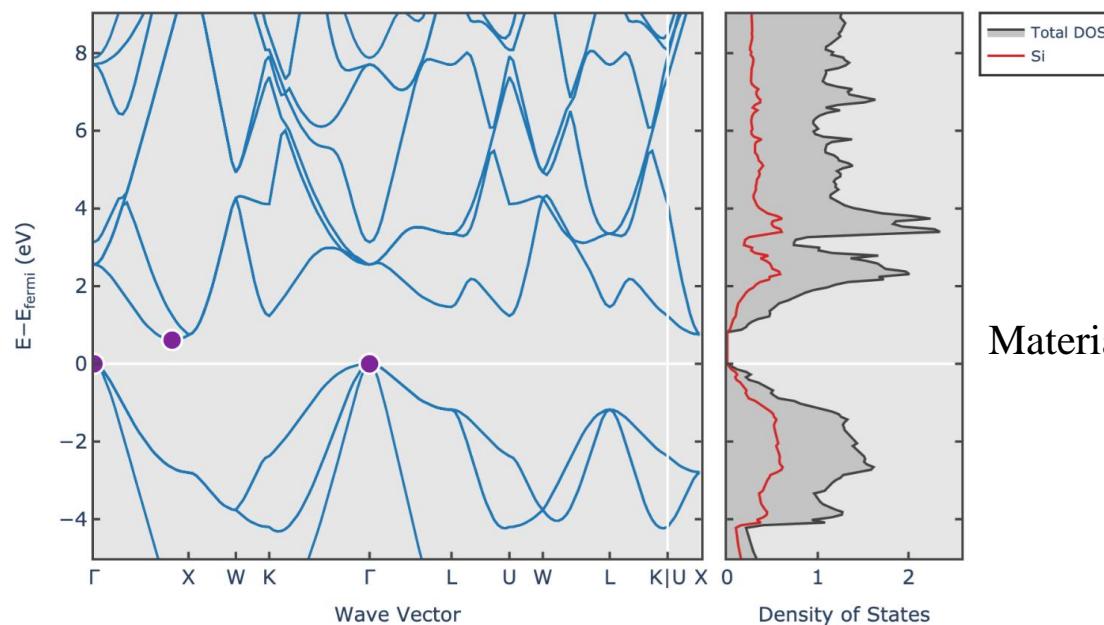


能带结构与态密度计算

Band structure and Density of states

在第一性原理计算中。能带结构 (band structure) 与态密度 (density of states, DOS) 是其中最为常见且具有互补性的两类表征方法，它们分别强调电子能量色散关系 $E(k)$ 与电子能量分布统计 $\rho(E)$ 。

能带和倒空间的k矢量有关，DOS只是和能量相关，两者相互关联



Material Project 中 Si 的能带和 DOS 图

态密度计算

态密度计算 (Density of states)

$$\rho(E) = \frac{1}{N_k} \sum_{i,\mathbf{k}} \delta(\varepsilon_{i,\mathbf{k}} - E) = \frac{\Omega_{\text{cell}}}{(2\pi)^d} \int_{\text{BZ}} d\mathbf{k} \delta(\varepsilon_{i,\mathbf{k}} - E)$$

定义：态密度表示每单位能量和每单位体积中包含的电子状态数
 $\rho(E)dE$ 表示单位体积中能量处于 $E+dE$ 之间的电子态的数目

需在布里渊区对波矢 \mathbf{k} 做积分（离散求和），对 \mathbf{k} 点网格有收敛性要求

重要参数：ISMEAR

SIGMA

NEDOS

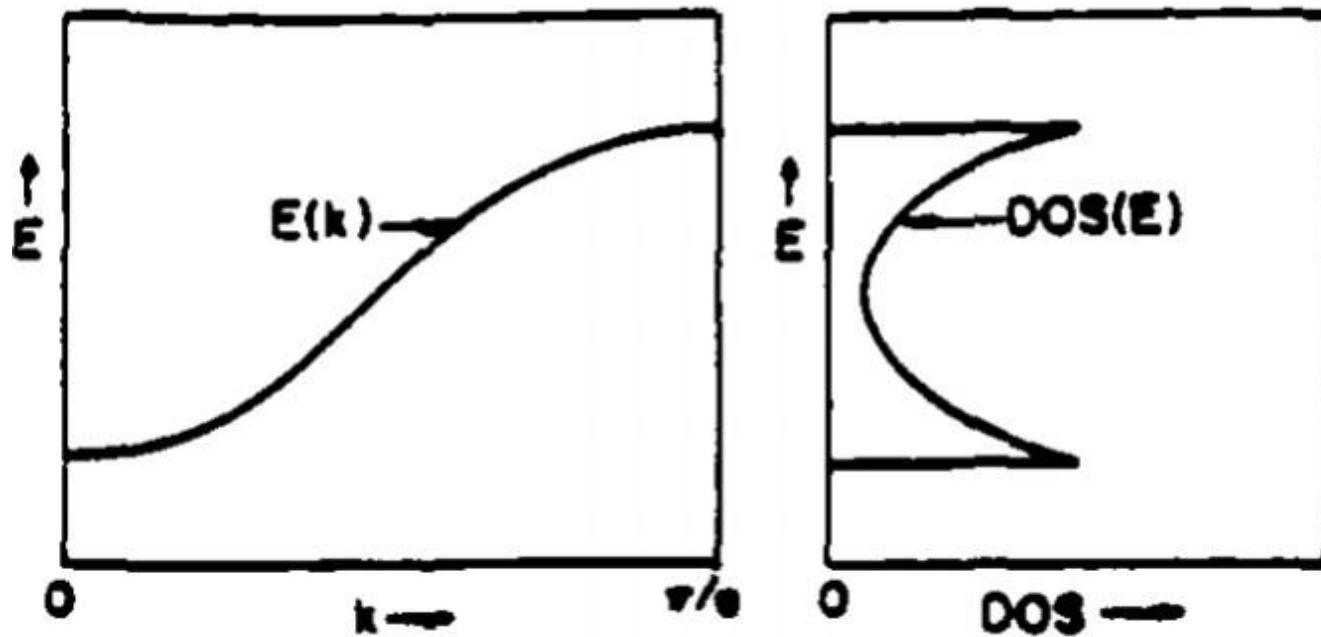
KPOINTS

展宽方法

展宽宽度

DOS的能量点数

足够密的 \mathbf{k} 点

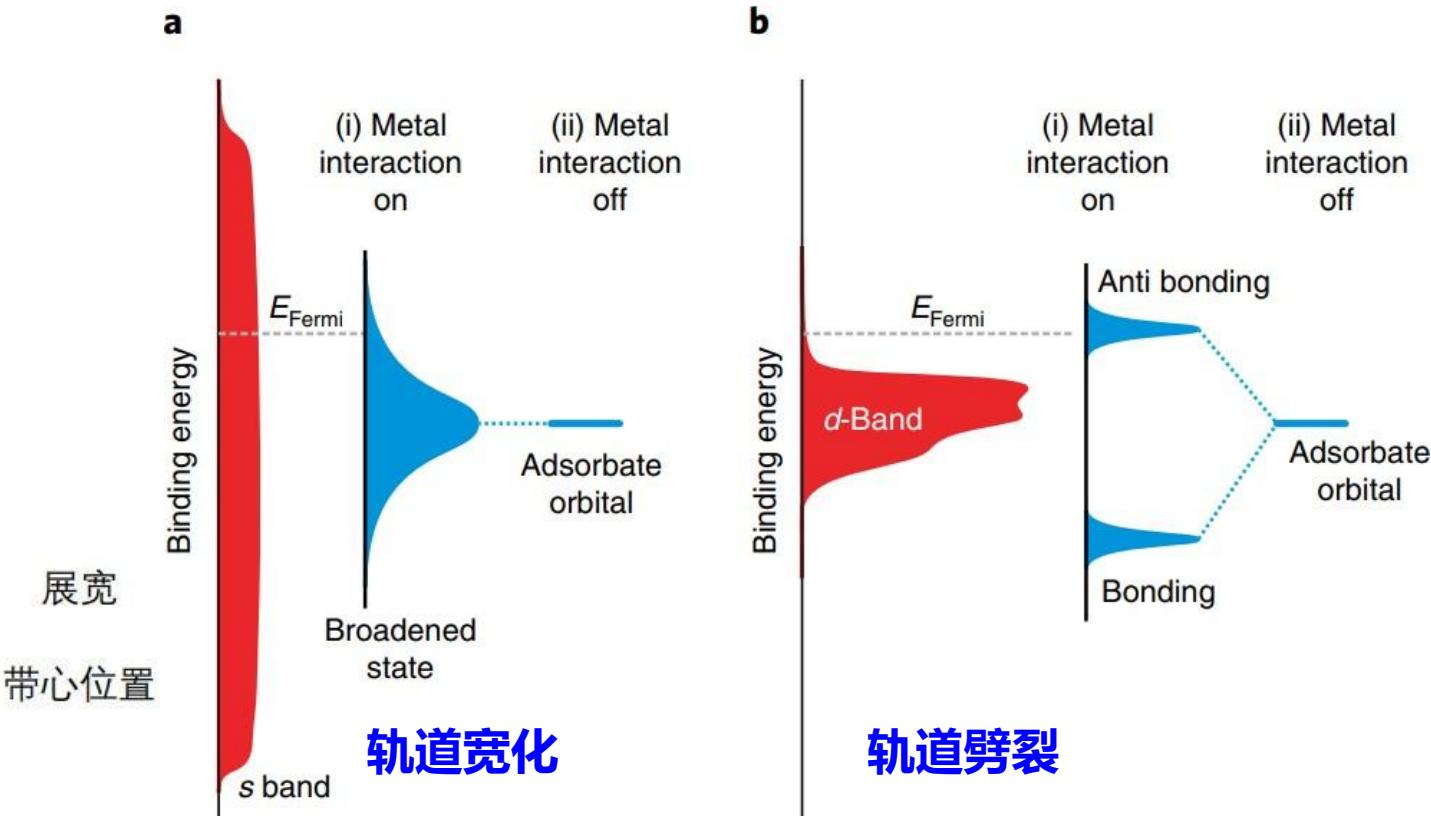
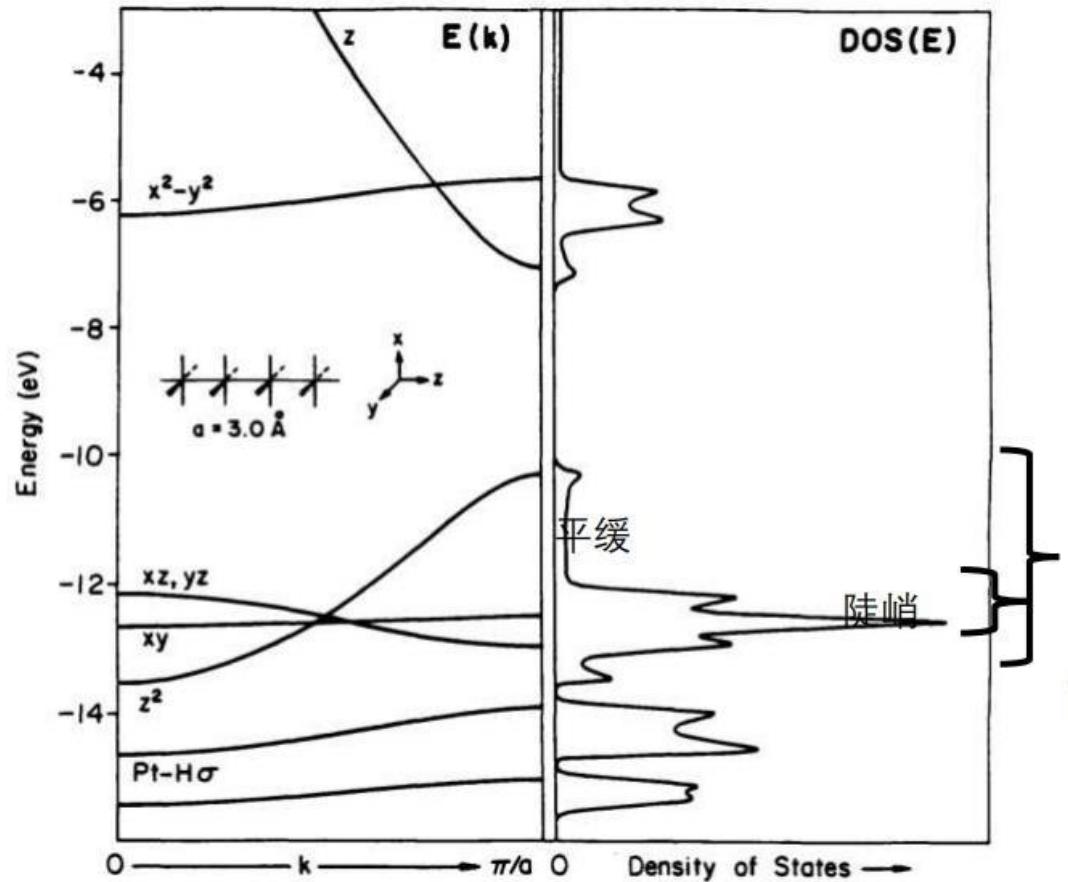


(对能带中的K进行积分 在E上进行投影 DOS)

1. 一般来说能带越密集/平缓的地方，单位能量范围内态越多，所以DOS也越大，能带越稀疏/陡峭的地方态密度就越小。
2. 对DOS积分就能得到电子数目，比如上图只有一条能带，上面占据了两个电子，那么对应的DOS图的积分也会是2，代表这个能量范围里的态上有两个电子。 所以DOS的展宽/位置就成了影响体系性质的关键因素

例子——判断电子局域和离域: PtH₄一维分子链

s d轨道和吸附物相互作用

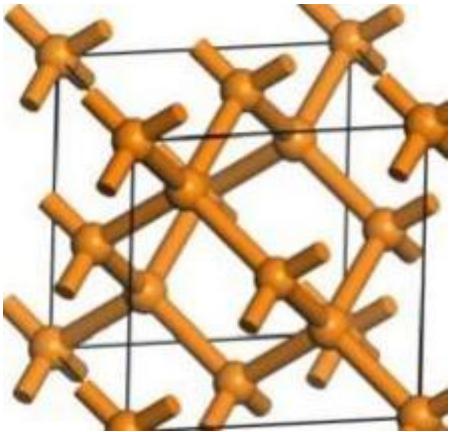


Nature Chemistry | VOL 10 | OCTOBER 2018 | 1008–1015

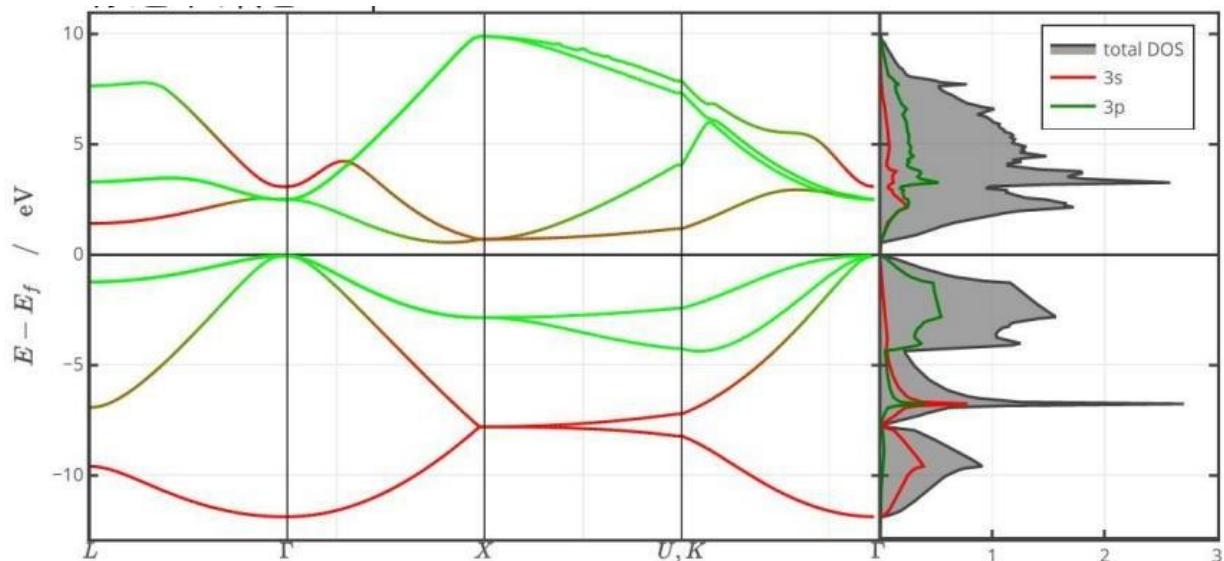
- 根据DOS的展宽就能判断原子轨道之间的作用强弱程度，带心位置能影响体系和其他分子的相互作用。
- 比如dz²轨道，能带比较宽，dos能量跨度比较大，轨道离域，相互作用强
- 比如dxy dxz轨道，能带接近于平带，dos峰尖锐，轨道较局域，作用比较弱

案例——DOS的轨道贡献

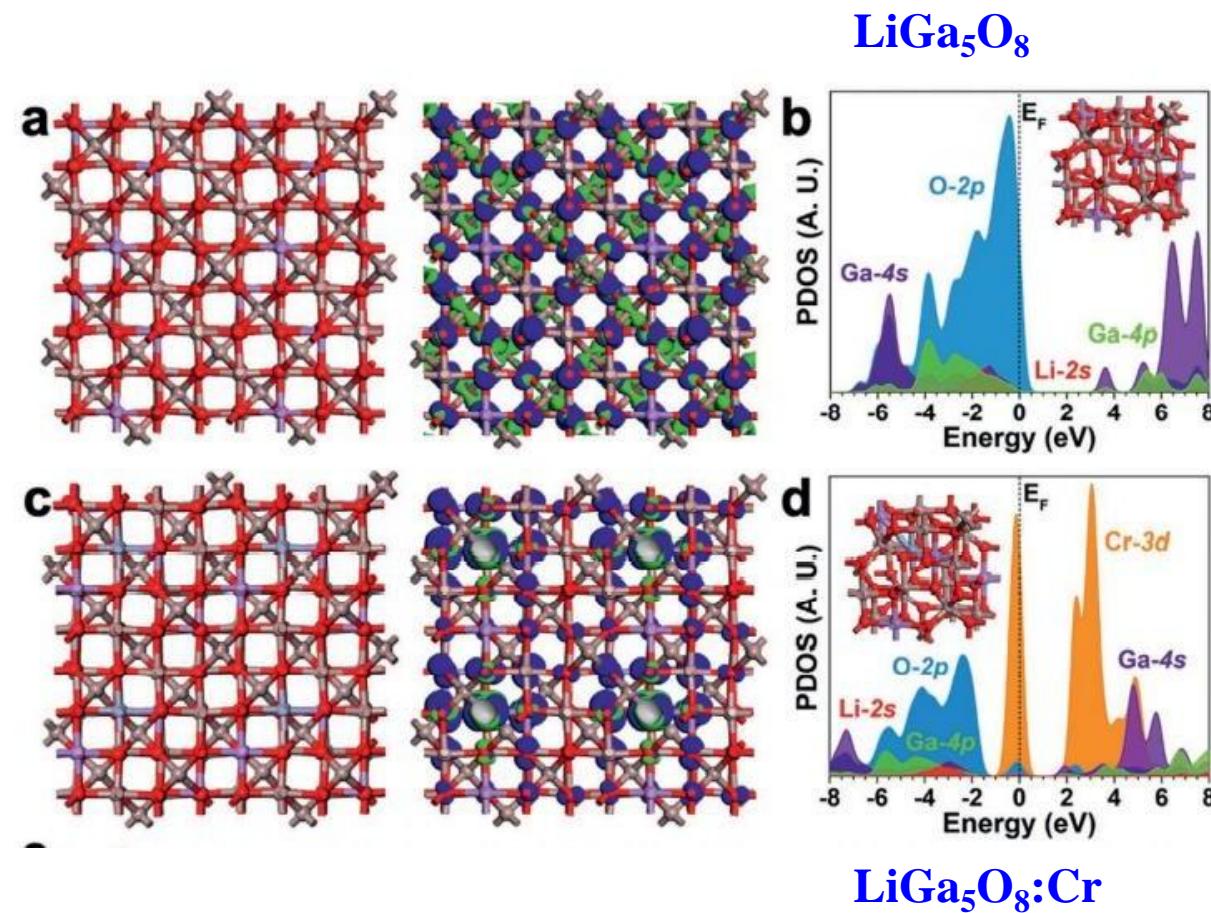
程序会把 E_{fermi} 对齐到0 eV的位置，所以纵坐标是 $E - E_f$



Bulk Si



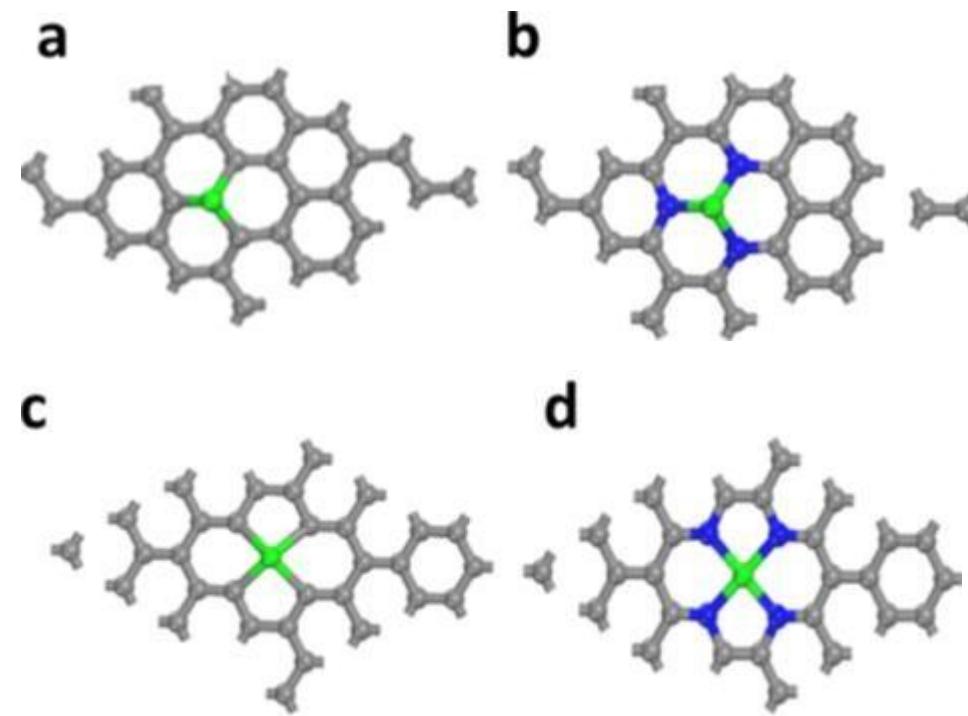
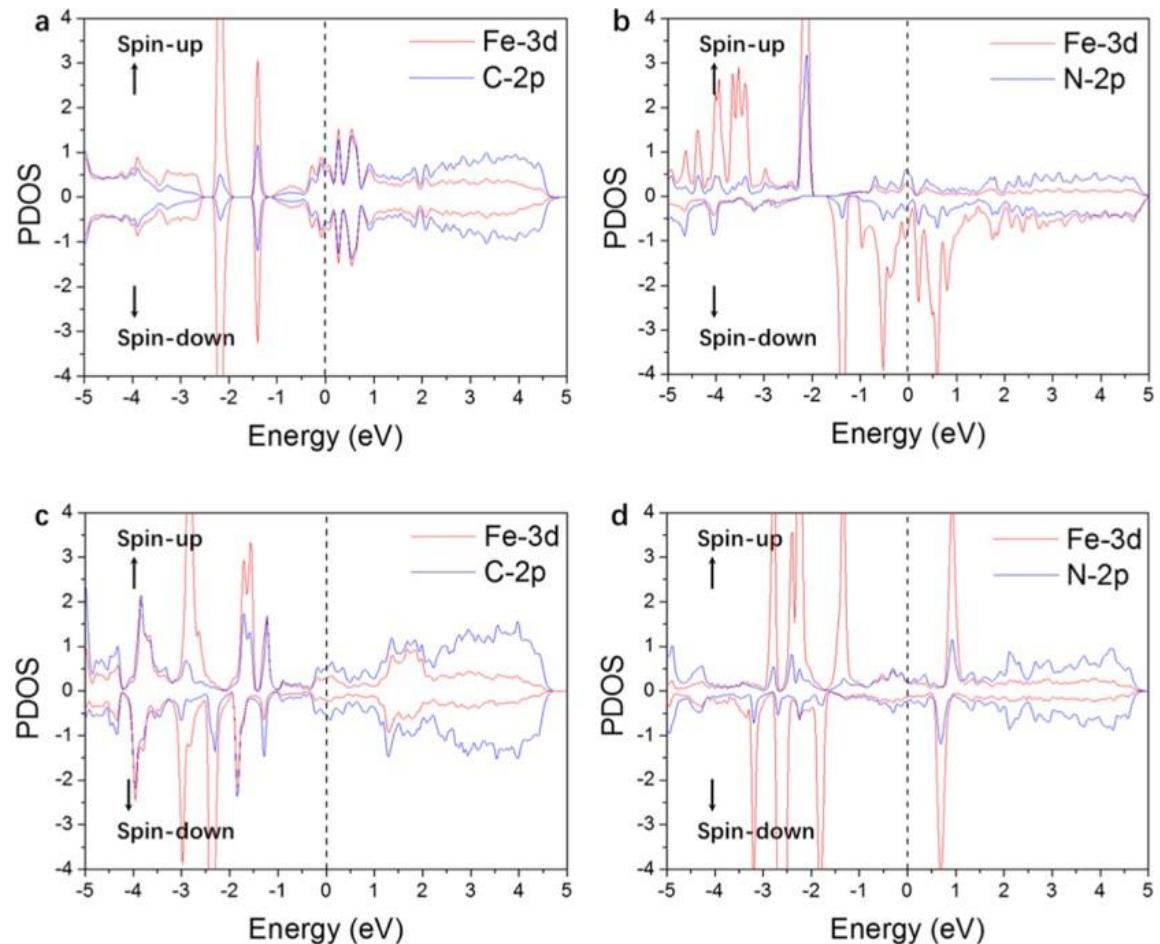
3s轨道贡献比较小



Adv. Funct. Mater. 2021, 31, 2010685

不同原子不同轨道对总态密度的贡献

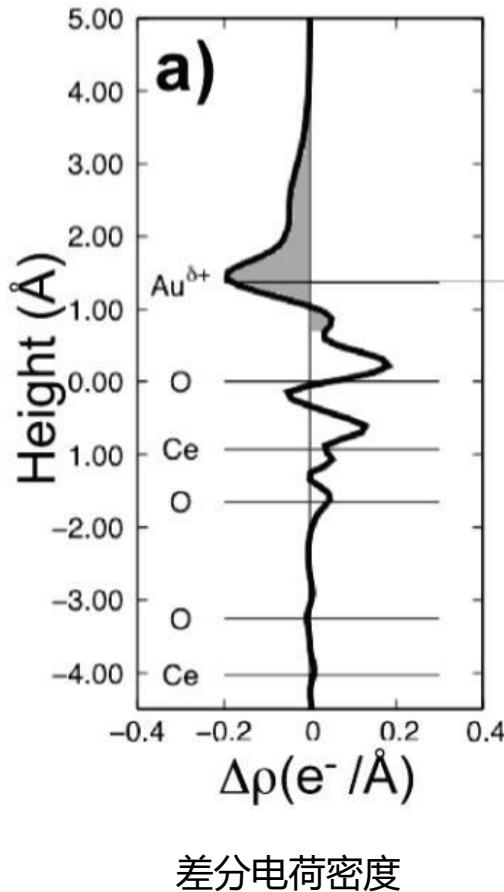
案例——不同自旋电子的态密度



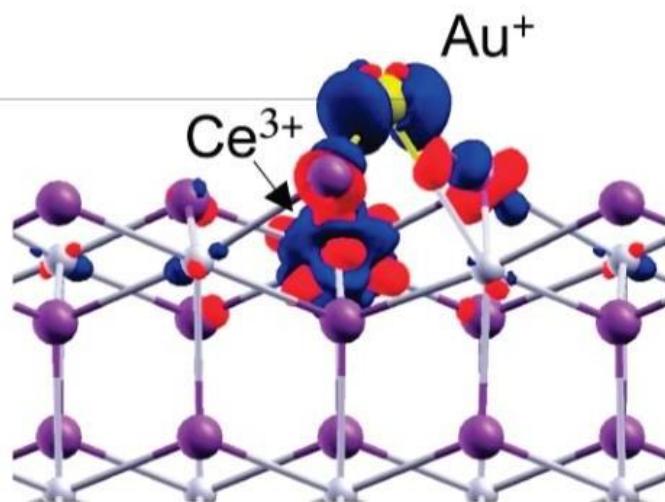
单铁原子 (Fe) 负载在缺陷石墨烯上 (N掺杂或不掺杂)

DOS上下自旋对称则无磁矩，不对称则有净磁矩

案例——研究相互作用模型 (1)



b)

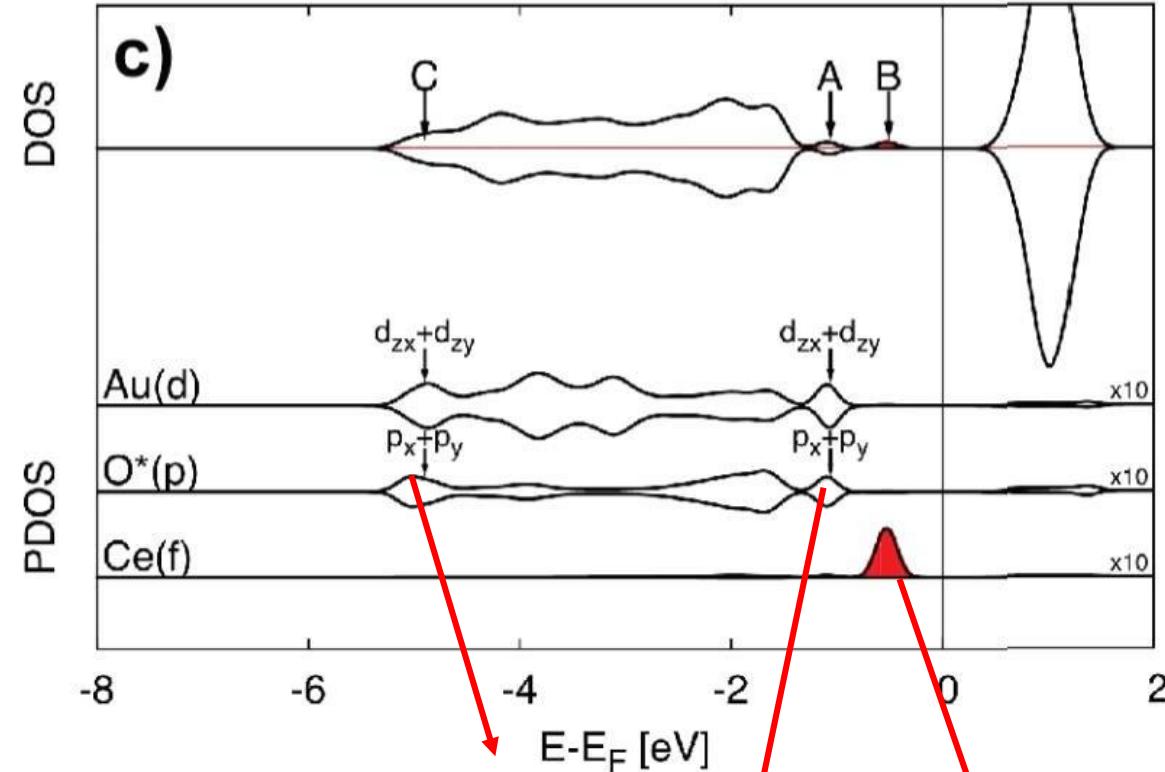


判断离子键看孤立的峰
判断共价键看重叠的峰

Au@bridge

Ce 4f¹ 5d¹ 6s²
Au 6s¹

Ce的4f空轨道



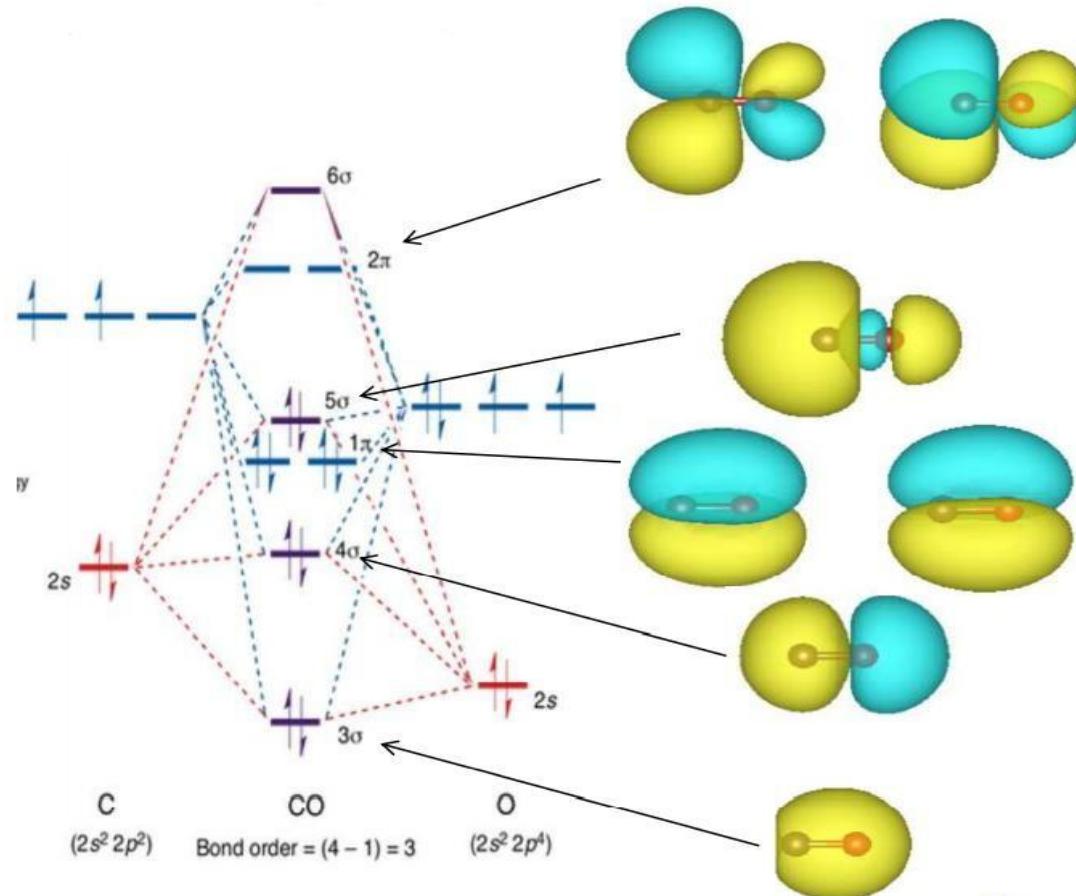
O-Au轨道重叠作用比较大，
共价键

Ce 4f占据一个局
域电子（电子转移），
 $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$

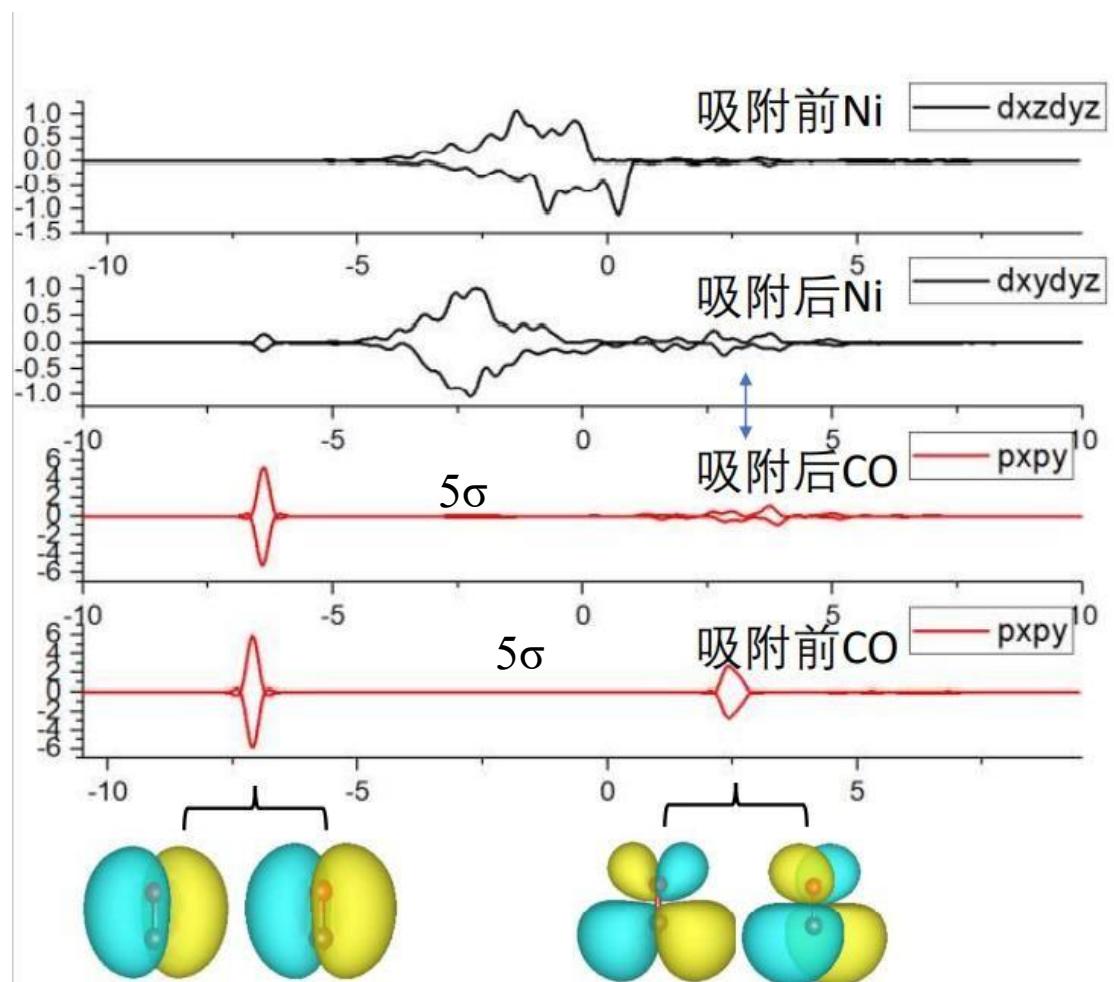
说明Au向CeO₂转移电子，形成Au⁺和Ce³⁺

案例——研究相互作用模型 (2)

CBM VBM 周期性体系
HOMO LUMO 分子体系



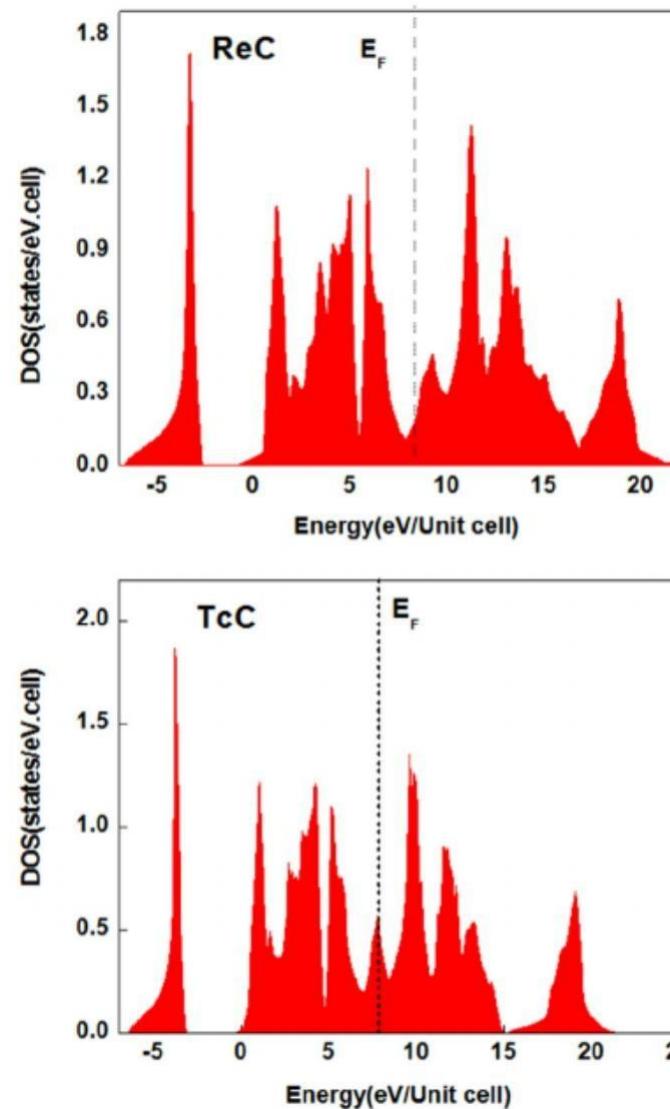
https://mp.weixin.qq.com/s/pc1_YxEJmsAPdiR165jYQQ



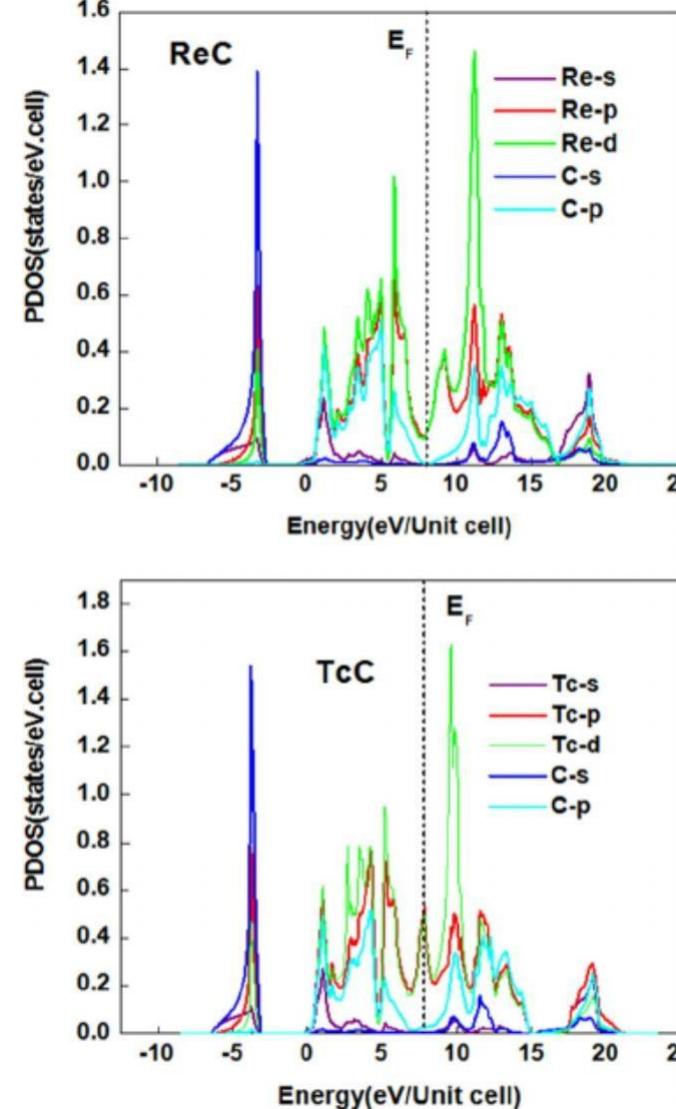
5σ 和 $2\pi^*$ 轨道，与 Ni 的 d 带发生杂化，形成了 5σ 成键和 Ni- $2\pi^*$ 反键。CO 的 5σ 轨道上的电子转移至 Ni 的 d 轨道，使 5σ 轨道发生左移，Ni 的 d 轨道上的电子转移到 CO 的 $2\pi^*$ 轨道，使 $2\pi^*$ 轨道发生分裂，部分进入成键轨道

Density of states计算 (fermi能级未归0)

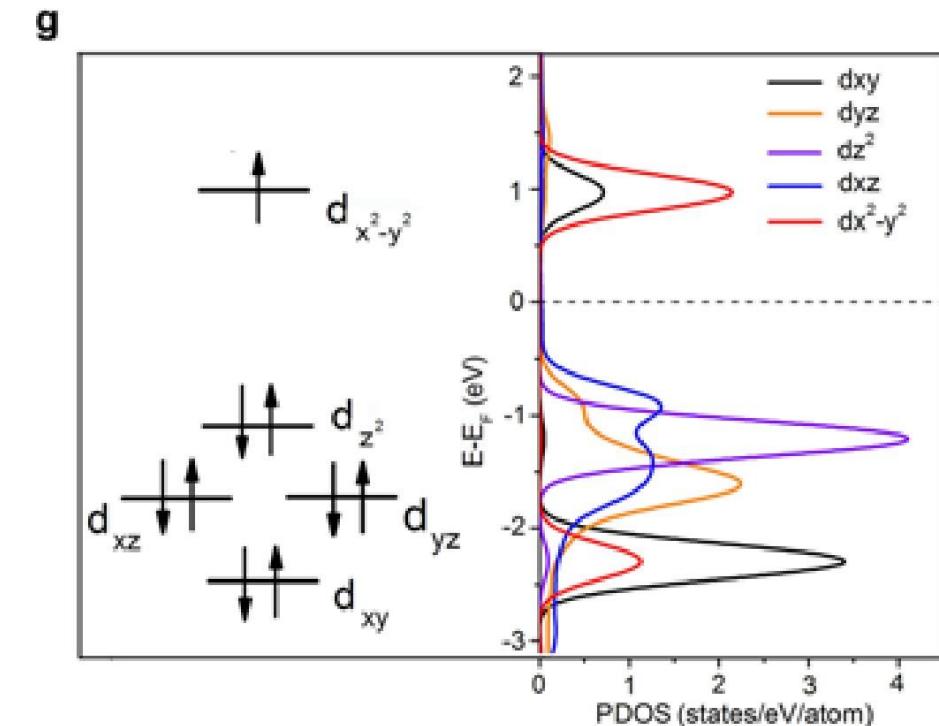
TDOS-total DOS



局域态密度 (LDOS) -s, p, d, f 轨道



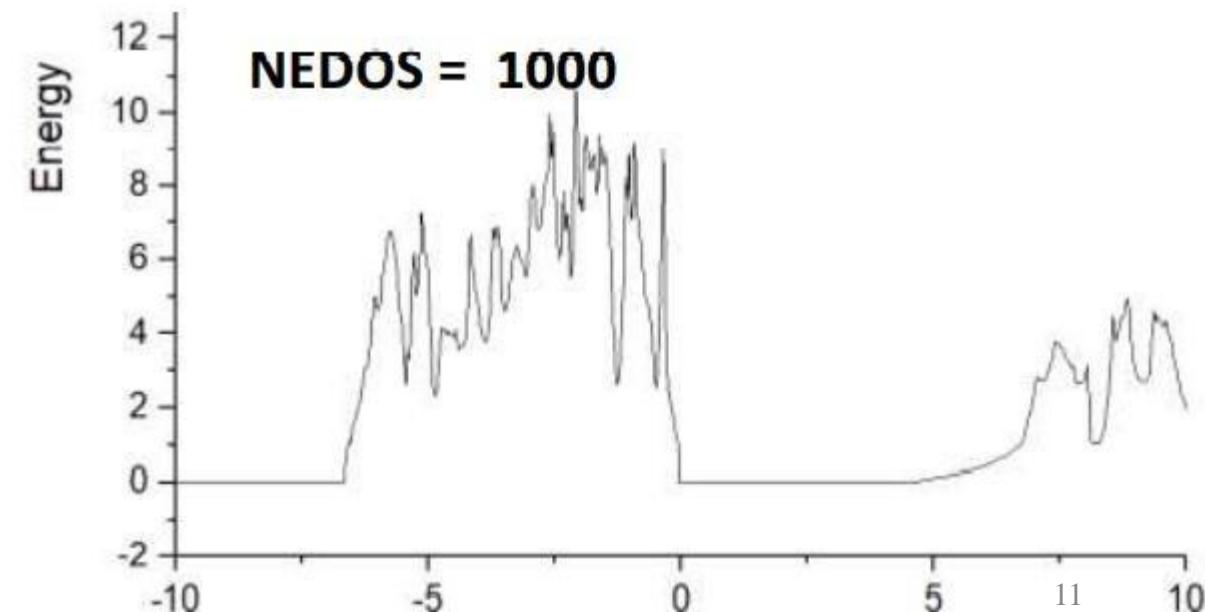
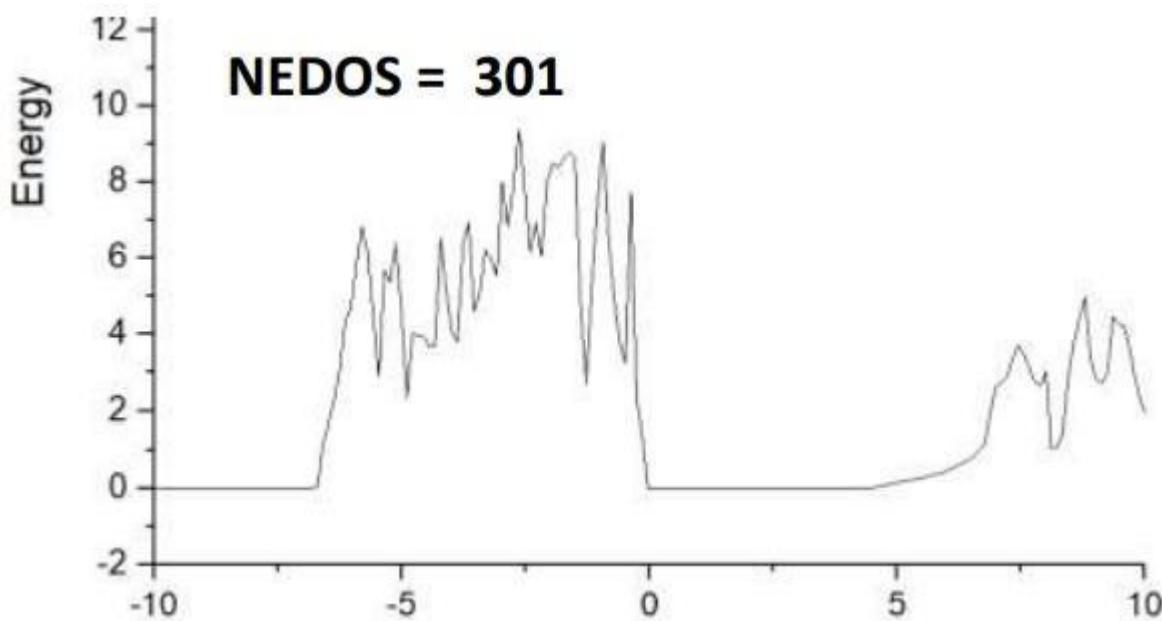
投影态密度 (PDOS)



- LORBIT = 10 把态密度分解到每个原子以及原子的spd轨道上面，称为为局域态密度，Local DOS (LDOS)。
- LORBIT = 11 在10的基础上，还进一步分解到px, py, pz等轨道上，称为投影态密度 (Projected DOS) 或者分波态密度 (Partial DOS)，即PDOS。
- 所以LORBIT = 11可以提供我们更多的信息。

态密度DOS计算-KPOINTS, NEDOS

- KPOINTS: K点数目的选取，K点数目越高，DOS质量越高，一般我们 $k \cdot a = 30-45$ 左右就可以了
- NEDOS数目越多，DOS质量也越高，它是把DOS的能量区间（横坐标）范围分成NEDOS个点，然后作图，一般NEDOS=3001就够了
- NEDOS↑ → DOSCAR, vasprun.xml↑, 占用空间越大
- 如果DOS的峰太尖，可以提高NEDOS，插入更多的点



态密度DOS计算 ISMEAR, SIGMA

1. ISMEAR -5 (四面体方法),0 (GS方法), 1 (MP方法)

1.ISMEAR=-5适于所有体系DOS的计算，但是**K点数目绝对不能小于4**，否则会报错

VERY BAD NEWS! internal error in subroutine IBZKPT:

Tetrahedron method fails for NKPT<4. NKPT= 1

2. ISMEAR=-5, SIGMA可以不用管了

3. ISMEAR=-5, 不能用于体系的优化和能带计算，因为不能准确处理Fermi能级处的电子占据问题，导致力的计算出现误差

2. 如果你的体系很大，直接用的Gamma单点计算，那么K点数目肯定小于4，这个时候ISMEAR禁止等于-5，

1. 建议ISMEAR=0或者1，这个时候SIGMA需要注意了

2. ISMEAR=0，适用于**所有体系**的计算，SIGMA = 0.01~0.05就可以了

3. ISMEAR=1，适于**金属体系**的计算，需要很高精度的SIGMA，一般SIGMA = 0.2就够了

3. 一般我们直接用ISMEAR = 0了，因为这个方法得到的DOS谱图相比于ISMEAR=-5更光滑，更好看

态密度DOS计算方法

一步计算

NSW=0

LORBIT=11/10

ISMEAR=0

SIGMA=0.05

NEDOS=3001，高密度K点

二步计算

步骤一：静态计算(scf获得电荷文件
CHGCAR):

NSW=0

ISMEAR=0

LORBIT=11

LCHARG=T

步骤二：读入CHGCAR

ISTART=1

ICHARG=11

LCHAGR=F

SIGMA=0.05

NEDOS=3001，高密度K点

后处理vaspkit → 11

Vaspkit处理DOS的步骤

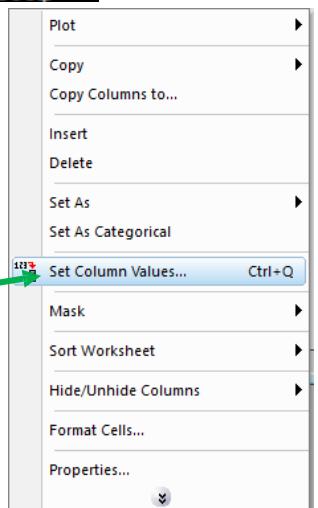
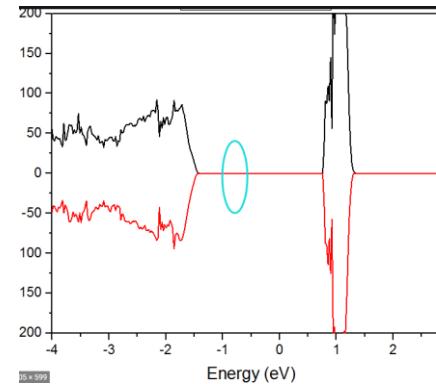
vaspkit → 11

```
[CMS@doge Cu]$ cd dos/  
[CMS@doge dos]$ ls  
INCAR KPOINTS LORBIT10 LORBIT11 POSCAR POTCAR vasp.5.4.4.pbs
```

```
[CMS@doge LORBIT10]$ vaspkit  
\\\\\\\\\  
/ \ \ Hey, you must know what you are doing.  
+---.000o--()--o000.-----+  
A Pre- and Post-Processing Program for VASP Code  
VASPKIT Version: 0.73 (20 Apr. 2019)  
Developed by Wei WANG (wangwei@me.com)  
Contributor: Nan XU (tamas@zju.edu.cn)  
+---.0000-----+  
( ) Oooo.  
\ ( ( )  
\_) ) /  
===== Structural Options =====  
1) VASP Input Files Generator 2) Elastic-Properties  
3) K-Path Generator 4) Structure Editor  
5) Catalysis-ElectroChemical Kit 6) Symmetry Search  
lobsterin" 6L, 123C  
===== Electronic Options =====  
11) Density-of-States 21) DFT Band-Structure  
23) 3D Band-Structure 25) Hybrid-DFT Band-Structure  
26) Fermi-Surface 28) Band-Structure Unfolding
```

```
-->>  
11  
===== DOS Options =====  
111) Total Density-of-States  
112) Projected Density-of-States for Selected Atoms  
113) Projected Density-of-States for Each Element  
114) The Sum of Projected Density-of-States for Selected Atoms  
115) The Sum of Projected DOS for Selected Atoms and Orbitals  
0) Quit  
9) Back  
-->>  
111  
-->> (01) Reading Input Parameters From INCAR File...  
-->> (02) Reading Fermi Energy from DOSCAR File...  
oooooooooooo The Fermi Energy will be set to zero eV ooooooooooooo  
-->> (03) Reading DOS Data From DOSCAR File...  
-->> (04) Written TDOS.dat and ITDOS.dat Files!  
+-->
```

Vaspkit自动把fermi能级平移到0，
就是把横坐标的能量直接减去E_{fermi}，
如果想要得到没减过fermi能级的图，
则把现在得到的图横坐标加上fermi
能级能量 (origin直接可以操作，设
置列值加上E_{fermi})



vaspkit处理DOS的步骤，计算DOS前查看OSZICAR最后一列mag是不是等于0，如果等于0则没有自旋，DOS可以关了ISPIN，如果有的话则一定要开

```
-->>
11
    DOS Options =
111) Total Density-of-States
112) Projected Density-of-States for Selected Atoms
113) Projected Density-of-States for Each Element
114) The Sum of Projected Density-of-States for Selected Atoms
115) The Sum of Projected DOS for Selected Atoms and Orbitals

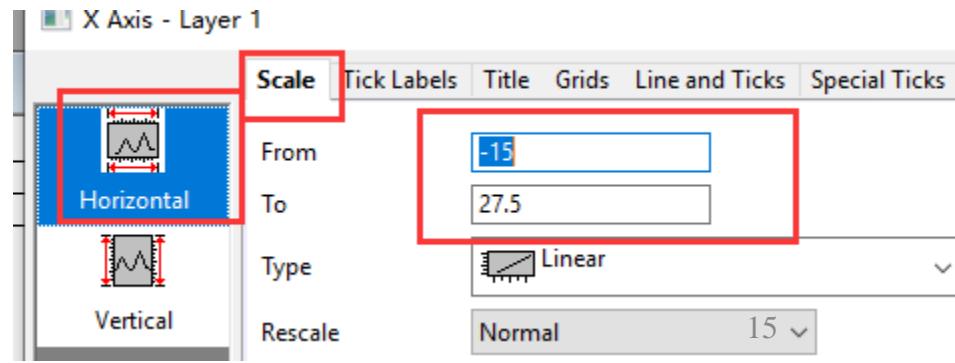
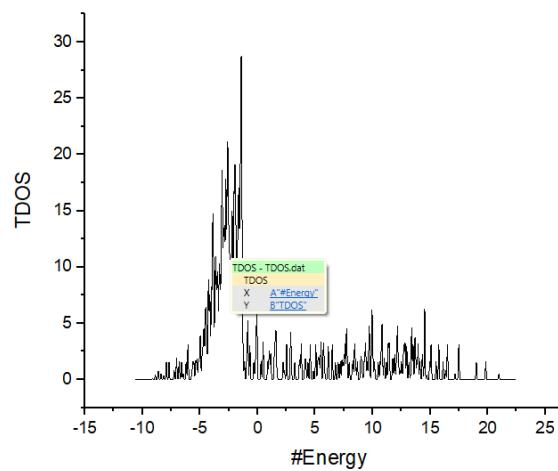
0) Quit
9) Back
-->>
111
-->> (01) Reading Input Parameters From INCAR File...
-->> (02) Reading Fermi Energy from DOSCAR File...
0000000000 The Fermi Energy will be set to zero eV 0000000000000000
-->> (03) Reading DOS Data From DOSCAR File...
-->> (04) Written TDOS.dat and ITDOS.dat Files!
+
```

111 → 体系总DOS，直接用TDOS.dat文件作图即可，这里第一列是横坐标能量，第二列是纵坐标态密度，因为Cu是没有磁矩的，所以我关了ISPIN，直接删除就可→得到的TDOS直接拖入origin作图

	#Energy	TDOS
1	-10.63672	0.00000
2	-10.62572	0.00000
3	-10.61472	0.00000
4	-10.60372	0.00000
5	-10.59272	0.00000
6	-10.58172	0.00000
7	-10.57072	0.00000
8	-10.55872	0.00000
9	-10.54772	0.00000
10	-10.53672	0.00000
11	-10.52572	0.00000
12	-10.51472	0.00000
13	-10.50372	0.00000

	A(X)	B(Y)
Long Name	#Energy	TDOS
Units		
Comments		
F(x)=		
Sparklines		
1	-10.63672	0
2	-10.62572	0
3	-10.61472	0
4	-10.60372	0
5	-10.59272	0
6	-10.58172	0
7	-10.57072	0
8	-10.55872	0
9	-10.54772	0
10	-10.53672	0
11	-10.52572	0
12	-10.51472	0
13	-10.50372	0
14	-10.49272	0
15	-10.48172	0
16	-10.47072	0
17	-10.45972	0
18	-10.44872	0
19	-10.43772	0
20	-10.42672	0
21	-10.41572	0
22	-10.40472	0
23	-10.39372	0
24	-10.38272	0
25	-10.37172	0
26	-10.36072	0
27	-10.34972	0
28	-10.33872	0
29	-10.32772	0
30	-10.31672	0
31	-10.30572	0
32	-10.29372	0
33	-10.28272	0
34	-10.27172	0
35	-10.26072	0
36	-10.24972	0
37	-10.23872	0
38	-10.22772	0
39	-10.21672	0
40	-10.20572	0
41	-10.19472	0
42	-10.18372	0
43	-10.17272	0
44	-10.16172	0
45	-10.15072	0
46	-10.13972	0
47	-10.12872	0

1. 选中数据
2. 作图
3. 双击很横坐标或者纵坐标，修改横纵坐标取值范围，一般改横坐标比较多，因为我们只考虑fermi能级附近的态密度（-5~5之内大致可以，具体情况视实际情况定）



PDOS讲白了就是投影得到某个原子的DOS LDOS就是投影到具体轨道上的DOS

```
-->> 11
===== DOS Options =====
111) Total Density-of-States
112) Projected Density-of-States for Selected Atoms
113) Projected Density-of-States for Each Element
114) The Sum of Projected Density-of-States for Selected Atoms
115) The Sum of Projected DOS for Selected Atoms and Orbitals
```

112 → 得到选中原子的PDOS，基本就是直接给出所有原子的PDOS，自己选自己需要的

```
[CMS@doge dos]$ head POSCAR
graphite\(2\)\(0\)\(1\)\(2\)
 1.00000000000000
 7.380000114399996 0.0000000000000000 0.0000000000000000
 -3.690000057199998 6.3912675790000000 0.0000000000000000
 0.0000000000000000 0.0000000000000000 10.0000000000000000
C Cu H
17 1 1
Direct
-0.0095713766827253 -0.0056505244885387 0.0848699638956381
0.0951535004651247 0.2164065235231978 0.0816850869779018
[CMS@doge dos]$ vasopkit
```

```
-->> 112
-->> (01) Reading Input Parameters From INCAR File...
-->> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV oooooooooooooooo
-->> (03) Reading DOS Data From DOSCAR File...
-->> (04) Reading Structural Parameters from POSCAR File...
|-----|
Input the element-symbol and/or atom-index to SUM [Total-atom: 19]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)

-->>
C Cu H
-->> (05) Written SELECTED_ATOM_LIST File!
-->> (06) Written PDOS_A1.dat Files!
-->> (07) Written Integrated IPDOS_A1.dat Files!
-->> (08) Written PDOS_A2.dat Files!
-->> (09) Written Integrated IPDOS_A2.dat Files!
-->> (10) Written PDOS_A3.dat Files!
-->> (11) Written Integrated IPDOS_A3.dat Files!
-->> (12) Written PDOS_A4.dat Files!
-->> (13) Written Integrated IPDOS_A4.dat Files!
-->> (14) Written PDOS_A5.dat Files!
-->> (15) Written Integrated IPDOS_A5.dat Files!
-->> (16) Written PDOS_A6.dat Files!
```

113 → 得到按原子种类分类的DOS，比如体系有Cu, C, O三种元素，数目都不一定，那么可以得到这些元素的总PDOS

```
-->> 113
-->> (01) Reading Input Parameters From INCAR File...
-->> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV oooooooooooooooo
-->> (03) Reading DOS Data From DOSCAR File...
-->> (04) Reading Structural Parameters from POSCAR File...
-->> (05) Written PDOS_C.dat Files!
-->> (06) Written Integrated IPDOS_C.dat Files!
-->> (07) Written PDOS_Cu.dat Files!
-->> (08) Written Integrated IPDOS_Cu.dat Files!
-->> (09) Written PDOS_H.dat Files!
-->> (10) Written Integrated IPDOS_H.dat Files!
+-----+
```

114 → 得到选中原子的DOS之和，有的时候并不要所有的原子总和，只要局部，这个时候，只需要输入局部的原子序数，eg.这里我只要石墨烯中1,2,3号元素的DOS之和，就可以这样输

```
-->> 114
-->> (01) Reading Input Parameters From INCAR File...
-->> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV ooooooooooooo
-->> (03) Reading DOS Data From DOSCAR File...
-->> (04) Reading Structural Parameters from POSCAR File...
|-----|
Input the element-symbol and/or atom-index to SUM [Total-atom: 19]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)

-->>
C 1-3
-->> (05) Written SELECTED_ATOM_LIST File!
-->> (06) Written PDOS_SUM.dat Files!
-->> (07) Written Integrated IPDOS_SUM.dat Files!
```

115 → 把不同原子的不同轨道的DOS集在一起

例如1. LORBIT=11的时候，我想把Cu的s p d轨道画出来

依次输入： Cu → s → Cu → px py pz → Cu → dxy dyz dz2 dxz dx2 → PDOS_USER.dat作图

```
115 ----->
--> (01) Reading Input Parameters From INCAR File...
--> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV ooooooooooooo
--> (03) Reading DOS Data From DOSCAR File...
--> (04) Reading Structural Parameters from POSCAR File...
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!

Cu ----->
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2 f-3 ~ f3, "all" for summing ALL.
----->
s
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!

Cu ----->
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2 f-3 ~ f3, "all" for summing ALL.
----->
py pz px
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!

Cu ----->
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2 f-3 ~ f3, "all" for summing ALL.
----->
dxy dyz dz2 dxz dx2
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
--> (05) Written PDOS_USER.dat Files!
```



例如1. LORBIT=11的时候，我想把Cu100-CO的被吸附的Cu以及C O原子相应原子轨道画出来

```
115 ----->
--> (01) Reading Input Parameters
--> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV ooooooooooooo
--> (03) Reading DOS Data From DOSCAR File...
--> (04) Reading Structural Parameters from POSCAR File...
+----->
| Selective Dynamics
+----->
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
14
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
C
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
O
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
U
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
py pz px
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
C
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
O
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
px
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
C
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
O
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
py
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
C
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
O
Input the Orbitals to Sum
Which orbital? s py pz px dxy dyz dz2 dxz dx2
----->
pz
Input the element-symbol and/or atom-index to SUM [Total-atom: 4]
(Free Format is OK, e.g., C Fe H 1-4 7 8 24)
Press "Enter" if you want to end entry!
----->
--> (05) Written PDOS_USER.dat Files!
```

LORBIT=10, 只能得到 s p d tot总能量,

1	#Energy	s	p	d	tot
2	-10.63672	0.00000	0.00000	0.00000	0.00000
3	-10.62572	0.00000	0.00000	0.00000	0.00000
4	-10.61472	0.00000	0.00000	0.00000	0.00000
5	-10.60372	0.00000	0.00000	0.00000	0.00000
6	-10.59272	0.00000	0.00000	0.00000	0.00000

LORBIT=11。可以得到px py pz ...具体轨道的能量，如果想得到p轨道总能量，可以把px+py+pz轨道能量之和加在一起，(origin操作)就免去再计算的麻烦

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)	K(Y)	L(Y)
Long Name	#Energy	s	py	pz	px	dxy	dyz	dz2	dxz	dx2	tot	
Units												
Comments												
F(x)=												
Sparklines												
18	-8.07869	0	0	0	0	0	0	0	0	0	0	0
19	-8.01269	0	0	0	0	0	0	0	0	0	0	0
20	-7.94669	0	0	0	0	0	0	0	0	0	0	0
21	-7.88169	0	0	0	0	0	0	0	0	0	0	0
22	-7.81569	-1E-5	0	0	0	0	0	0	0	0	-1E-5	0
23	-7.75069	-8E-5	0	0	0	0	0	0	0	0	-8E-5	0
24	-7.68469	-3.5E-4	0	-1E-5	0	0	0	0	0	0	-3.6E-4	0

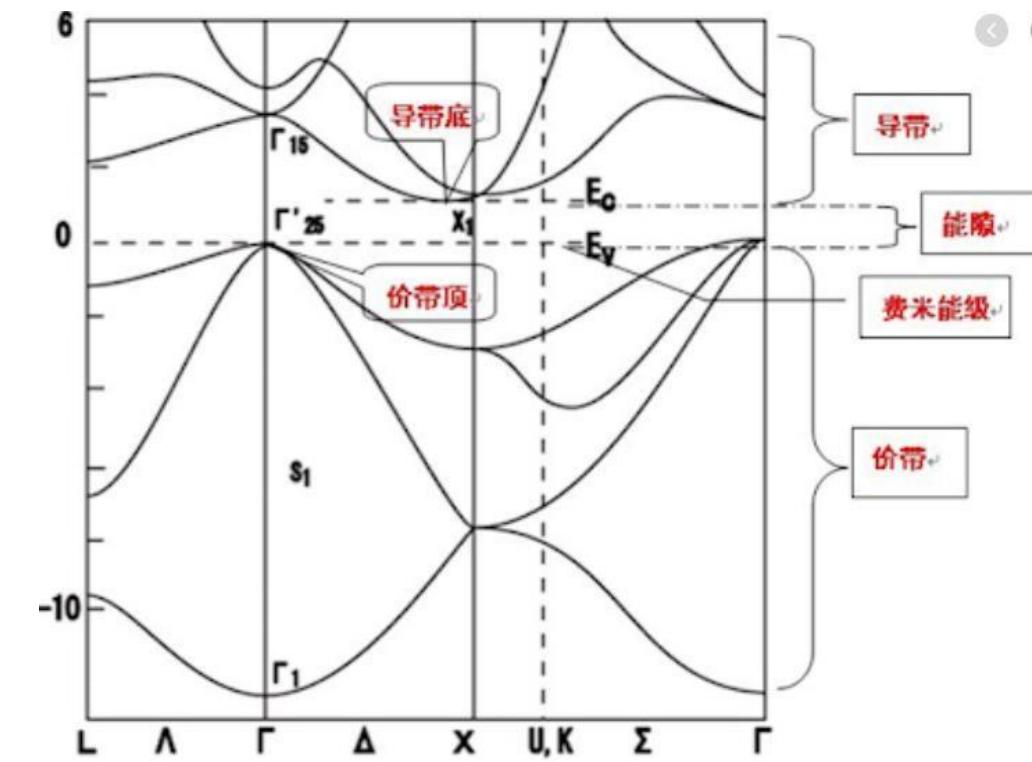
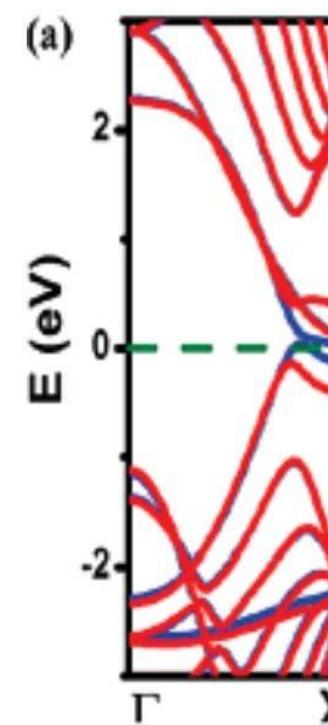
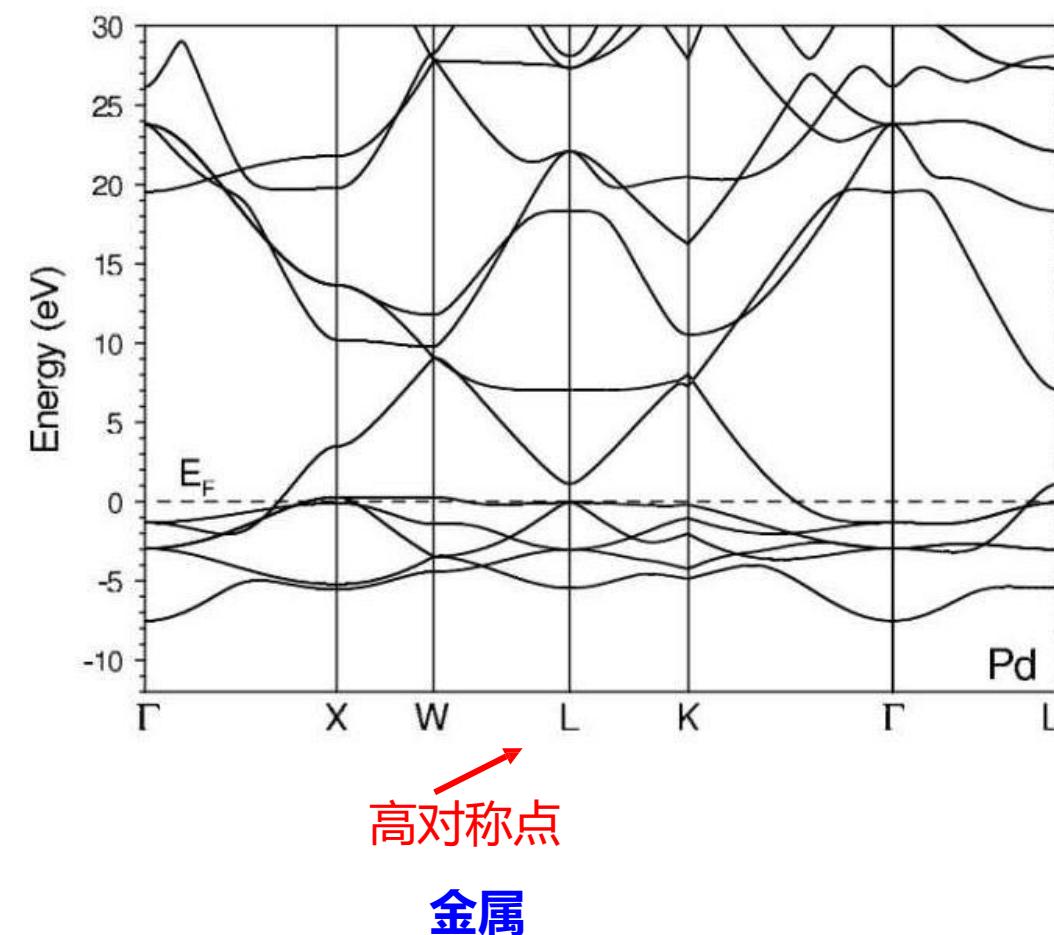
能带计算

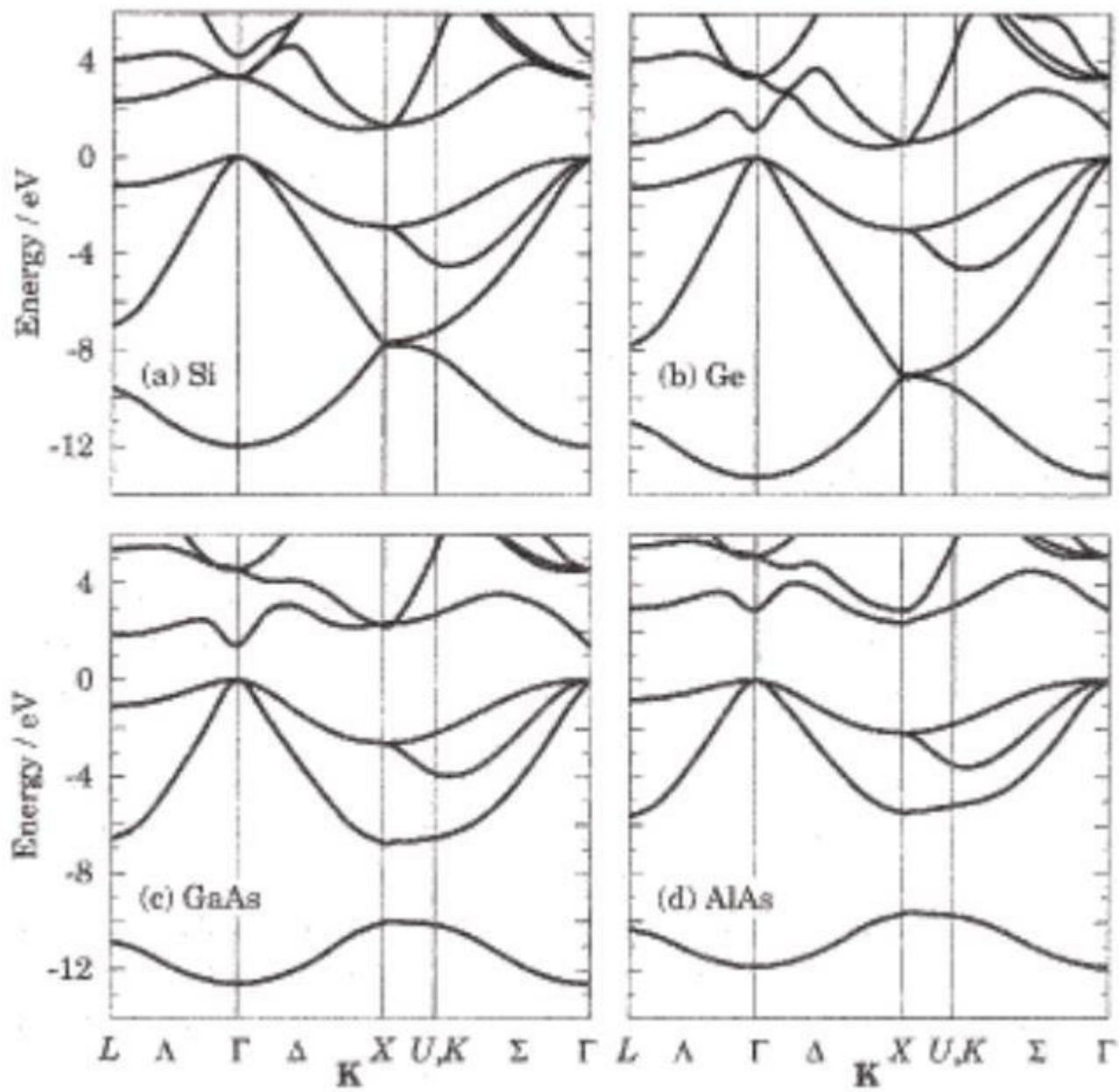
Band计算

1. 金属? 半金属? 半导体?

2. 直接带隙? 间接带隙?

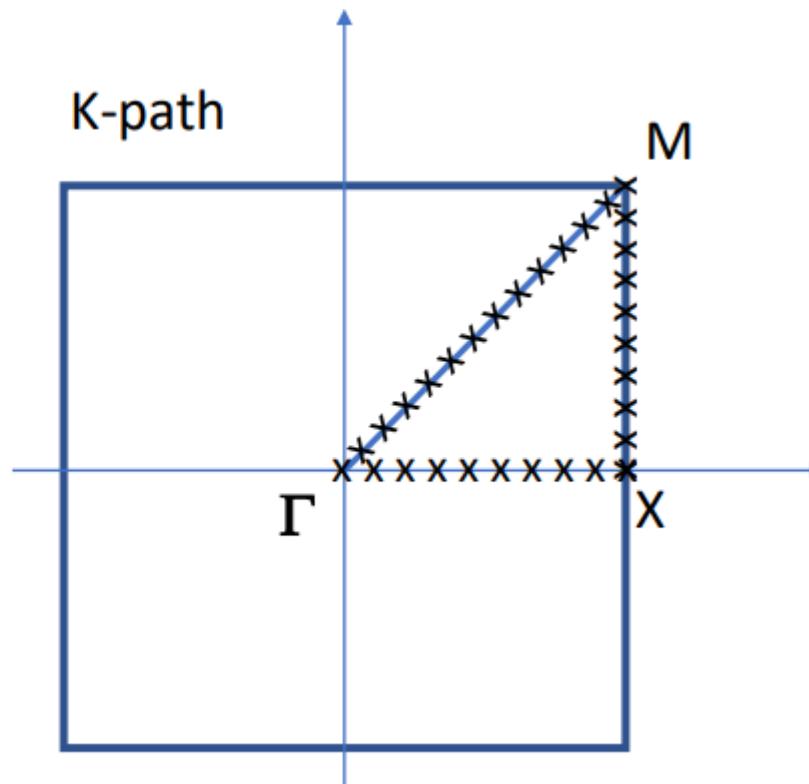
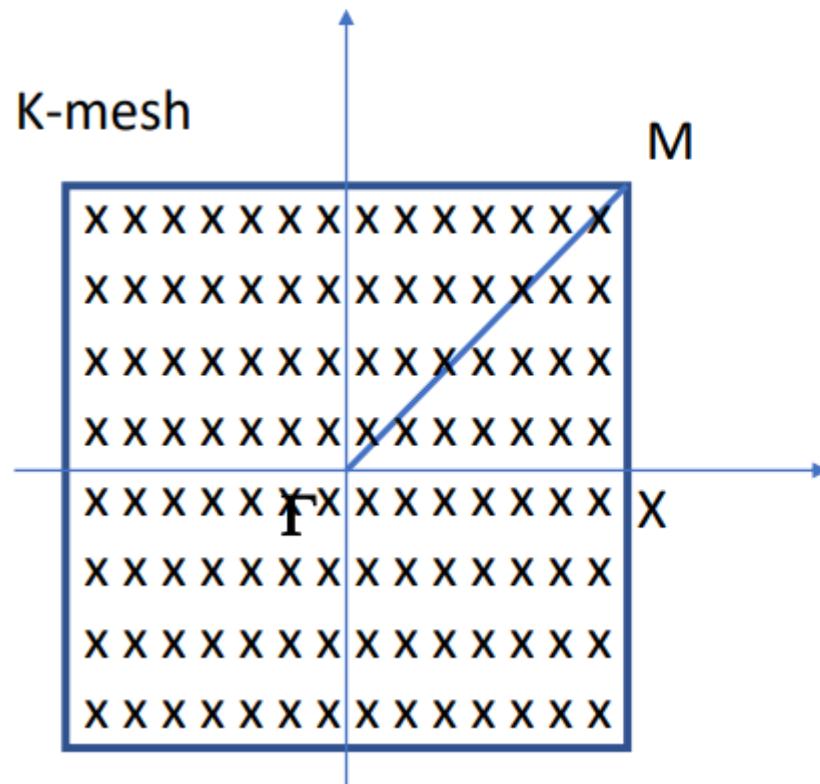
1. 金属: 能带穿过fermi能级
2. 半金属: 自旋向上 (or向下) 存在带隙, 半导体性质, 但是自旋向下 (or向上) 没有带隙, 金属性质
3. 半导体: 存在明显的带隙 E_g





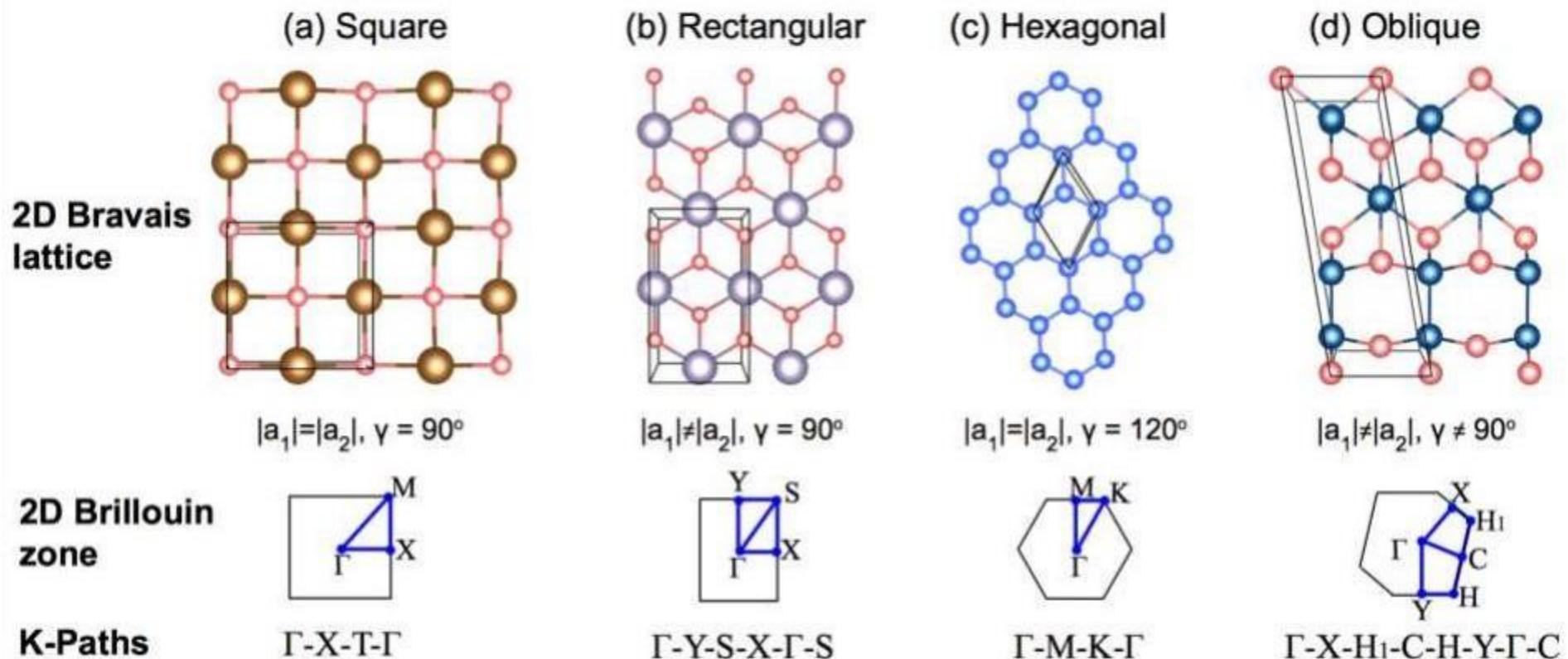
能带计算k点选取

1. (自洽) 非能带计算, K点都是在布里渊区均匀撒点的, 这样可以较好的还原实空间中的电荷密度等信息。
2. 但是, 能带计算的K点的选择是在布里渊区的边界上的, 这些K点不能很好的体现实空间的电荷密度, 所以我们要选一些高对称的k点, 所谓的算能带结构, 就是算这些高对称点的连线上的能级。



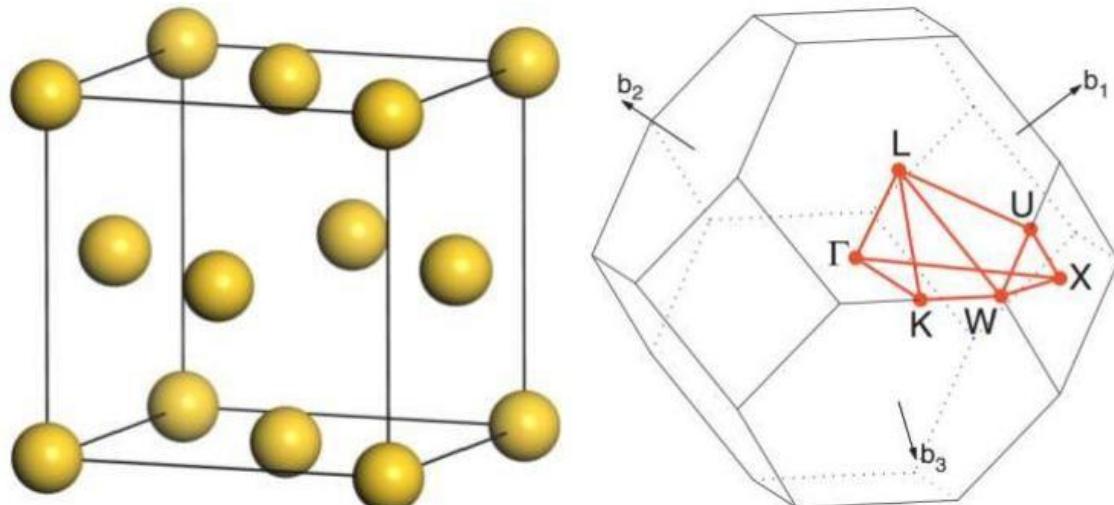
二维体系布里渊区

二维体系，那么K点的取值就是两个数字的组合： $k_x \ k_y$



三维体系的布里渊区

此时，倒空间和布里渊区是三维的，K点的取值就是三个数字的组合： $k_x k_y k_z$ 。三维布里渊区边界不可能一笔画完，所以能带图中会出现“断点”，用“|”标记。



$\Gamma-X-U | K-\Gamma-L-W-X$

K-Path Generated by VASPKIT.

20 #表示每小段路径中插值的K点的数目，如果默认的数值都算不动的话，可以考虑将其设小

Line-Mode
Reciprocal

0.0000000000	0.0000000000	0.0000000000	GAMMA
0.5000000000	0.0000000000	0.5000000000	X
0.5000000000	0.0000000000	0.5000000000	X
0.6250000000	0.2500000000	0.6250000000	U
0.3750000000	0.3750000000	0.7500000000	K
0.0000000000	0.0000000000	0.0000000000	GAMMA
0.0000000000	0.0000000000	0.0000000000	GAMMA
0.5000000000	0.5000000000	0.5000000000	L
0.5000000000	0.5000000000	0.5000000000	L
0.5000000000	0.2500000000	0.7500000000	W
0.5000000000	0.2500000000	0.7500000000	W
0.5000000000	0.0000000000	0.5000000000	X

BCC金属Fe的第一布里渊区，高对称点路径

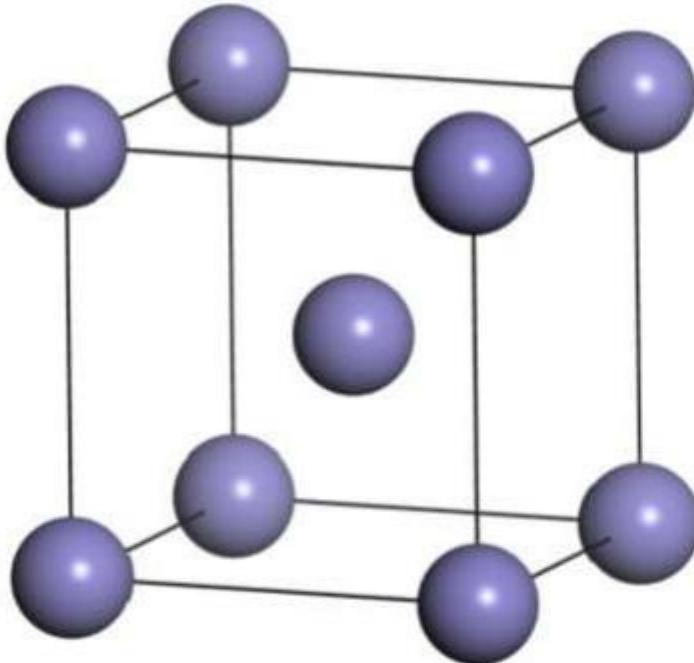
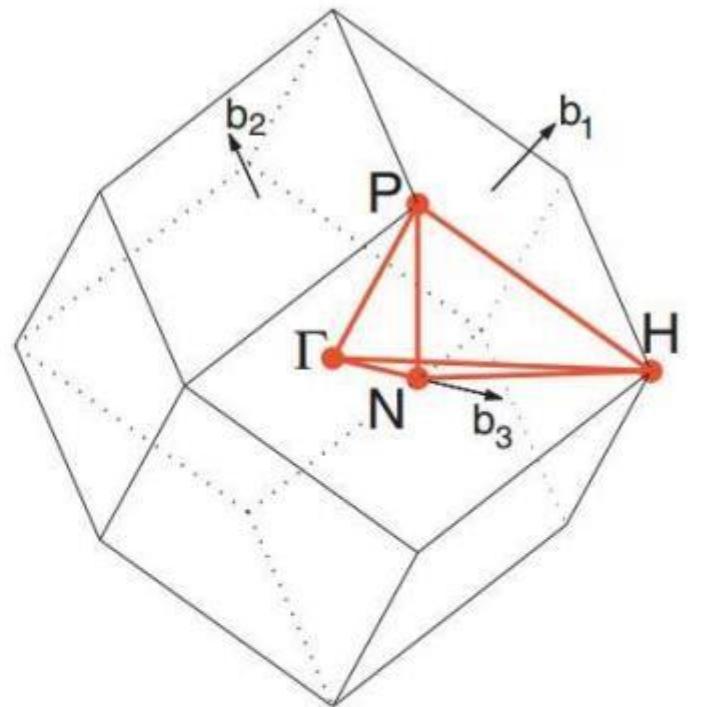


Table 4
Symmetry \mathbf{k} -points of BCC lattice.



$\Gamma-H-N-\Gamma-P-H \mid P-N$

$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$	$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$
0	0	0	Γ	$1/4$	$1/4$
$1/2$	$-1/2$	$1/2$	H	0	$1/2$

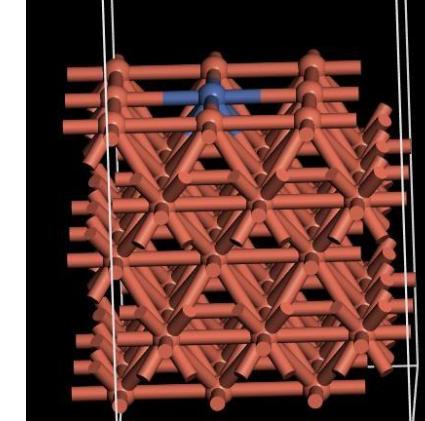
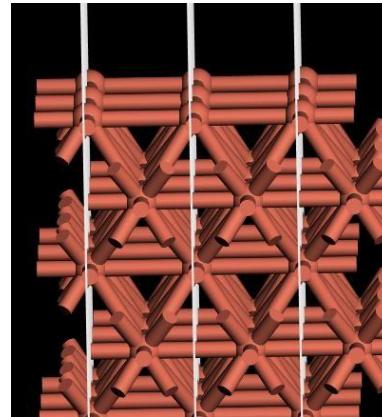
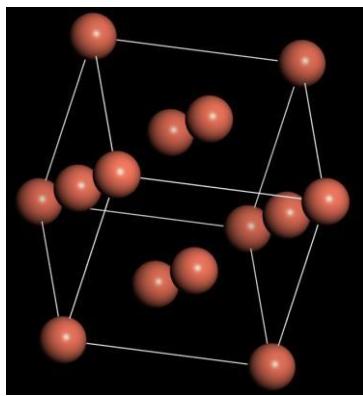
生成高对称点路径

- ① 结构网站生成<https://www.materialscloud.org/work/tools/seekpath>
- ② 判断体系的布里渊区形状自己生成，参考论文High-throughput electronic band structure calculations: Challenges and tools
- ③ 一些脚本，如VASPKIT
- ④ 建议使用后两种方法生成K点后，与结构网站对应一下

注意：

能带是材料的本征性质，一般我们用原胞计算就行

1. 比如我们知道Cu111 Cu100的能带，那么我们直接算cubic Cu的能带就行；如果我们想算石墨烯的band，那么我们直接算最小的胞就行
2. 如果计算Cu111面掺杂Fe之后的band，那么这个掺杂后的体系其实就是原胞；如果计算掺Cu后的石墨烯的band，那么这个掺Cu石墨烯就是原胞



能带计算方法

- **只能分步计算：**由于在能带计算时k点是一些在倒空间高对称线上的点，不能进行自洽计算。
- 参考网址：<https://blog.shishiruqi.com/2019/07/11/band2/>
- 也就是计算能带的时候，**自洽计算是必须的一步**；

BAND计算步骤

以体相Cu为例：

- 步骤一：优化体相 (opt)
- 步骤二：静态计算(scf， 得到电荷文件CHGCAR)

NSW=0 LCHARG=T

- 步骤三：非自洽计算，读入CHGCAR
- cp INCAR POTCAR CONTCAR CHGCAR band

ISTART=1

ICHARG=11

LCHARG=F

ISMEAR=0

准备高对称点KPOINTS，使用 vaspykit 得到 vaspykit → 3 →根据自己的实际情况选择1D 2D 3D材料），将生成的KPATH.in 文件名改为KPOINTS

步骤四：提交作业计算，完成后数据处理，输入vaspykit → 21

K-Path Generated by VASPKIT.			
20			
Line-Mode			
Reciprocal			
0.0000000000	0.0000000000	0.0000000000	GAMMA
0.5000000000	0.0000000000	0.5000000000	X
0.5000000000	0.0000000000	0.5000000000	X
0.6250000000	0.2500000000	0.6250000000	U
0.3750000000	0.3750000000	0.7500000000	K
0.0000000000	0.0000000000	0.0000000000	GAMMA
0.0000000000	0.0000000000	0.0000000000	GAMMA
0.5000000000	0.5000000000	0.5000000000	L
0.5000000000	0.5000000000	0.5000000000	L
0.5000000000	0.2500000000	0.7500000000	W
0.5000000000	0.2500000000	0.7500000000	W
0.5000000000	0.0000000000	0.5000000000	X

21

```
=====
Band Options =====
211) Band-Structure
212) Projected Band-Structure for Selected Atoms
213) Projected Band-Structure for Each Element
214) The Sum of Projected Band-Structure for Selected Atoms

0) Quit
9) Back
-->>
211
-->> (01) Reading Input Parameters From INCAR File...
-->> (02) Reading Fermi-Energy from DOSCAR File...
oooooooooooo The Fermi Energy will be set to zero eV ooooooooooooo
-->> (03) Reading Energy-Levels From EIGENVAL File...
-->> (04) Reading Structural Parameters from POSCAR File...
-->> (05) Reading K-Paths From KPOINTS File...
-->> (06) Written BAND.dat File!
-->> (07) Written BAND REFORMATTED.dat File!
-->> (08) Written KLINE.S.dat File!
-->> (09) Written KLABELS File!
-->> (10) Written BAND_GAP File!
```

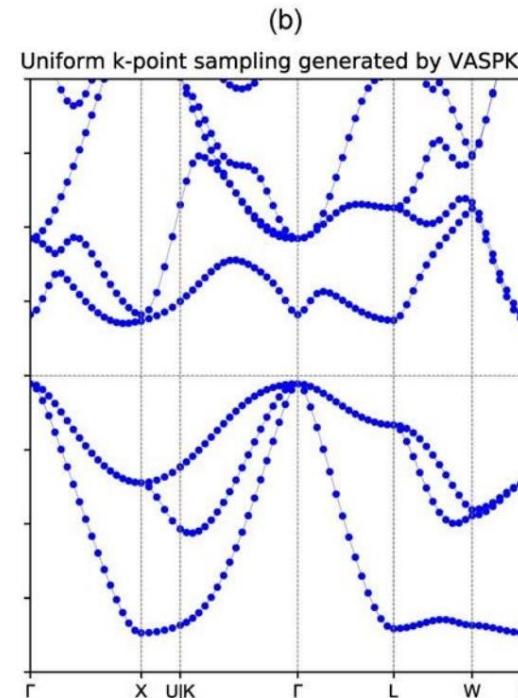
BAND.dat文件就是总的能带图， 横坐标是横坐标（高对称点位于每隔20个点数据处，因为我们之前设的是每隔20个点插入一个高对称点， 纵坐标是能带）

```
1 K-Path Energy-Level
2 #Band-index 1
3 0.000 -9.1516
4 0.065 -9.1348
5 0.129 -9.0842
6 0.194 -9.0002
7 0.259 -8.8832
8 0.323 -8.7337
9 0.388 -8.5525
10 0.453 -8.3405
11 0.518 -8.0992
12 0.582 -7.8301
```

```
[CMS@doge band]$ vi KLINE.S.dat
[CMS@doge band]$ vi KLABELS

1 K-Label K-Coordinate in band-structure plots
2 GAMMA 0.000
3 X 1.229
4 U|K 1.761
5 GAMMA 3.358
6 L 4.863
7 W 5.478
8 X 6.092
9
10
11 * Give the label for each high symmetry point in KPOINTS (KPATH.in) file. Otherwise, they will be identified as 'Undefined' in KLABELS file
```

KLABELS文件给出第一列高对称点的排序。第二列给出这些高对称点出现的横坐标，其实直接看这个文件就可以顺利插入高对称点



```
[tc-xxxxx band]$ vi BAND_GAP
+----- Summary -----
Band Character: Indirect
Band Gap (eV): 0.6677
Eigenvalue of VBM (eV): 5.8258
Eigenvalue of CBM (eV): 6.4936
HOMO & LUMO Bands: 16 17
Location of VBM: 0.000000 0.000000 0.000000
Location of CBM: 0.019737 0.019737 0.039474
```

BAND_GAP文件可以直接得出：

- (1) 半导体是什么类型半导体？直接带隙？间接带隙？
- (2) 半导体的带隙值
- (3) CBM, VBM的值以及位置

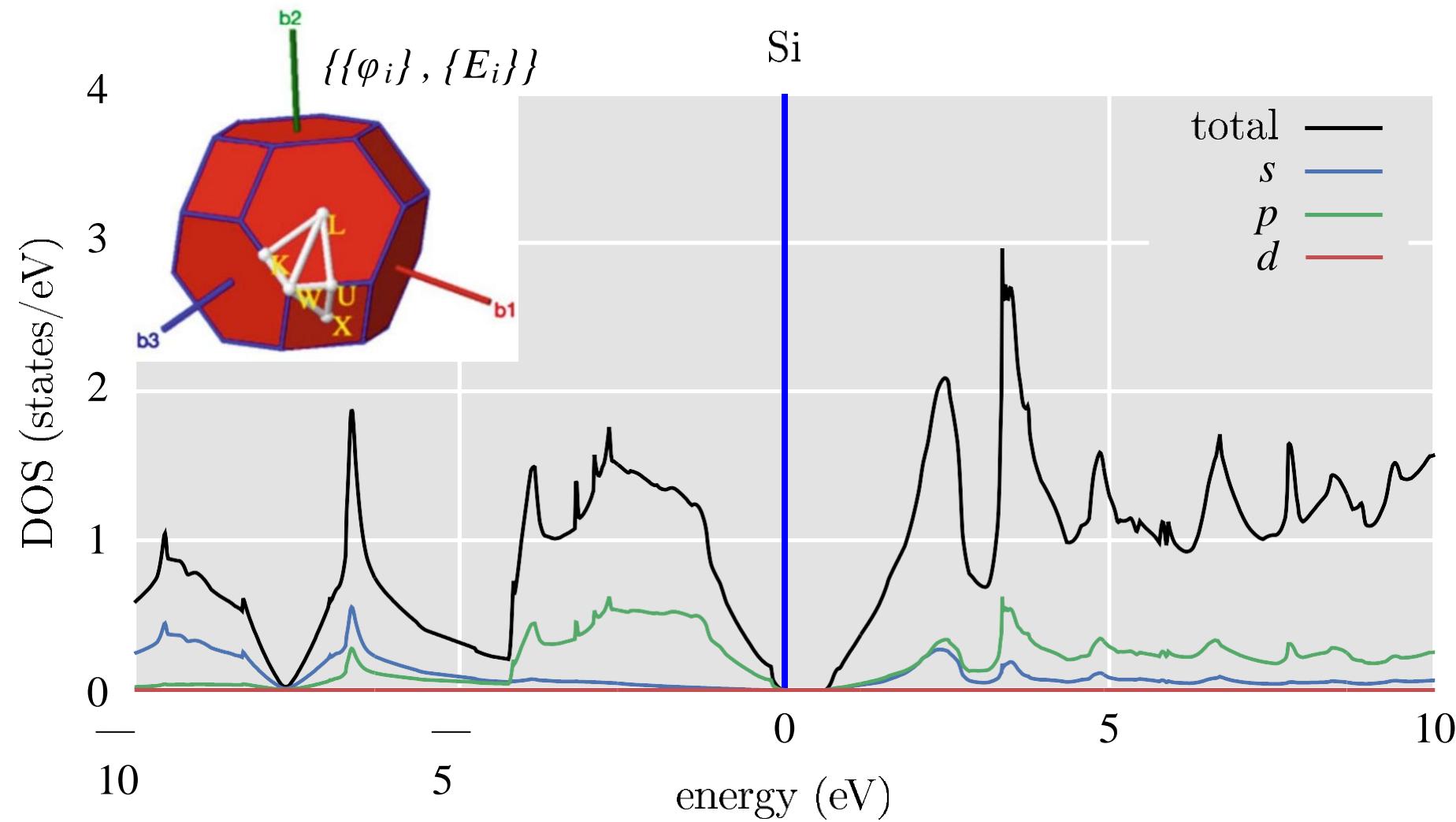
Example 1: Si DOS calculations

INCAR (Si DOS):

```
SYSTEM=Si
NBANDS=39      # KBIN::XVASP_INCAR_GetNBANDS #
ISYM=2
ENMAX=343.483 # 1.4*ENMAX (245.345) of pseudopotentials
EDIFF=1E-6     # high accuracy required
ISMEAR=-5      # Performing RELAX_STATIC (tetrahedron method with Blochl corrections
SIGMA=0.05     # Performing RELAX_STATIC
                # (so the DOS will not spill too much from band edges)
NSW=0         # Performing RELAX_STATIC
                # (zero ionic steps, so no relax, just static)
IBRION=2       # Performing RELAX_STATIC (relax con grad, but single step
                # so no relax)
ISIF=2         # Performing RELAX_STATIC (relax ions, but single step so no relax) (electronic steps max)
NELM=12        # Performing
0
NELMIN=2        # Performing RELAX_STATIC (electronic steps min)
LORBIT=10        # Performing RELAX_STATIC (get spin decomposition)
LCHARG=.TRUE. # Performing RELAX_STATIC
#LAECHG=.TRUE.  # Performing RELAX_STATIC (Bader ON)
LWAVE=.FALSE.    # Performing RELAX_STATIC
PREC=ACCURAT E
EMIN= -30.0      # Performing RELAX_STATIC (aleksey) force search for EMIN (DOS E min)
EMAX= 45.0        # Performing RELAX_STATIC (aleksey) (DOS E max)
NEDOS= 5000       # Performing RELAX_STATIC (aleksey) (number of E steps)
```

print well-converged
CHGCAR for BANDS

Example 1: Si DOS calculations



Example 2: Si band structure calculations

INCAR (Si BANDS):

```
SYSTEM=Si  
NBANDS=39      # KBIN::XVASP_INCAR_GetNBANDS #  
ISYM=2          SYMMETRY=ON  
ENMAX=343.483  # 1.4*ENMAX (245.345) of pseudopotentials # high  
EDIFF=1E-6      accuracy required  
ISMEAR=0        # Performing RELAX_STATIC_BANDS  
                # (put back Gauss, use 1 if metals)  
  
SIGMA=0.05     # Performing RELAX_STATIC_BANDS  
                # (so the DOS will not spill too much from band edges)  
  
NSW=0          # Performing  
IBRION=2        # Performing RELAX_STATIC_BANDS  
ISIF=2          # Performing RELAX_STATIC_BANDS  
NELM=120         # Performing RELAX_STATIC_BANDS  
NELMIN=2         # Performing RELAX_STATIC_BANDS  
LORBIT=10        # Performing RELAX_STATIC_BANDS  
LCHARG=.FALSE.   # Performing RELAX_STATIC_BANDS  
#LAECHG=.TRUE.   # Performing RELAX_STATIC_BANDS (Bader ON)  
LWAVE=.FALSE.    # Performing RELAX_STATIC_BANDS  
PREC=ACCURATE   # Performing RELAX_STATIC_BANDS (aleksey)  
ICHARG=11      # Performing RELAX_STATIC_BANDS (use CHGCAR.static)  
RELAX_STATIC_BANDS
```

use input CHGCAR
from STATIC

Example 2: Si band structure calculations

KPOINTS (Si):

FCC (face-centered cubic) G-X-W-K-G-L-U-W-L-K U-X 20! 20 grids

Line-mode
reciprocal

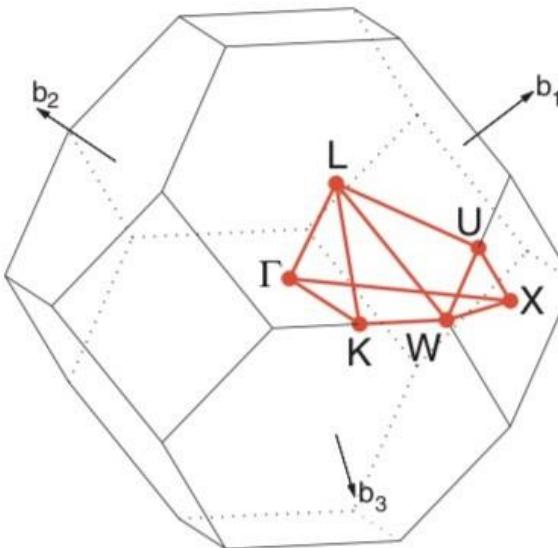


Fig. 2. Brillouin zone of FCC lattice. Path: Γ -X-W-K- Γ -L-U-W-L-K|U-X. An example of band structure using this path is given in Fig. 27.

Table 3
Symmetry \mathbf{k} -points of FCC lattice.

$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$	$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$
0	0	0	Γ	$5/8$	$1/4$
$3/8$	$3/8$	$3/4$	K	$1/2$	$1/4$
$1/2$	$1/2$	$1/2$	L	$1/2$	0

Example 2: Si band structure calculations

KPOINTS (Si BANDS):

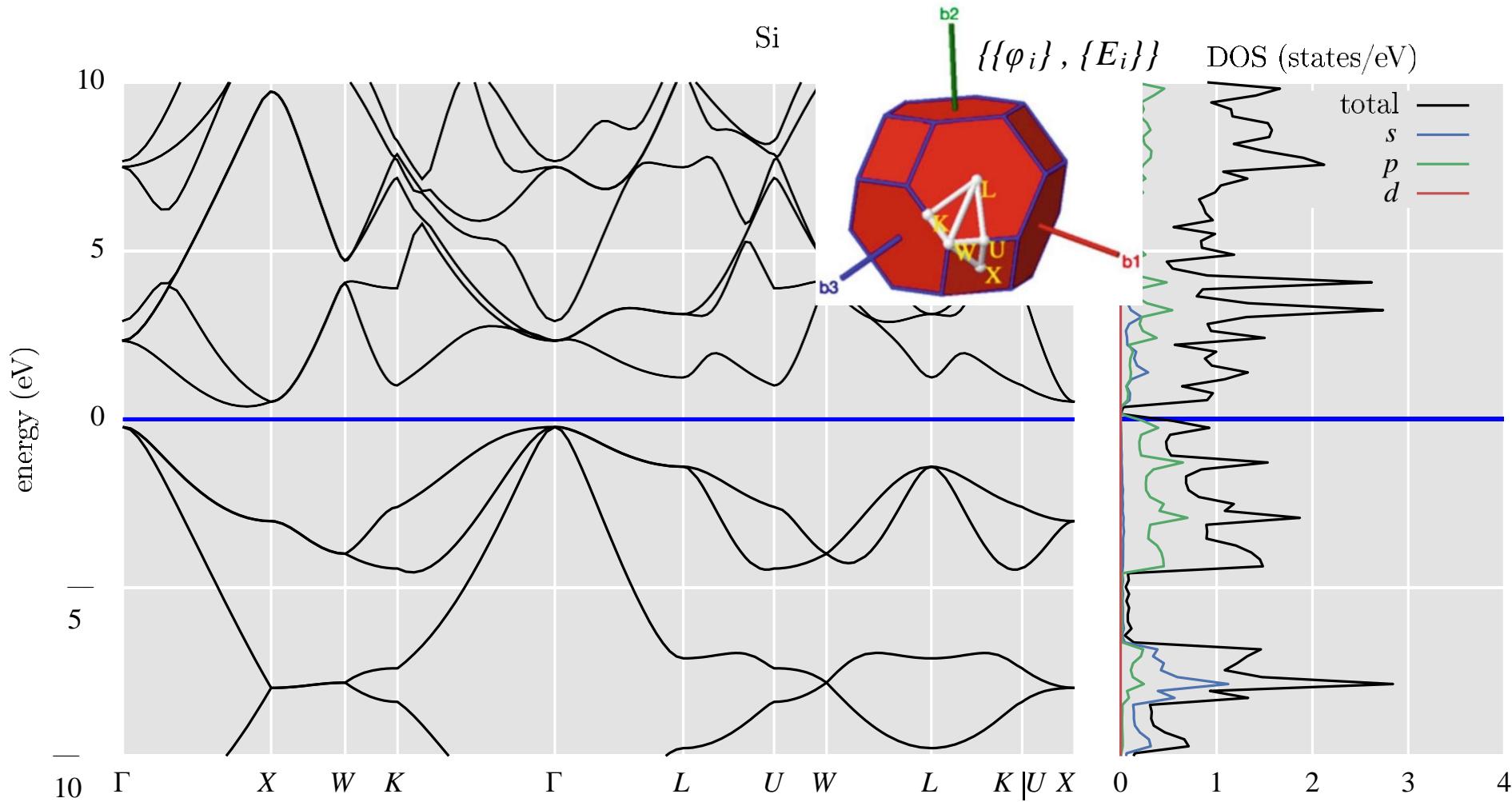
FCC (face-centered cubic) G-X-W-K-G-L-U-W-L-K U-X

20 ! 20 grids

Line-mode reciprocal

0.0000	0.0000	0.0000	! \Gamma
0.5000	0.0000	0.5000	! X
0.5000	0.0000	0.5000	! X
0.5000	0.2500	0.7500	! W
0.3750	0.3750	0.7500	! K
0.3750	0.3750	0.7500	! K
0.0000	0.0000	0.0000	! \Gamma
0.0000	0.0000	0.0000	! \Gamma
0.5000	0.5000	0.5000	! L
0.6250	0.2500	0.6250	! U
0.6250	0.2500	0.6250	! U
0.5000	0.2500	0.7500	! W
0.5000	0.5000	0.5000	! L
0.5000	0.5000	0.5000	! L
0.3750	0.3750	0.7500	! K
0.6250	0.2500	0.6250	! U
0.5000	0.0000	0.5000	! X

Example 2: Si band structure calculations



练习

- 计算体相Cu的态密度，比较参数ISMEAR=0, 1, -5的区别，并分析体相Cu的态密度主要由哪个轨道贡献。
- 计算体相Si和Cu的能带，比较分析。与实验值比较，带隙类型一致吗？DFT低估还是高估带隙？
- **可选做：**计算Cu(111), Cu(100)表面吸附CO分子的吸附能，根据吸附能判断最稳定构型（是hollow, top, 还是bridge?），计算吸附CO的Cu位点和CO的态密度变化。

吸附位点解释：<https://zhuanlan.zhihu.com/p/646095577>