密度泛函理论简介

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Outline

- Hartree-Fock理论简介
- 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
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- 半经验电子结构计算
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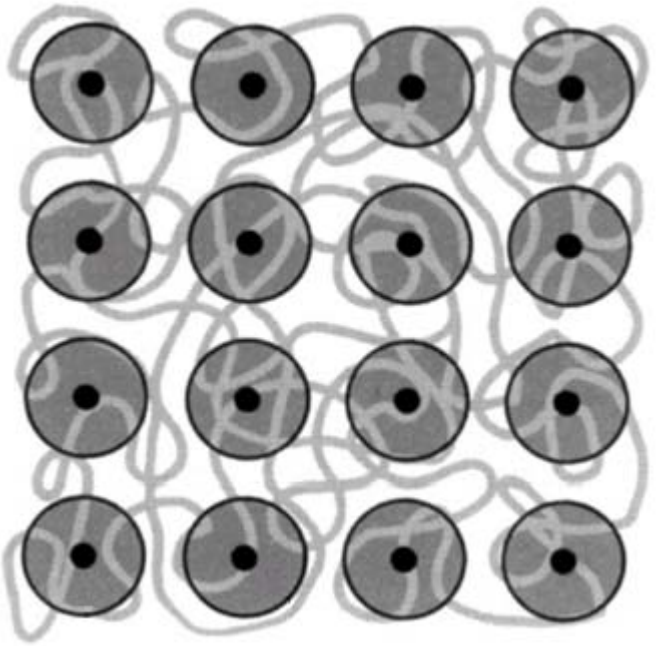
微观世界的量子力学描述

- 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

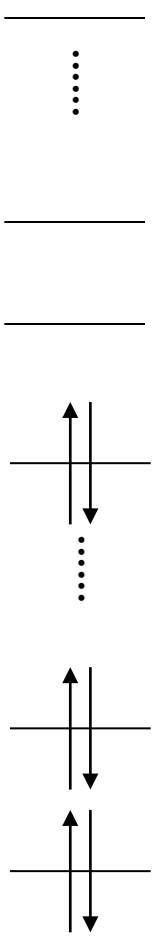
- 分子轨道

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

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

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

$$E = \sum_i \varepsilon_i$$



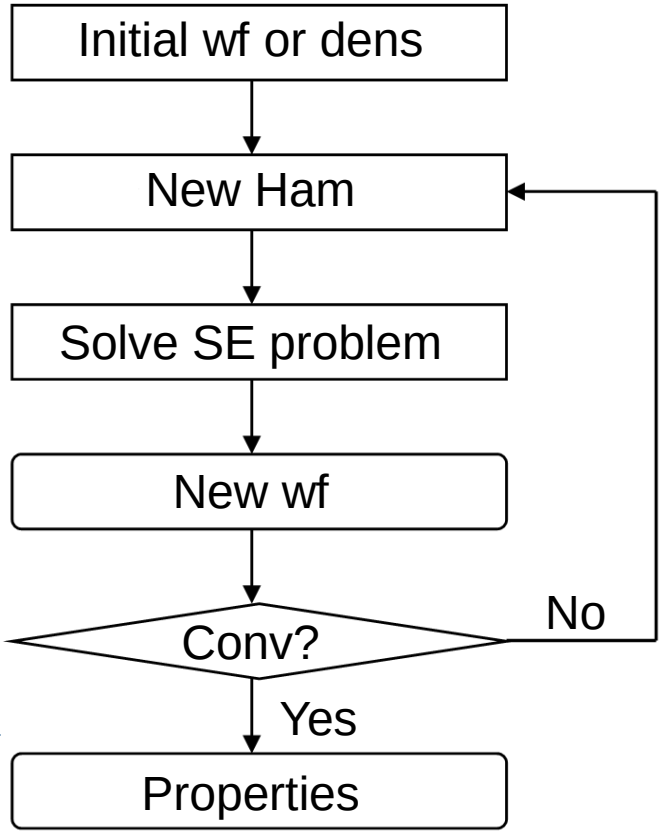
平均场近似

- 单电子哈密顿量由变分得到

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

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

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



Slater行列式

- 交换反对称性

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

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

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

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

Hatree-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

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

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

原子基组

- 一般形式

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

- Slater型轨道(STO)

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

- Gaussian型轨道(GTO)

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

- 收缩高斯基组(STO-*n*G)
- 分裂基组与分裂价基
- 极化函数
- 弥散函数
- 例子
  - 6-311++G(3df, 2pd)
- 平面波基组
- 原子基组优化

J. Phys.: Condens. Matter, **18**, 1347 (2006)

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

↓

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

↓ BO

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

↓ 单电子近似

Hamiltonian: 忽略电子电子相互作用→平均场

波函数(变分法): HP→SD

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

Hatree-Fock理论的局限性

- 电子关联效应

- 后HF方法
  - 组态相互作用

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

  - 耦合簇方法

$$\psi_{cc} = e^{\hat{T}} \psi_{HF}$$

  - MP微扰方法

$$\hat{H}^{(0)} = \sum_i \hat{f}_i \qquad \psi^{(0)} = \psi_{HF}$$

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

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

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

Hohenberg-Kohn定理：DFT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。

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

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

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

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

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

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

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

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

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

- 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

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

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

- 关联项

$$E_C[n] = F[n] - (T_S[n] + U_H[n] + E_X[n])$$

$$= \langle \psi_n^{\min} | \hat{\hat{\hat{\hat{T}}}} + U | \psi_n^{\min} \rangle - \langle \psi_n^{SD} | T + U | \psi_n^{SD} \rangle$$

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
  - PBE

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)

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

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

- Slater potential → KLI → CEDA
- Kohn-Sham vs orbital-specific potentials

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

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

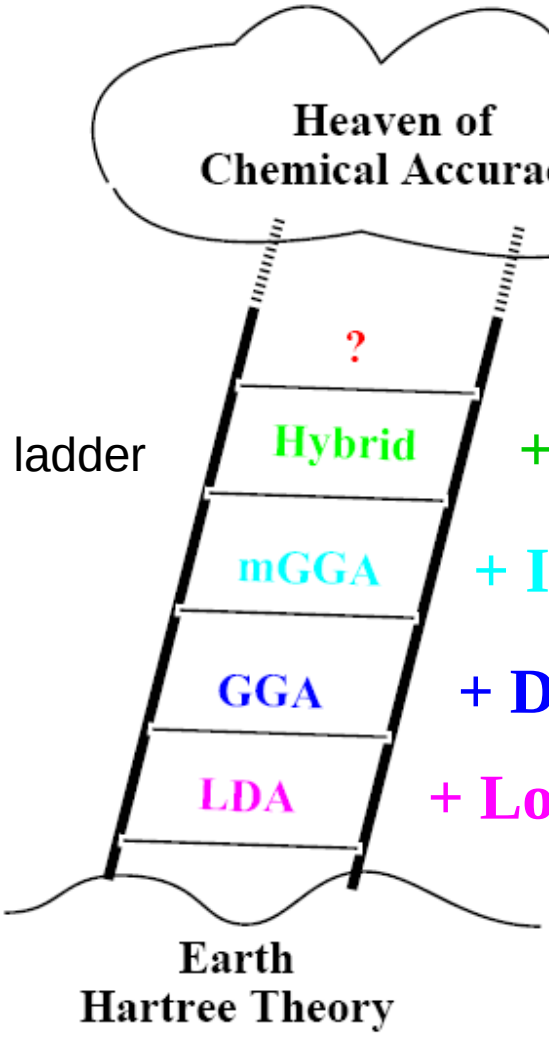
- 双杂化

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

- 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

自相互作用误差

- 单电子体系

$$E_C[n] = 0$$

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

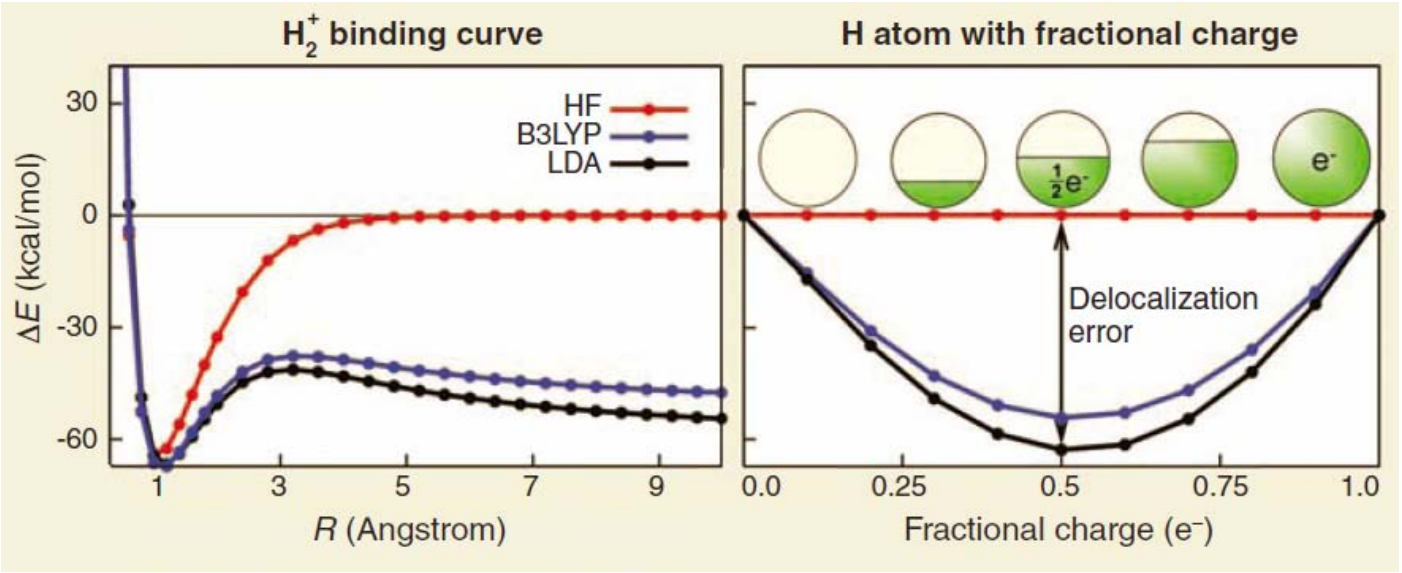
- 自相互作用修正

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

- 头痛医头，脚痛医脚？

离域化误差

- H_2^+分子离子解离

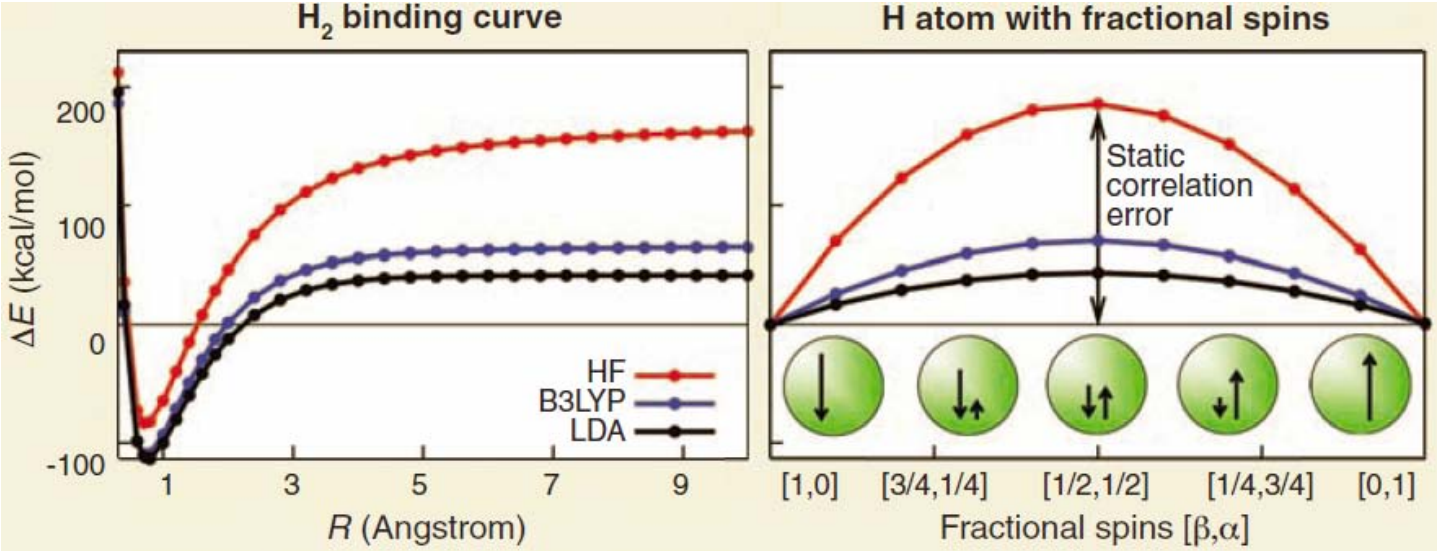


- 低估活化能，高估电导，低估能隙，...

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

静态关联误差

- H_2分子解离



- broken-symmetry open-shell calculation

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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

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

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

DFT+D

- DFT-D

$$E_{DFT-D} = E_{KS} + C_6 R^{-6} f_{dmp}(R)$$

- vdW-DF

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

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

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

$$S_{\mu\nu} = \delta_{\mu\nu}$$

$$(\mu\nu \mid \lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu \mid \lambda\lambda) \qquad (\mu\mu \mid \lambda\lambda) = \gamma_{AB}$$

$$\gamma_{AA} = IP_A - EA_A \qquad \gamma_{AB} = \frac{\gamma_{AA} + \gamma_{BB}}{2 + r_{AB}(\gamma_{AA} + \gamma_{BB})}$$

$$\langle \mu \mid -\frac{1}{2}\nabla^2 - \sum_k \frac{Z_k}{r_k} \mid \mu \rangle = -\mathrm{IP}_\mu - \sum_k (Z_k - \delta_{Z_A Z_k})\,\gamma_{Ak}$$

$$\langle \mu \mid -\frac{1}{2}\nabla^2 - \sum_k \frac{Z_k}{r_k} \mid \nu \rangle = \frac{(\beta_A + \beta_B)S_{\mu\nu}}{2}$$

- 孤对电子、空间取向

intermediate neglect of differential overlap

- INDO
  - (ss|ss) = Gss
  - (ss|pp) = Gsp
  - (pp|pp) = Gpp
  - (pp|p′ p′) = Gpp′
  - (sp|sp) = Lsp
- INDO/S (ZINDO/S)
- MINDO/3
  - 对s和p轨道使用不同的ζ，定义对参数β_{AB}

neglect of diatomic differential overlap (I)

- NDDO, 直接考虑不同轨道间的双中心双电子积分
- modified neglect of differential overlap (MNDO)

$$F_{\mu\mu} = U_{\mu} - \sum_{B \neq A} Z_B (\mu\mu \mid s_B s_B) + \sum_{\nu \in A} P_{\nu\nu} [(\mu\mu \mid \nu\nu) - \frac{1}{2} (\mu\nu \mid \mu\nu)] + \sum_{B} \sum_{\lambda \in B} \sum_{\sigma \in B} P_{\lambda\sigma} (\mu\mu \mid \lambda\sigma)$$

$$F_{\mu\nu} = \frac{1}{2} (\beta_{\mu} + \beta_{\nu}) S_{\mu\nu} - \frac{1}{2} \sum_{\lambda \in A} \sum_{\sigma \in B} P_{\lambda\sigma} (\mu\lambda \mid \nu\sigma)$$

$$V_N = \sum_{k<l} Z_k Z_l (s_k s_k \mid s_l s_l)(1 + e^{-\alpha_k r_{kl}} + e^{-\alpha_l r_{kl}})$$

neglect of diatomic differential overlap (II)

- Austin Model 1 (AM1)

$$V_N(A,B) = V_{AB}^{\mathrm{MNDO}} + \frac{Z_A Z_B}{r_{AB}} \sum_{i=1}^{4} [a_{A,i} e^{-b_{A,i}(r_{AB}-c_{A,i})^2} + a_{B,i} e^{-b_{B,i}(r_{AB}-c_{B,i})^2}]$$

- parameterized model 3 (PM3)
  - 用两个高斯参数代替AM1中的4个参数，并做更强的拟合
  - PM5中加入d轨道
  - PM6在核-核排斥项中采用对参数

$$V_N^{\mathrm{PM6}}(A,B) = Z_A Z_B (s_A s_A \mid s_B s_B)(1 + \chi_{AB} e^{-\alpha_{AB}(r_{AB}+0.0003 r_{AB}^6)})$$

- pairwise distance directed Gaussian function (PDDG)

$$V_N^{PDDG}(A,B) = (\frac{1}{n_A + n_B}) \sum_{i=1}^{2} \sum_{j=1}^{2} (n_A P_{i,A} + n_B P_{j,B}) e^{-[(r_{AB}-D_{i,A}-D_{j,B})^2/10]}$$

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

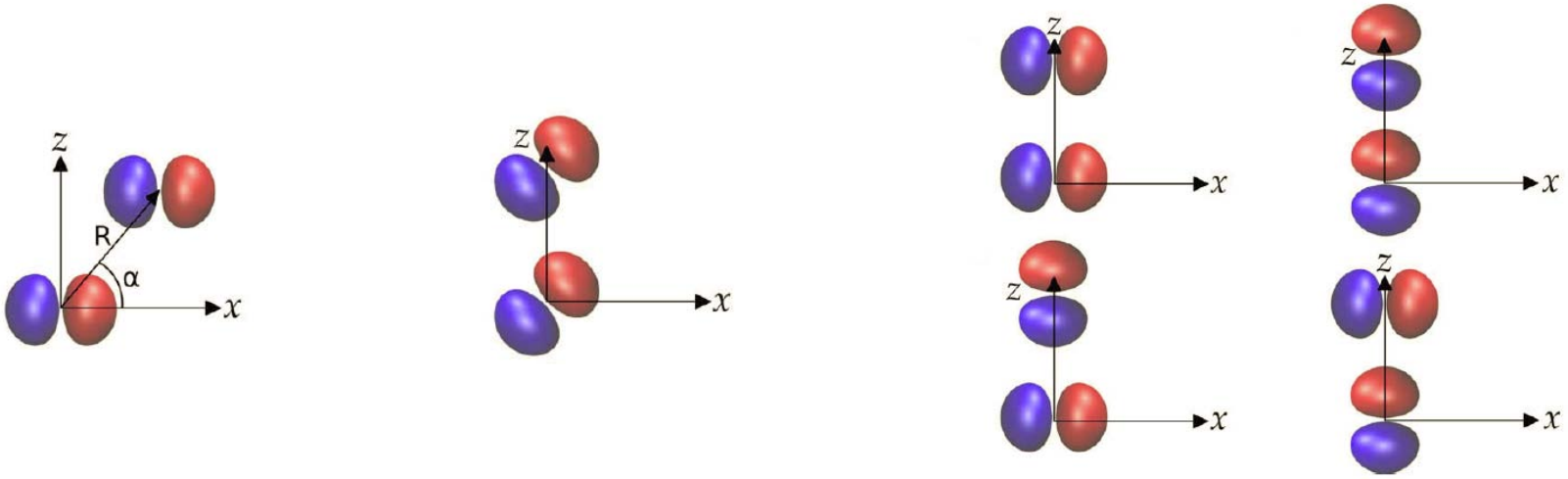
- TB近似可以作为一种插值方法
- SK在参数化Hamiltonian矩阵元时，所采用的近似
  - 正交化基组
  - 只考虑较近的原子之间的相互作用
  - 只考虑特定能量区间里的原子轨道
  - 假设Hamiltonian可以分解为原子中心对称项之和，忽略双中心以上的项

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

- 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

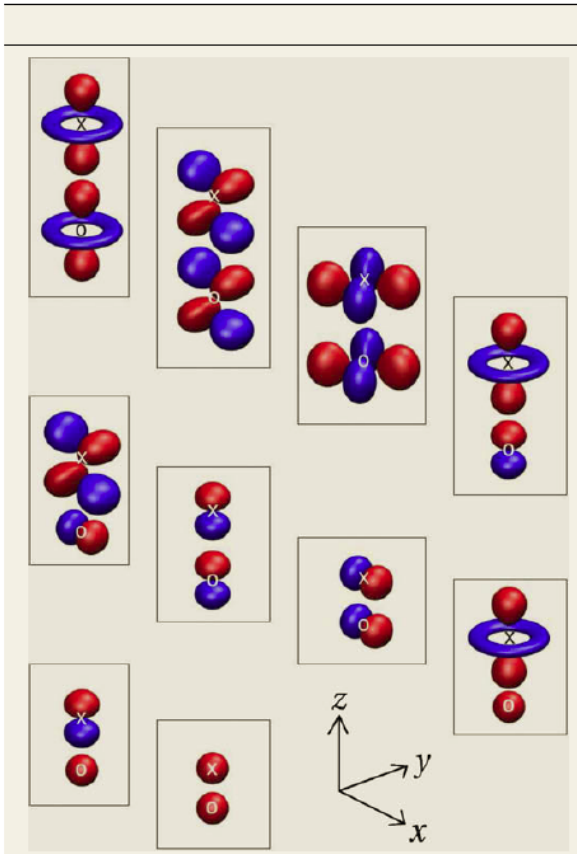
- 双中心积分可以通过方向余弦由一组SK积分求得



- 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,



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

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

Density-Functional Tight-Binding

- On-site term

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

- Hopping term

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

- 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

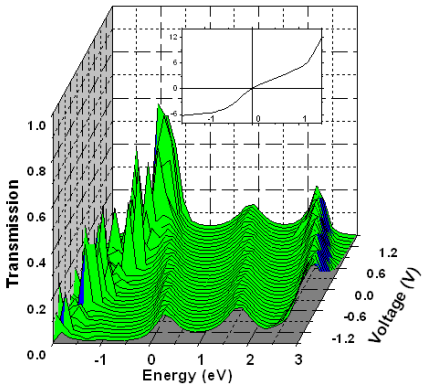
$$h_{\mu\nu} = h_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_K^N (\gamma_{IK} + \gamma_{JK}) \Delta q_K \pm \frac{1}{2} S_{\mu\nu} \sum_{l" \in I} (W_{Ill"} + W_{Il'l"}) P_{Il"} \qquad \mu \in I, \nu \in J$$

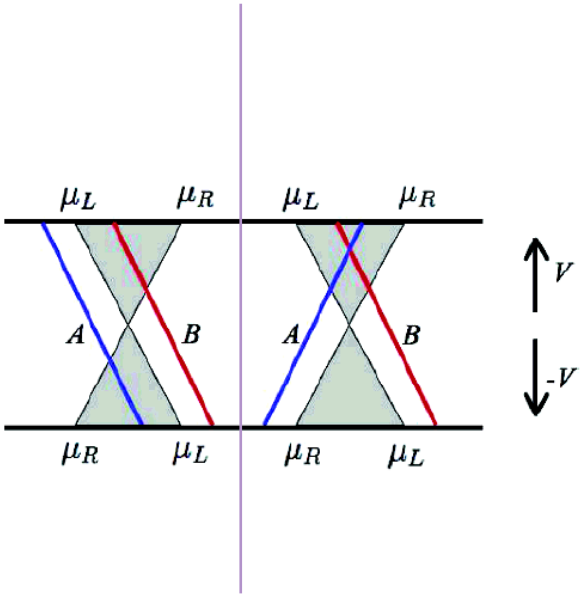
- Total Energy

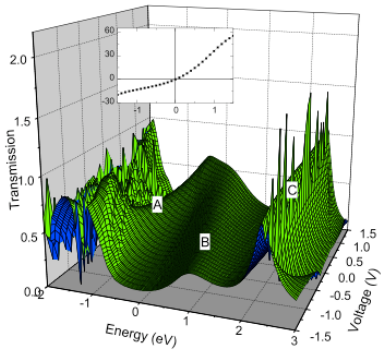
$$E_{nscc} + E_{scc} + E_{rep} \qquad E_{nscc} = \sum_n f_n \sum_{\mu\nu} c_{n\mu}^* c_{n\nu} h_{\mu\nu}^0$$

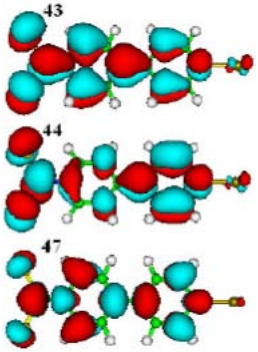
理论设计

- Molecular diode based on dithiol anchoring group

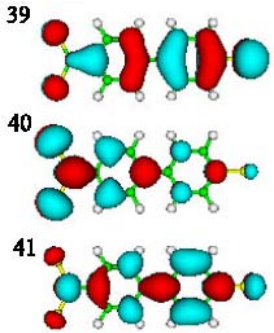








$$I(V) = G_0 \int_{-\infty}^{\infty} dE\, T(E)[f_L(E-\mu_L) - f_R(E-\mu_R)]$$



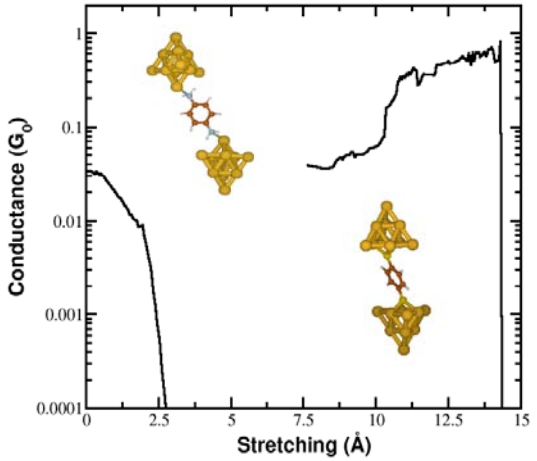
BPE: Coupling Strength

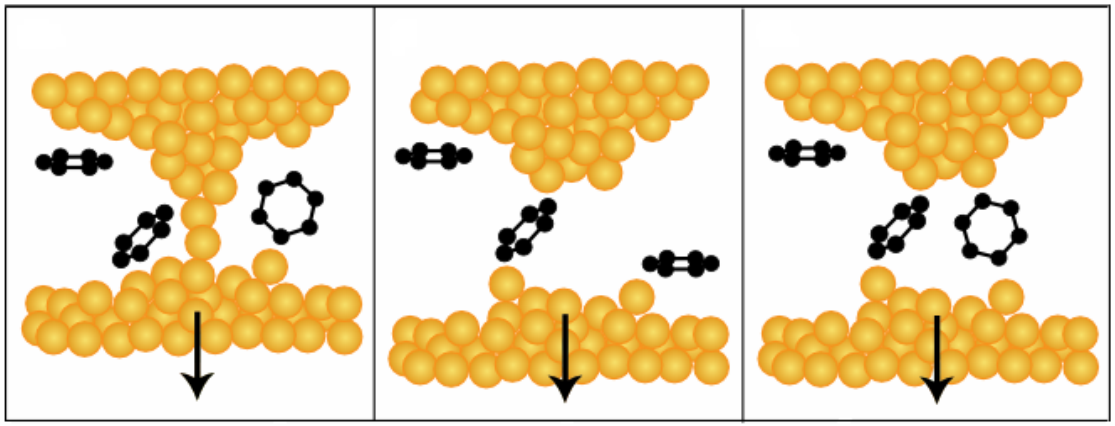
BPH: Orbital Interaction

JPCB, **110**, 9893 (2006); 19116 (2006)

计算表征

- Anchoring group in molecular junctions
  - Adsorption geometry
  - Transmission
  - Virtual STM break junction

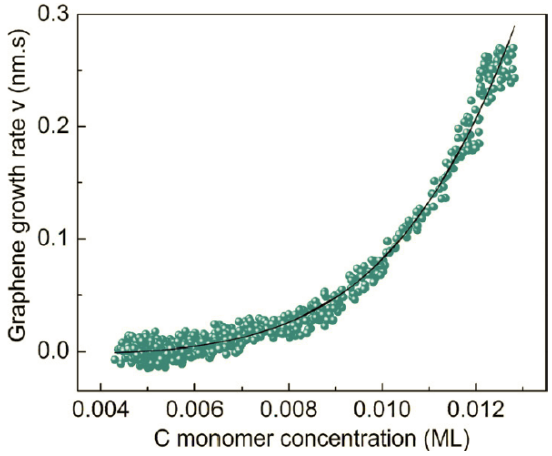




PRB, **76**, 035415 (2007)

生长机理

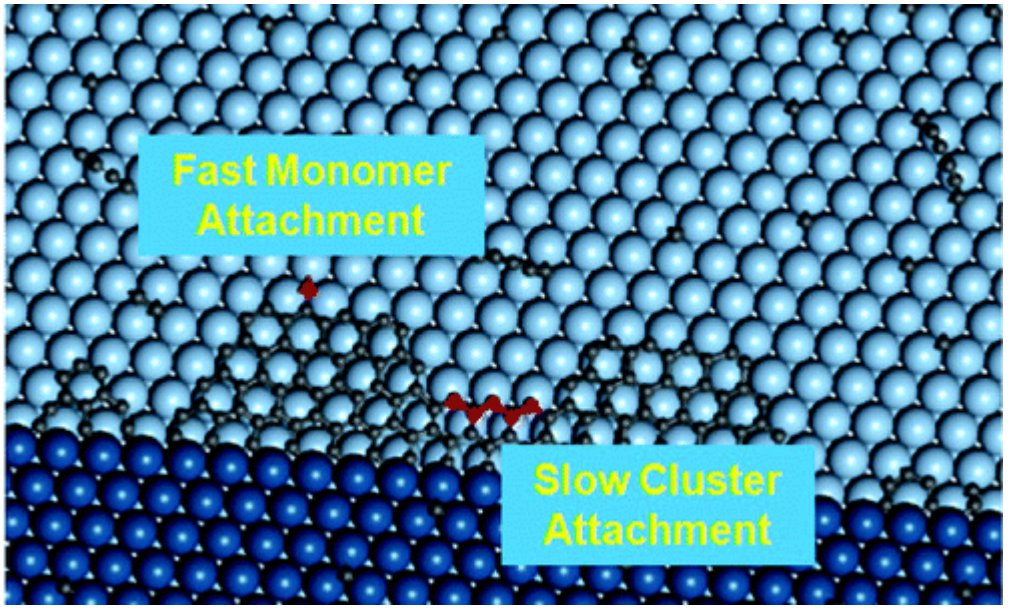
- Nonlinear growth of graphene



$$\upsilon \propto \left[\left(\frac{c}{c^{eq}}\right)^{n} - 1\right] \quad \text{with } n \approx 5.$$

New J. Phys. **10, 093026 (2008); 11, 063046 (2009)**

非线性生长行为表明存在多粒子协同效应



First principles calculations

Standing-on-the-front kMC simulations

JACS, **134**, 6045 (2012)

Conclusions

- By working with the density, DFT reaches a good balance between efficiency and accuracy.
- Significant errors exist for some kinds of problems.
- DFT is widely used in electronic structure calculations and other field in condensed matter physics.

Thank You!