中国科学技术大学本科生课程

量子化学

Quantum Chemistry

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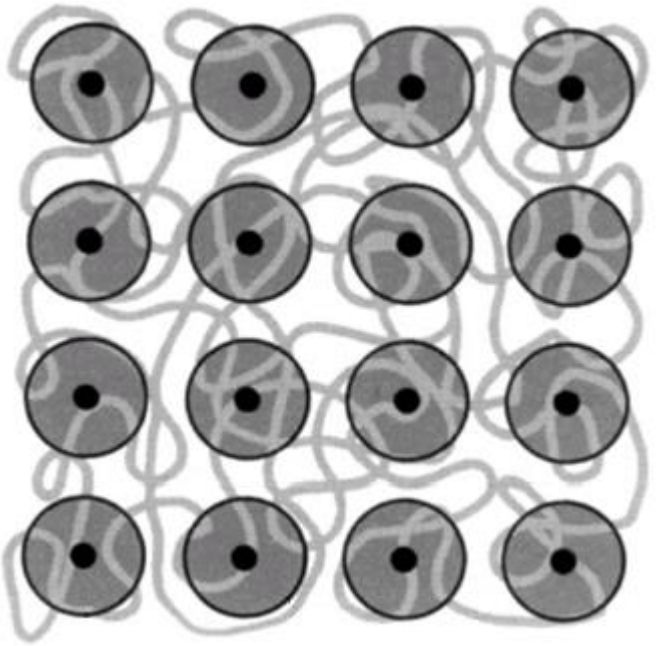
第五章 计算量子化学初步

微观世界的量子力学描述

- 为什么需要微观描述
  - 宏观性质的微观起源
  - 微观操纵与调控
- 物理模型
  - 原子核+电子
  - 电子结构理论
- 数学描述
  - 薛定谔方程



$$\hat{H}\psi(\mathbf{r},\mathbf{R}) = E\psi(\mathbf{r},\mathbf{R})$$

$$\hat{H} = -\sum_I \frac{\hbar^2}{2m_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_i \sum_I \frac{e^2 Z_I}{r_{iI}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{I<J} \frac{e^2 Z_I Z_J}{r_{IJ}}$$

波恩-奥本海默(BO)近似

- 对原子核和电子进行分离变量

$$\hat{H} = -\sum_I \frac{\hbar^2}{2m_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_i\sum_I \frac{e^2 Z_I}{r_{iI}} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{I<J}\frac{e^2 Z_I Z_J}{r_{IJ}}$$

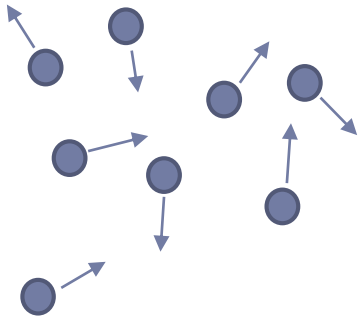
$$\psi(\mathbf{r},\mathbf{R}) = \psi_N(\mathbf{R})\cdot\psi_{el}(\mathbf{r};\mathbf{R})$$

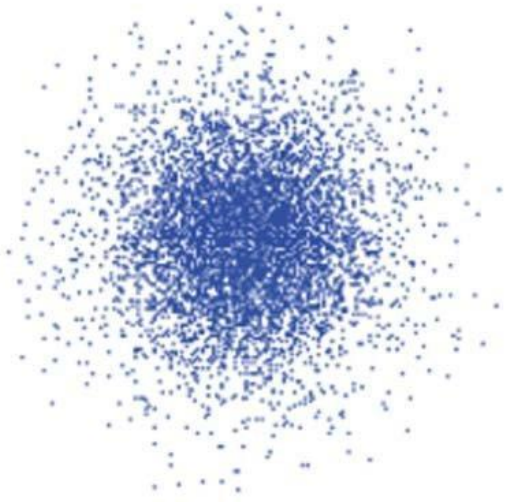
$$\hat{H}_{el}(\mathbf{R})\psi_{el}(\mathbf{r}) = E(\mathbf{R})\psi_{el}(\mathbf{r})$$

- 知道势能面E(R)以后可得到几何构型，反应能，过渡态，…
- 绝热近似 (eV >> 300K)

电子结构问题

Schrodinger Equation $\hat{H}\,\Psi\left(\vec{r};\vec{R}\right) = E(\vec{R})\Psi\left(\vec{r};\vec{R}\right)$





Macroscopic Particle

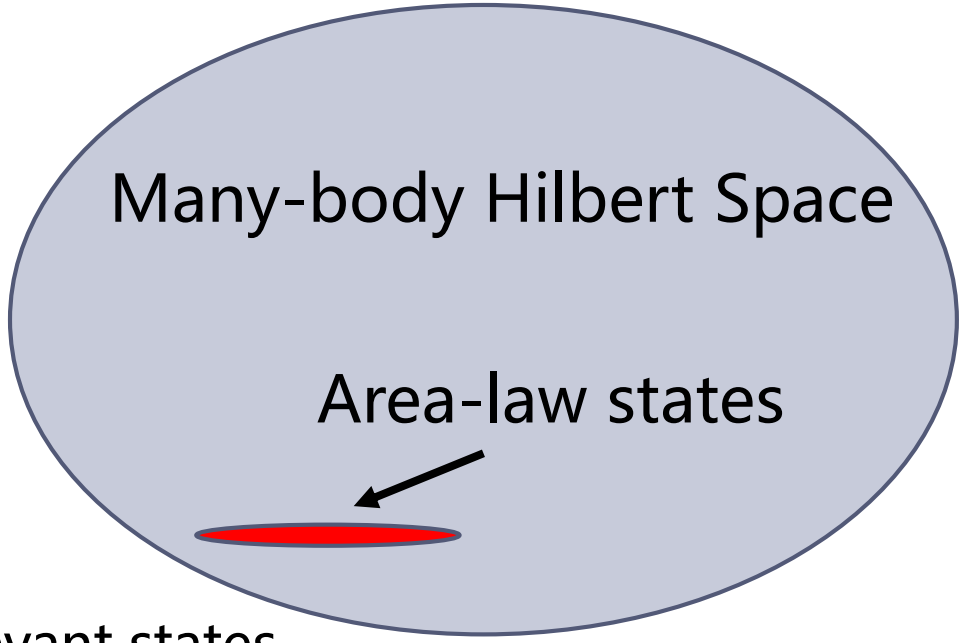
$(\vec{r}_1, \vec{p}_1; \ldots; \vec{r}_N, \vec{p}_N)$

Microscopic Particle

$\Psi(\vec{r}_1, \ldots, \vec{r}_N)$

希尔伯特空间

Low-energy states of realistic Hamiltonians are heavily constrained by locality so that they must obey the entanglement area-law.



Corner of relevant states

Orús, Ann. Phys. 349, 117 (2014)

单电子近似

- 假定电子间无相互作用

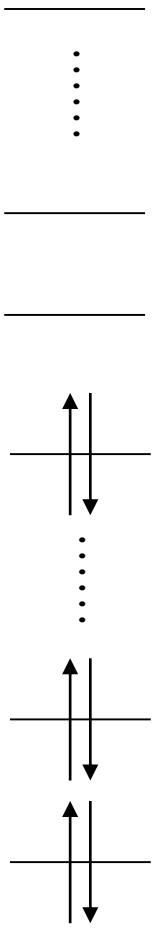
$$\hat{H} = \sum_i \hat{h}_i$$

$$\hat{h}_i = -\frac{\hbar^2}{2m_i}\nabla_i - \sum_I \frac{e^2 Z_I}{r_{iI}}$$

- 求解单电子方程，得到分子轨道

$$\psi_{HP} = \varphi_1\varphi_2\cdots\varphi_n$$

$$E = \sum_i \varepsilon_i$$



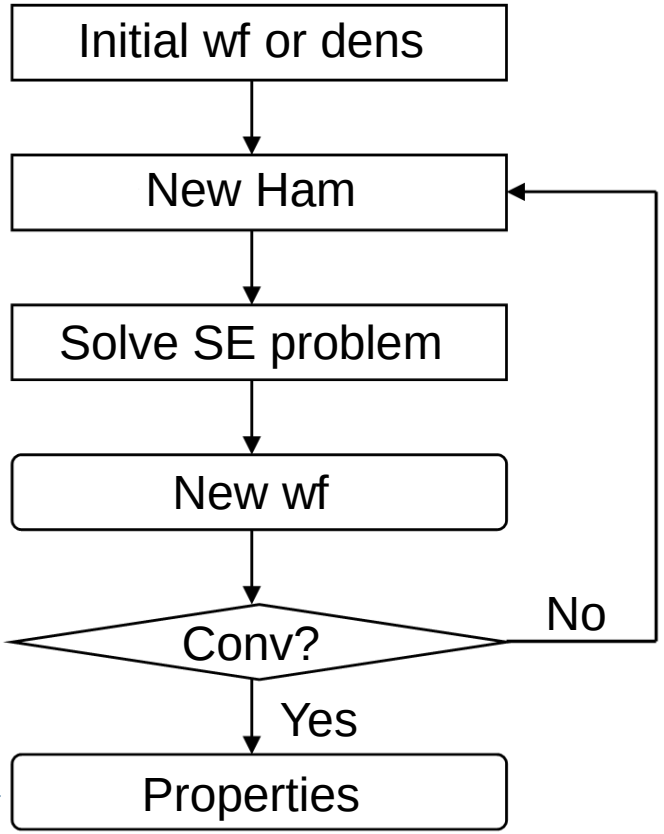
平均场近似

- 单电子哈密顿量可以通过变分得到

$$\hat{h}_i = -\frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_I \frac{e^2 Z_I}{r_{iI}} + v_i \qquad v_i = \sum_{j\neq i}\int \frac{e\rho_j}{r_{ij}} d\mathbf{r}_j \qquad \rho_j = |\varphi_j|^2 e$$

$$E^{HP} = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i\neq j}\iint \frac{|\varphi_i|^2 |\varphi_j|^2 e^2}{r_{ij}} d\mathbf{r}_i d\mathbf{r}_j$$

- 自洽求解(Hartree自洽场)
  - 收敛判据
  - Mixing algorithms



Slater行列式

- 交换反对称性

$$\hat{P}_{12}\left[\varphi_a(1)\varphi_b(2)\right]=\varphi_a(2)\varphi_b(1)\neq-\varphi_a(1)\varphi_b(2)$$

$$\psi_A=\frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2)-\varphi_a(2)\varphi_b(1)\right]$$

$$\psi_{SD}=\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_a(1) & \varphi_b(1)\\ \varphi_a(2) & \varphi_b(2)\end{vmatrix}$$

$$\psi_{SD}\left(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N\right)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1)\\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_N(2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N)\end{vmatrix}=\left|\varphi_1,\varphi_2\cdots\varphi_N\right\rangle$$

- Pauli不相容原理

Hartree-Fock自洽场

- 交换相互作用

$$\int \psi_{SD} \frac{1}{r_{12}} \psi_{SD} d\mathbf{r}_1 d\mathbf{r}_2 = J_{ab} - K_{ab}$$

$$J_{ab} = \int \psi_{HP} \frac{1}{r_{12}} \psi_{HP} d\mathbf{r}_1 d\mathbf{r}_2 = \int \varphi_a^2(1) \frac{1}{r_{12}} \varphi_b^2(2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$K_{ab} = \int \varphi_a(1) \varphi_b(1) \frac{1}{r_{12}} \varphi_a(2) \varphi_b(2) d\mathbf{r}_1 d\mathbf{r}_2$$

- LCAO

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{\hbar^2}{2m_e} \nabla^2 \right| \nu \right\rangle - \sum_I Z_I \left\langle \mu \left| \frac{1}{r_I} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma) \right]$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu(1) \phi_\nu(1) \frac{e^2}{r_{12}} \phi_\lambda(2) \phi_\sigma(2) d\mathbf{r}_1 d\mathbf{r}_2 \qquad P_{\lambda\sigma} = 2\sum_i^{occ} a_{\lambda i} a_{\sigma i}$$

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)=\hat{H}\psi(\mathbf{r},t)$$

↓

$$\hat{H}\psi(\mathbf{r})=E\psi(\mathbf{r})$$

↓ BO

$$\hat{H}(\mathbf{R})\psi(\mathbf{r})=E(\mathbf{R})\psi(\mathbf{r})$$

↓ 单电子近似

Hamiltonian: 忽略e-e相互作用→平均场(变分)

多体波函数：HP→SD

$$\hat{h}_i\varphi_i=\varepsilon_i\varphi_i$$

Beyond Hartree-Fock

- 电子关联效应

$$E_{\text{corr}} = E_{\text{nonrel}} - E_{\text{HF}}$$

  - 静态关联

    Weak or broken bonds involving a large occupation of antibonding orbitals cannot be described by a single determinant.

  - 动态关联

    Remaining correlation associated with the instantaneous short-range electron-electron interactions.

多体微扰方法

- 二阶Moller-Plesset (MP2)微扰

$$\hat{H}^{(0)} = \sum_i \hat{f}_i \qquad \psi_0^{(0)} = \psi_{HF} \qquad \hat{H}^{(0)}\psi_0^{(0)} = \left(\sum_{m=1}^{n} \varepsilon_m\right)\psi_0^{(0)}$$

$$E_0^{(0)} + E_0^{(1)} = E_{\mathrm{HF}}$$

$$E_0^{(2)} = \sum_{s\neq 0} \frac{|\langle \psi_s^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_s^{(0)}}$$

$$= \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \frac{|\langle ab | r_{12}^{-1} | ij \rangle - \langle ab | r_{12}^{-1} | ji \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

- MP2 does not work well at geometries far from equilibrium
- CASPT2

组态相互作用(CI)

- 从CIS到Full CI

$$|\psi\rangle = C_0 |\psi_0\rangle + \sum_{a}^{vir}\sum_{i}^{occ} C_i^a |\psi_i^a\rangle + \sum_{a<b}^{vir}\sum_{i<j}^{occ} C_{ij}^{ab} |\psi_{ij}^{ab}\rangle + \ldots$$

- MCSCF
  - CASSCF
  - RASSCF
- MRCI

耦合簇方法(CC)

- Size Consistency
- CC wavefunction ansatz

$$\psi = e^{\hat{T}}\psi_{HF} \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n \qquad \hat{T}_1\psi_0 = \sum_{a=n+1}^{\infty}\sum_{i=1}^{n} t_i^a \psi_i^a$$

$$\langle \psi_0 | \hat{H} | e^{\hat{T}}\psi_0 \rangle = E\langle \psi_0 | e^{\hat{T}}\psi_0 \rangle = E$$

$$\langle \psi_{ij}^{ab} | \hat{H} | e^{\hat{T}}\psi_0 \rangle = \langle \psi_0 | \hat{H} | e^{\hat{T}}\psi_0 \rangle \langle \psi_{ij}^{ab} | e^{\hat{T}}\psi_0 \rangle$$

- CCD

$$\langle \psi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2)\psi_0 \rangle = (E_{\mathrm{HF}} + \langle \psi_0 | \hat{H} | \hat{T}_2\psi_0 \rangle)\langle \psi_{ij}^{ab} | \hat{T}_2\psi_0 \rangle$$

传统的量子力学范式

- 波函数作为核心量

  外势v(r)→多体波函数→可观测的物理量(observables)

- 电荷密度

$$n(\mathbf{r}) = N\int d\mathbf{r}_2 \int d\mathbf{r}_3 ... \int d\mathbf{r}_n \psi^*(\mathbf{r}\mathbf{r}_2...\mathbf{r}_n)\psi(\mathbf{r}\mathbf{r}_2...\mathbf{r}_n)$$

- 单体算符

$$\langle\psi|\hat{o}|\psi\rangle = \int \psi^*(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)\sum_i \hat{o}_i\psi(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N$$

$$= N\int \psi^*(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)\hat{o}_1\psi(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N = \int d\mathbf{r}\hat{o}n(\mathbf{r})$$

Hohenberg-Kohn定理：量子力学新范式

- 定理一：全同费米子系统非简并基态的密度n唯一地决定了外势。

$$E_a^0 < \langle \psi_b^0 | \hat{H}_a | \psi_b^0 \rangle$$
$$= \langle \psi_b^0 | \hat{H}_a - \hat{H}_b + \hat{H}_b | \psi_b^0 \rangle$$
$$= \langle \psi_b^0 | \hat{v}_a - \hat{v}_b | \psi_b^0 \rangle + E_b^0$$

$$E_a^o < \int d\mathbf{r}[v_a - v_b]n^0(\mathbf{r}) + E_b^0$$

$$E_b^o < \int d\mathbf{r}[v_b - v_a]n^0(\mathbf{r}) + E_a^0$$

$$E_a^0 + E_b^0 < E_a^0 + E_b^0$$

Hohenberg-Kohn定理：变分法

- 定理二：给定外势v，存在F[n]定义在所有非简并基态密度n上，使得下述能量泛函当 n 取基态电子密度时取得唯一的最小值

$$E_v[n] = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + F[n]$$

$$\begin{aligned} E &= \min_{\psi} \langle \psi | \hat{H} | \psi \rangle = \min_{n} \min_{\psi \to n} \langle \psi | \hat{H} | \psi \rangle \\ &= \min_{n} [\min_{\psi \to n} \langle \psi | \hat{T} + \hat{U} | \psi \rangle + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r})] \\ &= \min_{n} \{F[n] + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r})\} \end{aligned}$$

交换关联能

- Levi泛函可写成动能和势能两部分

$$F[n]=T[n]+U[n]$$

- 动能的主要部分：

$$T_S[n]=-\frac{\hbar^2}{2m}\sum_i^n\int d\mathbf{r}\varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})$$

- 势能的主要部分：

$$U_H[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- 其余部分：

$$E_{XC}=E_{tot}-T_S-V-U_H=(T-T_S)+(U-U_H)$$

Kohn-Sham方程

- 电子密度

$$n(\mathbf{r}) = \sum_{i}^{occ} |j_i(\mathbf{r})|^2$$

- 变分可得

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

- Total energy

$$E_{KS} = \sum_{i}^{N}\varepsilon_i - \int d\mathbf{r} v_{eff}(\mathbf{r})n(\mathbf{r}) + \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

交换关联泛函

- 交换项

$$E_X[n] = \langle \psi_n^{SD} | \hat{U} | \psi_n^{SD} \rangle - U_H[n]$$

$$\langle \psi_n^{SD} | \hat{T} + \hat{U} | \psi_n^{SD} \rangle = T_S[n] + U_H[n] + E_X[n]$$

- 关联项

$$\begin{aligned} E_C[n] &= F[n] - (T_S[n] + U_H[n] + E_X[n]) \\ &= \langle \psi_n^{\min} | \hat{T} + \hat{U} | \psi_n^{\min} \rangle - \langle \psi_n^{SD} | \hat{T} + \hat{U} | \psi_n^{SD} \rangle \end{aligned}$$

局域密度近似(LDA)

- 交换关联能量密度

$$E_{XC}^{LDA}[n]=\int d\mathbf{r}n(\mathbf{r})\varepsilon_{XC}(n)$$

- 不同LDA间大同小异：
  - 交换

$$E_{X}^{LDA}\propto\int d\mathbf{r}n^{\frac{4}{3}}(\mathbf{r})$$

  - 关联：对精确QMC结果的不同参数化模型

    PW92, PZ81, VWN80

- 低估的交换能(~10%)，高估的关联能(~200%)

广义梯度近似(GGA)

- 引入密度梯度

$$E_{XC} \propto \int d\mathbf{r} f(n, \nabla n)$$

- 约化密度梯度

$$s = \frac{|\nabla n|}{n^{4/3}}$$

- 经验泛函 vs. 第一性原理泛函
  - BLYP etc popular in CHEM
  - PBE etc popular in PHYS

PBE Family

- PBE
  - Only satisfy conditions which are energetically significant.

$$E_X^{GGA} = \int d^3r\, n\epsilon_X^{unif}(n)F_X(s)$$

$$F_X(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \qquad \kappa = 0.804 \quad \mu = 0.2195$$

- revPBE: κ=1.245
- RPBE:

$$F_X(s) = 1 + \kappa(1 - e^{-\mu s^2/\kappa})$$

- PBEsol

$$\mu_{GE} = 10/81 \approx 0.1235$$

$$E_c[n] = \int d^3r n(\mathbf{r})\{\epsilon_c^{unif}(n(\mathbf{r})) + \beta t^2(\mathbf{r}) + \ldots\} \qquad \mu = \pi^2\beta/3$$

$\beta = 0.046 \approx 0.0375$ to best fit TPSS results

杂化密度泛函

- 引入精确交换

$$E_{XC} = aE_X^{exact} + (1-a)E_{XC}^{GGA}$$

- 三参数杂化泛函

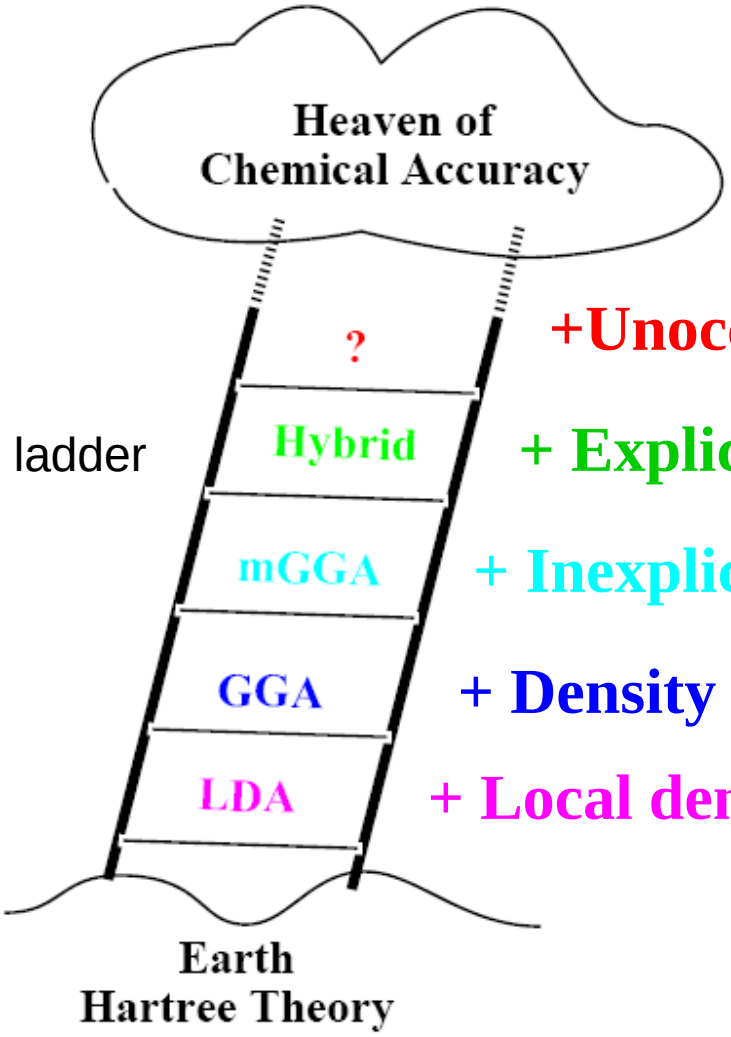
$$E_{XC}^{B3LYP} = a_0 E_X^{exact} + (1-a_0)E_X^{slater} + a_X E_X^B + a_c E_C^{VWN} + (1-a_c)E_C^{LYP}$$

- 屏蔽杂化泛函

$$\frac{1}{r} = \frac{1-\mathrm{erf}(\omega r)}{r} + \frac{\mathrm{erf}(\omega r)}{r}$$

$$E_{XC}^{HSE} = aE_X^{HF,SR} + (1-a)E_X^{PBE,SR} + E_X^{PBE,LR} + E_C^{PBE}$$

Jacobi之梯



jacob's ladder

+Unoccupied orbital information

+ Explicit occupied orbital information

+ Inexplicit occupied orbital information

+ Density gradient

+ Local density

DFT-D

- DFT-D

$$E_{DFT-D} = E_{KS} + C_6 R^{-6} f_{dmp}(R) \qquad C_6^{ij} = 2\,\frac{C_6^i C_6^j}{C_6^i + C_6^j}$$

- DFT-D2

$$f_{d,6}(r_{ij}) = \frac{s_6}{1 + e^{-d(r_{ij}/(s_R R_{0ij})-1)}}, \qquad R_{0ij} = R_{0i} + R_{0j}, \qquad C_6^{ij} = \sqrt{C_6^i C_6^j}$$

- DFT-D3

Dispersion coefficients from (TD)DFT A_mH_n and B_kH_l reference molecules

$$E_{\text{disp}} = -\frac{1}{2}\sum_{i=1}^{N_{at}}\sum_{j=1}^{N_{at}}\sum_{\mathbf{L}}{}' f_{d,6}(r_{ij,L})\,\frac{C_{6ij}}{r_{ij,L}^6} + f_{d,8}(r_{ij,L})\,\frac{C_{8ij}}{r_{ij,L}^8},$$

Zero damping

$$f_{d,n}(r_{ij}) = \frac{s_n}{1 + 6(r_{ij}/(s_{R,n} R_{0ij}))^{-\alpha_n}},$$

BJ damping

$$f_{d,n}(r_{ij}) = \frac{s_n\, r_{ij}^n}{r_{ij}^n + (a_1\, R_{0ij} + a_2)^n},$$

$$E^{(3)} = \sum_{ABC} f_{d,(3)}(\bar{r}_{ABC}) E^{ABC}, \qquad E^{ABC} = \frac{C_9^{ABC}(3\cos\theta_a \cos\theta_b \cos\theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3}$$

vdW-DF

- vdW-DF

$$E_{vdW-DF} = E^{GGA} + (E_c^{LDA} + E_c^{nl} - E_c^{GGA})$$

$$E_c^{nl} = \frac{1}{2}\iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1, q_2, r_{12})n(\mathbf{r}_2)$$

- opt-X
  - optB88-vdW
  - optB86b-vdW
- vdW-DF2
  - rPW86
  - Z_{ab}=-1.887

数值离散

- 单电子方程

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

- 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, $n = 0, \ldots, \pm N$, 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					
$N=2$	$-\frac{5}{2}$	$\frac{4}{3}$	$-\frac{1}{12}$				
$N=3$	$-\frac{49}{18}$	$\frac{3}{2}$	$-\frac{3}{20}$	$\frac{1}{90}$			
$N=4$	$-\frac{205}{72}$	$\frac{8}{5}$	$-\frac{1}{5}$	$\frac{8}{315}$	$-\frac{1}{560}$		
$N=5$	$-\frac{5269}{1800}$	$\frac{5}{3}$	$-\frac{5}{21}$	$\frac{5}{126}$	$-\frac{5}{1008}$	$\frac{1}{3150}$	
$N=6$	$-\frac{5369}{1800}$	$\frac{12}{7}$	$-\frac{15}{56}$	$\frac{10}{189}$	$-\frac{1}{112}$	$\frac{2}{1925}$	$-\frac{1}{16632}$

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)

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

  - 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, x2-y2, 3z2-r2
- 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

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

- 通用的完备基组(平面波基组)

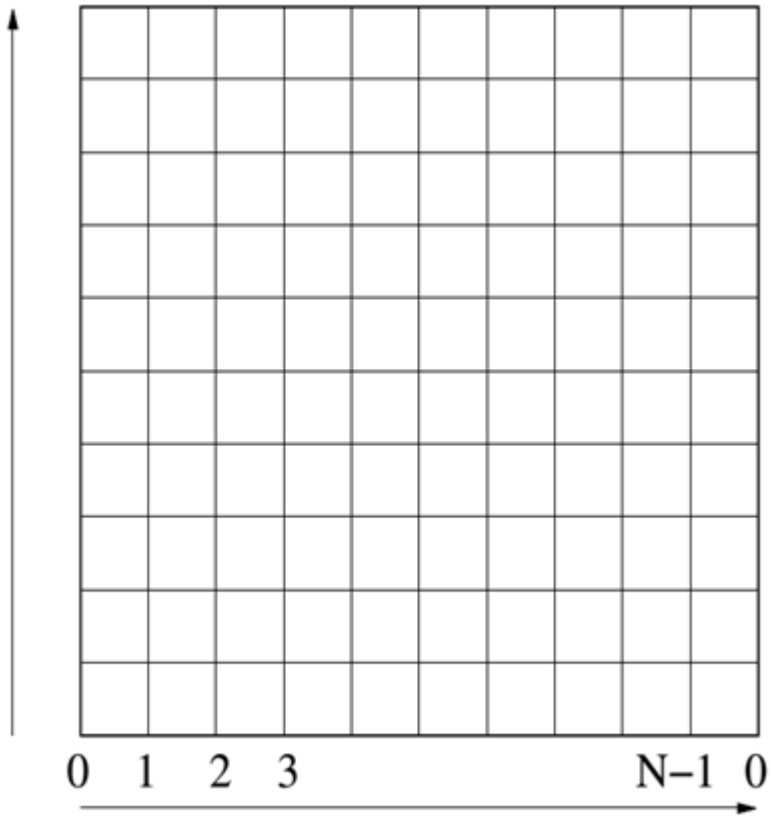
$$\varphi_n(\mathbf{r})=\int C_n(\mathbf{g})e^{i\mathbf{g}\cdot\mathbf{r}}d\mathbf{g}$$

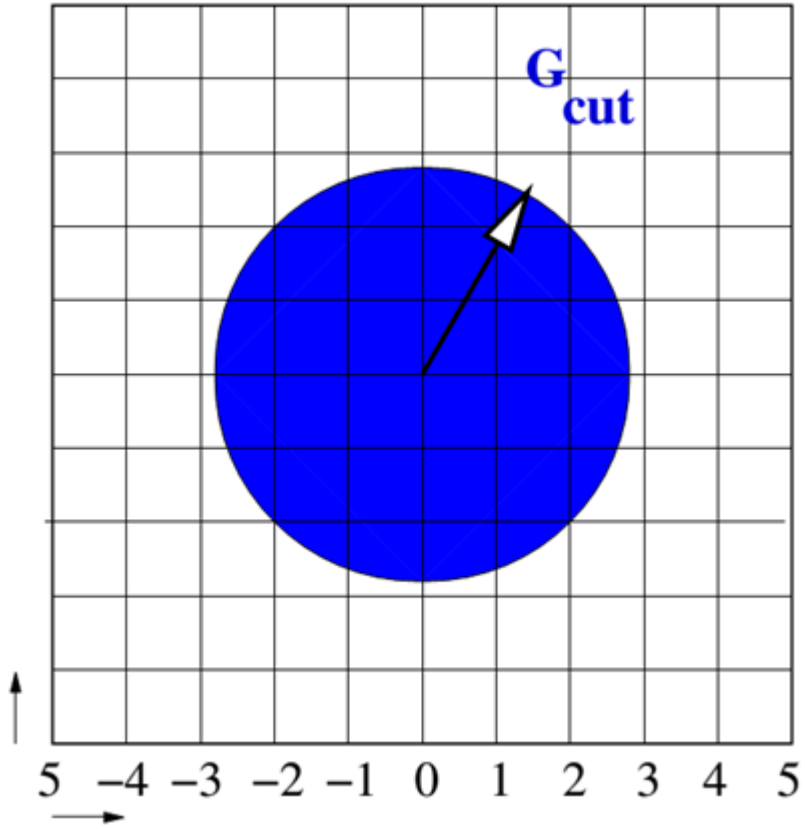
- 离散傅立叶变换

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

  - 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。

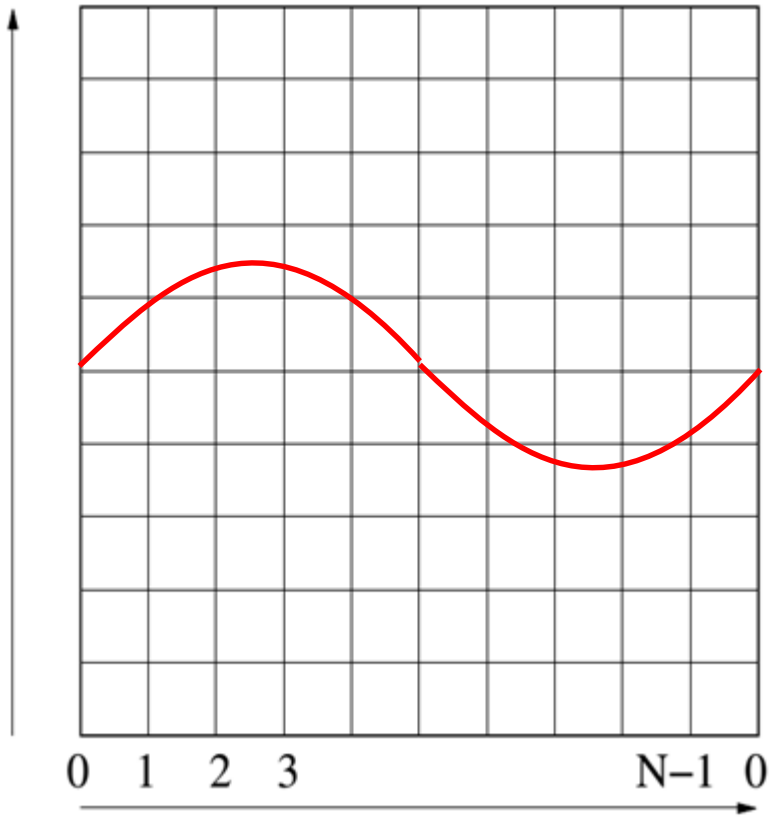
实空间与k空间对应

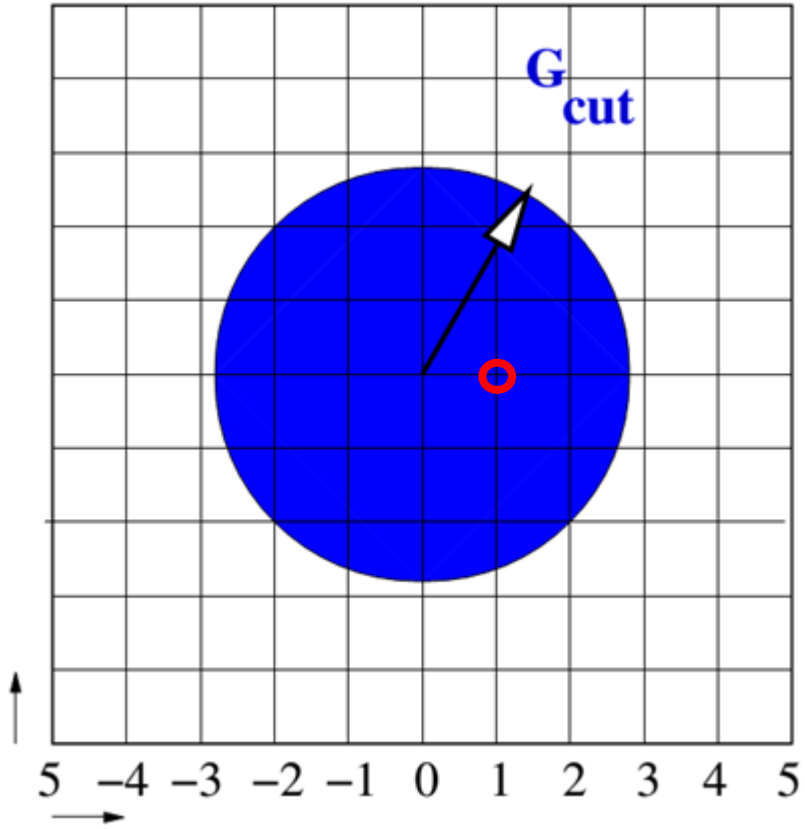




$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

实空间与k空间对应





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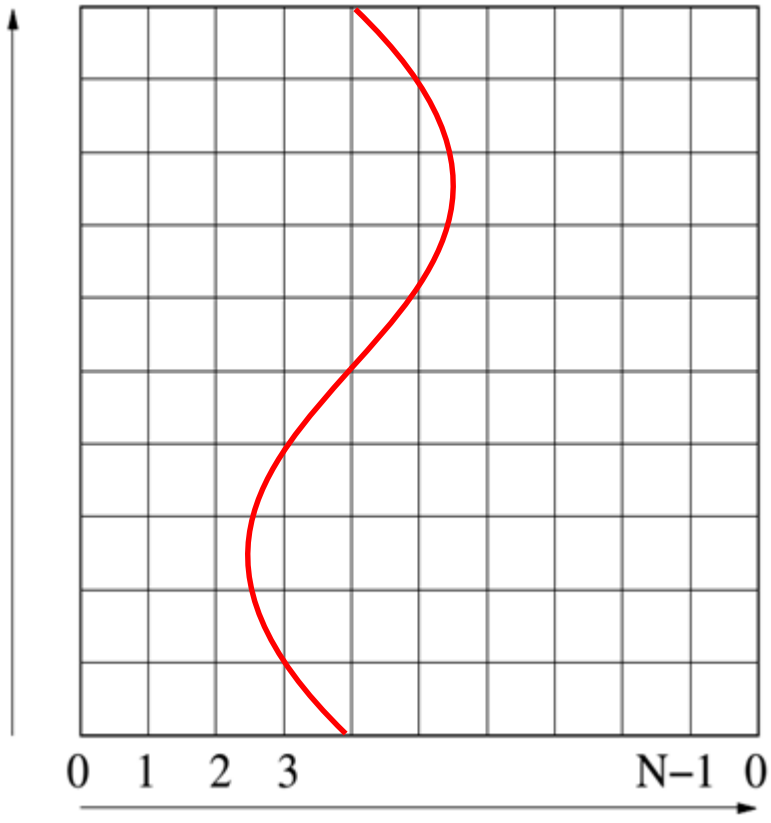
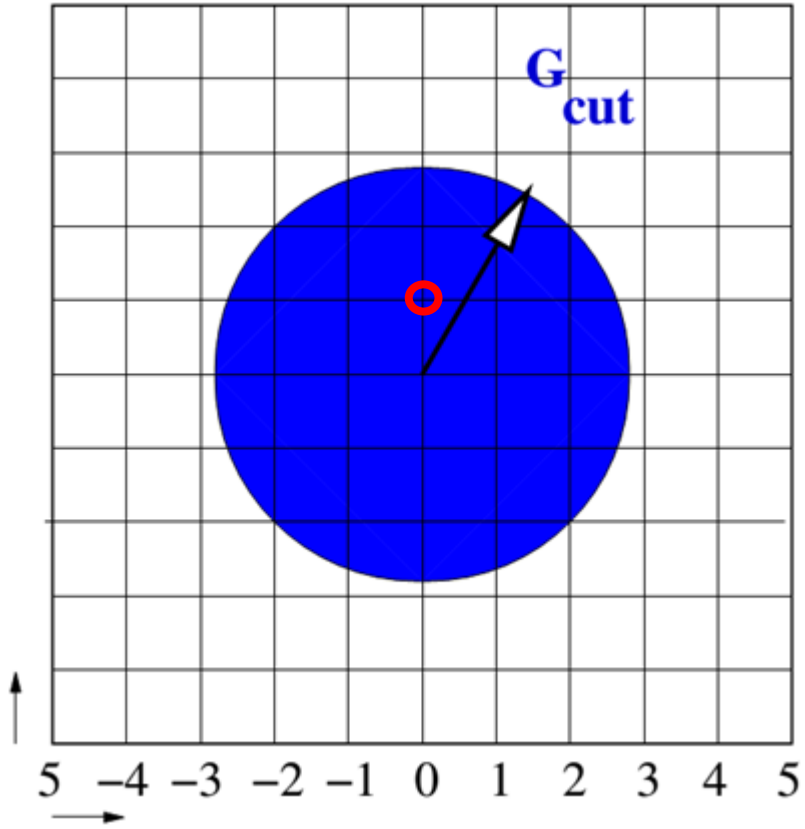
实空间与k空间对应





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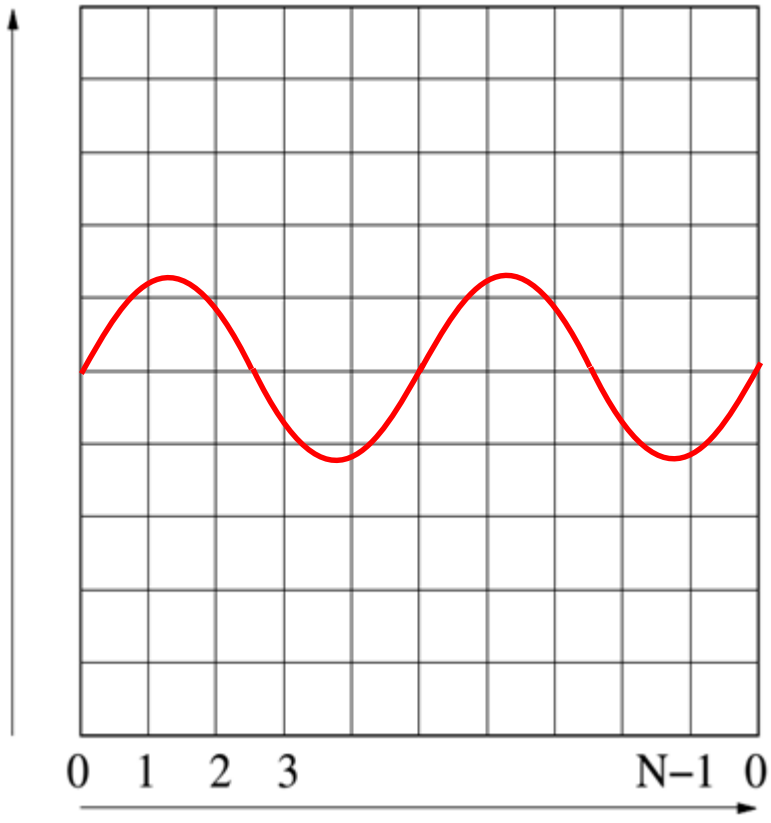
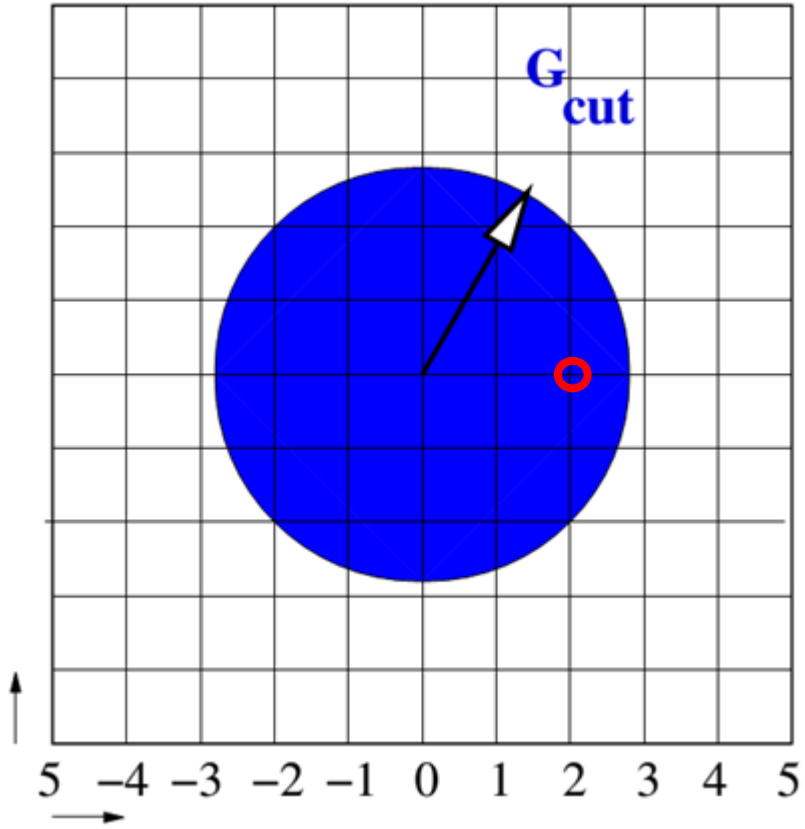
实空间与k空间对应





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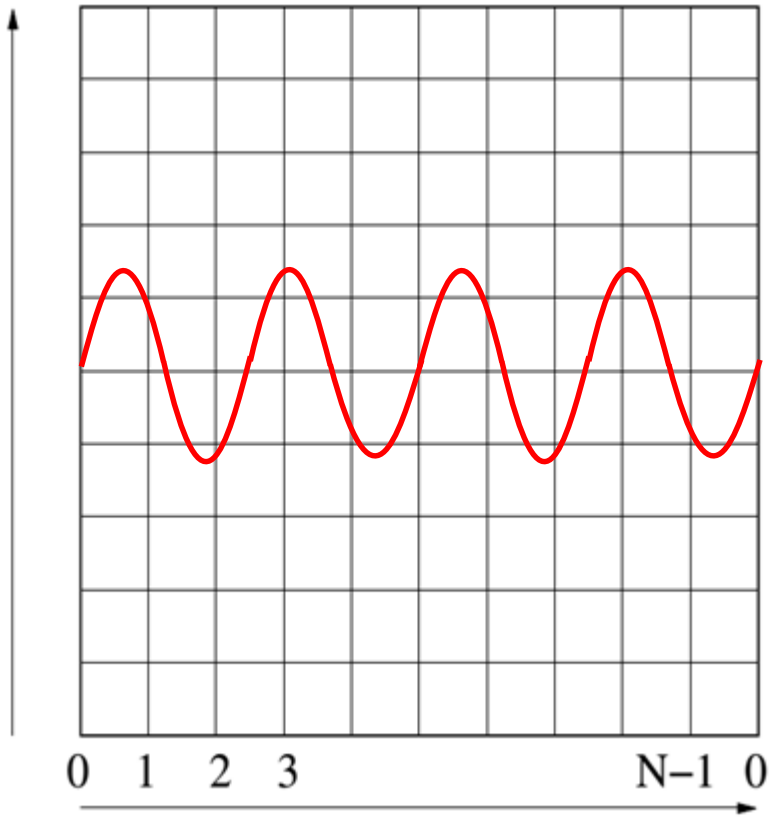
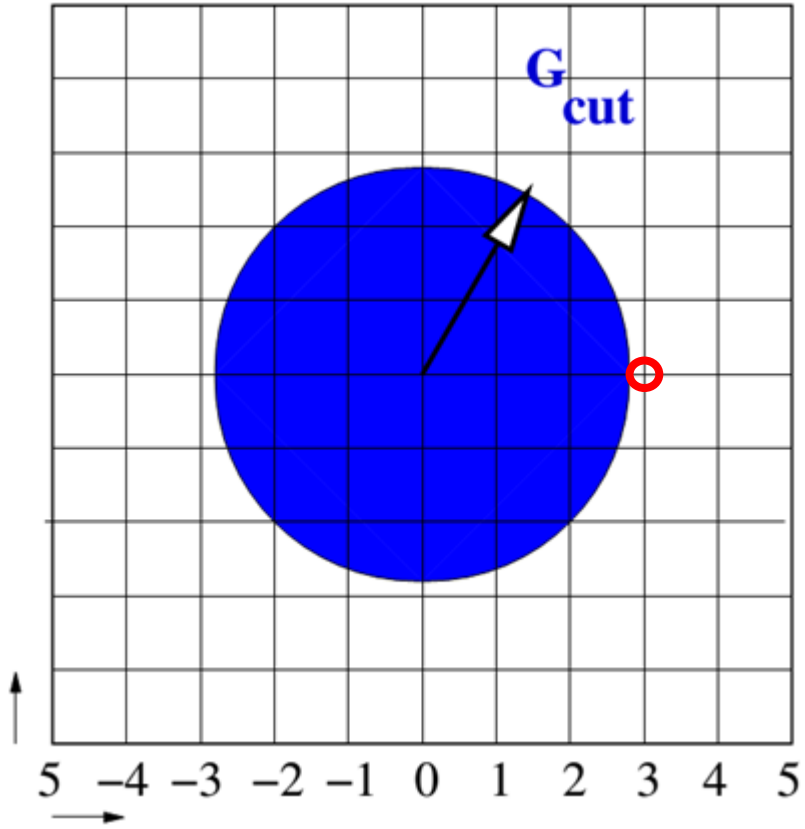
实空间与k空间对应





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平面波基组

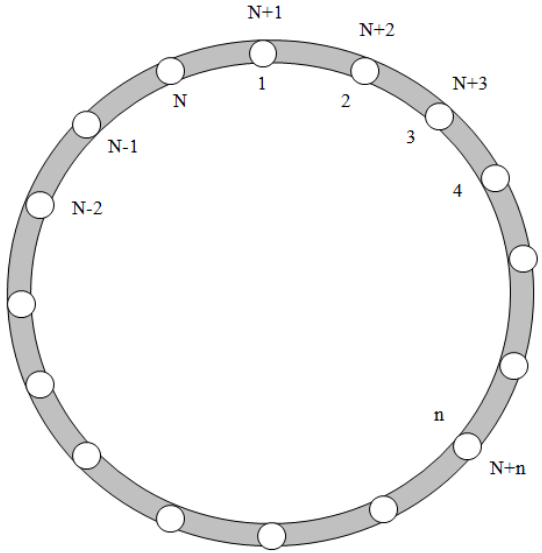
- 单粒子波函数(非周期)的离散化
  - 周期性边界条件 (布洛赫定理)

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

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

  - 波恩－冯卡曼边界条件

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



基于HF理论的半经验算法

- HF计算的瓶颈：N^4个双电子积分
- Motivation
  - 加快计算速度
  - 通过做化学上的正确的近似，原则上还有可能包含部分关联效应，提高精度。
  - 更易得到解析的梯度
- complete neglect of differential overlap (CNDO)
- intermediate neglect of differential overlap (INDO)
- neglect of diatomic differential overlap (NDDO)
  - MNDO、AM1、PM3、PDDG

Extended Huckel Theory

- 忽略芯电子，对价电子采用STO，这样可以得到重迭矩阵S
- 哈密顿矩阵

$$H_{\mu\mu} = -VSIP$$

$$H_{\mu\nu} = \frac{1.75}{2}(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$$

- 定性的分子轨道分析

Slater-Koster紧束缚近似

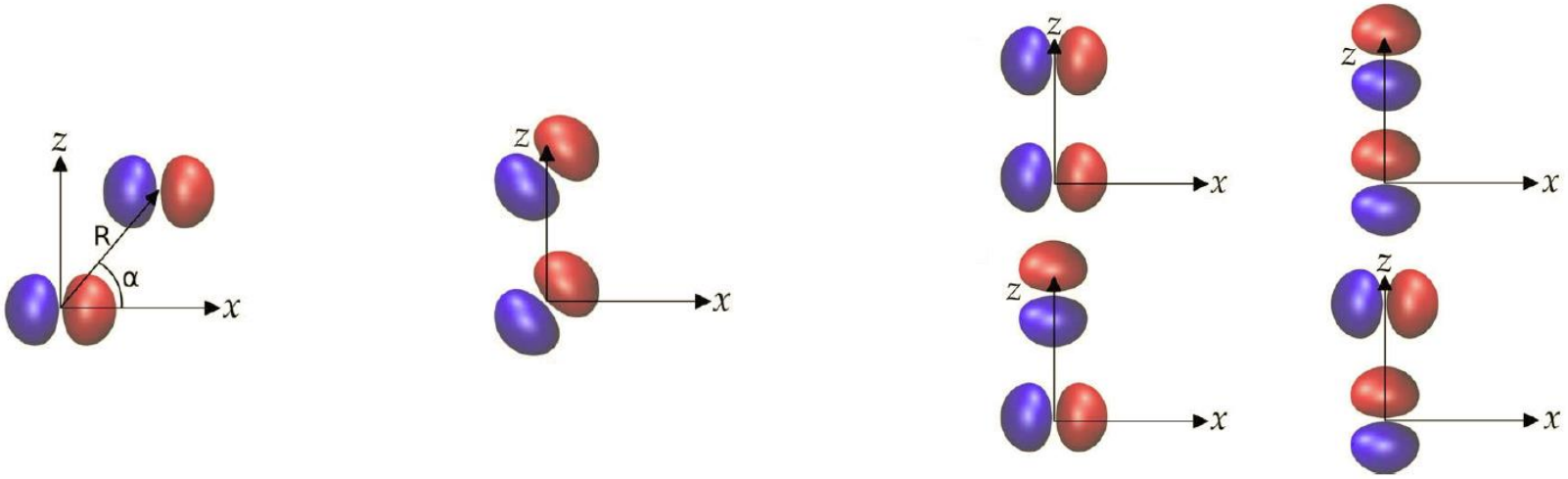
- TB近似可以作为一种插值方法
- SK在参数化Hamiltonian矩阵元时，所采用的近似
  - 正交化基组
  - 只考虑较近的原子之间的相互作用
  - 只考虑特定能量区间里的原子轨道
  - 假设Hamiltonian可以分解为原子中心对称项之和，忽略双中心以上的项

$$\int \phi_n^*(\mathbf{r}-\mathbf{R}_i)\hat{h}\phi_m(\mathbf{r}-\mathbf{R}_j)d^3r$$

- 引入重迭矩阵:产生更多的参数，同时避免Lowdin正交化带来的离域性。

Slater-Koster Transformation

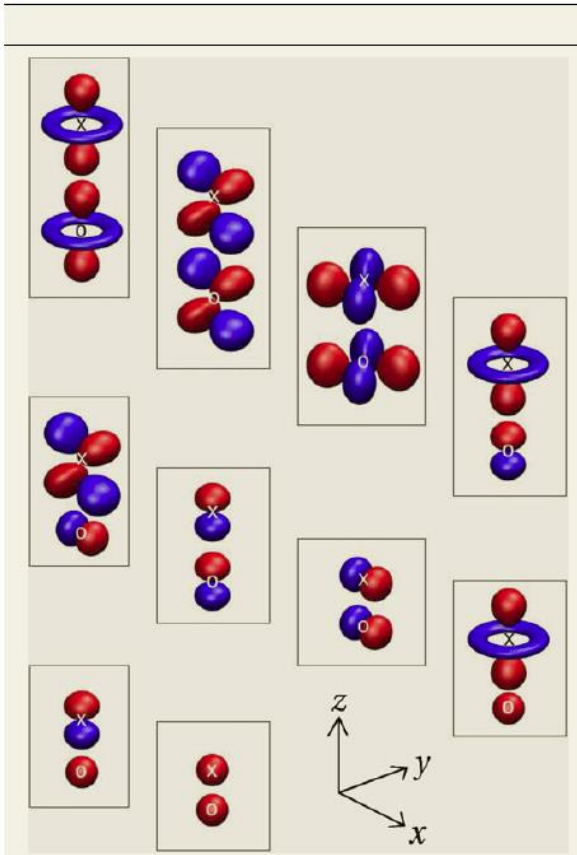
- 双中心积分可以通过方向余弦由一组SK积分求得



- 列表、解析关系[PRB 69, 233101]

Slater-Koster Transformation

- 只考虑s,p,d轨道，SK积分的个数为14个：ssσ, spσ, ppσ, ppπ, sdσ, pdσ, pdπ, ddσ, ddπ, ddδ, psσ, dsσ, dpσ, dpπ



τ	$\tilde{Y}_{\tau_1}(\theta_1,\varphi)$	$\tilde{Y}_{\tau_2}(\theta_2,\varphi)$
$dd\sigma$	$d_{3z^2-r^2}$	$d_{3z^2-r^2}$
$dd\pi$	d_{zx}	d_{zx}
$dd\delta$	d_{xy}	d_{xy}
$pd\sigma$	p_z	$d_{3z^2-r^2}$
$pd\pi$	p_x	d_{zx}
$pp\sigma$	p_z	p_z
$pp\pi$	p_x	p_x
$sd\sigma$	s	$d_{3z^3-r^2}$
$sp\sigma$	s	p_z
$ss\sigma$	s	s

$$S_{\mu\nu}(\tau) = S_{\nu\mu}(\tau)\cdot(-1)^{l_\mu+l_\nu}$$

Quantum Computation

"*Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical.*"

Feynman, Int. J. Theor. Phys. 21,467 (1982)

Classical

0

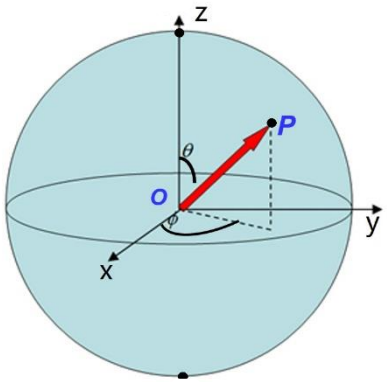
1

N $|\psi\rangle = |0\rangle \text{ or } |1\rangle$

Universal Bit Operator

$\{NAND, NOR, NOT\}$

Quantum



$|\psi\rangle = a|0\rangle + b|1\rangle$ 2^N

$= \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$

Universal Qubit Operators

$\{H, T, CNOT\}$

Two Qubits and Entanglement

Basis set

$$00 \equiv \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\end{bmatrix} \qquad 01 \equiv \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\1\\0\\0\end{bmatrix}$$

$$10 \equiv \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\1\\0\end{bmatrix} \qquad 11 \equiv \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

Composite state

$$\begin{bmatrix}\alpha\\\beta\end{bmatrix} \otimes \begin{bmatrix}\gamma\\\delta\end{bmatrix} = \begin{bmatrix}\alpha\begin{bmatrix}\gamma\\\delta\end{bmatrix}\\ \beta\begin{bmatrix}\gamma\\\delta\end{bmatrix}\end{bmatrix} = \begin{bmatrix}\alpha\gamma\\\alpha\delta\\\beta\gamma\\\beta\delta\end{bmatrix}$$

Bell set

$$\psi \otimes \phi = \begin{bmatrix}1/\sqrt{2}\\0\\0\\1/\sqrt{2}\end{bmatrix} \quad ?$$

Quantum Gates

T gate $T = \begin{bmatrix} 1 & 0 \\ 0 & e^{i\pi/4} \end{bmatrix}$

Hadamard gate $H = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$

Pauli gates $X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = HT^4H$ $Y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = T^2HT^4HT^6$ $Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = T^4$

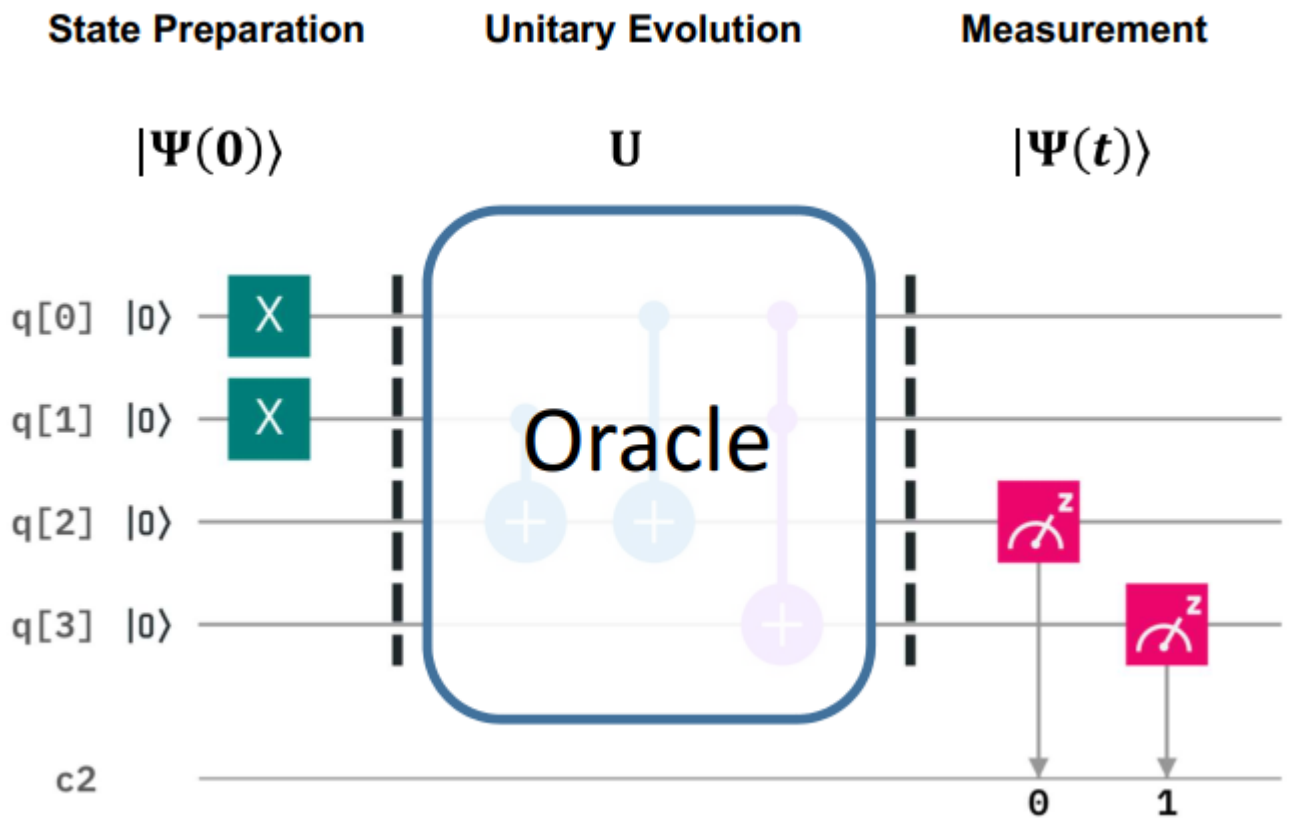
CNOT gates $\mathrm{CNOT} = \begin{bmatrix} 1\,0\,0\,0 \\ 0\,1\,0\,0 \\ 0\,0\,0\,1 \\ 0\,0\,1\,0 \end{bmatrix}$

$|00\rangle \rightarrow |00\rangle$
$|01\rangle \rightarrow |01\rangle$
$|10\rangle \rightarrow |11\rangle$
$|11\rangle \rightarrow |10\rangle$

Entangling gate

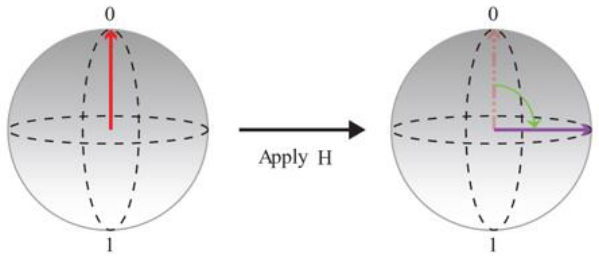
$$\begin{bmatrix} a\,b \\ c\,d \end{bmatrix} \otimes \begin{bmatrix} e\,f \\ g\,h \end{bmatrix} = \begin{bmatrix} ae\;af\;be\;bf \\ ag\;ah\;bg\;bh \\ ce\;cf\;de\;df \\ cg\;ch\;dg\;dh \end{bmatrix}$$

Quantum Algorithm

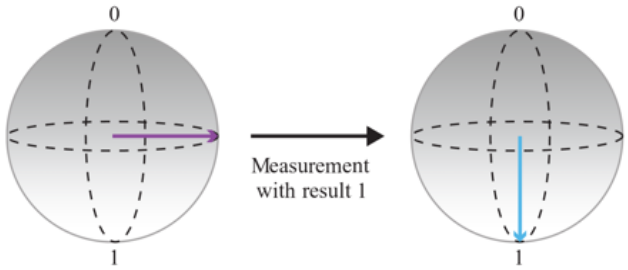


Random Number Generator

- start with a qubit initialized in the state 0
- apply H to create a superposition in which the probabilities for 0 and 1 are the same



- measure the qubit and save the output

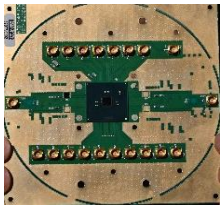


- call this operation several times to create binary random number 100101001010

Quantum Computers

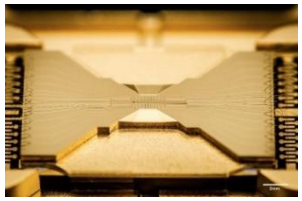
Q System One

2019.01
IBM



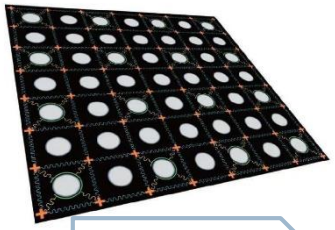
Horse Ridge

2019.12
Intel



QV4000000

2020.10
IonQ

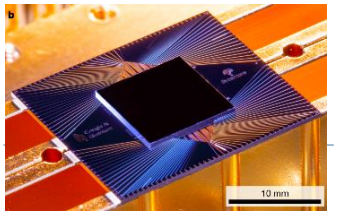


祖冲之号

2021.05
USTC

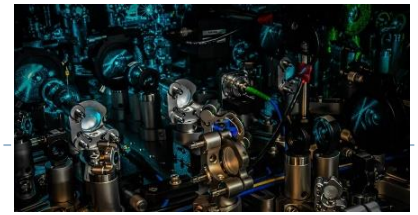
2019.09
Google

Sycamore



2020.10
Honeywell

QV128



2020.12
USTC

九章

Variational Quantum Eigensolver

- A hybrid quantum-classical algorithm
- Parametrized wave function

$$|\Psi(\theta)\rangle = U(\theta)|\Psi_0\rangle$$

$U(\theta)$ is a unitary operator or a product of unitary operators

- Rayleigh-Ritz variational principle

$$|\Psi\rangle = e^{\hat{T}-\hat{T}^+}|\Psi_0\rangle$$

$$E = \min_{\theta}\langle\Psi(\theta)\left|\hat{H}\right|\Psi(\theta)\rangle$$

Peruzzo, et. al, *Nature Comm.* 5, 4213 (2014)

本章小结

- ✓ 单电子近似与Hartree-Fock理论；
- ✓ 电子关联与后HF方法；
- ✓ 密度泛函理论与交换关联泛函；
- ✓ 单电子方程离散化与基组；
- ✓ 半经验电子结构计算方法；
- ✓ 量子计算化学(Quantum^2 Chemistry)。