中国科学技术大学本科生课程

应用量子化学(H)
Applied Quantum Chemistry

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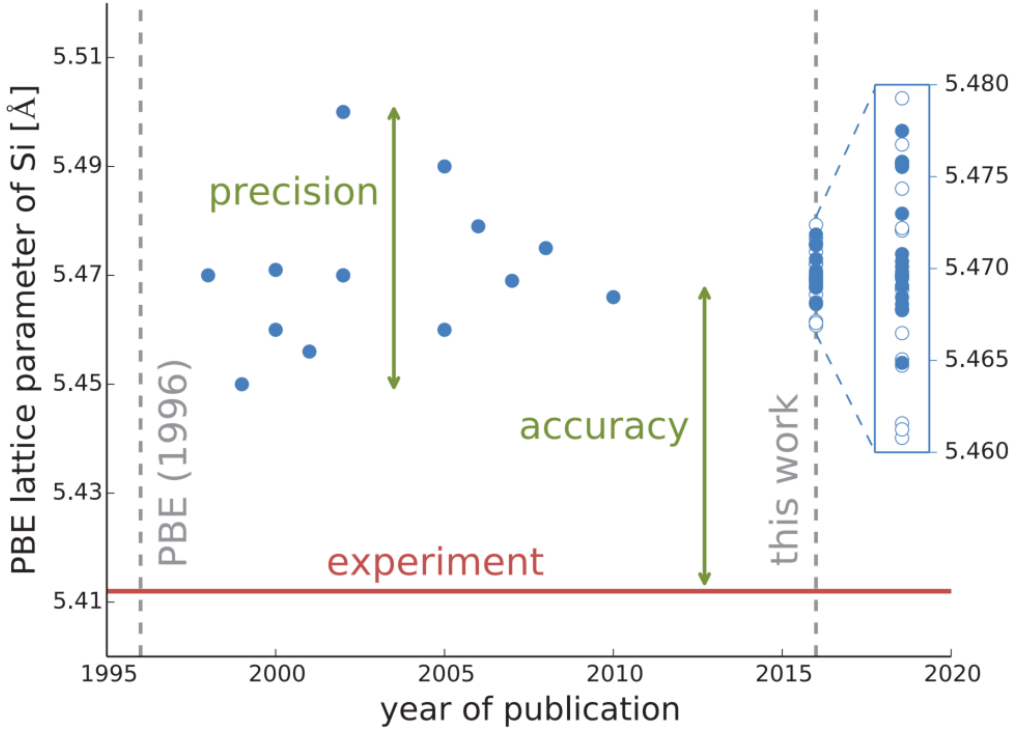
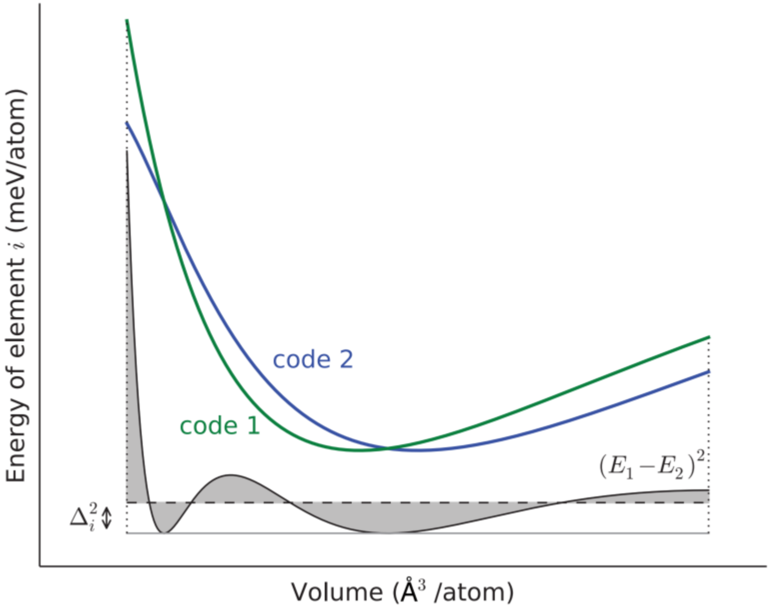
2022年春季学期

第四章 数值方法

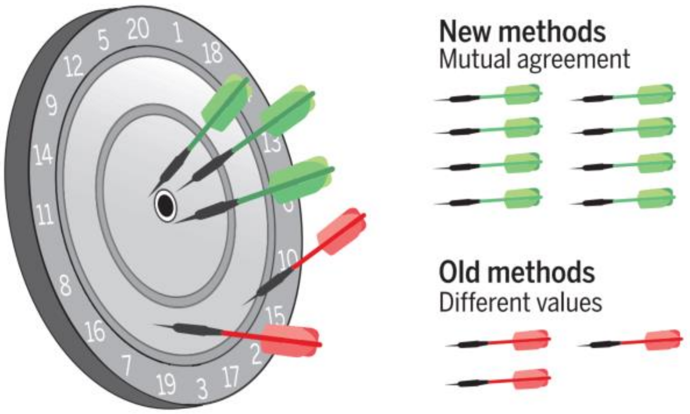
计算结果可重复性



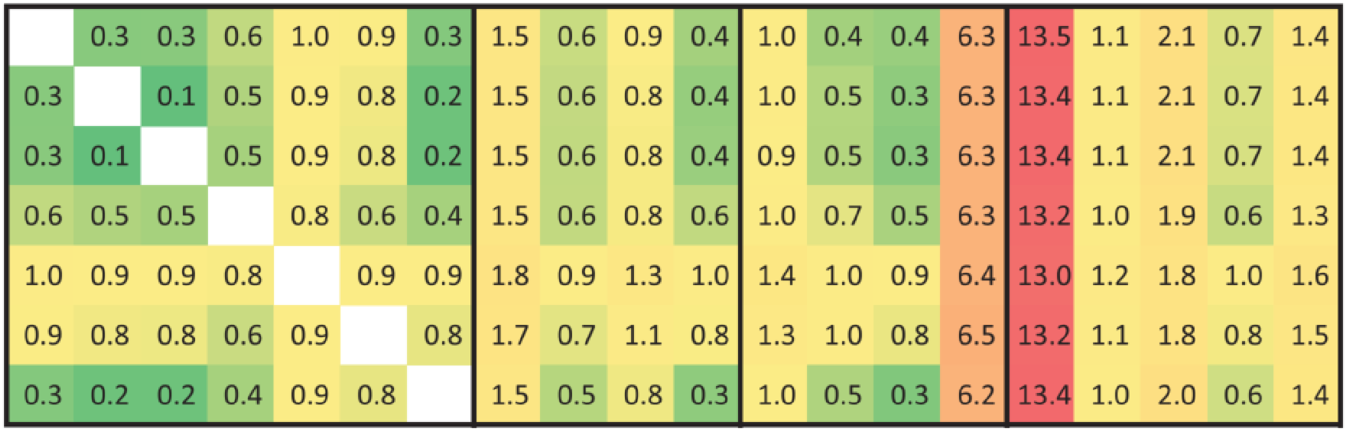


Science 351, 1415 (2016)

计算结果可重复性



Scorecard



	0.3	0.3	0.6	1.0	0.9	0.3	1.5	0.6	0.9	0.4	1.0	0.4	0.4	6.3	13.5	1.1	2.1	0.7	1.4
0.3		0.1	0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	1.0	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.3	0.1		0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	0.9	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.6	0.5	0.5		0.8	0.6	0.4	1.5	0.6	0.8	0.6	1.0	0.7	0.5	6.3	13.2	1.0	1.9	0.6	1.3
1.0	0.9	0.9	0.8		0.9	0.9	1.8	0.9	1.3	1.0	1.4	1.0	0.9	6.4	13.0	1.2	1.8	1.0	1.6
0.9	0.8	0.8	0.6	0.9		0.8	1.7	0.7	1.1	0.8	1.3	1.0	0.8	6.5	13.2	1.1	1.8	0.8	1.5
0.3	0.2	0.2	0.4	0.9	0.8		1.5	0.5	0.8	0.3	1.0	0.5	0.3	6.2	13.4	1.0	2.0	0.6	1.4

Science 351, 1415 (2016)

主要内容

- 原子基组
- 平面波基组
- 赝势方法
- 自洽场方法

数值离散

可以通过划分实空间网格来离散薛定谔/HF/KS方程。

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

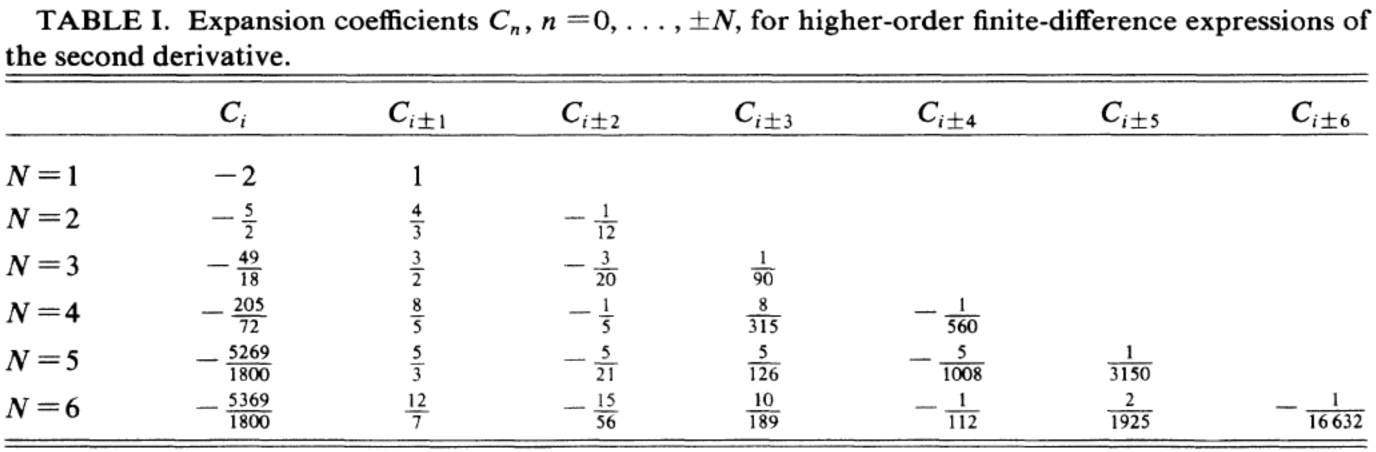


TABLE I. Expansion coefficients C_n, $n=0,\dots,\pm N$, for higher-order finite-difference expressions of the second derivative.

	C_i	$C_{i\pm1}$	$C_{i\pm2}$	$C_{i\pm3}$	$C_{i\pm4}$	$C_{i\pm5}$	$C_{i\pm6}$
$N=1$	-2	1					
$N=2$	$-\frac{5}{2}$	$\frac{4}{3}$	$-\frac{1}{12}$				
$N=3$	$-\frac{49}{18}$	$\frac{3}{2}$	$-\frac{3}{20}$	$\frac{1}{90}$			
$N=4$	$-\frac{205}{72}$	$\frac{8}{5}$	$-\frac{1}{5}$	$\frac{8}{315}$	$-\frac{1}{560}$		
$N=5$	$-\frac{5269}{1800}$	$\frac{5}{3}$	$-\frac{5}{21}$	$\frac{5}{126}$	$-\frac{5}{1008}$	$\frac{1}{3150}$	
$N=6$	$-\frac{5369}{1800}$	$\frac{12}{7}$	$-\frac{15}{56}$	$\frac{10}{189}$	$-\frac{1}{112}$	$\frac{2}{1925}$	$-\frac{1}{16632}$

* 适应网格

使用实空间网格需要显式的确定边界条件。

边界条件

*固定(fixed/close)边界条件

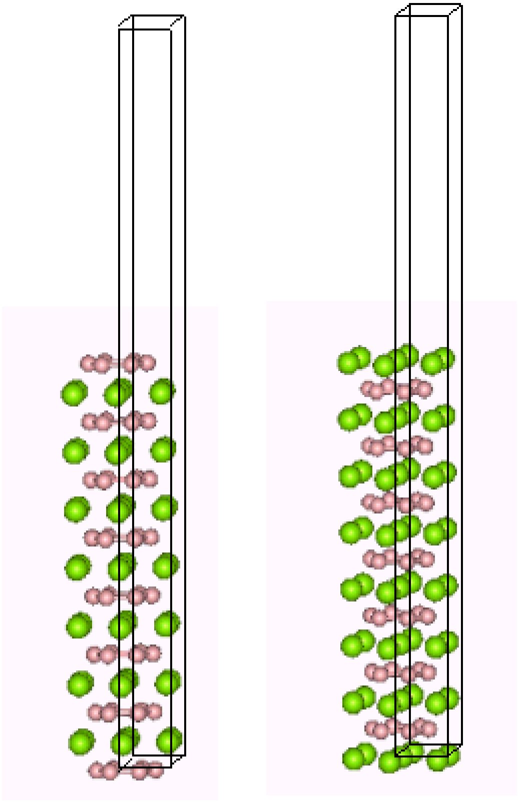
$$y(x_0,t) = 0$$

*自由(free/open)边界条件

$$\frac{\partial y(x_0,t)}{x} = 0$$

*周期性边界条件

*超胞模型：0维、1维、2维和表面体系



*边界条件可以隐式的由基组函数确定

§ 4.1 原子基组

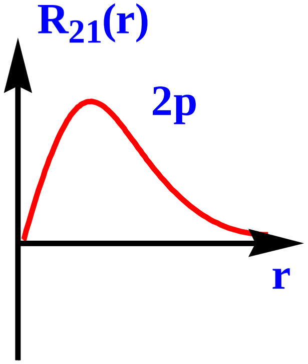
一、 Slater型轨道函数与Gaussian 型轨道函数

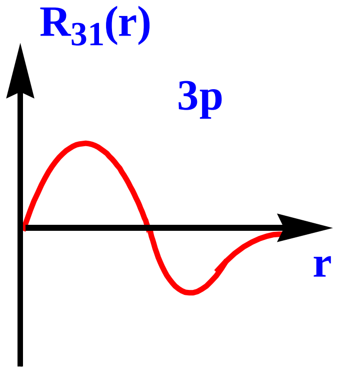
$$\varphi_i = \sum_{\nu=1}^{m} C_{\nu i}\chi_\nu \qquad \{\chi_\nu\}$$：基函数

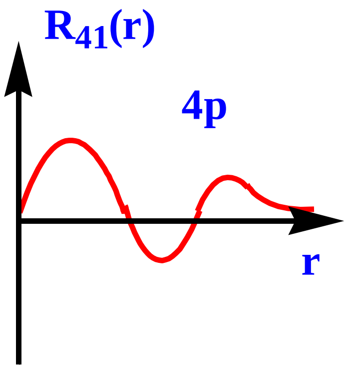
类氢轨道：$\chi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)$

$$R_{n\ell}(r) = N_{n\ell}\, e^{-\frac{Zr}{n}} \left(\frac{2Z}{n} r\right)^{\ell} L_{n+\ell}^{2\ell+1}\left(\frac{2Z}{n} r\right)$$ （核位于坐标原点）

$$R_{nl}(r) \sim r^{l}(a_0 + a_1 r + \cdots + a_{n-l-1} r^{n-l-1})e^{-\zeta\ r}$$







正交性：

- 不同，波函数角度部分保证；
- 相同，多项式。

Slater型轨道 (STO)

$$\chi_{nlm}(\vec{r}) = R_n(r,\zeta)Y_{lm}(\theta,\varphi)$$

$$R_n(r,\zeta) = N_{n\zeta}\, r^{n-1} e^{-\zeta r}$$

$$N_{n\zeta} = \frac{(2\zeta)^{(2n+1)/2}}{\sqrt{(2n)!}}$$

* ζ ---*orbital* exponents, $\sim n, l$

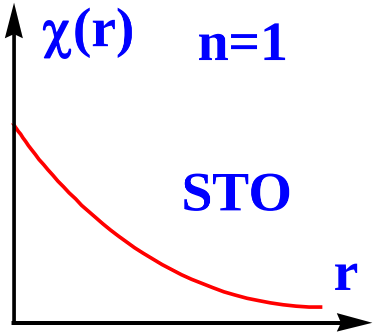
* 轨道指数(orbital exponents)为正值，反映原子轨道的弥散程度(空间分布的大小)。轨道指数越小，轨道越弥散。可通过对原子做变分法或SCF计算得到。

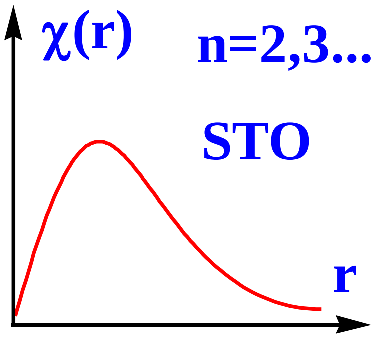
$$\chi_{1s}(\vec{r}) = (\zeta/\pi)^{1/2} e^{-\zeta r}$$

$$\chi_{2s}(\vec{r}) = (\zeta^5/3\pi)^{1/2} r e^{-\zeta r}$$

$$\chi_{2px}(\vec{r}) = (\zeta^5/\pi)^{1/2} x e^{-\zeta r}$$

$$\chi_{3s}(\vec{r}) = (\zeta^7/45\pi)^{1/2} r^2 e^{-\zeta r}$$





Slater型轨道 (STO)

* 直角坐标系下： $\chi_{abc} = N_{abc} x^a y^b z^c e^{-\zeta\ r}$

例如： $p_x:\ a = 1,\ b = c = 0$

$d_{xy}:\ a = b = 1,\ c = 0$

* 如若核位于 $\vec{R}_A$ 处，则公式中的坐标变量替换为：

$$x \to x - X_A,\quad y \to y - Y_A,\ z \to z - Z_A$$

$$r \to \left|\vec{r} - \vec{R}_A\right|$$

* 完备STO的线性组合可以得到类氢原子轨道；r→0时(核附近)有正确的渐进行为(尖点条件)。

* STO的问题：计算双电子多中心积分困难(没有解析表达式)。

$$(\mu\nu|\lambda\sigma) = \int d\vec{r}_1\, d\vec{r}_2\, \chi_\mu^*(\vec{r}_{A1})\chi_\nu(\vec{r}_{B1}) r_{12}^{-1} \chi_\lambda^*(\vec{r}_{C2})\chi_\sigma(\vec{r}_{D1})$$

Gaussian型函数 (GTO)

$$\chi_{nlm} = R_n(r,\alpha)Y_{lm}(\theta,\varphi)$$

$$R_n(r,\alpha) = N_{n\alpha}\, r^{n-1} e^{-\alpha\ r^2}$$

* $\alpha --- orbital$ exponents, $\sim n,l$

* 直角坐标系下(核位于坐标原点)：

$$\chi_{pqt} = N_{pqt} x^p y^q z^t e^{-\alpha\ r^2}$$

$$N_{pqt} = \left[\frac{(8\alpha)^{p+q+t}\ p!q!t!}{(2p)!(2q)!(2t)!}\right]^{1/2} \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

例如： p_x ： $p=1,\ q=t=0$ ； d_{xy} ： $p=q=1,\ t=0$

S. F. Boys, Proc. Roy. Soc. A200, 42 (1950)

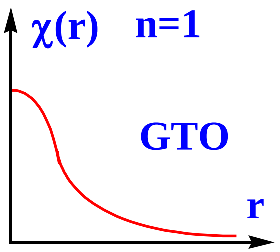
Gaussian型函数 (GTO)

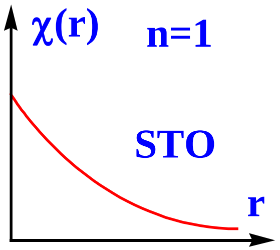
因为$x^2+y^2+z^2$是球形的，六个d轨道可以表示成5个正则d轨道：xy, yz, xz, x^2-y^2, $3z^2-r^2$

	i	**j**	**k**			**i**	**j**	**k**	
Σ=0	0	0	0	s	Σ=2	1	1	0	d_{xy}
Σ=1	1	0	0	p_x		1	0	1	d_{xz}
	0	1	0	P_y		0	1	1	d_{yz}
	0	0	1	p_z		2	0	0	d_{x2}
						0	2	0	d_{y2}
						0	0	2	d_{z2}

* 单个GTO描写原子轨道精度较差。(核附近的渐进行为不正确)

例：H原子，能量差~15%



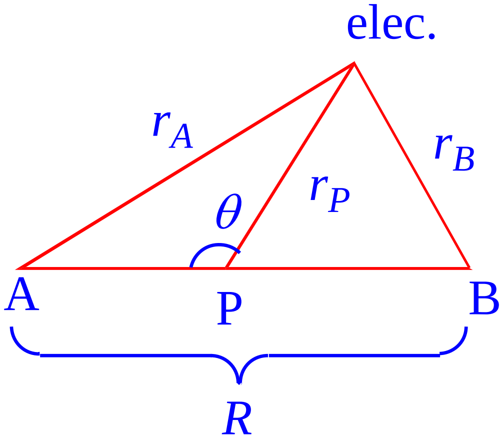


Gaussian型函数 (GTO)

* GTO的优点：三维积分化为一维积分，多中心积分化为单中心积分。

GTO的乘积定理：

$$e^{-ar_A^2}e^{-br_B^2} = Ke^{-(a+b)r_P^2}$$



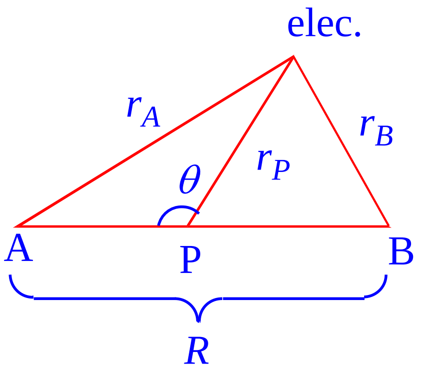
其中：

$$\begin{cases} K = e^{-\frac{ab}{a+b}R^2} \\ \overline{AP} = \dfrac{b}{a+b}R, \quad \overline{BP} = \dfrac{a}{a+b}R \end{cases}$$

从而，两个中心不同的Gaussian函数的乘积可以合并为一个新的Gaussian函数(两个中心浮动到一个新中心)。

Gaussian型函数 (GTO)

证明： 令： $\overline{AP}=\frac{b}{a+b}R,\quad \overline{BP}=\frac{a}{a+b}R$



由余弦定理： $r_A^2=r_P^2+\overline{AP}^2-2\cdot\overline{AP}r_P\cos\theta$

可得： $$\overline{BP}\,r_A^2=\overline{BP}(r_P^2+\overline{AP}^2-2\cdot\overline{AP}\cdot r_P\cos\theta)$$

同理： $$\overline{AP}\,r_B^2=\overline{AP}(r_P^2+\overline{BP}^2+2\cdot\overline{BP}\cdot r_P\cos\theta)$$

$$\overline{BP}\,r_A^2+\overline{AP}\,r_B^2=(\overline{AP}+\overline{BP})\cdot r_P^2+\overline{BP}\cdot\overline{AP}^2+\overline{AP}\cdot\overline{BP}^2$$

$$=R\cdot r_P^2+\overline{BP}\cdot\overline{AP}\cdot R$$

$$\frac{a}{a+b}R\cdot r_A^2+\frac{b}{a+b}R\cdot r_B^2=R\cdot r_P^2+R^3\cdot\frac{ab}{(a+b)^2}$$

Gaussian型函数 (GTO)

$$\frac{a}{a+b}R\cdot r_A^2+\frac{b}{a+b}R\cdot r_B^2=R\cdot r_P^2+R^3\cdot\frac{ab}{(a+b)^2}$$

两边同时 $\times\dfrac{a+b}{R}$

$$a\cdot r_A^2+b\cdot r_B^2=(a+b)\cdot r_P^2+R^2\cdot\frac{ab}{a+b}$$

取指数：

$$e^{-ar_A^2}e^{-br_B^2}=e^{-(a+b)r_P^2}\cdot e^{-\frac{ab}{a+b}\cdot R^2}$$

故：

$$e^{-ar_A^2}e^{-br_B^2}=Ke^{-(a+b)r_P^2}$$

$$K=e^{-\frac{ab}{a+b}\cdot R^2}$$

收缩的Gaussian函数 (STO-*n*G)

单个Gaussian 型函数用于描写原子轨道结果很差。实际计算一般用几个Gaussian 型函数(primitives)逼近(收缩到)一个原子轨道。

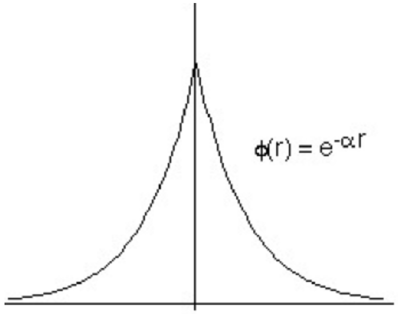
$$\chi_{\mu}^{CGF}\left(\vec{r}-\vec{R}_A\right)=\sum_{p=1}^{L} d_{p\mu}\, g_p\left(\alpha_{p\mu},\vec{r}-\vec{R}_A\right)$$

式中：$d_{p\mu}$ 为收缩系数，L为收缩长度，

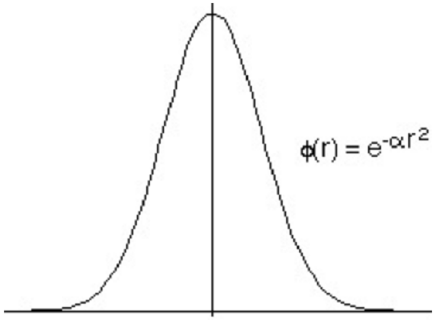
$g_p\left(\alpha_{p\mu},\vec{r}-\vec{R}_A\right)$ 为第 p 个归一化的Gaussian基函数，轨道指数为$\alpha_{p\mu}$，轨道中心为R_A

可以选择cGF 逼近Slater轨道或Hartree-Fock原子轨道。

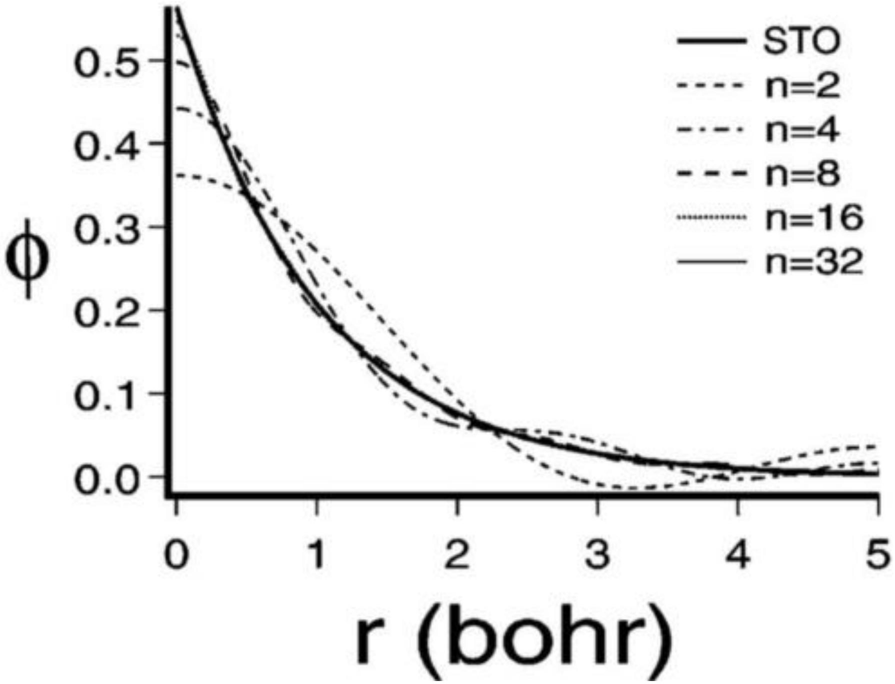
收缩的Gaussian函数 (STO-*n*G)



Slater-type 1s orbital



Gaussian-type 1s orbital



常用高斯基组

1、 最小基组(STO-*n*G)

对于原子内层和价层的每一个AO，使用一个STO。因此，对氧是5个基函数(2s1p)。用*n*个Gaussian原函数的组合表示STO，其中收缩系数和轨道指数的选择使其逼近一个Slater函数。例：STO-3G, STO-4G, STO-6G

2、 双 Zeta(DZ)基

每个AO用两个轨道指数(Zeta)不同的基函数表示.对C2H2分子，碳需要两个1s STO，两个2s STO，两个2px，两个2py，两个2pz。氢需要两个1s。记为(4s2p/2s)。同理有三zeta(TZ)等基组

W.J. Hehre, R.F. Stewart, J.A. Pople, J. Chem. Phys. **51**, 2657 (1969)

常用高斯基组

3、分裂价(SV)基

内层轨道用一个基函数表示，价层轨道两个(或三个)指数(Zeta)不同的基函数表示，分别称为VDZ和VTZ.

如：6-31G: 内层AO用一个基函数(STO-6G)，价层AO用两个基 (STO-3G和STO-1G)

4、极化基

W.J. Hehre, R.F. Stewart, J.A. Pople, J. Chem. Phys. **51**, 2657 (1969)

常用高斯基组

6-31G(d) (也写作 6-31G*)：对Li-Ca添加一组直角坐标d高斯函数(6个)，对Sc-Zn添加一组直角坐标f高斯函数(10个)。

6-31G(d,p) (也写作6-31G**)：在6-31G*的基础上对氢和He原子添加一组p高斯函数(3个)。

6-311G(3df,3pd) 在非氢原子上加的三组d函数(15个)和一组f函数(7个)，在氢原子上加的三组p函数(9个)和一组d函数(5个)。

* 增加极化函数的目的是为了反映原子结合成分子后，轨道(或电子云)的变形(角度的可调性)。

常用高斯基组

5、 弥散基

为了反映负离子或高激发态下电子可以出现在离原子较远的位置，有时在计算中要增增加“弥散函数”(额外增加的、轨道指数较小的函数)。

6-31+G 对非氢原子添加四个弥散函数，s和px, py, pz

6-31++G 除了非氢元素以外，对氢元素也添加一个弥散s函数

应用：含有孤对电子的体系，阴离子(Anion)，以及其他带有明显负电荷的体系，激发态体系(excited state)，含有低的离子化能的体系，以及纯酸的体系，计算极化等。

有时候，如研究电子阴离子化合物，需要增加鬼原子或平面波

其他原子基组

* Dunning's correlation consistent basis sets (相关一致基组):

cc-pVDZ：价层双分裂，大致相当于6-31G**，因为二者对H都是[2s1p]对第一周期元素都是[3s2p1d]。

cc-pVTZ：价层三分裂，非氢原子加2个d函数和1个f函数, 氢原子加2个p函数和1个d函数；

从cc-pvDZ到cc-pvTZ，除了每个AO用到的cGF增加一组外，还要增加一组更高角动量的基函数。

从低级别到高级别基组增加的函数是对关联能贡献大小相当的，因此叫cc基组。

其他原子基组

aug-cc-pVTZ: one set of diffuse function for each angular momentum. 在通常的体系中，对H增加弥散函数意义不大，如果在aug-基础上去掉H的弥散函数，称为jul-基组。进一步去掉其他弥散函数可以得到jun-,may-,apr-基组。例如，aug-cc-pVTZ对碳原子有s,p,d,f弥散函数。如果去掉碳的f弥散函数，去掉H的所有弥散函数，就得到jun-cc-pVTZ基组。

* 赝势基组

赝势法：对重原子只处理价层和次价层，核和内层电子的作用用一个有效静电势代替(相对论效应可合并进去)。

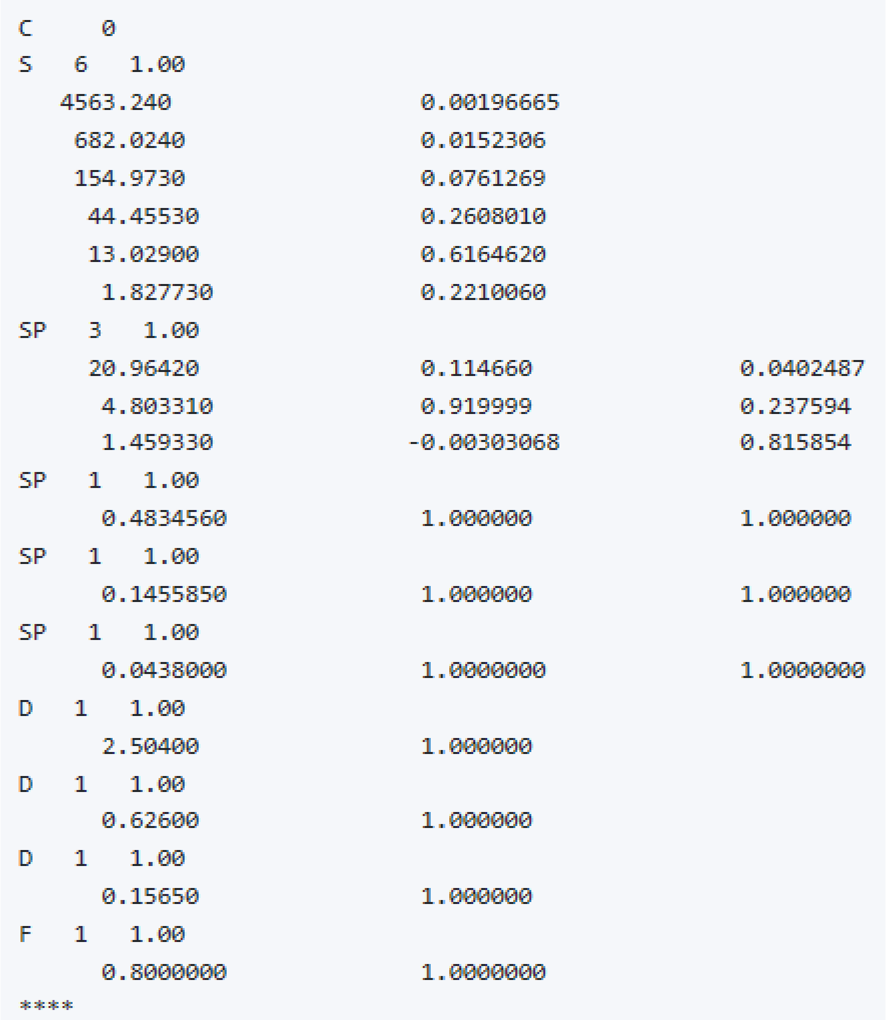
lanl2mb：相当于最小基(较少用)；

lanl2dz：相当于价层双分裂(常用)。

Basis Set Exchange数据库

https://www.basissetexchange.org/

6-311++G(3df,3pd)



```
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S   6   1.00
   4563.240               0.00196665
    682.0240              0.0152306
    154.9730              0.0761269
     44.45530             0.2608010
     13.02900             0.6164620
      1.827730            0.2210060
SP   3   1.00
     20.96420             0.114660               0.0402487
      4.803310            0.919999               0.237594
      1.459330           -0.00303068             0.815854
SP   1   1.00
      0.4834560           1.000000               1.000000
SP   1   1.00
      0.1455850           1.000000               1.000000
SP   1   1.00
      0.0438000           1.0000000              1.0000000
D   1   1.00
      2.50400             1.000000
D   1   1.00
      0.62600             1.000000
D   1   1.00
      0.15650             1.000000
F   1   1.00
      0.8000000           1.0000000
****
```

Carbon

s-type cGF with 6 G, scale factor

orbital exponents and contraction coefficients

s-and *p*-type cGF with 3 G

s-and *p*-type cGF with 1 G

diffuse function

d-type cGF with 1 G

f-type cGF with 1 G

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。

优点：

①分子解离成原子exactly。

②Confining 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。

习题

1.以STO和GTO为尝试变分函数，计算H原子基态能量，并与精确解比较。

2. Slater型函数的径向部分为 $R_n(r,\zeta)=N_{n\zeta}r^{n-1}e^{-\zeta r}$，试计算其归一化因子$N_{n\zeta}$。

3.若用RHF/STO-3G计算水分子,试问：
(1)使用了多少个基函数(basis);
(2)使用了多少个Gauss原函数(primitive gaussians);
(3)可以得到个分子轨道(含自旋)?
(4)若在此基础上做水的Full-CI计算，涉及多少个组态?

4.给出一个HF/6-31G*和HF/6-31G**能量相同的分子。

§ 4.2 平面波基组

傅里叶变换

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

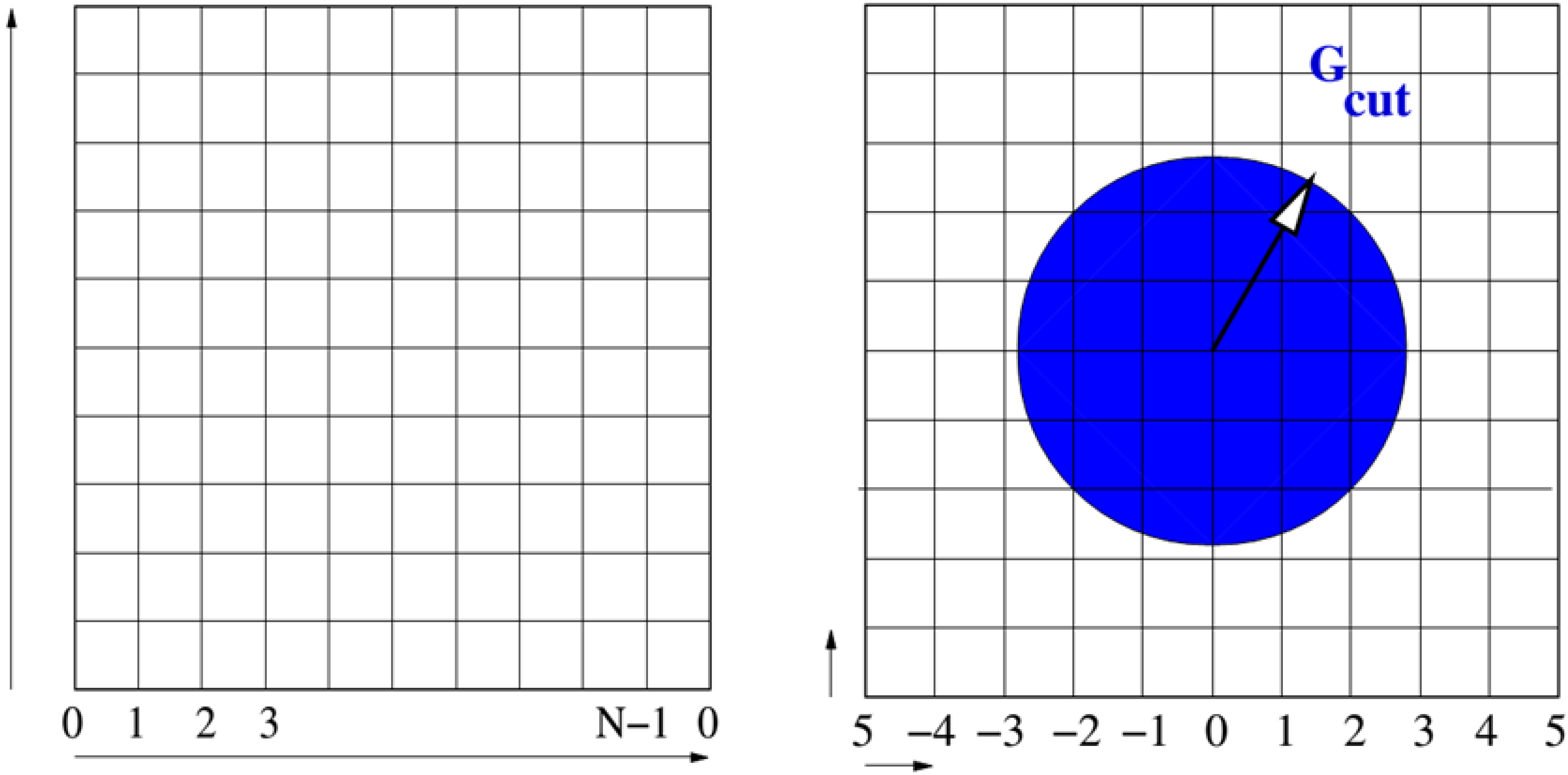
离散傅里叶变换（周期性边界条件）

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

平面波基组？

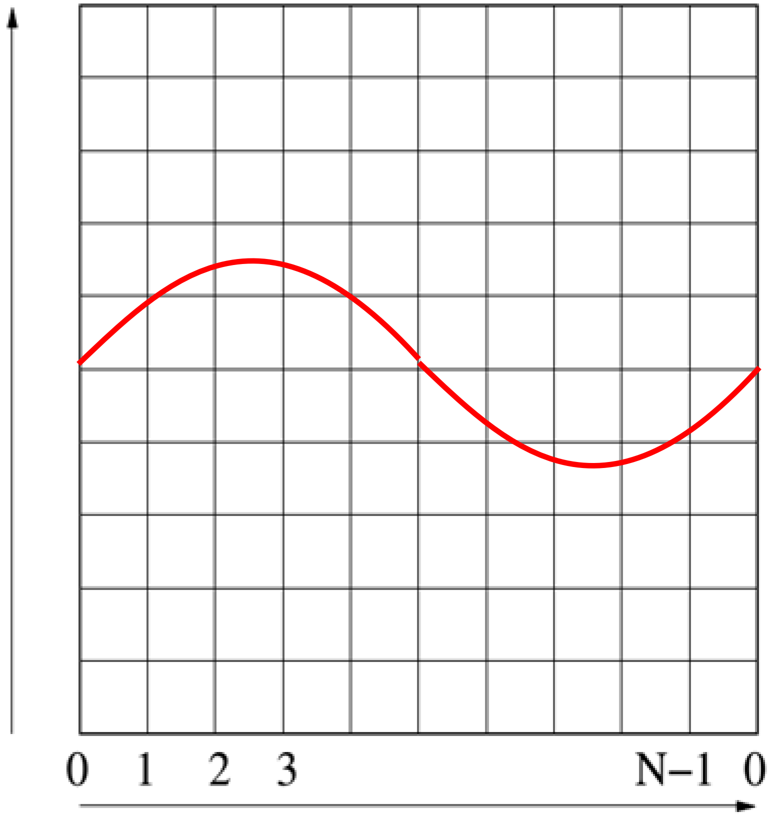
$$\varphi_n(\boldsymbol{r})=\sum_{\boldsymbol{g}}C_n(\boldsymbol{g})e^{i\boldsymbol{g}\cdot\boldsymbol{r}}$$

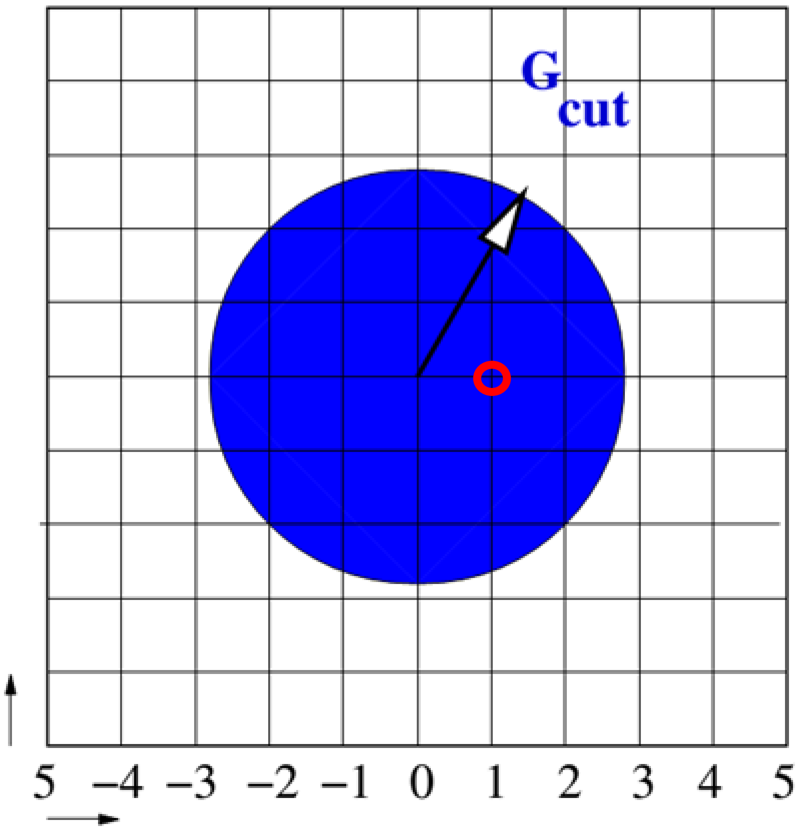
实空间与倒易空间的对应



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

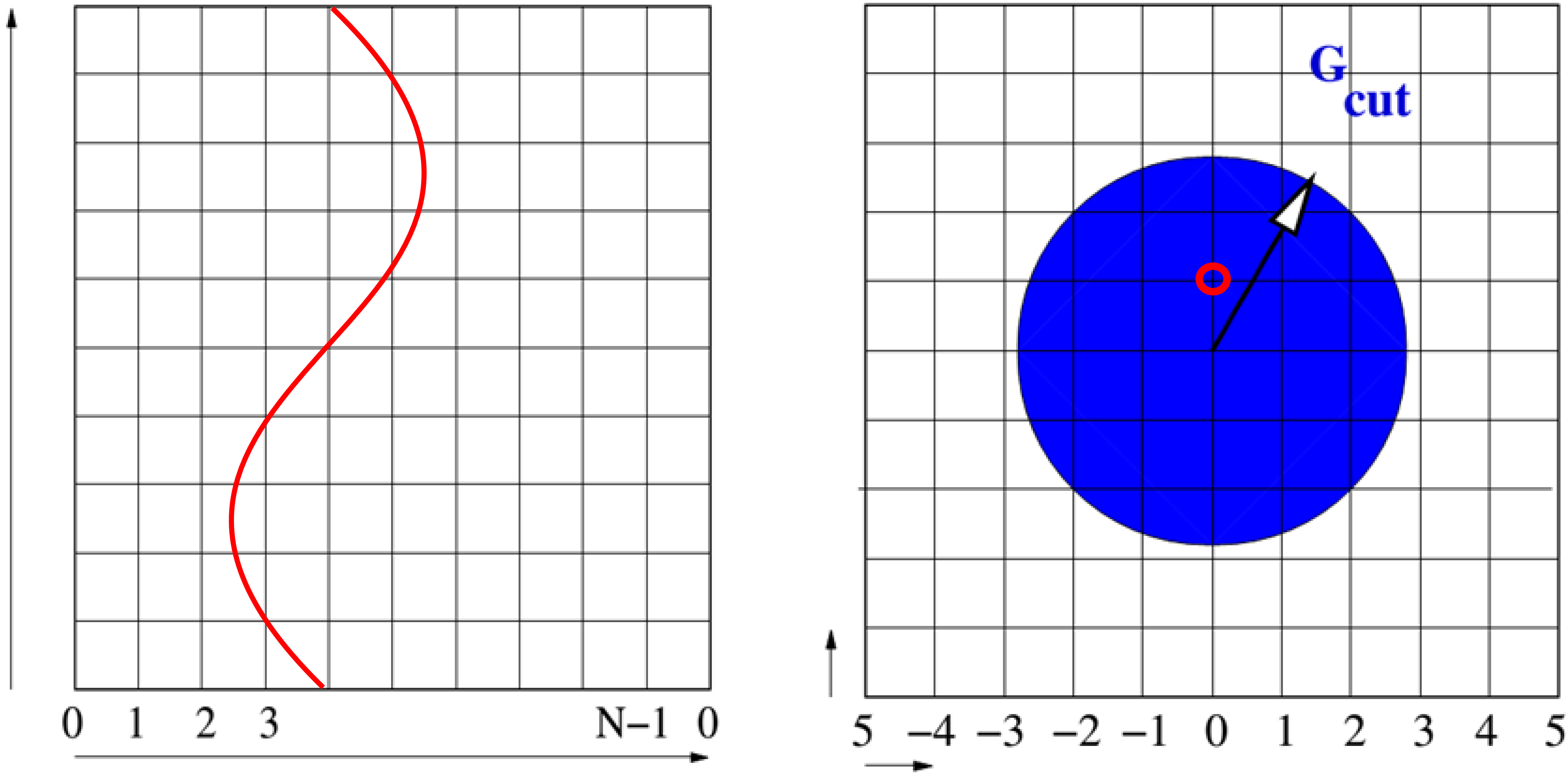
实空间与倒易空间的对应





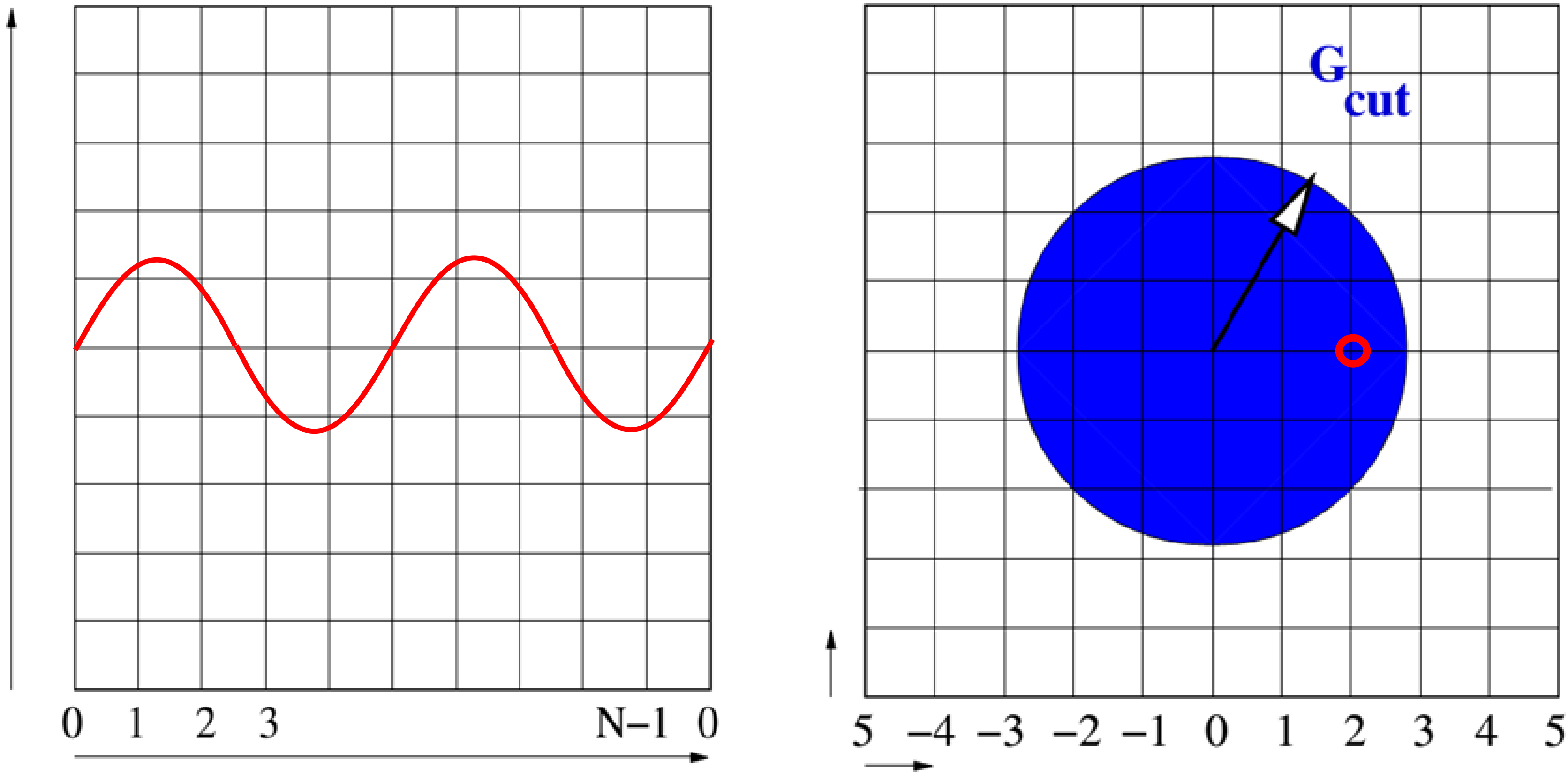
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \xleftrightarrow{\text{FFT}} C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

实空间与倒易空间的对应



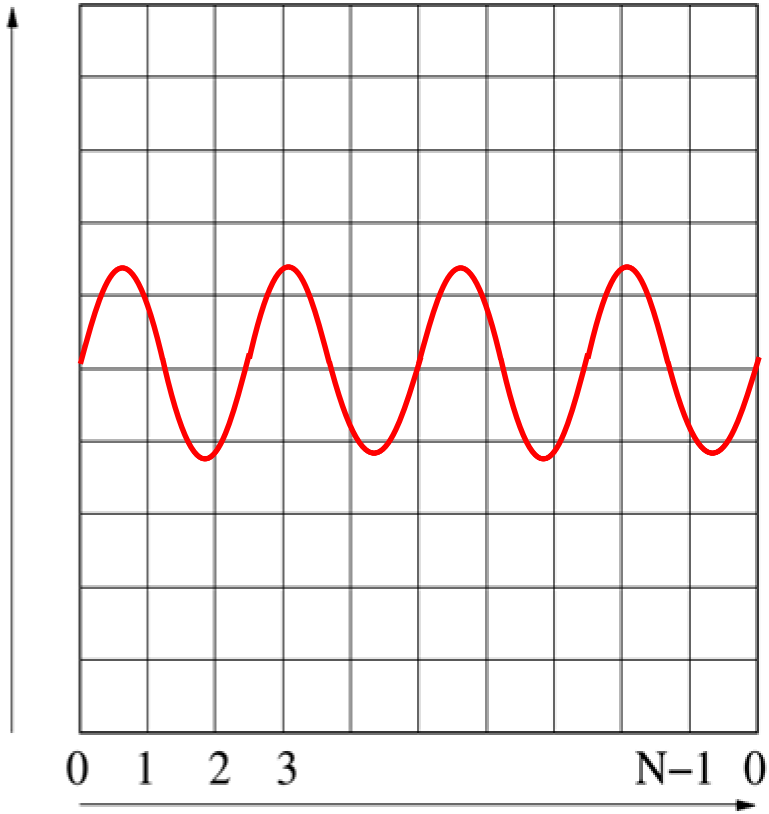
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \xleftrightarrow{\text{FFT}} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

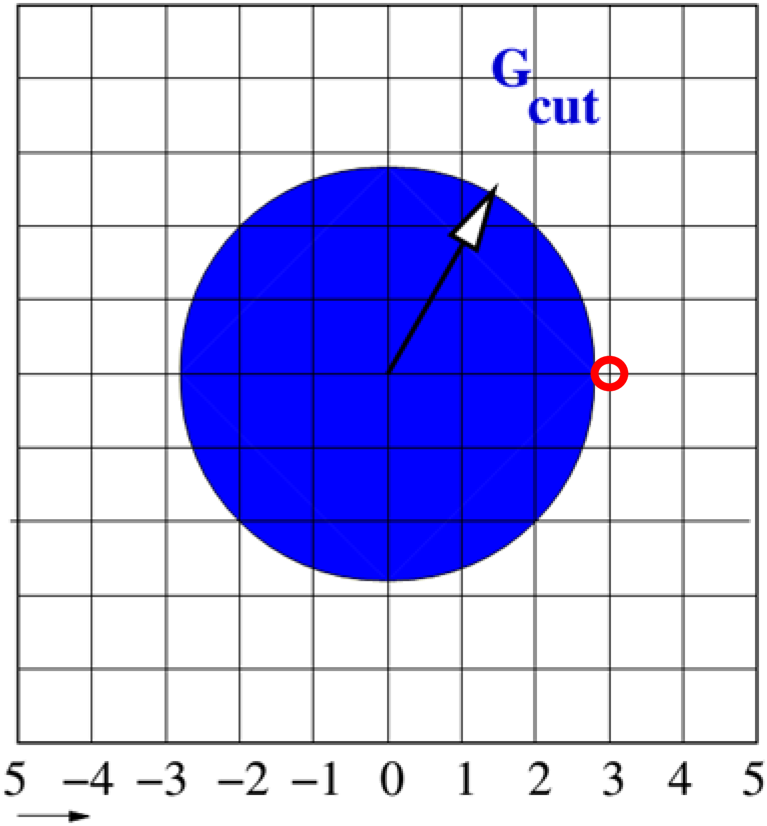
实空间与倒易空间的对应



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

实空间与倒易空间的对应





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

周期性边界条件与离散化

傅里叶变换

$$A(\boldsymbol{k}) = \frac{1}{\Omega}\int_{\Omega} F(\boldsymbol{r})e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}d\boldsymbol{r}$$

$$= \frac{1}{\Omega}\int_{\Omega} F(\boldsymbol{r}+\boldsymbol{R_n})e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}d\boldsymbol{r}$$

$$A(\boldsymbol{k})\left(1-e^{i\boldsymbol{k}\cdot\boldsymbol{R}_n}\right)=0$$

$$= \frac{1}{\Omega}\int_{\Omega} F(\boldsymbol{r}')e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'}d\boldsymbol{r}'\cdot e^{i\boldsymbol{k}\cdot\boldsymbol{R}_n}$$

倒易空间点阵

$$e^{i\boldsymbol{G}_n\boldsymbol{R}_n}=1 \qquad \boldsymbol{G_n}\cdot\boldsymbol{R_n}=2\pi m$$

$$\boldsymbol{G_n}=h_1\boldsymbol{b}_1+h_2\boldsymbol{b}_2+h_3\boldsymbol{b}_3$$

Bloch定理

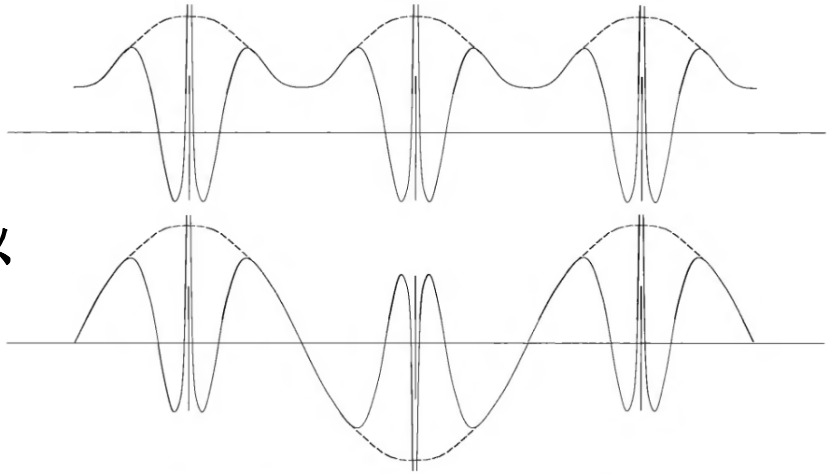
一般说来波函数的对称性可以不同于哈密顿量的对称性。例如，自由粒子的波函数为平面波而不是恒等函数。

周期体系：

$$[\hat{h},\hat{t}]=0 \qquad \varphi(\boldsymbol{r}+n_1\boldsymbol{R})=\hat{t}^{n_1}\varphi(\boldsymbol{r})=\lambda^{n_1}\varphi(\boldsymbol{r})$$

$$\lambda(n_1+n_2)=\lambda(n_1)\lambda(n_2) \quad \lambda=\exp(i\boldsymbol{k}\cdot\boldsymbol{R}_n)$$

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



布洛赫波函数中的周期部分满足以下方程，只需在一个单胞中求解

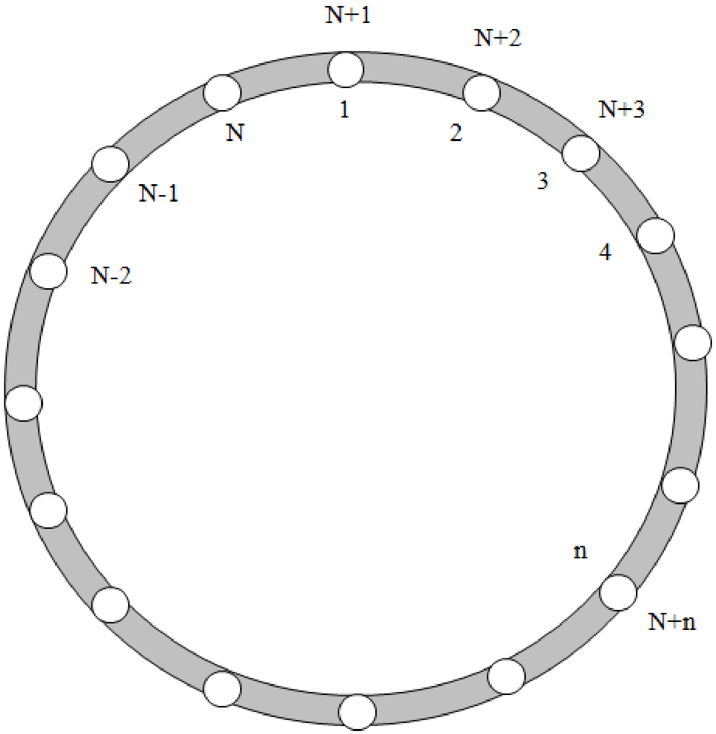
$$e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\hat{H}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{i,\boldsymbol{k}}(\boldsymbol{r})=\varepsilon_{i,\boldsymbol{k}}u_{i,\boldsymbol{k}}(\boldsymbol{r})$$

$$\hat{H}(\boldsymbol{k})u_{i,\boldsymbol{k}}(\boldsymbol{r})=\left[-\frac{\hbar^2}{2m_e}(\nabla+i\boldsymbol{k})^2+V(\boldsymbol{r})\right]u_{i,\boldsymbol{k}}(\boldsymbol{r})=\varepsilon_{i,\boldsymbol{k}}u_{i,\boldsymbol{k}}(\boldsymbol{r})$$

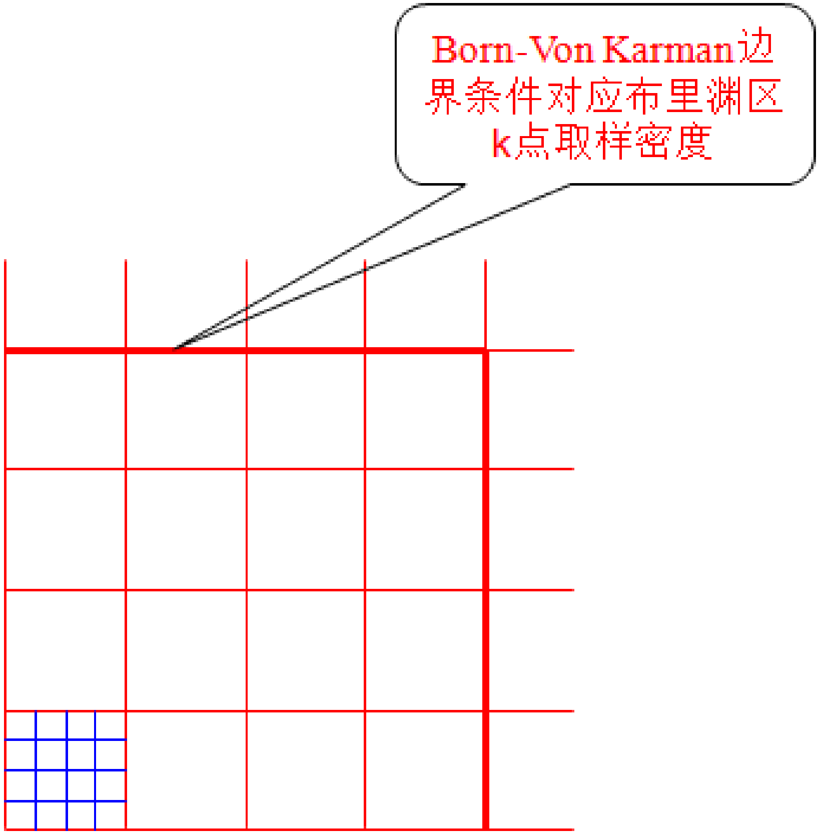
波矢的离散化

Born-von Karman 边界条件

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

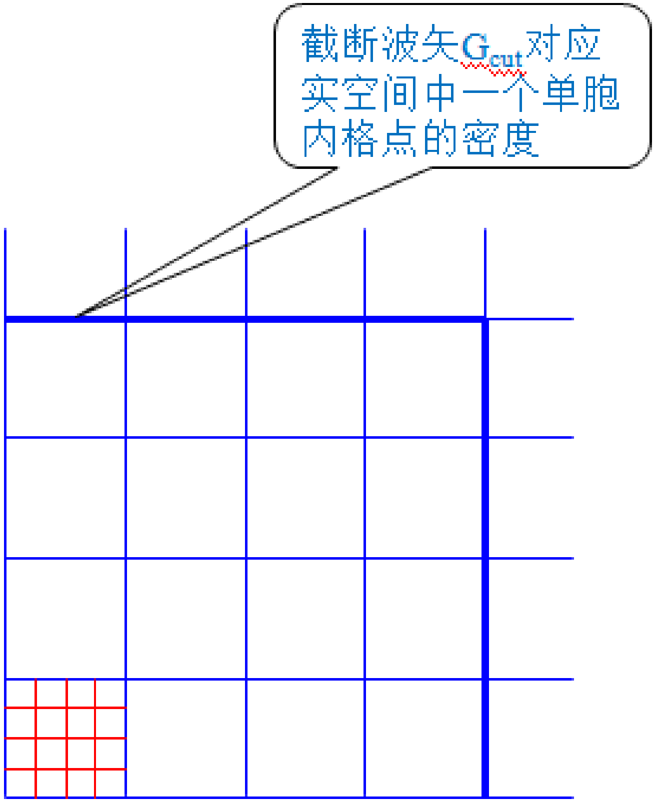


实空间与倒易空间的对应



Born-Von Karman边界条件对应布里渊区k点取样密度

Real space



截断波矢G_{cut}对应实空间中一个单胞内格点的密度

Reciprocal space

平面波基组

- 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

$$V_{\mathrm{xc},\mathbf{r}} = V_{\mathrm{xc}}[\rho_{\mathbf{r}}] \qquad \{V_{\mathrm{xc},\mathbf{r}}\} \to \{V_{\mathrm{xc},\mathbf{G}}\}$$

  - Hartree势

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

  - Add all contribution, then FFT back to real space

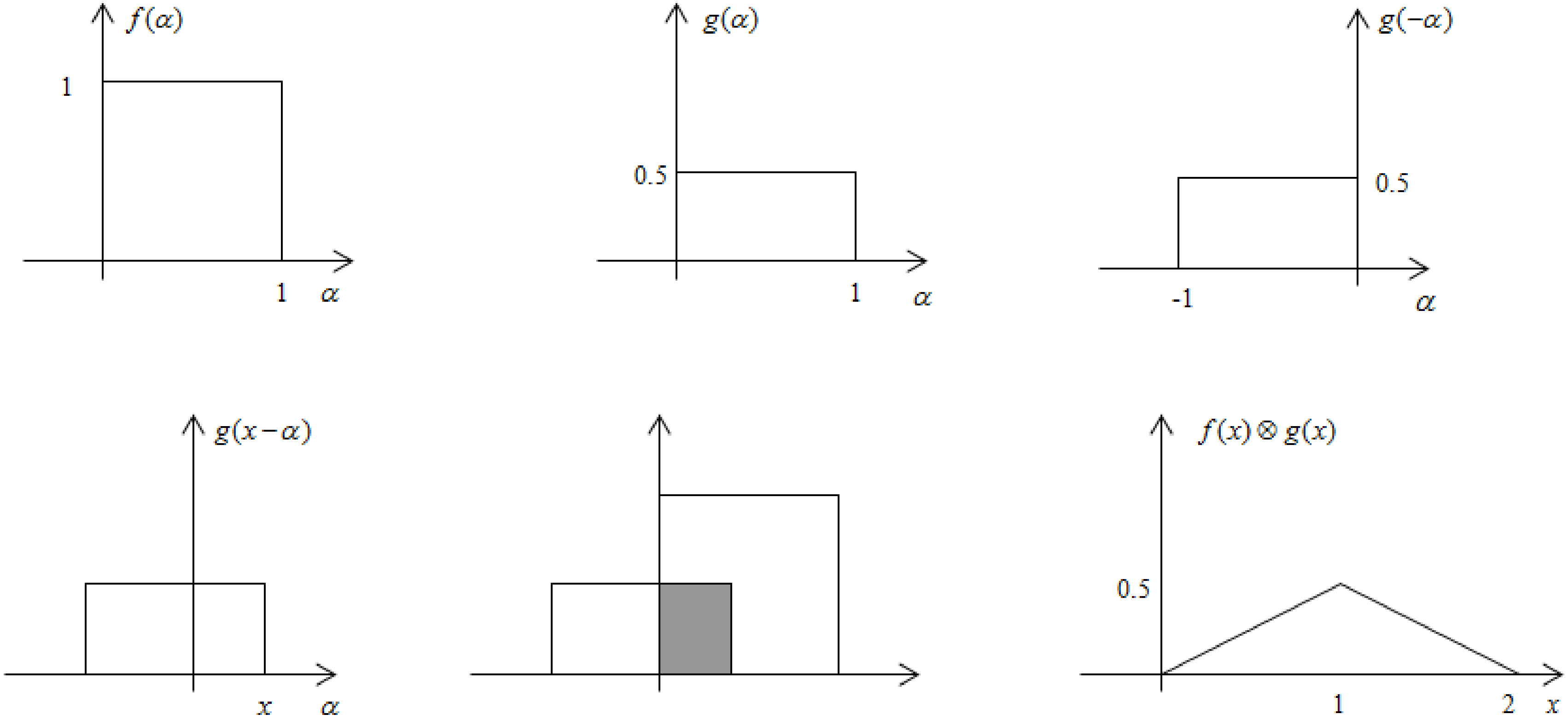
$$V_{\mathbf{G}} = V_{\mathrm{H},\mathbf{G}} + V_{\mathrm{xc},\mathbf{G}} + V_{\mathrm{ext},\mathbf{G}} \qquad \{V_{\mathbf{G}}\} \to \{V_{\mathbf{r}}\}$$

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

卷积

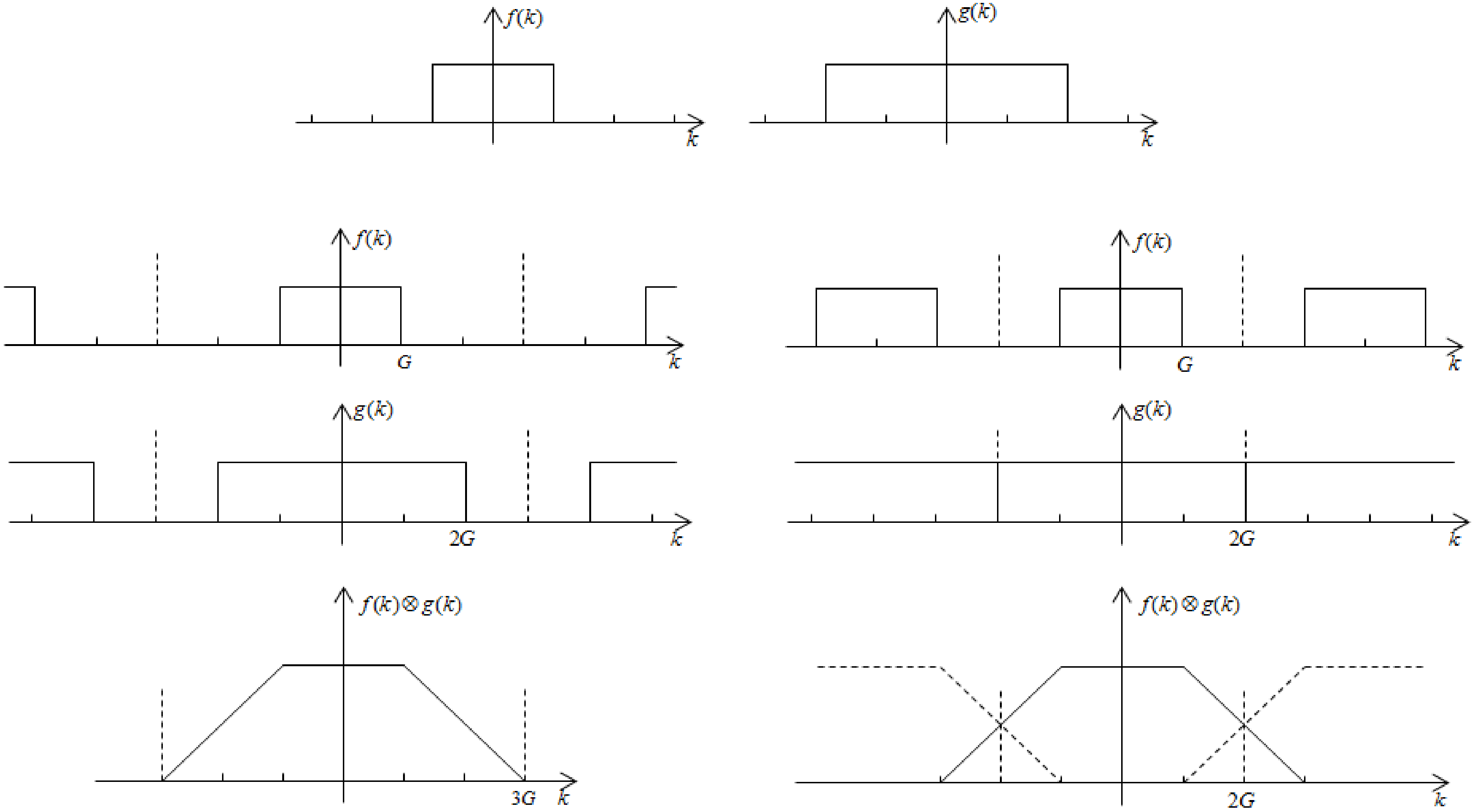
卷积的定义

$$f(x)\otimes g(x)=\int_{-\infty}^{+\infty}f(\alpha)g(x-\alpha)d\alpha \qquad f(k)\otimes g(k)=\frac{1}{M}\sum_{m=0}^{M-1}f(m)g(k-m)$$



倒空间卷积

卷积定理：实空间两个函数的乘积对应着倒空间的卷积

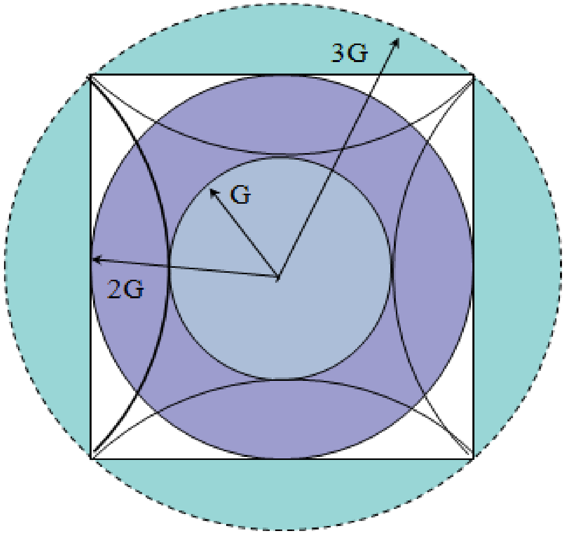


缠绕误差

- 电荷密度($2G_{\mathrm{cut}}$)
- 有效势($2G_{\mathrm{cut}}$以内分量才有意义)

$$\langle \mathbf{G}'|v_{eff}|\mathbf{G}\rangle = \sum_n v_{eff}(\mathbf{G}_n)\boldsymbol{\delta}_{\mathbf{G}'-\mathbf{G},\mathbf{G}_n}$$

- 单电子方程



GPW混合基组

- 用高斯基组表示波函数
- 同时用一套辅助的平面波基组来表示密度

- 类似resolution of the identity (RI)的思想

§4.3 赝势方法

- 模守恒赝势 (Norm conserving pseudopotential)
- 超软赝势 (Ultrasoft pseudopotential)
- 投影缀加波方法 (Projector augmented wave)

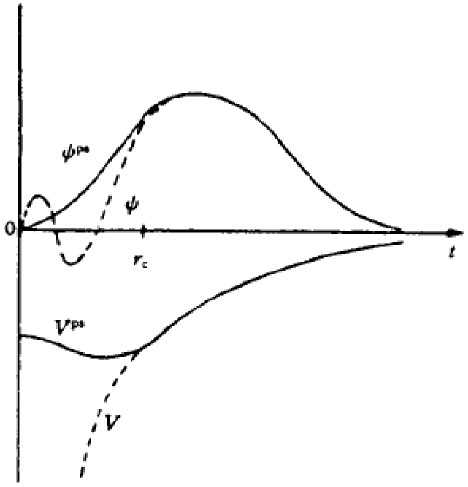
Pseudopotential

- The same scattering properties (phase shifts modulo 2π) can be reproduced by different potentials.
- Ionic pseudopotential
  - Replace the strong Coulomb potential of the nucleus and the effects of the tightly bound core electrons by an effective ionic potential acting on the valence electrons (frozen core).
  - Semilocal *l*-dependent potential

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

$$= v_{loc}(r) + \sum_{lm} |Y_{lm}\rangle\, \delta v_l(r) \langle Y_{lm}|$$

$$\delta V_l(r) = 0 \;\; \text{for} \;\; r > R_c$$



PP Construction

1. Calculation of the all electron atom in a reference state (only for the radial part)

$$\varphi(\boldsymbol{r}) = [u_{n,l}(r)/r]Y_{lm} \quad -\frac{1}{2}\frac{d^2}{dr^2}u_{n,l}(\boldsymbol{r}) + \left[\frac{l(l+1)}{2r^2} + V_{ext}(\boldsymbol{r}) - \varepsilon_{n,l}\right]u_{n,l}(\boldsymbol{r}) = 0$$

2. Construction of the pseudo valence orbitals $\varphi^{ps}(\boldsymbol{r})$
3. Get screened PP from an inversion of the Schrodinger equation

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

4. Removal of the electrostatic and xc components due to the valence electrons from the screened PP, i.e. "unscreening"

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

Core Corrections

- Nonlinear core-valence xc scheme $v^{xc}[\rho_0^{PS}] \longrightarrow v^{xc}[\rho^{core} + \rho_0^{PS}]$
- Partial core density

$$V_l^{ps}(r) \longrightarrow V_l^{ps,scr}(r) - V^H[\rho_0^{ps}; r] - V^{XC}[\rho_0^{ps} + \tilde{\rho}_0^{core}; r]$$

$$E^{tot} \longrightarrow \sum_i f_i \langle \psi_i | T + \hat{V}^{ps} | \psi_i \rangle + E^H[\rho^{ps}] + E^{XC}[\rho^{ps} + \tilde{\rho}_0^{core}]$$

$$\tilde{\rho}_0^{core}(r) = \begin{cases} \rho_0^{core}(r) & r \geq r^{nlc} \\ c_0 + \sum_{i=3}^{6} c_i r^i & r \leq r^{nlc} \end{cases}$$

- It’s reasonable to set r^{nlc} to about the radius where the full core density drops below the valence electron density.

Norm-Conserving Pseudopotential

- Requirements for a good pseudopotential
  - All-electron and pseudo valence eigenvalues agree for a chosen "prototype" atomic configuration
  - All-electron and pseudo valence wavefunctions agree beyond a chosen core radius r_c.
  - The logarithmic derivatives of the all-electron and pseudo wavefunctions agree at r_c.
  - The integrated charge inside r_c for each wavefunction agrees (norm conserving condition).
  - The first energy derivative of the logarithmic derivatives of the all-electron and pseudo wave function agrees at r_c.

$$2\pi\left[(r\varphi)^2\frac{d}{d\epsilon}\frac{d}{dr}\ln\varphi\right]_R = 4\pi\int_0^R \varphi^2 r^2 dr$$

Choice of the Core Radii

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

Separable Pseudopotential Operator

- Kleinman-Bylander scheme

$$\hat{V}_{\mathrm{NL}} = V_{\mathrm{local}}(\boldsymbol{r}) + \sum_{lm} \frac{\left|\psi_{lm}^{\mathrm{PS}} \delta V_l\right\rangle \left\langle \delta V_l \psi_{lm}^{\mathrm{PS}}\right|}{\left\langle \psi_{lm}^{\mathrm{PS}} \middle| \delta V_l \middle| \psi_{lm}^{\mathrm{PS}} \right\rangle}$$

  - Reduce number of integrals from N(N+1)/2 to N

$$\int j_l(kr)\, \delta v(r) j_l(k'r) r^2 dr P_l(\cos\theta_{kk'})$$

$$\int j_l(kr)\chi(r) r^2 dr \int j_l(k'r)\chi(r) r^2 dr\, P_l(\cos\theta_{kk'})$$

  - ghost state, avoid using too attractive local potential, sometime treat semicore state as a valence state is necessary.

- Without constructing the semilocal potential

$$\left|\chi_{lm}\right\rangle = (\varepsilon_l - T - v_{loc}) \left|\varphi_{lm}^{ps}\right\rangle$$

$$v_{NL} = \sum_{lm} \frac{\left|\chi_{lm}\right\rangle\left\langle\chi_{lm}\right|}{\left\langle \chi_{lm} \middle| \varphi_{lm}^{ps} \right\rangle}$$

ψ_{lm}^{PS} is a solution of $\hat{\mathrm{H}}\psi_{lm}^{\mathrm{PS}} = \varepsilon_l \psi_{lm}^{\mathrm{PS}}$

Multiple Reference Energies

- Construct pseudofunctions ψ_s at different energies ε_s
  Define matrix $$B_{s,s'} = \langle \psi_s | \chi_{s'} \rangle$$

$$\chi_s\ (\boldsymbol{r}) \equiv \left\{ \varepsilon_l - \left[-\frac{1}{2} \nabla^2 + V_{\text{local}}(\boldsymbol{r}) \right] \right\} \psi_s\ (\boldsymbol{r})$$

- Define projectors $$\beta_s = \sum_{s'} B^{-1}_{s,s'} \chi_{s'} \qquad \langle \psi_s | \beta_{s'} \rangle = \delta_{s,s'}$$

$$\delta \hat{V}_{\text{NL}} = \sum_{lm} \left[\sum_{s,s'} B_{s,s'} \left| \beta_s \rangle \langle \beta_{s'} \right| \right]_{lm}$$

ψ_s is a solution of $\hat{\mathrm{H}} \psi_s = \varepsilon_s \psi_s$

- Generalized norm conserving condition

$$4\pi \int_0^{r_c} \tilde{\phi}_i\ (r) \tilde{\phi}_j(r) r^2 dr = 4\pi \int_0^{r_c} \phi_i\ (r) \phi_j(r) r^2 dr \quad \forall i, j$$

Ultrasoft Pseudopotential

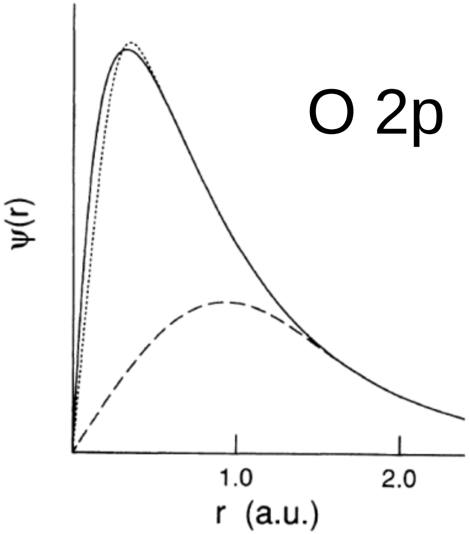
- Relax the NC constraint

$$Q_{nm}(r) = \psi_n^*(r)\psi_m(r) - \tilde{\psi}_n^*(r)\tilde{\psi}_m(r)$$

$$q_{nm} = \int d\boldsymbol{r} Q_{nm}(\boldsymbol{r}) = \langle \psi_n | \psi_m \rangle_R - \langle \tilde{\psi}_m | \tilde{\psi}_n \rangle_R$$

$$S = 1 + \sum_{nm,I} q_{nm} |\beta_n^I\rangle \langle \beta_m^I|$$

$$\langle \tilde{\psi}_i | \hat{S} | \tilde{\psi}_{i'} \rangle = \delta_{i,i'} \qquad \langle \tilde{\psi}_i | S | \tilde{\psi}_j \rangle_R = \langle \psi_i | \psi_j \rangle_R$$



PRB **1990**, 41, 7892

- Charge

$$n(\boldsymbol{r}) = \sum_i \left[|\tilde{\psi}_i(\boldsymbol{r})|^2 + \sum_{nm,I} Q_{nm}^I(\boldsymbol{r}) \langle \tilde{\psi}_i | \beta_n^I \rangle \langle \beta_m^I | \tilde{\psi}_i \rangle \right]$$

Typically, the augmentation charge Q_{nm} should be pseudized

USPP Construction

- An all-electron calculation on a free atom to get $V_{\mathrm{AE}}(r)$
- At reference energies get $|\psi_n\rangle$, $(T+V_{AE}-\epsilon_n)|\psi_n\rangle = 0$
- Construct pseudo-wave-function and a smooth $V_{\mathrm{loc}}(r)$
- Obtain projectors

$$|\chi_n\rangle = (\epsilon_n - T - V_{\mathrm{loc}})\big|\tilde{\psi}_n\big\rangle \qquad B_{nm} = \langle\tilde{\psi}_n|\chi_m\rangle \qquad |\beta_n\rangle = \sum_m (B^{-1})_{mn}|\chi_m\rangle$$

$$\left(T + V_{\mathrm{loc}} + \sum_{nm} D_{nm}|\beta_n\rangle\langle\beta_m|\right)|\tilde{\psi}_n\rangle = \epsilon_n\left(1 + \sum_{nm} q_{nm}|\beta_n\rangle\langle\beta_m|\right)|\tilde{\psi}_n\rangle$$ is satisfied

$$D_{nm} = B_{nm} + \epsilon_m q_{nm}$$

- Unscreening

$$V_{\mathrm{loc}}^{\mathrm{ion}}(r) = V_{\mathrm{loc}}(r) - \int d\boldsymbol{r}' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \mu_{\mathrm{xc}}(r)$$

$$D_{nm}^{(0)} = D_{nm} - \int d\boldsymbol{r}' V_{\mathrm{loc}}(\boldsymbol{r}') n(\boldsymbol{r}')$$

USPP as an AE Method

- Meaning of D

$$D_{ij} = \left\langle \tilde{\phi}_i \middle| \left(\frac{\hbar^2}{2m_e}\Delta - V_{\mathrm{loc}} + \varepsilon_j \right) \middle| \tilde{\phi}_j \right\rangle + \varepsilon_j Q_{ij}$$

$$= \left\langle \tilde{\phi}_i \middle| \frac{\hbar^2}{2m_e}\Delta - V_{\mathrm{loc}} \middle| \tilde{\phi}_j \right\rangle + \varepsilon_j \left(\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle + Q_{ij} \right)$$

$$= -\left\langle \tilde{\phi}_i \middle| -\frac{\hbar^2}{2m_e}\Delta + V_{\mathrm{loc}} \middle| \tilde{\phi}_j \right\rangle + \varepsilon_j \left(\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle + \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle \right)$$

$$= -\left\langle \tilde{\phi}_i \middle| -\frac{\hbar^2}{2m_e}\Delta + V_{\mathrm{loc}} \middle| \tilde{\phi}_j \right\rangle + \langle \phi_i | \varepsilon_j | \phi_j \rangle$$

$$= -\underbrace{\left\langle \tilde{\phi}_i \middle| -\frac{\hbar^2}{2m_e}\Delta + V_{\mathrm{loc}} \middle| \tilde{\phi}_j \right\rangle}_{\text{energy pseudo onsite}} + \underbrace{\left\langle \phi_i \middle| -\frac{\hbar^2}{2m_e}\Delta + V_{\mathrm{AE}} \middle| \phi_j \right\rangle}_{\text{energy AE onsite}}$$

One-Electron Equation

- Generalized eigen problem

$$E_{\text{tot}}\left[\{\tilde{\psi}_i\},\{\boldsymbol{R}_{\boldsymbol{I}}\}\right] = \sum_i \langle\tilde{\psi}_i|-\nabla^2 + V_{NL}|\tilde{\psi}_i\rangle + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{\text{xc}}[n] + \int d\boldsymbol{r}V_{\text{loc}}^{\text{ion}}(\boldsymbol{r})n(\boldsymbol{r}) + U(\{\boldsymbol{R}_{\boldsymbol{I}}\})$$

$$\frac{\delta E_{\text{tot}}}{\delta\tilde{\psi}_i^*(\boldsymbol{r})} = \epsilon_i S\tilde{\psi}_i(\boldsymbol{r})$$

$$V_{NL} = \sum_{nm,I} D_{nm}^{(0)}\,|\beta_n^I\rangle\langle\beta_m^I|$$

$$\frac{\delta n(\boldsymbol{r}')}{\delta\tilde{\psi}_i^*(\boldsymbol{r})} = \tilde{\psi}_i(\boldsymbol{r}')\delta(\boldsymbol{r}'-\boldsymbol{r}) + \sum_{nm,I} Q_{nm}^I(\boldsymbol{r}')\beta_n^I(\boldsymbol{r})\langle\beta_m^I|\tilde{\psi}_i\rangle$$

$$H|\tilde{\psi}_i\rangle = \epsilon_i S|\tilde{\psi}_i\rangle$$

$$H = -\nabla^2 + V_{\text{eff}} + \sum_{nm,I} D_{nm}^I\,|\beta_n^I\rangle\langle\beta_m^I|$$

$$V_{\text{eff}}(\boldsymbol{r}) = \frac{\delta E_{\text{tot}}}{\delta n(\boldsymbol{r})} = V_{\text{loc}}^{\text{ion}}(\boldsymbol{r}) + \int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \mu_{\text{xc}}(\boldsymbol{r})$$

$$D_{nm}^I = D_{nm}^{(0)} + \int d\boldsymbol{r}V_{\text{eff}}(\boldsymbol{r})Q_{nm}^I(\boldsymbol{r})$$

Projector Augmented Wave Method

- Transform operator

$$\left|\psi_n\right\rangle = \hat{\mathcal{T}}\left|\tilde{\psi}_n\right\rangle \qquad \hat{\mathcal{T}}^\dagger \hat{\mathrm{H}} \hat{\mathcal{T}}\left|\tilde{\psi}_n\right\rangle = \epsilon_n \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}}\left|\tilde{\psi}_n\right\rangle$$

- Expansion with partial waves

$$\hat{\mathcal{T}} = 1 + \sum_a \hat{\mathcal{T}}^a$$

only modify the wave function close to the nuclei

$$|\phi_i^a\rangle = (1 + \hat{\mathcal{T}}^a)|\tilde{\phi}_i^a\rangle \iff \hat{\mathcal{T}}^a|\tilde{\phi}_i^a\rangle = |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle$$

- Projectors

$$\left|\tilde{\psi}_n\right\rangle = \sum_i P_{ni}^a|\tilde{\phi}_i^a\rangle \qquad \left|\psi_n\right\rangle = \hat{\mathcal{T}}\left|\tilde{\psi}_n\right\rangle = \sum_i P_{ni}^a|\phi_i^a\rangle \,, \quad \text{for } |\mathbf{r} - \mathbf{R}^a| < r_c^a$$

$$P_{ni}^a = \langle\tilde{p}_i^a|\tilde{\psi}_n\rangle$$

requirement of linear transform

$$\sum_i |\tilde{\phi}_i^a\rangle\langle\tilde{p}_i^a| = 1$$

the completeness relation

$$\left\langle\tilde{p}_{i_1}^a\middle|\tilde{\phi}_{i_2}^a\right\rangle = \delta_{i_1,i_2}, \quad \text{for } |\mathbf{r} - \mathbf{R}^a| < r_c^a$$

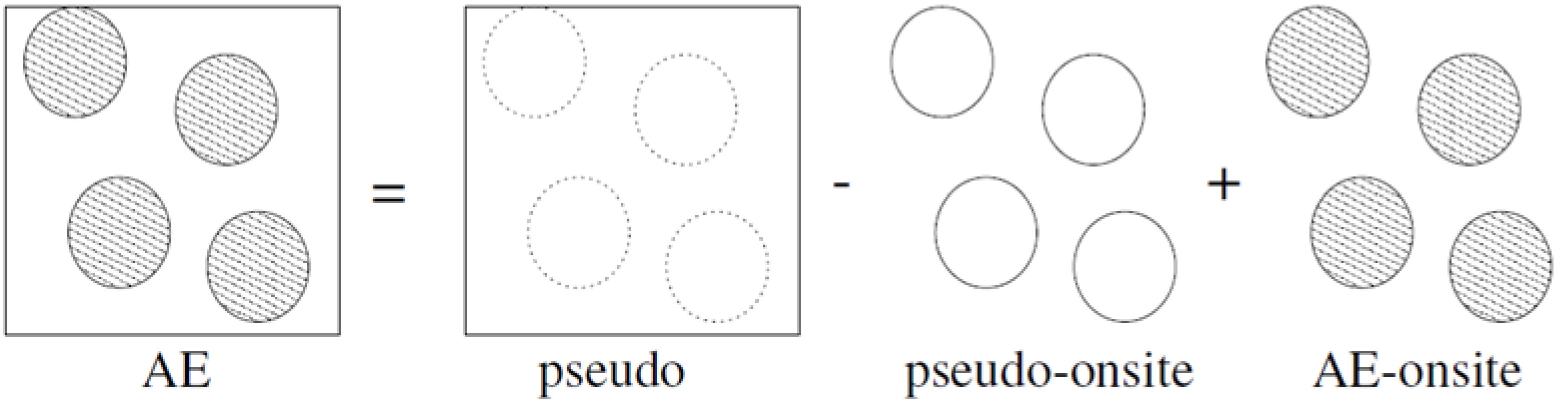
biorthogonality

The PAW Transform

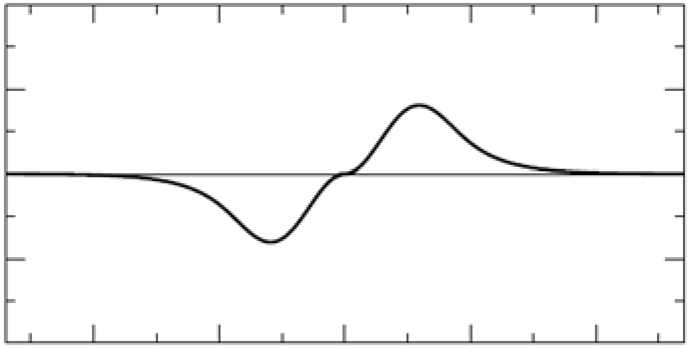
$$\hat{\mathcal{T}} = 1 + \sum_a \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle\tilde{p}_i^a|$$

- Let $c_{lm\epsilon} = \langle\tilde{p}_{lm\epsilon}|\tilde{\psi}_n\rangle$, we have

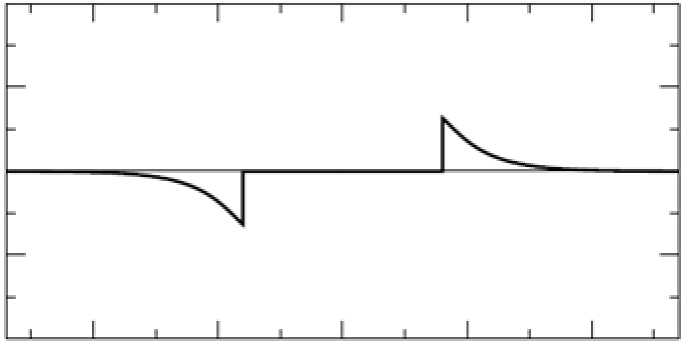
$$|\psi_n\rangle = |\tilde{\psi}_n\rangle - \sum|\tilde{\phi}_{lm\epsilon}\rangle\, c_{lm\epsilon} + \sum|\phi_{lm\epsilon}\rangle\, c_{lm\epsilon}$$



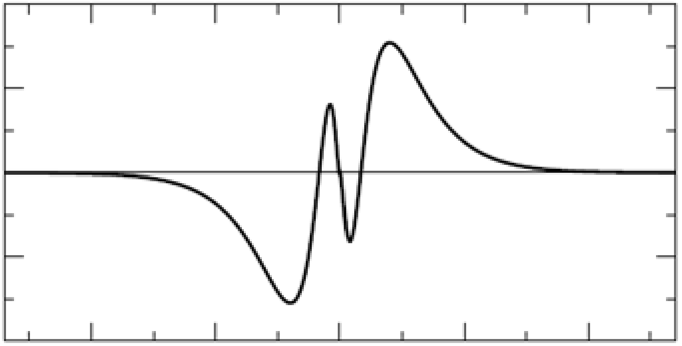
$$|\tilde{\psi}_n\rangle$$



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



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



Charge Density

- All-electron charge density

$$n(\boldsymbol{r}) = \tilde{n}(\boldsymbol{r}) + n^1(\boldsymbol{r}) - \tilde{n}^1(\boldsymbol{r})$$

$$\tilde{n}(\boldsymbol{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \tilde{\Psi}_n \rangle$$

on a plane-wave grid

$$n^1(\boldsymbol{r}) = \sum_{(i,j)} \rho_{ij} \langle \phi_i | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \phi_j \rangle$$

on a radial support grid

$$\tilde{n}^1(\boldsymbol{r}) = \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \tilde{\phi}_j \rangle$$

$$\rho_{ij} = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_n \rangle$$

- Frozen core

n_c frozen core AE charge density

$n_{Zc} = n_Z + n_c$

$\tilde{n}_c$ partial core charge density

$\tilde{n}_{Zc}$ pseudized core density

Hartree Energy

- Charge decomposition

compensation charge

$$n_T = n + n_{Zc} = \underbrace{(\tilde{n} + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T} + \underbrace{(n^1 + n_{Zc})}_{n^1_T} - \underbrace{(\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}^1_T}$$

$$\frac{1}{2}(n_T)(n_T) = \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) + \left(n^1_T - \tilde{n}^1_T\right)(\tilde{n}_T) + \frac{1}{2}\left(n^1_T - \tilde{n}^1_T\right)\left(n^1_T - \tilde{n}^1_T\right)$$

replace $\tilde{n}_T$ by $\tilde{n}^1_T$

an approximation for an incomplete set of projectors

$$= \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) - \frac{1}{2}\overline{\left(\tilde{n}^1_T\right)\left(\tilde{n}^1_T\right)} + \frac{1}{2}\overline{\left(n^1_T\right)\left(n^1_T\right)}$$

- Compensation charge (for valence electrons)

$$\int_{\Omega_r} (n^1 - \tilde{n}^1 - \hat{n})\,|\boldsymbol{r} - \boldsymbol{R}|^l Y_L^*(\widehat{\boldsymbol{r} - \boldsymbol{R}})\,d\boldsymbol{r} = 0$$

$$\hat{n} = \sum_{(i,j),L} \rho_{ij}\hat{Q}^L_{ij}(\boldsymbol{r}) \qquad \hat{Q}^L_{ij}(\boldsymbol{r}) = q^L_{ij}\, g_l(|\boldsymbol{r} - \boldsymbol{R}|)\, Y_L(\widehat{\boldsymbol{r} - \boldsymbol{R}})$$

moments of AE-augmentation functions

Exchange-Correlation Energy

- Charge decomposition

$$n_c + n = (\tilde{n} + \hat{n} + \tilde{n}_c) + (n^1 + n_c) - (\tilde{n}^1 + \hat{n} + \tilde{n}_c)$$

- For local or semilocal xc functional and a complete set of projectors

$$E_{xc} = E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + \overline{E_{xc}[n^1 + n_c]} - \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]}$$

Total Energy

- Three terms

$$E = \tilde{E} + E^1 - \tilde{E}^1$$

$$\tilde{E} = \sum_n f_n \left\langle \tilde{\Psi}_n \middle| -\frac{1}{2}\Delta \middle| \tilde{\Psi}_n \right\rangle + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + E_H[\tilde{n} + \hat{n}] + \int v_H[\tilde{n}_{Zc}][\tilde{n}(\boldsymbol{r}) + \hat{n}(\boldsymbol{r})]\, d\boldsymbol{r} + U(\boldsymbol{R}, Z_{ion})$$

$$\tilde{E}^1 = \sum_{(i,j)} \rho_{ij} \left\langle \tilde{\phi}_i \middle| -\frac{1}{2}\Delta \middle| \tilde{\phi}_j \right\rangle + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]} + \overline{E_H[\tilde{n}^1 + \hat{n}]} + \int_{\Omega_r} v_H[\tilde{n}_{Zc}][\tilde{n}^1(\boldsymbol{r}) + \hat{n}(\boldsymbol{r})] d\boldsymbol{r}$$

$$E^1 = \sum_{(i,j)} \rho_{ij} \left\langle \phi_i \middle| -\frac{1}{2}\Delta \middle| \phi_j \right\rangle + \overline{E_{xc}[n^1 + n_c]} + \overline{E_H[n^1]} + \int_{\Omega_r} v_H[n_{Zc}] n^1(\boldsymbol{r}) d\boldsymbol{r}$$

Generalized Eigenvalue Problem

- Overlap

$$S[\{\boldsymbol{R}\}] = 1 + \sum_{i} |\tilde{p}_i\rangle\, q_{ij}\, \langle\tilde{p}_j| \qquad q_{ij} = \langle\phi_i|\phi_j\rangle - \langle\tilde{\phi}_i|\tilde{\phi}_j\rangle$$

$$\langle\widetilde{\Psi}_n|S|\widetilde{\Psi}_m\rangle = \delta_{nm}$$

- Hamiltonian

$$\tilde{\rho} = \sum_{n} f_n \left|\widetilde{\Psi}_n\right\rangle\!\left\langle\widetilde{\Psi}_n\right| \qquad H = \frac{dE}{d\tilde{\rho}} = \frac{\partial E}{\partial\tilde{\rho}} + \int \frac{\delta E}{\delta\tilde{n}(\boldsymbol{r})} \underbrace{\frac{\partial\tilde{n}(\boldsymbol{r})}{\partial\tilde{\rho}}}_{|r\rangle\langle r|} d\boldsymbol{r} + \sum_{(i,j)} \frac{\partial E}{\partial\rho_{ij}} \underbrace{\frac{\partial\rho_{ij}}{\partial\tilde{\rho}}}_{|\tilde{p}_i\rangle\langle\tilde{p}_j|}$$

$$H[\rho,\{\boldsymbol{R}\}] = -\frac{1}{2}\Delta + \tilde{v}_{\mathrm{eff}} + \sum_{(i,j)} |\tilde{p}_i\rangle\left(\widehat{D}_{ij} + D^1_{ij} - \widetilde{D}^1_{ij}\right)\langle\tilde{p}_j|$$

$$\tilde{v}_{\mathrm{eff}} = v_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c]$$

Corrections to Hamiltonian

$$\widehat{D}_{ij} = \frac{\partial \tilde{E}}{\partial \rho_{ij}} = \int \frac{\delta E}{\delta \hat{n}(\boldsymbol{r})} \frac{\partial \hat{n}(\boldsymbol{r})}{\partial \rho_{ij}} d\boldsymbol{r} = \sum_{L} \int \tilde{v}_{\text{eff}}(\boldsymbol{r}) \hat{Q}_{ij}^{L}(\boldsymbol{r}) d\boldsymbol{r}$$

$$D_{ij}^{1} = \frac{\partial E^{1}}{\partial \rho_{ij}} = \left\langle \phi_i \middle| -\frac{1}{2}\Delta + v_{\text{eff}}^{1} \middle| \phi_j \right\rangle$$

$$v_{\text{eff}}^{1}[n^1] = v_H[n^1 + n_{Zc}] + v_{xc}[n^1 + n_c]$$

$$\widetilde{D}_{ij}^{1} = \frac{\partial \tilde{E}^{1}}{\partial \rho_{ij}} = \left\langle \tilde{\phi}_i \middle| -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}}^{1} \middle| \tilde{\phi}_j \right\rangle + \sum_{L} \int_{\Omega_r} d\boldsymbol{r}\, \tilde{v}_{\text{eff}}^{1}(\boldsymbol{r}) \hat{Q}_{ij}^{L}(\boldsymbol{r})$$

$$\tilde{v}_{\text{eff}}^{1}[\tilde{n}^1] = v_H[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]$$

PAW Dataset

- AE and PS partial waves ϕ_i and $\tilde{\phi}_i$
- Projector functions $\tilde{p}_i$
- Core-charge density n_c , pseudized core charge density $\tilde{n}_{Zc}$ and the partial electronic core-charge density $\tilde{n}_c$
- The compensation functions $g_l(\mathrm{r})$
  - A double grid technique can be used for not-so-soft compensation charge $\hat{n}$

From PAW to USPP

- The total energy functional of the US-PP method can be obtained by linearization of the PAW energy functional around the atomic reference occupancies ρ_{ij}^{a}
- In the following limiting case, USPP method is strictly equivalent the PAW method

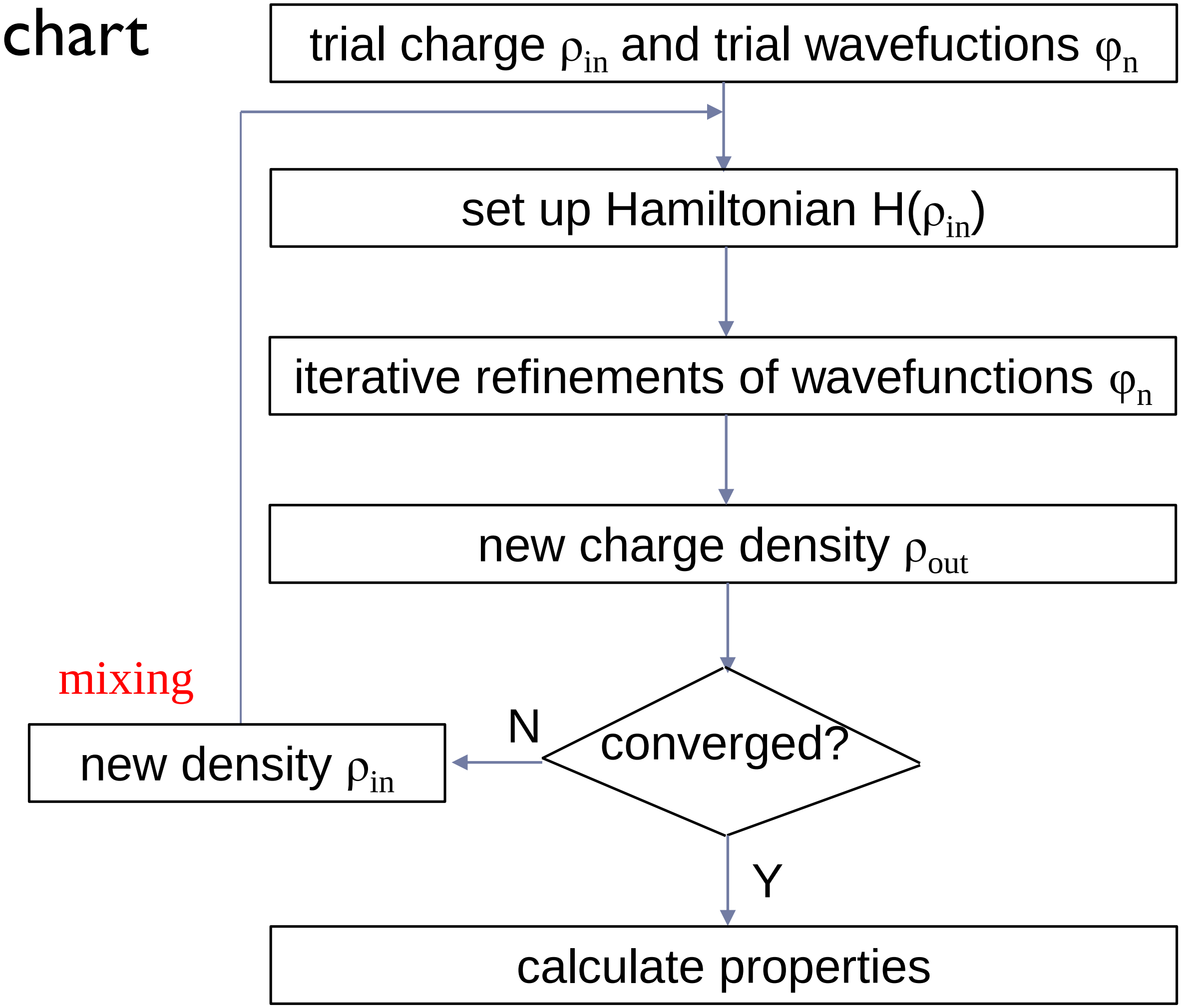
$$\hat{n} = n^1 - \tilde{n}^1 \qquad \tilde{n}_c = n_c \qquad \tilde{n}_{Zc} = n_{Zc}$$

§4.4 自洽场方法

- 矩阵对角化的迭代算法
- 布里渊区积分
- Smear方法
- Mixing方法

Self-Consistent Field

- Flow chart



trial charge ρ_{in} and trial wavefuctions φ_n

set up Hamiltonian $H(\rho_{in})$

v_{eff}

iterative refinements of wavefunctions φ_n

eigenvalue problem/minimization

new charge density ρ_{out}

k-sampling, smearing

converged?

energy

N

new density ρ_{in}

mixing

Y

calculate properties

Effective Potential

- Hartree potential
  - calculate the integral $v_H(\boldsymbol{r}) = \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}'$
  - solve the Poisson equation $\nabla^2 \mathrm{v}_H = -4\pi\rho$
- xc potential
  - local potential
  - OEP method
  - GKS scheme

Iterative Matrix Diagonalization

- Only interested in part of the eigenvalues
- Krylov subspace method
- Lanczos iteration

INPUT： NBANDS

$$\varphi_2 = c_2(\hat{h}\varphi_1 - h_{11}\varphi_1)$$

$$\varphi_{n+1} = c_{n+1}(\hat{h}\varphi_n - h_{nn}\varphi_n - h_{n,n-1}\varphi_{n-1}) \qquad h_{\mathrm{ij}} = \langle\varphi_{\mathrm{i}}|\hat{h}|\varphi_{\mathrm{j}}\rangle$$

$$\langle\varphi_{\mathrm{i}}|\varphi_{\mathrm{j}}\rangle = \delta_{ij}$$

a tridiagonal matrix in the iterative subspace

Iterative Matrix Diagonalization

- Rayleigh quotient

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

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

residual vector

- Trace minimization

$$\min_{X^* X = I} \frac{1}{2} \mathrm{Tr}(X^* A X) \qquad X \in \mathbb{C}^{n \times k}$$

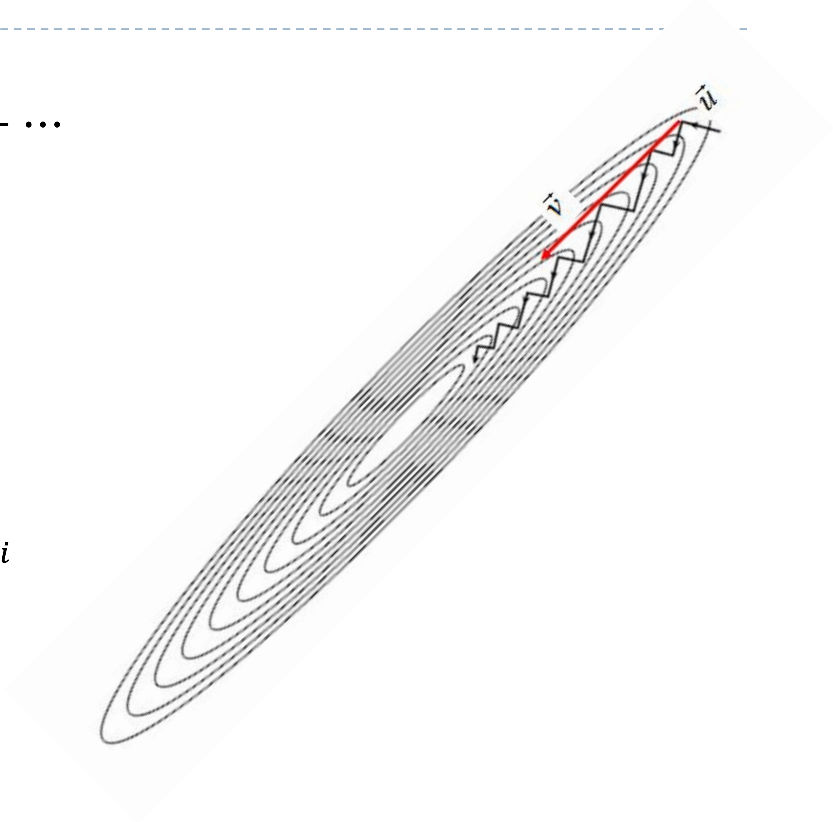
$$R = (I - XX^*)AX = AX - X(X^* AX)$$

concurrency of matrix operation

Multidimensional Optimization

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

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



- Steepest descent

$$x_{i+1} = x_i + \alpha^{i+1} g_i \qquad g = -\left.\frac{\partial F(x)}{\partial x}\right|_{x=x_i}$$

- Conjugated gradient

$$\nabla f = A\boldsymbol{x} - \boldsymbol{b}; \qquad \delta(\nabla f) = A\delta\boldsymbol{x}$$

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

$$\boldsymbol{h}_{i+1} = \boldsymbol{g}_{i+1} + \gamma_i \boldsymbol{h}_i \qquad \gamma_i = \frac{\boldsymbol{g}_{i+1}\cdot\boldsymbol{g}_{i+1}}{\boldsymbol{g}_i\cdot\boldsymbol{g}_i}$$

Multidimensional Optimization

- Quasi Newton methods

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

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

$$\lim H_i \longrightarrow A^{-1}$$

Broyden， BFGS

Preconditioning

- find a matrix K which gives the exact error of the wave function

  if $\varphi - \varphi^{ap} = \delta\varphi$, then $R[\varphi^{ap} + \delta\varphi] = R[\varphi^{ap}] + \left(\hat{h} - \varepsilon^{ap}\hat{I}\right)\delta\varphi = 0$

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

- Condition number
- Teter preconditioning: diagonal matrix, for large G the kinetic term dominates H, for small G becomes a constant

  $$\langle G|K|G'\rangle = \delta_{GG'} \frac{27 + 18x + 12x^2 + 8x^3}{27 + 18x + 12x^2 + 8x^3 + 16x^4} \qquad x = \frac{\hbar^2}{2m}\frac{G^2}{1.5E^{\mathrm{kin}}(\boldsymbol{R})}$$

  $$|p_n\rangle = K|R_n\rangle \qquad |\phi_n'\rangle = |\phi_n\rangle + \lambda|p_n\rangle$$

Davidson and LOBPCG Method

- Davidson iteration
  - include n eigenvectors and n residual vectors
  - solve the 2n×2n eigenvalue problem, got the n lowest-energy eigenvectors
- Locally optimal block preconditioned conjugate gradient (LOBPCG) algorithm

$$X \leftarrow XC_X + WC_W + PC_P$$

Rayleigh-Ritz procedure

$$W = (I - XX^*)TR$$

search direction

$$TR = T\big(AX - X(X^*AX)\big)$$

preconditioned residual

$$P = (I - XX^*)(W'C'_W - P'C'_P)$$

conjugate direction

Sequential (Band-by-Band) Algorithms

- Steepest descent

$$g_n = \left(1 - \sum_{n'} |\phi_{n'}\rangle\langle\phi_{n'}|\boldsymbol{S}\right) |p_n\rangle$$

  - 1D minimization along the search direction is a 2x2 eigenvalue problem

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

Rayleigh-Ritz scheme

  - at each step, a new residual vector is introduced, leading to a larger iterative subspace

$$\langle b_i|\boldsymbol{H} - \epsilon\boldsymbol{S}|b_j\rangle = 0 \qquad b_{i,i=1,N-1} = \{\phi_n/g_n^1/g_n^2/g_n^3/\cdots\}$$

- Conjugated gradient
  - conjugate each new search direction to the previous directions

$$|f^M\rangle = |p_m^M\rangle + \frac{\langle p_m^M|g_m^M\rangle}{\langle p_m^{M-1}|g_m^{M-1}\rangle}|f^{M-1}\rangle \qquad \{|\phi_m^M\rangle/|f^M\rangle\}$$

Block Davidson Method

- Block Davidson scheme
  - select a subset in all bands, do Davidson iteration

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

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

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

  - After all subsets are converged, do a Raighly-Ritz optimization for the final eigenvectors $\{\phi_k | k = 1, \ldots, N_{\text{bands}}\}$

Projected Preconditioned CG

- Gradient projection techniques for constrained optimization

$$\bar{x} \leftarrow x + \gamma s \qquad x \leftarrow M_Q \bar{x},$$

- PPCG algorithm

$$\bar{X} \leftarrow X C_X + W C_W + P C_P \qquad X \leftarrow M_Q \bar{X}$$

Restrict C_X, C_W, and C_P to be block diagonal

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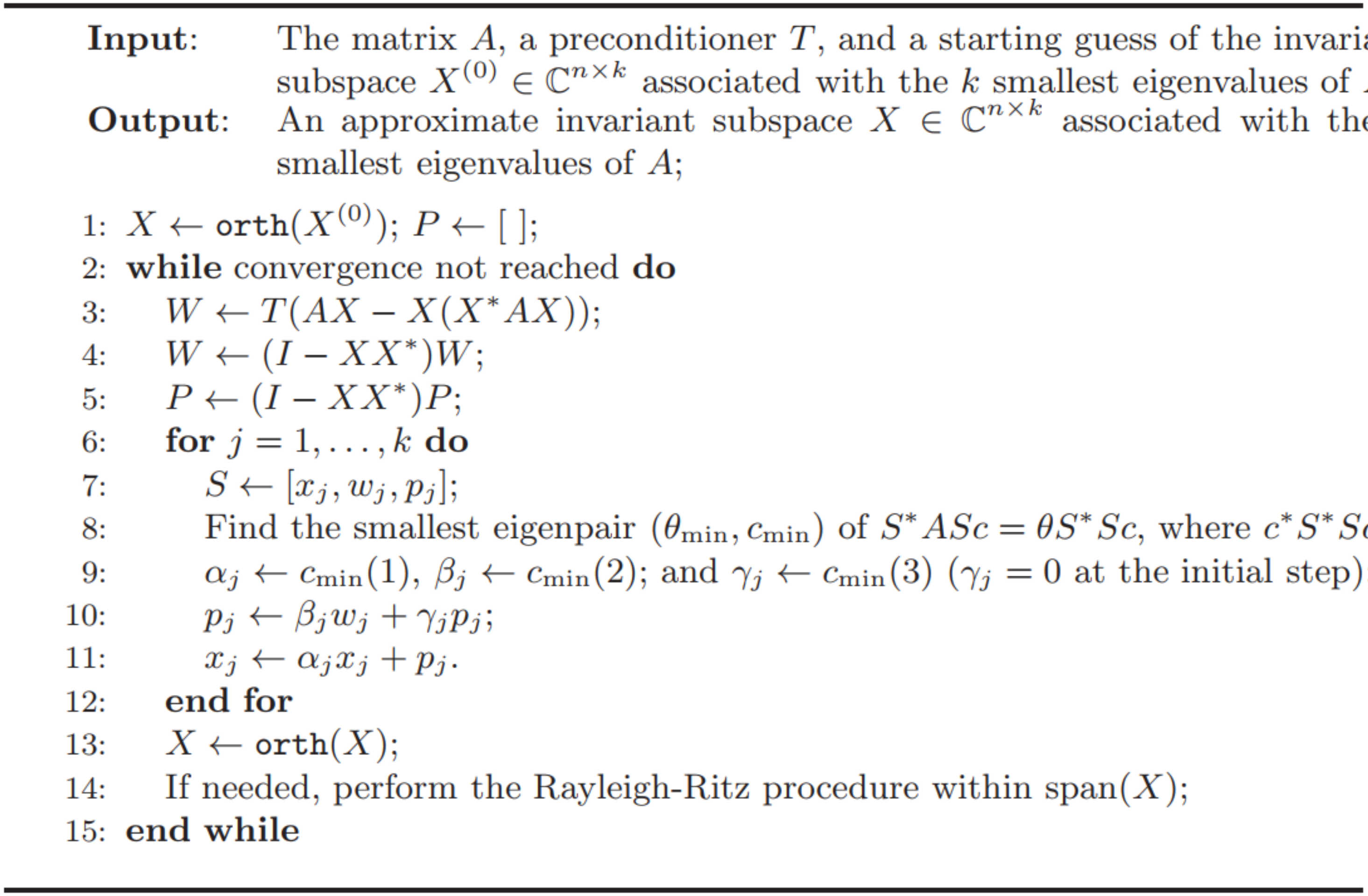
Projected Preconditioned CG

- PPCG algorithm with block size = 1



Input: The matrix A, a preconditioner T, and a starting guess of the invariant subspace $X^{(0)} \in \mathbb{C}^{n\times k}$ associated with the k smallest eigenvalues of A;

Output: An approximate invariant subspace $X \in \mathbb{C}^{n\times k}$ associated with the k smallest eigenvalues of A;

```
$X \leftarrow$ orth($X^{(0)}$); $P \leftarrow [\,]$;
while convergence not reached do
    $W \leftarrow T(AX - X(X^*AX))$;
    $W \leftarrow (I - XX^*)W$;
    $P \leftarrow (I - XX^*)P$;
    for $j = 1, \ldots, k$ do
        $S \leftarrow [x_j, w_j, p_j]$;
        Find the smallest eigenpair $(\theta_{\min}, c_{\min})$ of $S^*ASc = \theta S^*Sc$, where $c^*S^*Sc = 1$;
        $\alpha_j \leftarrow c_{\min}(1)$, $\beta_j \leftarrow c_{\min}(2)$; and $\gamma_j \leftarrow c_{\min}(3)$ ($\gamma_j = 0$ at the initial step);
        $p_j \leftarrow \beta_j w_j + \gamma_j p_j$;
        $x_j \leftarrow \alpha_j x_j + p_j$.
    end for
    $X \leftarrow$ orth($X$);
    If needed, perform the Rayleigh-Ritz procedure within span($X$);
end while
```

Residual Minimization

- **Residual Minimization - direct inversion in the iterative subspace (RMM-DIIS)**
  - minimize the norm of the residual vector instead of the Rayleigh Ritz quotient

$$\langle R[\varphi_{n+1}] | R[\varphi_{n+1}] \rangle$$

  - because the norm of the residual vector has an unconstrained minimum at each eigenvector, orthonormalization becomes unnecessary.
  - fast, but always finds the vector which is closest to the initial trial vector.

RMM-DIIS

- calculate a preconditioned residual vector
- perform a trial step along this direction

$$\left|\phi_m^1\right\rangle = \left|\phi_m^0\right\rangle + \lambda K \left|R_m^0\right\rangle \qquad \left|R_m^1\right\rangle = \left|R(\phi_m^1)\right\rangle$$

- search for the linear combination

$$\left|\bar{\phi}^M\right\rangle = \sum_{i=0}^{M} \alpha_i \left|\phi_m^i\right\rangle \quad \text{with } M = 1$$

$$\left|\bar{R}^M\right\rangle = \left|R\left(\bar{\phi}^M\right)\right\rangle = \sum_{i=0}^{M} \alpha_i \left|R_m^i\right\rangle$$

$$\sum_{j=0}^{M} \left\langle R_m^i \middle| R_m^j \right\rangle \alpha_j = \epsilon \sum_{j=0}^{M} \left\langle \phi_m^i \middle| S \middle| \phi_m^j \right\rangle \alpha_j$$

Integration over the BZ

- Charge density

$$\rho = \sum_{n}^{occ} \varphi_{n\boldsymbol{k}}^{*}(\boldsymbol{r})\varphi_{n\boldsymbol{k}}(\boldsymbol{r}) d\boldsymbol{r} d\boldsymbol{k}$$

- Numerically, integral is a weighted summation

$$\frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \Rightarrow \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}}$$

- The integrand is a smooth and periodic function of **k**

$$f_i(\boldsymbol{k}) = \sum_{\boldsymbol{T}} f_i(\boldsymbol{T})\, e^{i\boldsymbol{k}\cdot\boldsymbol{T}}$$

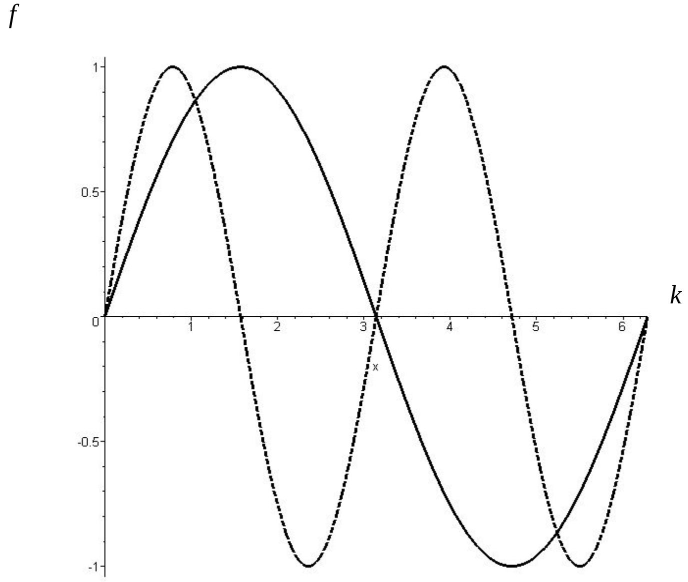
Special Points

- A one-dimensional example

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

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

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

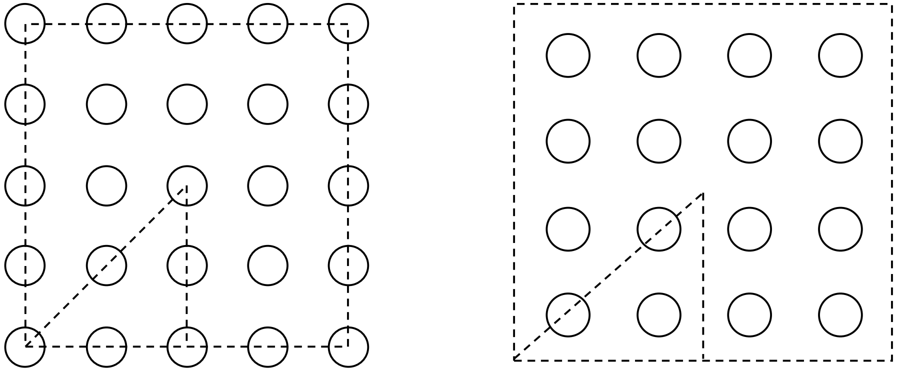


Monkhorst-Pack points

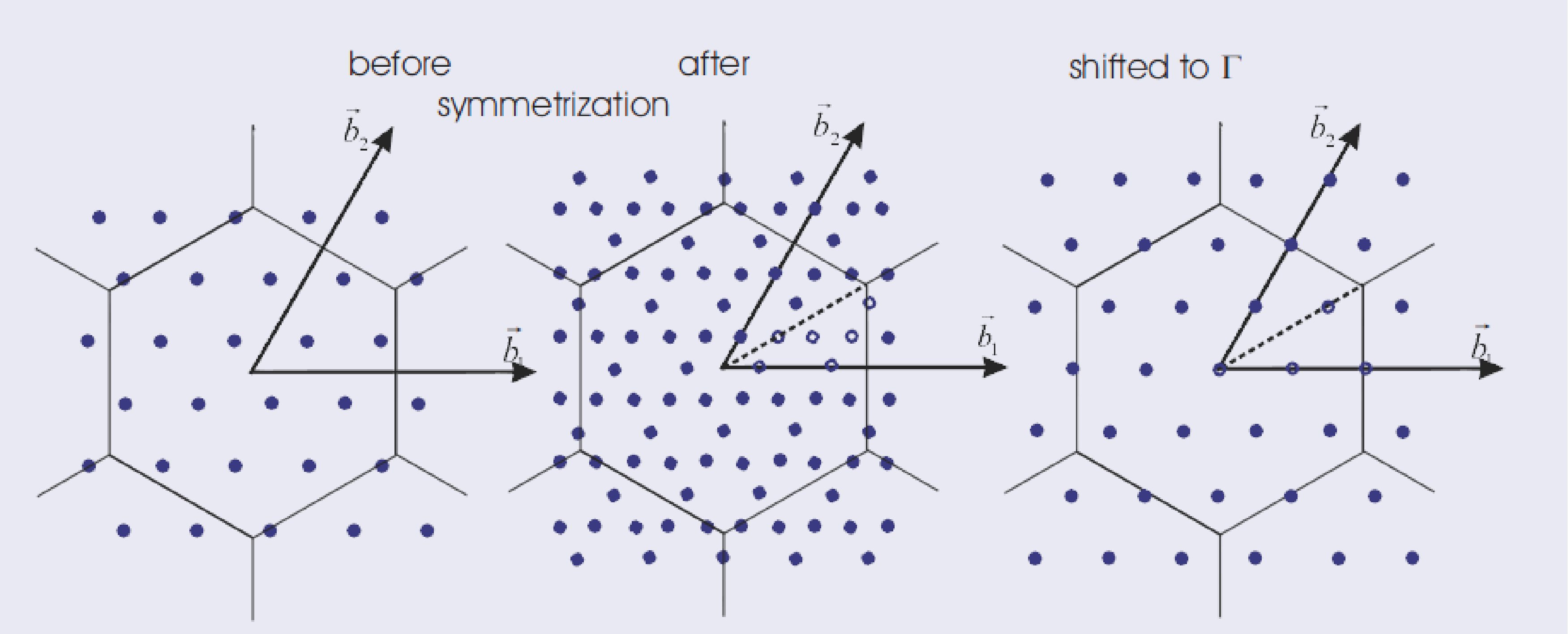
- Reduce from 3D to 1D
- Fractional coordinates

$$\mu_r = (2r - n_k - 1)/2n_k \quad r = 1,2,3,\ldots,n_k$$

- Offset from the Γ point



- For hexagonal lattice, the Γ point should be included

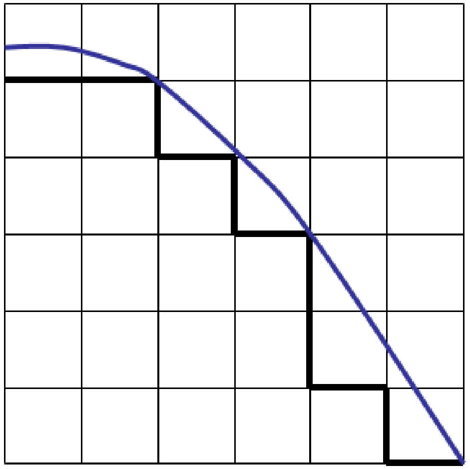


Difference between Metal and Insulator

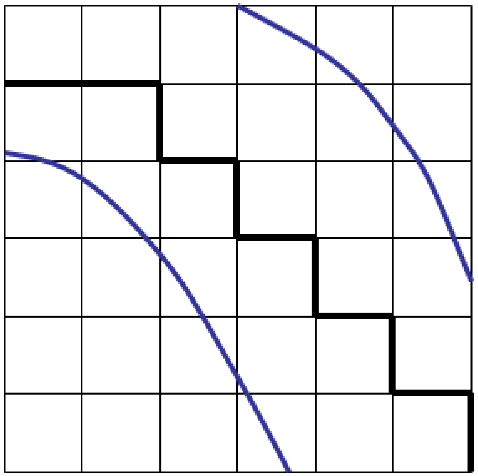
- Occupation is a step function at zero temperature

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

- More k points are required for metal



metal: a sharp
Fermi surface



insulator: a
band gap

Smearing

- Fermi-Dirac distribution

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

- Energy is no longer variational with respect to the partial occupancies f
- New variational function: free energy

$$F = E - \sum_{n\mathbf{k}} \omega_{\mathbf{k}} \sigma S(f_{n\mathbf{k}})$$

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

Fermi-Dirac function

- From F to f

$$\begin{aligned}
&(1) && F = E - \textstyle\sum_n \sigma S(f_n) \\
&(2) && S(f) = -[f\ln f + (1-f)\ln(1-f)] \\
&(3) && \sigma = k_B T \\
&(4) && \tfrac{\partial}{\partial f_n}\,[F - \mu(\textstyle\sum_n f_n - N)] = 0 \\
(1),(4) \longrightarrow\ &(5) && \frac{\partial E}{\partial f_n} - \sigma\frac{\partial S}{\partial f_n} - \mu = 0 \\
(2) \longrightarrow\ &(6) && \tfrac{\partial S}{\partial f} = -[\ln f + 1 - \ln(1-f) - 1] = \ln\tfrac{1-f}{f} \\
&(7) && \frac{\partial E}{\partial f_n} = \varepsilon_n \\
(5)-(7) \longrightarrow\ &(8) && \varepsilon_n - \sigma\ln\frac{1-f_n}{f_n} - \mu = 0 \\
(8) \longrightarrow\ &(9) && \exp\left[\tfrac{\varepsilon_n-\mu}{\sigma}\right] = \tfrac{1}{f_n} + 1 \\
(9) \longrightarrow\ & && f_n = \tfrac{1}{\exp\left[\frac{\varepsilon_{nk}-\mu}{\sigma}\right]+1}
\end{aligned}$$

- The reduced occupation probability below the Fermi energy are not compensated by the occupation probability above the Fermi energy.

Gaussian Smearing

- Broadening energy levels with Gaussian function, f becomes an integral of the Gaussian function

$$f(\varepsilon) = \frac{1}{2}[1 - \mathrm{erf}(\frac{\varepsilon-\mu}{\sigma})]$$

- The error function does not have an analytical inversion, entropy and free energy can not be written in f

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

- σ has no physical interpretation.
- Forces are calculated as derivatives of F(σ), not necessarily equal to force at E(0)

Gaussian Smearing

- Extrapolation to σ → 0: Because the dependence of the free energy and the Kohn-Sham energy on the smearing width is the same (to first order), averaging the two values gives a much better approximation to the T = 0 K result

$$
\begin{aligned}
& F(\sigma) \approx E(0) + \gamma\sigma^2 && (1)\\
& F(\sigma) = E(\sigma) - \sigma S(\sigma) && (2)\\
& S(\sigma) = -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma\sigma && (3)\\
(1) - (3) \longrightarrow\quad & E(\sigma) \approx E(0) - \gamma\sigma^2 && (4)\\
(1) + (4) \longrightarrow\quad & E(0) \approx \frac{1}{2}\big(F(\sigma) + E(\sigma)\big) &&
\end{aligned}
$$

Methfessel & Paxton Smearing

- Expansion of step function in a complete set of orthogonal functions, Gaussian smearing is the 0th order

$$f_0(x) = \frac{1}{2}\left(1 - \mathrm{erf}(x)\right)$$

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

$$S_N(x) = \frac{1}{2} A_N H_{2N}(x) e^{-x^2}$$

$$\text{with: } A_n = \frac{(-1)^n}{n!4^n\sqrt{\pi}}$$

- Extrapolation to σ → 0

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

- If entropy $S = \sigma \sum_n S_N(f_n)$ is small, $\hat{E}(\sigma) \approx F(\sigma) \approx E(\sigma) \approx E(0)$, force are accurate within the same limit.
- Not suitable for insulator, occupation may be >1.

Phys. Rev. B **1989** 40, 3616

Cold Smearing

- A broadening scheme leading to an occupation function that is positive definite.

$$\tilde{\delta}(x) = \frac{2}{\sqrt{\pi}} e^{-\left[x-\left(1/\sqrt{2}\right)\right]^2}\left(2-\sqrt{2}x\right) \qquad x = \frac{\mu-\epsilon}{\sigma}$$

$$f_i = \int_{-\infty}^{x_i} \tilde{\delta}(x)dx \qquad x_i = \frac{\mu-\tilde{\epsilon}_i}{\sigma}$$

$$S = \sum_i s_i$$

$$s_i = \frac{1}{\sqrt{\pi}} e^{-\left[x_i-\left(1/\sqrt{2}\right)\right]^2}\left(1-\sqrt{2}x_i\right)$$

Phys. Rev. Lett. **1999** 82, 3296

Linear Tetrahedron Method

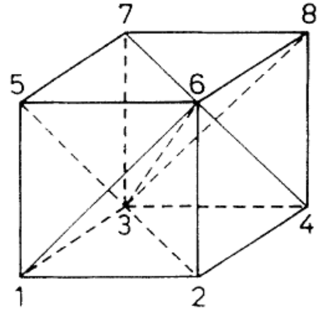
- Dividing up BZ into tetrahedra
  - Linear interpolation of the function to be integrated within these tetrahedral
  - integration of the interpolated function
- k-space integral
  - Interpolation

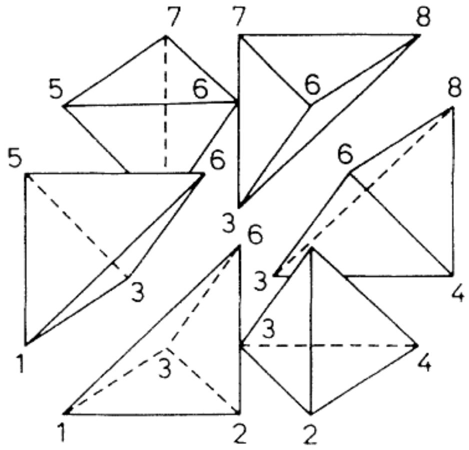
$$\bar{X}_n(\boldsymbol{k}) = \sum_j c_j\,(\boldsymbol{k}) X_n(\boldsymbol{k}_j)$$

  - remapping of the tetrahedra onto the k-points

$$I = \sum_{nj} \omega_{nj}\,(\boldsymbol{k}) X_n(\boldsymbol{k}_j)$$

$$\omega_{nj} = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\Omega_{\mathrm{BZ}}} d\boldsymbol{k}\, c_j(\boldsymbol{k}) f(\varepsilon_n(\boldsymbol{k}))$$

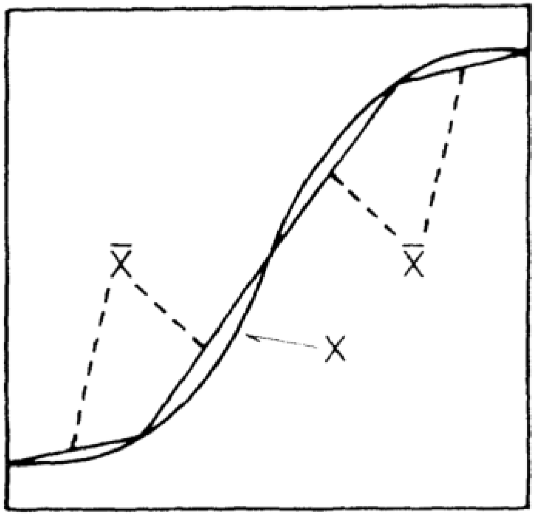




Blöchl Correction

- Linear interpolation under- or overestimates the real curvature
- For full bands these errors cancel
- Corrections for metal

$$\delta\omega_{\boldsymbol{kn}} = \sum_{\mathrm{T}} \frac{1}{40} D_{\mathrm{T}}(\varepsilon_{\mathrm{F}}) \sum_{j=1}^{4} \left(\varepsilon_{jn} - \varepsilon_{\boldsymbol{kn}}\right)$$



- Best k-point convergence for energy
- With Blöchl corrections the new effective partial occupancies do not minimize the ground state total energy

Energy functional

- KS energy functional

$$E_{KS} = T_S[n] + E_{pot}[n] \qquad T_S[n] = E_S - \int d\boldsymbol{r} v^{in}(\boldsymbol{r})\, n^{out}(\boldsymbol{r}) \qquad E_S = \sum_{i}^{N} \varepsilon_i$$

$$E_{pot} = \int d\boldsymbol{r} v_{ext}(\boldsymbol{r})\, n(\boldsymbol{r}) + E_H[n] + E_{XC}[n]$$

- KS energy as a functional of effective potential

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

- Harris-Foulkes functional

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

  - widely used in energy estimation in non-SCF calculations, no need to calculate n^{out}

Mixing

Linear Mixing

$$n_{i+1}^{in} = \alpha n_i^{out} + (1-\alpha) n_i^{in}$$
$$= n_i^{in} + \alpha\left(n_i^{out} - n_i^{in}\right)$$

charge density residual

$$R\left[n_i^{in}\right] = n_i^{out}\left[n_i^{in}\right] - n_i^{in}$$

- large α works well for strongly bound, rigid systems, while for soft systems, such as metal surfaces convergence can be difficult.

INPUT： AMIX

- charge sloshing problem

$$\delta v^{out}(\boldsymbol{G}) = \sum_{\boldsymbol{G}'} \varepsilon(\boldsymbol{G}, \boldsymbol{G}')\delta v^{in}(\boldsymbol{G}')$$

$$\alpha < \frac{1}{\varepsilon(\boldsymbol{G}_{\min})}$$

- Kerker preconditioning: damping the oscillations in the low-q components of the charge density.

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

INPUT： BMIX

Broyden Mixing

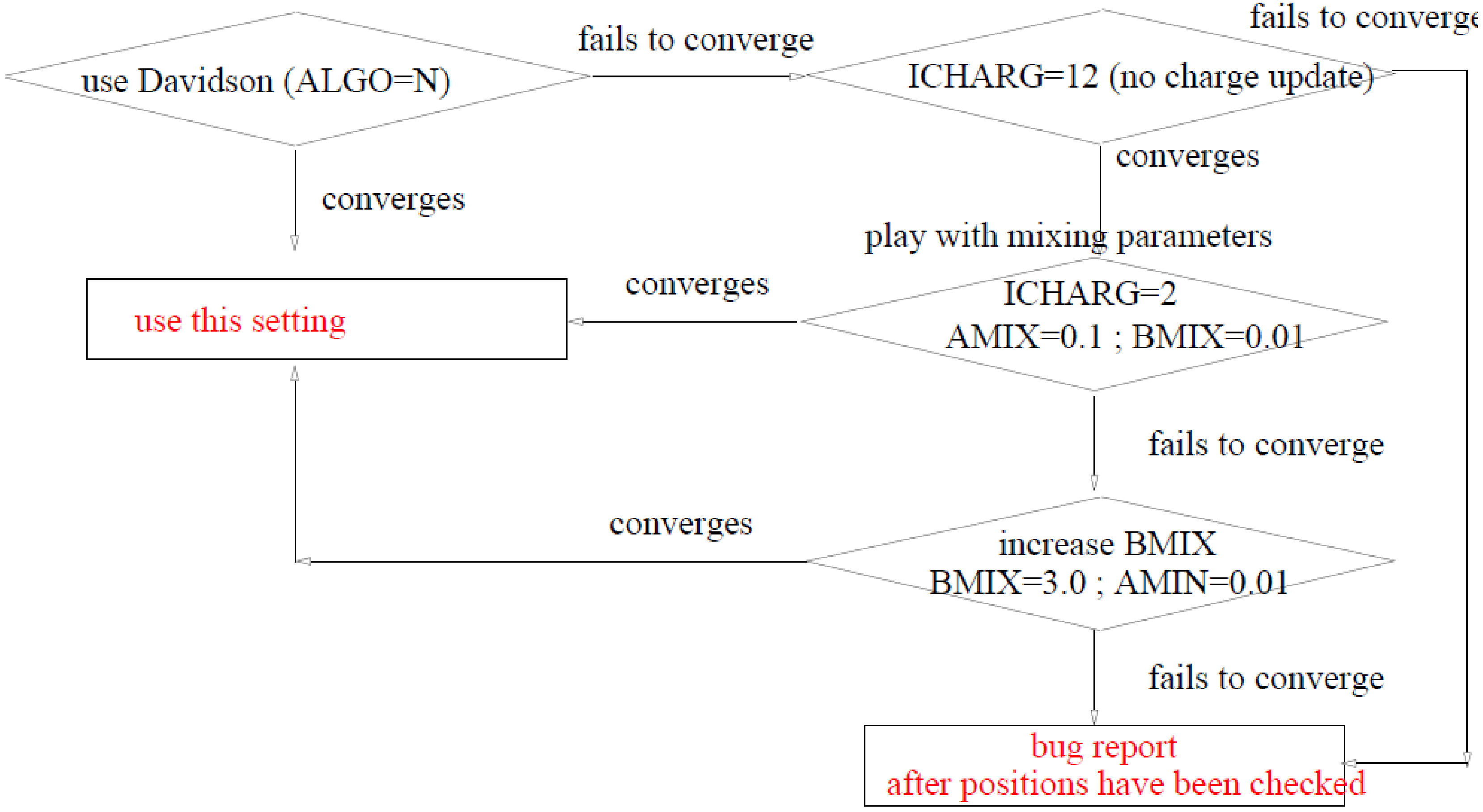
- linear mixing is similar to quasi-Newton-Raphson iteration $\mathbf{x}_{i+1}=\mathbf{x}_i-\mathbf{J}^{-1}\mathbf{R}_i$
- Using $\mathbf{J}_0=\alpha\mathbf{I}$ as the initial Jacobian, using quasi-Newton scheme, update **J** at every step

Pulay Mixing

- RMM-DIIS like
  - Find the linear combination coefficients of several densities.
  - Minimize the normal of the residue vector subject to the constraint of conserving the number of electrons (DIIS like)
  - It is desirable to reuse the approximation for the charge dielectric function which was obtained in previous ionic steps to reduce the number of electronic steps during relaxations and MD.

INPUT：MAXMIX

If SCF Convergence Fails



use Davidson (ALGO=N)

fails to converge

ICHARG=12 (no charge update)

fails to converge

converges

converges

play with mixing parameters

use this setting

converges

ICHARG=2
AMIX=0.1 ; BMIX=0.01

fails to converge

converges

increase BMIX
BMIX=3.0 ; AMIN=0.01

fails to converge

bug report
after positions have been checked