

电子结构分析初步

李震宇 (USTC)

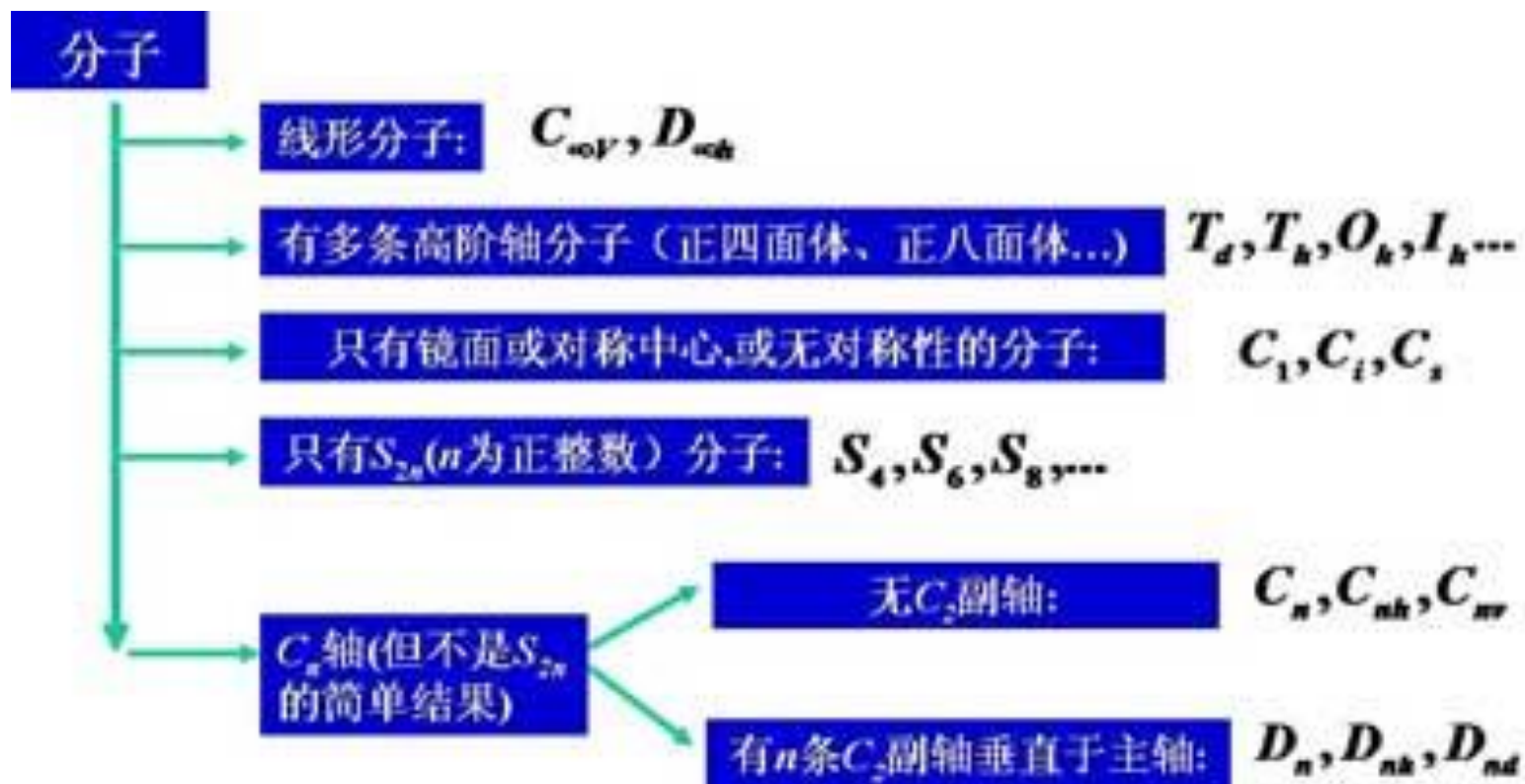
Outline

- ▶ 几何结构与可视化工具
- ▶ 电荷/自旋密度相关
 - ▶ 电荷布居
 - ▶ 极化与偶极修正
 - ▶ 磁性
- ▶ 单电子轨道相关
 - ▶ 能带与态密度
 - ▶ Instabilities
- ▶ 总能相关
 - ▶ 力、应力

分子结构

▶ 开放边界条件

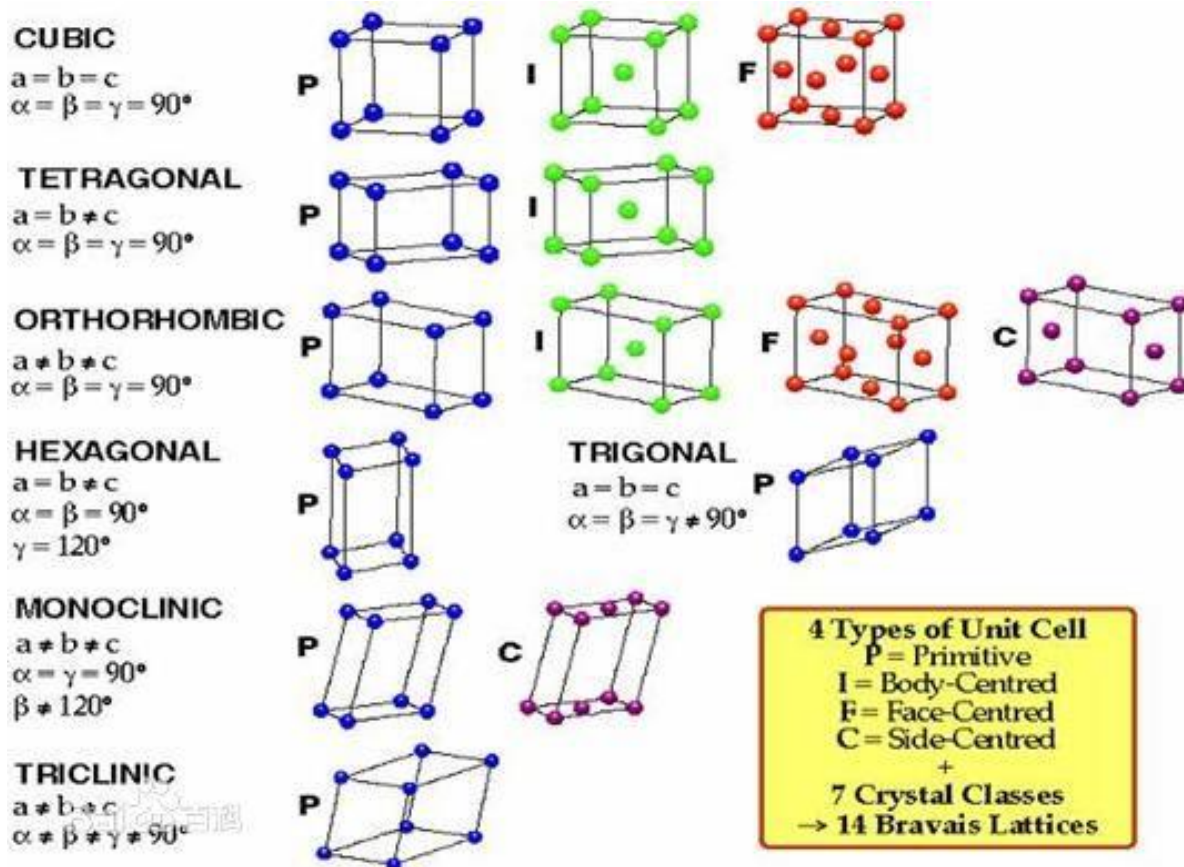
▶ 点群对称性



晶体结构

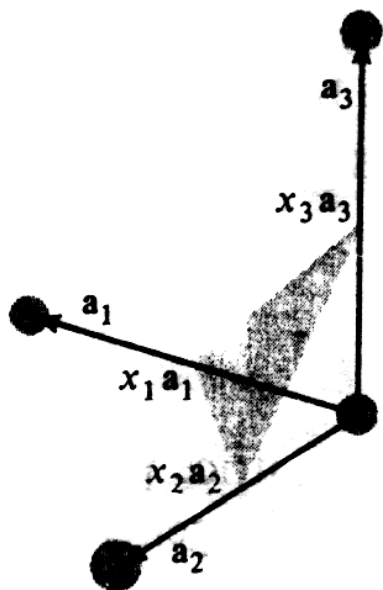
▶ 周期边界条件(PBC)

▶ 7个晶系、14种布拉伐格子、230种空间群对称性

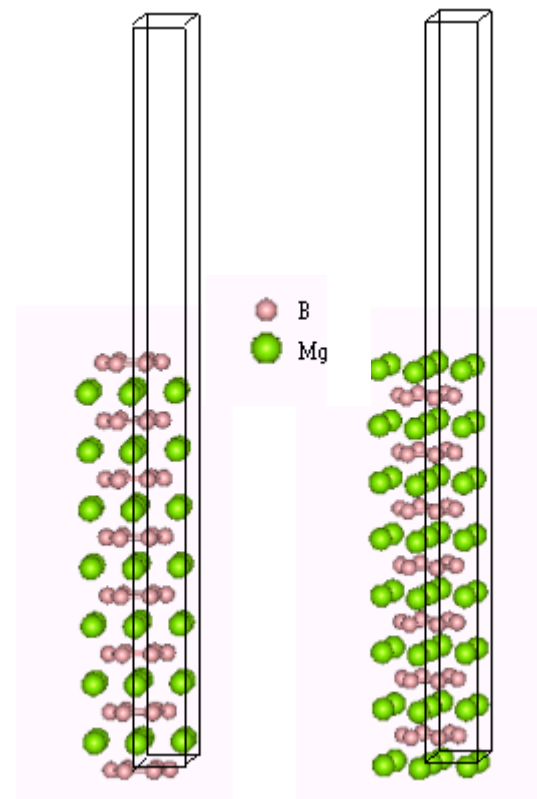


PBC的扩展

- ▶ 超胞
- ▶ 表面结构与Slab模型
 - ▶ 晶向: $[l_1 l_2 l_3]$ $\langle l_1 l_2 l_3 \rangle$
 - ▶ 晶面、Miller指数: (hkl) $\{hkl\}$

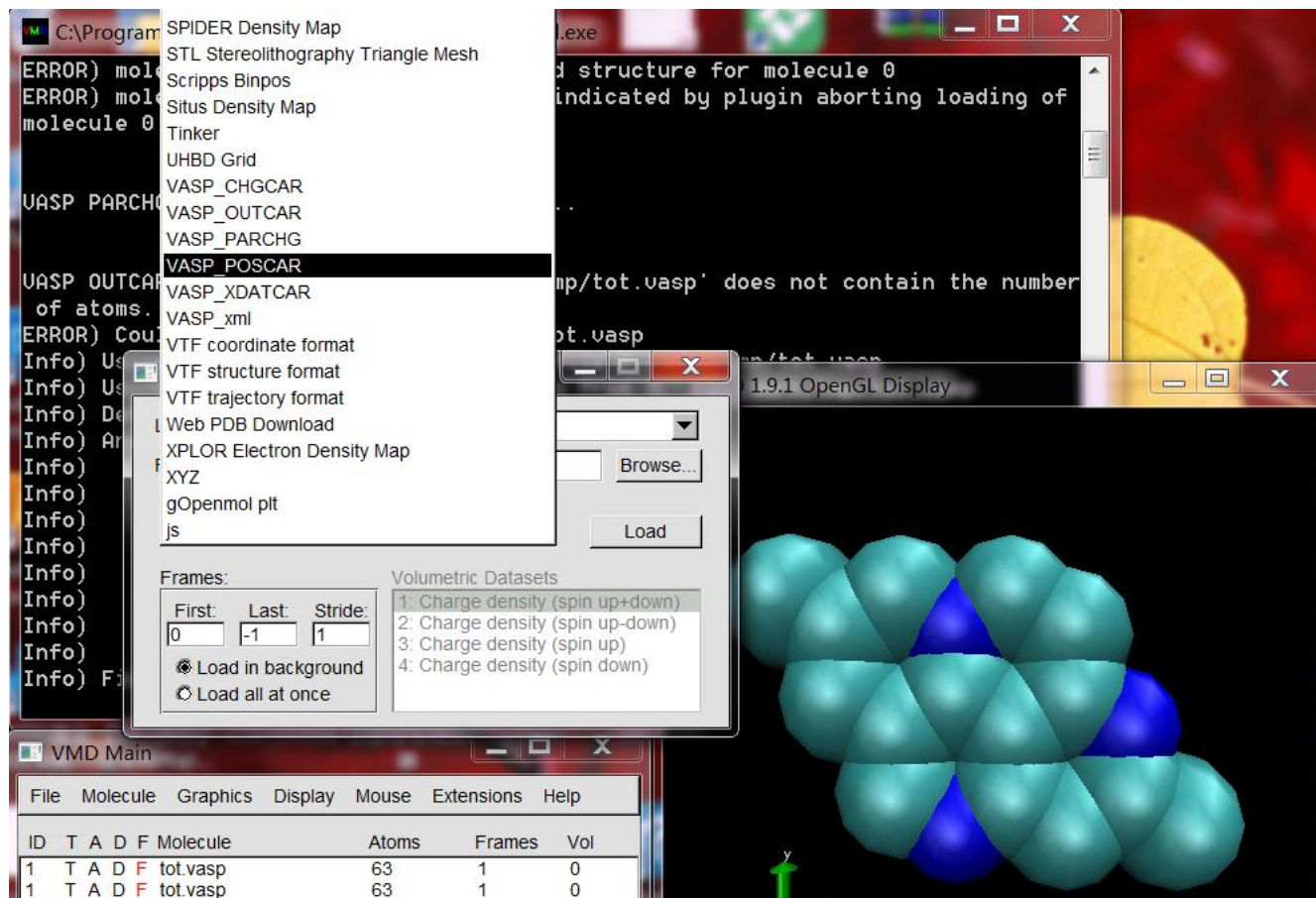


$$\frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} = h : k : l$$



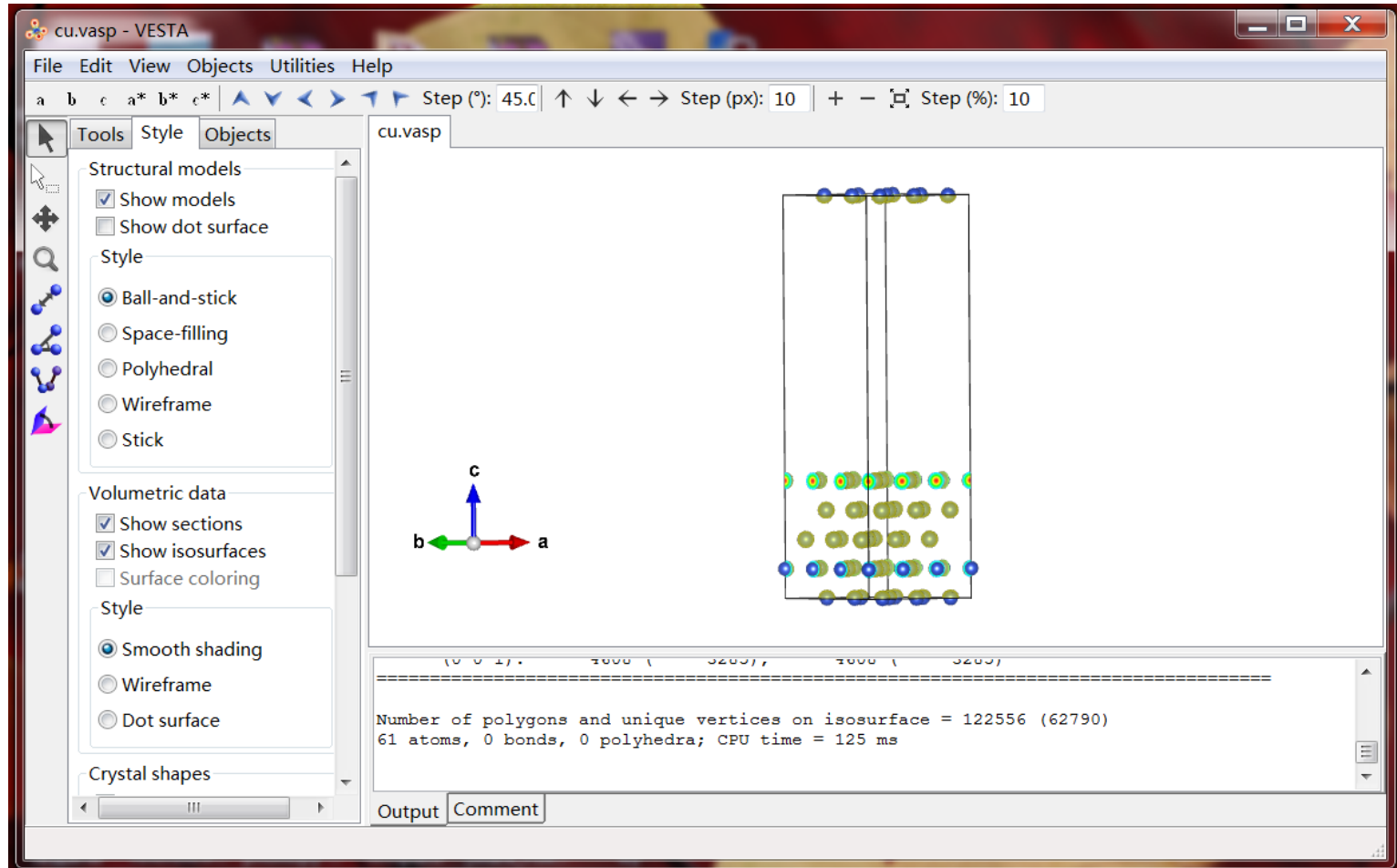
VMD

► <http://www.ks.uiuc.edu/Research/vmd/>



VESTA

► <http://jp-minerals.org/vesta/en/>



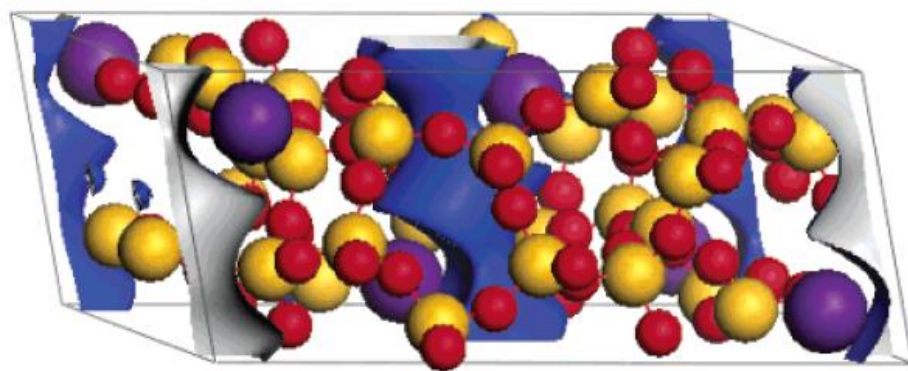
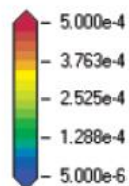
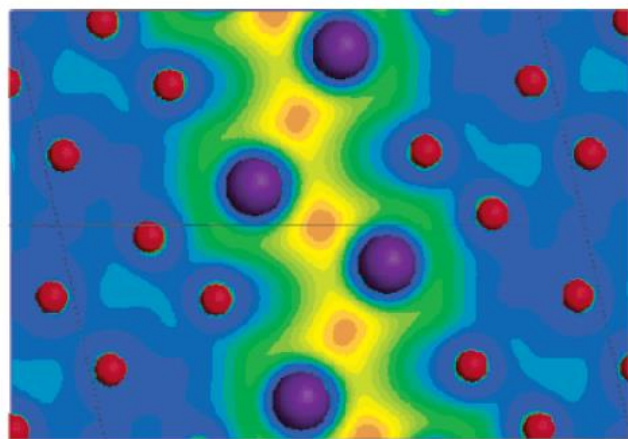
其他软件

- ▶ **P4VASP**
 - ▶ <http://www.p4vasp.at/>
- ▶ **VASP Data Viewer**
 - ▶ <http://vaspview.sourceforge.net/>
- ▶ **Xcrysden**
 - ▶ <http://www.xcrysden.org/>
- ▶ **Molden**
 - ▶ <http://www.cmbi.ru.nl/molden/molden.html>
- ▶ **Materials Studio**
 - ▶ <http://accelrys.com/products/materials-studio/>
- ▶ **MedeA**
 - ▶ <http://www.materialsdesign.com/medea/medea-vasp-52>



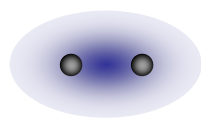
电荷密度分布

- ▶ 可视化
 - ▶ Isosurface
 - ▶ Contour map

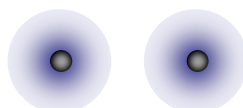


电荷转移

▶ 化学键

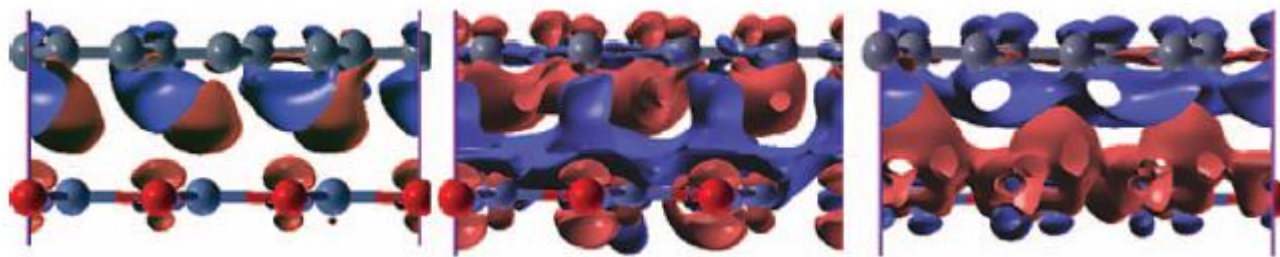


共价键



离子键

▶ 差分电荷密度



G/ZnO

G/Al-ZnO

G/Li-ZnO



基于分子轨道的布居分析

▶ Mulliken布居

$$N = \text{Tr}(PS) = \sum_{\mu} (PS)_{\mu\mu}$$

$$P_{\mu\nu} = \sum_{i,j}^{occ} c_{i\mu} c_{j\nu} \quad \varphi = \sum_{\mu} c_{i\mu} \chi_{\mu} \quad S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$$

▶ Löwdin布居

▶ 先对基组作正交化，使得对基矢的依赖变小

▶ 自然布居分析

▶ 先作Occupancy-weighted正交化得到NAO

▶ 基本可以达到基组收敛，但仍趋向于高估电荷布居。



基于整体性质的布居分析

▶ 静电势拟合

- ▶ conformational dependence for flexible molecules
- ▶ ill-conditioned, especially for inner atoms

▶ Hirshfeld布居

$$\rho_d = \rho(\mathbf{r}) - \sum_{\alpha} \rho_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha})$$

$$q_{\alpha} = \int \rho_d(\mathbf{r}) W_{\alpha}(\mathbf{r}) d\mathbf{r} \quad W_{\alpha}(\mathbf{r}) = \rho_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}) \left[\sum_{\beta} \rho_{\beta}(\mathbf{r} - \mathbf{R}_{\beta}) \right]^{-1}$$

▶ AIM by Bader

- ▶ 拓扑分析: zero flux surface

$$\nabla \rho \cdot \mathbf{n} = 0$$



电子局域化函数

- ▶ 电子局域化程度可以通过球平均条件对分布几率来描述，其最低阶(二阶)Taylor展开系数为

$$D_{\sigma} = \tau_{\sigma} - \frac{1}{4} \frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}}$$

- ▶ 一个正比于局域化程度的归一ELF函数可以通过均匀电子气作为参考体系得到

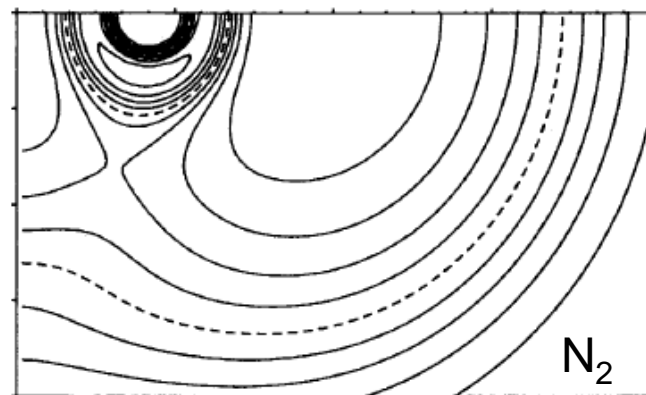
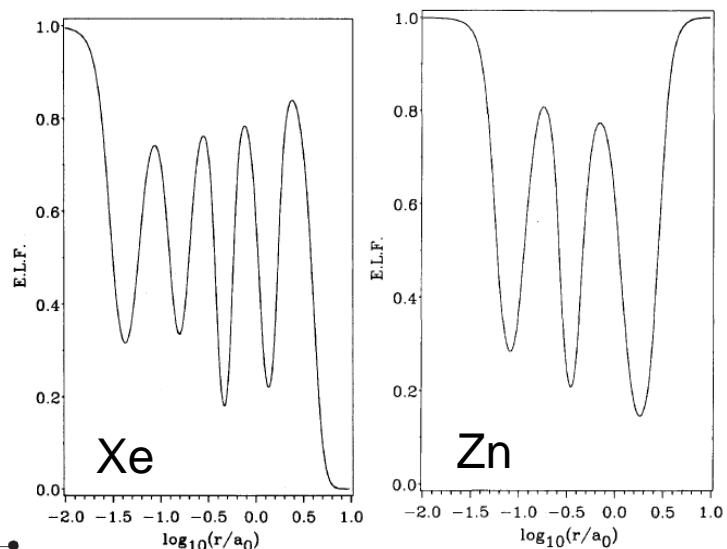
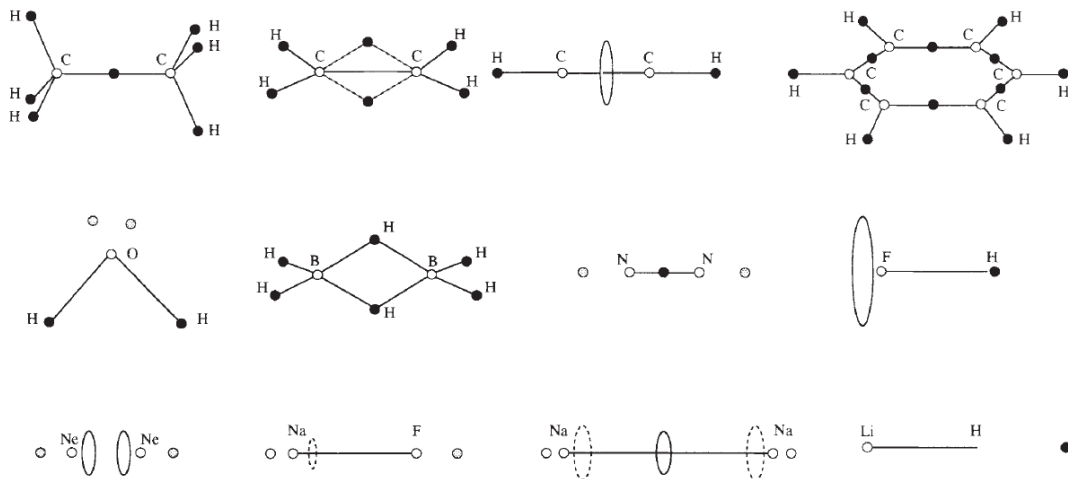
$$\text{ELF} = (1 + \chi_{\sigma}^2)^{-1}$$

$$\chi_{\sigma} = D_{\sigma} / D_{\sigma}^0 \quad D_{\sigma}^0 = \frac{3}{5} (6\pi^2)^{2/3} \rho_{\sigma}^{5/3}$$



ELF的应用

- ▶ 原子壳层结构
- ▶ 分子中的电子局域化程度
- ▶ 成键类型分析
 - ▶ 局域吸引子：键、非键、芯



极化与Berry位相

- ▶ 在周期边界条件下偶极矩 \mathbf{P} 的方向与单胞取法有关

$$+ - \boxed{+ -} \boxed{+ -} -$$

- ▶ Well-defined 的量为

$$\nabla \cdot \mathbf{P}(\mathbf{r}, t) = -\delta n(\mathbf{r}, t)$$

- ▶ 绝缘体宏观极化率的变化对应初末态波函数的相位差

$$\Delta \mathbf{P} = \int_{\lambda_1}^{\lambda_2} \frac{\partial \mathbf{P}}{\partial \lambda} d\lambda = \mathbf{P}(\lambda_2) - \mathbf{P}(\lambda_1)$$

$$\mathbf{P}(\lambda) = -\frac{fie}{(2\pi)^3} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} \langle u_{n\mathbf{k}}^{(\lambda)} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}}^{(\lambda)} \rangle$$



偶极修正

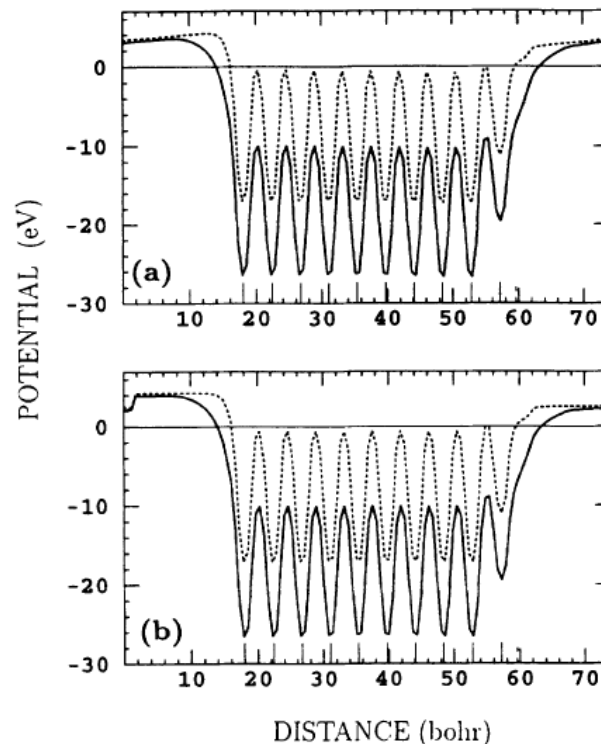
- ▶ Slab模型中存在垂直表面的偶极矩时，PBC导致体系的能量随单胞大小收敛很慢
- ▶ 在真空中增加一个偶极层自洽地抵消表面偶极层静电势

$$\phi^{ext}(\mathbf{r}) = -\frac{4\pi\mu}{\Omega} [z - a_3\theta(z_0 - z)] \quad 0 \leq z < a_3$$

- ▶ 外加电场

$$\mathbf{E}(\mathbf{r}) = -\nabla\phi^{ext}(\mathbf{r})$$

- ▶ 能量的修正 $\Delta E = -\mu E$
- ▶ 力的修正 $\Delta F_l[n] = -Z_l E(\mathbf{R}_l)$



磁性

▶ 自旋密度泛函理论

▶ 波函数变成旋量

$$|\Phi\rangle = \begin{pmatrix} |\Psi^\uparrow\rangle \\ |\Psi^\downarrow\rangle \end{pmatrix} \quad n^{\alpha\beta}(\mathbf{r}) = \sum_n f_n \langle \Psi_n^\beta | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_n^\alpha \rangle$$

▶ 密度变成 2×2 矩阵 $\overset{\leftrightarrow}{n}(\mathbf{r})$

$$n_{\text{Tr}}(\mathbf{r}) \equiv \text{Tr} [n^{\alpha\beta}(\mathbf{r})] = \sum_\alpha n^{\alpha\alpha}(\mathbf{r})$$

$$n^{\alpha\beta}(\mathbf{r}) = (n_{\text{Tr}}(\mathbf{r})\delta_{\alpha\beta} + \vec{m}(\mathbf{r}) \cdot \vec{\sigma}_{\alpha\beta}) / 2$$

$$\vec{m}(\mathbf{r}) = \sum_{\alpha\beta} n^{\alpha\beta}(\mathbf{r}) \cdot \vec{\sigma}_{\alpha\beta}$$

▶ 密度泛函

$$E = \sum_\alpha \sum_n f_n \langle \Psi_n^\alpha | -\frac{1}{2}\Delta | \Psi_n^\alpha \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n_{\text{Tr}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_{\text{Tr}}(\mathbf{r}) n_{\text{Tr}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\overset{\leftrightarrow}{n}(\mathbf{r})]$$

▶ KS方程

$$\sum_\beta H^{\alpha\beta} |\Psi_n^\beta\rangle = \epsilon_n S^{\alpha\alpha} |\Psi_n^\alpha\rangle$$

$$V_{\text{xc}}^{\alpha\beta}[\overset{\leftrightarrow}{n}(\mathbf{r})](\mathbf{r}) = \frac{\delta E_{\text{xc}}[\overset{\leftrightarrow}{n}(\mathbf{r})]}{\delta n^{\beta\alpha}(\mathbf{r})}$$

$$H^{\alpha\beta} = -\frac{1}{2}\Delta\delta_{\alpha\beta} + V_{\text{ext}}(\mathbf{r})\delta_{\alpha\beta} + \int d\mathbf{r}' \frac{n_{\text{Tr}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta_{\alpha\beta} + V_{\text{xc}}^{\alpha\beta}[\overset{\leftrightarrow}{n}(\mathbf{r})](\mathbf{r})$$

自旋密度泛函理论

- ▶ 通常只有在 $\vec{m}(\mathbf{r}) = m_z(\mathbf{r})$, 也即密度矩阵是对角的情况下才容易得到交换关联能量的可靠近似

$$E_{\text{xc}} = \int n_{\text{Tr}}(\mathbf{r}) \varepsilon_{\text{xc}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] d\mathbf{r}$$

- ▶ 可以通过对角化 $\vec{n}(\mathbf{r})$ 得到 $V_{\text{xc}}^{\alpha\beta}(\mathbf{r})$ 的表达式
- ▶ 或者等价地通过如下定义得到 $V_{\text{xc}}^{\alpha\beta}(\mathbf{r})$

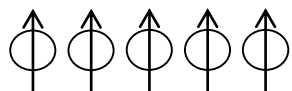
$$n_{\uparrow}(\mathbf{r}) = \frac{1}{2}[n_{\text{Tr}}(\mathbf{r}) + |\vec{m}(\mathbf{r})|], \quad n_{\downarrow}(\mathbf{r}) = \frac{1}{2}[n_{\text{Tr}}(\mathbf{r}) - |\vec{m}(\mathbf{r})|], \quad \hat{m}(\mathbf{r}) = \frac{\vec{m}(\mathbf{r})}{|\vec{m}(\mathbf{r})|}$$

$$V_{\text{xc}}^{\alpha\beta}(\mathbf{r}) = \frac{1}{2} \left[\frac{\delta E_{\text{xc}}}{\delta n_{\uparrow}(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta n_{\downarrow}(\mathbf{r})} \right] \delta_{\alpha\beta} + \frac{1}{2} \left[\frac{\delta E_{\text{xc}}}{\delta n_{\uparrow}(\mathbf{r})} - \frac{\delta E_{\text{xc}}}{\delta n_{\downarrow}(\mathbf{r})} \right] \hat{m}(\mathbf{r}) \cdot \vec{\sigma}_{\alpha\beta}$$

- ▶ 对共线(collinear)磁性体系, KS哈密顿矩阵是对角的

共线磁序

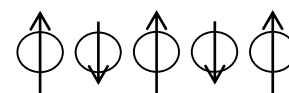
▶ FM、AFM、SDW...



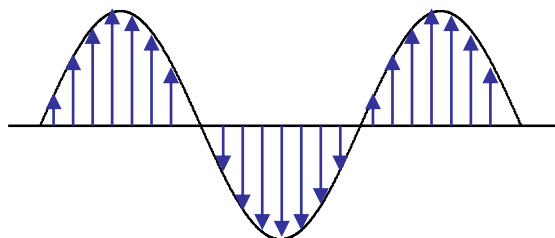
铁磁



反铁磁



亚铁磁



自旋密度波



非共线磁序与旋轨耦合

▶ 非共线KS方程

$$\begin{pmatrix} H^{\alpha\alpha} & V_{xc}^{\alpha\beta} \\ V_{xc}^{\beta\alpha} & H^{\beta\beta} \end{pmatrix} \begin{pmatrix} |\Psi_n^\alpha\rangle \\ |\Psi_n^\beta\rangle \end{pmatrix} = \epsilon_n \begin{pmatrix} |\Psi_n^\alpha\rangle \\ |\Psi_n^\beta\rangle \end{pmatrix}$$

▶ 自旋轨道耦合

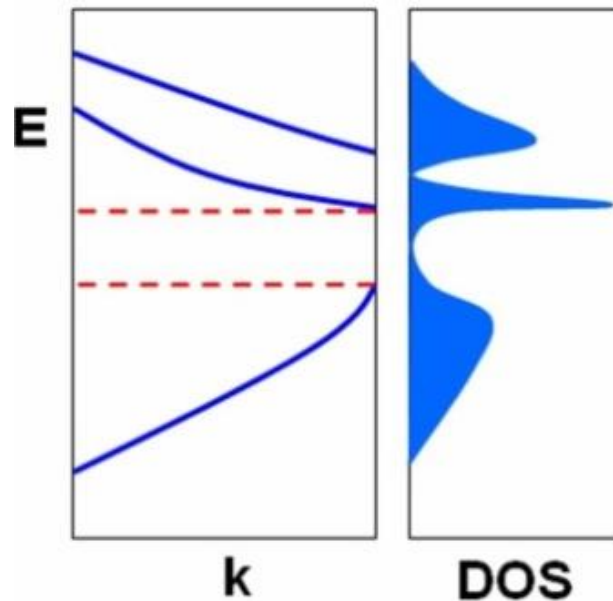
$$H_{\text{SOI}}^{\alpha\beta} = \frac{\hbar^2}{(2m_e c)^2} \sum_{i,j} \langle \phi_i | \frac{1}{r} \frac{dV_{\text{spher}}}{dr} | \phi_j \rangle | \tilde{p}_i \rangle \vec{\sigma}_{\alpha\beta} \cdot \vec{L}_{ij} \langle \tilde{p}_j |$$



能带结构

- ▶ 能带结构给出单电子态能量随k点的变化
- ▶ 常和态密度画在一起

$$D(\varepsilon) = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \delta(\varepsilon - \varepsilon_n(\mathbf{k}))$$

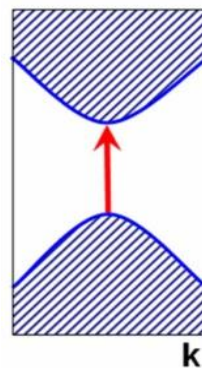
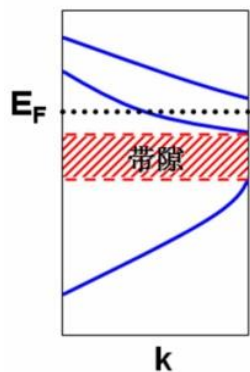
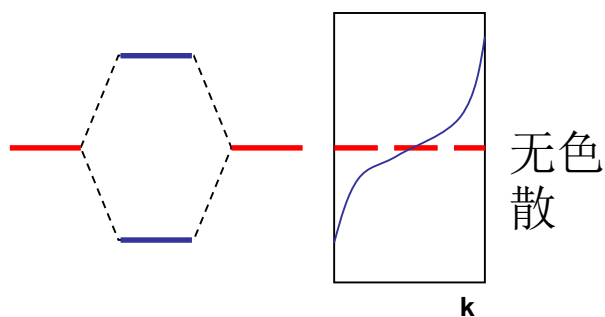


色散与带隙

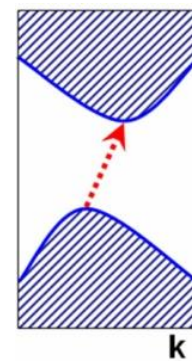
▶ 色散

▶ 相互作用越强，色散越强

▶ 能隙



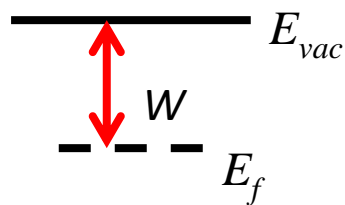
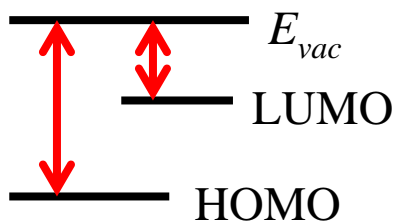
直接带隙
(强光学吸收)



间接带隙
(弱光学吸收)

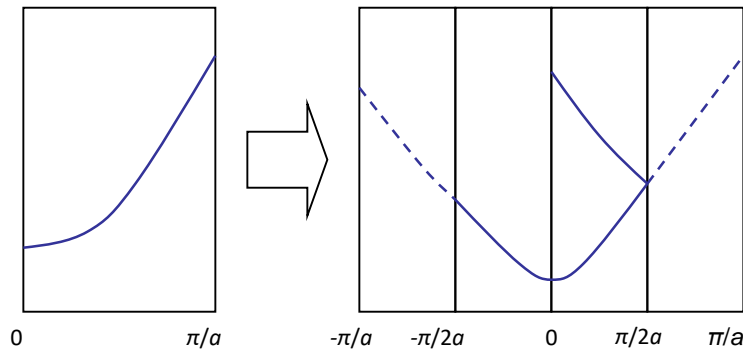
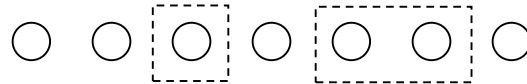
IP、AE、WF

- ▶ 电离能(IP)为拿走一个电子所需要的能量
- ▶ 电子亲和能(EA)为得到一个电子所释放的能量
 - ▶ IP和EA可以通过 Δ SCF方法计算
- ▶ 功函数为电子从金属逃逸时所需要克服的功
 - ▶ 真空能级等于无穷远处有效势的值，为了加快收敛，通常只考虑静电部分
 - ▶ 计算功函数时最好完全避免wrap around error



能带折叠与投影

- ▶ 选取不同大小的原胞时，其对应的布里渊区会发生相应的变化



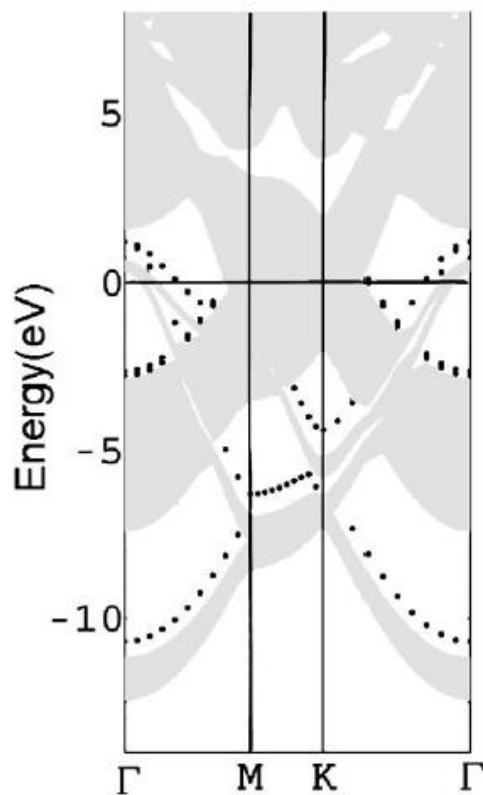
单胞取
一个原
子

单胞取
两个原
子

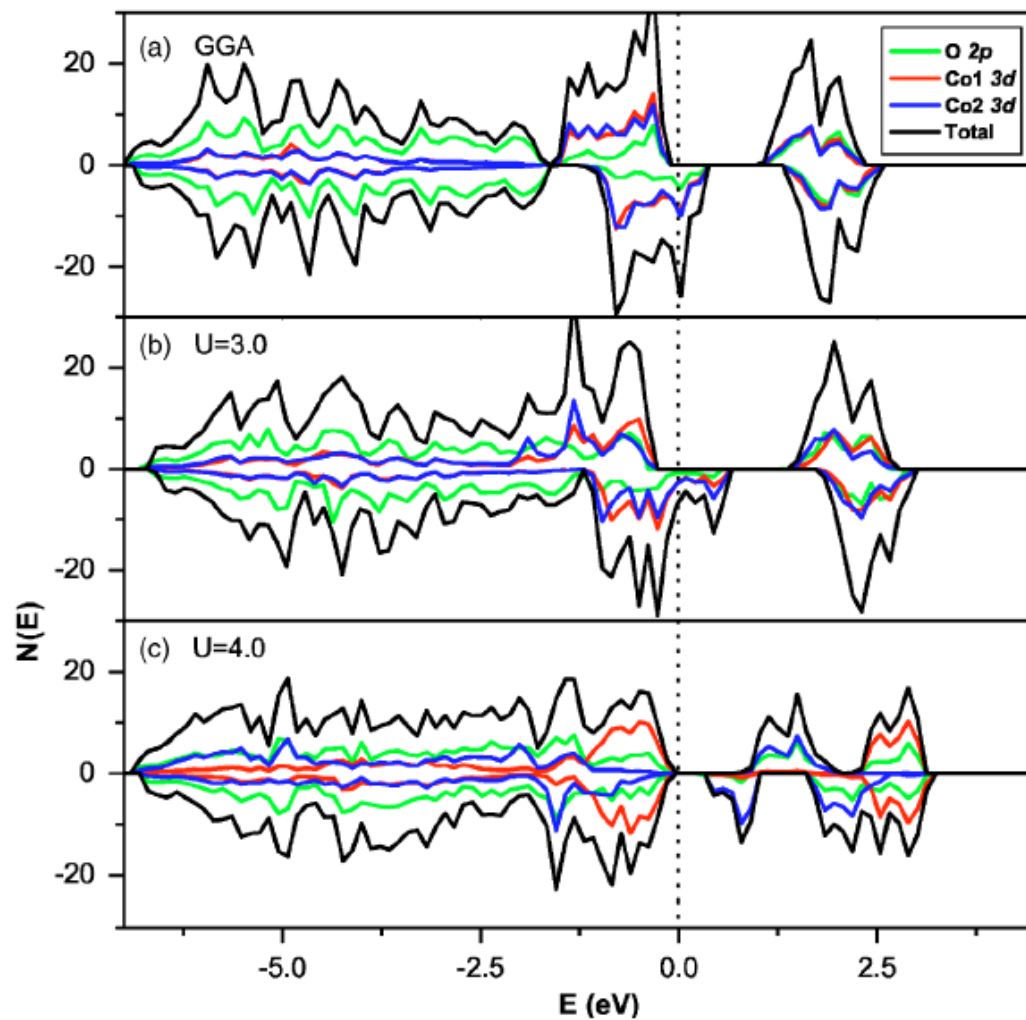


能带投影

- ▶ 对低维体系，为了清楚的识别表面态，常将高维带结构投影到低维

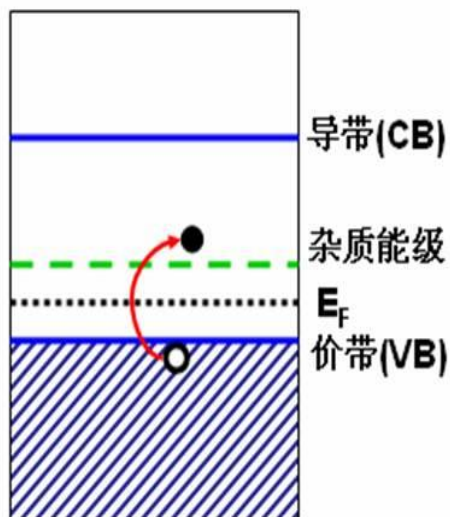


分态密度

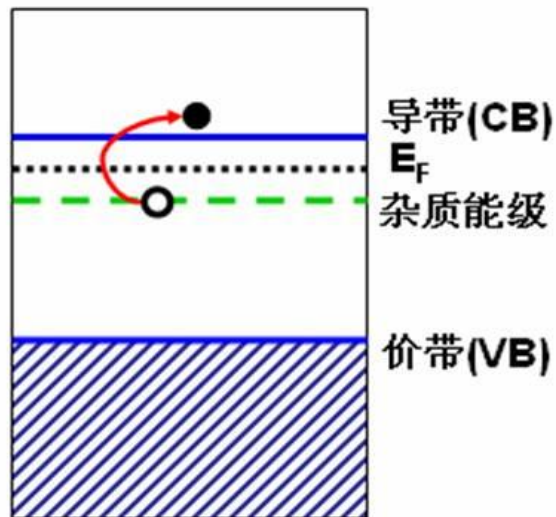


半导体掺杂

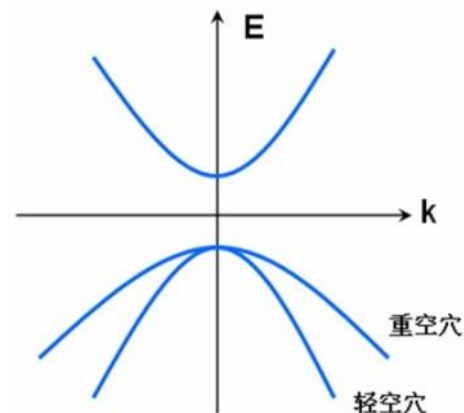
▶ p型和n型掺杂



p型掺杂



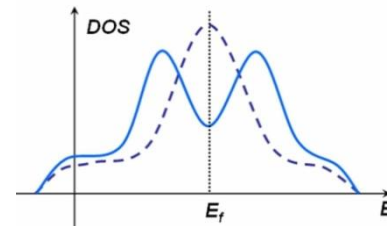
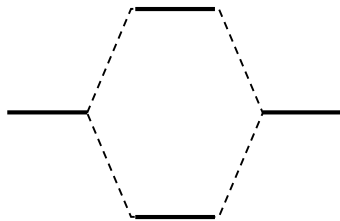
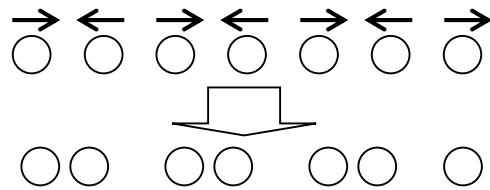
n型掺杂



- ▶ 载流子有效质量
$$m^* = \hbar^2 / \frac{\partial E^2}{\partial \mathbf{k}^2}$$

Instabilities

- ▶ Large DOS at E_f suggests an instability
- ▶ Peierls相变
 - ▶ 当一维原子链中的原子两两结合时，会形成成键态和反键态，但由于有贡献的是占据态，因此体系的总能会降低。



Stoner铁磁理论

- ▶ 考虑自旋极化很小的情形

$$v_{xc}^{\pm}(\mathbf{r}) = v_{xc}^0(\mathbf{r}) \mp m(\mathbf{r}) \tilde{v}[n(\mathbf{r})] \doteq v_{xc}^0(\mathbf{r}) \mp \frac{1}{2} IM$$

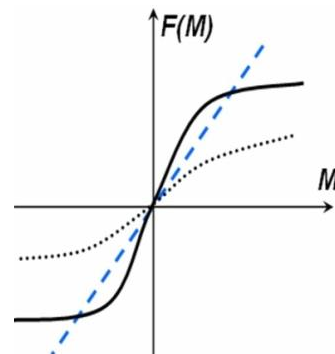
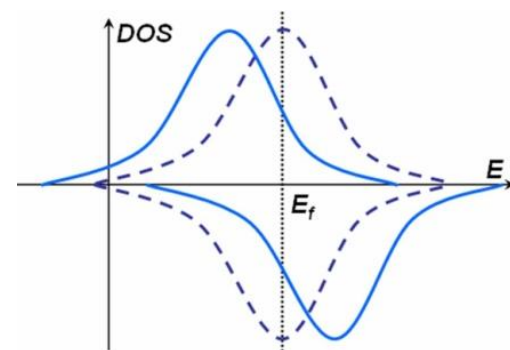
- ▶ 修正为常数则波函数不变，态密度发生平移

$$M = \int^{E_F} [n^0(E + \frac{1}{2} IM) - n^0(E - \frac{1}{2} IM)] dE = F(M)$$

- ▶ 有磁矩的条件 $F'(0) > 1$ ，即 $ln^0(E_F) > 1$

- ▶ 3d易形成铁磁

$$W_{3d} < W_{4d} < W_{5d} \Rightarrow n_{3d}^0 > n_{4d}^0 > n_{5d}^0$$



原子受力

- ▶ 能量的梯度

$$\mathbf{g} = -\frac{dE}{d\mathbf{R}} = \mathbf{F}$$

- ▶ Hellmann-Feynman 定理

$$\frac{\partial E}{\partial \mathbf{R}} = \langle \psi | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \psi \rangle$$

- ▶ 成立的条件：(1) $|\psi\rangle$ 是 \hat{H} 的本征函数；
(2) $|\psi\rangle$ 正交归一，即 $\frac{\partial}{\partial \mathbf{R}} \langle \psi | \psi \rangle = 0$
- ▶ MP2、CC 等不满足变分原理的方法不适用
- ▶ 对依赖原子位置的不完备基组不适用



状态方程(EOS)

- ▶ 如果已知压强与体积的关系，通过对压强 $P = -\frac{dE}{d\Omega}$ 积分可以得到能量与体积的关系
- ▶ 拟合状态方程可以得到体模量

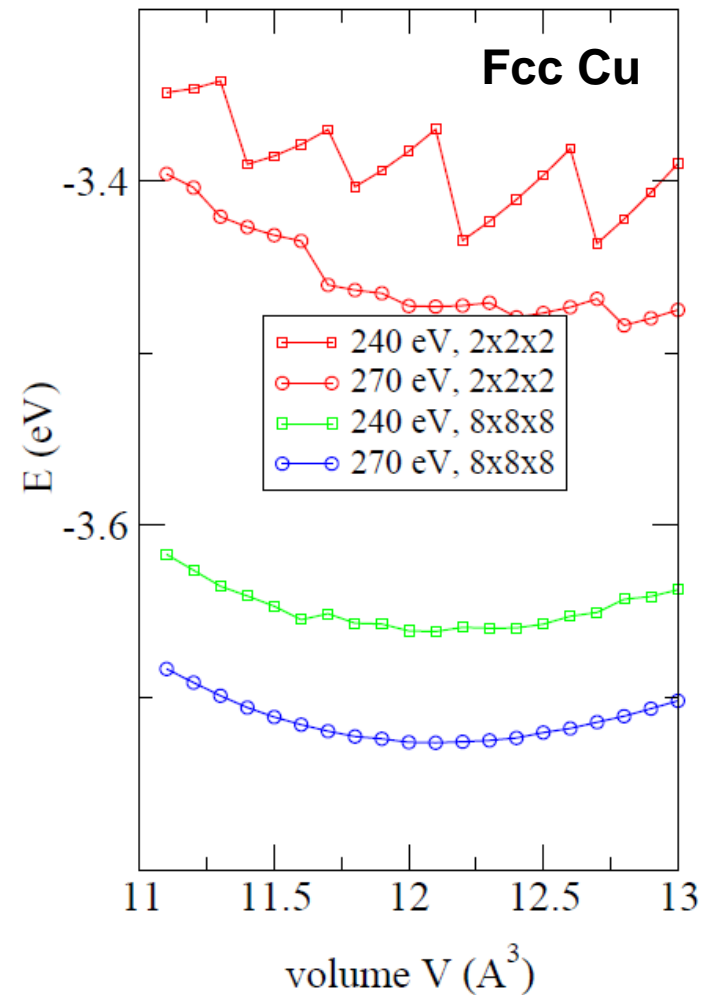
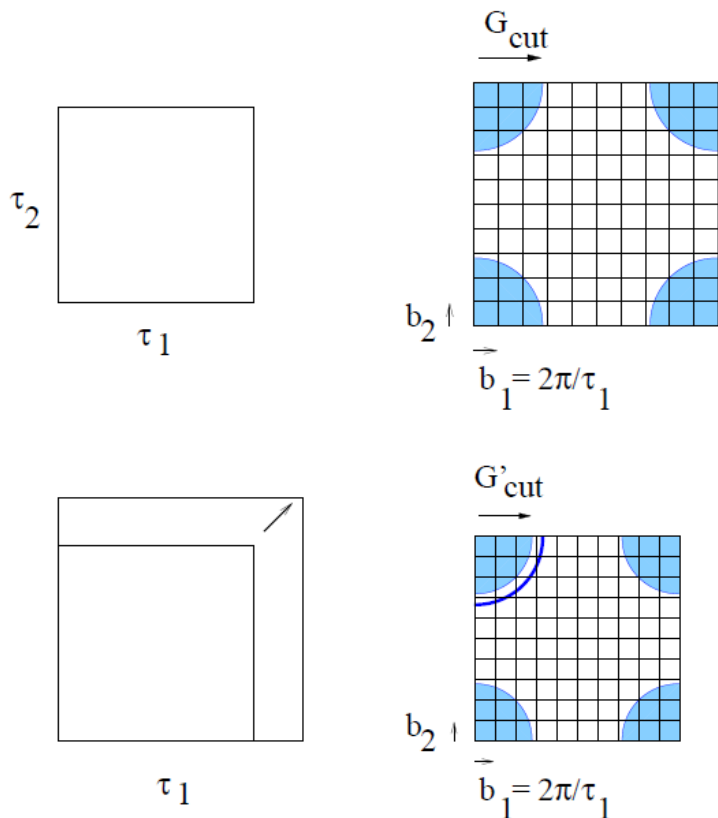
$$B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2 E}{d\Omega^2}$$

- ▶ Equilibrium volume and shape of a crystal depend on the XC-type used:
 - ▶ LDA: overbinding ! a0 too small
 - ▶ PBE, PW91: underbinding ! a0 too large
 - ▶ results are improved using specially designed functionals(PBEsol, HSE),...
-



基组截断

- ▶ basis set changes discontinuously
- ▶ increase ENCUT (by 30%) to perform lattice relaxations



弹性力学性质

- ▶ Elasticity: stress-strain relation (应力——应变关系)

$$\mathbf{r}_\alpha \rightarrow (\delta_{\alpha\beta} + \varepsilon_{\alpha\beta})\mathbf{r}_\beta$$

▶ 应力张量:

$$\sigma_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial E}{\partial \varepsilon_{\alpha\beta}}$$

弹性系数:

$$C_{\alpha\beta;\gamma\delta} = -\frac{\partial \sigma_{\alpha\beta}}{\partial \varepsilon_{\gamma\delta}}$$



上机实践

- ▶ 体相Si能带结构
- ▶ 体相Si态密度
- ▶ 体相MgB₂分态密度
- ▶ 体相MgB₂电荷转移(Bader布居分析)
- ▶ Ni(110)表面态

