

电子结构计算主要算法

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Outline

- ▶ 单电子方程的离散化
 - ▶ 实空间网格
 - ▶ 原子基组
 - ▶ 平面波基组
- ▶ 赝势
 - ▶ 模守恒赝势、超软赝势
 - ▶ 投影缀加波方法
- ▶ 自洽场
 - ▶ 求解单电子波函数
 - ▶ 求解电荷密度
- ▶ 几何优化

数值离散

▶ 单电子方程

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r})\right]\varphi_i = \varepsilon_i\varphi_i$$

▶ 实空间网格

▶ 边界条件

▶ 开放边界条件

▶ 周期性边界条件

▶ 矩阵形式(本征值问题)



有限差分

- ▶ 中心差分
- ▶ 高阶差分

$$\frac{\partial^2 \Psi}{\partial x^2} = \sum_{n=-N}^N C_n \Psi(x_i + nh, y_j, z_k) + O(h^{2N+2})$$

TABLE I. Expansion coefficients C_n , $n = 0, \dots, \pm N$, for higher-order finite-difference expressions of the second derivative.

	C_i	$C_{i\pm 1}$	$C_{i\pm 2}$	$C_{i\pm 3}$	$C_{i\pm 4}$	$C_{i\pm 5}$	$C_{i\pm 6}$
$N=1$	-2	1					
$N=2$	$-\frac{5}{2}$	$\frac{4}{3}$	$-\frac{1}{12}$				
$N=3$	$-\frac{49}{18}$	$\frac{3}{2}$	$-\frac{3}{20}$	$\frac{1}{90}$			
$N=4$	$-\frac{205}{72}$	$\frac{8}{5}$	$-\frac{1}{5}$	$\frac{8}{315}$	$-\frac{1}{560}$		
$N=5$	$-\frac{5269}{1800}$	$\frac{5}{3}$	$-\frac{5}{21}$	$\frac{5}{126}$	$-\frac{5}{1008}$	$\frac{1}{3150}$	
$N=6$	$-\frac{5369}{1800}$	$\frac{12}{7}$	$-\frac{15}{56}$	$\frac{10}{189}$	$-\frac{1}{112}$	$\frac{2}{1925}$	$-\frac{1}{16632}$

原子基组

▶ 原子轨道的线性组合(LCAO)

$$\chi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$$

▶ Slater-type orbital (STO)

$$\chi(r, \theta, \phi) \propto r^{n-1} e^{-\zeta r} Y_{lm}$$

- ▶ 计算三中心和四中心双电子积分比较困难，一般采用数值积分方法(ADF)
- ▶ 只需要确定Slater指数就可以得到一个基函数，因此对重金属元素很容易得到可用的基组



Gaussian-type orbital (GTO)

- ▶ 在 Gaussian 函数前面加上不同的因子

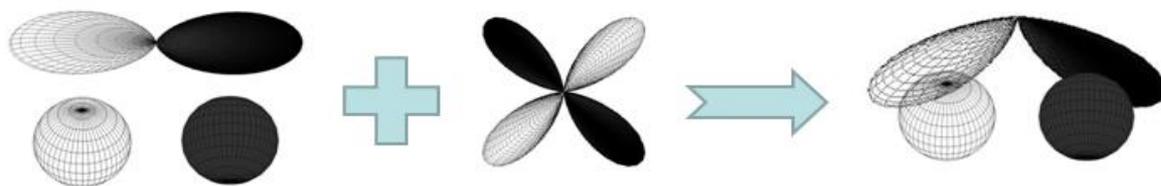
$$\chi(x, y, z) \propto x^i y^j z^k e^{-\alpha r^2}$$

- ▶ i、j、k之和为0、1、2分别对应s、p、d轨道
 - ▶ 5个正则d轨道： $xy, yz, xz, x^2-y^2, 3z^2-r^2$
 - ▶ GTO乘积定理：两个高斯函数的积仍是高斯函数
 - ▶ 三维积分变成独立的三个一维积分
 - ▶ GTO并不是一种轨道： r 大的时候衰减太快，而在原子核处又没有尖点(cusp)。
 - ▶ Gaussian函数没有节点：没法只用一个高斯函数来表示价轨道
-



Gaussian基组

- ▶ 收缩高斯基组(STO-3G)
- ▶ 分裂基组(multi- ζ)与分裂价基(3-21G)
- ▶ 极化基组(6-31G**, 6-311G(3df,3pd))



- ▶ 弥散函数(6-31++G)
- ▶ **练习**: 用6-311++G(3df, 2pd)计算H₂O时, 用到多少个轨道, 多少个GTO?



数值原子基组

- ▶ 直接作(赝)原子轨道计算, 存储径向函数, 样条插值
 - ▶ 分子解离成原子 exactly
 - ▶ Confining Potential, energy shift, 局域基组
- ▶ 极化、扩展等轨道可以通过离子、激发态、类氢原子、电场微扰等方法产生。



傅立叶变换

▶ 傅立叶变换

$$F(k) = \int_{-\infty}^{+\infty} f(x) e^{-2\pi i k x} dx \quad f(x) = \int_{-\infty}^{+\infty} F(k) e^{2\pi i k x} dk$$

▶ 通用的完备基组(平面波基组)

$$\varphi_n(\mathbf{r}) = \int C_n(\mathbf{g}) e^{i\mathbf{g}\cdot\mathbf{r}} d\mathbf{g}$$

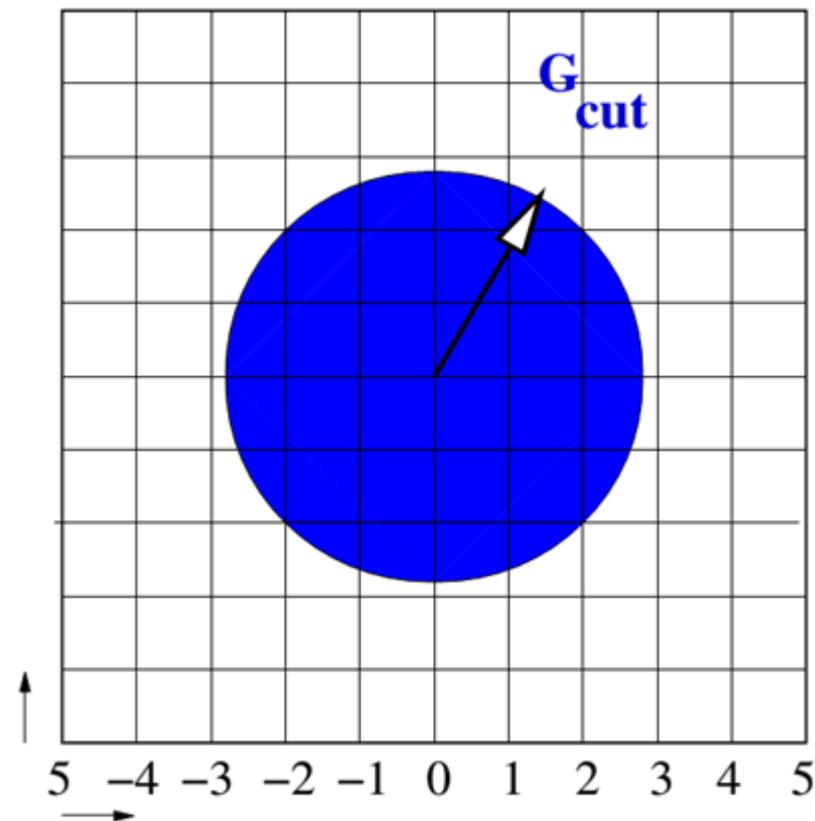
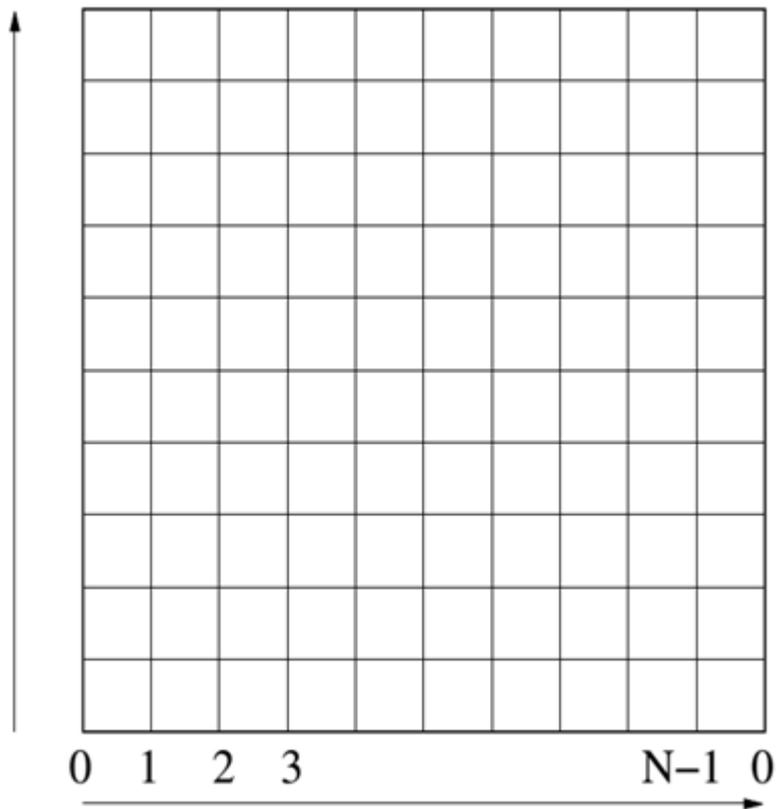
▶ 离散傅立叶变换

$$F(k) = \frac{1}{N} \sum_{x=0}^{N-1} f(x) e^{-\frac{2\pi}{N} i k x} \quad f(x) = \sum_{k=0}^{N-1} F(k) e^{\frac{2\pi}{N} i k x}$$

- ▶ 当 f 为实数时, 有 N 个实空间变量, 对应倒空间中 $[1, (N-1)/2]$ 区间内的, $(N-1)/2$ 个复数, 以及 0 和 $N/2$ 两个实数。

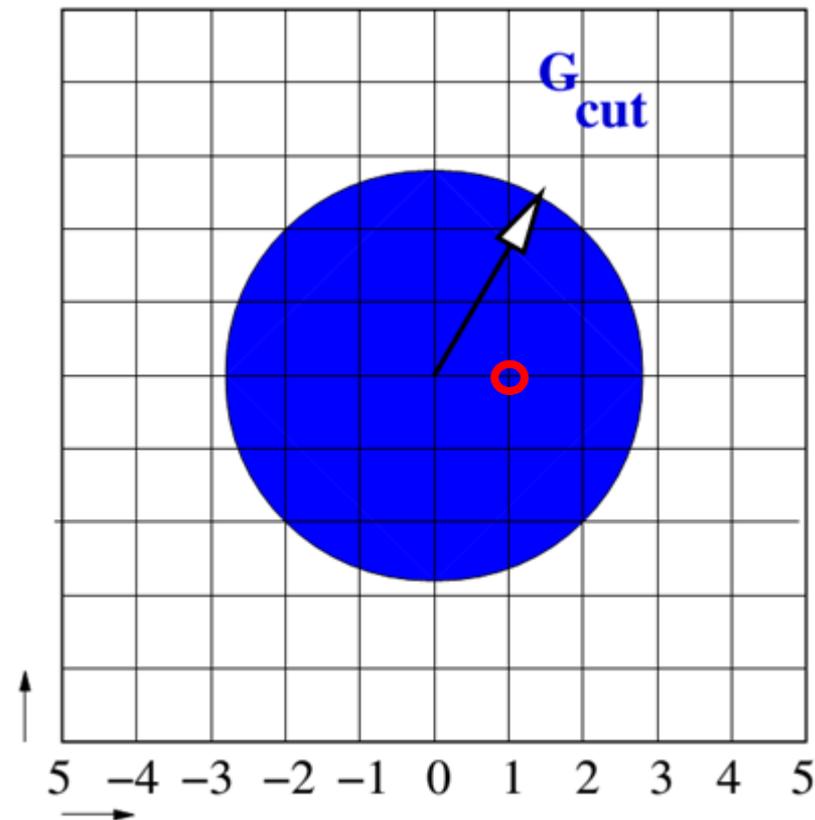
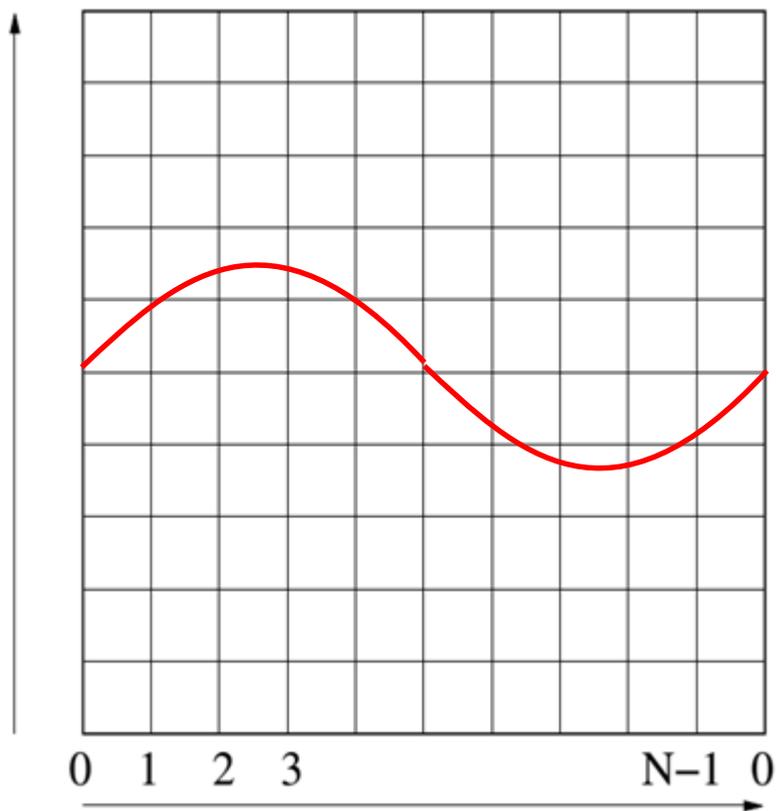


实空间与k空间对应



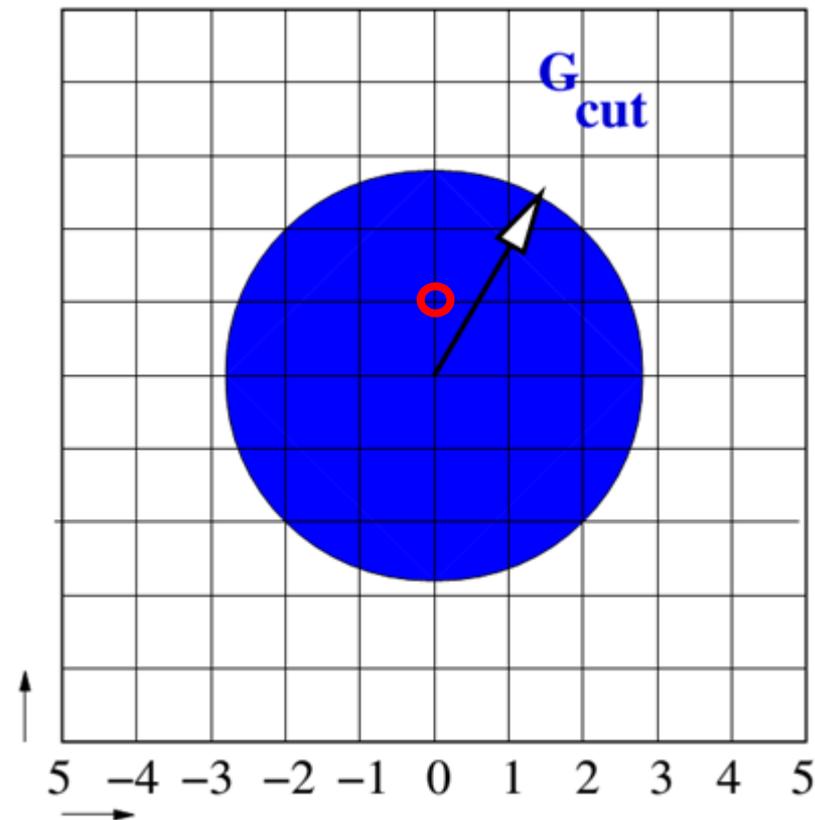
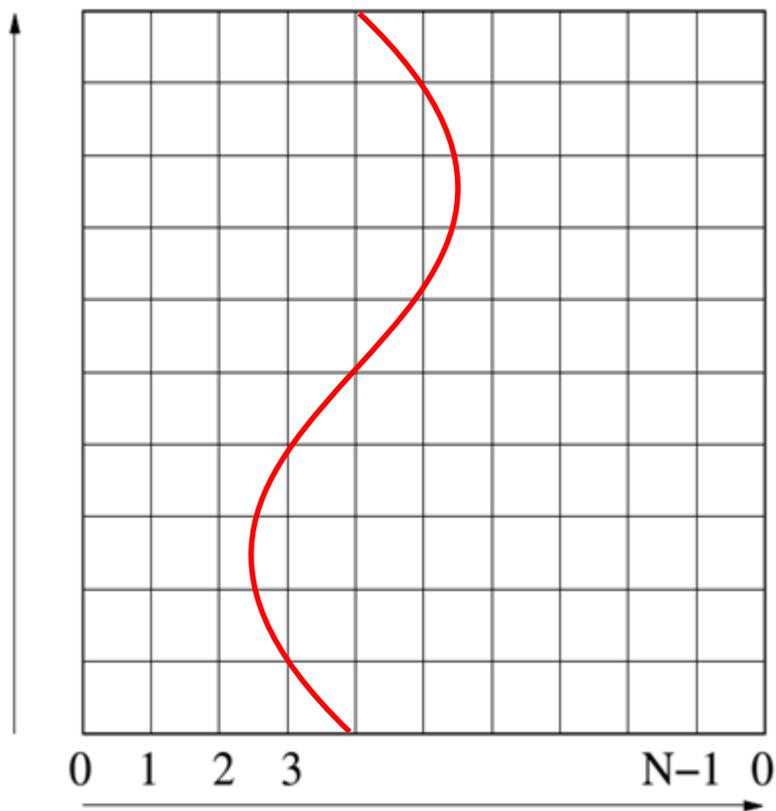
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \xleftrightarrow{\text{FFT}} C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

实空间与k空间对应



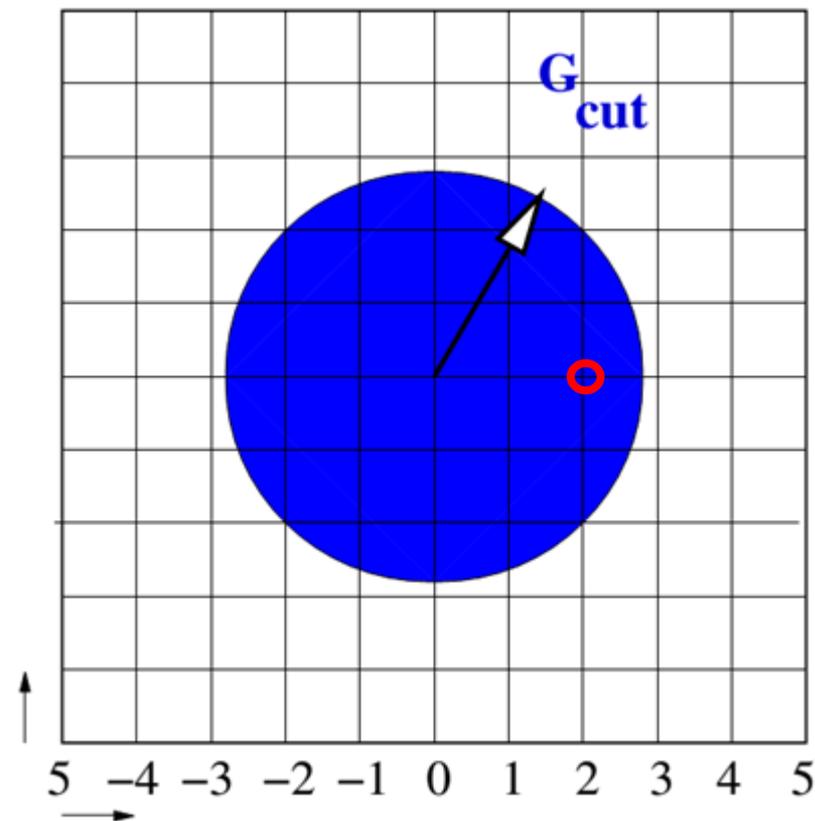
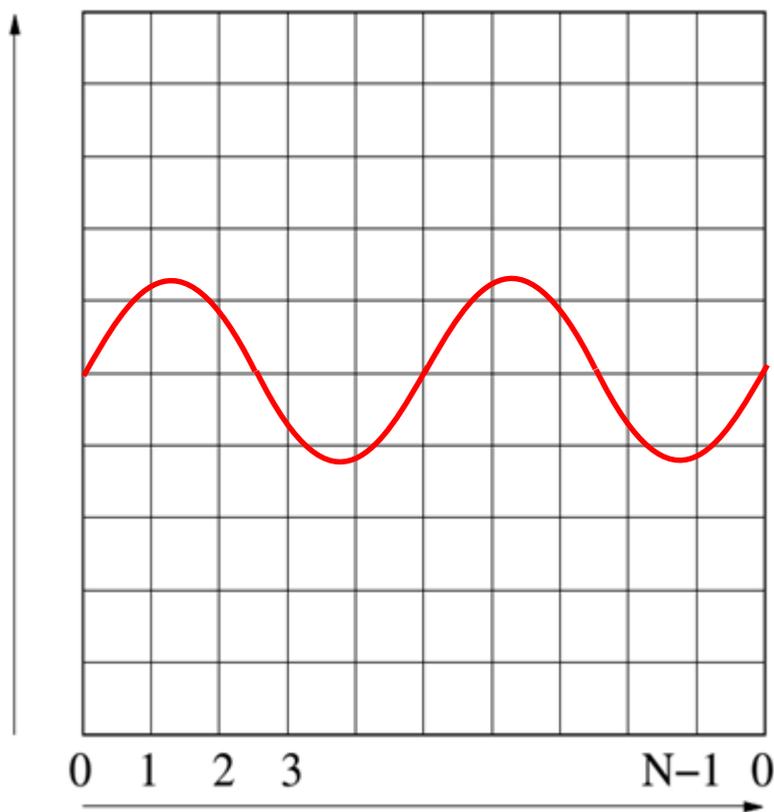
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实空间与k空间对应



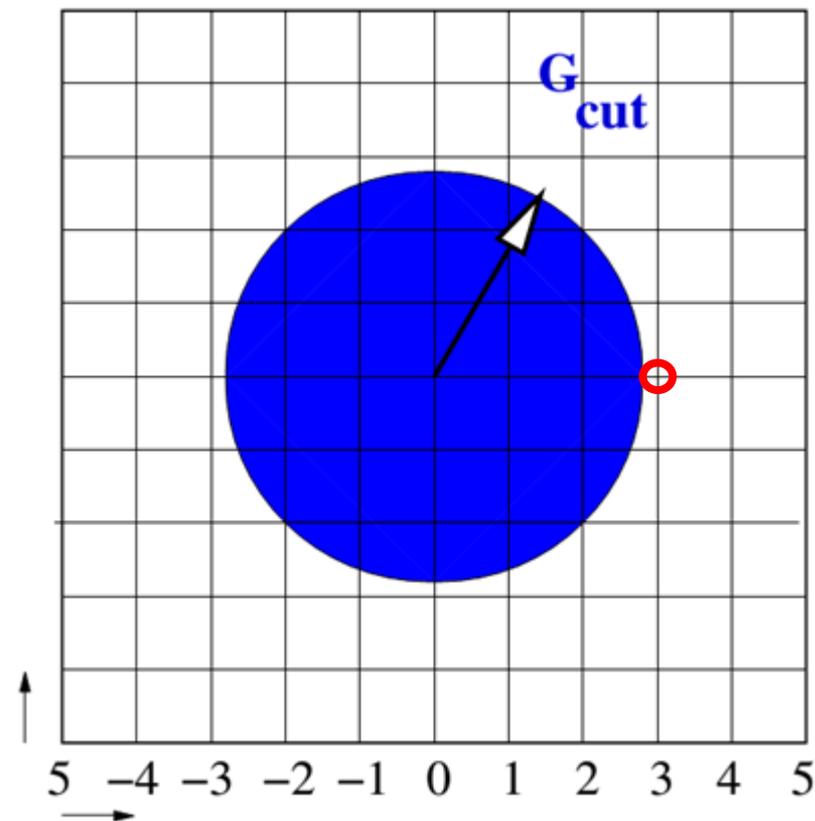
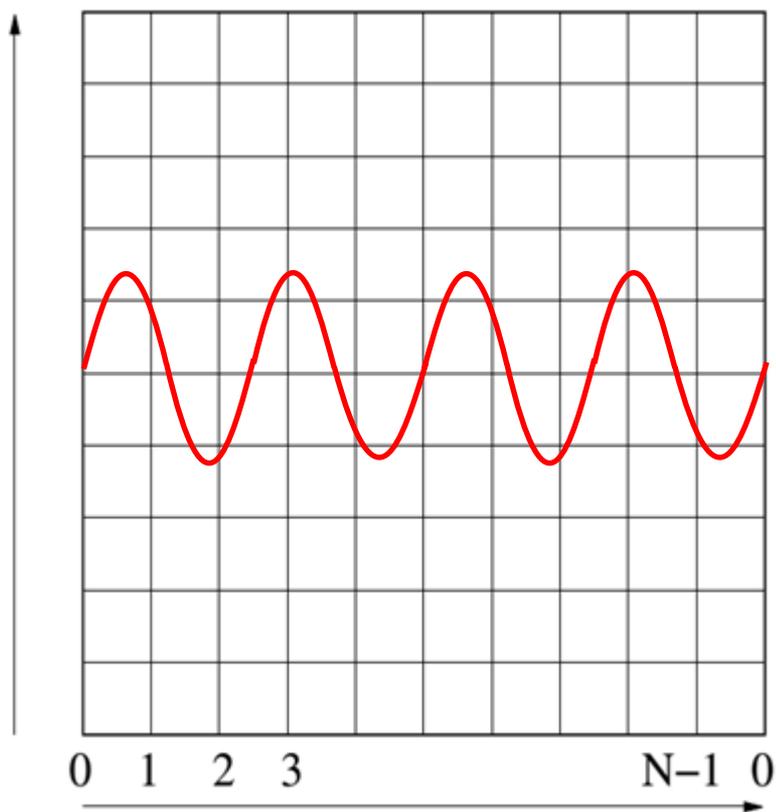
$$C_{\mathbf{r}nk} = \sum_{\mathbf{G}} C_{\mathbf{G}nk} e^{i\mathbf{G}\mathbf{r}} \xleftrightarrow{\text{FFT}} C_{\mathbf{G}nk} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}nk} e^{-i\mathbf{G}\mathbf{r}}$$

实空间与k空间对应



$$C_{rnk} = \sum_{\mathbf{G}} C_{\mathbf{G}nk} e^{i\mathbf{G}\mathbf{r}} \xleftrightarrow{\text{FFT}} C_{\mathbf{G}nk} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{rnk} e^{-i\mathbf{G}\mathbf{r}}$$

实空间与k空间对应



$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \xleftrightarrow{\text{FFT}} C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

平面波基组

▶ 单粒子波函数(非周期)的离散化

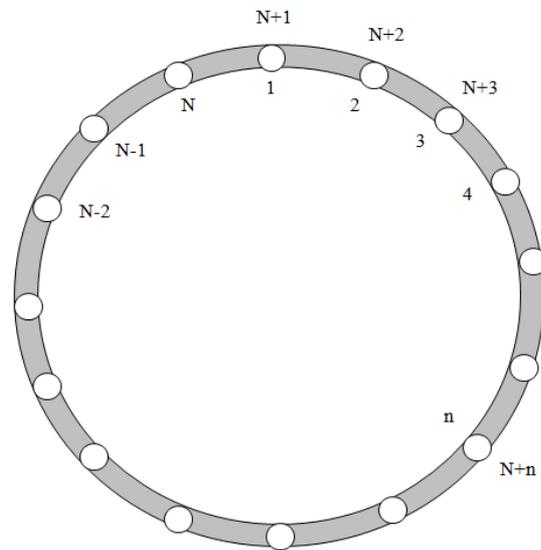
▶ 周期性边界条件 (布洛赫定理)

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

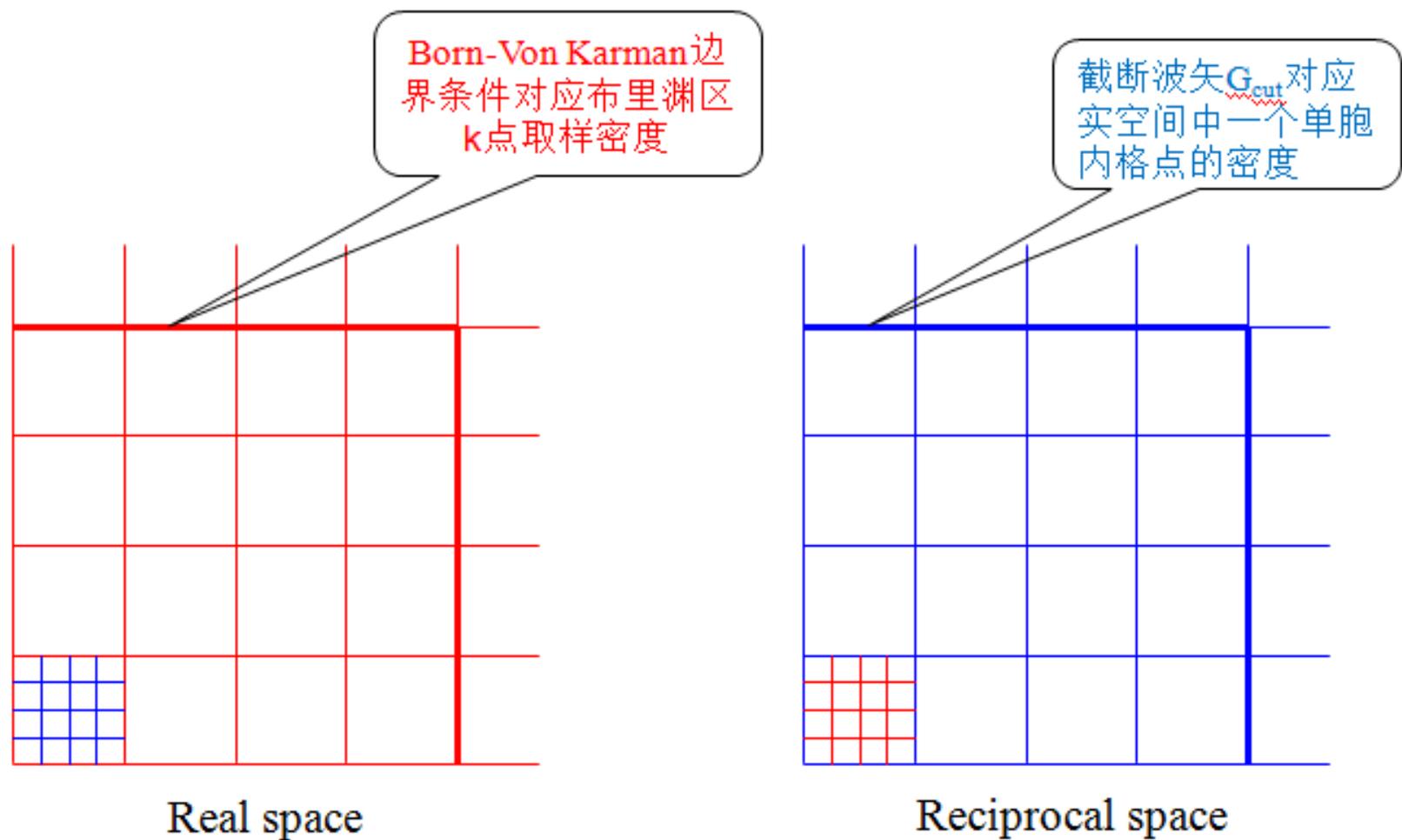
$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

▶ 波恩-冯卡曼边界条件

$$\varphi_n = \varphi_{N+n} \Rightarrow e^{ikNR} = 1 \Rightarrow k = \frac{2\pi}{NR} m$$



实空间与倒易空间



哈密顿算符

▶ 动能

$$\langle \mathbf{G} + \mathbf{k} | -\frac{1}{2}\Delta | \psi_{n\mathbf{k}} \rangle = \frac{1}{2} |\mathbf{G} + \mathbf{k}|^2 C_{\mathbf{G}n\mathbf{k}}$$

▶ 势能

▶ 交换关联势

Evaluate in real space, then FFT to k-space

$$V_{\text{xc},\mathbf{r}} = V_{\text{xc}}[\rho_{\mathbf{r}}] \quad \{V_{\text{xc},\mathbf{r}}\} \rightarrow \{V_{\text{xc},\mathbf{G}}\}$$

▶ Hartree势

Poisson equation in k-space $V_{\text{H},\mathbf{G}} = \frac{4\pi}{|\mathbf{G}|^2} \rho_{\mathbf{G}}$

▶ Add all contribution, then FFT back to real space

$$V_{\mathbf{G}} = V_{\text{H},\mathbf{G}} + V_{\text{xc},\mathbf{G}} + V_{\text{ext},\mathbf{G}} \quad \{V_{\mathbf{G}}\} \rightarrow \{V_{\mathbf{r}}\}$$

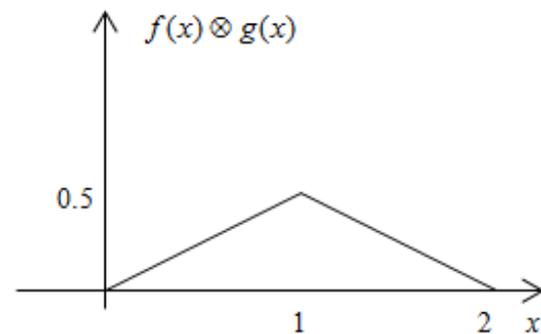
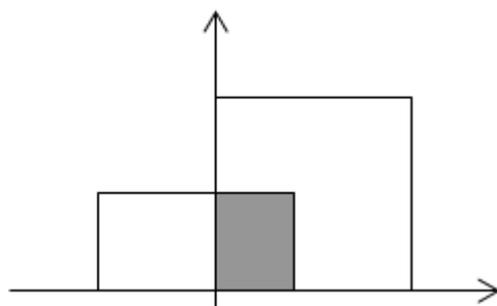
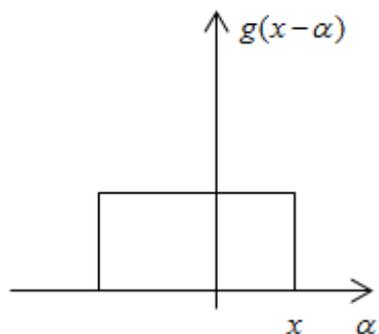
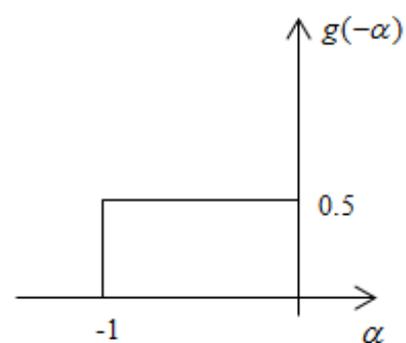
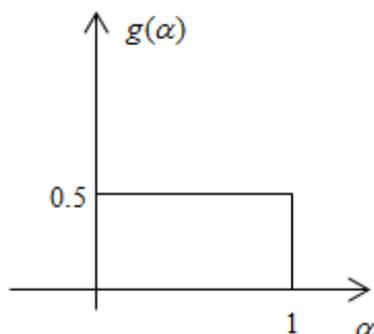
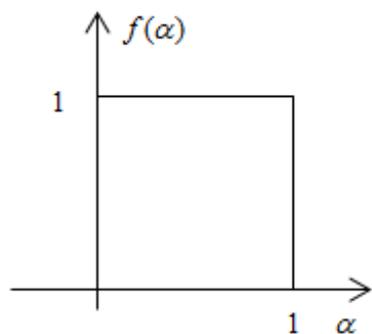
$$\langle \mathbf{G} + \mathbf{k} | V | \psi_{n\mathbf{k}} \rangle = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} V_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$



卷积

卷积的定义

$$f(x) \otimes g(x) = \int_{-\infty}^{+\infty} f(\alpha)g(x-\alpha)d\alpha$$



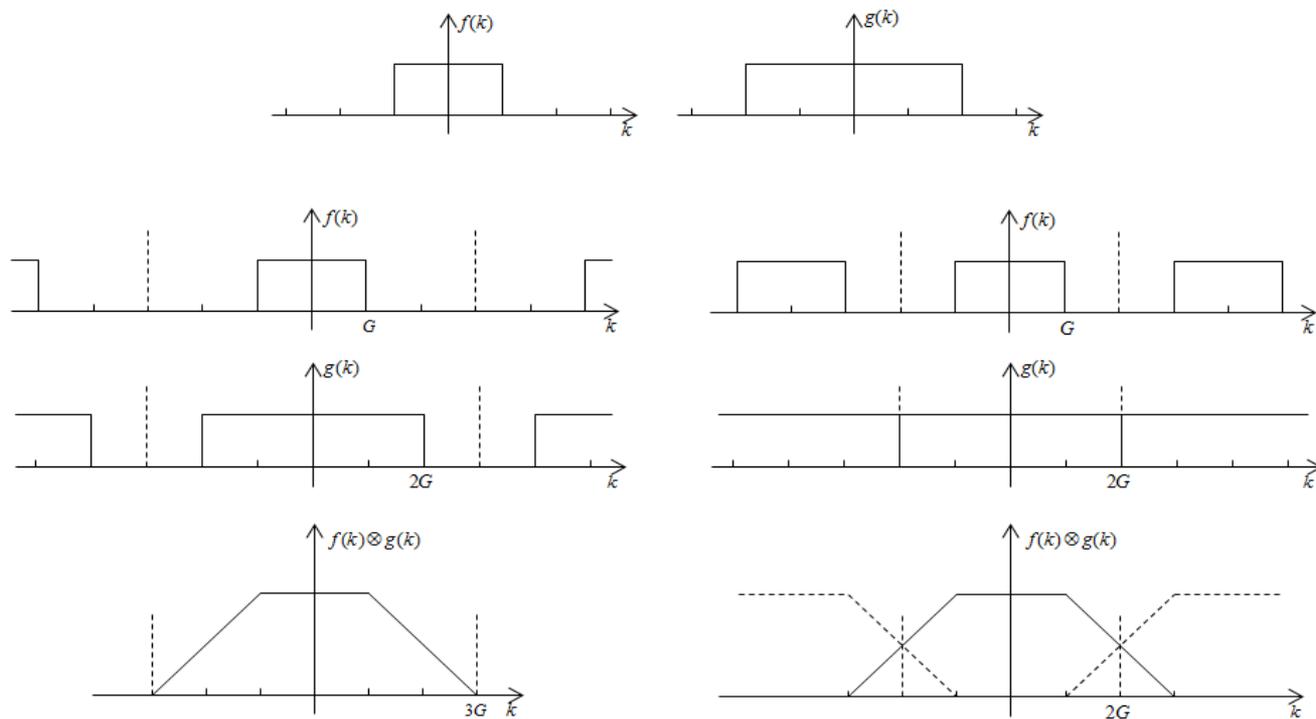
卷积与截断半径

▶ 卷积定理

- ▶ 实空间中的乘积对应倒空间中的卷积，两者互为Fourier变换，反之亦然

$$f(k) \otimes g(k) = \frac{1}{M} \sum_{m=0}^{M-1} f(m)g(k-m)$$

▶ 倒空间卷积

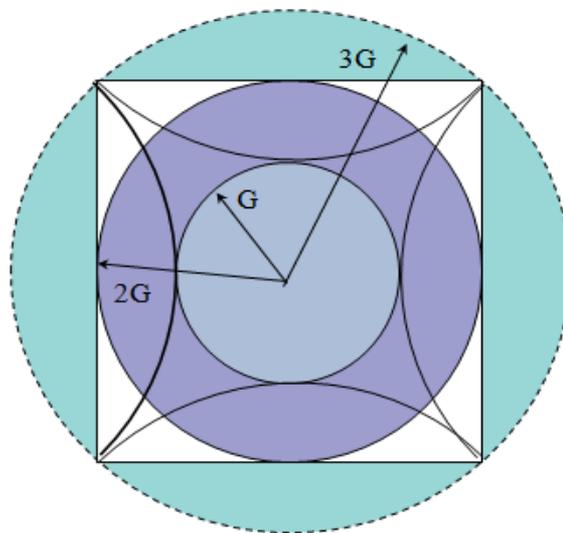


Wrap around error

- ▶ 电荷密度 ($2G_{\text{cut}}$)
- ▶ 有效势 ($2G_{\text{cut}}$ 内有意义)

$$\langle \mathbf{G}' | v_{\text{eff}} | \mathbf{G} \rangle = \sum_n v_{\text{eff}}(\mathbf{G}_n) \delta_{\mathbf{G}'-\mathbf{G}, \mathbf{G}_n}$$

- ▶ 单电子方程



赝势

▶ 芯电子与价电子

▶ 原子形成分子与固体时，芯电子基本保持不变

▶ 泡利不相容原理 → 原子轨道相互正交 → 价电子态快速振荡

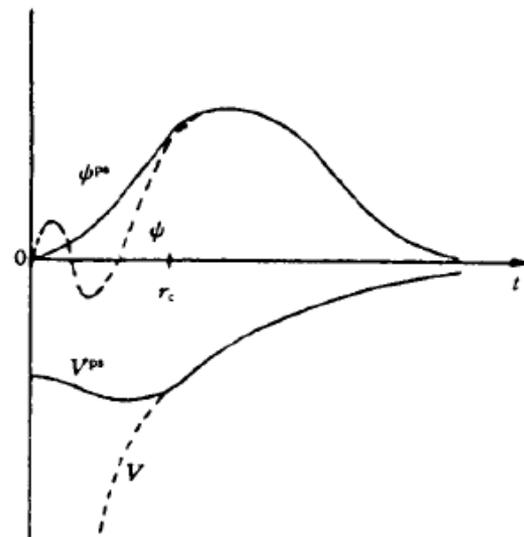
▶ 赝势：对赝波函数的散射性质与原子核及芯电子对价波函数的散射性质相同

▶ 赝波函数通常变化缓慢

▶ 需要的基函数较少

▶ 没有径向节点

▶ 无需求解内层电子



赝势构造步骤

1. 原子全电子计算，只需考虑径向部分 $\varphi(\mathbf{r}) = [u_l(r)/r]Y_{lm}$
2. 构造赝价波函数 $\varphi^{ps}(\mathbf{r})$
3. 反演得到总的赝势

$$v_l^{tot}(r) = \varepsilon_l - \frac{\hbar^2}{2m_e} \left[\frac{l(l+1)}{r^2} - \frac{\frac{d^2}{dr^2} u_l^{ps}(r)}{u_l^{ps}(r)} \right]$$

4. 去屏蔽

$$v_l^{PS} = v_l^{tot} - v^H[\rho_0^{PS}] - v^{xc}[\rho_0^{PS}]$$

▶ 芯修正 $v^{xc}[\rho_0^{PS}] \rightarrow v^{xc}[\rho^{core} + \rho_0^{PS}]$

▶ 部分芯修正

r^{nlc} 通常选核密度降到
低于价电子密度的点

$$\tilde{\rho}_o^{core}(r) = \begin{cases} \rho_o^{core}(r) & r \geq r^{nlc} \\ c_o + \sum_{i=3}^l c_i r^i & r \leq r^{nlc} \end{cases}$$

模守恒赝势

▶ 赝波函数限制条件

- ▶ 光滑, 无节点
- ▶ 对某种典型的电子组态, 赝本征值与真实本征值相等
- ▶ 真实波函数与赝波函数在芯半径 r_c 外相等
- ▶ 在芯半径内与真实波函数电荷密度积分相同(模守恒)

▶ 模守恒条件保证了径向波函数的对数微分对能量的导数在参考能量处相等

▶ 芯半径的选择

- ▶ Big enough to make soft Psp
- ▶ Small enough to keep good transferability
- ▶ Not too small to be very close to the outmost radial node



Kleinman-Bylander近似

- ▶ 不同的角动量感受到不同的势

$$\hat{v}^{PS} = \sum_{lm} |Y_{lm}\rangle v_l(r) \langle Y_{lm}|$$

- ▶ 在较远处都趋于库仑势 Z/r

$$v_l(r) = v_{loc}(r) + \delta v_l(r) \quad \hat{v}^{PS} = v_{loc}(r) + \sum_{lm} |Y_{lm}\rangle \delta v_l(r) \langle Y_{lm}|$$

- ▶ Kleinman-Bylander可分离格式

$$\sum_{lm} |Y_{lm}\rangle \delta v_l(r) \langle Y_{lm}| = \sum_{lm} |\chi_{lm}^{KB}\rangle E_l^{KB} \langle \chi_{lm}^{KB}|$$

- ▶ 积分数目由约 $N(N+1)/2$ 个变为 N 个
- ▶ ghost state



超软赝势(USPP)

▶ 非局域赝势

$$v_{NL} = \frac{|\chi_i\rangle\langle\chi_i|}{\langle\chi_i|\varphi_i^{PS}\rangle} \quad |\chi_i\rangle = (\varepsilon_i - T - v_{loc})|\varphi_i^{PS}\rangle$$

▶ 多能量参考点

$$B_{ij} = \langle\varphi_i^{PS}|\chi_j\rangle \quad |\beta_i\rangle = \sum_j (B^{-1})_{ji}|\chi_j\rangle \quad v_{NL} = \sum_{ij} B_{ij}|\beta_i\rangle\langle\beta_j| \quad \psi(r)$$

▶ 容易验证 $(T + v_{loc} + v_{NL})|\varphi_i^{PS}\rangle = \varepsilon_i|\varphi_i^{PS}\rangle$

▶ 模守恒条件成立时, B_{ij} 和 v_{NL} 是厄米的

$$Q_{ij} = \langle\varphi_i|\varphi_j\rangle_R - \langle\varphi_i^{PS}|\varphi_j^{PS}\rangle_R = 0$$

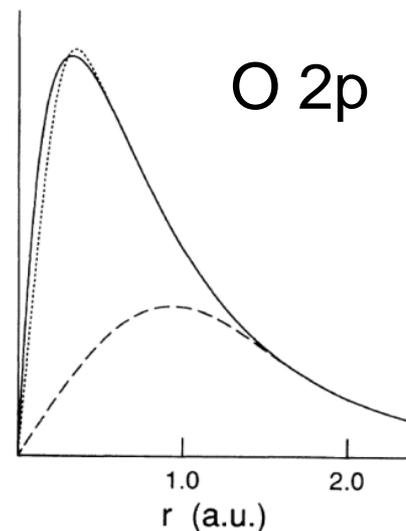
▶ 除去模守恒条件

$$S = 1 + \sum_{ij} Q_{ij}|\beta_i\rangle\langle\beta_j|$$

$$v_{NL} = \sum_{ij} (B_{ij} + \varepsilon_j Q_{ij})|\beta_i\rangle\langle\beta_j|$$

$$\langle\varphi_i^{PS}|S|\varphi_j^{PS}\rangle_R = \langle\varphi_i|\varphi_j\rangle_R \quad (T + v_{loc} + v_{NL})|\varphi_i^{PS}\rangle = \varepsilon_i S|\varphi_i^{PS}\rangle$$

▶ 电荷密度、能量、力需重新定义



PRB 1990, 41, 7892

投影缀加波方法(PAW)

- ▶ 考虑赝波函数与全电子波函数之间的变换

$$\varphi = \hat{T}\tilde{\varphi}, \quad \hat{T} = \hat{I} + \sum_R \hat{T}_R$$

- ▶ 在原子周围做分波展开

$$|\varphi\rangle = |\tilde{\varphi}\rangle + \sum_m c_m \{|\varphi_m\rangle - |\tilde{\varphi}_m\rangle\}$$

$$c_m = \langle \tilde{p}_m | \tilde{\varphi} \rangle$$

$$\hat{T} = \hat{I} + \sum_m \{|\varphi_m\rangle - |\tilde{\varphi}_m\rangle\} \langle \tilde{p}_m |$$

- ▶ 通过求得赝波函数能量, 电荷密度等信息

$$\tilde{A} = T^\dagger A T$$



PAW变换

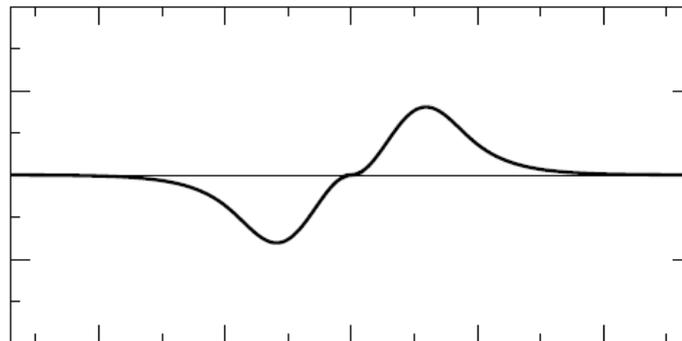
▶ 令 $c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon} | \tilde{\psi}_n \rangle$, 有

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle - \sum |\tilde{\phi}_{lm\epsilon}\rangle c_{lm\epsilon} + \sum |\phi_{lm\epsilon}\rangle c_{lm\epsilon}$$

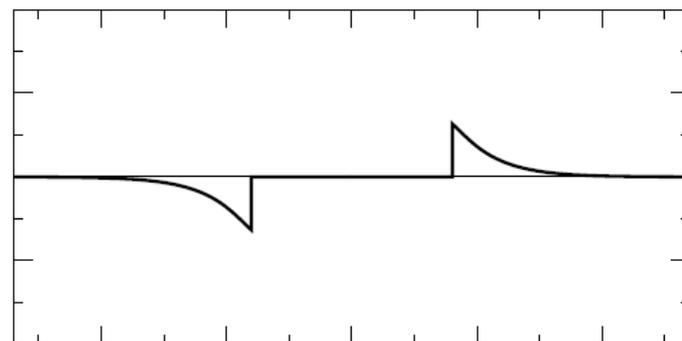
AE = pseudo - pseudo-onsite + AE-onsite



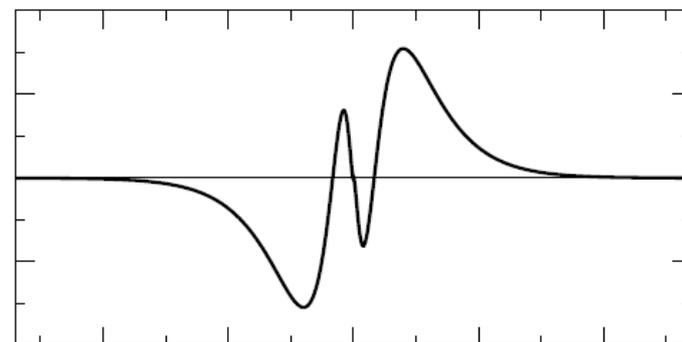
$$|\tilde{\psi}_n\rangle$$



$$|\tilde{\psi}_n\rangle - \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n \rangle$$



$$|\tilde{\psi}_n\rangle - \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n \rangle + \sum_i |\phi_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n \rangle$$



算符变换

- ▶ 对任意局域算符存在对应的赝算符

$$\tilde{A} = A + \sum_{ij} |\tilde{p}_i\rangle \left(\langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j |$$
$$\langle \psi | A | \psi \rangle = \langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$$

- ▶ 电荷密度

$$\begin{aligned} \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle &= \langle \tilde{\psi} | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\psi} \rangle + \sum_{ij} \langle \tilde{\psi} | \tilde{p}_i \rangle \left(\langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle - \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | \tilde{\psi} \rangle \\ &= \tilde{\rho}(\mathbf{r}) - \tilde{\rho}^1(\mathbf{r}) + \rho^1(\mathbf{r}) \end{aligned}$$

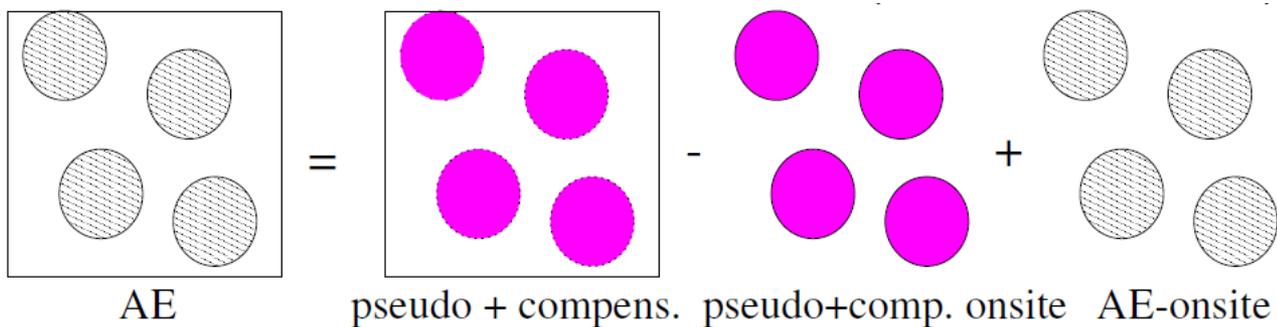
- ▶ 动能

$$\underbrace{\sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2} \Delta | \tilde{\psi}_n \rangle}_{\tilde{E}} - \underbrace{\sum_{\text{site } (i,j)} \sum \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2} \Delta | \tilde{\phi}_j \rangle}_{\tilde{E}^1} + \underbrace{\sum_{\text{site } (i,j)} \sum \rho_{ij} \langle \phi_i | -\frac{1}{2} \Delta | \phi_j \rangle}_{E^1}$$

$$\rho_{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \quad \text{on site density matrix}$$

Hartree能

- ▶ 赝波函数与全电子波函数在球内的模不相等
- ▶ 在处理长程静电相互作用时常引入补偿电荷



- ▶ Hartree能 $E_H = \tilde{E} - \tilde{E}^1 + E^1$

$$E_H[\tilde{\rho} + \hat{\rho}] - \sum_{\text{sites}} E_H[\tilde{\rho}^1 + \hat{\rho}^1] + \sum_{\text{sites}} E_H[\rho^1]$$

单中心赝电荷 单中心补偿电荷



总能

▶ 总能可以写成三项之和 $E = \tilde{E} + E^1 - \tilde{E}^1$

$$\begin{aligned} \tilde{E} = & \sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2} \Delta | \tilde{\psi}_n \rangle + E_{xc}[\tilde{\rho} + \hat{\rho} + \tilde{\rho}_c] + \\ & E_H[\tilde{\rho} + \hat{\rho}] + \int v_H[\tilde{\rho}_{Zc}] (\tilde{\rho}(\mathbf{r}) + \hat{\rho}(\mathbf{r})) d^3\mathbf{r} + U(\mathbf{R}, Z_{\text{ion}}) \end{aligned}$$

$$\begin{aligned} \tilde{E}^1 = & \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \overline{E_{xc}[\tilde{\rho}^1 + \hat{\rho} + \tilde{\rho}_c]} + \right. \\ & \left. \overline{E_H[\tilde{\rho}^1 + \hat{\rho}]} + \int_{\Omega_r} v_H[\tilde{\rho}_{Zc}] (\tilde{\rho}^1(\mathbf{r}) + \hat{\rho}(\mathbf{r})) d^3\mathbf{r} \right\} \end{aligned}$$

$$\begin{aligned} E^1 = & \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2} \Delta | \phi_j \rangle + \overline{E_{xc}[\rho^1 + \rho_c]} + \right. \\ & \left. \overline{E_H[\rho^1]} + \int_{\Omega_r} v_H[\rho_{Zc}] \rho^1(\mathbf{r}) d^3\mathbf{r} \right\} \end{aligned}$$



赝波函数

- 赝波函数是PAW方法的变分变量，可通过如下方程自洽求解

$$\left(-\frac{1}{2}\Delta + \tilde{V}_{\text{eff}} + \sum_{ii} |\tilde{p}_i\rangle (D_{ij} + \dots) \langle \tilde{p}_j| \right) |\tilde{\psi}_n\rangle = \epsilon_n \left(1 + \sum_{ii} |\tilde{p}_i\rangle Q_{ij} \langle \tilde{p}_j| \right) |\tilde{\psi}_n\rangle$$

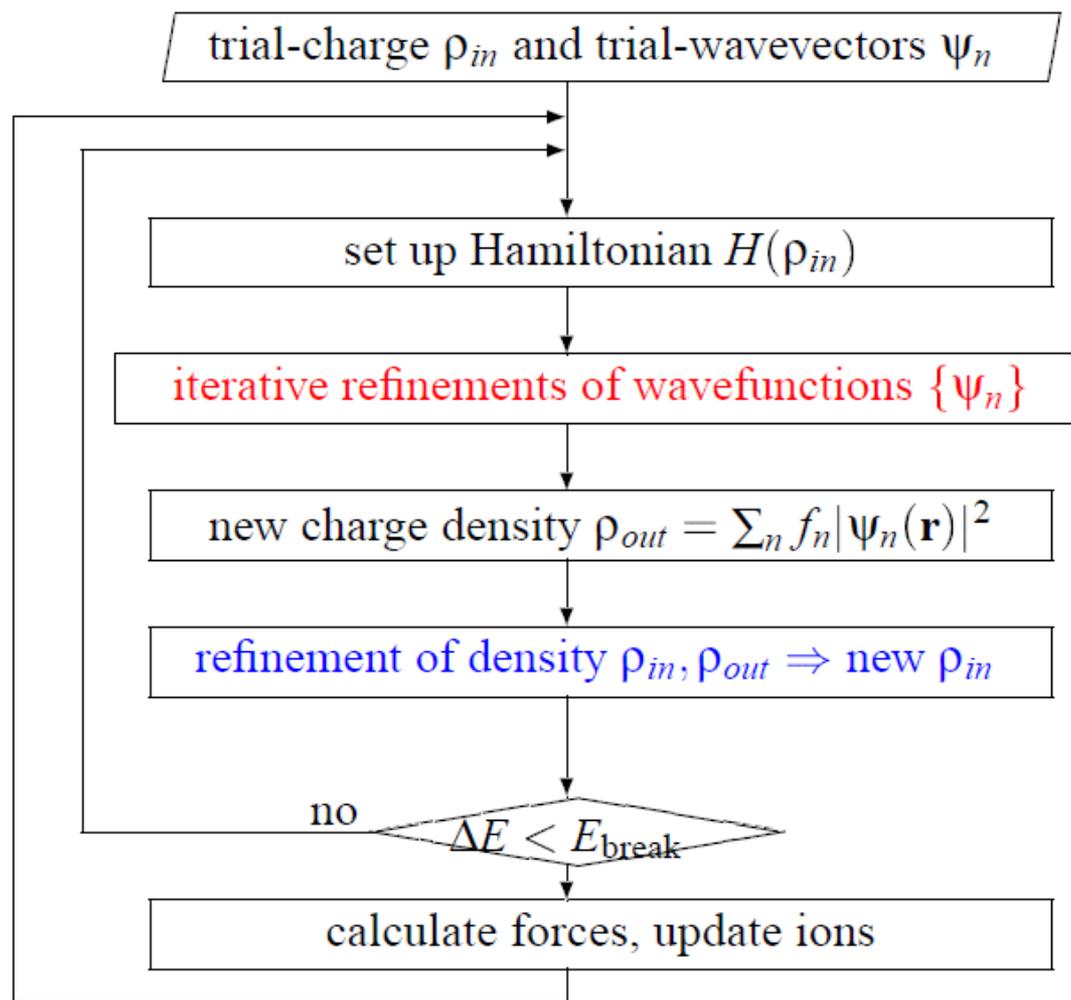
$$D_{ij} = \langle \phi_i | -\frac{1}{2}\Delta + v_{\text{eff}}^1[\rho_v^1] | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}}^1[\tilde{\rho}_v^1] | \tilde{\phi}_j \rangle$$

$$\rho_v^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \quad \tilde{\rho}_v^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle$$

- 如果分波函数在PAW球内形成完备基组，全电子波函数与芯态正交，这正是PAW方法被认为是一种全电子方法的原因

Al	3p 3s 2p 2s 1s	
effective Al	2p 1s	nodeless
PAW Al	3p 3s	with nodal structure

自洽场迭代



- ▶ 两圈循环优化波函数和密度
- ▶ 内层循环优化波函数：CG, DIIS, Davidson 算法
- ▶ 外层循环优化电荷密度：DIIS 算法

多维优化

▶ 最速下降法

$$g = -\frac{\partial F(x)}{\partial x} \Big|_{x=x_i} \quad x_{i+1} = x_i + \alpha^{i+1} g_i$$

▶ 共轭梯度法



$$f(\mathbf{x}) = f(\mathbf{P}) + \sum_i \frac{\partial f}{\partial x_i} x_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 f}{\partial x_i \partial x_j} x_i x_j + \dots$$

$$\approx c - \mathbf{b} \cdot \mathbf{x} + \frac{1}{2} \mathbf{x} \cdot \mathbf{A} \cdot \mathbf{x}$$

$$\nabla f = \mathbf{A}\mathbf{x} - \mathbf{b}; \quad \delta(\nabla f) = \mathbf{A}\delta\mathbf{x}$$

$$\mathbf{u} \cdot [\delta(\nabla f)] = 0 \Rightarrow \mathbf{u} \cdot \mathbf{A} \cdot \mathbf{v} = 0$$

▶ 拟牛顿法

$$f(\mathbf{x} + \delta) = f(\mathbf{x}) + \nabla f(\mathbf{x})\delta + \frac{1}{2} \delta \mathbf{A} \delta$$

$$\nabla f(\mathbf{x} + \delta) = 0 \Rightarrow \delta = -\mathbf{A}^{-1} \nabla f(\mathbf{x})$$

$$\lim H_i \rightarrow \mathbf{A}^{-1} \quad \text{Broyden方法, BFGS}$$

矩阵本征值问题的迭代算法

▶ Krylov子空间方法(Lanczos迭代)

$$\varphi_{n+1} = c_{n+1}(\hat{h}\varphi_n - h_{nn}\varphi_n - h_{n,n-1}\varphi_{n-1}) \quad h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle$$

▶ 残量

$$R[\varphi^{ap}] = (\hat{h} - \varepsilon^{ap} \hat{I}) | \varphi^{ap} \rangle$$

$$\varepsilon^{ap} = \frac{\langle \varphi^{ap} | \hat{h} | \varphi^{ap} \rangle}{\langle \varphi^{ap} | \varphi^{ap} \rangle}$$

▶ 预处理(preconditioning)

$$\begin{aligned} \delta\varphi &= -(\hat{h} - \varepsilon^{ap} \hat{I})^{-1} R[\varphi^{ap}] \\ &= KR[\varphi^{ap}] \end{aligned}$$

- ▶ Teter预处理矩阵：对角矩阵，对大的G矢收敛到动能，对小的G矢趋于一个常量

$$\langle \mathbf{G} | \mathbf{K} | \mathbf{G}' \rangle = \delta_{\mathbf{G}\mathbf{G}'} \frac{27 + 18x + 12x^2 + 8x^3}{27 + 18x + 12x^2 + 8x^3 + 16x^4}$$

$$|p_n\rangle = \mathbf{K} |R_n\rangle.$$

$$x = \frac{\hbar^2}{2m} \frac{G^2}{1.5E^{\text{kin}}(\mathbf{R})},$$

单带优化

▶ 最速下降法

$$g_n = (1 - \sum_{n'} |\phi_{n'}\rangle \langle \phi_{n'} | \mathbf{S} | p_n \rangle).$$

- ▶ 沿残量方向优化本征值等价于一个 2×2 的本征值问题

$$\langle b_i | \mathbf{H} - \epsilon \mathbf{S} | b_j \rangle = 0, \quad b_{i,i=1,2} = \{\phi_n / g_n\}.$$

- ▶ 每个迭代步引入一个新残量，逐步扩大迭代子空间

$$\langle b_i | \mathbf{H} - \epsilon \mathbf{S} | b_j \rangle = 0 \quad b_{i,i=1,N-1} = \{\phi_n / g_n^1 / g_n^2 / g_n^3 / \dots\}.$$

▶ 共轭梯度法

- ▶ 每步引入的新矢量与之前搜索方向共轭
-



多带优化

▶ Davidson迭代

- ▶ 同时考虑n个本征矢，引入n个残量
- ▶ 解 $2n \times 2n$ 本征值问题，取能量最低的n个波函数

▶ 块Davidson方法

- ▶ 在所有带中取一个子集，进行Davidson迭代

$$\{\phi_n | n = 1, \dots, N_{\text{bands}}\} \Rightarrow \{\phi_k^1 | k = 1, \dots, n_1\}$$

$$\left\{ \phi_k^1 / g_k^1 = \left(1 - \sum_{n=1}^{N_{\text{bands}}} |\phi_n\rangle \langle \phi_n | \mathbf{S} \right) \mathbf{K} (\mathbf{H} - \epsilon_{\text{app}} \mathbf{S}) \phi_k^1 \mid k = 1, \dots, n_1 \right\} \quad \{\phi_k^2 | k = 1, n_1\}$$

$$\left\{ \phi_k^2 / g_k^1 / g_k^2 = \left(1 - \sum_{n=1}^{N_{\text{bands}}} |\phi_n\rangle \langle \phi_n | \mathbf{S} \right) \mathbf{K} (\mathbf{H} - \epsilon_{\text{app}} \mathbf{S}) \phi_k^2 \mid k = 1, \dots, n_1 \right\}$$

- ▶ 所有子集收敛以后，进行一个整体的Raleigh Ritz优化

$$\{\phi_k | k = 1, \dots, N_{\text{bands}}\}$$



残量优化方法

▶ RMM-DIIS

- ▶ 不优化本征值，而是优化 $\langle R[\varphi_{n+1}] | R[\varphi_{n+1}] \rangle$,
- ▶ 同样对应一个迭代子空间的本征值问题
- ▶ 因为残量的模对每个本征态都是极小值，所以不需要先对残量做正交归一化
- ▶ 趋向于找到与最初设置相近的极值点，在初值不好的时候会丢掉一些值



布里渊区积分

▶ 电荷密度

$$\rho = \sum_n \int_{BZ} \varphi_{nk}^*(\mathbf{r}) \varphi_{nk}(\mathbf{r}) d\mathbf{r} dk$$

▶ 不失一般性，积分可以离散成加权求和

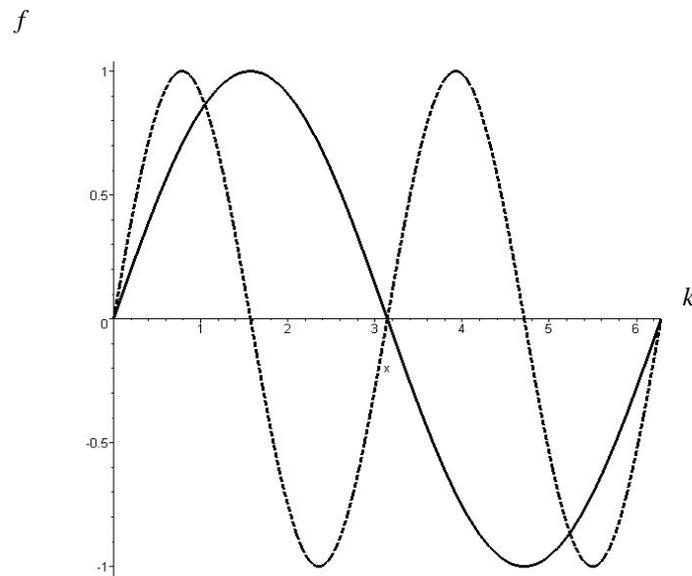
$$\frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \Rightarrow \sum_{\mathbf{k}} w_{\mathbf{k}}$$

▶ 特殊点的选取

$$f_2(k) = A_0 + A_1 \sin(k) + A_2 \sin(2k)$$

$$I = \int_0^{2\pi} f_2(k) dk = A_0$$

$$= f_2\left(k = \frac{\pi}{2}\right) + f_2\left(k = \frac{3\pi}{2}\right)$$

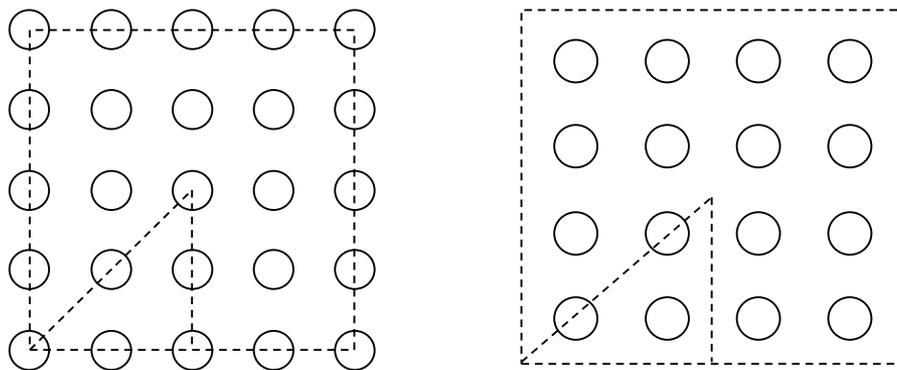


Monkhorst-Pack 取样法

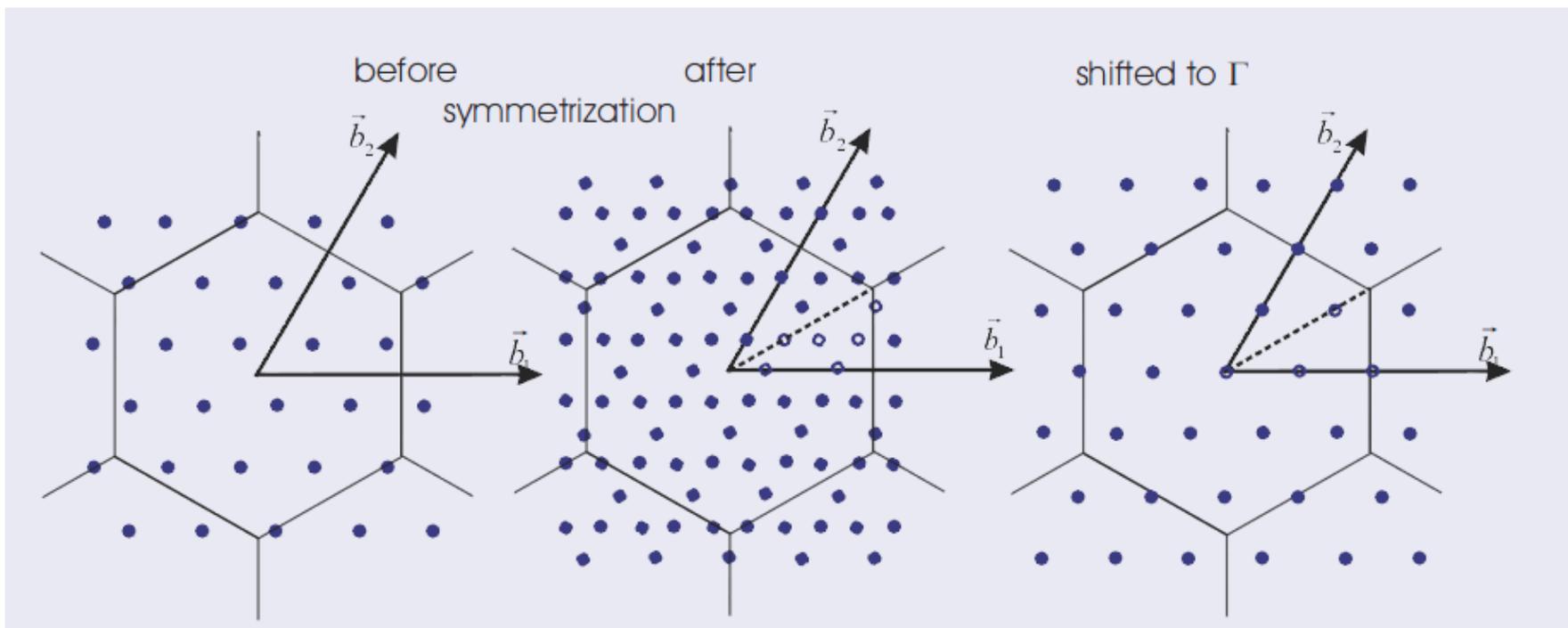
- ▶ 将三维问题转化为三个一维问题
- ▶ 特殊k点的分数坐标

$$u_r = (2r - n_k - 1) / 2n_k \quad r = 1, 2, 3, \dots, n_k$$

- ▶ 对偶数分割不包括原点，以减少计算量



- ▶ 对六角晶格，应该将Gamma点包含在k网格中

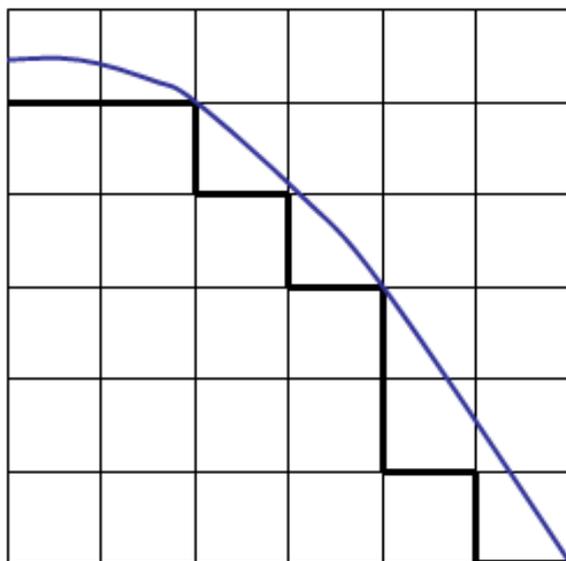


金属与绝缘体

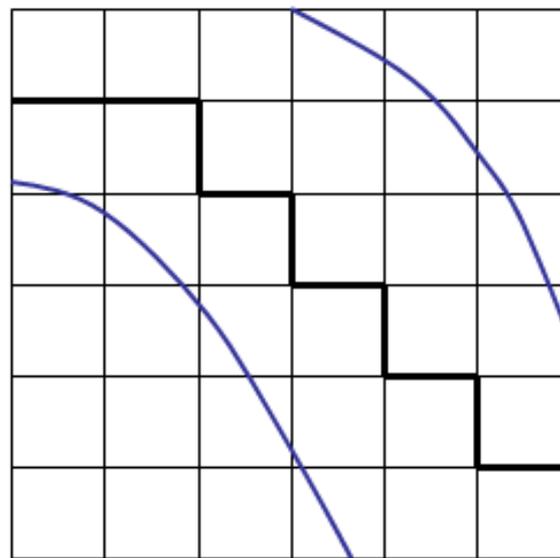
- ▶ 占据数零温下为阶跃函数

$$\sum_n \frac{1}{\Omega_{BZ}} \int_{BZ} \langle \varphi_n(\mathbf{k}) | \hat{X} | \varphi_n(\mathbf{k}) \rangle \theta(\varepsilon_{nk} - \mu) d\mathbf{k}$$

- ▶ 与绝缘体比较，金属需要更密的k点取样



金属



绝缘体

分数占据(SMEAR)

▶ Fermi-Dirac 分布

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_b T}} + 1}$$

- ▶ 能量对分数占据 f 不再满足变分原理
- ▶ 新的变分函数是自由能 F ，包括熵的贡献

$$F = E - \sum_{nk} \omega_k \sigma S(f_{nk})$$

$$S(f) = - [f \ln f + (1 - f) \ln(1 - f)]$$



Gaussian Smearing

- ▶ 将能级展宽成高斯函数，积分可得

$$f(\varepsilon) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{\varepsilon - \mu}{k_B T} \right) \right]$$

- ▶ 熵不能通过f表达， σ 没有物理意义

$$S \left(\frac{\varepsilon - \mu}{\sigma} \right) = \frac{1}{2\sqrt{\pi}} \exp \left[- \left(\frac{\varepsilon - \mu}{\sigma} \right)^2 \right]$$

- ▶ 力通过自由能微分得到，不同于E(0)的力，解决办法：

$$\begin{aligned} F(\sigma) &\approx E(0) + \gamma\sigma^2(1) \\ F(\sigma) &= E(\sigma) - \sigma S(\sigma)(2) \\ S(\sigma) &= -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma\sigma(3) \end{aligned}$$

$$(1) - (3) \rightarrow E(\sigma) \approx E(0) - \gamma\sigma^2(4)$$

$$(1) + (4) \rightarrow E(0) \approx \frac{1}{2} (F(\sigma) + E(\sigma))$$

$$E(T \rightarrow 0) = E_0 = \frac{1}{2} (F + E)$$

Methfessel & Paxton Smearing

- ▶ 将阶梯函数用一组正交函数展开，Gauss是其零阶近似

$$f_N(x) = f_0(x) + \sum_{m=1}^N A_m H_{2m-1}(x) e^{-x^2}$$

- ▶ 能量外推

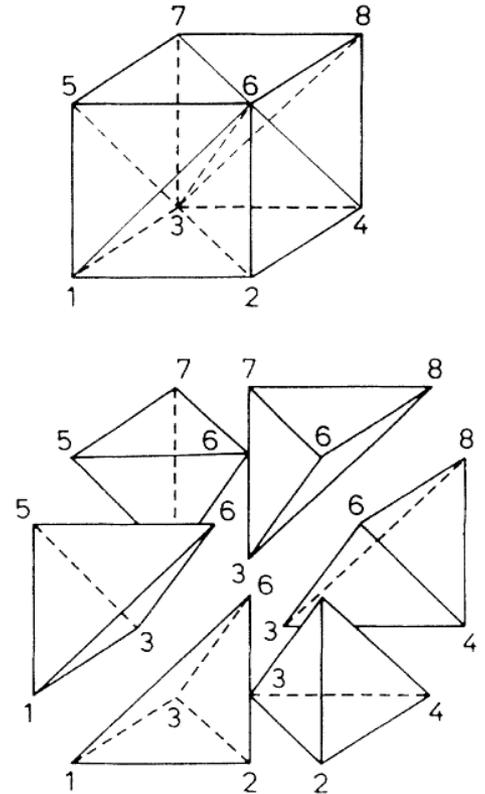
$$E(0) \approx \hat{E}(\sigma) = \frac{1}{N+2} ((N+1)F(\sigma) + E(\sigma))$$

- ▶ 高阶MP方法中F里的熵贡献较小，计算的力更准。
 - ▶ 不适用与半导体/绝缘体，占据数可能大于1
-



Tetrahedron Integration

- ▶ 在由四个k点组成四面体内做线性插值
- ▶ 对金属误差抵消不完全，调整BZ积分时k点的权重 (Blöchl Correction)
- ▶ 对分数占据不满足变分原理
- ▶ best k-point convergence for energy
- ▶ k meshes for tetrahedra BZ-integration have to include Gamma and the k-points at the BZ edges



Mixing

▶ Linear Mixing

$$\begin{aligned} n_{i+1}^{in} &= \alpha n_i^{out} + (1-\alpha)n_i^{in} \\ &= n_i^{in} + \alpha(n_i^{out} - n_i^{in}) \end{aligned} \quad \alpha < \frac{2}{\tilde{\chi}_{\max}^{-1}} = 2\tilde{\chi}_{\min}$$

- ▶ 对束缚很强的刚性系统，可以取较大的，而对于金属表面之类的较软的系统，则比较困难
- ▶ 平面波情形，charge sloshing problem

$$\delta v^{out}(\mathbf{G}) = \sum_{\mathbf{G}'} \varepsilon(\mathbf{G}, \mathbf{G}') \delta v^{in}(\mathbf{G}') \quad \alpha < 1/\varepsilon(\mathbf{G}_{\min})$$

- ▶ Kerker Mixing: 对介电函数做Thomas-Fermi屏蔽近似

$$\varepsilon(|\mathbf{G}|) = \frac{|\mathbf{G}|^2}{|\mathbf{G}|^2 + G_{\max}^2}$$



Broyden Mixing

- ▶ linear mixing可以类比于Quasi-Newton-Raphson迭代
 $\mathbf{x}_{i+1} = \mathbf{x}_i - \mathbf{J}^{-1} \mathbf{R}_i$
- ▶ 采用 $\mathbf{J}_0 = \alpha \mathbf{I}$ 作为初始的Jacobian，通过quasi-Newton弛豫，逐步更新 \mathbf{J}

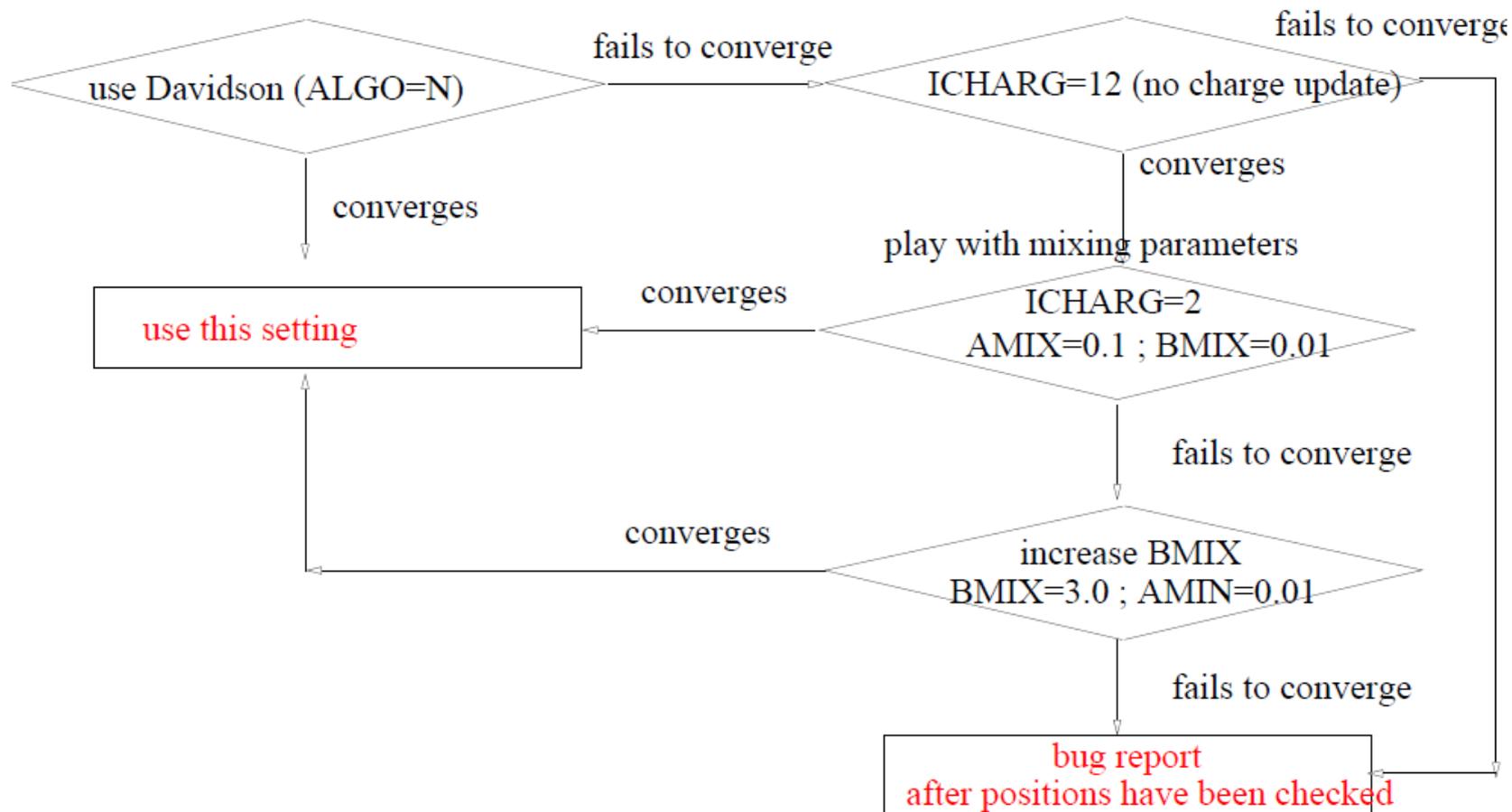


Pulay Mixing

- ▶ RMM-DIIS like
 - ▶ 求几个密度的线性组合系数
 - ▶ Minimize the normal of the residue vector subject to the constraint of conserving the number of electron (DIIS like)



If SCF Convergence Fails



能量泛函

▶ KS能量泛函

$$E_{KS} = T_S[n] + E_{pot}[n]$$

$$E_{pot} = \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r}) + E_H[n] + E_{XC}[n] \quad T_S[n] = E_S - \int d\mathbf{r} v^{in}(\mathbf{r})n^{out}(\mathbf{r}) \quad E_S = \sum_i^N \varepsilon_i$$

▶ 有效势泛函

$$E_{KS}[v^{in}] = E_S[v^{in}] - \int d\mathbf{r} v^{in}(\mathbf{r})n^{out}(\mathbf{r}) + E_{pot}[n^{out}]$$

▶ Harris-Foulkes泛函

$$E_{HF}[n^{in}] = E_S[v_{n^{in}}] - \int d\mathbf{r} v_{n^{in}}(\mathbf{r})n^{in}(\mathbf{r}) + E_{pot}[n^{in}]$$

- ▶ 主要用在非自洽计算时的能量估计，无需计算 n^{out}



几何优化

- ▶ 数学上等价于寻找函数最小值

$$f(\vec{x}) = a + \vec{b}\vec{x} + \frac{1}{2}\vec{x}\mathbf{B}\vec{x} = \bar{a} + \frac{1}{2}(\vec{x} - \vec{x}^0)\mathbf{B}(\vec{x} - \vec{x}^0) \quad \mathbf{B}_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

- ▶ 梯度

$$\vec{g}(\vec{x}) = \frac{\partial f}{\partial \vec{x}} = \mathbf{B}(\vec{x} - \vec{x}^0)$$

- ▶ 牛顿法

$$\vec{x} = \vec{x}^1 - \mathbf{B}^{-1}\vec{g}(\vec{x}^1)$$

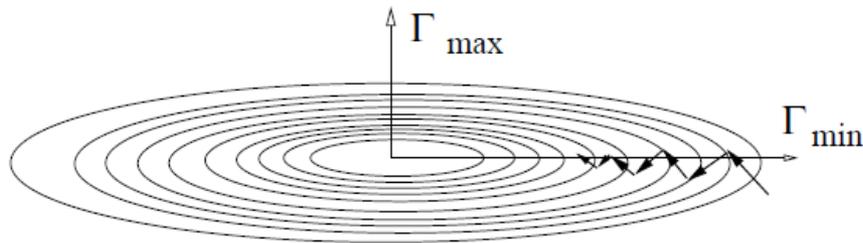


最速下降法

- ▶ the highest frequency mode determines the maximum stable step-width, but the soft modes converge slowest

- ▶ Number of iterations

$$k \propto \frac{\Gamma_{\max}}{\Gamma_{\min}}$$



Steepest Descent Algorithm

- 1 guess \vec{x}^1
- 2 calculate $\vec{g}(\vec{x}^1)$
- 3 step along the steepest descent direction
$$\vec{x}^2 = \vec{x}^1 - \frac{1}{\Gamma_{\max}} \vec{g}(\vec{x}^1)$$
- 4 repeat 2+3 \rightarrow converged geometry

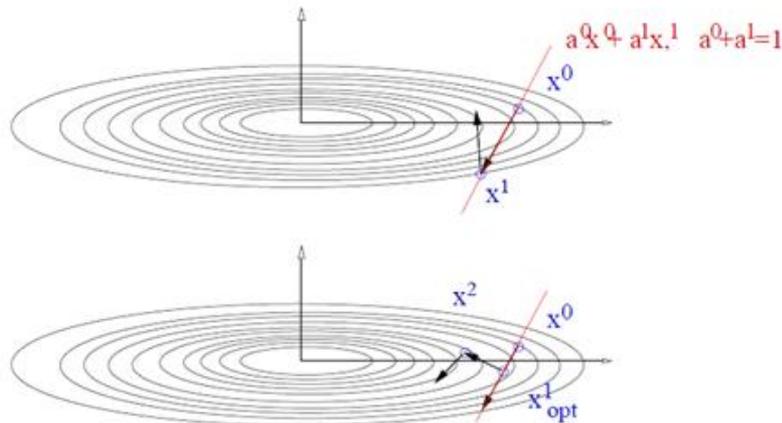
DIIS

- ▶ gradient is linear in it's arguments for a quadratic function

$$\begin{aligned} \vec{g}\left(\sum_i \alpha^i \vec{x}^i\right) &= \mathbf{B} \left(\sum_i \alpha^i \vec{x}^i - \vec{x}^0 \right) = \mathbf{B} \left(\sum_i \alpha^i \vec{x}^i - \sum_i \alpha^i \vec{x}^0 \right) \\ &= \sum_i \alpha_i \mathbf{B}(\vec{x}^i - \vec{x}^0) = \sum_i \alpha_i \vec{g}^i. \end{aligned}$$

- ▶ Number of interations
- ▶ POTIM, NFREE

$$\propto \sqrt{\frac{\Gamma_{\max}}{\Gamma_{\min}}}$$

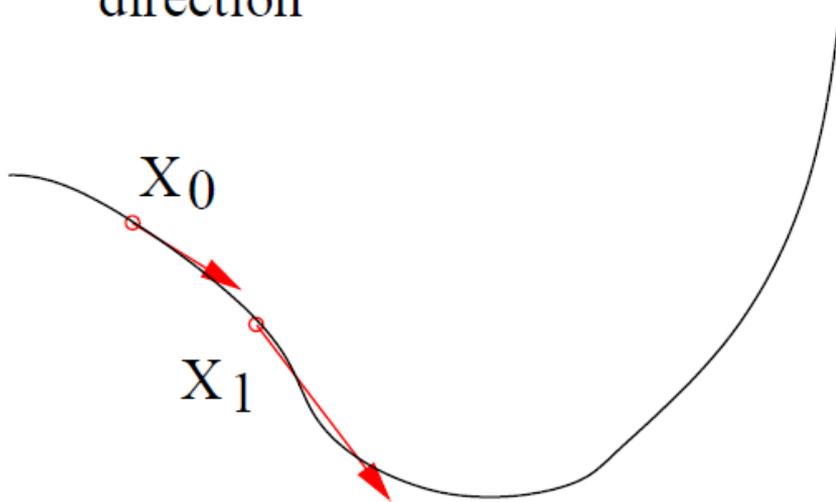


full DIIS

- steepest descent step (sds)
- opt. position \vec{x}_{opt}^1
- sds from \vec{x}_{opt}^1 along $\vec{g}_{\text{opt}} \rightarrow \vec{x}^2$
- $\rightarrow \vec{g}(\vec{x}^2)$
- linearity \rightarrow gradient is known in 2D
- minimize f exactly

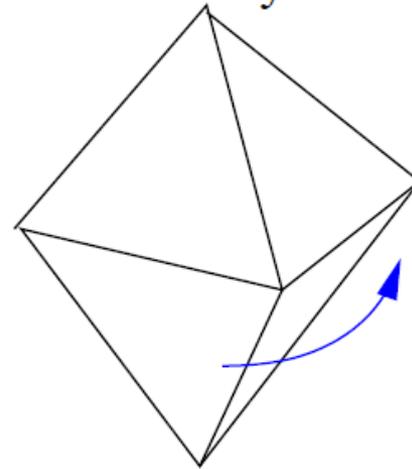
Trouble Cases for DIIS

force increases along the search direction



DIIS is dead, since it considers the forces only
it will move uphill instead of down

rigid unit modes i.e. in perovskites (rotation)
molecular systems (rotation)

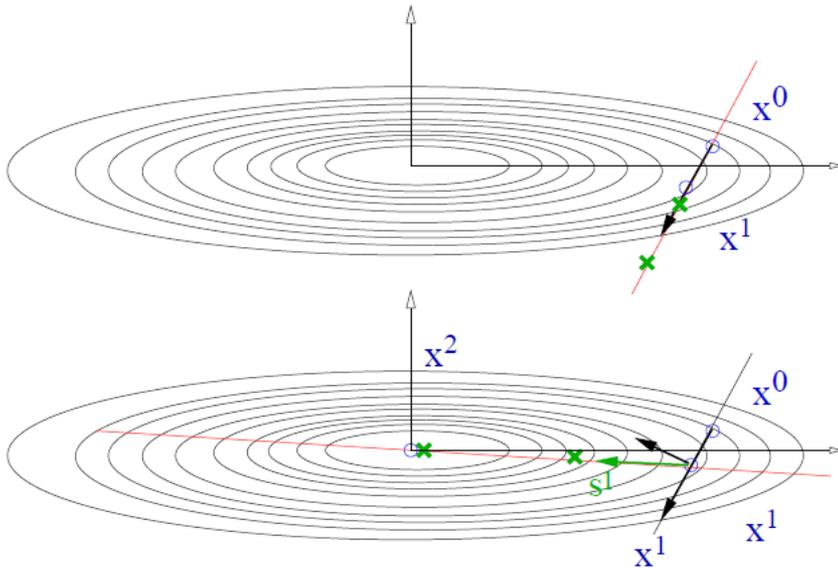


in cartesian coordinates the Hessian matrix changes when the octahedron rotates!



CG

- ▶ line minimisations is done using a variant of Brent algorithm
- ▶ POTIM



The CG Algorithm

- sds from \vec{x}^0 along \vec{g}^0
- trial step(s) x ,
 $N_x \geq 1$), $\longrightarrow \vec{x}^1$
- \longrightarrow new $\vec{g}^1 = \vec{g}(\vec{x}^1)$
- conjugate $\vec{g}^1 : \longrightarrow, \vec{s}^1$
- \vec{s}^1 points directly towards the minimum
- minimization along \vec{s}^1

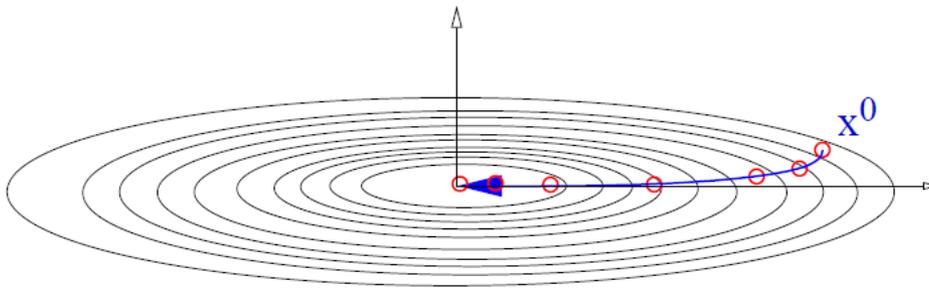
Damped MD

- ▶ equation of motion

$$\ddot{\vec{x}} = -2 * \alpha \vec{g}(\vec{x}) - \mu \dot{\vec{x}}$$

- ▶ α (POTIM) must be as large as possible, but without leading to divergence
- ▶ SMASS must be set to

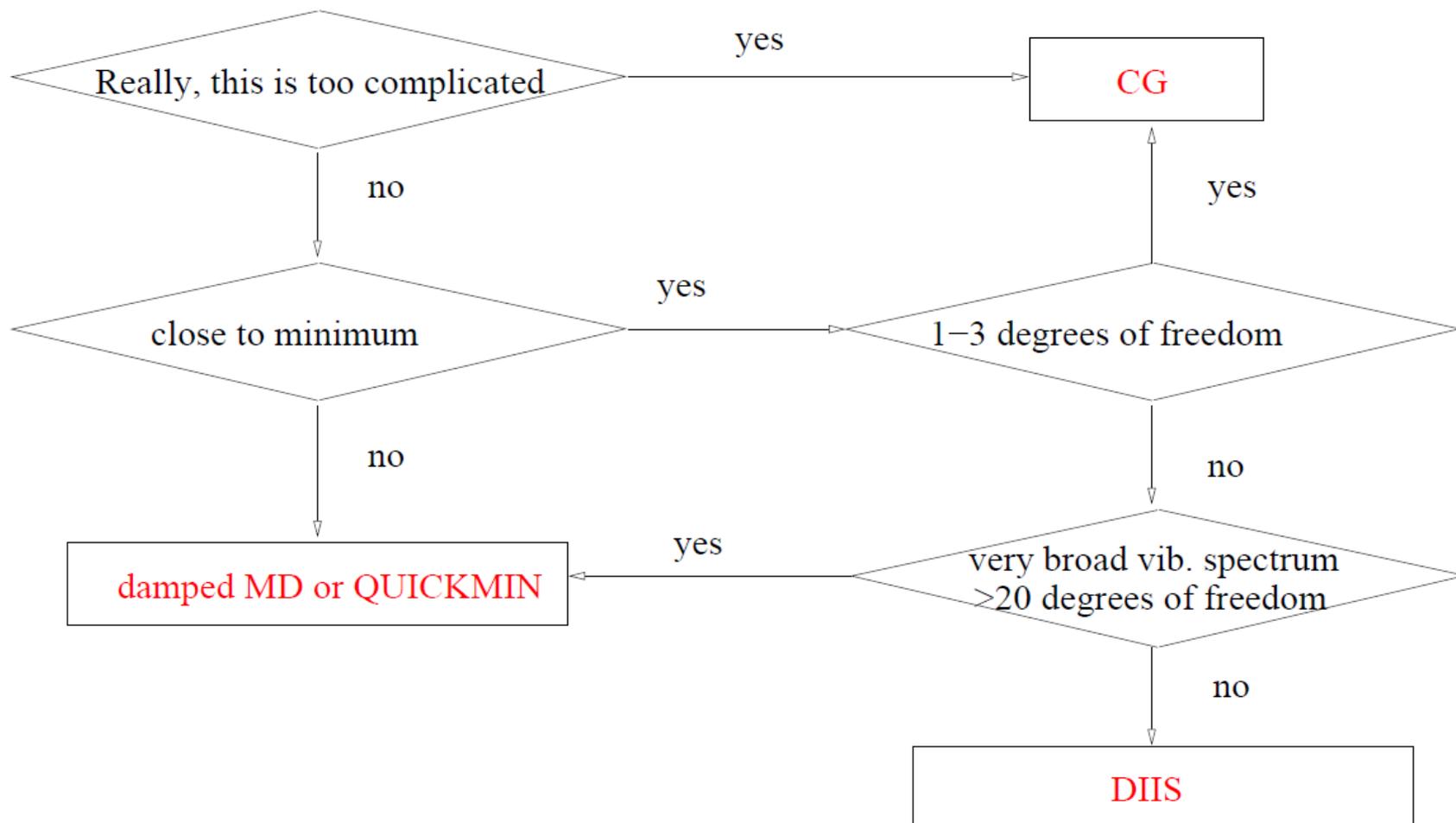
$$\mu \approx 2 \sqrt{\Gamma_{\min} / \Gamma_{\max}}$$



Damped MD (MD)

- “rolling ball” with friction (μ)
- μ too small: minimum overshoot, back-acceleration
- μ too large: relaxation slows down (like SD)

几何优化算法选择



上机实践

- ▶ 石墨烯能量收敛测试
 - ▶ K sampling
 - ▶ Ecut
 - ▶ Real space grid
- ▶ 测试mixing参数对石墨烯SCF收敛的影响

