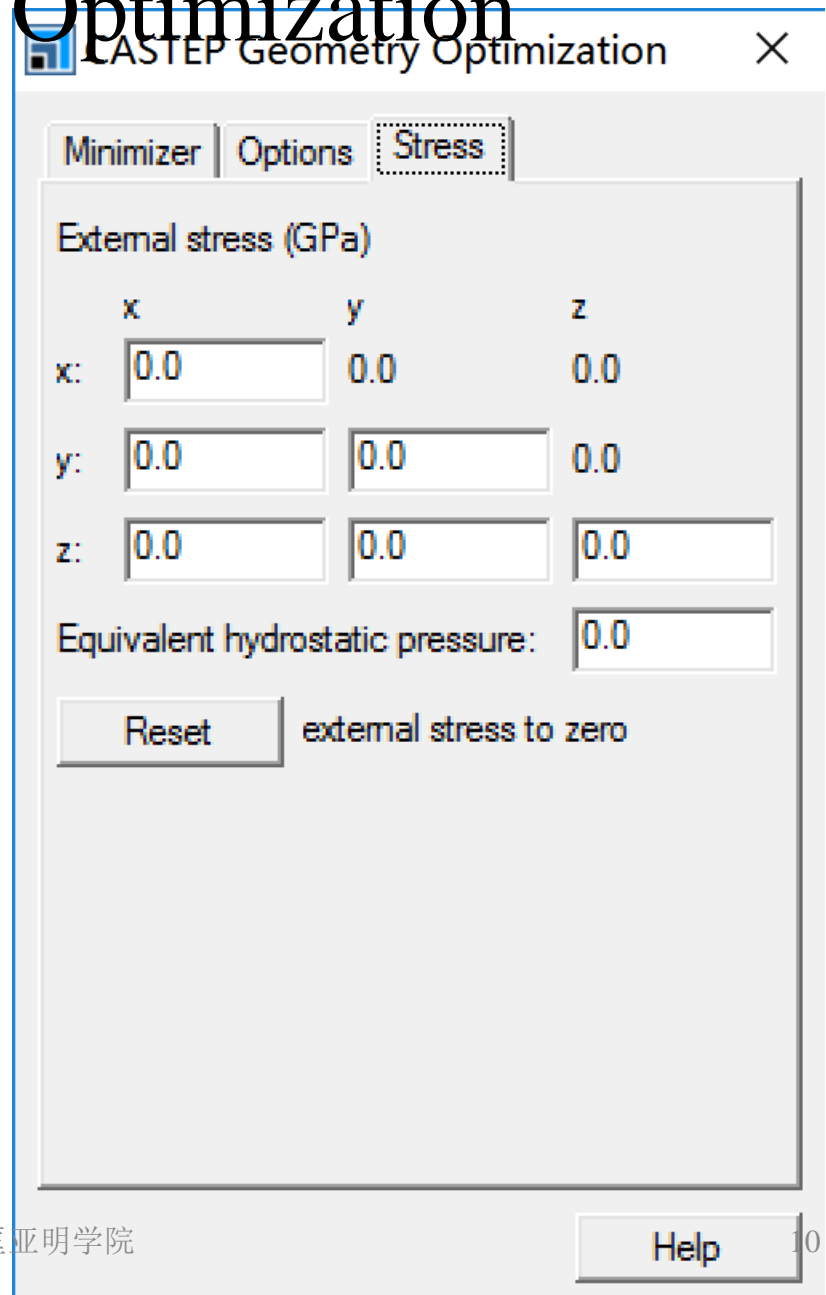
→ More... for **Options**



2. Geometry Optimization

CASTEP Calculation

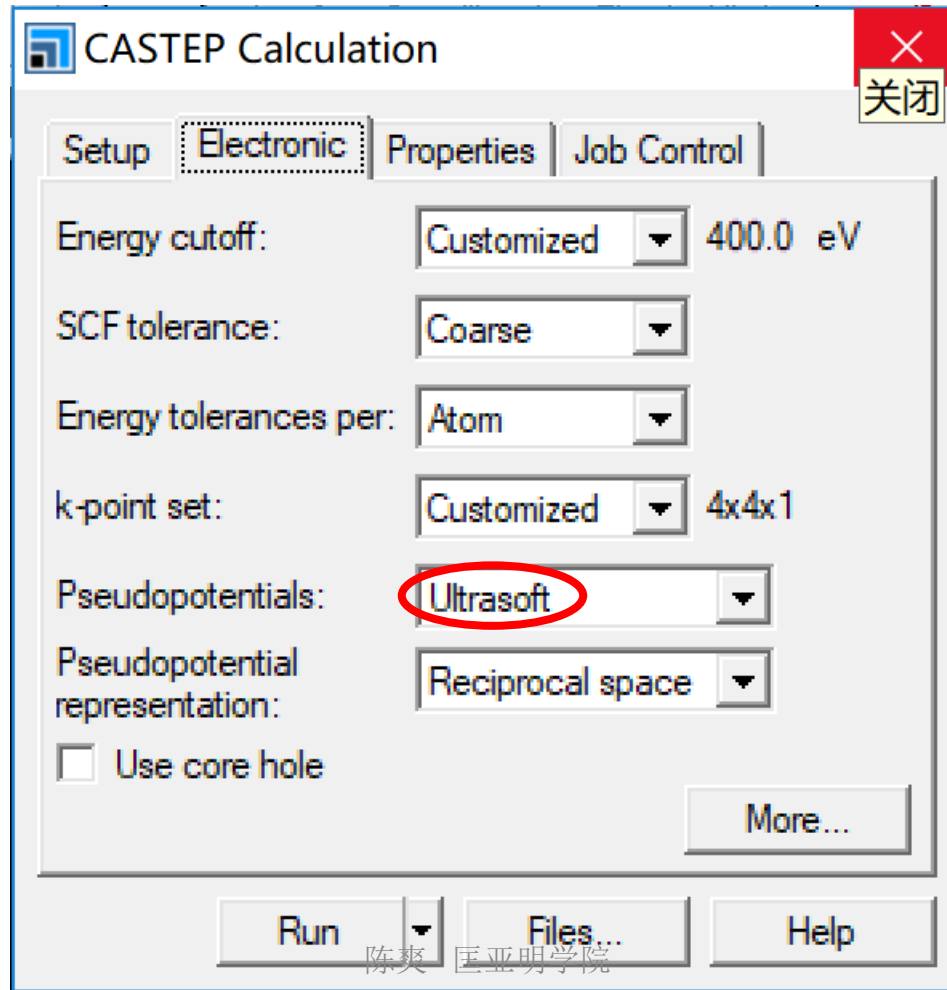
Setup → More... for **Stress**
(默认设置没有更改)



2. Geometry Optimization

CASTEP Calculation

Electronic



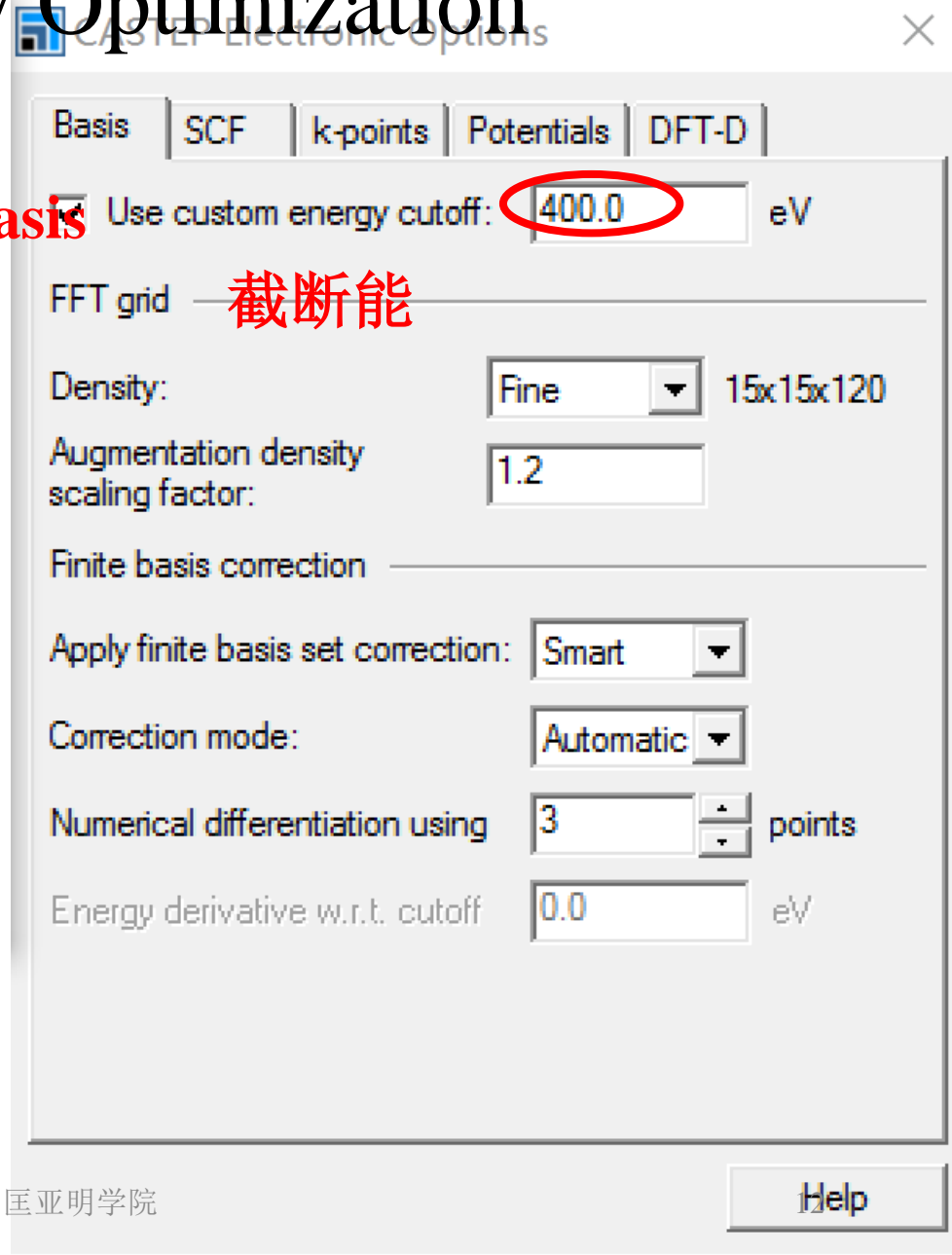
超软赝势

2. Geometry Optimization

CASTEP Calculation

Electronic

→ More... for Basis



The image shows the 'CASTEP Electronic Options' dialog box. The 'Basis' tab is selected. The 'Use custom energy cutoff' checkbox is checked, and the value '400.0' is entered in the adjacent text box, which is circled in red. The unit 'eV' is shown to the right. Below this, the 'FFT grid' is set to '15x15x120'. The 'Density' is set to 'Fine' and the 'Augmentation density scaling factor' is '1.2'. Under 'Finite basis correction', 'Apply finite basis set correction' is set to 'Smart', 'Correction mode' is 'Automatic', 'Numerical differentiation using' is '3' points, and 'Energy derivative w.r.t. cutoff' is '0.0' eV. A red label '截断能' (cutoff energy) is placed next to the energy cutoff field. A 'Help' button is at the bottom right.

CASTEP Electronic Options

Basis | SCF | k-points | Potentials | DFT-D

☒ Use custom energy cutoff: 400.0 eV

FFT grid — 截断能

Density: Fine 15x15x120

Augmentation density scaling factor: 1.2

Finite basis correction

Apply finite basis set correction: Smart

Correction mode: Automatic

Numerical differentiation using 3 points

Energy derivative w.r.t. cutoff 0.0 eV

Help

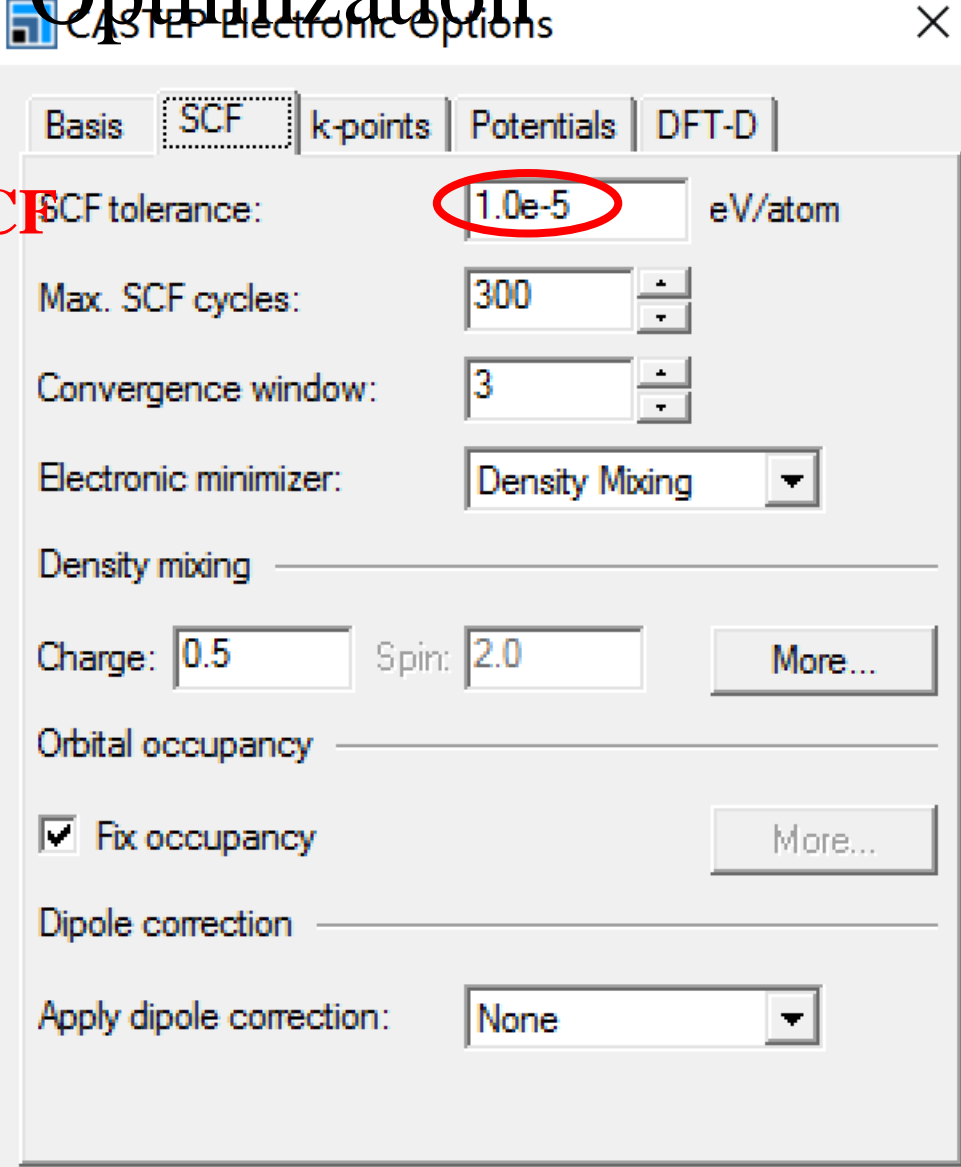
2. Geometry Optimization

CASTEP Calculation

Electronic

→ More... for SCF

自洽收敛标准：
两次波函数更新能量差



The image shows the 'CASTEP Electronic Options' dialog box. The 'SCF' tab is selected. The 'SCF tolerance' is set to $1.0\text{e-}5$ eV/atom, which is circled in red. Other settings include 'Max. SCF cycles' at 300, 'Convergence window' at 3, and 'Electronic minimizer' set to 'Density Mixing'. There are 'More...' buttons for 'Density mixing', 'Orbital occupancy', and 'Dipole correction'. The 'Charge' is 0.5 and 'Spin' is 2.0. The 'Apply dipole correction' is set to 'None'. A 'Help' button is at the bottom right.

Option	Value
SCF tolerance	$1.0\text{e-}5$ eV/atom
Max. SCF cycles	300
Convergence window	3
Electronic minimizer	Density Mixing
Charge	0.5
Spin	2.0
Orbital occupancy	Fix occupancy (checked)
Apply dipole correction	None

2. Geometry Optimization

CASTEP Calculation

Electronic

→ More... for **k-points**

CASTEP Electronic Options

×

Basis | SCF | **k-points** | Potentials | DFT-D

Gamma point only

☐ Quality: Coarse

☐ Separation: 0.05 1/Å

☒ Custom grid parameters

Monkhorst-Pack grid

	a	b	c
Grid parameters:	4	4	1
Actual spacing:	0.11735	0.11735	0.05 1/Å
Origin shift:	0	0	0

Display points...

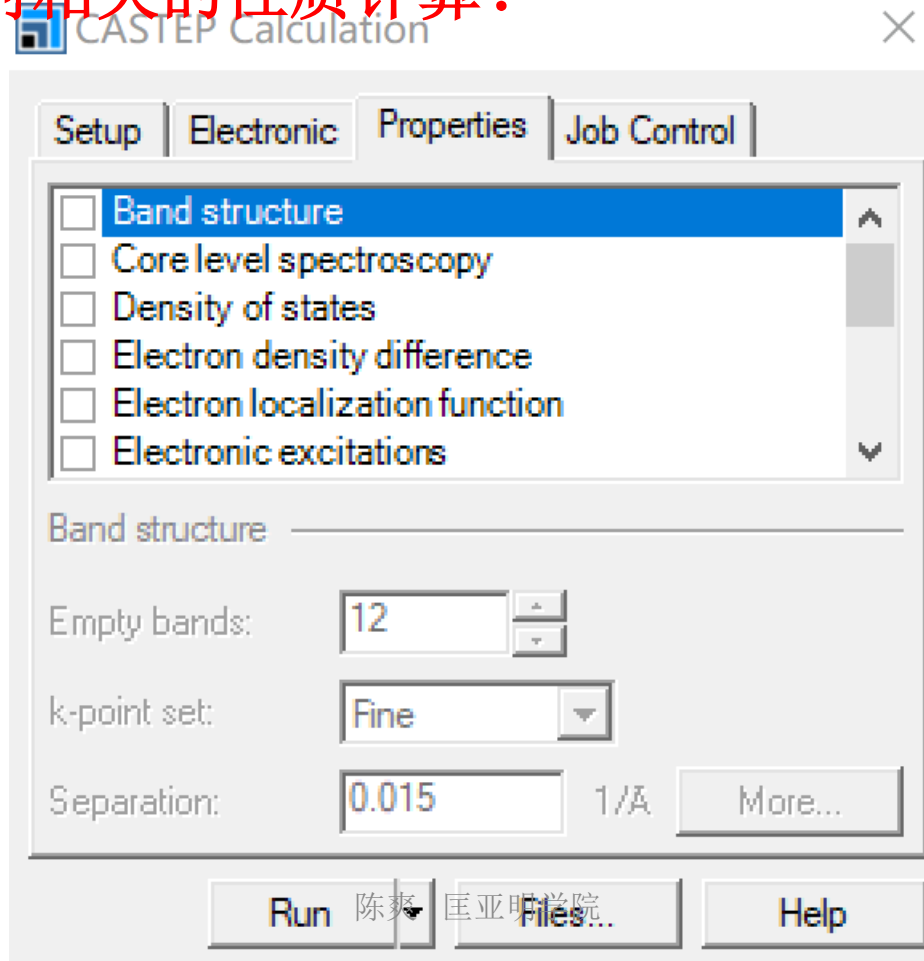
1d Help

2. Geometry Optimization

CASTEP Calculation

Properties

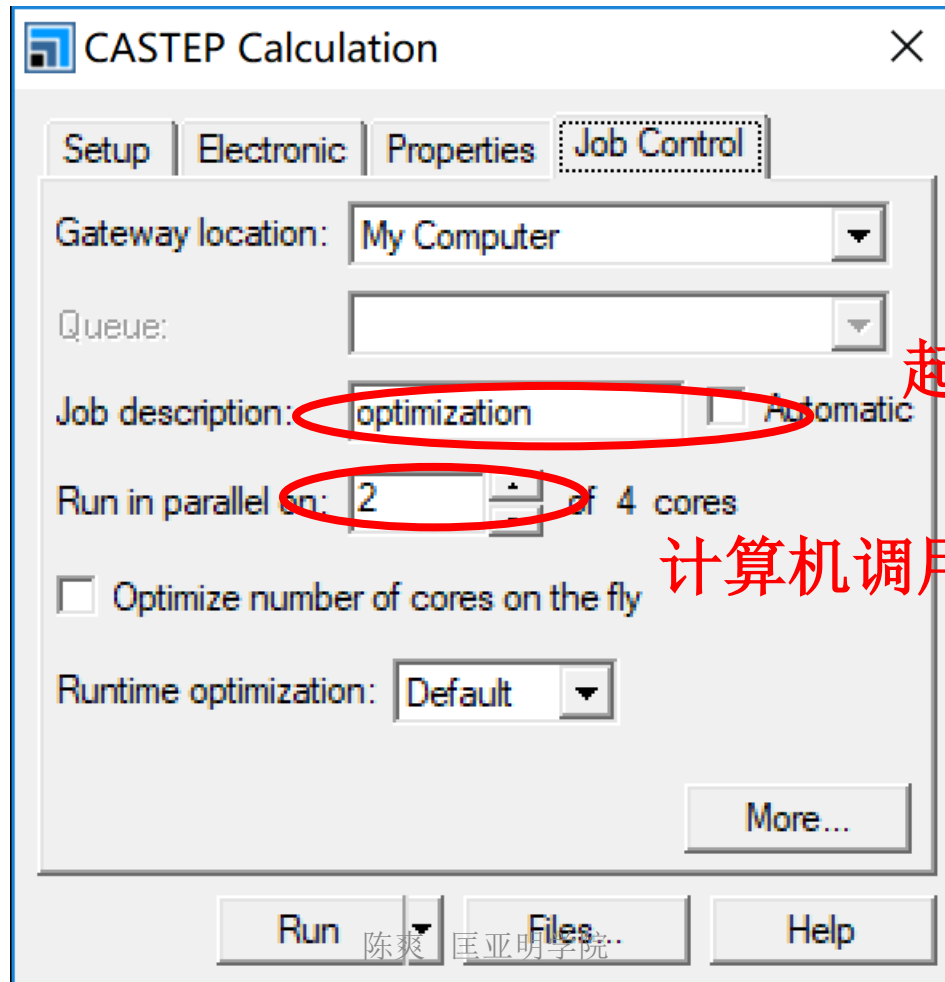
不要勾选任何相关的性质计算！



2. Geometry Optimization

CASTEP Calculation

Job Control



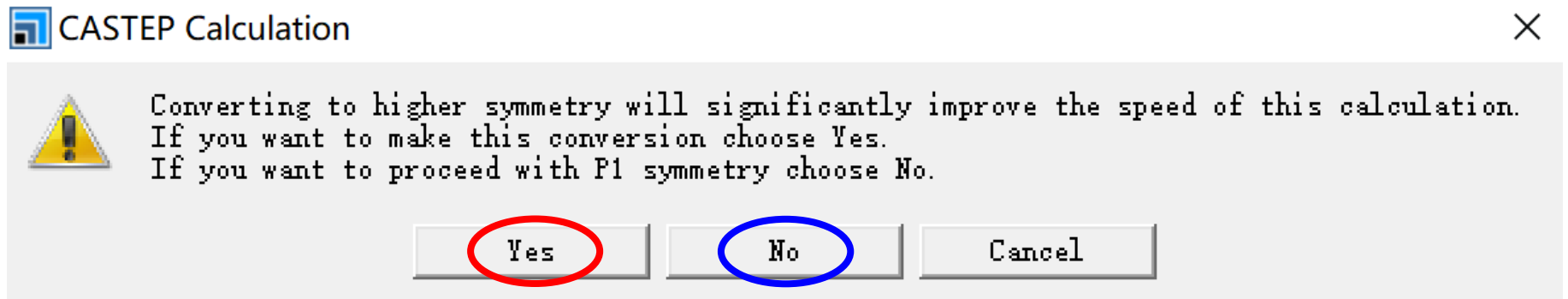
起文件名

计算机调用核数

2. Geometry Optimization

CASTEP Calculation

After submitting this job:



回到2个原子的
六方单胞

还是4个原子的
正交单胞

3. Charge Density

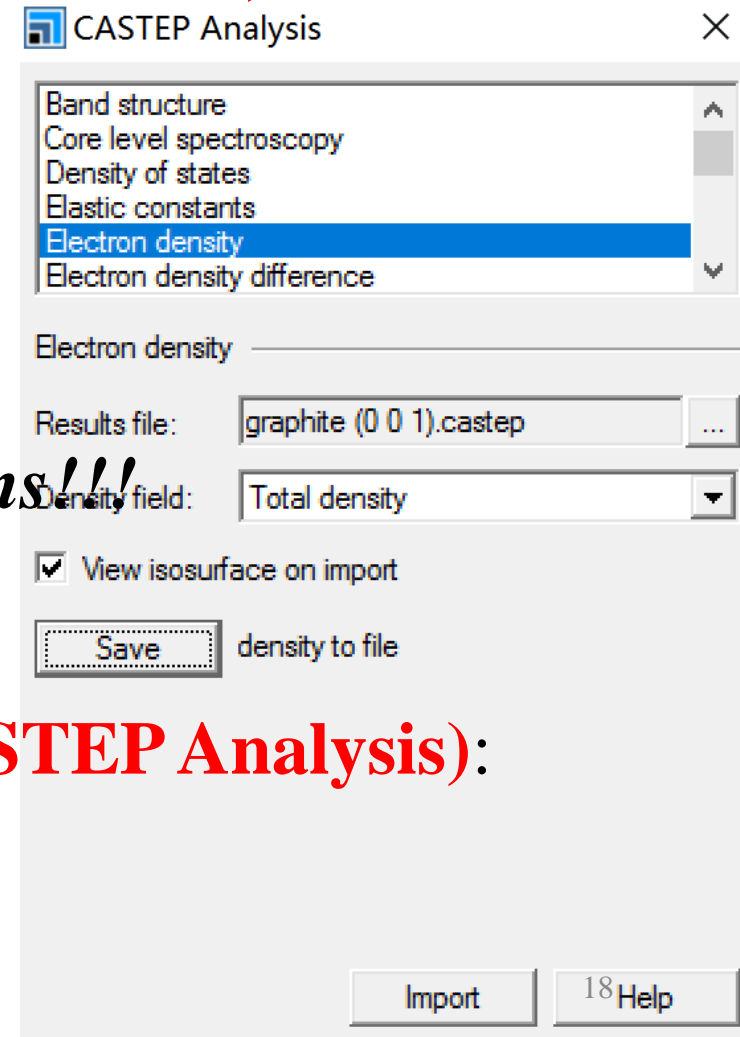
(1) Setting for higher-computational-accuracy single-point calculations (**CASTEP Calculation**):

- ① Task: Energy
- ② K -point set: $8 \times 8 \times 1$
- ③ SCF tolerance: $10\text{e-}6$ eV/atom

Taking the optimal structure (.xsd)
for the following property calculations!!!*

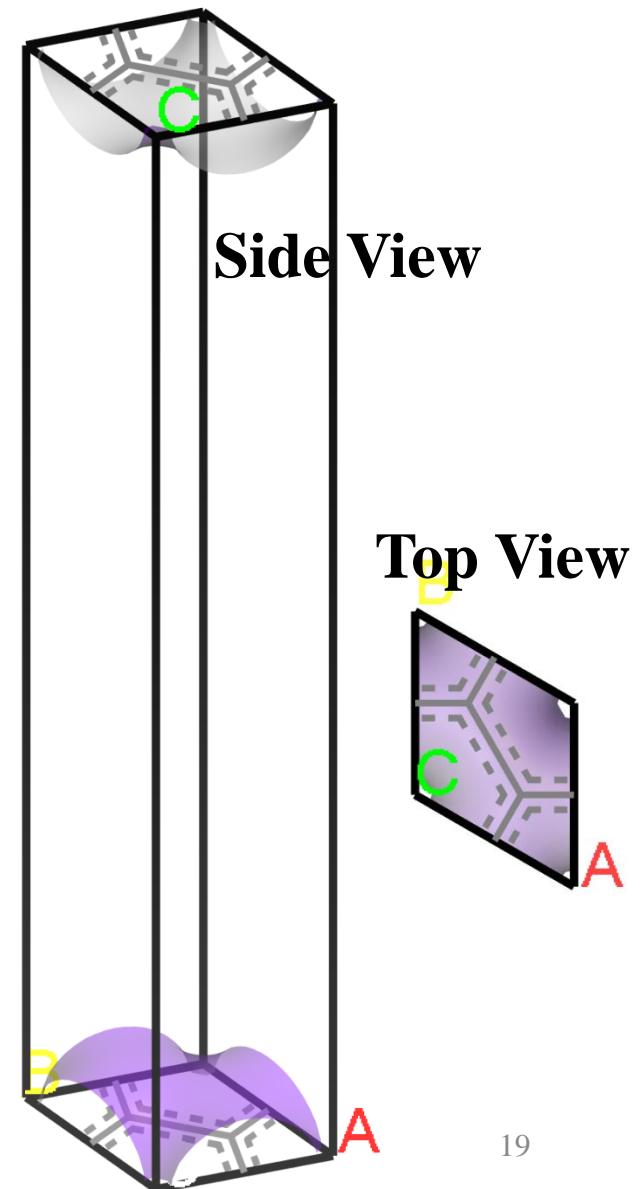
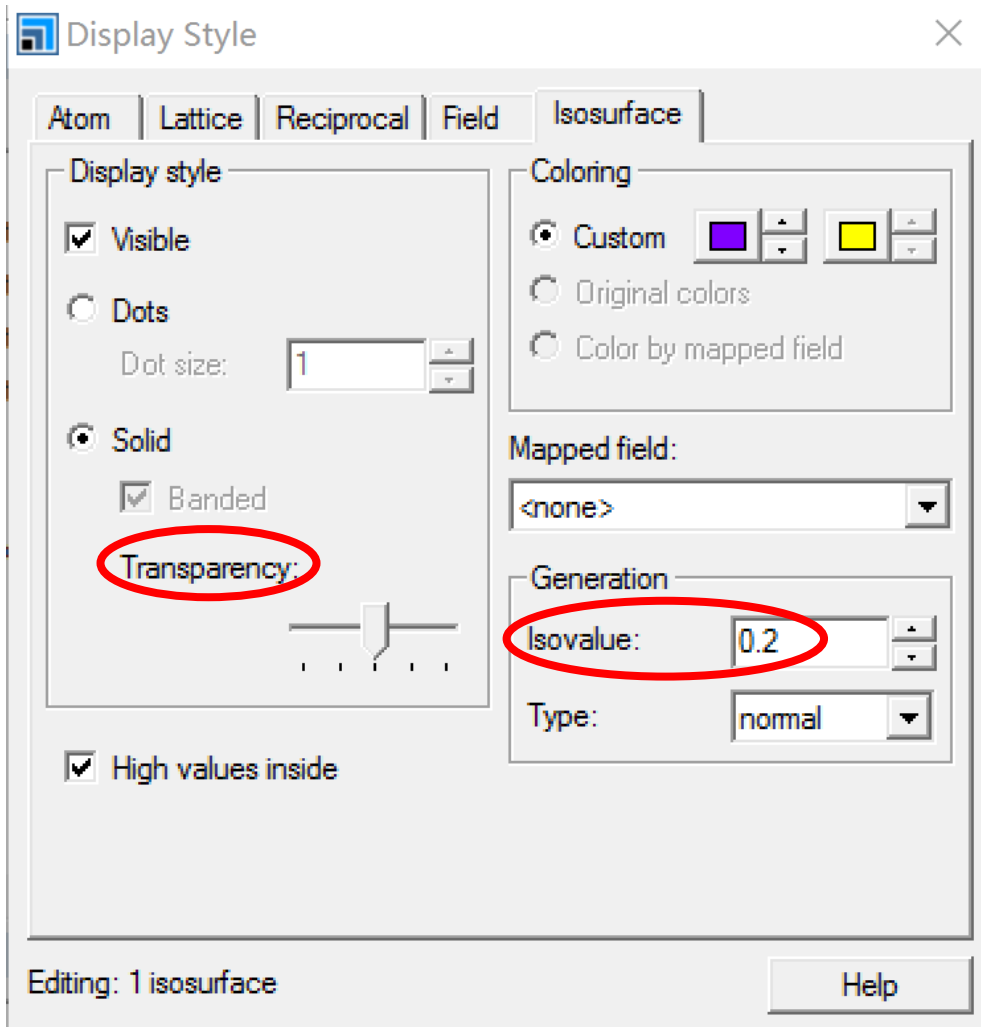
(2) Visualize charge density (**CASTEP Analysis**):

- ① Select “Electron density”
- ② Import



3. Charge Density

(3) Change “Display Style”

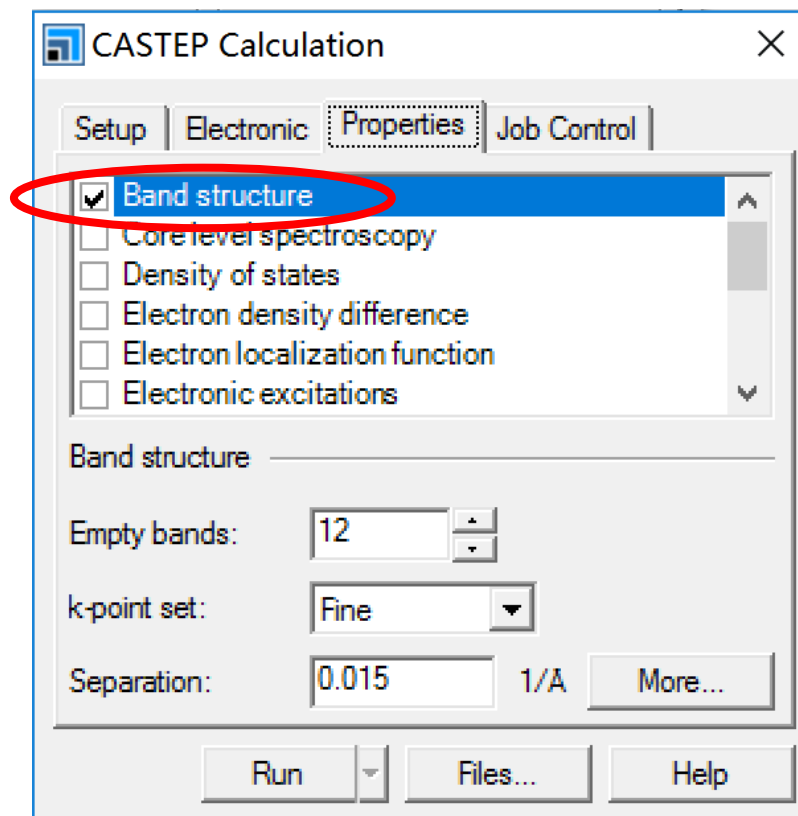


4. Band Structure

(1) Setting:

① Setup → Task: Properties

② Properties → Mark “Band structure”



4. Band Structure

(1) Setting:

③ Set high-symmetry K points: “Tools → Brillouin Zone Path”

高对称点信息的获取:

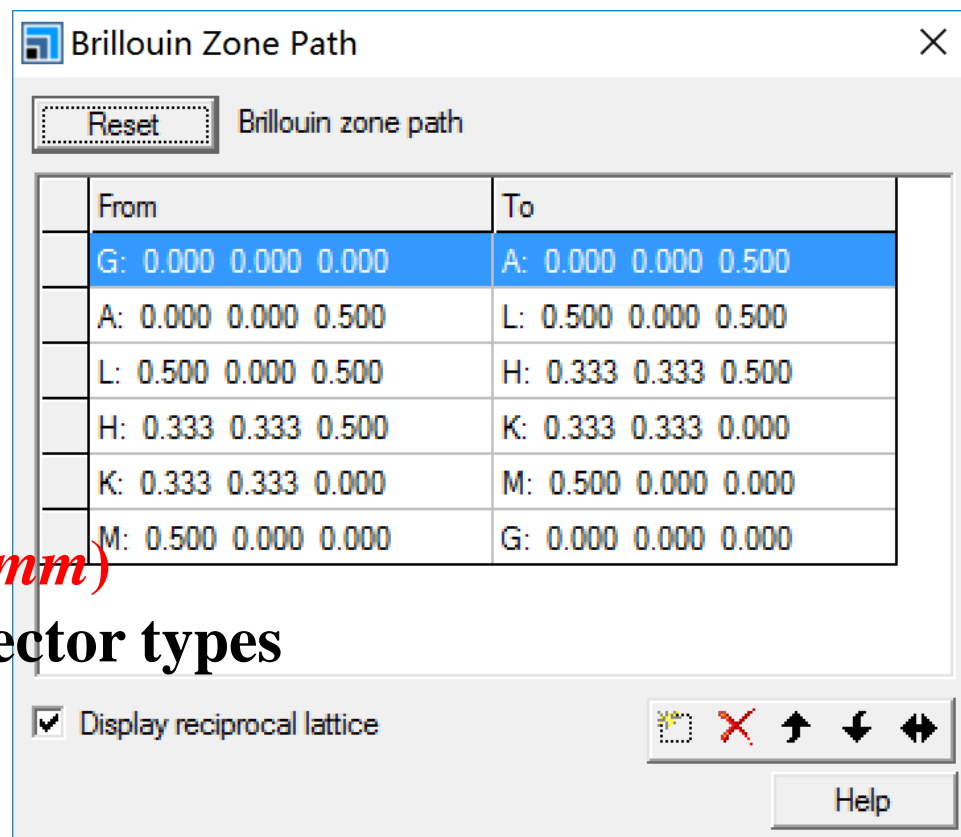
借助网站<http://cryst.ehu.es/>

→ Space-group symmetry

→ KVEC for k vectors

→ Choose space group ($P6/mmm$)

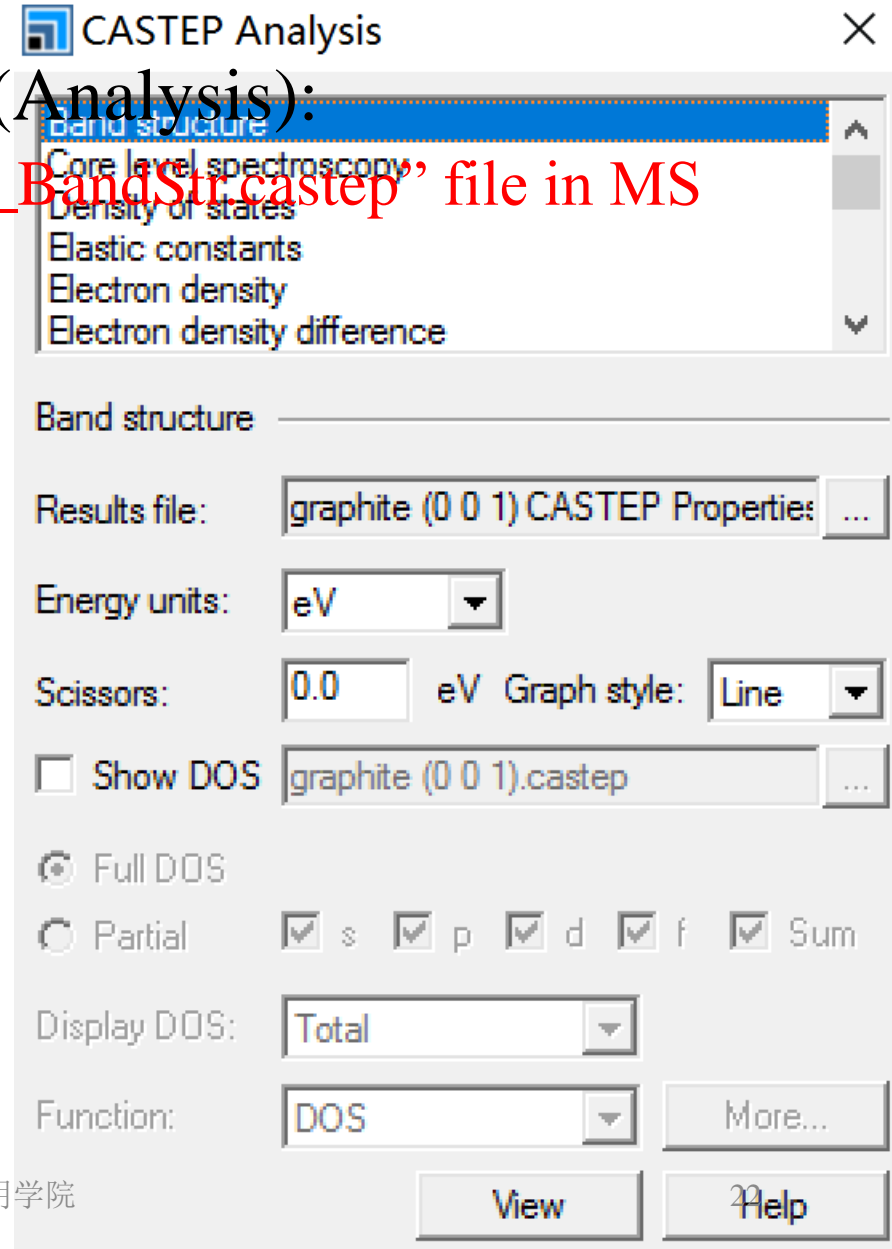
→ Comparative listing of k -vector types



4. Band Structure

(2) Visualize band structure (Analysis):

- ① Open file “band structure_BandStr.castep” file in MS window
- ② Select “Band structure”
- ③ View



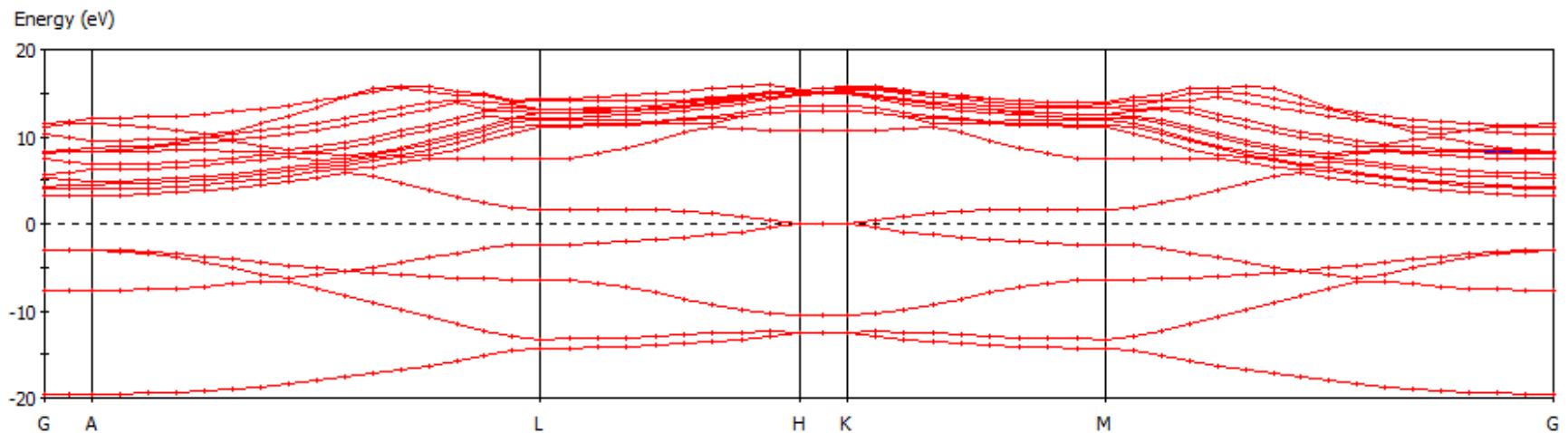
4. Band Structure

Brillouin Zone Path

Reset Brillouin zone path

From	To
G: 0.000 0.000 0.000	A: 0.000 0.000 0.500
A: 0.000 0.000 0.500	L: 0.500 0.000 0.500
L: 0.500 0.000 0.500	H: 0.333 0.333 0.500
H: 0.333 0.333 0.500	K: 0.333 0.333 0.000
K: 0.333 0.333 0.000	M: 0.500 0.000 0.000
M: 0.500 0.000 0.000	G: 0.000 0.000 0.000

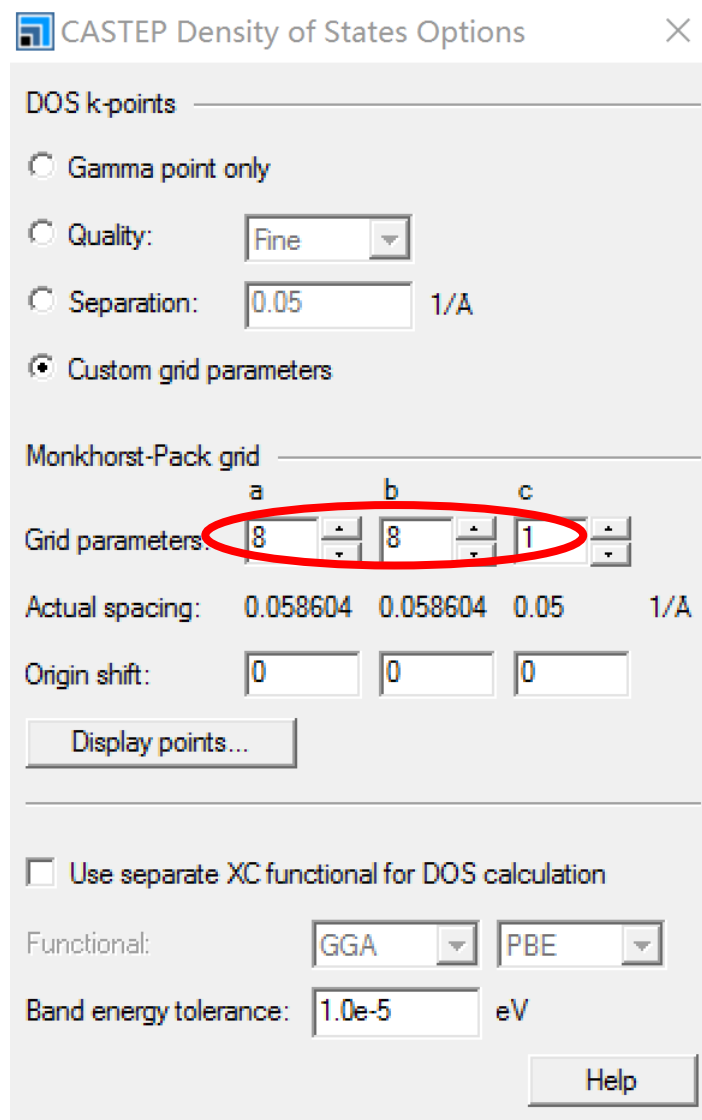
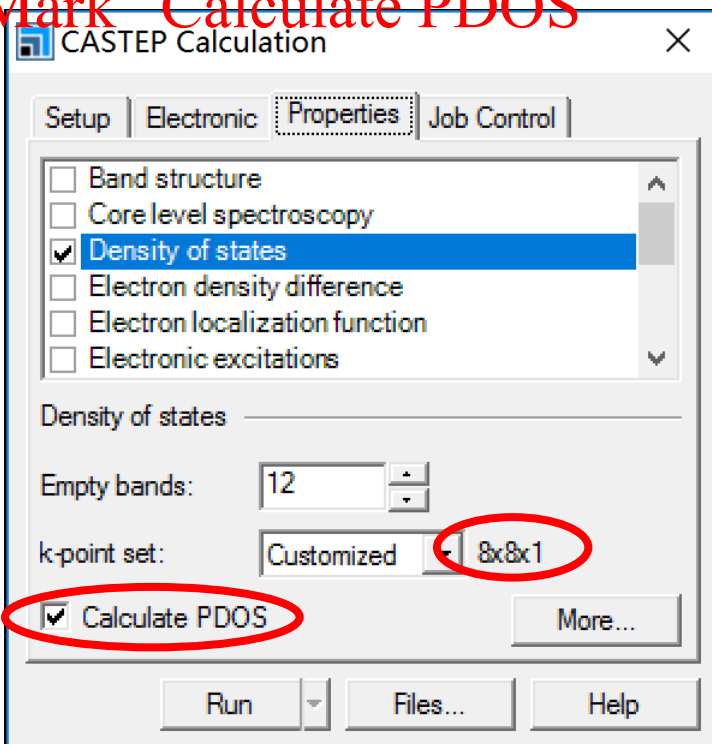
CASTEP Band Structure
Band gap is 0.019 eV



5. Density of States (DOS & PDOS)

(1) Setting **(Calculation)**:

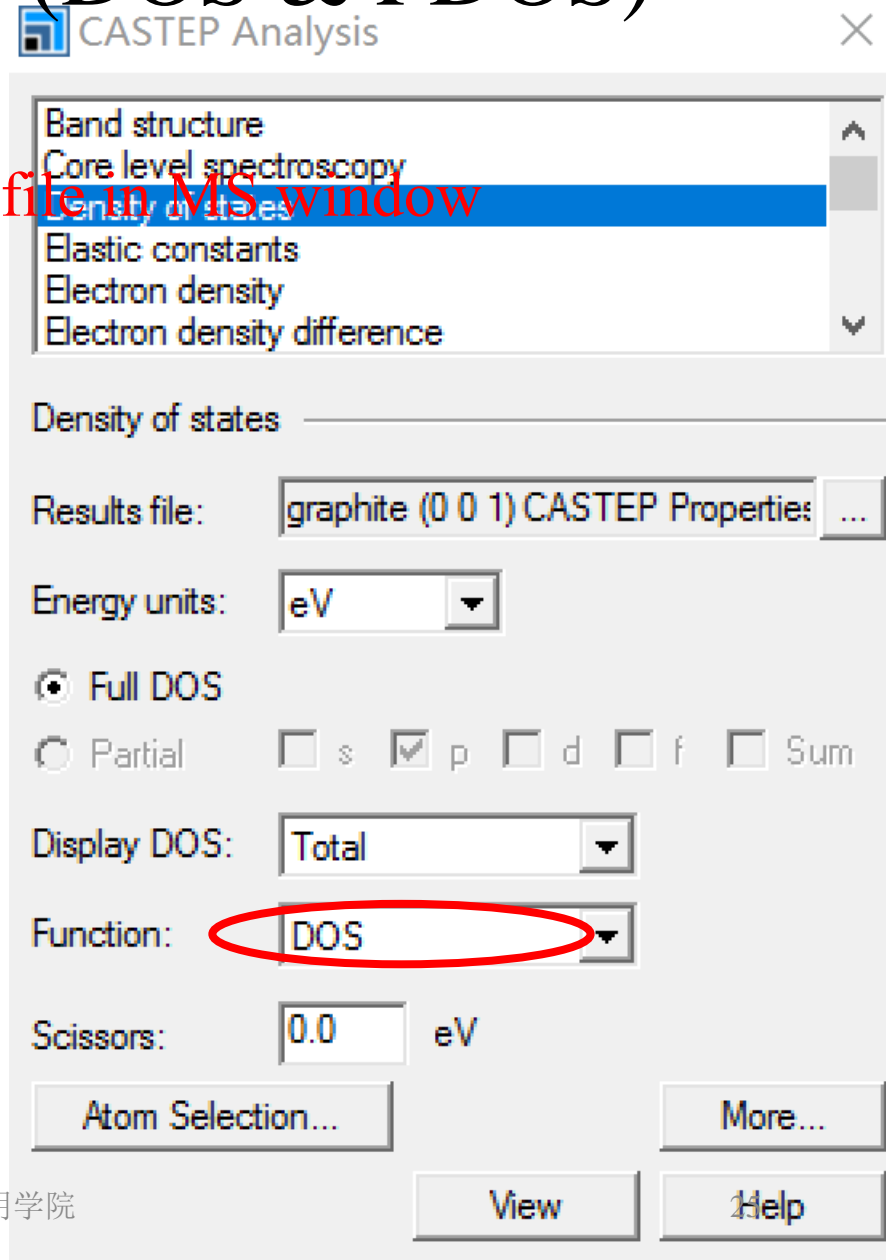
- ① Task: Properties
- ② Properties: Mark “Density of states”
- ③ More... for k-point set
- ④ Mark “Calculate PDOS”



5. Density of States (DOS & PDOS)

(2) Visualize DOS (**Analysis**):

- ① Open file “DOS_DOS.castep” file in MS window
- ② Select “Density of states”
- ③ Select “Full DOS” or “Partial”
- ④ View



5. Density of States (DOS & PDOS)

