电子结构理论简介

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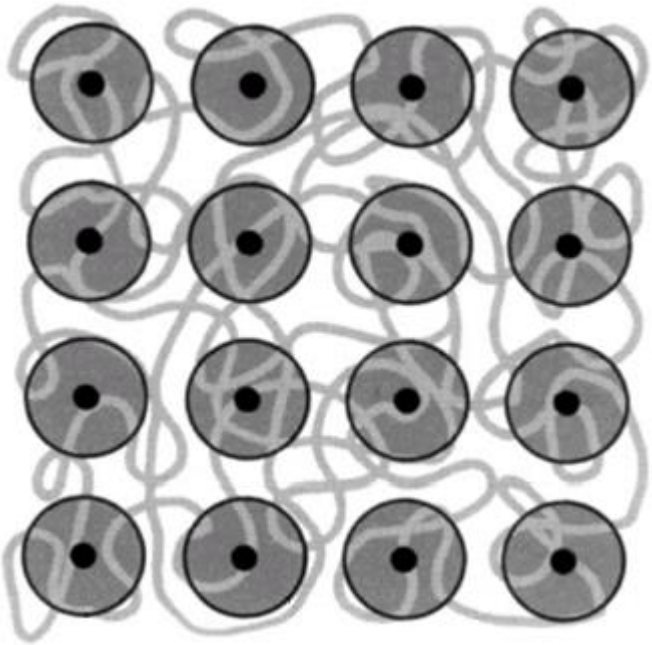
Outline

- Hartree-Fock理论及post-HF方法
- DFT理论框架
  - Hohenberg-Kohn定理：多体理论
  - Kohn-Sham方程：有效单体理论
- 交换关联泛函
  - Jacob之梯
  - 误差分析
- 准粒子模型
  - GW近似
- 半经验电子结构模型

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)

单电子近似

- 假定电子间无相互作用

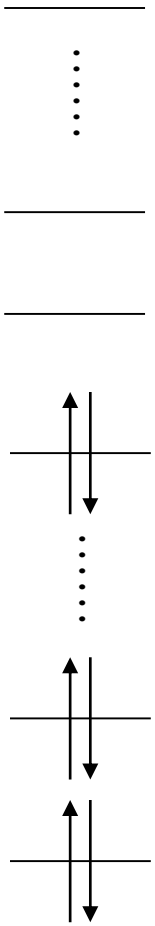
$$\hat{H} = \sum_i \hat{h}_i$$

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

- 求解单电子方程，得到分子轨道

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

$$E = \sum_i \varepsilon_i$$



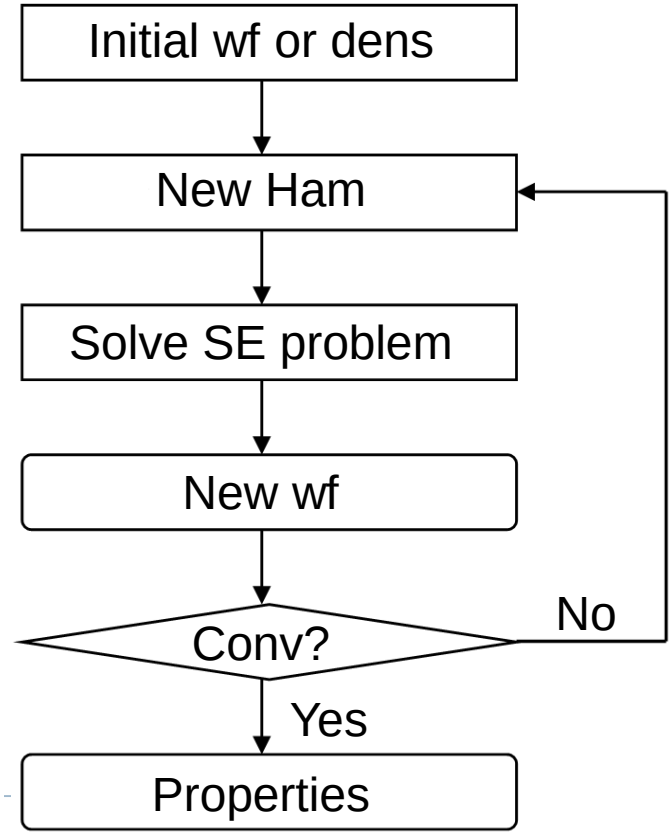
平均场近似

- 单电子哈密顿量可以通过变分得到

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

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

- 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不相容原理与交换相互作用

Hartree-Fock自洽场

- 用Slater行列式作为多体波函数

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

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

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

- LCAO

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

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

Koopmann定理

- 单电子轨道能量等于N电子体系从第j个轨道上取走一个电子并保持N－l个电子状态不不变的总能变化值。

$$\varepsilon_j = \int \varphi_j^*(\vec{r})\varepsilon_j\varphi_j(\vec{r})\,d\vec{r} = \left\langle \Phi_N \middle| H_N \middle| \Phi_N \right\rangle - \left\langle \Phi_{N-1} \middle| H_{N-1} \middle| \Phi_{N-1} \right\rangle$$

- 推广：系统中一个电子由状态j转移到态i而引起系统能量的变化为对应分子轨道能量差。

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

$$\downarrow$$

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

$$\downarrow \text{ BO}$$

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

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

$$\downarrow$$

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

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.

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

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

耦合簇方法(CC)

- 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

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

- 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。

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

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

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

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

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

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

KS轨道与能量

- KS轨道并不是严格意义上的单电子轨道。KS轨道的引入仅需要保证上面的电子密度表达式，并没有对应的多体波函数。
- Overall the KS orbitals are a good basis for qualitative interpretation of molecular orbitals.
- Koopmans' theorem in DFT: the eigenvalue of the uppermost occupied KS orbital equals the exact ionization potential.

JACS **1999**, 121, 3414; *PRL* **1982**, 49, 1691; *PRB* **1985**, 31, 3231

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

其他GGA泛函

- AM05
  - subsystem functional approach

$$X = 1 - \alpha s^2/(1 + \alpha s^2),$$

$$\hat{\epsilon}_x(\mathbf{r};[n]) = \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r}))[X + (1 - X)F_x(s)],$$

$$\epsilon_c(\mathbf{r};[n]) = \epsilon_c^{\mathrm{LDA}}(n(\mathbf{r}))[X + (1 - X)\gamma],$$

$$F_x^{\mathrm{LAA}}(s) = (cs^2 + 1)/(cs^2/F_x^b + 1),$$

Linear Airy Approximation

meta-GGA

- 引入密度拉普拉斯或者动能密度

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

- 无法直接计算泛函微分：OEP (OPM)

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta n(\mathbf{r})}$$

$$= \int d^3\mathbf{r}' \int d^3\mathbf{r}'' \sum_i [\frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} \frac{\delta v_s(\mathbf{r}'')}{\delta n(\mathbf{r})} + c.c]$$

- Self consistent mGGA

$$v_{\mathrm{xc}}^{\mathrm{MGGA}}(\mathbf{r})\psi_n(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{MGGA}}}{\delta n}\psi_n \to \left[\frac{\partial e_{\mathrm{xc}}^{\mathrm{MGGA}}}{\partial n} - \nabla \cdot \left(\frac{\partial e_{\mathrm{xc}}^{\mathrm{MGGA}}}{\partial \nabla n}\right)\right]\psi_n - \frac{1}{2}\nabla \cdot \left\{\frac{\partial e_{\mathrm{xc}}^{\mathrm{MGGA}}}{\partial \tau}\nabla \psi_n\right\},$$

$$v_{\mathrm{xc}}^{\mathrm{MGGA}}(\mathbf{r}) \to v_{\mathrm{xc}}^{\mathrm{GGA}}(\mathbf{r}) - \frac{1}{2}\nabla \cdot \{\mu_{\mathrm{xc}}(\mathbf{r})\nabla\}$$

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

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

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

双杂化泛函

- 三参数杂化泛函

$$E_{XC}^{B3} = E_{XC}^{LDA} + c_1(E_X^{exact} - E_X^{LDA}) + c_2 \Delta E_X^{GGA} + c_3 \Delta E_C^{GGA}$$

- 双杂化

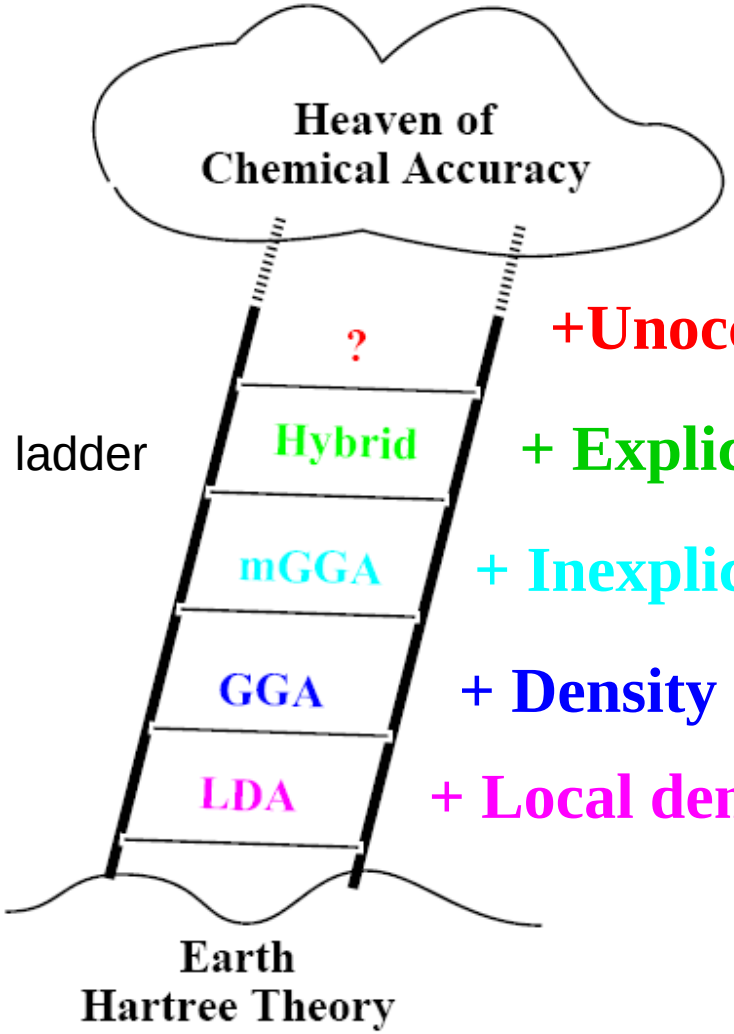
$$E_{XC}^{DH} = E_{XC}^{LDA} + c_1(E_X^{exact} - E_X^{LDA}) + c_2 \Delta E_X^{GGA} + c_3(E_C^{PT2} - E_C^{LDA}) + c_4 \Delta E_C^{GGA}$$

- PT2

$$E_C^{PT2} = -\frac{1}{4}\sum_{ij}\sum_{\alpha\beta}\frac{|\langle \varphi_i \varphi_j | \hat{v}_{ee} | \varphi_\alpha \varphi_\beta \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_\alpha - \varepsilon_\beta}$$

Jacobi之梯

jacob's ladder



+Unoccupied orbital information

+ Explicit occupied orbital information

+ Inexplicit occupied orbital information

+ Density gradient

+ Local density

DFT+U

- Mott绝缘体，on-site库仑排斥
- Hubbard模型

$$H = -t \sum_{<i,j>,\sigma} (c_{i,\sigma}^{\dagger} c_{j,\sigma} + h.c.) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

- 加入一个惩罚函数

$$E^{DFT+U} = E^{DFT} + U^{eff} \sum_{\sigma} \left(\sum_{m_i} n_{m_i m_i}^{\sigma} - \sum_{m_1 m_2} n_{m_1 m_2}^{\sigma} n_{m_2 m_1}^{\sigma} \right)$$

- Molecular DFT+U
  - CO on Rh(111) surface

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

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

- 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

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

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

DFT-TS

- DFT-TS

$$C_{6AB} = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)d\omega,$$

$$\alpha_i = \nu_i\,\alpha_i^{free}, \quad C_{6ii} = \nu_i^2\,C_{6ii}^{free}, \quad R_{0i} = \left(\frac{\alpha_i}{\alpha_i^{free}}\right)^{\frac{1}{3}} R_{0i}^{free}.$$

$$\nu_i = \frac{\int r^3\,w_i(\mathbf{r})\mathbf{n}(\mathbf{r})\,\mathbf{d^3r}}{\int r^3\,n_i^{free}(\mathbf{r})\,\mathbf{d^3r}}, \qquad C_{6ij} = \frac{2C_{6ii}\,C_{6jj}}{[\frac{\alpha_j}{\alpha_i}C_{6ii} + \frac{\alpha_i}{\alpha_j}C_{6jj}]}. \qquad R_{0ij} = R_{0i} + R_{0j}.$$

Hirshfeld partitioning

- TS+SCS

$$\alpha_i^{SCS}(\omega) = \alpha_i(\omega) - \alpha_i(\omega)\sum_{i\neq j}\tau_{ij}\alpha_j^{SCS}(\omega), \qquad \alpha_i(\omega) = \frac{\alpha_i}{1+(\omega/\omega_i)^2}, \qquad \omega_i = \frac{4}{3}\frac{C_{6ii}}{(\alpha_i)^2}$$

$$C_{6ii} = \frac{3}{\pi}\int_0^\infty \alpha_i^{SCS}(\omega)\alpha_i^{SCS}(\omega)\,d\omega. \qquad R_{0i}^{SCS} = \left(\frac{\alpha_i^{SCS}}{\alpha_i}\right)^{1/3} R_{0i}.$$

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

自相互作用误差

- 单电子体系

$$E_C[n]=0$$

$$E_X[n]=-E_H[n]$$

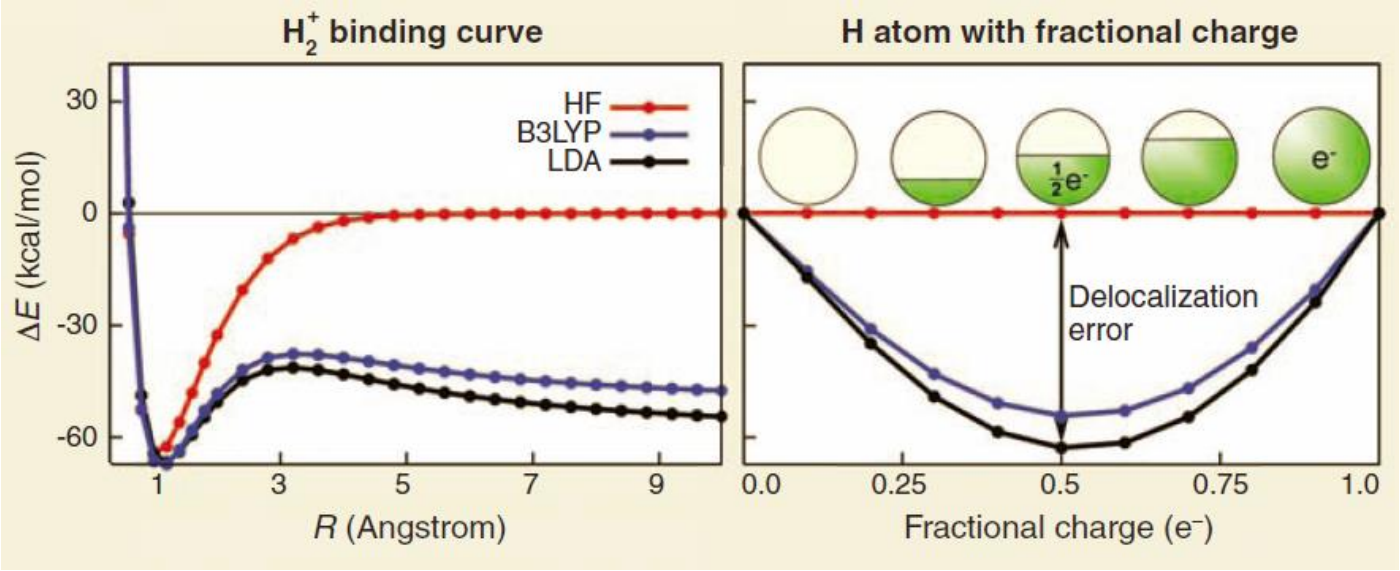
- 自相互作用修正

$$E_{XC}^{SIC}[n]=E_{XC}[n]-\sum_i^N(E_H[n_i]+E_{XC}[n_i])$$

- 头痛医头，脚痛医脚？

离域化误差

- H_2^+分子离子解离

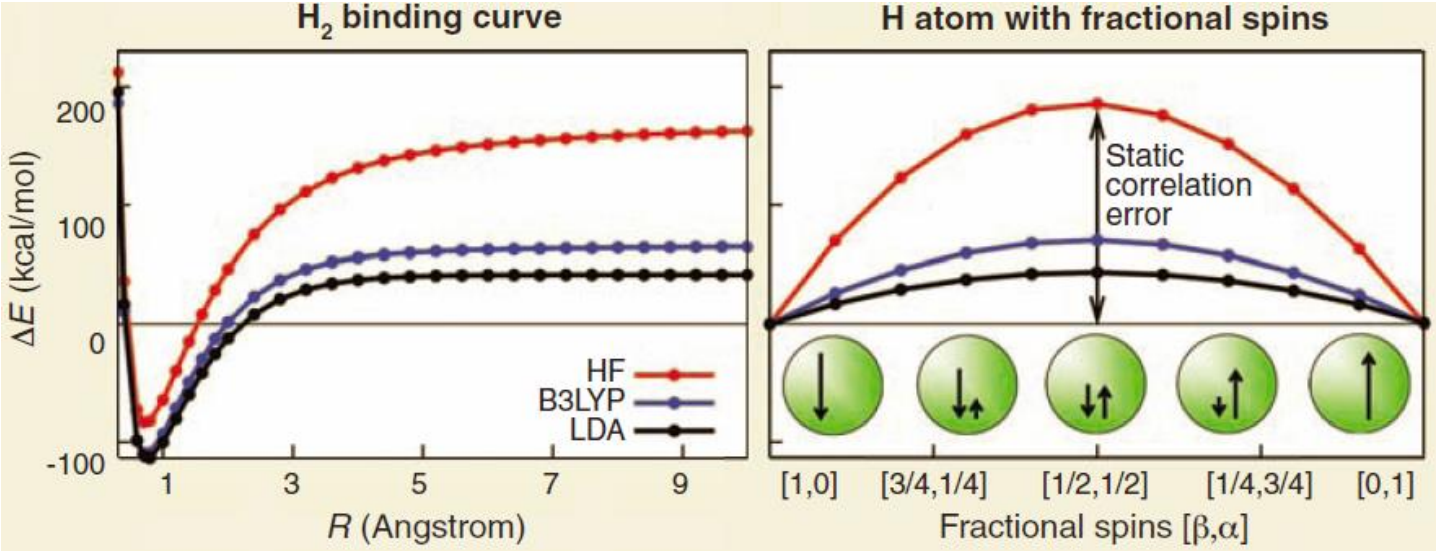


- 低估活化能，高估电导，低估能隙，...

Science, **321**, 792 (2008)

静态关联误差

- H_2分子解离



- broken-symmetry open-shell calculation

Science, **321**, 792 (2008)

准粒子与自能

- 准粒子方程

$$\left[-\frac{1}{2}\nabla^2 + V_H + V_{ext}\right]\Psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_i)\Psi_i(\mathbf{r}')d\mathbf{r}' = E_i\Psi_i(\mathbf{r})$$

- Hedin自洽方程组

$$\begin{aligned}
\Sigma(12) &= i\int d(34)G(14)W(1^+3)\Gamma(423) \\
W(12) &= v(12) + \int d(34)v(42)P(34)W(13) \\
P(12) &= -i\int d(34)G(23)G(42)\Gamma(341) \\
\Gamma(123) &= \delta(12)\delta(13) + \int d(4567)\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)
\end{aligned}$$

典型近似

- Hartree近似

$$\Sigma(12) = 0$$

- Hartree-Fock近似

$$\Sigma(12) = iG(12)v(12)$$

- DFT-LDA

$$\Sigma(12) = V_{xc}(1)\delta(12)$$

GW近似

- 所有的量都可以通过格林函数表达

GW

$$\Sigma(12) = i\int d(34)G(14)W(1^{+}3)\Gamma(423)$$

$$W(12) = v(12) + \int d(34)v(42)P(34)W(13)$$

$$P(12) = -i\int d(34)G(23)G(42)\Gamma(341)$$

$$\Gamma(123) = \delta(12)\delta(13) + \cancel{\int d(4567)\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)}$$

GW计算

- G0W0
  - DFT→unocc orb, WAVEDER→G0,W0→Σ correction
- GW0
  - Iterating G and keeping W fixed to the initial DFT W_0
- scGW0
  - Orbitals are updated as well

$$(\mathbf{T}+\mathbf{V})\phi+\left(\mathbf{\Sigma}(E_0)-\frac{d\mathbf{\Sigma}(E_0)}{dE_0}E_0\right)\phi=E\left(1-\frac{d\mathbf{\Sigma}(E_0)}{dE_0}\right)\phi$$

- GW/scGW

Practical Approaches

- Use G0W0, GW0, or possibly scGW0 on top of PBE, if PBE yields reasonable screening for host
- Possibly try G0W0 on top of HSE, if PBE is not reasonable, slightly too large band gaps because RPA screening is not great for HSE

ACFDT-RPA

- Adiabatic connection technique

$$\hat{H}_\lambda = \hat{T} + \hat{v}^\lambda_{\text{ext}} + \lambda \hat{V}_{\text{ee}} \quad (\text{where } 0 \le \lambda \le 1) \qquad \hat{H}_\lambda |\Phi_\lambda[n]\rangle = E_\lambda |\Phi_\lambda[n]\rangle$$

$$U^\lambda_{\text{XC}} = \langle \Phi_\lambda[n] | V_{\text{ee}} | \Phi_\lambda[n] \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad E^{\text{exact}}_{\text{xc}} = \int_0^1 d\lambda\, U^\lambda_{\text{XC}}$$

- ACFDT

$$\underbrace{U^\lambda_{\text{XC}}}_{\text{Fluctuation}} = -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \left[-\frac{1}{\pi} \int_0^\infty d\omega \underbrace{\text{Im}\chi_\lambda(\mathbf{r}, \mathbf{r}', \omega)}_{\text{Dissipation}} - n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right]$$

$$\chi_\lambda(\mathbf{r}, \mathbf{r}', t - t') = \partial n(\mathbf{r}, t) / \partial v^\lambda_{\text{ext}}(\mathbf{r}', t')$$

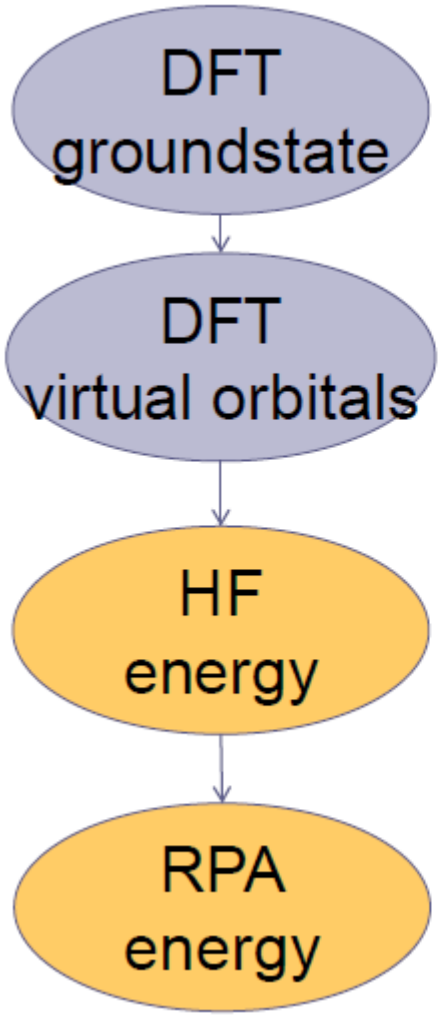
- RPA

$$\chi_\lambda = \chi_0 + \chi_0 (\lambda v + f^\lambda_{\text{xc}}) \chi_\lambda \qquad f_{\text{xc}} = 0$$

$$E^{\text{RPA}}_{\text{xc}} = E^{\text{exact}}_{\text{x}} + E^{\text{RPA}}_{\text{c}} \qquad E^{\text{RPA}}_{\text{c}} = \frac{1}{2\pi} \int_0^\infty d\omega \, \text{Tr} \left[\ln(1 - \chi_0(i\omega) v) + \chi_0(i\omega) v \right]$$

$$\text{Tr} = \int d\mathbf{r} \int d\mathbf{r}'$$

VASP flow chart



EDIFF = 1E-8
ISMEAR = 0 ; SIGMA = 0.1

NBANDS = maximum # of plane waves
ALGO = Exact ; NELM = 1
ISMEAR = 0 ; SIGMA = 0.1
LOPTICS = .TRUE.

ALGO = Eigenval ; NELM = 1
LWAVE = .FALSE.
LHFCALC = .TRUE. ; AEXX= 1.0
ISMEAR = 0 ; SIGMA = 0.1

NBANDS = maximum # of plane waves
ALGO = ACFDT
SIGMA = about ¼ of DFT gap
NOMEGA = 16

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

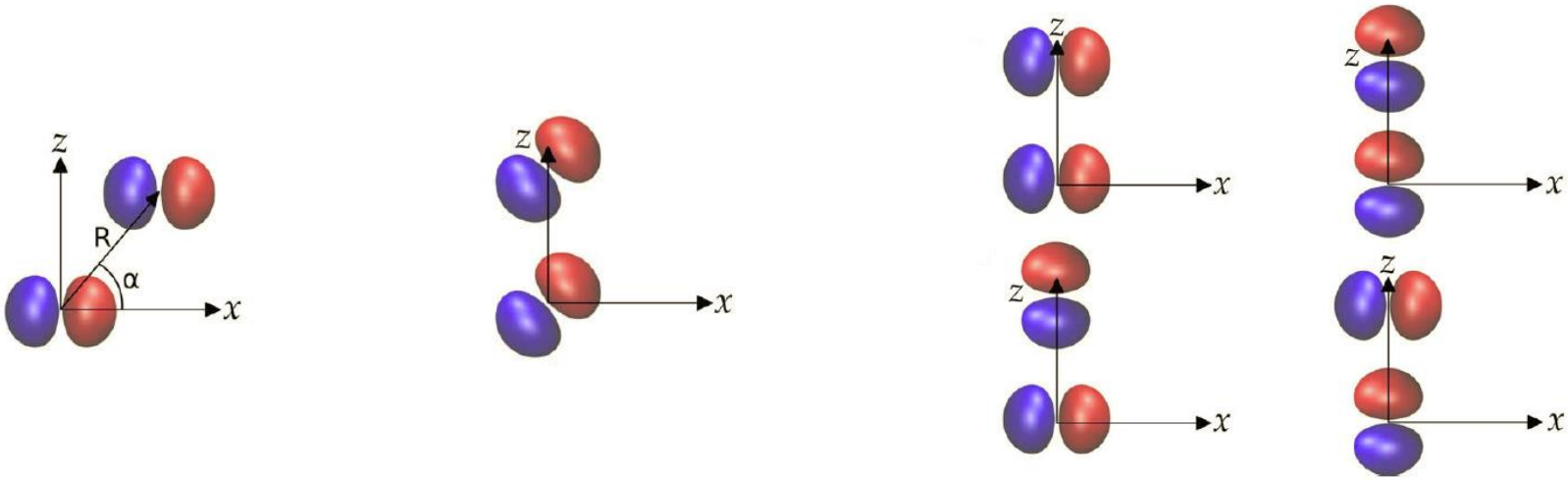
- TB近似可以作为一种插值方法
- SK在参数化Hamiltonian矩阵元时，所采用的近似
  - 正交化基组
  - 只考虑较近的原子之间的相互作用
  - 只考虑特定能量区间里的原子轨道
  - 假设Hamiltonian可以分解为原子中心对称项之和，忽略双中心以上的项

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

- 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

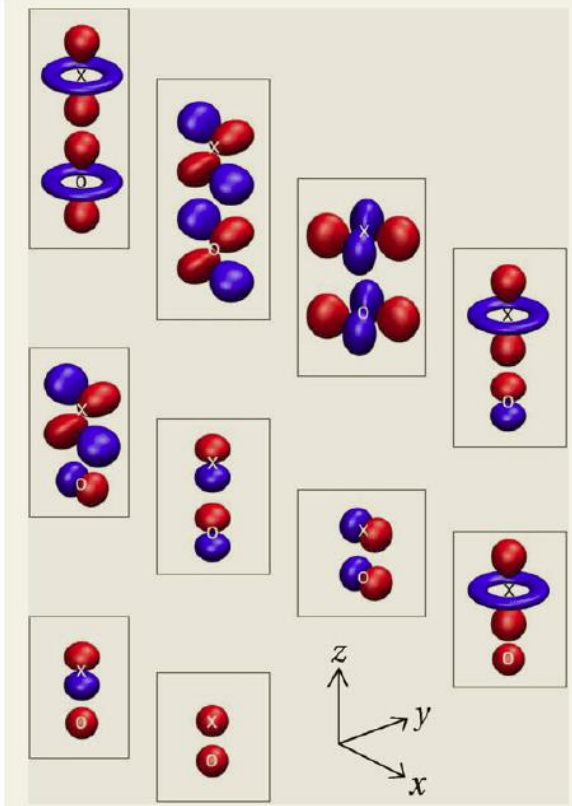
- 双中心积分可以通过方向余弦由一组SK积分求得



- 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

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

NRL-TB

- 体系的总能

$$E = \int \frac{d^3k}{(2\pi)^3} \sum_n \varepsilon_n(\mathbf{k}) + F[n(\mathbf{r})]$$

$$\varepsilon_n'(\mathbf{k}) = \varepsilon_n(\mathbf{k}) + \frac{F[n(\mathbf{r})]}{N_e}$$

- On-site term

$$\rho_I = \sum_J e^{-\lambda^2 R_{IJ}} F(R_{IJ}) \qquad F(R) = \frac{\theta(R_C - R)}{1 + e^{\frac{R - R_C}{l} + 5}}$$

$$h_{Il} = a_l + b_l \rho^{\frac{2}{3}} + c_l \rho^{\frac{4}{3}} + d_l \rho^2$$

NRL-TB

- Hopping term

$$h_{ll'\mu}(R) = (e_{ll'\mu} + f_{ll'\mu}R + g_{ll'\mu}R^2)e^{-h_{ll'\mu}^2 R}F(R)$$

- 1+12+4*10*2=93 parameters
- Modified like-atom hopping term

$$s_{ll'\mu}(R) = (\delta_{ll'} + p_{ll'\mu}R + q_{ll'\mu}R^2 + r_{ll'\mu}R^3)e^{-s_{ll'\mu}^2 R}F(R)$$

DFT Total Energy

- KS total energy

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

- Two-order expression

$$\begin{aligned} E[\delta n] \approx & \sum_a f_a \langle \varphi_a | -\frac{1}{2}\nabla^2 + v_{ext} + v_H[n_0] + v_{xc}[n_0] | \varphi_a \rangle \\ & + \frac{1}{2} \int\int d\mathbf{r} d\mathbf{r}' \left(\frac{\delta^2 E_{xc}[n_0]}{\delta n \delta n'} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \delta n \delta n' \\ & - \frac{1}{2} \int d\mathbf{r} v_H[n_0](\mathbf{r}) n_0(\mathbf{r}) + E_{xc}[n_0] + E_{II} - \int d\mathbf{r} v_{xc}[n_0](\mathbf{r}) n_0(\mathbf{r}) \end{aligned}$$

Density-Functional Tight-Binding

- On-site term

$$[\hat{T} + v_{eff}[n_I^0] + (\frac{r}{r_0})^2]\phi_\nu(\mathbf{r}) = \varepsilon_\nu \phi_\nu(\mathbf{r})$$

- Hopping term

$$h_{\mu\nu}^0 = \left\langle \phi_\mu \middle| \hat{T} + v_{eff}[n_I^0 + n_J^0] \middle| \phi_\nu \right\rangle$$

- Repulsive term: polynomial or spline

$$V_{rep}(R) = \begin{cases} \sum_{n=2}^{NP} d_n (R_C - R)^n & R < R_C \\ 0 & otherwise \end{cases}$$

Second-Order SCC-DFTB

- 能量修正

$$E_{2nd} = E_{coul} = \frac{1}{2}\sum_{I,J}^{N} \Delta q_I \Delta q_J \gamma_{IJ}$$

$$\gamma_{II} \approx U_I = \frac{\partial E^{at}[\rho_I^0]}{\partial^2 q_I} = \frac{\partial \varepsilon_{HOMO}}{\partial n_{HOMO}}$$

$$\gamma_{IJ} = \iint' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \frac{\tau_I^3}{8\pi} e^{-\tau_I|\mathbf{r}'-\mathbf{R}_I|} \frac{\tau_J^3}{8\pi} e^{-\tau_J|\mathbf{r}-\mathbf{R}_J|} \qquad \tau_I = \frac{16}{5} U_I$$

- 自旋极化

$$\frac{1}{2}\sum_{I}^{N}\sum_{l\in I}\sum_{l'\in I} P_{Il} P_{Il'} W_{Ill'} \qquad W_{Ill'} = \frac{1}{2}\left(\frac{\partial \varepsilon_{l\uparrow}}{\partial n_{l'\uparrow}} - \frac{\partial \varepsilon_{l\uparrow}}{\partial n_{l'\downarrow}}\right)_{P=0}$$

Second-Order SCC-DFTB

- Population

$$\Delta q_I = \sum_i^{occ} \sum_{\mu \in I} \sum_{\nu}^{N} \left(n_i^{\uparrow} c_{\mu i}^{\uparrow} c_{\nu i}^{\uparrow} + n_i^{\downarrow} c_{\mu i}^{\downarrow} c_{\nu i}^{\downarrow} \right) S_{\mu\nu} - q_I^0$$

$$P_{Il} = \sum_i^{occ} \sum_{\mu \in I} \sum_{\nu}^{N} \left(n_i^{\uparrow} c_{\mu i}^{\uparrow} c_{\nu i}^{\uparrow} - n_i^{\downarrow} c_{\mu i}^{\downarrow} c_{\nu i}^{\downarrow} \right) S_{\mu\nu}$$

- Hamiltonian

$$h_{\mu\nu} = h_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_K^N (\gamma_{IK} + \gamma_{JK}) \Delta q_K \pm \frac{1}{2} S_{\mu\nu} \sum_{l'' \in I} (W_{Ill''} + W_{II'l''}) P_{II''} \qquad \mu \in I, \nu \in J$$

- Total Energy

$$E_{nscc} + E_{scc} + E_{rep} \qquad E_{nscc} = \sum_n f_n \sum_{\mu\nu} c_{n\mu}^* c_{n\nu} h_{\mu\nu}^0$$

上机实践

- 计算Si能隙
  - LDA/GGA
  - HSE
  - G0W0
- 计算苯dimer势能面
  - LDA/GGA
  - DFT-D2/D3
  - vdW-DF/optB86b