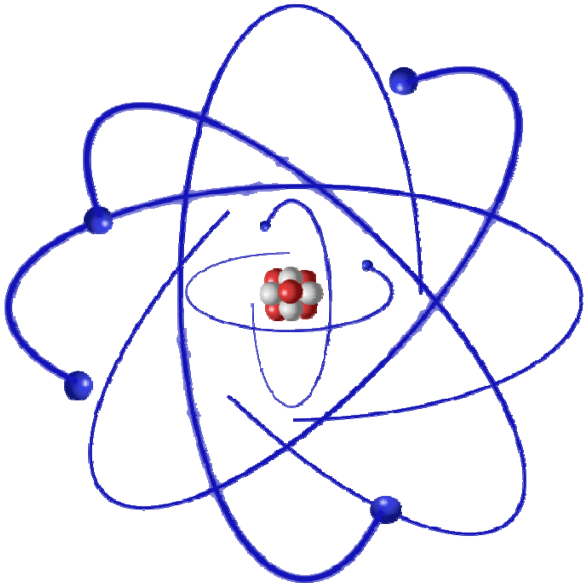


第十一讲：现代电子结构计算方法

N-Particle System Problem

$$H\psi = E\psi$$

Remember
the good old days of the
1-electron H-atom??

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

They're
over!

$$H = -\sum_{i=1}^{N}\frac{\hbar^2}{2M_i}\nabla^2_{\mathbf{R}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ i\neq j}}^{N}\frac{Z_iZ_je^2}{|\mathbf{R}_i-\mathbf{R}_j|} - \frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_ie^2}{|\mathbf{R}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}$$

kinetic energy of ions

potential energy of ions

kinetic energy of electrons

electron-electron interaction

electron-ion interaction

Multi-Atom-Multi-Electron Schrödinger Equation

$$H(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n)\,\Psi(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n) = E\,\Psi(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n)$$

近似I：绝热近似

Born-Oppenheimer Approximation (skinless version)

- mass of nuclei exceeds that of the electrons by a factor of 1000 or more
- we can neglect the kinetic energy of the nuclei
- treat the ion-ion interaction classically
- significantly simplifies the Hamiltonian for the electrons:

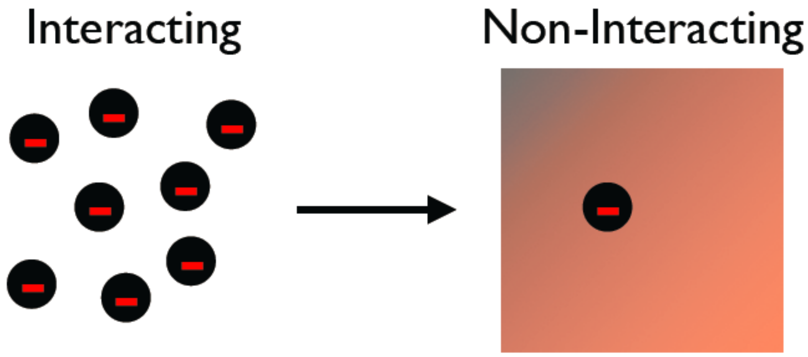

Born


Oppenheimer

This term is just an external potential V(r_j)

$$H = -\frac{h^2}{2m}\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i\neq j}}^{n}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

近似II：单电子近似



体系Hamilton量简化

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

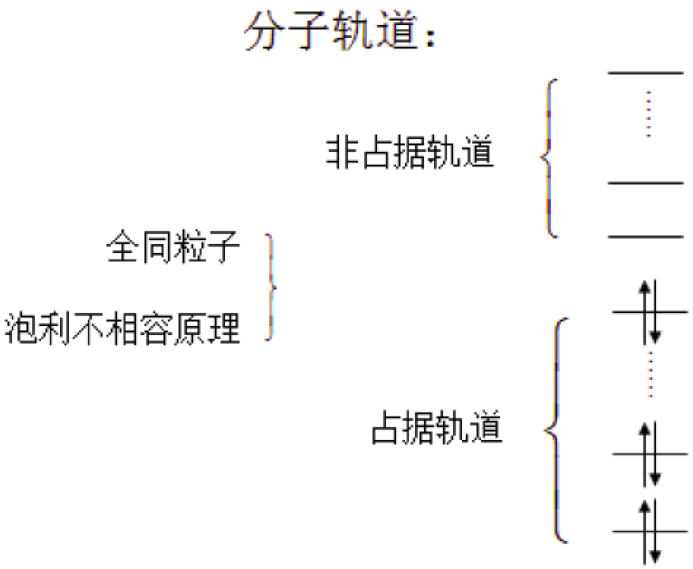
单电子薛定谔方程 $\hat{h}_i \varphi_i = \varepsilon_i \varphi_i$

φ_i 为单电子波函数 or 分子轨道(MO)

本征值 ε_i 为对应的分子能级

任何两个粒子不能有完全相同的量子数

(n, l, m, s) 其中s = ±1/2 自旋量子数



无相互作用多体波函数？

Write wavefunction as a simple product of single particle states: Hartree 积 （HP多体波函数）

$$\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)=\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)\ldots\varphi_n(\boldsymbol{r}_n)$$

Hard　　　　Product of Easy

Total energy

$$E=\sum_i \varepsilon_i$$

近似III：平均场近似

- 对HP多体波函数

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

$$v_i = \sum_{j\neq i}\int \frac{\rho_j}{r_{ij}}\, d\mathbf{r}_j \qquad \rho_j = \left|\varphi_j\right|^2 e$$

Hartree Approximation: the electrons do not interact explicitly with the others, but each electron interacts with the medium potential given by the other electrons

变分法

$$E = \sum_{i=1}^{N} H_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} J_{ij}$$

- 单电子积分项

$$H_i = \int \Phi_i(i) h_i \Phi_i(i) d\tau_i = \int \Phi_i(i)\left[-\frac{1}{2}\nabla_i^2 + \sum_{A=1}^{M} -\frac{Z_A}{r_{iA}}\right]\Phi_i(i) d\tau_i$$

- 库仑双电子积分
- 代表经典两个电荷密度之间的排斥作用（由 Φ_i and Φ_j 描述）

$$J_{ij} = \iint \Phi_i^2(1)\frac{1}{r_{12}}\Phi_j^2(2)d\tau_1 d\tau_2$$

Hartree 方程

$$\left[-\frac{1}{2}\nabla_i^2+\sum_{A=1}^{M}-\frac{Z_A}{r_{iA}}+\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\int\left|\Phi_j(j)\right|^2\frac{1}{r_{ij}}d\tau_j\right]\Phi_i(i)=\varepsilon_i\Phi_i(i)$$

$$\varepsilon_i=H_i+\sum_{\substack{j=1\\ j\neq i}}^{N}J_{ij}$$

- 分子轨道能量

$$E=\sum_{i=1}^{N}\varepsilon_i-\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}J_{ij}$$

总能量

In order to find Φ_i we need Φ_i ⇒ SCF procedure

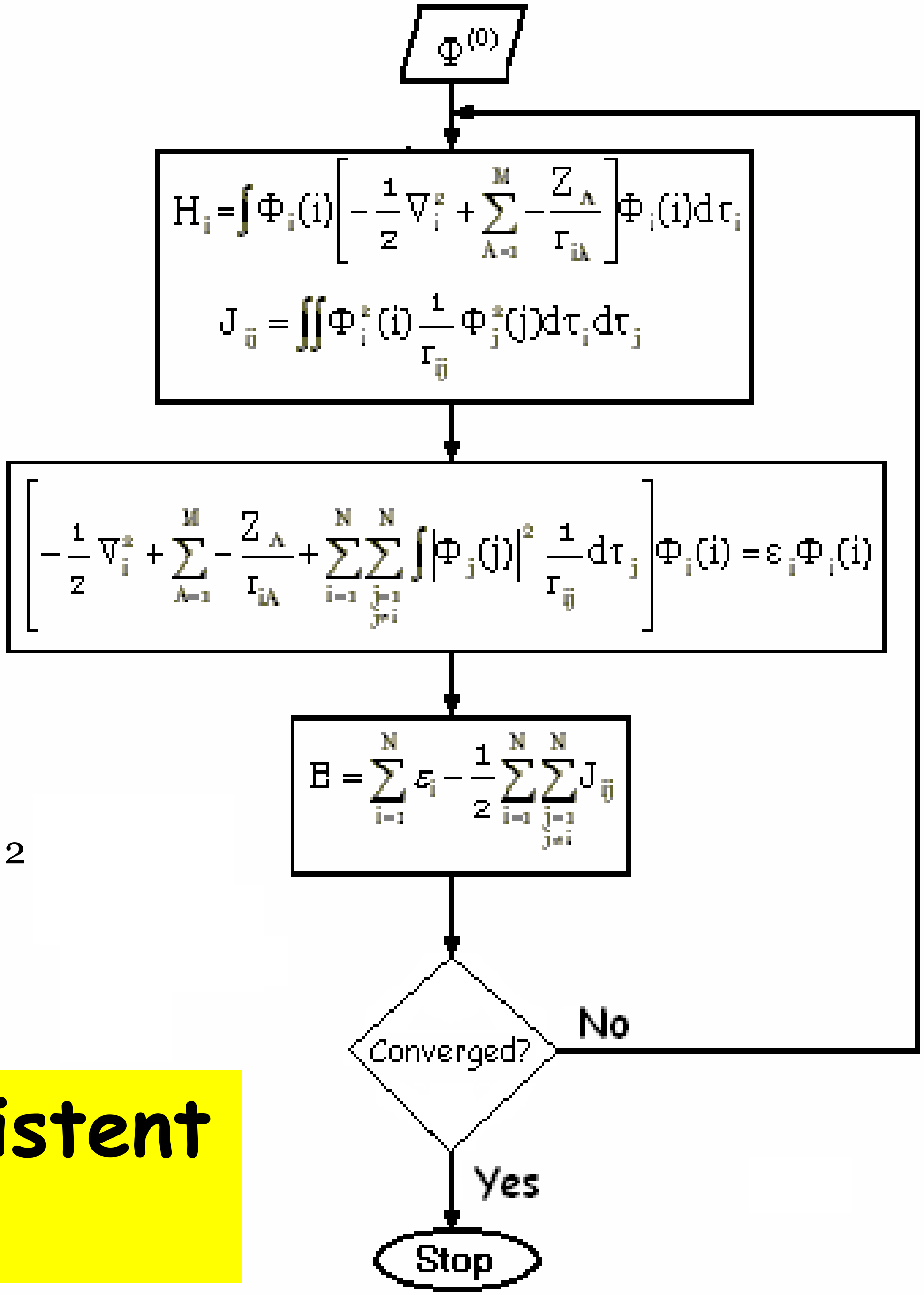
***i* 次迭代 电子密度分布**

$$\rho_i(r) = |\Phi_i(r)|^2$$

总电子密度

$$\rho_{tot}(r) = \sum_{i=1}^{N} \rho_i(r) = \sum_{i=1}^{N} |\Phi_i(r)|^2$$

Solution: Self-Consistent Field （SCF）



$$\Phi^{(0)}$$

$$H_i = \int \Phi_i(i) \left[-\frac{1}{2}\nabla_i^2 + \sum_{A=1}^{M} -\frac{Z_A}{r_{iA}} \right] \Phi_i(i) d\tau_i$$

$$J_{ij} = \iint \Phi_i^2(i) \frac{1}{r_{ij}} \Phi_j^2(j) d\tau_i d\tau_j$$

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_{A=1}^{M} -\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \int |\Phi_j(j)|^2 \frac{1}{r_{ij}} d\tau_j \right] \Phi_i(i) = \varepsilon_i \Phi_i(i)$$

$$E = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} J_{ij}$$

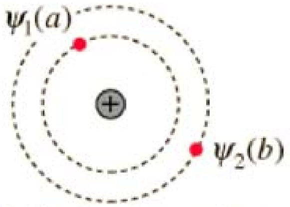
N个电子体系Slater波函数

HP 波函数

不满足电子（费米子）全同性要求的波函数反对成性

如：双粒子体系

$$\psi=\varphi_a(1)\varphi_b(2) \text{ 是两电子体系本征方程的解}$$



For fermions the negative sign must be used, so that the wavefunction goes to identically zero if the states a and b are identical.

交换算符P$_{12}$ $\hat{P}_{12}\left[\varphi_a(1)\varphi_b(2)\right]=\varphi_a(2)\varphi_b(1)\neq-\varphi_a(1)\varphi_b(2)$ **也是本征解**

则满足交换反对称条件的波函数：

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

Slater行列式形式（SD）

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

Fock, Slater 1930

N电子体系总波函数

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

单电子波函数

Hartree-Fock Solution

电子相互作用项

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

$$E = \left\langle \Psi^{SD} \middle| H \middle| \Psi^{SD} \right\rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ij})$$

$$H_i = \int \Phi_i^*(r) h_i \Phi_i(r) dr = \int \Phi_i^*(r) \left[-\frac{1}{2} \nabla_i^2 + v_i \right] \Phi_i(r) dr$$

$$J_{ij} = \iint \Phi_i^2(1) \frac{1}{r_{12}} \Phi_j^2(2) dr_1 dr_2$$

电子间的库仑排斥能

$$K_{ij} = \iint \Phi_i^*(r_1) \Phi_j^*(r_1) \frac{1}{|r_1 - r_2|} \Phi_i(r_2) \Phi_j(r_2) dr_1 dr_2$$

同自旋电子的交换能

exchange operator:

$$K_j(1)\Phi_i(1)=\left[\int \Phi_j(2)\frac{1}{r_{12}}\Phi_i(2)d\tau_2\right]\Phi_j(1)$$

Hartree-Fock equations:

$$\left[-\frac{1}{2}\nabla_i^2+v_i\right]\Phi_i(r)+\sum_{j=1}^{N}\int\left|\Phi_j(r')\right|^2\frac{1}{|r-r'|}\Phi_i(r)d\tau_j-\sum_{j=1}^{N}\int\Phi_j^*(r')\Phi_i(r')\frac{1}{|r-r'|}\Phi_j(r)d\tau_j=\varepsilon_i\Phi_i(r)$$

Fock operator:

$$f_i=h_i+\sum_{j=1}^{N}(J_j-K_j)$$

⇒ molecular orbital energies:

$$\varepsilon_i=\left\langle\Phi_i\middle|f_i\middle|\Phi_i\right\rangle=H_i+\sum_{j=1}^{N}(J_{ij}-K_{ij})$$

Hartree-Fock-Roothann Equation

Roothann Linear Combination of Atomic Orbital – Molecular Orbital (LCAO-MO)

$$\Phi_i = \sum_{\mu=1}^{K} c_{\mu i}\varphi_\mu$$ i=1,2,...,K $\{\varphi_\mu\}$ – a set of known functions

---

$$f(r_1)\sum_\nu c_{\nu i}\varphi_\nu(r_1) = \varepsilon_i \sum_\nu c_{\nu i}\varphi_\nu(r_1)$$ matrix equation for the $c_{\mu i}$ coefficients

Multiplying by $\varphi_\mu^*(r_1)$ on the left and integrating we get:

$$\sum_\nu c_{\nu i}\int \varphi_\mu^*(r_1) f(r_1)\varphi_\nu(r_1)dr_1 = \varepsilon_i \sum_\nu c_{\nu i}\int \varphi_\mu^*(r_1)\varphi_\nu(r_1)dr_1$$

$$F_{\mu\nu} = \int \varphi_\mu^*(r_1) f(r_1)\varphi_\nu(r_1)dr_1$$

- Fock matrix (KxK Hermitian matrix)

$$S_{\mu\nu} = \int \varphi_\mu^*(r_1)\varphi_\nu(r_1)dr_1$$

- overlap matrix (KxK Hermitian matrix)

$$\Rightarrow \quad \sum_\nu F_{\mu\nu}c_{\nu i} = \varepsilon_i \sum_\nu S_{\mu\nu}c_{\nu i}, \qquad i = 1,2,\ldots,K$$

- Roothaan equations

FC=SCε

HF问题转变为矩阵方程问题

系数矩阵
$$C=\begin{pmatrix} c_{11} & c_{12} & \dots & c_{1K} \\ c_{21} & c_{22} & \dots & c_{2K} \\ \dots & \dots & \dots & \dots \\ c_{K1} & c_{K2} & \dots & c_{KK} \end{pmatrix} \qquad \varepsilon=\begin{pmatrix} \varepsilon_1 & 0 & \dots & 0 \\ 0 & \varepsilon_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \varepsilon_K \end{pmatrix}$$

其中

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

$$(\mu\nu|\lambda\sigma)=\iint \phi_\mu(1)\phi_\nu(1)\frac{e^2}{r_{12}}\phi_\lambda(2)\phi_\sigma(2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

密度矩阵元 $P_{\mu\nu}=2\sum_a^{N/2} c_{\mu a}c_{\nu a}^*$

P S 矩阵 对角元 $P_{\mu\mu}S_{\mu\mu}$ - 原子轨道 φ_μ 上的电子布局

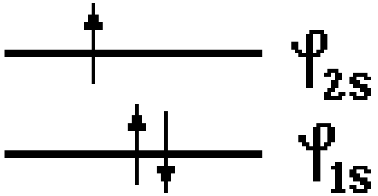
非对角元 $P_{\mu\nu}S_{\mu\nu}$ - 原子轨道 $\varphi_\mu\varphi_\nu$ 之间的电子密度布局

Restricted or Unrestricted HF

Restricted HF restricted wave-function

$$\Phi_1(x)=\varphi_1(r)\alpha(\omega) \quad \Phi_2(x)=\varphi_1(r)\beta(\omega)$$

Restricted wave-function for Li atom



$$\left|\Psi_{RHF}\right\rangle = \left|\varphi_{1s}\overline{\varphi}_{1s}\varphi_{2s}\right\rangle$$

But: $K_{1s(\alpha)2s(\alpha)} \neq 0$ and $K_{1s(\beta)2s(\alpha)}=0$

1s(α) and 1s(β) electrons will experience different potentials so that it will be more convenient to describe the two kind of electrons by different wave-functions

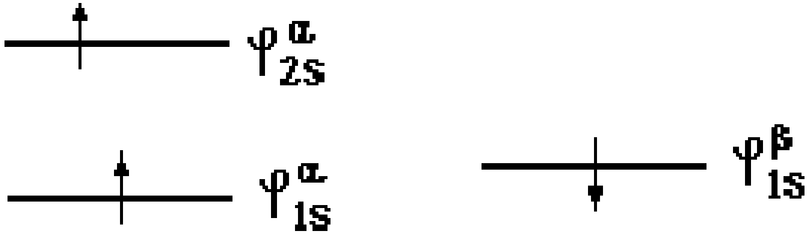
Restricted or Unrestricted HF

Unrestricted HF

No restriction on spatial wavefunction for spin orbit

$\Phi_1(x)=\varphi^{\alpha}{}_1(r)\alpha(\omega) \quad \Phi_2(x)=\varphi^{\beta}{}_1(r)\beta(\omega)$

Unrestricted wave-function for Li atom



$$|\Psi_{UHF}\rangle = |\varphi^{\alpha}_{1s}\ \overline{\varphi}^{\beta}_{1s}\ \varphi^{\alpha}_{2s}\rangle$$

$$\langle\varphi^{\alpha}_{i}|\varphi^{\alpha}_{j}\rangle = \delta_{ij} \qquad \langle\varphi^{\beta}_{i}|\varphi^{\beta}_{j}\rangle = \delta_{ij} \qquad \langle\varphi^{\alpha}_{i}|\varphi^{\beta}_{j}\rangle = S^{\alpha\beta}_{ij}$$

UHF solution: possible spin containment

Closed Shell System

RHF is good
RHF and UHF present same results

Open Shell System

UHF
优点：High efficient with two sets of spatial function
缺点：单行列式波函数不是$\langle S^2 \rangle$的本征波函数
高自旋态的混合 → 自旋污染

For an UHF wave-function, the expectation value of S^2 is:

$$\langle S^2 \rangle_{UHF} = \langle S^2 \rangle_{exact} + N^{\beta} - \sum_i^N \sum_j^N \left| S_{ij}^{\alpha\beta} \right|^2 \qquad \langle \varphi_i^{\alpha} | \varphi_j^{\alpha} \rangle = \delta_{ij} \qquad \langle \varphi_i^{\beta} | \varphi_j^{\beta} \rangle = \delta_{ij} \qquad \langle \varphi_i^{\alpha} | \varphi_j^{\beta} \rangle = S_{ij}^{\alpha\beta}$$

where:

$$\langle S^2 \rangle_{exact} = \left(\frac{N^{\alpha} - N^{\beta}}{2} \right) \left(\frac{N^{\alpha} - N^{\beta}}{2} + 1 \right)$$

$$\langle S^2 \rangle_{UHF} \geq \langle S^2 \rangle_{exact}$$

How to check?

Gaussian software, use iop(5/14)=2 输出 $<S^2>$

Number of unpaired electrons	s	$\langle S^2 \rangle$
0	0	0
1	0.5	0.75
2	1	2.0
3	1.5	3.75
4	2	6.0
5	2.5	8.75

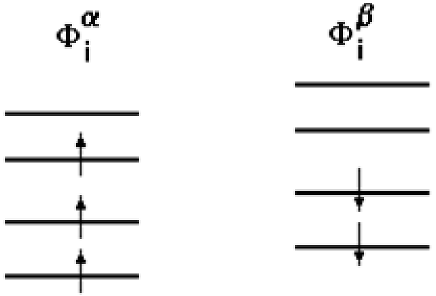
如果误差<10% ok

Recommended Solution

Restricted Open-Shell HF (ROHF)

波函数由多个slater行列式线性组合

1. Good for energy and wavefunction
2. Bad for spin-dependent properties



\- *approximately* a doublet

$$\left|{}^2\Psi\right\rangle = c_2^2\left|2\right\rangle + c_4^2\left|4\right\rangle + c_6^2\left|6\right\rangle + \dots$$

|2> - exact doublet state

|4> - exact quartet state

|6> - exact sextet state

对比

Unrestricted HF (UHF)

波函数由单个slater行列式线性组合

1. Energy: $E_{UHF} \leq E_{RHF}$ or E_{ROHF}
2. Good for spin-dependent properties

M. W. Wong, L. Radom, *J. Phys. Chem.* **99**, 8582 (1995).

J. Baker, A. Scheiner, J. Andzelm, *Chem. Phys. Lett.* **216**, 380 (1993).

Basis Set (基组)

$$\Psi = (N!)^{-1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_K(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_K(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_K(x_N) \end{vmatrix}$$

$$\Phi_i = \sum_{\mu=1}^{K} c_{\mu i} \varphi_\mu$$

if $\varphi_\mu \equiv$ AO → LCAO-MO
if $\varphi_\mu \neq$ AO → LCBF-MO

Slater Type Orbitals (STO)


John C. Slater (1900-1976)

类氢轨道

$$\varphi_i(\xi,n,l,m;r,\theta,\varphi) = Nr^{n-1}e^{-\xi r}Y_{lm}(\theta,\varphi)$$

ζ 轨道指数

- similar to atomic orbitals of the hydrogen atom
- more convenient (from the numerical calculation point of view) than AO, especially when n-l≥2 (radial part is simply r^2, r^3, ... and not a polinom)

$$\varphi_{1s} = \left(\frac{\xi_1^3}{\pi}\right)^{1/2} \exp(-\xi_1 r) \qquad \varphi_{2s} = \left(\frac{\xi_2^5}{96\pi}\right)^{1/2} r\exp\left(-\frac{\xi_2 r}{2}\right) \qquad \varphi_{2p_x} = \left(\frac{\xi_2^5}{32\pi}\right)^{1/2} x\exp\left(-\frac{\xi_2 r}{2}\right)$$

极小基组， 双ζ基组， 扩展基组（极化基组）

STO

Advantages:

- Physically, the exponential dependence on distance from the nucleus is very close to the exact hydrogenic orbitals.
- Ensures fairly rapid convergence with increasing number of functions.
- Use only one zeta parameter to fit the orbital

Disadvantages:

- Three and four center integrals cannot be performed analytically.
- No radial nodes. These can be introduced by making linear combinations of STOs.

Practical Use:

- Calculations of very high accuracy, atomic and diatomic systems.
- Semi-empirical methods where 3- and 4-center integrals are neglected.

Gaussian Type Orbitals (GTO)

$$G_A = N x_A^l y_A^m z_A^n e^{-arA^2}$$

◆ GTO的优点：

1. 因双中心函数乘积等于单中心函数（两个高斯函数的乘积仍是高斯函数），通过高斯函数可以把双中心积分变成单中心积分。
2. 高斯函数的指数为r^2的函数，可分解成$x^2+y^2+z^2$，把三维积分变成独立的三个一维积分，简化计算。

◆ GTO的缺点

1. 与Slater函数相比高斯函数在r大的时候衰减太快，而在原子核处又没有尖点(CUSP)。
2. GTO严格来说并不是一种轨道，高斯函数没有节点，无法只用一个高斯函数来表示价轨道。

Contracted Gaussian Type Orbitals (CGTO)

采用几个指数不同的高斯型函数拟合一个Slater型轨道，使得在r大的情况下的衰减特征趋近于原子轨道。

$$\chi = \sum_{a}^{N} C_a \chi^{GTO}(X, Y, Z; \alpha_a, i, j, k)$$

–采用了n个GTO，则记为 STO-nG (n = 2 ~ 6)
–原始（Primitive）基函数:用来拟合STO的单个GTO
–例如：常用的STO-3G，不具有足够的灵活度来描述价轨道的电子分布。

分裂基组与分裂价基（split-valence multi-ζ）：

- 一个原子轨道用几个STO来表示。
- 内层轨道可以通过一个STO获得较好的描述，价轨道偏离原子轨道较多，需要几个STO来表示。

3-21G

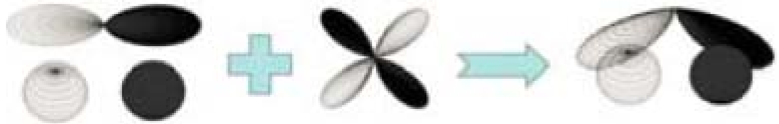
内层用三个Gaussian拟合的一个STO来描述
价层电子用2个STO来描述，分别由2个和1个Gaussian函数拟合

6-311G

内层电子用一个STO描述，它由6个gaussian函数拟合
价层电子用三个STO描述，分别由3,1和1个gaussian函数来拟合

极化基组（Polarization function):

- 对于各向异性环境中的原子，需要使用极化基组，如NH_3。
- 对H_2O，dxy轨道可以显著增加重叠。



◆ 例子

- **6-31G(d)（6-31G*）** 对非氢原子加上d轨道函数
- **6-31G(d,p)（6-31G**)** 对非氢原子加上d轨道函数，对氢原子加上p轨道函数
- **6-311G(3df,3pd)** 对非氢原子加上3个d轨道函数和一个f轨道函数，对于氢原子加上3个p轨道函数和1个d轨道函数

弥散函数（Diffusion function):

将在空间中比较弥散的s，p轨道的基函数（指数很小的函数）添加到基组中。

对于电子空间弥散明显的体系要增加弥散函数

如：

- 阴离子，含孤对电子
- 带明显负电荷体系
- 激发态体系
- 低离子化能体系
- 纯酸体系
- 计算极化的时候
- ….

例子：

6-31+G 对非氢原子加上s和p函数

6-31++G对非氢原子加上s, p函数，对氢原子加上s函数

采用6-311++G（3df，2pd）计算H_2O时，用到多少个轨道，多少个GTO？

Treating Core Electrons (ECP, RECP)

CREN Available for SC(4s) through Hs(0s6p6d)., A shape consistent basis set developed by Ermler and coworkers that has a large core region and small valence.

SBKJC VDZ Available for Li(4s4p) through Hg(7s7p5d), a relativistic basis set created by Stevens and coworkers to replace all but the outermost electrons. The double-zeta valence contraction is designed to have an accuracy comparable to that of the 3-21G all-electron basis set.

Hay-Wadt MB Available for K(5s5p) through Au(5s6p5d), this basis set contains the valence region with the outermost electrons and the previous shell of electrons. Elements beyond Kr are relativistic core potentials. This basis set uses a minimal valence contraction scheme.

Hay-Wadt VDZ Available for K(5s5p) through Au(5s6p5d), this basis 84 10 USING EXISTING BASIS SETS set is similar to Hay±Wadt MB, but it has a double-zeta valence contraction. This set is popular for transition metal modeling.

LANL2DZ Available for H(4s) through Pu(7s6p2d2f), this is a collection of double-zeta basis sets, which are all-electron sets prior to Na.

CRENBL Available for H(4s) through Hs(0s3p6d5f), this is a collection of shape-consistent sets, which use a large valence region and small core region.

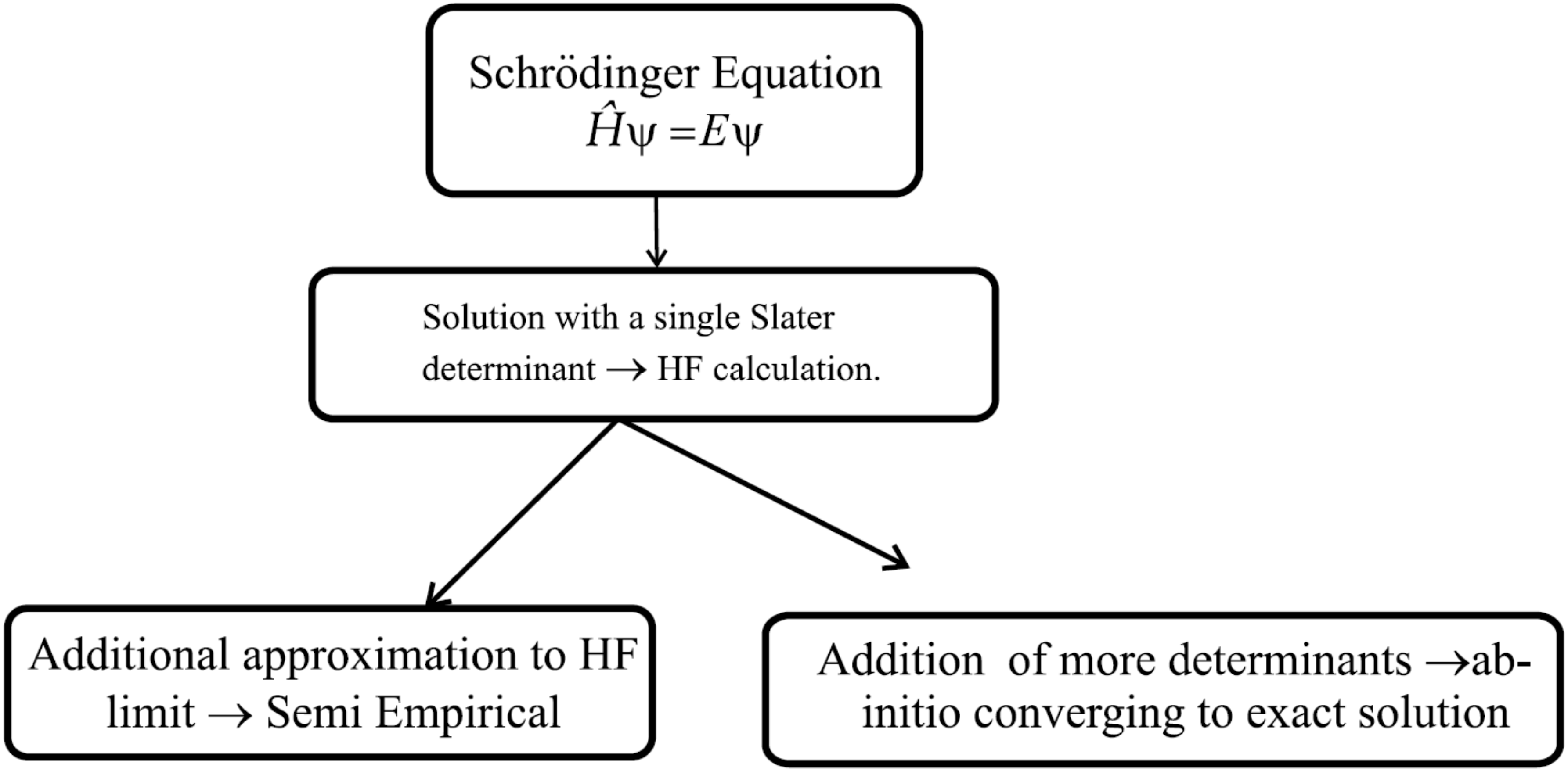
Dolg Also called Stuttgart sets, this is a collection of ECP sets currently under development by Dolg and coworkers. These sets are popular for heavy main group elements.

HF方法

结构预测较好，结合能误差较大

H_2	HF	exp
d(H-H) Ang	0.732	0.741
D_e(H-H) eV	3.49	4.75

What will be the next?



Schrödinger Equation

$\hat{H}\psi = E\psi$

Solution with a single Slater determinant → HF calculation.

Additional approximation to HF limit → Semi Empirical

Addition of more determinants →ab-initio converging to exact solution

Semi-empirical method

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

Simplify this part with either experimental data fitted parameter
or with *ab initial* fitting data fitted parameter

Advantage: very fast compared with *ab initio* method
Disadvantage: can be erratic, fewer properties can be predicted

Semiempirical methods are parameterized to reproduce various results:
geometry, energy (usually the heat of formation), dipole,
heats of reaction, ionization potentials

A few methods have been parameterized to reproduce a specific properties
NMR chemical shifts, electronic spectra …

Most Commonly Used Methods

Huckel

Earliest and Simplest, models only pi electrons in planar organic system
Only considering the nearest interaction, method used in class

Extended Huckel (or tight bonding)

Modeling the valence orbitals
Hamiltonian is built based on the orbital overlaps and experimental electron affinities and ionization energies.

$$H_{ij} = KS_{ij} (H_{ii} + H_{jj})/2$$

Oribtal overlap comes from the simple STO representation
Can be used for simulation of organic and inorganic materials
Can be used for band structure calculation, especially in physics NOW!
Fairly poor at predicting molecular geometries

ppp (Pariser-Parr-Pople) method

An extended Huckel method to deal with heteroatom
Can be used for less demanding for electronic effect (molecular mechanics)

Most Commonly Used Methods - 2

CNDO

Complete **N**eglect of **D**ifferential **O**verlap, the simplest one

Models valence orbitals with a minimal basis set of Slater Type Orbitals

Useful for hydrocarbon results, but little else

CNDO/2 method, an improved CNDO method

CNDO/s parameterized to reproduce electronic spectra, excited state

MINDO

Modified Intermediate Neglect of Differential Overlap

MINDO/1, MINDO/2, MINDO/3

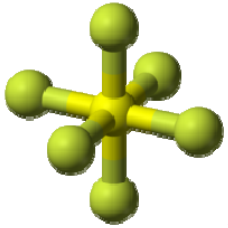
most reliable one

Some times used to obtain an initial guess for *ab initio* calculations.

Most Commonly Used Methods - 3

MNDO

Modified Neglect of Diatomic Overlap
Reasonable qualitative results for many organic systems, widely used


SF$_6$

Some qualitatively or quantitatively incorrect results:

- Underestimate electronic excitation energies
- Overestimate activation barrier
- Underestimate the barriers to bond rotation
- Wrong prediction of the unstability of hypervalent compounds and sterically crowded molecules
- Wrong prediction of the stability of four-member ring
- The prediction of structures is bad.
- …

Extended: MNDO/d including *d* orbital
can predict the stability of hypervalent compounds
MNDOC including electron correlation

Most Commonly Used Methods - 4

INDO

Intermediate Neglect of Diatomic Overlap
Was used for Organic compounds at one time.. History…

ZINDO

Zerner’s INDO method: Spectroscopic INDO method
The method is reparameterized for the purpose of reporducing electronic spectra results.
Can be used for: electronic spectra, UV transitions, and transition metal
Bad for Geometry Optimization.

SINDO

Symmetrically orthogonalized intermediate negloect of differential overlap
Design for binding energy and geometry of the 1st, 2nd elements and 3rd row transition metals

Most Commonly Used Methods - 5

AM1

Austin Model 1 (AM1)

Advantages:

- Generally predicts the heats of formation more accurately than MNDO
- Activation energies are improved over MNDO

Limitations:

1. It tends to poorly predict nitrogen pyramidalization
2. Limitation on energy:
   - Prediction of heat formation may inaccurate for molecules with large amount of charge localization
   - Prediction of rotational barrier to be one-third the actual barrier
   - Predicting five-member ring be too stable
3. Geometries involving phosphorus are predicted poorly
4. Systematic errors in alkyl group energies (too stable)
5. Hydrogen bond length correct, but wrong in direction…

AM1 predicts energies and geometries better than MNDO, but not as well as PM3.

Most Commonly Used Methods - 6

PM3

Use same questions as AM1 with an improved set of parameters
Most popular method for organic systems
More accurate than AM1 in hydrogen bond angle, but less in energy

Advance:
- The formation energies are more accurate than MNDO and AM1
- Hypervalent compounds are predicted more accurately.

Limitation:
- The rotation barrier around C-N bond in peptides is too low.
- Bonds between Si and the halide atoms are too short.
- Tend to predict incorrect electronic stats for germanium compounds.
- Tends to predict sp3 nitrogen being pyramidal
- Protons affinities are not accurate.
- The predicted charge on nitrogen is incorrect
- Nonbonded distances are too short.
- Hydrogen bond are too short by 0.1 angstrom

PM3 predicts engeries and bond lengths more accurately than AM1 or MNDO

Most Commonly Used Methods - 7

PM3/TM

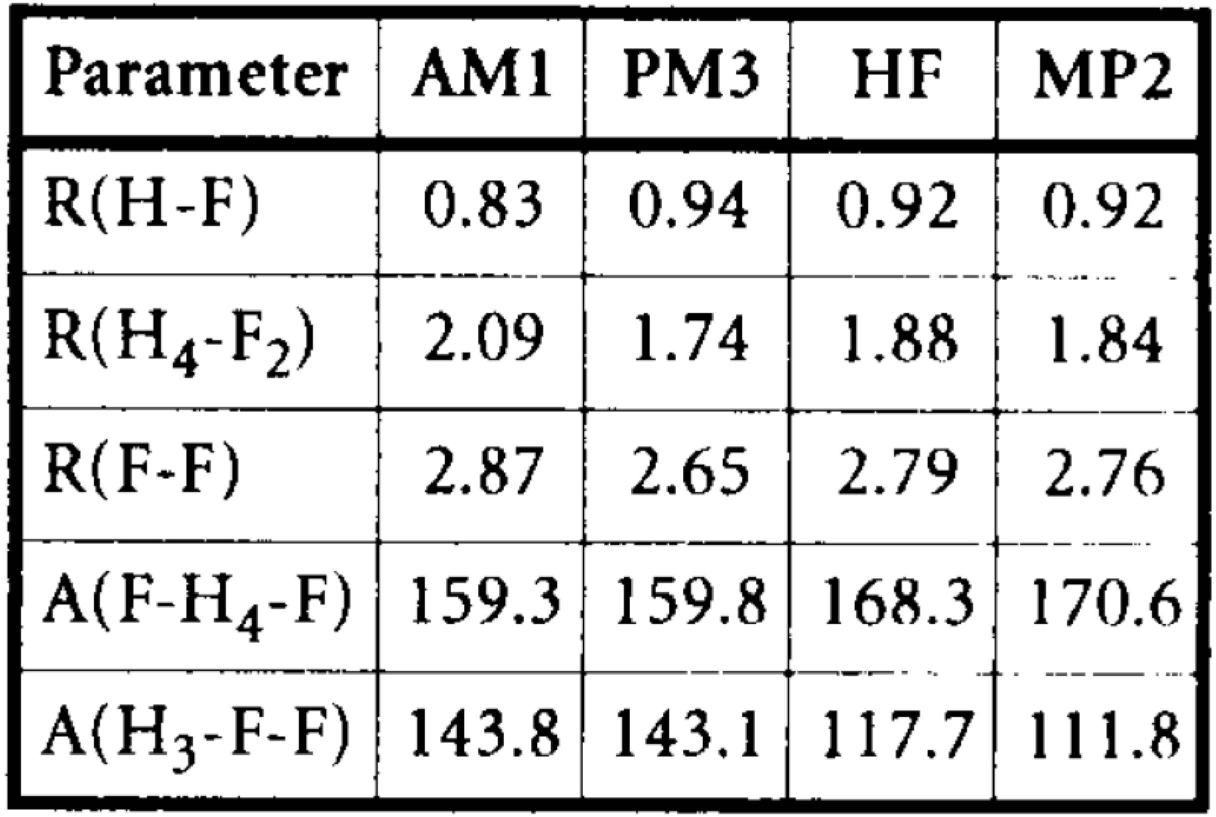
Extended PM3 method to include *d* orbitals
PM3/TM's parameterization isbased on reproducing geometries from Xray diffraction results, its results may be either reasonable or not.

TNDO

Typed Neglect of Differential Overlap
Parameterized for reproducing NMR chemical shift.

SAM1

Semi-ab initio method 1
It still neglects some of the integrals in HF, but including more than other semiempirical methods.
SAM1 are more accurate than AM1 and PM3 with more CPU times.
Vibrational frequencies computed are significantly more accurate than other semiempirical methods.



Parameter	AM1	PM3	HF	MP2
R(H-F)	0.83	0.94	0.92	0.92
R(H_4-F_2)	2.09	1.74	1.88	1.84
R(F-F)	2.87	2.65	2.79	2.76
A(F-H_4-F)	159.3	159.8	168.3	170.6
A(H_3-F-F)	143.8	143.1	117.7	111.8

Recommendation:
Semi-empirical methods may only be used for systems where parameters have been developed for all of their component atoms.

Types of problems: hydrogen bonding, transition structures, molecular containing atoms for which they are poorly parameterized, and so on,

电子关联与Post-HF方法

HF方法： 电子-电子作用 平均场近似

电子关联能 $E_c^{HF} = E_0 - E_{HF}$

E_0 - exact ground state energy
E_{HF} – HF energy for a given basis set

⇨ $E_c^{HF} < 0$ **HF**近似引起的误差 （大约总能的**0.3 ~ 2%** ）

Dynamical correlation – 电子运动瞬时相关
– 短程效应

Non-dynamical correlation – 与体系所处的状态有关，往往是由于单行列式波函数 ψ^{SD} 不能很好的描述基态。可能存在其它的行列式波函数具有接近的能量

⇨ multideterminantal wave-function

$$\Psi = a_0 \Psi^{HF} + \sum_i a_i \Psi_i$$

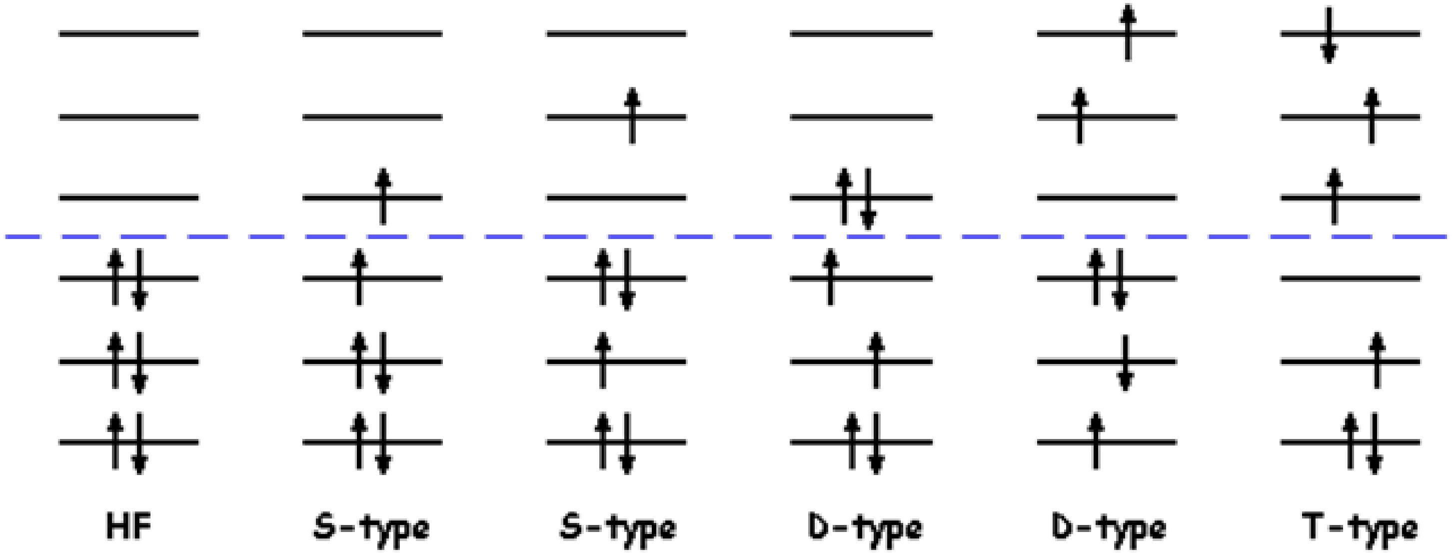
usually $a_0 \approx 1$

激发组态

Excited Slater Determinants (ESD)

考虑一个Closed-Shell System (RHF)，K个基函数构造分子轨道，体系电子数为N。则，占据轨道数(N/2)，空轨道数 K-N/2

改变基态电子的布局，可以得到基于HF基态波函数的S, D, T激发态Slater波函数

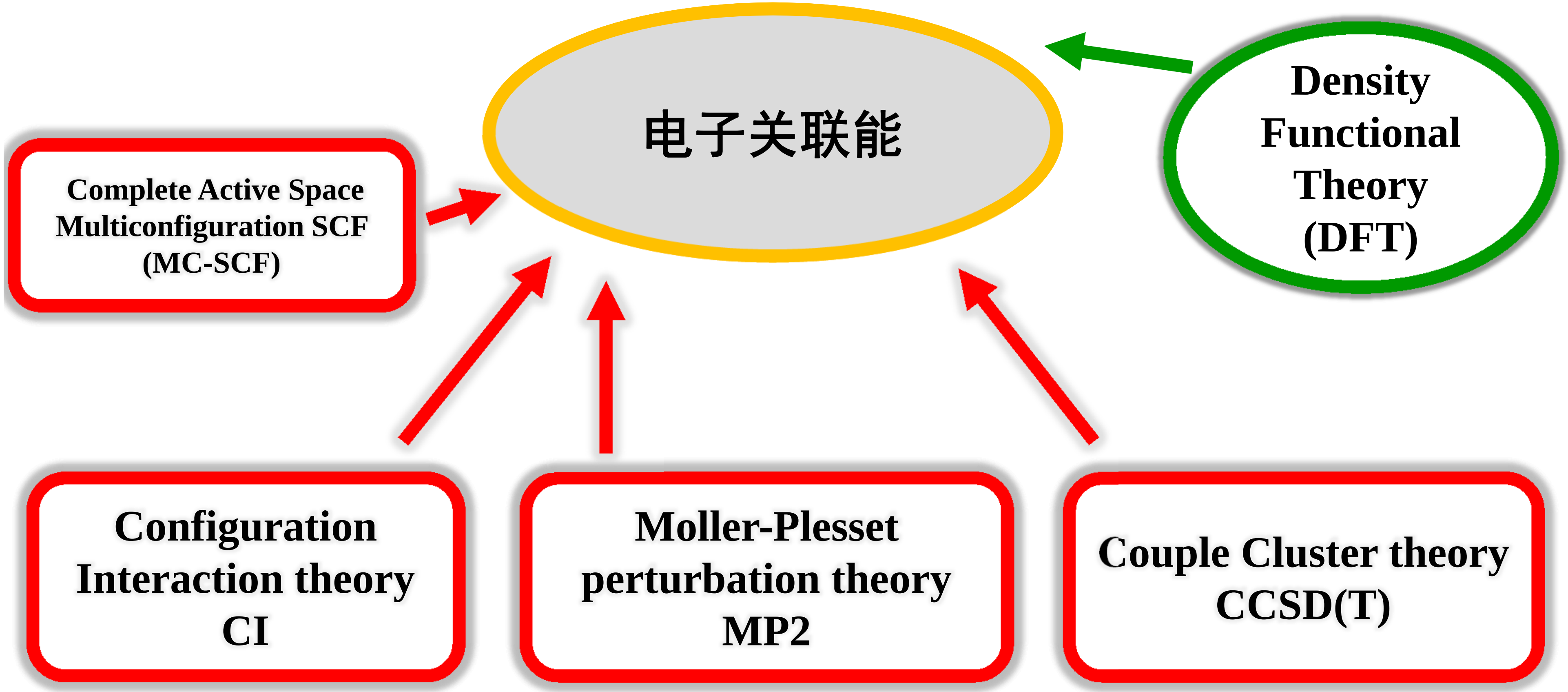


基组的数目决定ESD的数目

如果考虑所有的ESD函数，则电子-电子的相关能将被完全考虑

Practical Solutions

只对价电子的激发感兴趣，可以大大减少ESD数目



电子关联能

Complete Active Space Multiconfiguration SCF (MC-SCF)

Density Functional Theory (DFT)

Configuration Interaction theory CI

Moller-Plesset perturbation theory MP2

Couple Cluster theory CCSD(T)

Configuration Interaction (CI)

$$\Psi_{CI} = a_0\Psi_{SCF} + \sum_{S} a_S\Psi_S + \sum_{D} a_D\Psi_D + \sum_{T} a_T\Psi_T + \ldots$$

-**based on the variational principle**, including the slater determinant of excited states

The expansion coefficients are determined by imposing that the energy should be a minimum. The MOs used for building the excited determinants are taken from HF calculation and held fixed

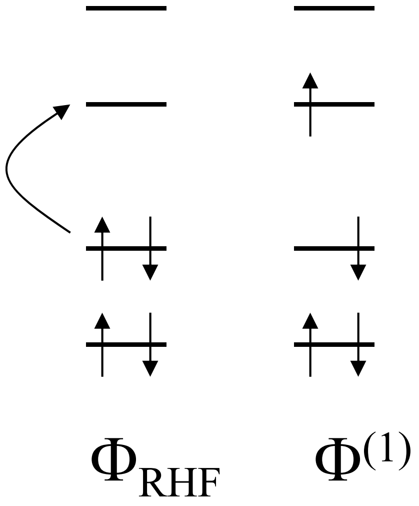
In the large basis set limit, all electron correlation methods scale at least as **N^5**

Example
Molecule: H_2O
Basis set: 6-31G(d) => 19BF => 38 spin MOs (10 occupied, 28 virtual)

The total number of excited determinants will be $C_{38}^{10} = 398637556$
Many of them will have different spin multiplicity and can therefore be left out in the calculation.
Generating only the singlet Configurational State Functions (CSF) we still obtain 1002001 determinants

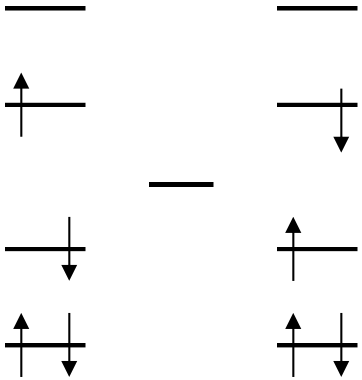
⇨ **Full CI method is only feasible for very small systems!!!**

Configuration State Functions



Consider a single excitation from the RHF reference.

Both Φ_{RHF} and $\Phi^{(1)}$ have S_z=0, but $\Phi^{(1)}$ is <u>not</u> an eigenfunction of S^2.



Singlet CSF

Linear combination of singly excited determinants <u>is</u> an eigenfunction of S^2.

<u>Configuration State Function, CSF</u>
(Spin Adapted Configuration, SAC)

Only CSFs that have the <u>same multiplicity</u> as the HF reference

$$\Phi(1,2) = \phi_1\alpha(1)\phi_2\beta(2) - \phi_1\alpha(2)\phi_2\beta(1)$$

Truncated CI methods 考虑有限激发态

$$\Psi_{CI} = a_0 \Psi_{SCF} + \sum_{S} a_S \Psi_S + \sum_{D} a_D \Psi_D + \sum_{T} a_T \Psi_T + \ldots$$

Truncating the expansion given above at level one =>

CIS - CI with only single excited determinants
CID - CI with only doubly excited determinants
CISD - CI with Singles and Doubles (scales as N^6)
CISDT - CI with Singles, Doubles and Triples (scales as N^8)
CISDTQ - CI with Singles, Doubles, Triples and Quadruples (scales as N^{10})
- gives results close to the full CI
- can only be applied to small molecules and small basis sets

CISD - the only CI method which is generally feasible for a large variety of systems
- recovers 80-90% of the available correlation energy

HF determinant 不会发生变化

CI's results can vary with the software, due to the HF reference state.

CI valid for excited state, however not for the energy of ground state

Multi-Configuration Self-Consistent Field Method (MCSCF)

CI method with the MOs are also varied, along with the coefficients of the CI expansion

MCSCF methods - are mainly used for generating a qualitatively correct wave-function
- recover the static part of the correlation (the energy lowering is due to the greater flexibility in the wave-function)

dynamic correlation – the correlation of the electrons' motions

In MCSCF methods the necessary configurations must be selected

⟹ **CASSCF (Complete Active Space SCF)**

- the selection of the configurations is done by partitioning the MOs into active and inactive spaces

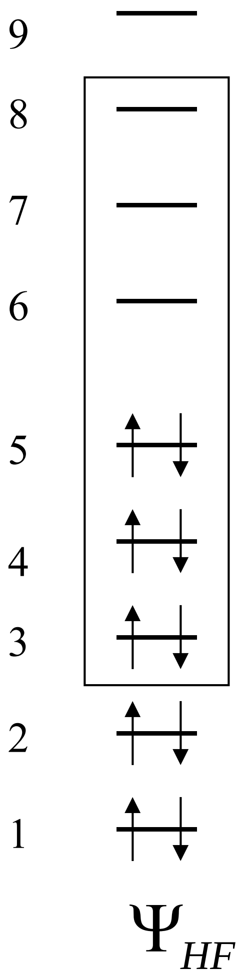
active MOs - some of the highest occupied and some of the lowest unoccupied MOs

Within the active MOs a full CI is performed

A more complete notation for this kind of methods is: [n,m]-CASSCF

- n electrons are distributed in all possible ways in m orbitals

H_2O MOs



Carry out Full CI ***and*** orbital optimization within a small active space.

Six-electron in six-orbital MCSCF is shown (written as [6,6]-CASSCF)

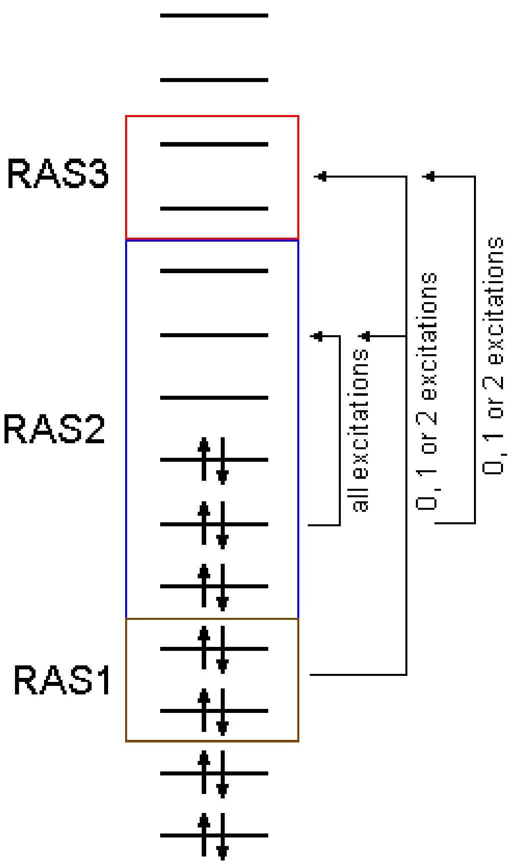
Complete Active Space Self-consistent Field (CASSCF)

Why?

1. To have a better description of the ground or excited state. Some molecules are not well-described by a single Slater determinant, e.g. O_3.
2. To describe bond breaking/formation; Transition States.
3. Open-shell system, especially low-spin.
4. Low lying energy level(s); mixing with the ground state produces a better description of the electronic state.

Alternative to CASSCF → Restricted Active Space SCF (RASSCF)

RASSCF – the active MOs are further divided into three sections: RAS1, RAS2 and RAS3



RAS1 space – MOs doubly occupied in the HF reference determinant

RAS2 space – both occupied and virtual MOs in the HF reference determinant

RAS3 space – MOs empty in the HF reference determinant

Configurations in RAS2 are generated by a full CI
Additional configurations are generated by allowing for example a maximum of two electrons to be excited from RAS1 and a maximum of two electrons to be excited to RAS3

⇩

RASSCF combines a full CI in a small number of MOs (RAS2) and a CISD in a larger MO space (RAS1 and RAS3)

Multi-Reference Configuration Interaction (MRCI)

The Configuration Interaction calculation uses MCSCF calculation wave-function,
not HF wave-function

More costly

Some notations for denoting this type calculations:

MCSCF+1+2 a MRCI calculation with single and double CI excitations
out of an MCSCF reference space
CASSCF+1+2

Coupled Cluster (CC) Methods

The idea in CC methods is to include all corrections of a given type to infinite order.
The wave-function is written as:

$$\Psi_{cc} = e^{\mathrm{T}}\Psi_0$$

where:

$$e^{\mathrm{T}} = 1 + \mathrm{T} + \mathrm{T}^2 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!}\mathrm{T}^k$$

with the cluster operator given by:

$$\mathrm{T} = \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3 + \ldots + \mathrm{T}_N$$

Acting on the HF reference wave function, the **T_i** operator generates all i-th excited Slater determinants:

$$\mathrm{T}_1\Psi_0 = \sum_{i}^{occ}\sum_{a}^{vir} t_i^a \Psi_i^a$$

$$\mathrm{T}_2\Psi_0 = \sum_{i<j}^{occ}\sum_{a<b}^{vir} t_{ij}^{ab} \Psi_{ij}^{ab}$$

$$\vdots$$

The exponential operator may be rewritten as:

$$e^{\mathrm{T}} = 1 + \mathrm{T}_1 + \left(\mathrm{T}_2 + \frac{1}{2}\mathrm{T}_1^2\right) + \left(\mathrm{T}_3 + \mathrm{T}_1\mathrm{T}_2 + \frac{1}{6}\mathrm{T}_1^3\right) + \ldots$$

First term generates the reference HF wave-function
Second term generates all singly excited determinants
First parentheses generates all doubly excited states (true doubly excited states by **T_2** or product of singly excited states by the product **$\mathrm{T}_1\mathrm{T}_1$**

The second parentheses generates all triply excited states, true (**T_3**) or products triples (**T_1T_2**, **$T_1T_1T_1$**)

The energy is given by:

$$E_{cc} = E_0 + \sum_{i<j}^{occ}\sum_{a<b}^{vir}\left(t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a\right)\left(\langle \Phi_i\Phi_j \mid \Phi_a\Phi_b\rangle - \langle \Phi_i\Phi_j \mid \Phi_b\Phi_a\rangle\right)$$

So, the coupled cluster correlation energy is determined completely by the singles and doubles amplitudes and the two-electron MO integrals

Truncated Coupled Cluster Methods

If all **T_N** operators are included in **T** the CC wave-function is equivalent to full CI wave-function, but this is possible only for the smallest systems.

⇨ Truncation of **T**

Including only the **T_1** operator there will be no improvement over HF, the lowest level of approximation being **$T=T_2$** (→ CCD=Coupled Cluster Doubles)

If **$T=T_1+T_2$** → CCSD → **scales as K^6** the only generally applicable model
If **$T=T_1+T_2+T_3$** → CCSDT → **scales as K^8**

Moller-Plesset Perturbation Theory

- **a perturbational method** in which the unperturbed Hamiltonian is chosen as a sum over Fock operators

Correlation was added as a perturbation

$$H_0 = \sum_{i=1}^{N} F_i = \sum_{i=1}^{N}\left(h_i + \sum_{j=1}^{N}(J_{ij} - K_{ij})\right) = \sum_{i=1}^{N} h_i + 2\langle V_{ee}\rangle$$

Zero order wave-function is the HF determinant
Zero order energy is the sum of MO energies

First order energy is exactly the HF energy

The correlation energy is recovered starting with the second order correction (MP2 method)

The first contribution to the correlation energy involves a sum over doubly excited determinants which can be generated by promoting two electrons from occupied MOs *i* and *j* to virtual MOs *a* and *b*. The explicit formula for the second order Moller-Plesset correction is

$$E(MP2) = \sum_{i<j}^{occ}\sum_{a<b}^{vir} \frac{\left[\langle \Phi_i\Phi_j \mid \Phi_a\Phi_b\rangle - \langle \Phi_i\Phi_j \mid \Phi_b\Phi_a\rangle\right]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

MP2 method

- scales as N^5
- accounts for cca. 80-90% of the correlation energy
- is fairly inexpensive (from the computational resources perspective) for systems with reasonable number of basis functions (100-200)

mp3, mp4 similar
mp5 is seldom done (N^{10} time complexity or worse)

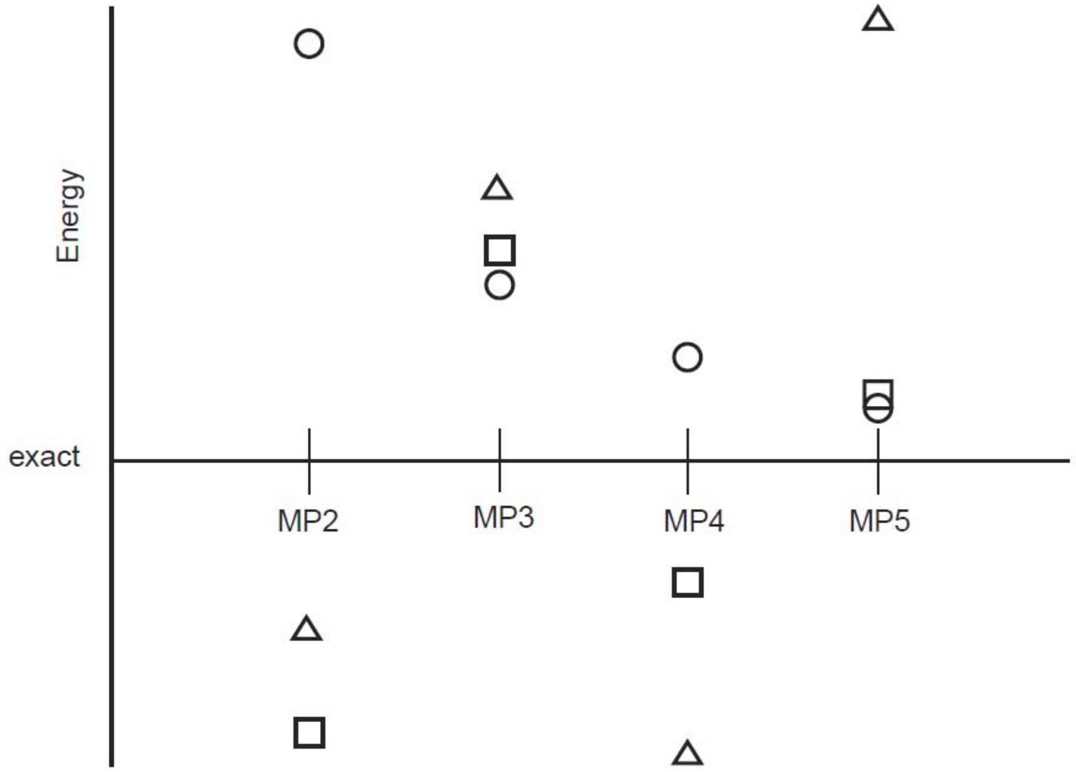


FIGURE 3.2 Possible results of increasing the order of Møller–Plesset calculations. The circles show monotonic convergence. The squares show oscillating convergence. The triangles show a diverging series.

Some systems: energies successively close to the total energy from mp2 to mp5
Some systems: energies occillattedly close to the total energy from mp2 to mp5
Some systems: energies diverse → single determinant reference is bad

Relative accuracy of energy

$$\text{HF} \ll \text{MP2} < \text{CISD} \cong \text{MP4} \cong \text{CCSD} < \text{CCSD(T)} < \text{CCSDT} < \text{Full CI}$$

Error in ab initio calculations:

1. The Born-Oppenheimer approximation
2. The use of an incomplete basis set
3. Incomplete correlation
4. The omission of relativistic effects

Calculation Cost

HF method scales as	N^4	(N - # of basis functions)
CI methods scale as	N^6-N^{10}	
MPn methods scale as	$>N^5$	
CC methods scale as	$>N^6$	

➡ **Correlated methods are not feasible for medium and large sized molecules!**

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{\hbar^2}{2m_e}\nabla^2 \right| \nu \right\rangle - \sum_I Z_I \left\langle \mu \left| \frac{1}{r_I} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma) \right]$$ 双电子四中心积分

Density functional theory (DFT)

- **1920s: Introduction of the Thomas-Fermi model.**
- **1964: Hohenberg-Kohn paper proving existence of exact DF.**
- **1965: Kohn-Sham scheme introduced.**
- **1970s and early 80s: LDA. DFT becomes useful.**
- **1985: Incorporation of DFT into molecular dynamics (Car-Parrinello)**

  (Now one of PRL's top 10 cited papers).
- **1988: Becke and LYP functionals. DFT useful for some chemistry.**
- **1998: Nobel prize awarded to Walter Kohn in chemistry for development of DFT.**

Basic Theory: The electron density is the essential

Hohenberg-Kohn Theorems

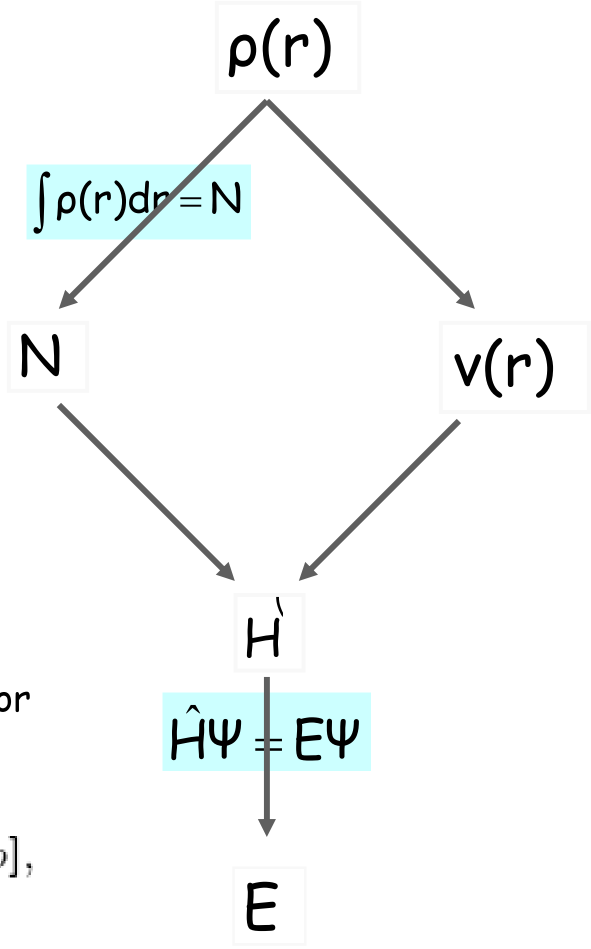
P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B 864 (1964)

The electronic Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 + \sum_{i}^{N} v(\mathbf{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

where the external potential is

$$v(\mathbf{r}_i) = -\sum_{Ai} \frac{Z_A}{r_{Ai}}$$



$\rho(r)$

$\int \rho(r)dr = N$

N

$v(r)$

$\hat{H}$

$\hat{H}\Psi = E\Psi$

E

First HK Theorem (**HK1**)

The external potential $V_{ext}(r)$ is (to within a constant) a unique functional of $\rho(r)$.

Since, in turn $V_{ext}(r)$ fixes H, the full many particle ground state is a uniquefunctional of $\rho(r)$.
Thus, the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system.

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r})V_{Ne}(\vec{r})d\vec{r} + F_{HK}[\rho],$$

$$F_{HK}[\rho] = T[\rho] + E_{ee}.$$

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0].$$

$$E_0[\rho_0] = \underbrace{\int \rho_0(\vec{r}) V_{Ne}\, d\vec{r}}_{\text{system dependent}} + \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{\text{universally valid}}.$$

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne}\, d\vec{r} + F_{HK}[\rho_0]$$

F_{HK}???

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] = \left\langle \Psi \middle| \hat{T} + \hat{V}_{ee} \middle| \Psi \right\rangle$$

$$E_{ee}[\rho] = \frac{1}{2} \int\int \frac{\rho(\vec{r}_1)\, \rho(\vec{r}_2)}{r_{12}}\, d\vec{r}_1 d\vec{r}_2 + E_{ncl}[\rho] = J[\rho] + E_{ncl}[\rho]$$

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r})V_{Ne}(\vec{r})d\vec{r} + F_{HK}[\rho]$$

with

$$F_{HK}[\rho] = \boxed{T[\rho]} + E_{ee}$$

$$E_{ee}[\rho] = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{non\_cl}[\rho] = \boxed{J[\rho]} + \boxed{E_{non\_cl}[\rho]}$$

Only $J[\rho]$ is known!

The explicit form of $T[\rho]$ and $E_{non\text{-}cl}[\rho]$ is the major challenge of DFT

$E_{non\_cl}[\rho]$ - contains all the effects of self-interaction correction and exchange and Coulomb correlation

Variational Principle in DFT

Second HK Theorem

The functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density.

Total energy function: $E_{V\,ext}[\rho] = <\Psi|\hat{T}+\hat{V}|\Psi> + <\Psi|\hat{V}_{ext}|\Psi>$

$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}]$ - variational principle

For any trial density ρ(r), which satisfies the necessary boundary conditions such as:

$\rho(r) \geq 0$ and $\int \rho(\vec{r})d\vec{r} = N$

and which is associated with some external potential V_{ext}, the energy obtained from the functional of F_{HK} represents an upper bound to the true ground state energy E_0.

First attempt: Thomas-Fermi model (1927)

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r}$$

L.H. Thomas, *Proc. Camb. Phil. Soc.*, 23, 542-548 (1927)
E. Fermi, *Rend. Acad., Lincei*, 6, 602-607 (1927)

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r} - Z\int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2$$

Problem in TF approximation: ignore correlation, and use local density approximation

Kohn and Sham (1965)

T[ρ] - kinetic energy of the system

Kohn and Sham proposed to calculate the exact kinetic energy of a non-interacting system with the same density as for the real interacting system.

$$T_{KS} = -\frac{1}{2}\sum_{i=1}^{N}\langle \Psi_i | \nabla^2 | \Psi_i \rangle$$

T_{KS} - kinetic energy of a fictitious non-interacting system of the same density ρ(r)

Ψ_i - are the orbitals for the non-interacting system (KS orbitals)

T_{ks} is not equal to the true kinetic energy of the system, but contains the major fraction of it
$T = T_{ks} + (T - T_{ks})$

Hohenberg-Kohn (1964) and Kohn-Sham (1965) ---Modern DFT

$$F_{HK}[\rho] = T_{KS}[\rho] + J[\rho] + E_{non\text{-}cl}[\rho]$$

$$E[\rho] = E_{Ne}[\rho] + T_{KS}[\rho] + J[\rho] + E_{xc}[\rho] =$$

$$-\sum_{i=1}^{N} \int \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} |\varphi_i(r_1)|^2 dr_1$$

$$-\frac{1}{2} \sum_{i=1}^{N} \langle \varphi_i | \nabla^2 | \varphi_i \rangle$$

$$+\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \iint |\varphi_i(r_1)|^2 \frac{1}{r_{12}} |\varphi_j(r_2)|^2 dr_1 dr_2$$

$$+E_{xc}[\rho]$$

$E_{xc}[\rho]$ includes everything which is unknown:

- exchange energy
- correlation energy
- correction of kinetic energy (T-T_{KS})

Question:
How can we uniquely determine the orbitals in our non-interacting reference system?
How can we define a potential such that it provides us with a slater determinant which is characterized by the same density as our real system?

Kohn-Sham Equations:

Minimize $E[\rho]$ with the conditions:

$$\int \rho(r)dr = N$$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

⇒

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(r_2)}{r_{12}} dr_2 + v_{xc}(r_1) - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}}\right] \varphi_i = \varepsilon_i \varphi_i$$

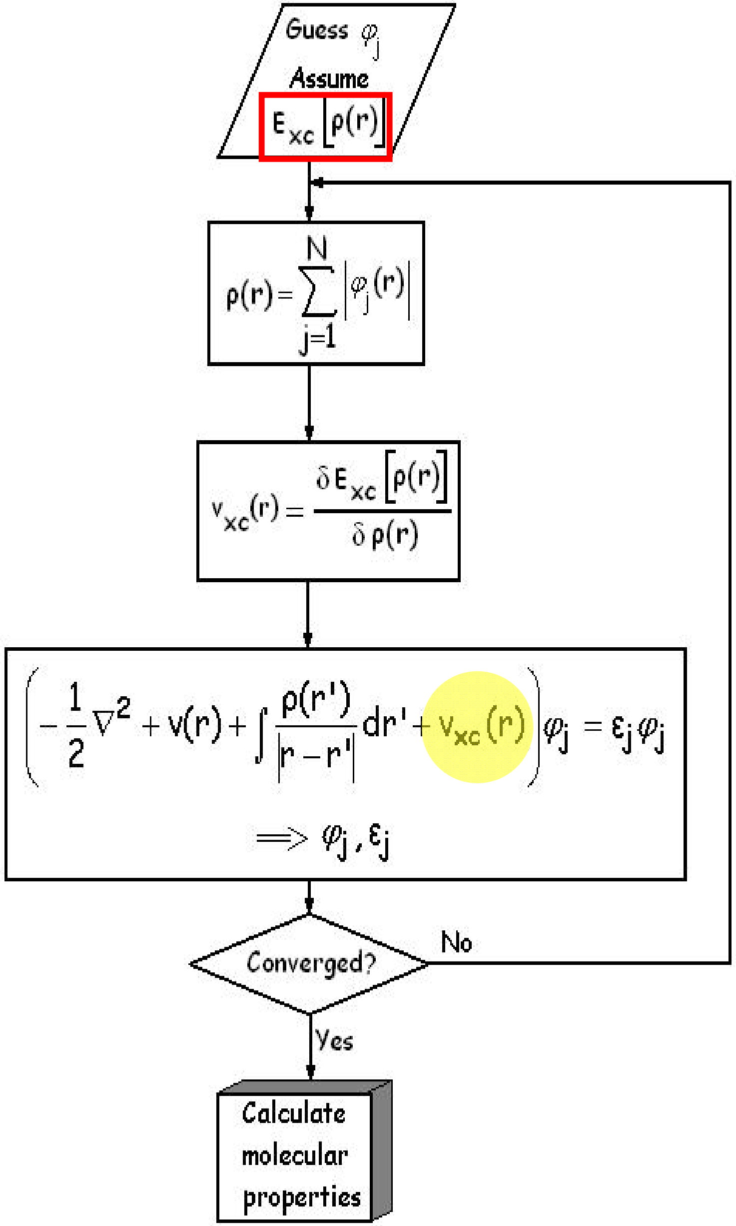
with:

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

Kohn-Sham Formalism

W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A 1133 (1965)



Guess φ_j

Assume

$E_{xc}\left[\rho(r)\right]$

$$\rho(r)=\sum_{j=1}^{N}\left|\varphi_j(r)\right|$$

$$v_{xc}(r)=\frac{\delta E_{xc}\left[\rho(r)\right]}{\delta\rho(r)}$$

$$\left(-\frac{1}{2}\nabla^2+v(r)+\int\frac{\rho(r')}{|r-r'|}dr'+v_{xc}(r)\right)\varphi_j=\varepsilon_j\varphi_j$$

$$\Longrightarrow \varphi_j,\varepsilon_j$$

Converged?

No

Yes

Calculate molecular properties

Kohn-Sham equations

$$\left(-\frac{1}{2}\nabla^2+v(r)+\int\frac{\rho(r')}{|r-r'|}dr'-\sum_i K_i(r)\right)\varphi_j=\varepsilon_j\varphi_j$$

Hartree-Fock equations

$E_{xc}[\rho]$ = ??

Local Density Approximation (LDA) – uniform electron gas

$$E_{xc}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r))dr$$

The exchange energy is about ten times larger than correlation in "standard" systems

ε_{xc} – the exchange-correlation energy per particle of a uniform electron gas of density ρ(r)
- depends on the density at r

$$\epsilon_{XC}(\rho(\vec{r})) = \epsilon_X(\rho(\vec{r})) + \epsilon_C(\rho(\vec{r}))$$

split into exchange and correlation contributions

$$\epsilon_X = -\frac{3}{4}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{1/3}$$

represents the exchange energy of an electron in a uniform electron gas of a particular density

$$E_X = C_X \int \rho^{4/3}(\mathbf{r})d\mathbf{r} \qquad C_X = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \quad \text{[Dirac]}$$

Slater exchange functional (S)

For the correlation part:

Monte-Carlo simulations of the homogenous electron gas – Ceperly and Alder

--- interpolation of these results → analytical expressions of ε_c

Vosko, Wilk & Nusair (1980) most widely used LDA → SVWN

Perdew &Wang (1992)

Local Spin Density Approximation (LSDA)

- variant of LDA for unrestricted formalism (open-shell systems)

Two spin-densities:

$$\rho_\alpha(\vec{r}) \text{ and } \rho_\beta(\vec{r})$$

$$\rho(\vec{r}) = \rho_\alpha(\vec{r}) + \rho_\beta(\vec{r})$$

$$E_{XC}^{LSD}[\rho_\alpha, \rho_\beta] = \int \rho(\vec{r})\varepsilon_{XC}(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}))\, d\vec{r}$$

Performance of LDA (LSDA)

- for atoms and molecules the exchange energy is usually underestimated by 10%, but this is compensated by an overestimation of correlation by 2 or 3 times.
- underbind core electrons and overbind atoms in molecules
- not able to reproduce the effects of bond breaking and forming

Molecules do not resemble a uniform electron gas!

Generalized Gradient Approximation (GGA)

$$E_{xc}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r), \nabla\rho(r), \ldots)dr$$

to account for the non-homogeneity of the true electron density → gradient

ε_{xc} depends on the density and its gradient at r

GGA E_{XC} is usually split into its exchange and correlation contributions:

$$E_{XC}^{GGA} = E_{X}^{GGA} + E_{C}^{GGA}$$

GGA 并不总是比LDA得到更好的结果，有时候会得到"更糟糕"的结果

$$E_{X}^{GGA} = E_{X}^{LDA} - \sum_{\sigma} \int F(s_\sigma)\, \rho_\sigma^{4/3}(\vec{r})\, d\vec{r}$$

$$s_\sigma(\vec{r}) = \frac{|\nabla\rho_\sigma(\vec{r})|}{\rho_\sigma^{4/3}(\vec{r})}$$

- the reduced gradient density
- interpreted as a local inhomogeneity parameter
- it has large values for large gradients and in regions of small densities
- it is zero for the homogenous electron gas

(1) Adjust ε_{xc} such that it satisfies all (or most) known properties of the exchange-correlation hole and energy.

PW91, PBE…

(2) Fit ε_{xc} to a large data-set own exactly known binding energies of atoms and molecules.

BLYP, OLYP, HCTH…

Forms of F for exchange functionals

First class (A.D. Becke, Phys. Rev. A, 38, 3098, 1988)

$$F^{B} = \frac{\beta s_\sigma^2}{1 + 6\beta s_\sigma \sinh^{-1} s_\sigma}$$

β= 0.0042 – empirical
Derived functionals: FT97, PW91, CAM(A) and CAM(B)

Second class (A. D. Becke, J. Chem. Phys 84, 4524, 1986; J. P. Perdew, Phys. Rev. B 33, 8822, 1986;J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett 77, 3865, 1996)

$$F^{P86} = \left(1 + 1.296\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^2 + 14\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^4 + 0.2\left(\frac{s_\sigma}{(24\pi^2)^{1/3}}\right)^6\right)^{1/15}$$

Derived functionals: B86, P, PBE

Correlation functionals
P86, PW91, LYP

Exchange-Correlation functionals

BLYP

$$\epsilon_x^{B88} = \epsilon_x^{LDA} \left[1 - \frac{\beta x^2}{2^{1/3} A_x (1 + 6\beta x \sinh^{-1}(x))} \right]$$

$$x = \frac{2^{1/3} |\nabla \rho|}{\rho^{4/3}} \quad , \quad A_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \quad , \quad \beta = 0.0042$$

$$\epsilon_c^{LYP} = - \frac{a}{1 + d\rho^{-1/3}} \left\{ \rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_w + \frac{1}{9} (t_w + \frac{1}{2} \nabla^2 \rho) \right] e^{-c\rho^{-1/3}} \right\}$$

$$t_w = \frac{1}{8} \left(\frac{|\nabla \rho|^2}{\rho} - \nabla^2 \rho \right) \quad , \quad C_F = \frac{3}{10} (3\pi^2)^{2/3}$$

$$a = 0.04918 \quad , \quad b = 0.132 \quad , \quad c = 0.2533 \quad , \quad d = 0.349$$

PW91

$$\epsilon_x^{PW91} = \epsilon_x^{LDA}[\rho]\left[\frac{1 + sa_1\sinh^{-1}(sa_2) + (a_3 + a_4e^{-100s^2})s^2}{1 + sa_1\sinh^{-1}(sa_2) + a_5s^4}\right]$$

$$a_1 = 0.19645 \quad , \quad a_2 = 7.7956 \quad , \quad a_3 = 0.2743 \quad , \quad a_4 = -0.1508 \quad , \quad a_5 = 0.004$$

$$\epsilon_c^{PW91} = \epsilon_c^{LDA}[\rho] + \rho H[\rho, s, t]$$

$$H = \frac{\beta^2}{2\alpha}\ln\left[1 + \frac{2\alpha(t^2 + At^4)}{\beta(1 + At^2 + A^2t^4)}\right] + C_{c0}[C_c(\rho) + C_{c1}]t^2e^{-100s^2}$$

$$A = \frac{2\alpha}{\beta}\left[\exp\left(-2\alpha\epsilon_c^{LDA}(\rho)/(\rho\beta^2)\right) - 1\right]^{-1} \quad , \quad t = \left(\frac{\pi}{3}\right)^{1/6}\frac{|\nabla\rho|}{4\rho^{7/6}}$$

$$\alpha = 0.09 \quad , \quad \beta = 0.0667263212 \quad , \quad C_{c0} = 15.7559 \quad , \quad C_{c1} = 0.0035521$$

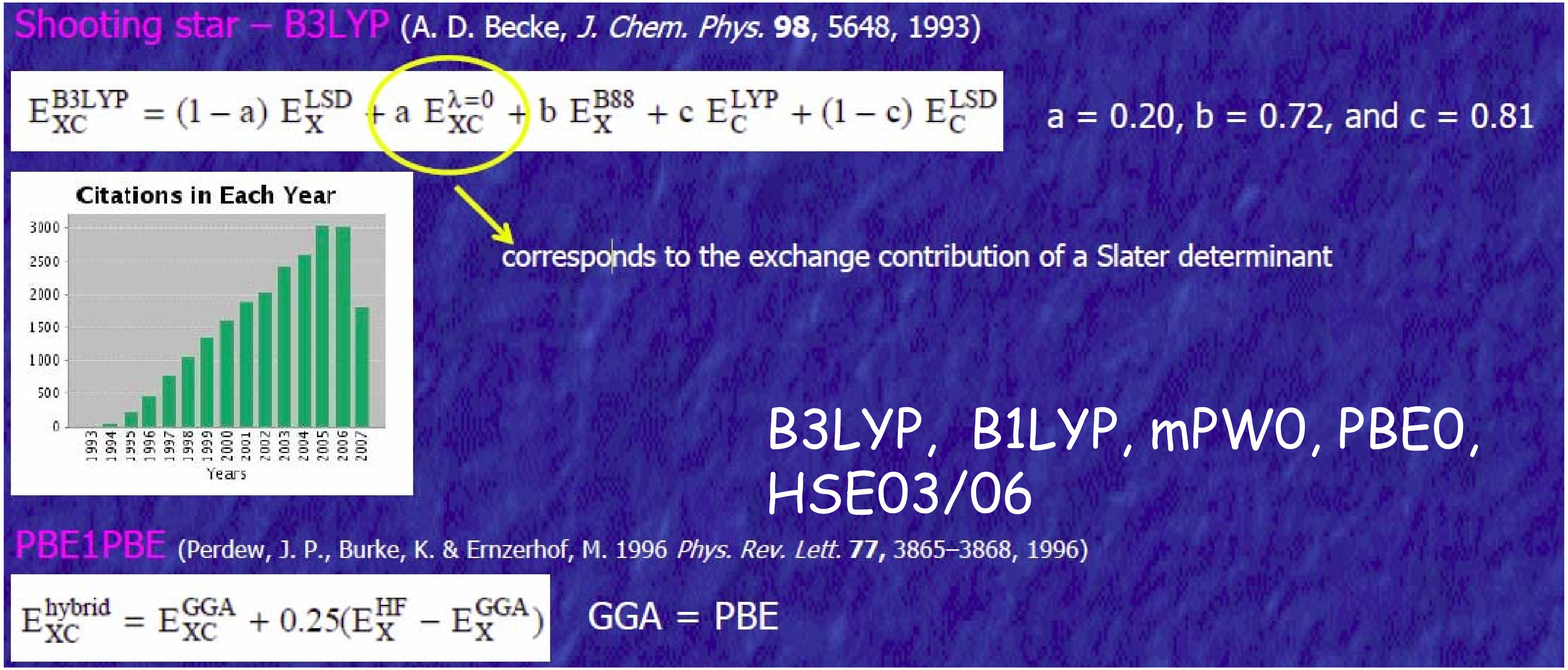
Hybrid Functionals

Since EX>>EC, an accurate expression for the exchange functional is a prerequisite for obtaining meaningful results from density functional theory.

$$E_{XC} = E_X^{exact} + E_C^{KS} \qquad E_{xc}^{hyb}[\rho] = \alpha E_x^{KS} + (1-\alpha)E_{xc}^{GGA}$$

E_X^{KS}-the exact exchange calculated with the exact KS wave function

α- fitting parameter



Shooting star – B3LYP (A. D. Becke, *J. Chem. Phys.* **98**, 5648, 1993)

$$E_{XC}^{B3LYP} = (1-a)\,E_X^{LSD} + a\,E_{XC}^{\lambda=0} + b\,E_X^{B88} + c\,E_C^{LYP} + (1-c)\,E_C^{LSD}$$

a = 0.20, b = 0.72, and c = 0.81

corresponds to the exchange contribution of a Slater determinant

Citations in Each Year

B3LYP, B1LYP, mPW0, PBE0, HSE03/06

PBE1PBE (Perdew, J. P., Burke, K. & Ernzerhof, M. 1996 *Phys. Rev. Lett.* **77,** 3865–3868, 1996)

$$E_{XC}^{hybrid} = E_{XC}^{GGA} + 0.25(E_X^{HF} - E_X^{GGA})$$

GGA = PBE

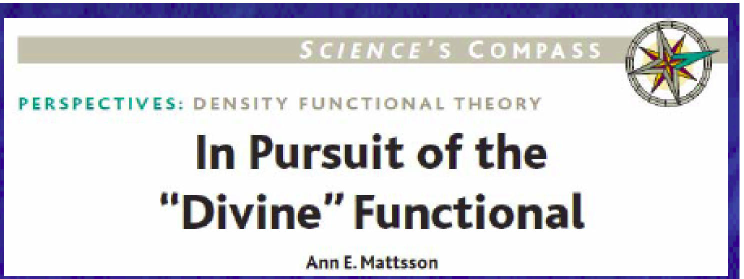
Meta-GGAs

The natural next step is to introduce higher derivatives into the functional, namely the density Laplacian, $\nabla^2\rho$ and the kinetic energy density, $\tau = \sum_i |\nabla\varphi_i|^2$

In the meta-GGA's, the exchange-correlation potential becomes orbital-dependent !

$$\varepsilon_{xc} = \varepsilon_{xc}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r}), \sum_i |\nabla\varphi_i|^2)$$

Jacob's ladder of DFT

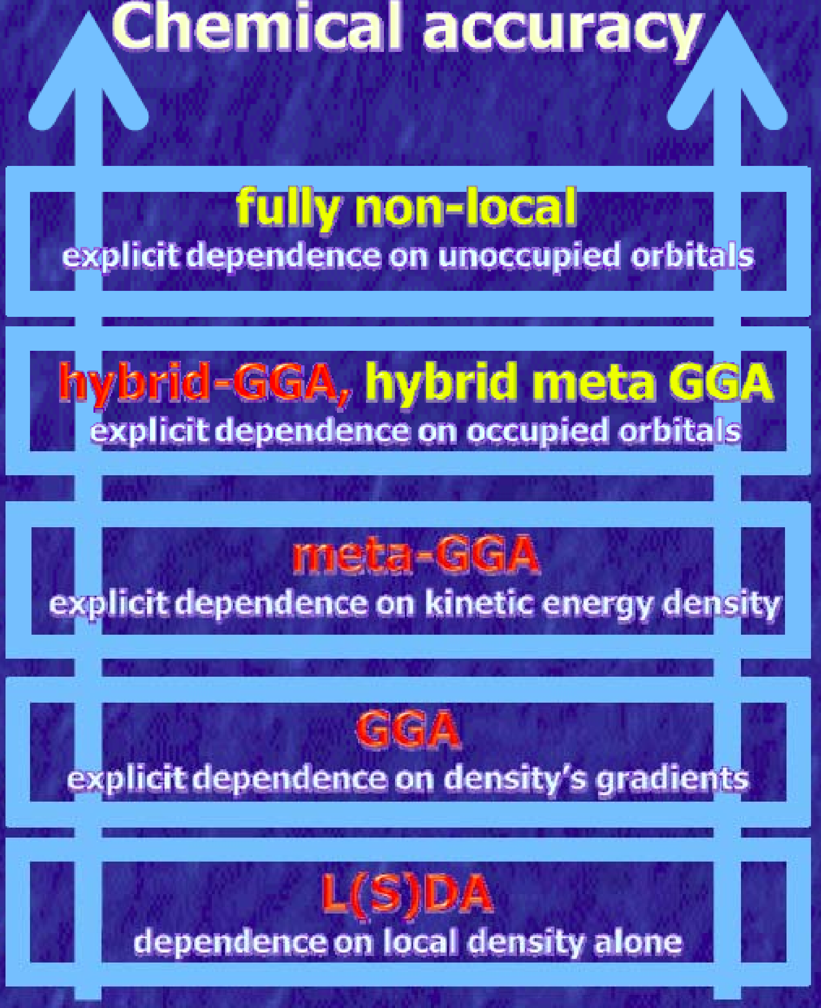


SCIENCE'S COMPASS

PERSPECTIVES: DENSITY FUNCTIONAL THEORY

In Pursuit of the "Divine" Functional

Ann E. Mattsson



Chemical accuracy

unocc. $\{\varphi_i\}$	**fully non-local** explicit dependence on unoccupied orbitals	Görling-Levy, 1994; Engel-Dreizler, 1999; Bartlett et el., 2005; B2-PLYP (Grimme et el., 2006)
occ. $\{\varphi_i\}$	**hybrid-GGA, hybrid meta GGA** explicit dependence on occupied orbitals	B3LYP, PBE1PBE PKZB, TPSS
$\nabla^2\rho$	**meta-GGA** explicit dependence on kinetic energy density	Proynov-Salahub-95
$\nabla\rho$	**GGA** explicit dependence on density's gradients	B88-P86, PW91, PBE
ρ	**L(S)DA** dependence on local density alone	S-VWN

Hartree world

Exchange and Correlation Functionals

E_x	
LDA	GGA
S(later)	B86 Becke, JCP 84, 4524 '86 B(88) Becke, PRA 38, 3098 '88 P(W86) Perdew, Wang, PRB 33, 8800 '86 P91 Perdew et al., PRB 46, 6671 '92 PBE Perdew, Burke, Ernzerhof, PRL 77, 3865, '96 revPBE Zhang, Yang, PRL 80, 890 '98 RPBE Hammer, Hansen, Norskov, PRB 59, 7413 '99

E_c	
LDA	GGA
(VBH) von Barth, Hedin, J. Phys. C 5, 1629 '72 VWN Vosko, Wilk, Nusair, Can. J. Phys. 58, 1200, '80 PW91 Perdew, Wang, PRB 45, 13244 '92	P(86) Perdew, PRB 33, 8822 '86 LYP Lee, Yang, Parr, PRB 37, 785 88' P91 (siehe links) PBE (siehe links)

ab-initio functionals:
fitted to theoretical data

semiempirical functionals:
fitted to experimental data

In practice: BLYP, B3LYP, BPW91, …

Classification of Density Functionals: GGA, hybrid, meta…

L(S)DA functionals:
SVWN, SVWN3, SVWN5,
SPWL

Pure GGA functionals:
BP86, BLYP
BPW91, OLYP, XLYP
G96LYP, PBEPBE
HCTH, BPBE
G96LYP, MPWLYP, MPWPW91,

Pure meta GGA (τ) functionals:
BB95, MPW1K
THCTH, VSXC, PBEKCIS
TPSS, TPSSKCIS, mPWB95

Hybrid GGA functionals
B3LYP, B3P86
B3PW91, PBE1PBE
O3LYP, KMLYP
B98, B971, B972
M052X, THCTH-HYB
TPSSH, BMK, MPW1K, MPW3LYP
BHandH, BHandHLYP
BHandHHYB, HSE2PBE
HSE1PBE, CAM-B3LYP

Hybrid meta-GGA functionals:
B1B95, BB1K
PBE1KCIS, VS98,
PKZB, BMK, TPSS1KCIS, TPSSh
M05, M05-2X, MPW1B95
MPWB1K, MPW1KCIS
PW6B95, PWB6K

S.F. Sousa, P.A. Fernandes, M.J. Ramos, J.Phys.Chem.A, 111, 10439 (2007)
Yi-Gui Wang, *J. Phys. Chem. A* 2009, *113,* 10867–10872
Gaussian 03

Comparison of methods: e.g. H_2O

method	E_{tot} [a.u.]	H-O [Å]	∠HOH [°]	vibrational modes [cm^{-1}]			dipole moment [D]
				bending	sym. stretch	asym. stretch	
HF	-76.065	0.940	106.2	1751	4229	4130	1.984
MP2	-76.408	0.958	104.0	1643	3978	3855	1.852
CCSD(T)	-76.421	0.958	104.1	1659	3952	3845	1.839
SVWN	-75.911	0.970	104.9	1571	3832	3737	1.930
RPBE	-76.465	0.968	104.0	1635	3815	3722	1.863
BP86	-76.477	0.970	104.1	1613	3789	3690	1.889
B3LYP	-76.472	0.961	105.1	1629	3905	3804	1.848
exp.	-76.438	0.958	104.5	1648	3943	3832	1.854
	> 4‰	> 1%	> 1%	> 3%			> 1%

Different functionals for different properties

- **Structure**: bond lengths, bond angles, dihedrals
- **Vibrational frequencies**: wavenumbers, IR intensity, Raman activity
- **Kinetics**: barrier heights
- **Thermochemistry**: atomization energies, binding energies, ionization potentials, electron affinities, heats of formation
- **Non-bonded interactions**: stacking, hydrogen bonding, charge transfer, weak interactions, dipole interactions, π-π interactions

What functional should I use?!

Depends on:
- your problem (system, the property investigated)
- availability and the computational costs

Atomization energies: $\text{SVWN} \ll \text{BP86} < \text{BLYP} \approx \text{BPW91} \ll \text{B3P86} < \underline{\text{B3LYP} \approx \text{B3PW91}}$

Ionization energy: - B3LYP – the best!

Electron afinities: $\text{BLYP} \approx \text{BPW91} \approx \text{B3LYP}$

Vibrational frequencies: - (BLYP), B3LYP, ...

MO5-2X - bond dissociation energies, **stacking and hydrogen-bonding interactions** in nucleobase pairs

Exchange-Correlation Functional

交换相关泛函的“好”与“不好”并不在于泛函本身，而在于如何在描述合适的体系使用正确的泛函

Some known limitations of DFT

Unknown the exact functional → an intrinsic uncertainty in energy between DFT and true ground state energy , and there is no direct way to estimate the magnitude of this uncertainty

Limited accuracy in the calculation of excited states.

Underestimated the band gaps of semiconductor

Inaccurate results in week van der Waals attractions

Failure to describe some strong-correlated system

Some recent developments

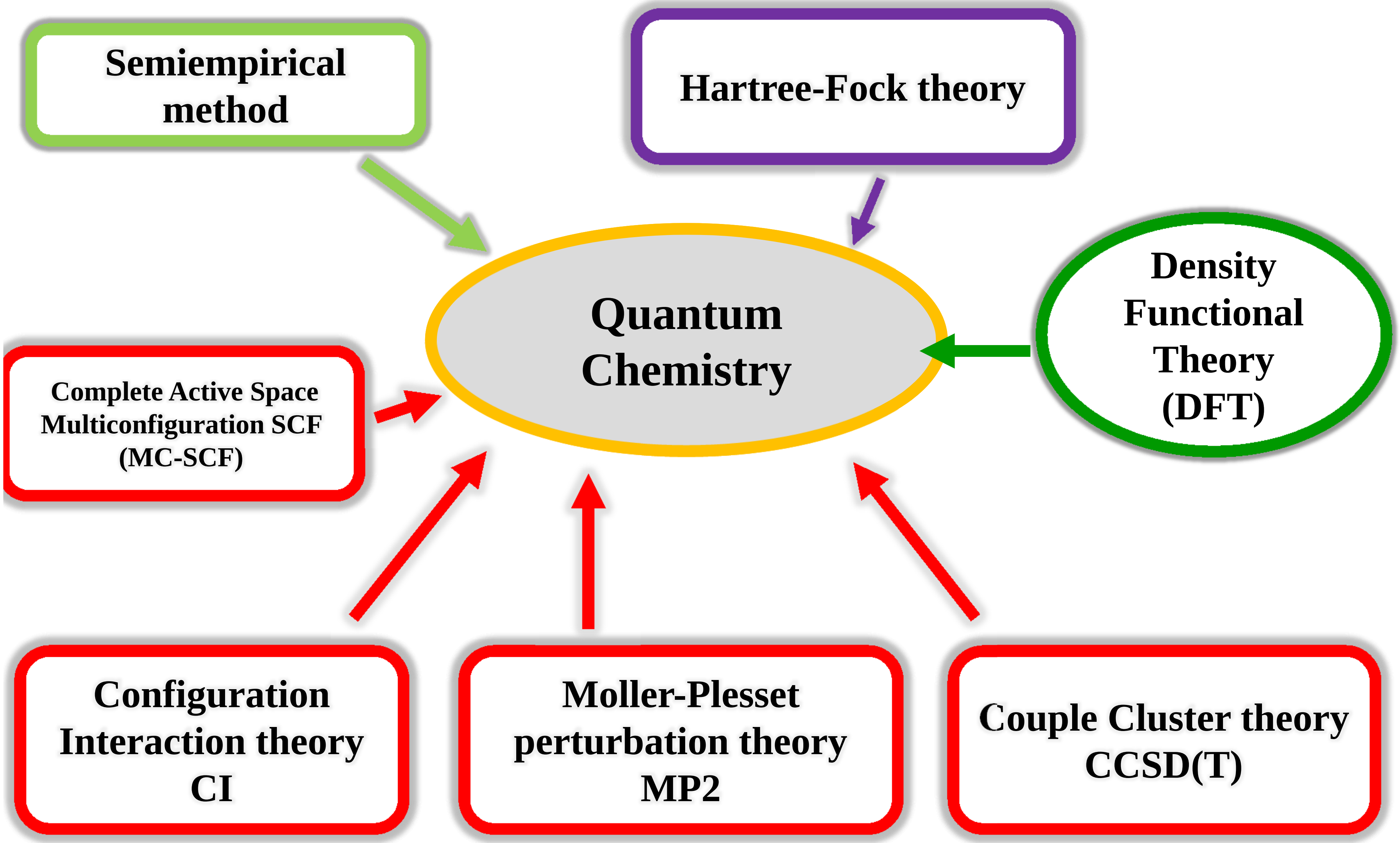
Linear scaling techniques (O(n))

LDA+U for strong correlated system

LDA+vdw for van der waals interaction

Non-collinear calculation

Practical Solutions



Semiempirical method

Hartree-Fock theory

Quantum Chemistry

Density Functional Theory (DFT)

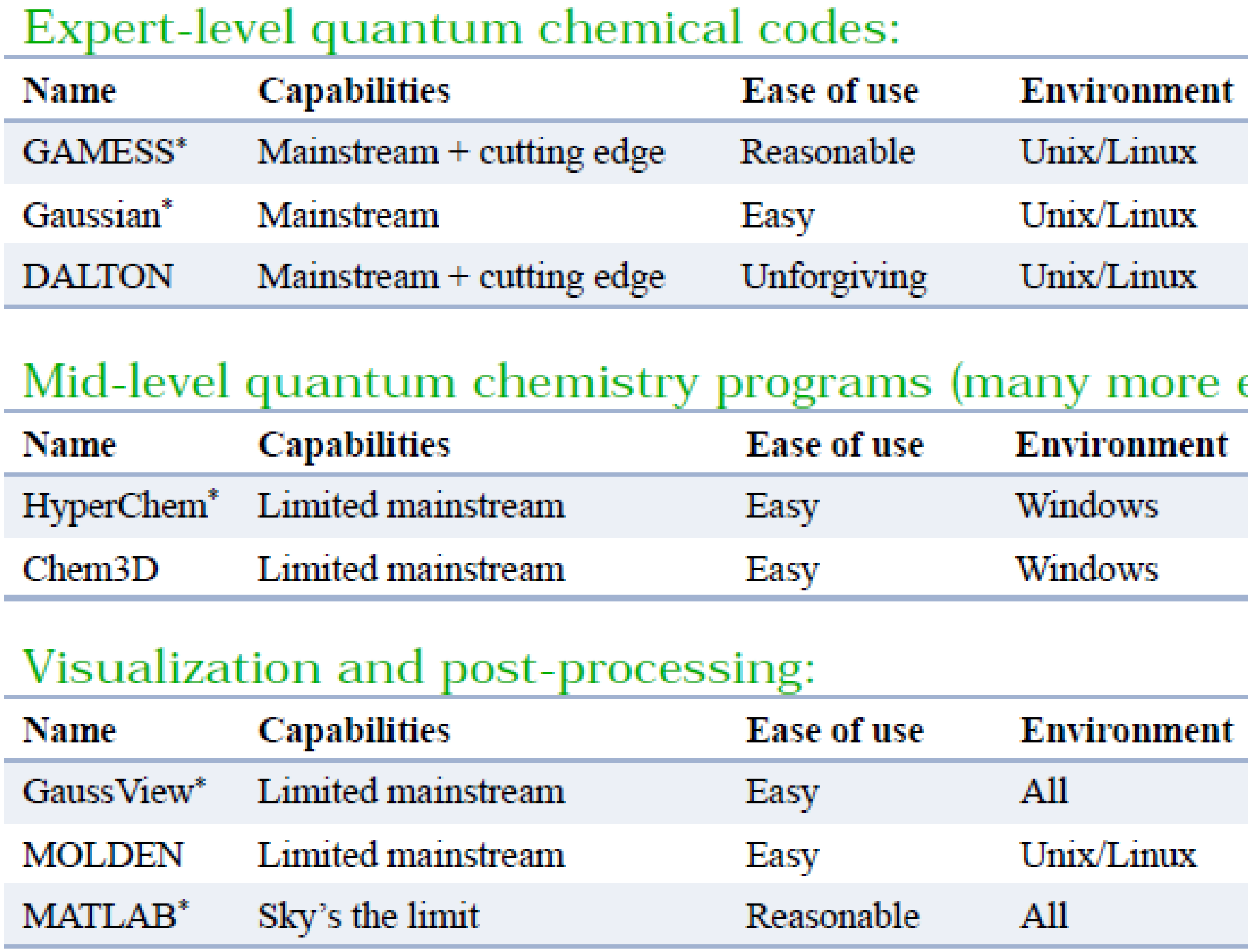
Complete Active Space Multiconfiguration SCF (MC-SCF)

Configuration Interaction theory CI

Moller-Plesset perturbation theory MP2

Couple Cluster theory CCSD(T)

Some tools for Quantum Chemistry



Expert-level quantum chemical codes:

Name	Capabilities	Ease of use	Environment
GAMESS*	Mainstream + cutting edge	Reasonable	Unix/Linux
Gaussian*	Mainstream	Easy	Unix/Linux
DALTON	Mainstream + cutting edge	Unforgiving	Unix/Linux

Mid-level quantum chemistry programs (many more

Name	Capabilities	Ease of use	Environment
HyperChem*	Limited mainstream	Easy	Windows
Chem3D	Limited mainstream	Easy	Windows

Visualization and post-processing:

Name	Capabilities	Ease of use	Environment
GaussView*	Limited mainstream	Easy	All
MOLDEN	Limited mainstream	Easy	Unix/Linux
MATLAB*	Sky's the limit	Reasonable	All

Modeling software

name	license	basis functions	pro/con
ABINIT	free	plane waves	very structured
ONETEP	pay	Wannier functions	linear scaling
Wien2k	pay	Y_{lm} + plane waves	very accurate
VASP	pay	plane waves	fast
PWscf	free	plane waves	fast

Kohn-Sham Orbitals

The orbitals satisfying the Kohn-Sham orbitals have no physical significance. Their only connection to the real world is that the sum of their squares add up to the exact density.

However, many authors recommend the KS orbitals as legitimate tools in qualitative MO considerations and this is due to the fact that the KS orbitals are not only associated with a one electron potential which includes all non-classical effects, but they are also consistent with the exact ground state density. Thus, in a sense, these orbitals are in a sense much closer to the real systems than the HF orbitals that neither reflect correlation effects nor do they yield the exact density.

On the other hand, the Slater determinant generated from the KS orbitals will not be confused with the true many-electron wave function! The exact wave function of the target system is simply not available in density functional theory! Accordingly, the eigenvalues εi connected to the KS orbitals do not have a strict physical meaning. In Kohn-Sham theory there is no equivalent of Koopmans' theorem, which could relate orbital energies to ionization energies. There is one exception though: as a direct consequence of the long range behavior of the charge density (its asymptotic exponential decay for large distances from all nuclei)

$$\rho(\vec{r}) \propto \exp[-2\sqrt{2I}\,|\vec{r}|]$$

the eigenvalue of the highest occupied orbital, ε_{max}, of the KS orbitals equals the negative of the exact ionization energy. This holds strictly only for ε_{max} resulting from the exact VXC, not for solutions obtained with approximations to the exchange-correlation potential.

J. Am. Chem. Soc. **1999,** *121,* 3414–3420

What Do the Kohn–Sham Orbitals and Eigenvalues Mean?

Ralf Stowasser and Roald Hoffmann*