

# 上一节课回顾

- 固体材料与纳米材料的最主要区别?
- 材料特性依赖于什么因素?
- 如何从理论上理解材料特性?
- 原子尺度到宏观尺度的材料设计
- 体系的哈密顿量

# 固体材料与纳米材料的最主要区别



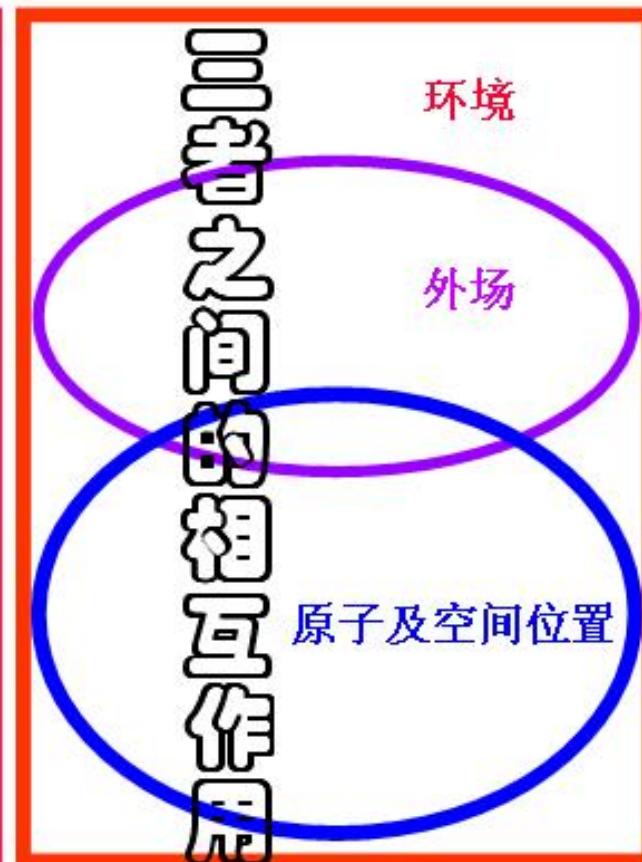
固体有平移对称性：  
理想情形没有表面和界面(或可忽略不计).

对固体材料，其特性是由几何结构与电子结构决定的，  
对纳米材料，其特性也是由几何结构与电子结构决定的

只要注意到上述的区别，研究固体材料的方法也可用于纳米材料的研究。但需要注意适用条件。

# 材料特性依赖于什么因素？

- 原子的空间位置：
  - 原子种类（键）
  - 空间位置
- 外场：
  - 电磁场
  - 温度
  - 压力
  - 辐射
- 环境效应：
  - 开放系, 耗散



物理的特性、  
化学的特性、  
生物的特性，  
与这三者有关

原子的空间位置最为重要：

i.e., Carbon: graphite, diamond, fullerenes, tubes

# 如何从理论上理解材料特性？

当不考虑外场和环境效应时，材料特性完全由原子种类和原子位置决定。(还原论观点)

- 给定原子种类，能否决定几何构型及力学特性？

原理：封闭体系的总能量极小态是稳定的。

问题：如何确定总能量及其极小化？

- 给定原子种类和几何结构，能否确定材料的电特性？

原理：用量子力学确定电子的状态（能量，密度等）

问题：如何求解多体量子力学问题？

# 原子尺度到宏观尺度的材料设计

- 首先找到原子的空间构型
  - With desired functions
  - With minimum total energy
- 从微观到介观再到宏观
  - By multi scale methods

原子尺度材料设计是建立在第一性原理电子结构计算基础上的。  
多尺度材料设计还与分子动力学及有限元有关。

理解与设计新材料的关键之一是理解材料结构与特性之间的关联。

结构依赖原子位置，而原子位置依赖于原子种类和所带电荷：

离子-离子间电磁相互作用

电子-电子间电磁相互作用

电子-离子间电磁相互作用

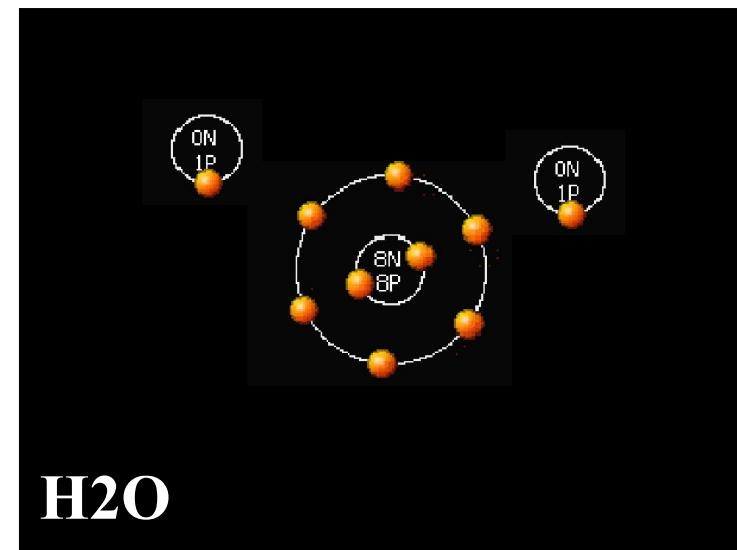
外场

# 最简单情形

- 当不考虑外场和环境效应时，材料特性完全由原子种类和原子位置决定。相互作用是电磁相互作用。

考虑水分子, H<sub>2</sub>O

- 1) 有几种原子核?
- 2) 有多少个电子? 有多少价电子?
- 3) 水分子的相互作用哈密顿量?
- 4) 外加电磁场的哈密顿量?
- 5) 外加压力对水分子会有那些改变?
- 6) 能否在量子力学框架严格求解水分子问题?



$$H(\{r_i\}, \{R_i\}) = T_{elec} + T_{nucl} + V_{nucl-nucl} + V_{nucl-elec} + V_{elec-elec}$$

- 哈密顿量是多体问题，如何求解？近似！

# 物理近似曾是一个笑话

## Spherical cow

[http://en.wikipedia.org/wiki/Spherical\\_cow](http://en.wikipedia.org/wiki/Spherical_cow)

From Wikipedia, the free encyclopedia

**Spherical cow** is a metaphor for highly simplified scientific **models** of complex real life phenomena.<sup>[1]</sup>

The phrase comes from a joke about **theoretical physicists**:

Milk production at a dairy farm was low, so the farmer wrote to the local university, asking for help from academia. A multidisciplinary team of professors was assembled, headed by a theoretical physicist, and two weeks of intensive on-site investigation took place. The scholars then returned to the university, notebooks crammed with data, where the task of writing the report was left to the team leader. Shortly thereafter the physicist returned to the farm, saying to the farmer "I have the solution, but it only works in the case of spherical cows in a vacuum."

It is told in many variants,<sup>[2]</sup> including a spherical horse in a vacuum, from a joke about a physicist who said he could predict the winner of any horse race to multiple decimal points - provided it was a perfectly elastic spherical horse moving through a vacuum.<sup>[3][4]</sup>

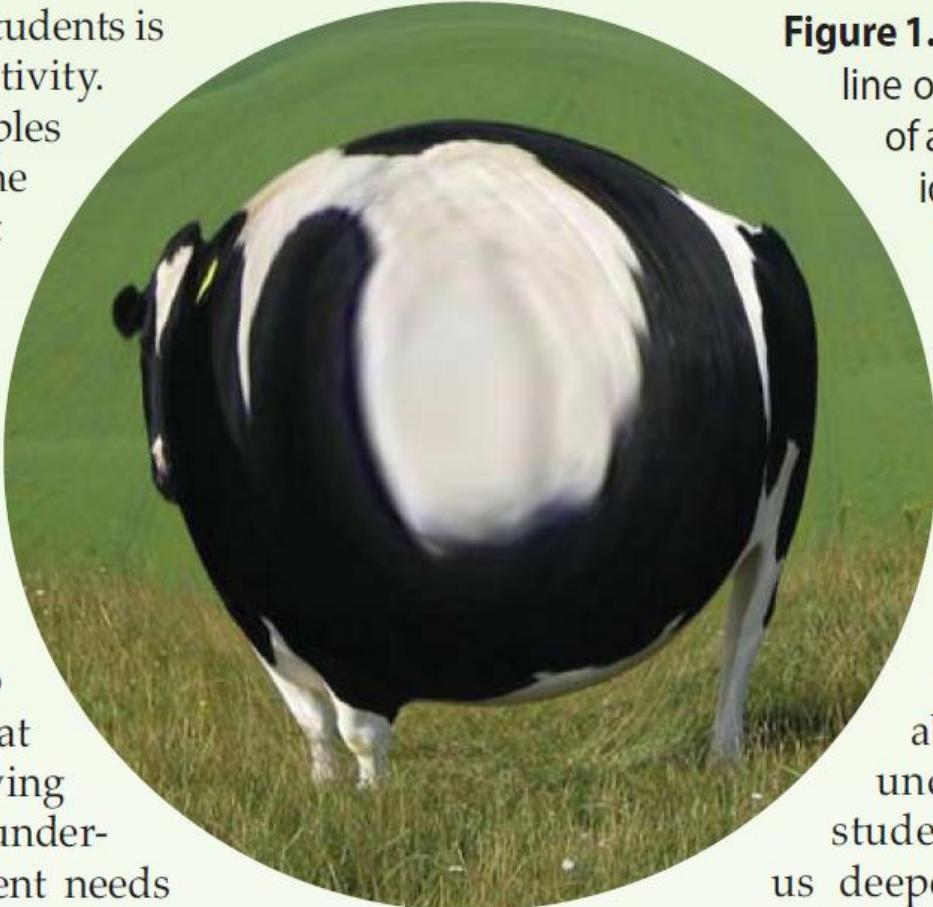
The point of the joke is that physicists will often reduce a problem to the simplest form they can imagine in order to make calculations more feasible, even though such simplification may hinder the model's application to reality.



A spherical cow jumps over the moon

# “First, we assume a spherical cow”

biology students is complex activity. Real examples from the field content reflect. But statements are trivial than expected. Of IPLS do more examples for sciences concerned to help recognize that the underlying a deeper understanding. Content needs



**Figure 1.** “First, we assume a spherical cow” is the punch line of a joke that pokes fun at the physicists’ manner of attacking problems. But for all its silliness, the joke identifies a bona fide aspect of physics culture that is not generally shared by colleagues in the life sciences. (Created by Erik Mazur and used with permission.)

合理近似  
是物理学  
的精髓

合理的近似  
是物理学  
的精髓

# 第2章 第一性原理方法

1. 密度泛函理论：原子单位，多粒子体系，绝热近似，哈特里近似，哈特里-福克近似，托马斯-费米理论，Hohenberg和Kohn的定理，Kohn-Sham方法，Kohn-Sham方程，交换关联能与LDA近似，Kohn-Sham方程的自洽求解，密度泛函理论的优缺点。
2. 总能量赝势方法I：赝势，动量空间的Kohn-Sham方程与总能量表达式，EWALD求和，发散项如何相消，动能截断，K空间抽样，超级原胞，力的计算，直接对角化，最陡下降法，CAR-PARRINELLO方法，ABINIT程序简介等。
3. 总能量赝势方法II：原子轨道，矩阵元的计算，总能量的计算，力的计算，SIESTA程序简介。
4. 应用于原子团簇
5. LAPW方法简介

# 第一性原理理论的重要性

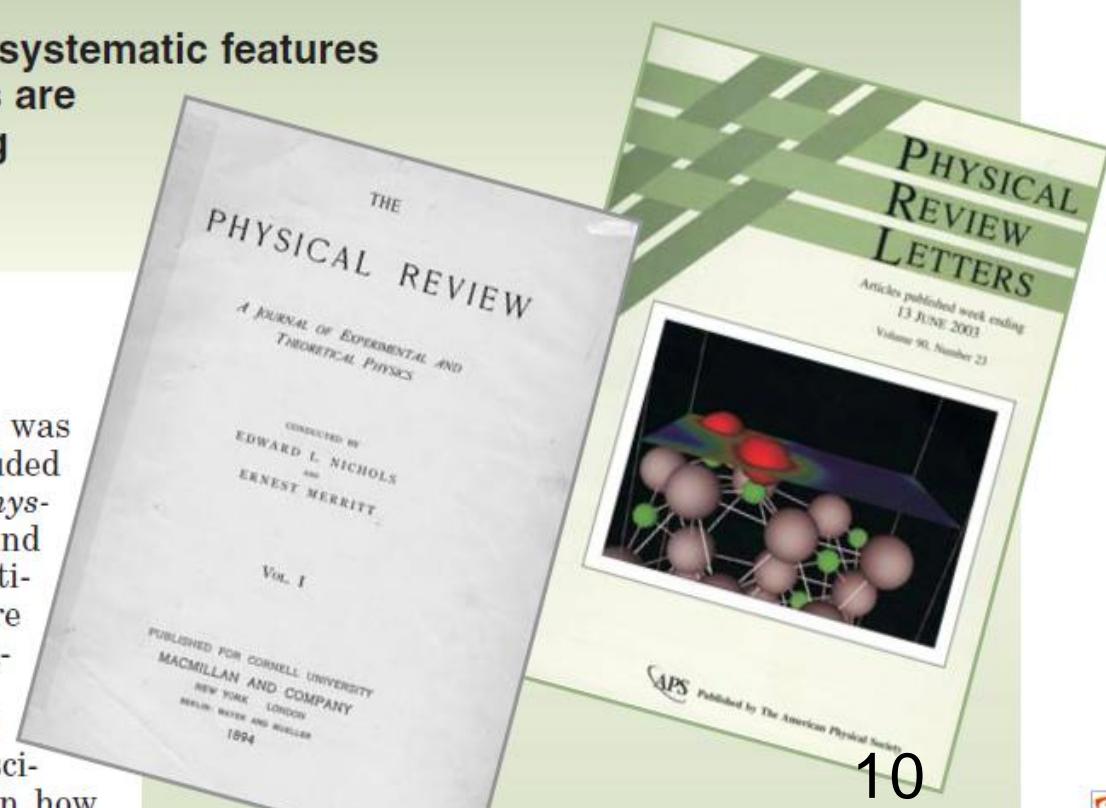
## Citation Statistics from 110 Years of *Physical Review*

Publicly available data reveal long-term systematic features about citation statistics and how papers are referenced. The data also tell fascinating citation histories of individual articles.

Sidney Redner

The first article published in the *Physical Review* was received in 1893; the journal's first volume included 6 issues and 24 articles. In the 20th century, the *Physical Review* branched into topical sections and spawned new journals (see figure 1). Today, all articles in the *Physical Review* family of journals (PR) are available online and, as a useful byproduct, all citations in PR articles are electronically available.

The citation data provide a treasure trove of quantitative information. As individuals who write scientific papers, most of us are keenly interested in how



# 最重要： 6/11

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

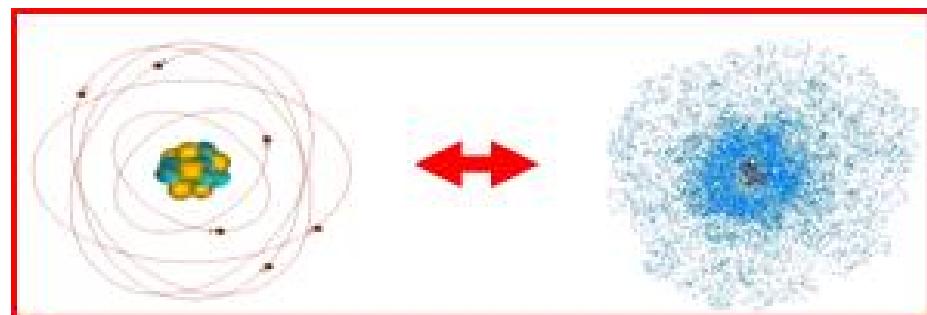
PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

# 第二章：第一性原理方法

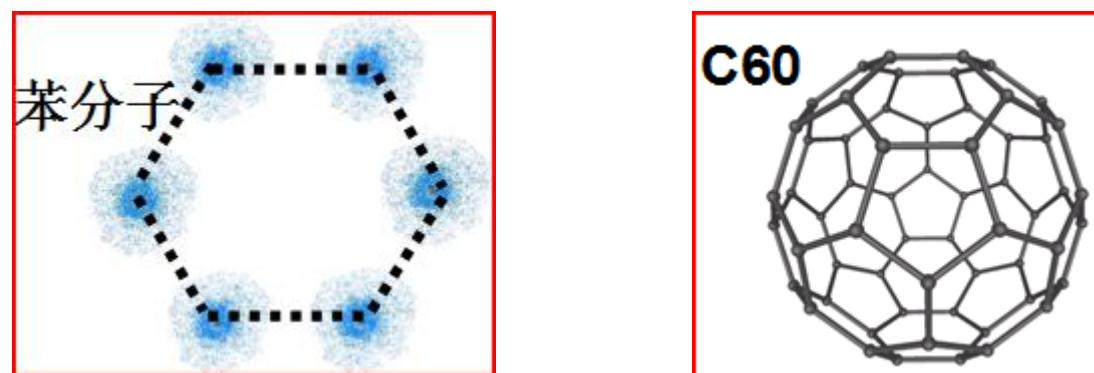
- 引论
- 绝热近似
- 平均场近似：
  - 哈特里-福克近似
  - 密度泛函理论
- 求解方法概述，优缺点
- 密度泛函理论的扩展

# 核、电子、原子、分子、晶体

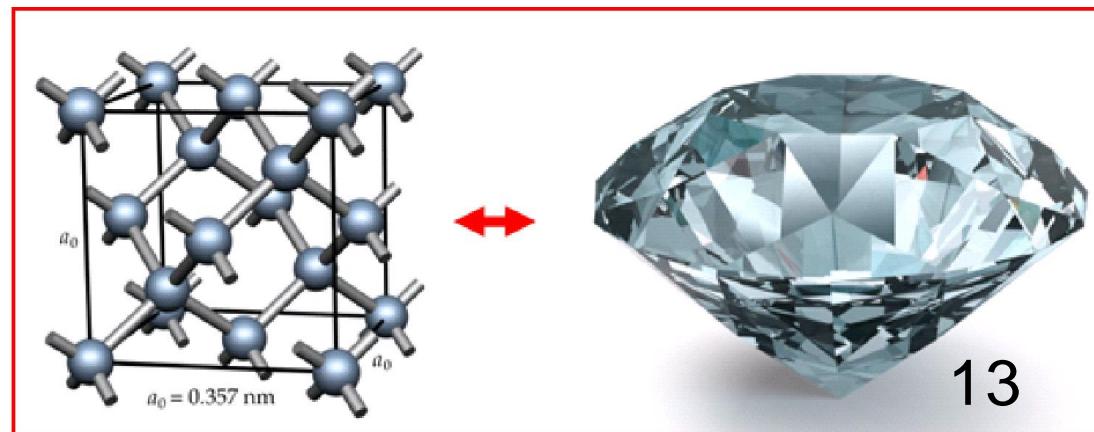
原子: 核 + 电子



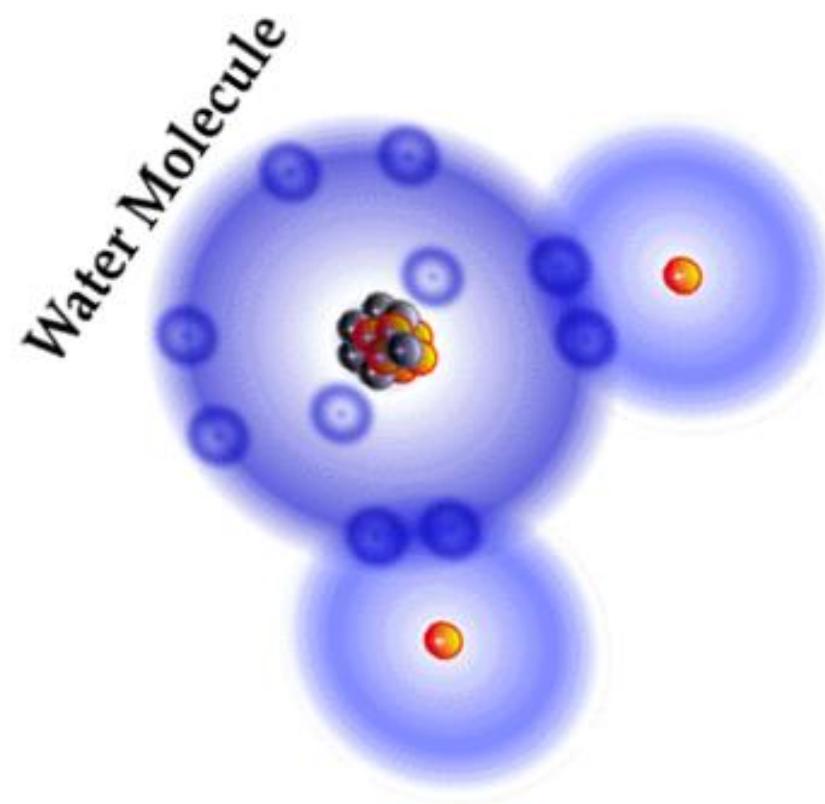
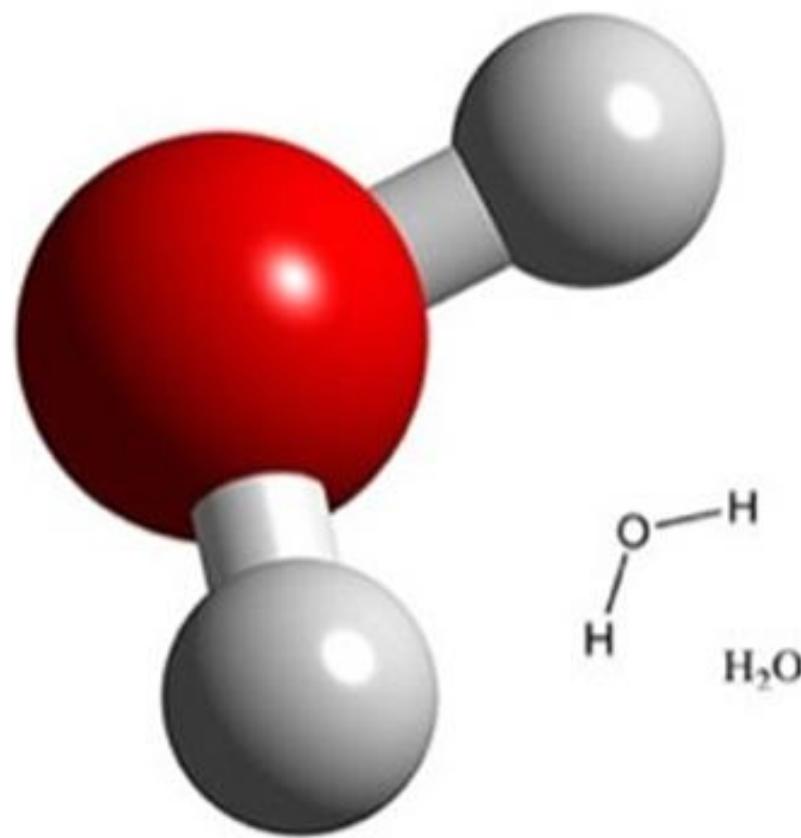
分子



固体  
(晶体)



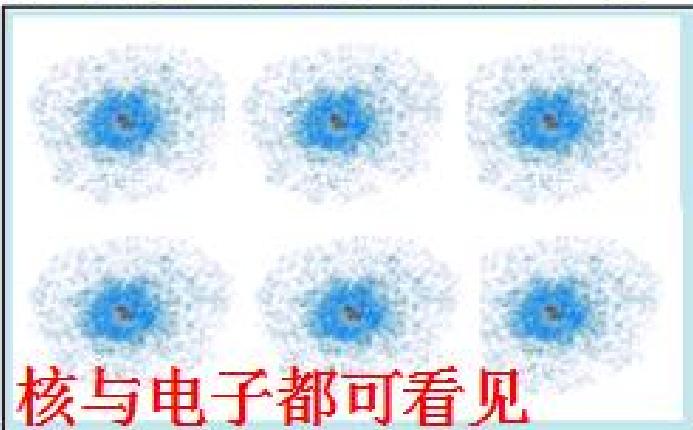
# 多体问题，例：Water: H<sub>2</sub>O



水分子组成：10个电子，3个原子核

# 绝热近似与平均场近似

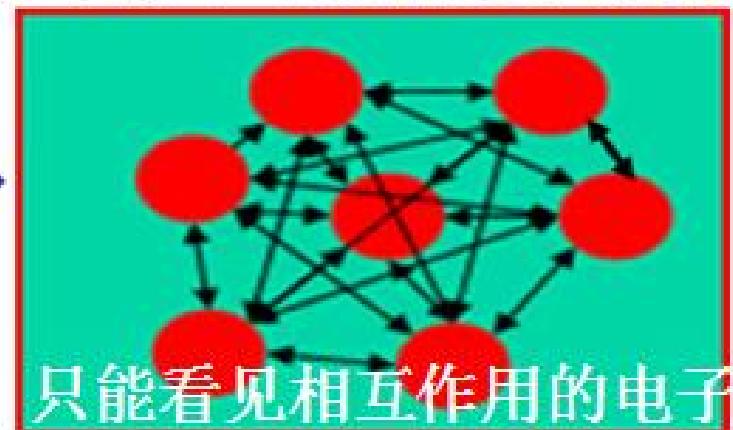
原子核与电子都在运动



核与电子都可看见

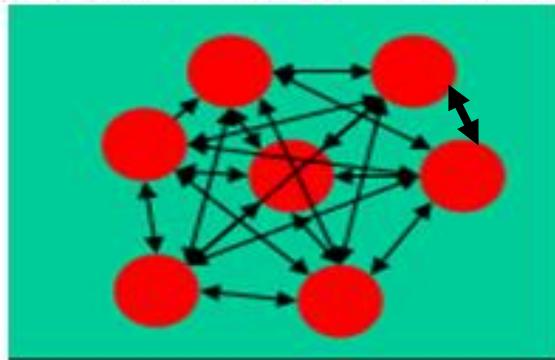
绝热  
近似

原子核不运动作为正电背景



只能看见相互作用的电子

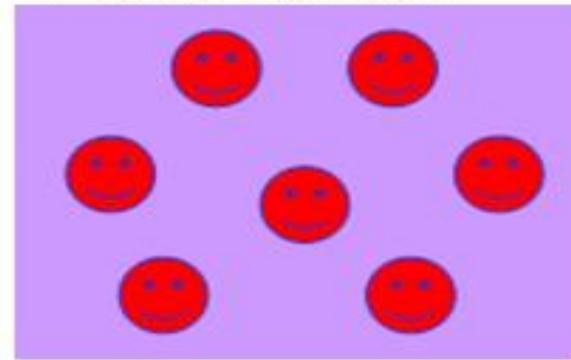
真实库仑相互作用：



相互作用的电子体系

平均场  
近似

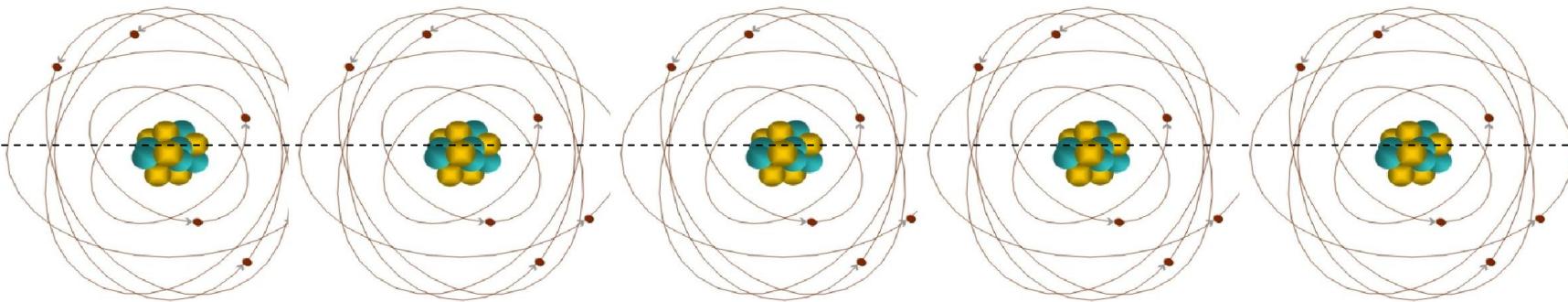
平均场有效势：



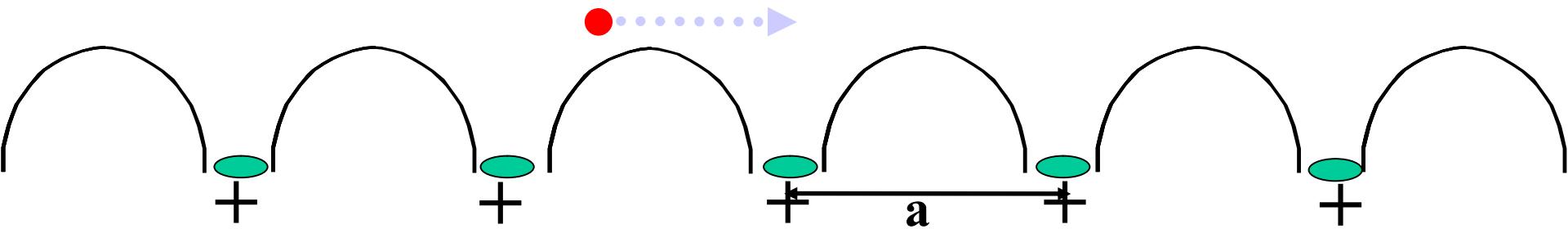
非相互作用的准粒子体系

# 例：1D 周期固体

1D无穷周期 – 真实: 无穷原子数目和无穷电子数目



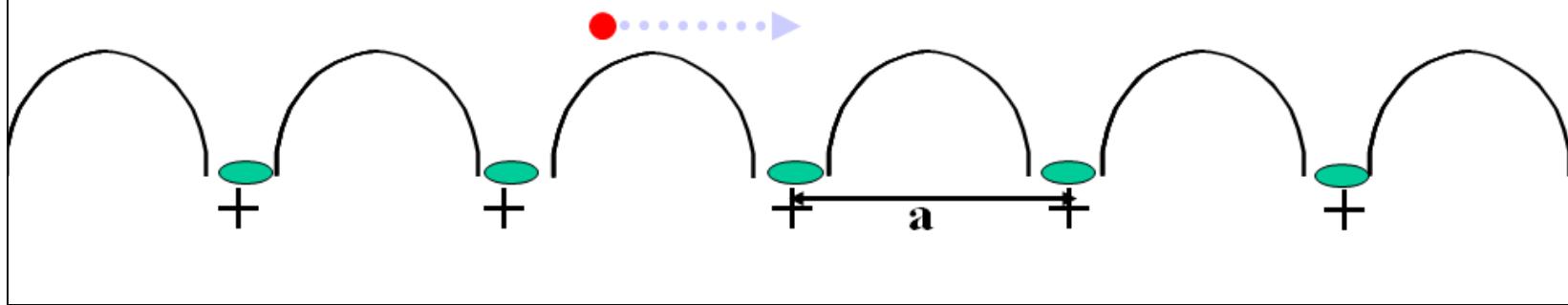
1D无穷周期 – 平均场近似: 单电子在周期势场中运动



密度泛函理论本质上是平均场，是固体及分子的最重要理论之一

# 思考题

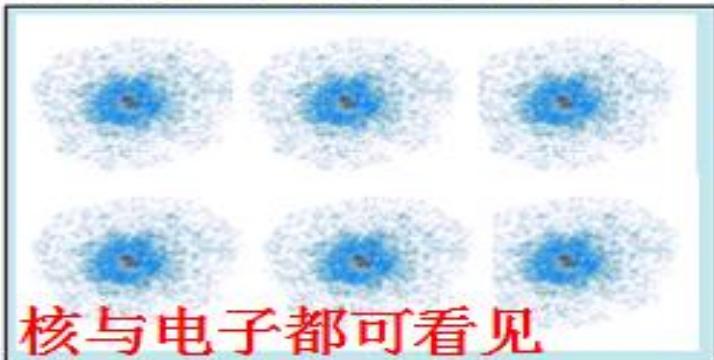
1D无穷周期 – 平均场近似: 单电子在周期势场中运动



“单电子在周期势场中运动”是否意味着是单电子问题？

- yes: 原来的电子都到哪里去了？
- no: 无穷多电子该如何处理，如何填充能级？

原子核与电子都在运动



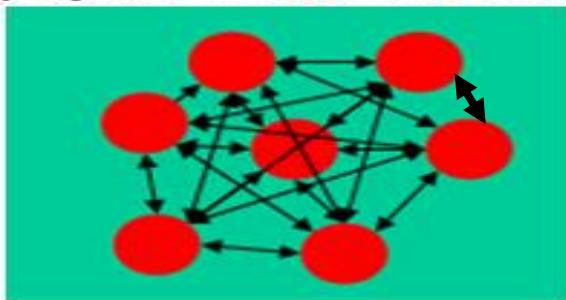
核与电子都可看见

绝热  
近似

原子核不运动作为正电背景



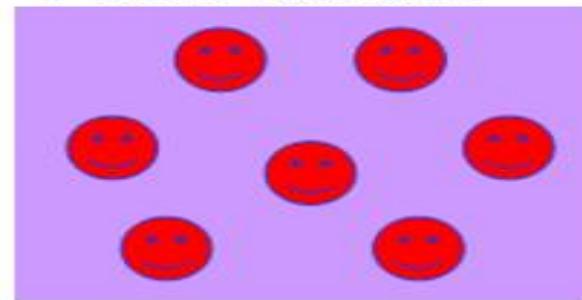
真实库仑相互作用：



相互作用的电子体系

平均场  
近似

平均场有效势：



非相互作用的准粒子体系

如何把这两个概念严格化？

# 密度泛函理论 I

1. 原子单位 Atomic unit
2. 多粒子体系 Many particle system
3. Born-Oppenheimer(绝热)近似
4. Hartree 近似
5. Hartree-Fock 近似
6. Thomas-Fermi 理论

# 密度泛函理论 II

- 7. Hohenberg and Kohn 定理
- 8. Kohn-Sham方法
- 9. Kohn-Sham方程
- 10. 交换关联与局域密度近似Exc and LDA
- 11. 自洽Kohn-Sham方程的编程求解
- 12. DFT的性能

# 1. 原子单位Atomic Units

## Atomic Units:

mass of electron  $m_e = 1$ , electron charge  $e = 1$ ,

Plank constant  $\hbar = 1$

the Gaussian electrostatic system(  $4\pi\epsilon_0 = 1$  for vacuum)

length is expressed in bohrs (1 bohr = 0.529177249 Å)

energy is in hartrees (1 hartree is 2 rydbergs, 1 Rydberg = 13.6 eV)

(the ground state energy of hydrogen atom is -1 rydberg, or 0.5 hartree)

# Atomic Units

## Atomic Unit

其本质是无量纲化：

The Schrodinger equation of H atom is

$$\left(-\frac{\hbar^2}{2m_e}\nabla'^2 - \frac{e^2}{r'}\right)\phi(r') = E'\phi(r'),$$

here  $\frac{1}{4\pi\varepsilon_0} = 1$ .

Let  $x' = \lambda x$ ,  $y' = \lambda y$ ,  $z' = \lambda z$ , then

$$\left(-\frac{\hbar^2}{2m_e\lambda^2}\nabla^2 - \frac{e^2}{\lambda r}\right)\phi(\lambda r) = E'\phi(\lambda r).$$

Assume that

$$\frac{\hbar^2}{m_e \lambda^2} = \frac{e^2}{\lambda} = E_{au}, \text{ and } E' = E E_{au}.$$

We have

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\psi(r) = E\psi(r).$$

It seems to take  $m_e = 1$ ,  $\hbar = 1$  and  $e = 1$ .

Now find  $\lambda$  and  $E_{au}$ . The length unit  $\lambda$  can be solved,

$$\lambda = \frac{\hbar^2}{e^2 m_e} = a_0 = 0.52918(\text{\AA}).$$

And energy unit

$$\begin{aligned} E_{au} &= \frac{e^2}{\lambda} = \frac{e^4}{\hbar^2} m_e = \frac{e^2}{a_0} \\ &= 27.211(\text{eV}) = 1(\text{Hartree}). \end{aligned}$$

Note that first Bohr radius is just  $a_0$ . The ground state energy of H atom is

$$-\frac{1}{2}E_{au} = -13.605(\text{eV}) = -1 \text{Rydberg.}$$

We define

$$\text{length: } 1 \text{ a.u.} = 0.52918(\text{\AA})$$

$$\text{energy: } 1 \text{ a.u.} = 27.211(\text{eV}).$$

And,

$$1 \text{ Hartree} = 2 \text{ Rydberg.}$$

# MD Time Unit

分子动力学单位

The Newton's equation is

$$-\frac{dU'(x')}{dx'} = m \frac{d^2x'}{dt'^2}.$$

Let  $U' = aU, x' = bx, t' = ct$ . Then

$$-\frac{a}{b} \frac{dU(bx)}{dx} = \frac{b}{c^2} m \frac{d^2x}{dt^2}.$$

Assume that

$$\frac{mb^2}{ac^2} = m_{au}.$$

The Newton's equation becomes

$$-\frac{dU(bx)}{dx} = m_{au} \frac{d^2x}{dt^2}.$$

We take the energy unit  $a = 1(\text{eV}) = 1.6 \times 10^{-19}$ , the length unit  $b = 1(\text{\AA}) = 10^{-10}$  and the mass  $m = m_{au} \times 1.66056 \times 10^{-27}$ . Thus, the time unit can be solved

$$c^2 = \frac{mb^2}{m_{au}a} = \frac{1.66 \times 10^{-27} \times (10^{-10})^2}{1.6 \times 10^{-19}} \approx 10^{-28},$$

or

$$c \approx 10^{-14}(\text{second}).$$

表明实际模拟时间很短！通常一秒都不到。

About the kinetic energy and temperature,

$$\frac{1}{2}m\left(\frac{dx'}{dt'}\right)^2 \rightarrow \frac{1}{2}m\frac{b^2}{c^2}\left(\frac{dx}{dt}\right)^2.$$

Hence  $m\frac{b^2}{c^2} = a m_{au} = m_{au}$  if  $a = 1$ (eV).

$$\frac{1}{2}m\left(\frac{dx'}{dt'}\right)^2 \rightarrow \frac{1}{2}m_{au}\left(\frac{dx}{dt}\right)^2(\text{eV}).$$

Temperature,

$$1(k_B T) = \frac{k_B T}{eV}(\text{eV}) = \frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} T(\text{K})(\text{eV}) \approx 0.86 \times 10^{-4} T(\text{K})(\text{eV}).$$

The kinetic energy at 300(K) is about  $0.0258(\text{eV}) = 25.8(\text{meV})$ .

一个物理量由它所具有的单位和一个数值来表征。  
无量纲化方法的好处：

- 模型所描述的规律应该独立于量纲的影响，在公式推导计算的过程中，要保证最后量纲的一致性；
- 进行无量纲化后可以发现问题的小项，从而忽略它们或利用它们进行近似微扰计算（不同量纲的物理量无法比较大小）。
- 无量纲物理量可进行超越函数的运算。

思考题：乘法可看成是加法的简写形式。  
为什么不同量纲物理量可以乘积，但不能做加法。

微信调侃人民币贬值的段子,错在哪里?  
 $1\text{元} = 100\text{分} = 10\text{分} * 10\text{分} = 0.1\text{元} * 0.1\text{元} = 0.01\text{元} = 1\text{分}$

# 无量纲化: 思考题

- 设有含时的单粒子薛丁格方程, 采用原子单位, 则时间的单位? (普郎克是个较小的数)
- 考虑电磁矢量势与标量势满足的微分方程的无量纲化问题。 (光速是个较大的数)

所有的模拟程序或计算都涉及无量纲问题, 这个细节对编程、程序使用都有用。

## 2. 哈密顿量与多体薛定格方程



Schrödinger Equation:  $H\psi = E\psi$

$$H = H(r_1, r_2, \dots, r_N; R_1, R_2, \dots, R_M)$$

$$\psi = \psi(r_1, r_2, \dots, r_N; R_1, R_2, \dots, R_M)$$

Erwin Schrödinger

任务：写出H，求解E， $\psi$

精确求解一般多体不可能



# 注解

1. 该课程不涉及相对论的多粒子体系量子力学问题：但自旋相关问题及自旋轨道相互作用等日趋重要；
2. 该课程不涉及含时的多粒子体系量子力学问题；
3. 该课程不涉及开放的多粒子体系量子力学问题。

# 封闭且无外场的多粒子系哈密顿量

## Many Particle System Hamiltonian:

The Hamiltonian

$$\hat{H}_{tot} = \hat{T}_{nucl} + \hat{T}_e + \hat{U}_{nucl} + \hat{V}_{ext} + \hat{U}_{ee}$$

where

I

$\hat{T}_{nucl}$  : kinetic energy of nuclei,

$$\hat{T}_{nucl} = \sum_{\alpha=1}^I -\frac{1}{2M_\alpha} \nabla_\alpha^2$$

$\hat{T}_e$  : kinetic energy of electrons,

$$\hat{T}_e = \sum_{i=1} \frac{1}{2} \nabla_i^2$$

$\hat{U}_{nucl}$  : interaction energy of nuclei (Coulombic repulsion),

$$\hat{U}_{nucl} = \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$$

where the  $Z_\alpha$  is the charge of an  $\alpha$ -th nucleus,

$$|R_\alpha - R_\beta| = \sqrt{(X_\beta - X_\alpha)^2 + (Y_\beta - Y_\alpha)^2 + (Z_\beta - Z_\alpha)^2}.$$

$\hat{V}_{ext}$  : external potential (the electrostatic potential between nuclei and electrons),

$$\hat{V}_{ext} = \sum_{i=1} \hat{v}_i \equiv \sum_{i=1} \left( \sum_{\alpha=1} \frac{-Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right)$$

where

$$|r_i - R_\alpha| = \sqrt{(x_i - X_\alpha)^2 + (y_i - Y_\alpha)^2 + (z_i - Z_\alpha)^2}.$$

标记惯例：电子： i, r,m 原子核： alpha, R,M

$\hat{U}_{ee}$  : electrostatic repulsion between electrons.

$$\hat{U}_{ee} = \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where

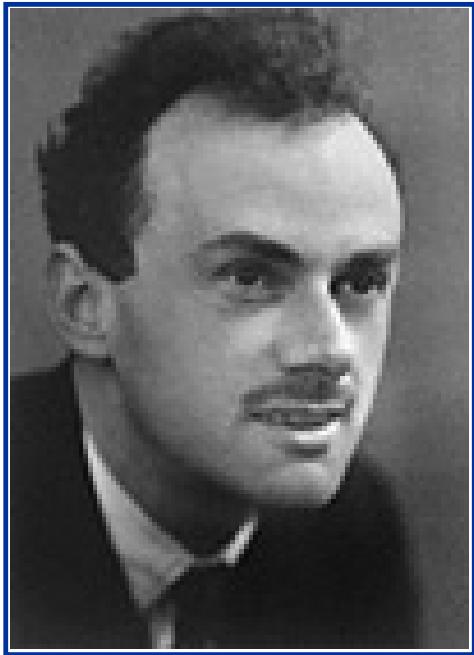
$$|\mathbf{r}_i - \mathbf{r}_j| = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}.$$

How to solve this equation? Stationary state:  $\hat{H}_{tot}\Phi(\{r_i\}, \{R_\alpha\}) = E_{tot}\Phi(\{r_i\}, \{R_\alpha\}).$

# 思考题：

- 能否写出有外加电场和磁场时的多体薛定格方程？
- 能否求解多体薛定格方程？如何求解？
- 假定对于无穷大体系（固体），多体薛定格方程中哪些项单独是可能发散的（尽管所有项的和是不会发散的）。

### 3. 多体问题太复杂了



P. A. M. Dirac

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

(1929年)

# 第一性原理、近似、半经验

- 化学领域，常把Hartree Fock+多组态方法称为第一性原理的计算，早期连DFT也不算，即使物理学家W. Kohn拿了化学Nobel奖，关于第一性原理的定义也各有不同。
- 第一性原理：其定义是相对的，最少的近似，最准确的结果
- 当写出多粒子哈密顿量时，就已经有近似了，至少没有考虑引力相互作用。
- 第一性原理并不一定比经验的理论好：重点是解决问题，而不是拼方法的“先进”。

# 第一性原理的定义 **ab initio, first principle**

在密度泛函理论没有建立以前， 第一性原理的定义： 根据没有引入参数的理论得到的计算方法。

比如基于**Hartree-Fock** 的理论， 包含组态相互作用**CI**， 二级多体微扰论**MP2**等。

# Ab initio: 全讲HF相关的计算

**Ab initio Calculations,**  
Ed. by P. Carsky and M. Urban,  
in Lecture notes in Chemistry,  
Springer 1980.

# First-Principles, 几乎全是讲DFT

**First-Principles Calculations in Real-Space Formalism - *Electronic Configurations and Transport Properties of Nanostructures,***

*Ed. by K. Hirose, T. Ono, Y. Fujimoto and S. Tsukamoto, Imperial College Press 2005.*

# 化学家对第一性原理的定义的讨论

- Should DFT methods be considered *ab initio* or semi-empirical? If *ab initio* is taken to mean the absence of fitting parameters, LSDA methods are *ab initio* but gradient corrected methods may or may not be.
- If *ab initio* is taken to mean that the method is based on theory, which in principle is able to produce the exact results, DFT methods are *ab initio*.
- Page 263, **Introduction to Computational Chemistry**, 2<sup>nd</sup> Ed., by F. Jensen, John Wiley & Sons Ltd 2007.

# 化学家对 AB INITIO 的新定义

- Ab initio molecular dynamics unifies approximate ab initio electronic structure theory (i.e. solving Schrodinger's wave equation numerically using, for instance, Hartree–Fock theory or the local density approximation within Kohn–Sham theory) and classical molecular dynamics (i.e. solving Newton's equation of motion numerically for a given interaction potential ...).
- Page 3, ***AB INITIO MOLECULAR DYNAMICS: BASIC THEORY AND ADVANCED METHODS*** by D. Marx and J. Hutter, Cambridge Univ. Press 2009.

# 当代趋势： HF， DFT， MC都是

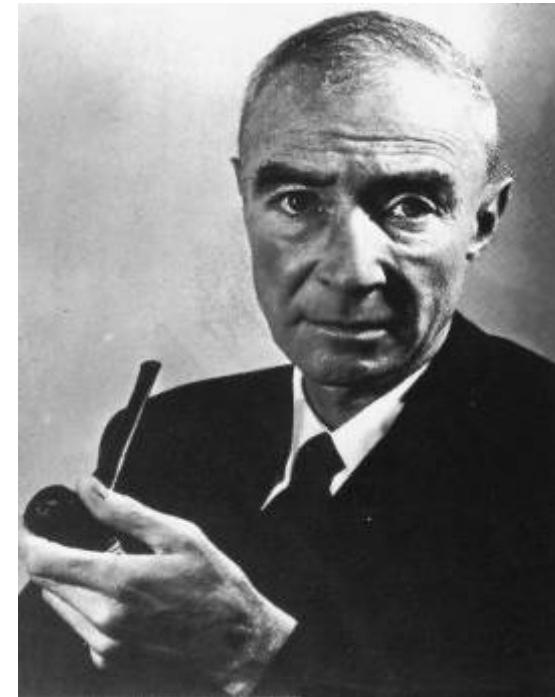
## Part VI Ab-Initio Methods in Physics and Chemistry

### 14 Ab-Initio Approach to the Many-Electron Problem

Alexander Quandt .....	415
14.1 Introduction .....	415
14.2 An Orbital Approach to Chemistry .....	419
14.3 Hartree-Fock Theory .....	427
14.4 Density Functional Theory .....	432
References .....	435

**Computational Many-particle Physics,**  
by H.Fehske,R.Schneider,A.Weibe,  
Springer 2008

# 4. Born-Oppenheimer近似



M. Born

R. Oppenheimer

把原子核坐标与电子坐标(取近似后)分离

# Born-Oppenheimer 原始论文

1927

Nr 20

## ANNALEN DER PHYSIK VIERTE FOLGE. BAND 84

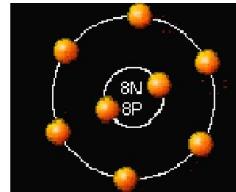
1. *Zur Quantentheorie der Moleküle;*  
*von M. Born und R. Oppenheimer*

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Moleküle erläutert.

注：1925年海森堡建立起矩阵力学；1926年薛定谔建立起波动力学 47



# 与电子比较原子核不易移动



Born-Oppenheimer Approximation

思考题：比较H中，k相等时  
核的动能与电子动能的比值



由电子和核组成的体系的理论处理通常考虑核的大质量效应而把它们的耦合分开。绝热近似就是基于这样的直觉：电子可以跟着核运动，当核位移时，电子波函数是平滑变化的。

● 电子很轻  
**electron**

moves around

too heavy to move

# 思考问题：近似的方法？

- 按动能区分不同的变量(高温、低温)
- 按空间区分不同的变量(局域、扩展)
- 按波长区分不同的变量(长波、短波)
- 按频率区分不同的变量(高频、低频)
- .....

数学物理方程中常见的快变量与慢变量的近似分离问题。

# Born-Oppenheimer Approx.

由于电子比核要轻许多，无论核运动到哪里，电子都可以瞬时调节其位置使之能跟随核的运动。(从微分方程的角度，电子的坐标是快变量，核的坐标是慢变量)。因此可以把电子的运动与核的运动分离。由一般方程出发

$$\hat{H}_{tot}\Phi(\{r_i\}, \{R_\alpha\}) = E_{tot}\Phi(\{r_i\}, \{R_\alpha\}).$$

设体系可分离变量，若只有一个态，设总波函数为

$$\Phi(\{r_i\}, \{R_\alpha\}) = \Psi(\{r_i\})\chi(\{R_\alpha\}),$$

若下列近似成立（一般不成立），

$$T_N \Psi(\{r_i\}) \chi(\{R_\alpha\}) = \Psi(\{r_i\}) T_N \chi(\{R_\alpha\}),$$

则电子的运动方程为

$$\hat{H}_{el} \Psi_{\{\mathbf{R}_\beta\}}(\{r_i\}) = E(\{R_\beta\}) \Psi_{\{\mathbf{R}_\beta\}}(\{r_i\}).$$

其中电子的哈密顿量为

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ext} + \hat{U}_{ee} = \sum_{i=1} \hat{h}_i + \hat{U}_{ee}$$

其中

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 + \hat{v}_i$$

注意电子波函数为  $\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\})$ , 可见电子波函数是以参数形式依赖于核坐标。实际上电子波函数与核的动能算符是不对易的。

通常都研究的是电子的问题，电子的运动方程可简写为

$$\hat{H}\Psi(\{r_i\}) = E\Psi(\{r_i\}).$$

同时要注意到,  $\hat{H}_{el} = \sum_{i=1} \hat{h}_i + \hat{U}_{ee}$  中,  $\sum_{i=1} \hat{h}_i$  部分是可以分离变量的, 然而  $\hat{U}_{ee}$  不能分离变量。凝聚态物理的复杂性, 包括强关联等都来源于此。

假设电子的运动仅以一种参数的方式依赖于核位置（当考虑电子的特性时，假设核的坐标是固定不变的）。则体系的总能量为

$$E_{tot} = \sum_{\alpha} \frac{P_{\alpha}^2}{2M_{\alpha}} + \sum_{\alpha < \beta} \frac{Z_{\alpha}Z_{\beta}}{|\mathbf{R}_{\alpha}-\mathbf{R}_{\beta}|} + E(\{R_{\beta}\}).$$

而原子核的运动方程是

$$(\hat{T}_{nucl} + \hat{U}_{nucl} + E(\{R_{\beta}\})\chi(\{R_{\alpha}\}) = E_{tot}\chi(\{R_{\alpha}\}).$$

此时核所受到的势能是

$$U_{tot}(\{R_{\beta}\}) = \sum_{\alpha < \beta} \frac{Z_{\alpha}Z_{\beta}}{|\mathbf{R}_{\alpha}-\mathbf{R}_{\beta}|} + E(\{R_{\beta}\}),$$

而原子核的运动方程是

$$(\hat{T}_{nucl} + \hat{U}_{nucl} + E(\{R_\beta\})\chi(\{R_\alpha\}) = E_{tot}\chi(\{R_\alpha\}).$$

此时核所受到的势能是

$$U_{tot}(\{R_\beta\}) = \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} + E(\{R_\beta\}),$$

核所受到的力是

$$\mathbf{F}_\beta = -\nabla_{\mathbf{R}_\beta} U_{tot}(\{R_\beta\}).$$

在一些文章里，也有把  $E_{tot}$  定义为  $U_{tot}$ ，因为零温下，核的动能只有零点能的贡献。

思考题：此处的总能量与固体物理中的可确定晶格常数的系统内能的关系？结合能？

$$\begin{aligned} H_{ion} &= E_{tot} = T_n + U_{nn} + E(\{R_\mu\}) \\ &\equiv T + U \end{aligned}$$

离子实的多体相互作用来自于电子

离子实部分如何求解？采用经典力学



思考题：为什么离子实部分采用经典力学就可以了？

用简谐近似描述核的运动，即只考虑核相对于平衡位置的位移到二级项。核的经典动力学是由振动的简正模式描述的，振动的量子化得到准粒子，即**声子**。

力:  $F_{\mu} = -\nabla_{\vec{R}_{\mu}} E_{tot}(\{R_{\mu}\})$

有核坐标的牛顿运动方程:

$$M_{R_{\mu}} \frac{d^2 R_{\mu}}{dt^2} = F_{\mu}$$

思考题: 离子实受到的力何时为零?  
如何计算动力学矩阵(晶格振动)?

# 绝热近似回顾：核与电子变量分离

总的哈密顿量为  $H_{tot} = T_e + U_{ee} + V_{ext} + T_N + U_{nucl}$ , 有定态方程  
 $H_{tot}\Phi(\{r_i\}, \{R_\alpha\}) = E_{tot}\Phi(\{r_i\}, \{R_\alpha\}).$

设可电子与核分离变量，且系统只有一个态

$\Phi(\{r_i\}, \{R_\alpha\}) = \Psi_{\{R_\alpha\}}(\{r_i\})\chi(\{R_\alpha\})$ . 令电子系统满足  
 $(T_e + U_{ee} + V_{ext})\Psi_{\{R_\alpha\}}(\{r_i\}) = E(\{R_\alpha\})\Psi_{\{R_\alpha\}}(\{r_i\}).$

由定态方程有

$$(E + T_N + U_{nucl})\Psi_{\{R_\alpha\}}(\{r_i\})\chi(\{R_\alpha\}) = E_{tot}\Psi_{\{R_\alpha\}}(\{r_i\})\chi(\{R_\alpha\})$$

若有对易关系  $T_N\Psi_{\{R_\alpha\}}(\{r_i\}) = \Psi_{\{R_\alpha\}}(\{r_i\})T_N$ , 则核满足方程

$$(E + T_N + U_{nucl})\chi(\{R_\alpha\}) = E_{tot}\chi(\{R_\alpha\}).$$

通常对易关系  $T_N\Psi_{\{R_\alpha\}}(\{r_i\}) = \Psi_{\{R_\alpha\}}(\{r_i\})T_N$  不成立，因为  
 $\Psi_{\{R_\alpha\}}(\{r_i\})$  与原子核的坐标有关。

思考题：用微扰方法讨论绝热近似(把电子质量与核质量之比作为微扰参量)

参考：谢希德《固体能带理论》；  
**Kohanoff, Electronic Structure.**

关注：

- 1) 与电子-声子耦合的关系
- 2) 与绝热位相 (Berry Phase) 的关系

注：DFT程序可计算e-p,Berry phase,不讲

# 多原子,多电子体系: 哈密顿量:

哈密顿量:  $H = T_n + U_{nn} + V_{ext} + T_e + U_{ee}$

$$T_n = \sum_{\mu} -\frac{1}{2M_{\mu}} \nabla_{\mu}^2$$

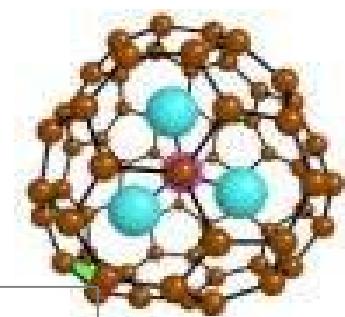
$$U_{nn} = \sum_{\mu < \nu} \frac{Z_{\mu} Z_{\nu}}{|\vec{R}_{\mu} - \vec{R}_{\nu}|}$$

$$V_{ext} = \sum_i \left( \sum_{\mu} \frac{-Z_{\mu}}{|\vec{r}_i - \vec{R}_{\mu}|} \right) = \sum_i v_i$$

如何求解?

$$T_e = \sum_i -\frac{1}{2m} \nabla_i^2$$

$$U_{ee} = \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$



# 绝热近似：电子运动与核运动分离

$$\text{电子: } \hat{H}_{el} = T_e + V_{ext} + U_{ee}$$

$$\equiv \sum_i \hat{h}_i + U_{ee}$$

$$\hat{H}_{el} \Psi(\{r_i\}) = E(\{R_\mu\}) \Psi(\{r_i\})$$

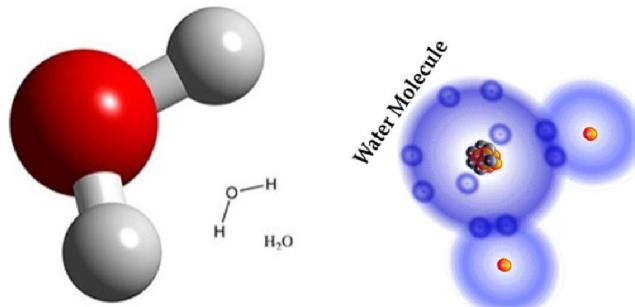
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$$\text{核: } H_{nucl} = T_n + U_{nn} + E(\{R_\mu\})$$

$$\equiv T_n + U_{tot} = E_{tot}$$

$$F_\mu = -\nabla_{\vec{R}_\mu} E_{tot}(\{R_\mu\})$$

多体问题，例：Water: H<sub>2</sub>O



## 绝热近似后：

水分子组成：10个电子，3个原子核

- 离子实部分可按牛顿运动方程求解，  
离子实-离子实相互作用势依赖于电子部分的能量
- 电子部分是求解多电子的薛定谔方程，  
电子间的相互作用势很复杂，电子部分的总势能依赖于电子与离子实的相互作用能

# 思考题

通常大系统的温度由系统的动能决定：

- 固体中电子体系的温度如何确定，如何估计？
- 固体系统中原子核的温度是否也可类似确定？
- 通常电子体系与原子核体系是否达到热平衡？
- 对一个分子，能否定义有意义的温度？
- 
- 为什么把电子体系与原子核体系分离的近似称为绝热近似？

# 绝热近似 – 纹身

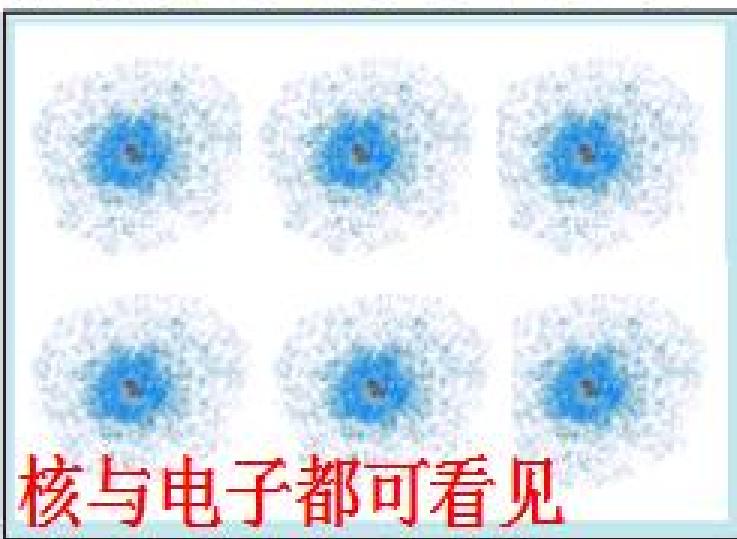
<http://blogs.discovermagazine.com/loom/2009/05/23/sigmas-from-shoulder-to-shoulder-science-tattoos/>

$$\begin{aligned}
 H = & -\frac{i}{\hbar} \sum_i \nabla_i^2 - \sum_a \frac{i}{2m_a} \nabla_a^2 - \sum_i \sum_a \frac{Z_a}{|\mathbf{r}_i - \mathbf{r}_a|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_a \sum_{\beta \neq a} \frac{Z_a Z_\beta}{|\mathbf{r}_a - \mathbf{r}_\beta|} \\
 \left[ -\frac{i}{\hbar} \sum_i \nabla_i^2 - \sum_i \sum_a \frac{Z_a}{|\mathbf{r}_i - \mathbf{r}_a|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\{\mathbf{r}_i\}; \{\mathbf{r}_a\}) = \mathcal{E}_e(\{\mathbf{r}_a\}) \Psi(\{\mathbf{r}_i\}; \{\mathbf{r}_a\}) \\
 \left[ -\sum_\beta \frac{1}{2m_\beta} \nabla_\beta^2 + \mathcal{E}_e(\{\mathbf{r}_a\}) + \frac{1}{2} \sum_\beta \sum_{\gamma \neq \beta} \frac{Z_\beta Z_\gamma}{|\mathbf{r}_\beta - \mathbf{r}_\gamma|} \right] \Phi(\{\mathbf{r}_a\}) = \mathcal{E} \Phi(\{\mathbf{r}_a\}).
 \end{aligned}$$

Joe writes, "My tattoo is 3 lines of equations, the top is the Born Oppenheimer Approximation, the second line is the equation in the form of a 3-Dimensional Schrödinger Equation, and the solution in the form of a Schrödinger Equation. As a biochemist and molecular biophysicist I studied a lot of this stuff and I must say, Schrödinger was my favorite and well, I had to do it. The ink was done at Red Sky Studios in Tucson, AZ by artist Lisa."

# 绝热近似图解

原子核与电子都在运动



核与电子都可看见

原子核不运动作为正电背景



只能看见相互作用的电子



思考问题：如果绝热近似不成立？  
如何解多核多电子问题？

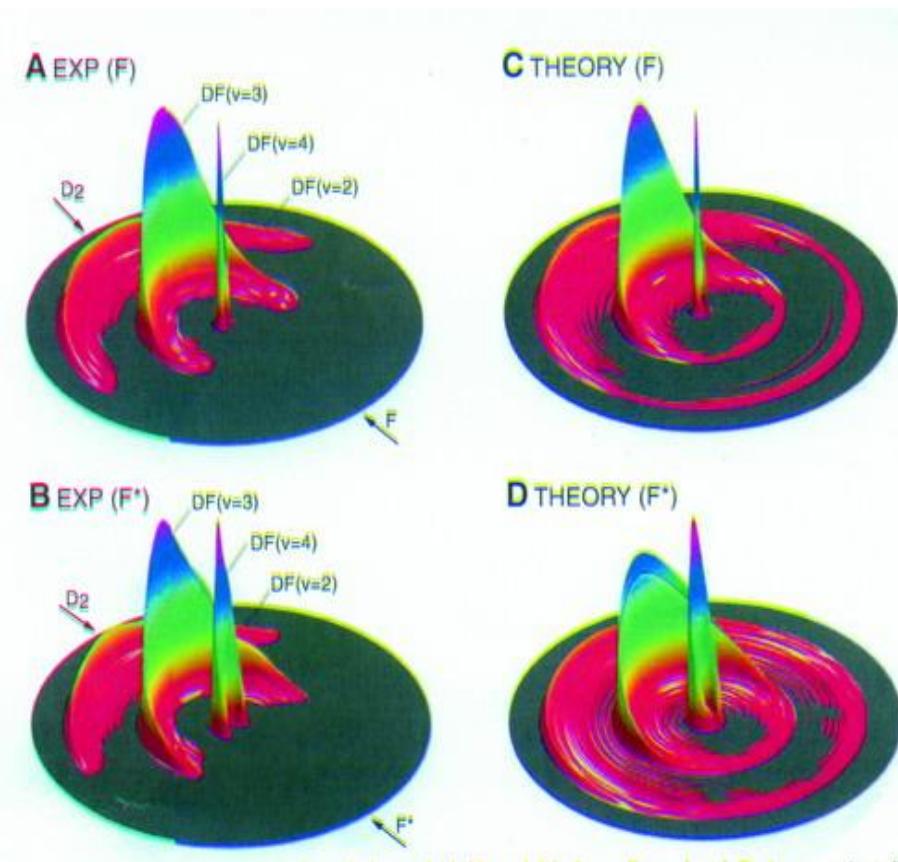
# 绝热近似是否一定成立?

- Breakdown of the Born-Oppenheimer approximation
- A review: Molecular Dynamics Beyond the Born-Oppenheimer Approximation
- A book: Beyond Born-Oppenheimer,  
by Michael Baer
- Born-Oppenheimer!  
Beyond BO(Ehrenfest)!  
Beyond Ehrenfest?

# Breakdown of the Born-Oppenheimer approximation in the F+o-D2→DF+D reaction

杨学明 ,大连化物所, *Science* 317, 1061(2007).

- 利用实验室自行研制的、先进的里德堡态氢原子飞行时间谱—交叉分子束仪器, 对氯加氢的反应进行了精确的交叉分子束实验研究, 测量了基态和激发态氯原子与氢分子反应的相对微分截面。在低碰撞能下, 他们发现氯原子自旋-轨道激发态的反应性与基态的相当, 这一结果说明波恩-奥本海默近似在这一反应中在低碰撞能时是失效的。但当碰撞能增加时, 他们发现氯原子自旋-轨道激发态的反应性与基态的相比变得越来越小, 这说明波恩-奥本海默近似在这一反应中在高碰撞能量时是有效的。



# A review: Molecular Dynamics Beyond the Born-Oppenheimer Approximation

- Molecular Dynamics Beyond the Born-Oppenheimer Approximation: Mixed Quantum-Classical Approaches,  
by Nikos L. Doltsinis,  
<http://www.fz-juelich.de/nic-series/volume31>, *in Computational Nanoscience: Do It Yourself*, J. Grotendorst, S. Blugel, D. Marx (Eds.), 2006

# nature materials

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*Nature Materials* 6, 198 - 201 (2007)

Published online: 11 February 2007 | doi:10.1038/nmat1846

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## Breakdown of the adiabatic Born–Oppenheimer approximation in graphene

Simone Pisana<sup>1</sup>, Michele Lazzeri<sup>2</sup>, Cinzia Casiraghi<sup>1</sup>, Kostya S. Novoselov<sup>3</sup>, A. K. Geim<sup>3</sup>, Andrea C. Ferrari<sup>1</sup> & Francesco Mauri<sup>2</sup>

The adiabatic Born–Oppenheimer approximation (ABO) has been the standard ansatz to describe the interaction between electrons and nuclei since the early days of quantum mechanics<sup>1, 2</sup>. ABO assumes that the lighter electrons adjust adiabatically to the motion of the heavier nuclei, remaining at any time in their instantaneous ground state. ABO is well justified when the energy gap between ground and excited electronic states is larger than the energy scale of the nuclear motion. In metals, the gap is zero and phenomena beyond ABO (such as phonon-mediated superconductivity or phonon-induced renormalization of the electronic properties) occur<sup>3</sup>. The use of ABO to describe lattice motion in metals is, therefore, questionable<sup>4, 5</sup>. In spite of this, ABO has proved effective for the accurate determination of chemical reactions<sup>6</sup>, molecular dynamics<sup>7, 8</sup> and phonon frequencies<sup>9, 10, 11</sup> in a wide range of metallic systems. Here, we show that ABO fails in graphene. Graphene, recently discovered in the free state<sup>12, 13</sup>, is a zero-bandgap semiconductor<sup>14</sup> that becomes a metal if the Fermi energy is tuned applying a gate voltage<sup>13, 15</sup>,  $V_g$ . This induces a stiffening of the Raman G peak that cannot be described within ABO.

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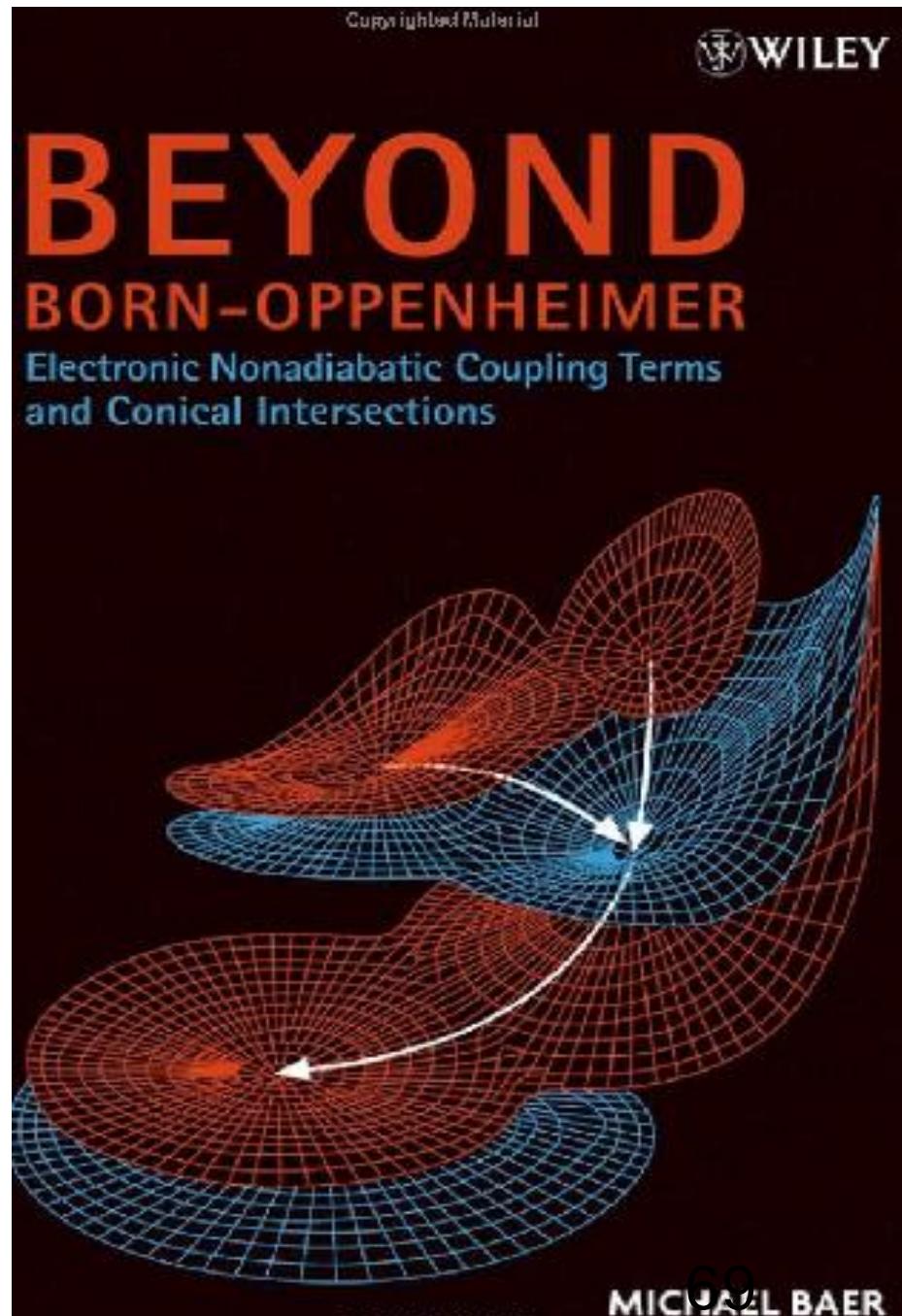
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- [Supplementary info](#)

# A Book:

- Beyond Born-Oppenheimer,  
by Michael Baer ,Wiley 2006

1. Mathematical Introduction.
2. Born-Oppenheimer Approach:  
Diabatization and Topological  
Matrix.
3. Model Studies.
4. Studies of Molecular Systems.
5. Degeneracy Points and Born—  
Oppenheimer Coupling Terms as  
Poles.
6. The Molecular Field.
7. Open Phase and the Berry Phase  
for Molecular Systems.
8. Extended Born-Oppenheimer  
Approximations.



# Born-Oppenheimer! Beyond BO(Ehrenfest)! Beyond Ehrenfest?

**Born-Oppenheimer MD, (电子波函数与时间无关)**

$$M_R \frac{\partial^2 R}{\partial^2 t} = - \frac{\partial}{\partial R} \min_{\Psi_0} \langle \Psi_0 \{R\} | H_{tot} | \Psi_0 \{R\} \rangle$$

$$H_{el} \Psi_0 (\{r\} \{R\}) = E_0 \Psi_0 (\{r\} \{R\})$$

最常用

**Ehrenfest MD (beyond BO)(电子波函数依赖时间)**

$$M_R \frac{\partial^2 R(t)}{\partial^2 t} = - \frac{\partial}{\partial R} \langle \Psi(t, \{R\}) | H_{tot} | \Psi(t, \{R\}) \rangle$$

$$i \frac{\partial \Psi(t, \{r\} \{R\})}{\partial t} = H_{el} \Psi(t, \{r\} \{R\})$$

# 绝热近似成立：多电子问题求解？

- 平均场及推广：
  - HF: CI(组态相互作用), MP2(多体微扰)
  - DFT: LDA(局域密度近似), LDA+U, GGA(梯度修正), GW(屏蔽自能), DMFT(动力学平均场), ...
- 强关联：
  - MC蒙特卡罗
  - DMRG(密度矩阵重整化群), 张量网格
  - 多体微扰(?)

该课程主要涉及平均场方法：  
把多电子问题化为单电子问题。

next

# 上一讲回顾

- 如何解多个原子和电子的问题?
  - 第一步：分离原子核体系与电子体系：绝热近似（条件？）
  - 第二步：把多电子体系近似为单电子体系（即  
将讲解）
- 技术问题：无量纲化（便于数学处理和物  
理分析：差分，风洞）
- 绝热近似有被违背的情形

# 关于绝热近似问题的补充

问题：

- 既然核动能与电子波函数不能严格对易，为何绝热近似还成立？
- 电子-声子相互作用？

# 总哈量

$$\begin{aligned}\hat{H}_{tot} &= \hat{T}_{nucl} + \hat{U}_{nucl} + \hat{T}_e + \hat{V}_{ext} + \hat{U}_{ee} \\ &= \hat{H}_{nucl} + \hat{H}_{el}\end{aligned}$$

若只有一个态，设总波函数为

$$\Phi(\{r_i\}, \{R_\alpha\}) = \Psi(\{r_i\})\chi(\{R_\alpha\}),$$

设电子哈量满足

$$\hat{H}_{el}\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\}) = E(\{R_\beta\})\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\})$$

这时

$$\hat{H}_{tot}\Phi(\{r_i\}, \{R_\alpha\}) = E_{tot}\Phi(\{r_i\}, \{R_\alpha\})$$

代入定义及假设

$$\begin{aligned} & (\hat{H}_{nucl} + \hat{H}_{el})\Psi(\{r_i\})\chi(\{R_\alpha\}) \\ = E_{tot}\Psi(\{r_i\})\chi(\{R_\alpha\}) \end{aligned}$$

$$\begin{aligned} & \hat{H}_{nucl}\Psi(\{r_i\})\chi(\{R_\alpha\}) + \hat{H}_{el}\Psi(\{r_i\})\chi(\{R_\alpha\}) \\ = E_{tot}\Psi(\{r_i\})\chi(\{R_\alpha\}) \end{aligned}$$

$$\begin{aligned} & \hat{H}_{nucl}\Psi(\{r_i\})\chi(\{R_\alpha\}) + E(\{R_\beta\})\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\})\chi(\{R_\alpha\}) \\ = E_{tot}\Psi(\{r_i\})\chi(\{R_\alpha\}) \end{aligned}$$

$$(\hat{T}_{nucl} + \hat{U}_{nucl})\Psi(\{r_i\})\chi(\{R_\alpha\})$$

$$+ E(\{R_\beta\})\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\})\chi(\{R_\alpha\})$$

$$= E_{tot}\Psi(\{r_i\})\chi(\{R_\alpha\})$$

$$\hat{T}_{nucl}(\Psi(\{r_i\})\chi(\{R_\alpha\}))$$

$$+ \hat{U}_{nucl}\Psi(\{r_i\})\chi(\{R_\alpha\})$$

$$+ E(\{R_\beta\})\Psi_{\{\mathbf{R}_\beta\}}(\{r_i\})\chi(\{R_\alpha\})$$

$$= E_{tot}\Psi(\{r_i\})\chi(\{R_\alpha\})$$

单独看第一项

$$\hat{T}_{nuc}(\Psi(\{r_i\})\chi(\{R_\alpha\}))$$

$$= - \sum_{\gamma} \frac{1}{2M_\gamma} \nabla_\gamma^2 (\Psi(\{r_i\})\chi(\{R_\alpha\}))$$

$$= - \sum_{\gamma} \frac{1}{2M_\gamma} \nabla_\gamma [\nabla_\gamma \Psi(\{r_i\}) \cdot \chi(\{R_\alpha\}) + \Psi(\{r_i\}) \cdot \nabla_\gamma \chi(\{R_\alpha\})]$$

$$= - \sum_{\gamma} \frac{1}{2M_\gamma} \nabla_\gamma^2 \Psi(\{r_i\}) \cdot \chi(\{R_\alpha\}) - \frac{1}{2M_\gamma} \nabla_\gamma \Psi(\{r_i\}) \cdot \nabla_\gamma \chi(\{R_\alpha\})$$

$$- \sum_{\gamma} \frac{1}{2M_\gamma} \nabla_\gamma \Psi(\{r_i\}) \cdot \nabla_\gamma \chi(\{R_\alpha\}) - \frac{1}{2M_\gamma} \Psi(\{r_i\}) \nabla_\gamma^2 \chi(\{R_\alpha\})$$

$$= [\hat{T}_{nuc} \Psi] \chi - \sum_{\gamma} \frac{1}{M_\gamma} \nabla_\gamma \Psi \cdot \nabla_\gamma \chi + \Psi [\hat{T}_{nuc} \chi]$$

前两项与非绝热有关，最后一项是绝热的结果。

采用微扰论看非绝热第一项对平均能量的贡献（一级）

$$\int d\mathbf{r} \int d\mathbf{R} \{\Psi^* \chi^* [\hat{T}_{nuc} \Psi] \chi\} \sim ?$$

其中注意多电子特性：

$$\Psi(\{\mathbf{r}_\alpha\}), \chi(\{\mathbf{R}_\alpha\}), d\mathbf{r} = \{d\mathbf{r}_i\}, d\mathbf{R} = \{d\mathbf{R}_\alpha\}.$$

该积分当电子坐标与核坐标重合时最大，设

$\mathbf{u}_{ia} = \mathbf{r}_i - \mathbf{R}_\alpha$ , 把电子波函数在  $\mathbf{R}_\alpha$  展开，则可近似得到对  $R$  的积分与对  $\mathbf{u}_{ia}$  可分别作出

$$\int d\mathbf{u}_{ia} \left[ \int d\mathbf{R} \chi^* \chi \right] \Psi^* [\hat{T}_{nuc} \Psi] \simeq \int d\mathbf{u}_{ia} \Psi^* [\hat{T}_{nuc} \Psi]$$

（细节自己补齐）此量正比于电子质量与核质量之比，量级约为  $10^{-5}$  可忽略不计。

采用微扰论看非绝热第二项对平均能量的贡献  
(一级)

$$-\frac{1}{M_\gamma} \int d\mathbf{r} \int d\mathbf{R} \{ \Psi^* \chi^* \nabla_\gamma \Psi \cdot \nabla_\gamma \chi \}$$

$$= -\frac{1}{M_\gamma} \int d\mathbf{R} \chi^* \nabla_\gamma \chi \cdot \int d\mathbf{r} \Psi^* \nabla_\gamma \Psi$$

电子波函数对固定核坐标满足归一性:

$$-\frac{1}{M_\gamma} \int d\mathbf{R} \chi^* \nabla_\gamma \chi \cdot \int d\mathbf{r} \Psi^* \nabla_\gamma \Psi = 0$$

该项的二级微扰不为零, 恰为电子-声子相互作用项。还涉及Berry Phase等。不在本课程讲解范围了。  
80

## 答疑：

# 原子核体系为什么不用薛定格方程求解？

- 1) 原子核体系也是多体问题，其薛定格方程无法简单解出。除非发展一套‘原子核的密度泛函理论’。确实有！【超冷原子系统的DFT，分子DFT，经典流体的DFT,聚合物体系的DFT】
- 2) 在零温情形，原子核动能只有零点能，其势能决定一切。采用经典力学即可解决问题。

# 答疑：结合能定义

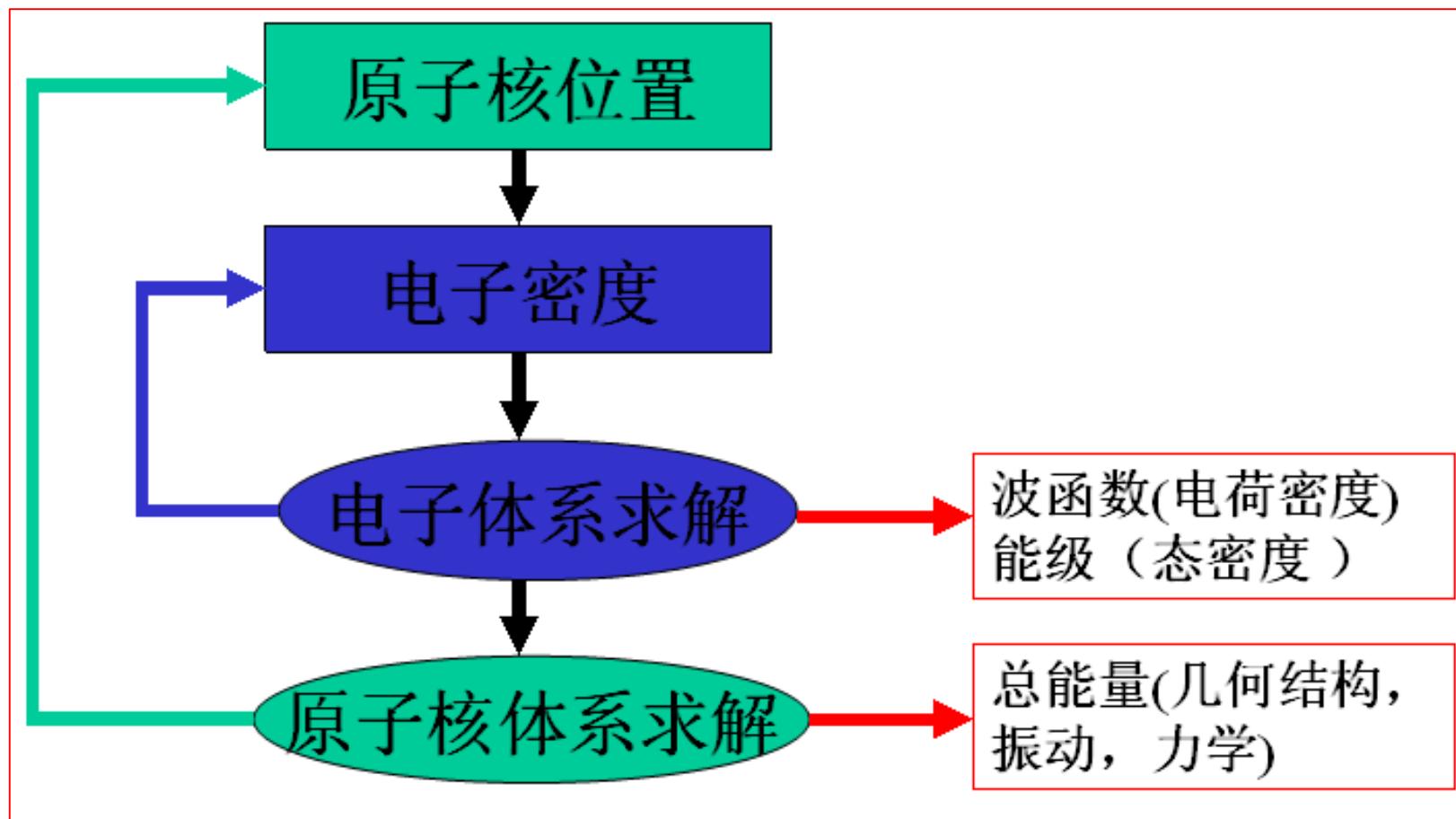
单原子晶体结合能 = [N原子体系总能量 + N原子体系零点能]/N  
- 单个原子体系总能量

思考题：

- 1)石墨烯的结合能如何计算？
- 2)对于两类原子构成的体系BN的结合能如何计算？
- 3)推广到多类原子构成的体系，其结合能如何计算？

答疑：

给定原子核解电子体系，原子核移动了该如何？



# 数学补充

- 泛函变分的知识，早已知晓
  - Fermat's principle[费马原理]，几何光学
  - Maupertuis' principle[莫佩提原理]，虚功原理
- 变分原理无处不在
  - 量子，电磁，场论，宇宙学，力学。 . .

# 补充：泛函、变分、分离变量等

从多元函数到泛函：

泛函的类比定义：

$$F(\varphi_1, \varphi_2, \dots, \varphi_n) \rightarrow F[\varphi(x)]$$

泛函导数的类比定义：

$$\begin{aligned} dF(\varphi_1, \varphi_2, \dots, \varphi_n) &= \sum_j \frac{\partial F}{\partial \varphi_j} d\varphi_j \\ \delta F[\varphi(x)] &= \int \frac{\delta F}{\delta \varphi} \delta \varphi \, dx \end{aligned}$$

泛函导数的计算： $\frac{\delta F[\varphi(x)]}{\delta \varphi(y)} = \lim_{\varepsilon \rightarrow 0} \frac{F[\varphi(x) + \varepsilon \delta(x - y)] - F[\varphi(x)]}{\varepsilon}$

# 一些变分的规则

$$\delta^2 J = \delta(\delta(J), \dots, \delta^k J) = \delta(\delta^{k-1} J)$$

$$\delta(J_1 + J_2) = \delta J_1 + \delta J_2, \text{ 线性} \quad \text{与微分的规则相对应}$$

$$\delta(J_1 J_2) = J_1 (\delta J_2) + (\delta J_1) J_2$$

$$J[y(x)] = \int_a^b F(x, y(x), y'(x)) dx$$

$$\delta J = \delta \int_a^b F(x, y, y') dx = \int_a^b \delta F(x, y, y') dx$$

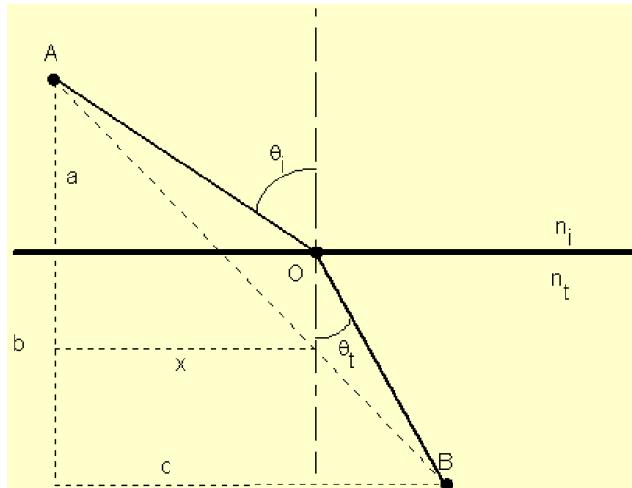
$$\delta F = \frac{\partial F}{\partial y} \delta y + \frac{\partial F}{\partial y'} \delta y'$$

$$\delta\left(\frac{dy}{dx}\right) = \frac{d}{dx}(\delta y)$$

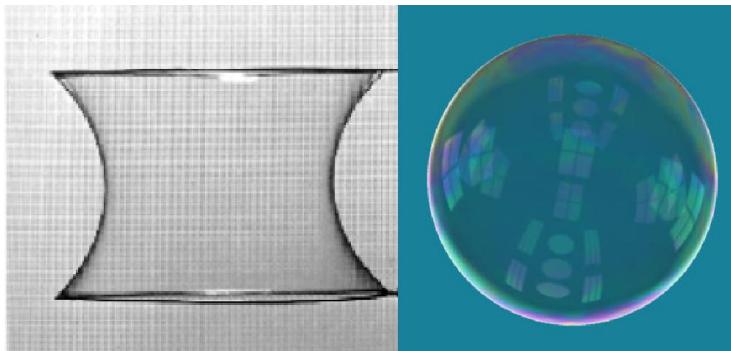
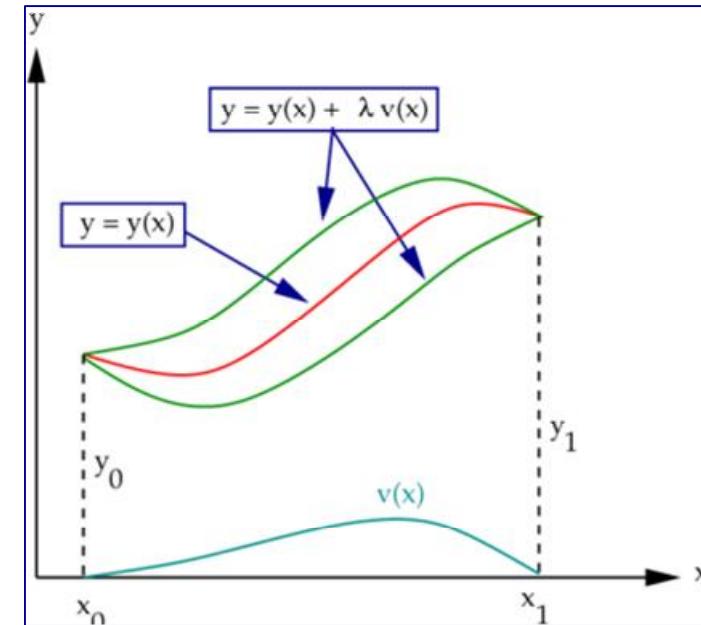
$$\delta x = dx$$

变分是多元微分的无穷维推广  
对多元函数，变分化为了微分

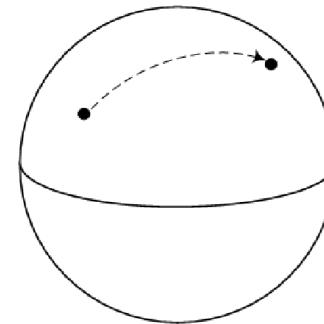
# 变分的物理意义：最优



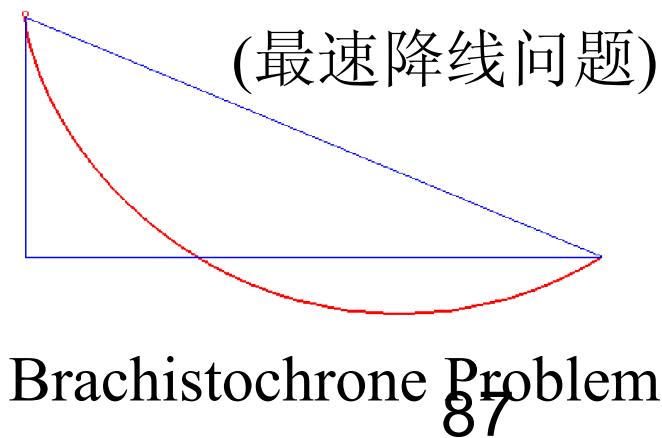
Fermat's Principle



Soap Film



Geodesics



Brachistochrone Problem  
87

(最速降线问题)

# 泛函的变分：

设有泛函  $F[\varphi(x)]$ , 极值条件为  $\delta F[\varphi] = 0$ , 可推出

$$\delta F[\varphi] = \int \frac{\delta F[\varphi(x)]}{\delta \varphi(x)} \delta \varphi(x) dx = 0.$$

由于  $\delta \varphi$  的任意性, 取  $\delta \varphi(x) = \delta(x - x_0)$ , 极值条件变为

$$\frac{\delta F[\varphi(x)]}{\delta \varphi(x)}|_{x=x_0} = 0.$$

对有条件  $G[\varphi] = 0$  的极值问题, 利用拉格朗日乘子法, 定义

$$\Omega[\varphi] = F[\varphi] - \lambda G[\varphi]$$

极值条件变为

$$\frac{\delta \Omega[\varphi]}{\delta \varphi} = 0.$$

薛定格方程的变分求解基于此。

思考题：限制条件是不等式该如何办？ (经济问题常遇到)  
88

若泛函含有导数，则可得到欧拉方程：设  $F[\varphi(x), \varphi'(x)]$ ，则固定边界的变分为

$$\begin{aligned}\delta F &= \int \frac{\delta F}{\delta \varphi} \delta \varphi dx + \int \frac{\delta F}{\delta \varphi'} \delta \varphi' dx \\ &= \int \frac{\delta F}{\delta \varphi} \delta \varphi dx + \int \frac{\delta F}{\delta \varphi'} \frac{d \delta \varphi}{dx} dx \\ &= \int \frac{\delta F}{\delta \varphi} \delta \varphi dx - \int \frac{d}{dx} \frac{\delta F}{\delta \varphi'} \delta \varphi dx\end{aligned}$$

令  $\delta F = 0$  有

$$\frac{\delta F}{\delta \varphi} - \frac{d}{dx} \frac{\delta F}{\delta \varphi'} = 0.$$

在讲量子分子动力学时要用到这样的欧拉方程。

对含有高阶导数，有广义的欧拉方程。

# 例： Euler-Lagrange Equation

作用量： $J[y(x)] = \int_a^b F(x, y(x), y'(x)) dx$

方程： $\frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) = 0$

思考题：推导广义欧拉方程

作用量： $J[y(x)] = \int_a^b F(x, y(x), y'(x), y''(x)) dx$

方程： $F_y - \frac{d}{dx} F_{y'} + \frac{d^2}{dx^2} F_{y''} = 0$

# 分离变量法相关的问题

设有哈密顿量

$$H(\{r_i\}) = \sum_i h(r_i),$$

且只有一个解

$$H(\{r_i\})\Phi(\{r_i\}) = E\Phi(\{r_i\}).$$

每个  $h(r_i)$  除自变量不同外，形式一样。

设  $h(r)$  有解

$$h(r)\varphi_j(r) = \epsilon_j\varphi_j(r).$$

则可定义

$$\Phi(\{r_i\}) = \varphi_{j_1}(r_1)\varphi_{j_2}(r_2)\cdots\varphi_{j_n}(r_n)$$

满足

$$H(\{r_i\})\Phi(\{r_i\}) = E\Phi(\{r_i\}).$$

证明：把 $\Phi(\{r_i\})$ 代入有

$$\begin{aligned} H(\{r_i\})\Phi(\{r_i\}) &= \sum_i h(r_i)\varphi_{j_1}(r_1)\varphi_{j_2}(r_2)\cdots\varphi_{j_n}(r_n) \\ &= (\epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_n})\varphi_{j_1}(r_1)\varphi_{j_2}(r_2)\cdots\varphi_{j_n}(r_n) \\ &\equiv E\varphi_{j_1}(r_1)\varphi_{j_2}(r_2)\cdots\varphi_{j_n}(r_n) \end{aligned}$$

可见总能量是单粒子能量的和：

$$E = \epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_n}.$$

如算符是和的形式，则解是乘积形式！

实际上这是分离变量的结果：设两粒子的情形

$$H(r_1, r_2) = h(r_1) + h(r_2),$$

应当满足方程

$$H(r_1, r_2)\Phi(r_1, r_2) = E\Phi(r_1, r_2).$$

由于可分离变量，设

$$\Phi(r_1, r_2) = \varphi(r_1)\varphi(r_2),$$

代入原方程有

$$H(r_1, r_2)\Phi(r_1, r_2) = E\Phi(r_1, r_2)$$

$$[h(r_1) + h(r_2)]\varphi(r_1)\varphi(r_2) = E\varphi(r_1)\varphi(r_2)$$

$$h(r_1)\varphi(r_1)\varphi(r_2) + h(r_2)\varphi(r_1)\varphi(r_2) = E\varphi(r_1)\varphi(r_2)$$

$$\frac{h(r_1)\varphi(r_1)}{\varphi(r_1)} + \frac{h(r_2)\varphi(r_2)}{\varphi(r_2)} = E$$

令：

$$\frac{h(r_1)\varphi(r_1)}{\varphi(r_1)} = \epsilon_1,$$

$$\frac{h(r_2)\varphi(r_2)}{\varphi(r_2)} = \epsilon_2,$$

得到：

$$h(r_1)\varphi(r_1) = \epsilon_1\varphi(r_1),$$

$$h(r_2)\varphi(r_2) = \epsilon_2\varphi(r_2),$$

$$E = \epsilon_1 + \epsilon_2.$$

可以推广到有限多粒子情形：  
如算符是和的形式，则解是乘积形式！

# 5. D.R. Hartree & V. A. Fock



The Hartree method 1928  
D.R. Hartree (1897-1958)  
Cambridge, UK

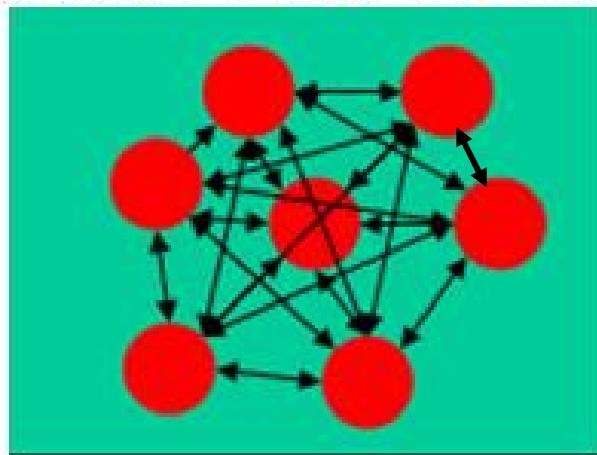


The Hartree-Fock method 1930  
V.A. Fock (1898–1974) Leningrad,  
Russia

Hartree-Fock 平均场概念现今仍被大量使用

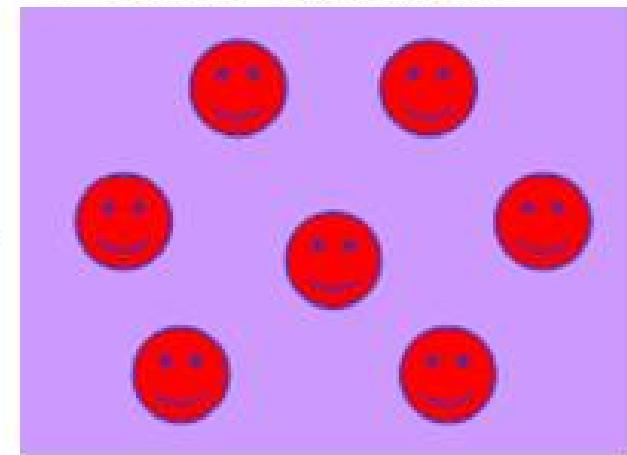
# 多电子体系的平均场概念

真实库仑相互作用：



相互作用的电子体系

平均场有效势：



非相互作用的准粒子体系

如何构造出较好的有效势？

## 5a. Hartree Approx.

# Hartree Approximation

对于所考虑的某个电子的运动，它与其它电子的相互作用的运动可以近似地看成是它在其它电子的平均密度所产生的电磁场中的运动（平均场理论）。假定对第*i*个电子而言，它感受到的其它电子的平均场为 $\hat{g}_i(\mathbf{r})$ ，则

$$\hat{U}_{ee} \approx \sum_{i=1} \hat{g}_i(\mathbf{r}),$$

then

$$\hat{H}_{el} = \sum_i \hat{h}_i + U_{ee}$$

$$\hat{H} \approx \sum_{i=1} \left( -\frac{1}{2} \nabla_i^2 + \hat{\nu}_i + \hat{g}_i \right) \equiv \sum_{i=1} \hat{H}_i$$

$$\hat{H} \approx \sum_{i=1} (-\frac{1}{2} \nabla_i^2 + \hat{v}_i + \hat{g}_i) \equiv \sum_{i=1} \hat{H}_i$$

整个哈密顿量在平均场的近似下是可以分离变量的。这样，多电子的Schrödinger方程可以化为 $N$ 个单电子的Schrödinger方程：

$$\hat{H}_i \phi_n(\mathbf{r}_i) = \epsilon_n \phi_n(\mathbf{r}_i),$$

由于 $\hat{g}_i$ 的形式还不知道，通过变分原理，可以把 $\hat{g}_i$ 找到：让

$$\Psi(\{\mathbf{r}_i\}) = \prod_i \phi_i(\mathbf{r}_i), \quad \langle \Psi | \Psi \rangle = 1$$

在如下的课件中，请注意状态标记与坐标标记的‘混乱’。

then

$$\langle \hat{H} \rangle_{hartree} =$$

$$\langle \Psi(\{r_i\}) | (\sum_{i=1} \hat{h}_i + \hat{U}_{ee}) | \Psi(\{r_i\}) \rangle$$

$$= \sum_{i=1} \langle \phi_i(\mathbf{r}) | \hat{h}_i | \phi_i(\mathbf{r}) \rangle$$

$$+ \frac{1}{2} \sum_{i \neq j} \langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle .$$

变分法的物理要求是体系的总能量存在最小值，先算总能量。

# Define the Coulomb integration (Coulomb energy)

$$\begin{aligned} J_{ij} &= \langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \rangle \\ &= \iint \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \iint \frac{\rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

总能量的计算：哈密顿量没有近似，波函数有近似。

可对总能量变分得到一个自治方程。

Variation:

$$\delta[\langle \hat{H} \rangle - \sum_i E_i (\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle - 1)] = 0,$$

$$\sum_{i=1} \langle \delta\phi_i(\mathbf{r}) | \hat{h}_i | \phi_i(\mathbf{r}) \rangle$$

$$+ \sum_{i \neq j} \langle \delta\phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle$$

$$- \sum_i E_i (\langle \delta\phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle) = 0.$$

Drop out summation over  $i$ ,

$$\begin{aligned} & \langle \delta\phi_i(\mathbf{r}) | \hat{h}_i | \phi_i(\mathbf{r}) \rangle \\ + \sum_{j(\neq i)} & \langle \delta\phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle \\ - E_i (\langle \delta\phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle) & = 0, \\ & \langle \delta\phi_i(\mathbf{r}) | \langle \hat{h}_i \\ + \sum_{j(\neq i)} & \langle \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_j(\mathbf{r}') \rangle - E_i \} | \phi_i(\mathbf{r}) \rangle & = 0. \end{aligned}$$

The  $\delta\phi_i(r)$  is arbitrary. Then

$$\{\hat{h}_i + \sum_{j(\neq i)} < \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_j(\mathbf{r}') >$$

$$- E_i\} |\phi_i(\mathbf{r}) > = 0$$

$$\{-\frac{1}{2}\nabla^2 + \hat{v} + \sum_{j(\neq i)} \int d\mathbf{r}' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\} |\phi_i(\mathbf{r}) > = E_i |\phi_i(\mathbf{r}) >$$

$$\{-\frac{1}{2}\nabla^2 + \hat{v} + \int d\mathbf{r}' \frac{\sum_{j(\neq i)} |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\} |\phi_i(\mathbf{r}) > = E_i |\phi_i(\mathbf{r}) >$$

$$(-\frac{1}{2}\nabla^2 + v + v_H) \phi \equiv (-\frac{1}{2}\nabla^2 + v_{eff}) \phi = E \phi$$

因此

$$\hat{g}(\mathbf{r}) = \sum_{j(\neq i)} \int d\mathbf{r}' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}.$$

这一项常称为Coulomb项或Hartree项.  
注意：需要自洽计算

$$H_i(\hat{g}_i(r)) \Rightarrow |\phi_i(r)|^2 \Rightarrow \hat{g}(r)$$

$$\Rightarrow H_i(\hat{g}_i(r)).$$

## 5b. 什么是自治

- 什么是自治？按照自身的逻辑推演，自己可以证明自己至少不是矛盾或者错误的。

自治场  $V_{eff}$

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i=1} \left| \phi_i(\mathbf{r}) \right|^2$$

$$V_{eff}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

这是关于波函数的非线性方程组：  $f(\phi) = 0$

# 迭代法

迭代法是逐次逼近方法

- 构造相应的迭代公式,
- 选取方程的初始近似根 $x_0$ ,
- 代入迭代公式反复校正根的近似值

例如,求方程的根

$$f(x) = x^3 - x - 1 = 0$$

- 首先将原方程改写成等价形式的迭代公式

$$x = g(x) = \sqrt[3]{x + 1}$$

- 初始近似根  $x_0 = 1.5$

- 得到

$$x_1 = g(x_0) = \sqrt[3]{x_0 + 1} = 1.35721$$

- 由于  $|x_0 - x_1| > 10^{-4}$

$$x_2 = g(x_1) = \sqrt[3]{x_1 + 1} = 1.33086$$

- • • • •

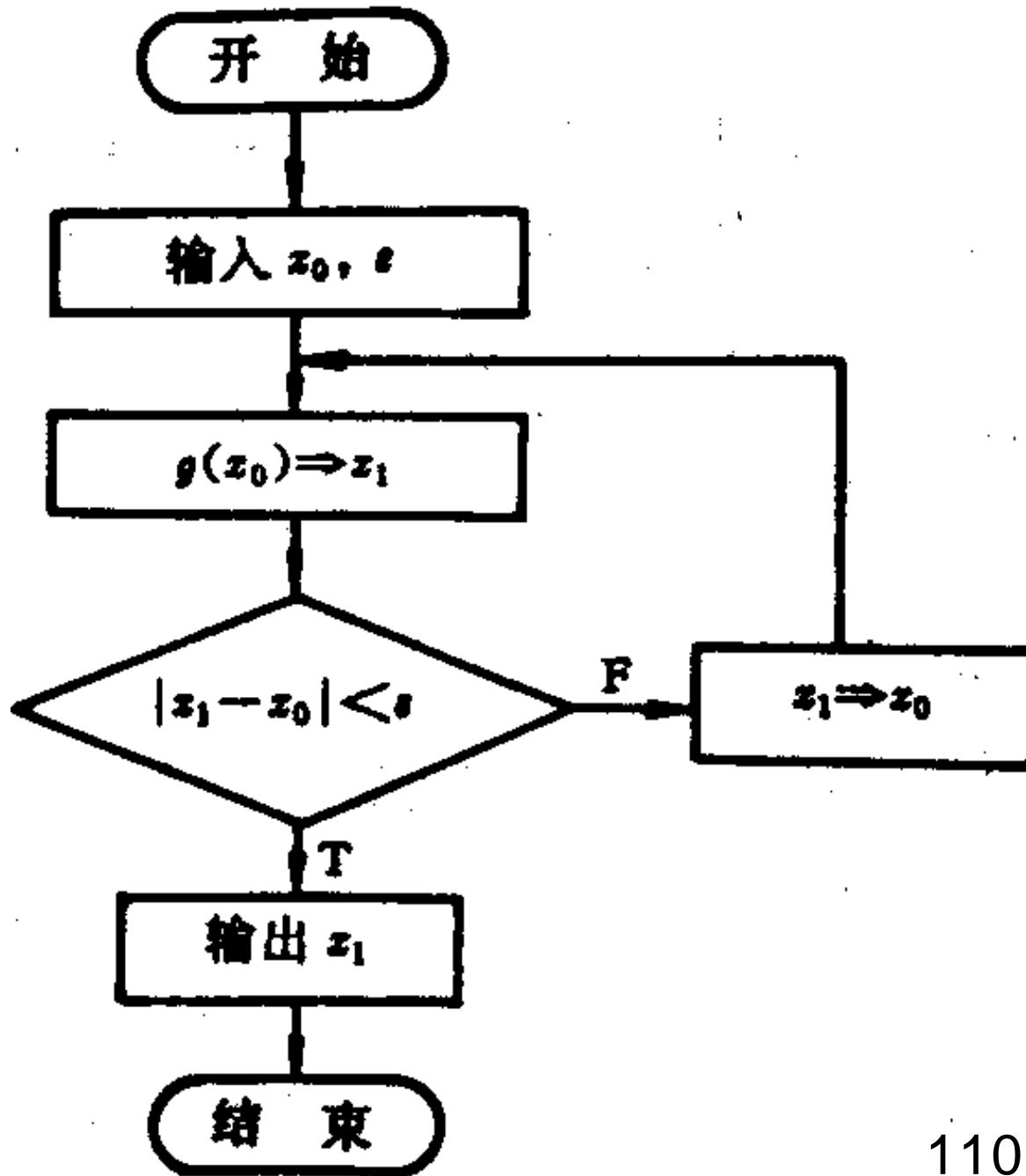
$$x_{k+1} = g(x_k) = \sqrt[3]{x_k + 1}$$

$k$	$x_k$	$k$	$x_k$
0	1. 5	5	1. 324 76
1	1. 357 21	6	1. 324 73
2	1. 330 86	7	1. 324 72
3	1. 325 88	8	1. 324 72
4	1. 324 94		

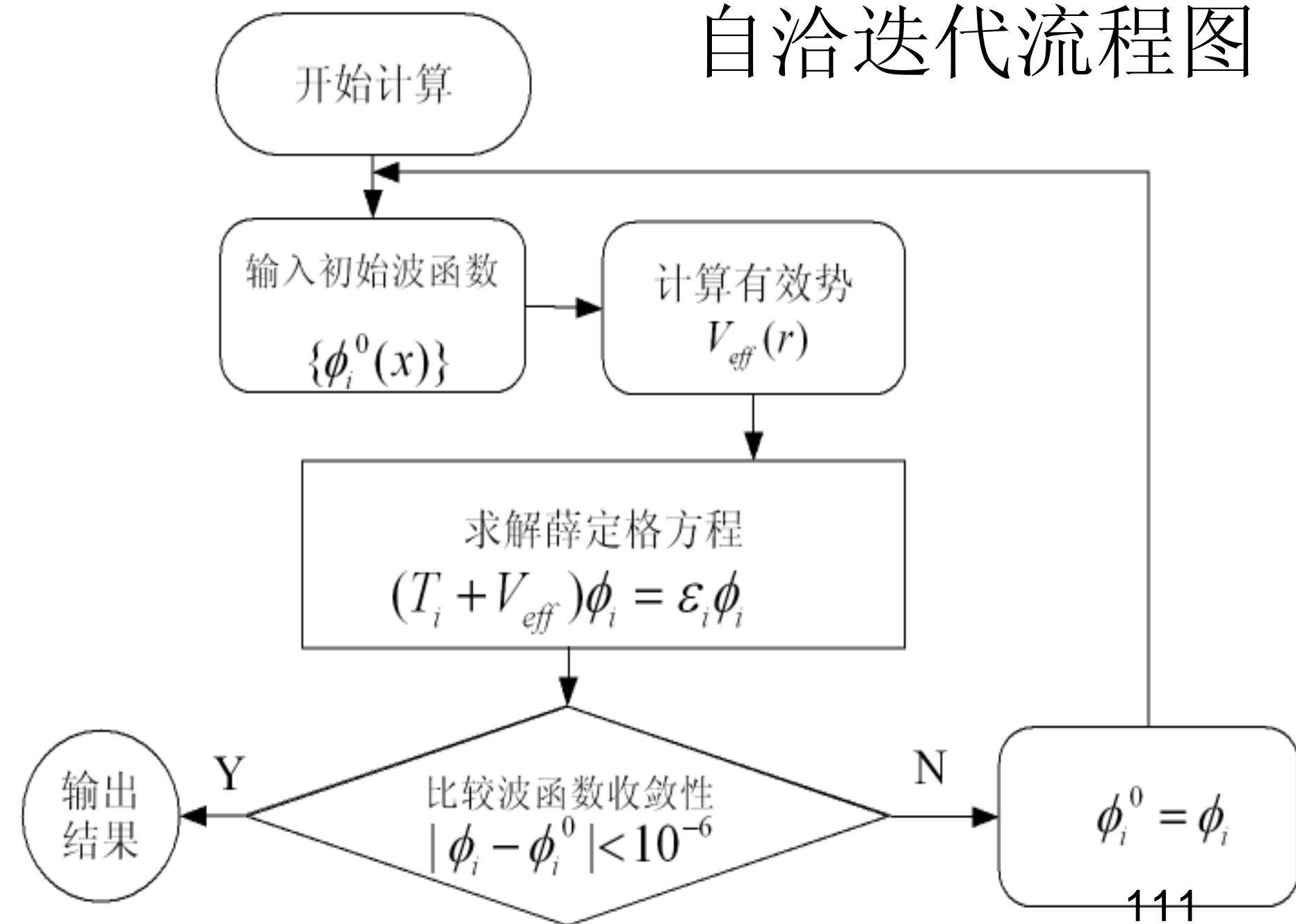
迭代法算法的计算步骤为：

- 1) 确定方程 $f(x)=0$ 的等价形式 $x=g(x)$ ；  
(为迭代收敛,要求 $g(x)$ 满足一定条件)
- 2) 选取初始值 $x_0$ , 按公式  $x_{k+1}=g(x_k)$ ,  $k=0,1,2,\dots$ 进行迭代;
- 3) 若  $|x_{k+1}-x_k| < \varepsilon$ , 则停止计算,  $x \approx x_{k+1}$ 。

## 迭代流程图



# 自洽迭代流程图



# Hartree 方法步骤：

1. 利用单电子波函数的乘积作为变分波函数
2. 计算体系总能量的平均值
3. 构造一个总能量附加波函数归一化条件的泛函
4. 对泛函取变分极小得到有效势的单电子方程
5. 对单电子方程自洽求解

多电子问题化为了单电子问题！

Hartree 方法缺点：没有考虑Pauli 不相容原理  
更没有考虑电子间的关联。

## 5c. Hartree-Fock Approx.

# Hartree-Fock近似

电子是费米子，由于Pauli不相容原理，对于多电子体系，没有两个电子可以由同一个电子波函数来描述。这样，体系的总波函数是由交换电子的标记所得的各种乘积项的反对称和构成。满足这样的对称性的总波函数可用行列式表达(Slater行列式)：

The total wave function is represented as a determinant (called Slater determinant):



$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}}$$

$\phi_1(\mathbf{r}_1)$	$\phi_2(\mathbf{r}_1)$	$\cdots$	$\phi_N(\mathbf{r}_1)$
$\phi_1(\mathbf{r}_2)$	$\phi_2(\mathbf{r}_2)$	$\cdots$	$\phi_N(\mathbf{r}_2)$
$\phi_1(\mathbf{r}_3)$	$\phi_2(\mathbf{r}_3)$	$\cdots$	$\phi_N(\mathbf{r}_3)$
.	.	.	.
.	.	.	.
.	.	.	.
$\phi_1(\mathbf{r}_N)$	$\phi_2(\mathbf{r}_N)$	$\cdots$	$\phi_N(\mathbf{r}_N)$

考虑两个电子的体系，让我们看看Slater行列式有那些特性：

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \end{vmatrix}$$
$$= \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)]$$

如果我们交换电子的标记  $1 \rightarrow 2$  和  $2 \rightarrow 1$  我们有

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \end{vmatrix}$$
$$= \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) - \phi_2(\mathbf{r}_2)\phi_1(\mathbf{r}_1)]$$

即具有反对称性： $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$ .

如果我们假定两个电子由同一个自旋轨道描述

$$\phi_1 = \phi_2 = \phi$$

我们有：

$$\begin{aligned}\Psi(\mathbf{r}_2, \mathbf{r}_1) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi(\mathbf{r}_2) & \phi(\mathbf{r}_2) \\ \phi(\mathbf{r}_1) & \phi(\mathbf{r}_1) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [\phi(\mathbf{r}_2)\phi(\mathbf{r}_1) - \phi(\mathbf{r}_2)\phi(\mathbf{r}_1)] \equiv 0\end{aligned}$$

即，Slater行列式满足Pauli不相容原理。

单行列式波函数 $\Psi$ 下的总能量的期望值是:

$$\langle H \rangle_{HF} = \langle \Psi | H | \Psi \rangle$$

$$= \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij})$$

其中:

$$H_i = \int \phi_i^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla_i^2 + \hat{v}_i \right] \phi_i(\mathbf{r}) d\mathbf{r},$$

$J_{ij}$  是前面定义的Coulomb积分,  $K_{ij}$  是新的项称为交换几分, 定义为

$$K_{ij} = \iint \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2.$$

$K_{ij}$  对总能量的贡献成为交换能  $E_x = -K_{ij}$ .

注意  $K_{ij}$  在形式上相似于  $J_{ij}$  但是单粒子波函数  $\phi_i$  和  $\phi_j$  交换了。注意，为使得  $K_{ij}$  不为零，电子  $i$  和  $j$  必须有相同的自旋（自旋部分的正交归一性）。库仑积分有简单的物理解释：电子  $i$  和  $j$  的电荷密度间的纯静电相互作用。可是交换积分没有这样的简单物理解释。交换积分  $K_{ij}$  来自于行列式波函数  $\Psi$ ，与要求波函数的反对称性或要求电子满足泡利原理有关。

当  $i = j$  时，有  $J_{ij}$  和  $K_{ij}$  相等。这点很重要，说明电子与自己的相互作用不会对总能量有影响。可以证明库仑积分  $J_{ij}$  大于或等于交换积分  $K_{ij}$  且都为正数。

# 思考问题

- 把单粒子波函数明确写为坐标部分与自旋部分,重新推导Hartree-Fock近似,明确交换积分中自旋平行与自旋反平行对交换积分的贡献。

利用变分原理，可得到Hartree-Fock本征方程，

$$\hat{f}(r_1)\phi_i(r_1) = \epsilon_i\phi_i(r_1)$$

其中Fock算符  $\hat{f}(r_1)$  定义为：

$$\hat{f}(r_1) = \hat{h}(r_1) + \sum_a [\hat{j}_a(\mathbf{r}_1) - \hat{k}_a(\mathbf{r}_1)].$$

单粒子项  $\hat{h}(r_1)$  的定义同前面。  
库仑算符定义为，

库仑算符定义为,

$$\begin{aligned}\hat{j}_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1) &= \phi_b(\mathbf{r}_1) \int |\phi_a(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \\ &= \phi_b(\mathbf{r}_1) \int \rho_a(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2\end{aligned}$$

交换算符定义为

$$\hat{k}_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1) = \phi_a(\mathbf{r}_1) \int \phi_a^*(\mathbf{r}_2)\phi_b(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2.$$

注意两者的差别。

# Hartree-Fock方程是一个单粒子方程

$$\hat{f}(r_1)\phi_i(r_1) = \epsilon_i\phi_i(r_1)$$

where the Fock operator  $\hat{f}(r_1)$  is defined as:

$$\hat{f}(r_1) = \hat{h}(r_1) + \sum_a [\hat{j}_a(\mathbf{r}_1) - \hat{k}_a(\mathbf{r}_1)].$$

$$[-\frac{1}{2}\nabla^2 + v(r) + v_H]\phi_a(r)$$

$$- \sum_j \phi_j(r) \int \phi_j^*(r_2) \frac{1}{|r - r_2|} \phi_a(r_2) dr_2$$

$$= \epsilon_a \phi_a(r)$$

如何推导出？和Hartree情形相仿  
122

# 5d. Hartree-Fock方程的导出细节

- 利用单行列式波函数作为变分波函数
- 计算总能量的平均值
- 构造一个总能量附加波函数归一化条件的泛函
- 对泛函取变分极小得到Hartree-Fock方程

# 用hartree波函数算平均值

三个粒子的哈密顿量为

$$\begin{aligned} & H(r_1, r_2, r_3) \\ = & h(r_1) + h(r_2) + h(r_3) \\ & + \frac{1}{|r_1 - r_2|} + \frac{1}{|r_1 - r_3|} + \frac{1}{|r_2 - r_3|} \end{aligned}$$

设有哈特利波函数

$$\Psi(r_1, r_2, r_3) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3),$$

且有正交归一性  $\langle\phi_i|\phi_j\rangle = \delta_{ij}$

## 计算平均值

$$\langle \Psi(r_1, r_2, r_3) | H(r_1, r_2, r_3) | \Psi(r_1, r_2, r_3) \rangle$$

$$= \int \phi_1^*(r_1) \phi_2^*(r_2) \phi_3^*(r_3) H(r_1, r_2, r_3) \phi_1(r_1) \phi_2(r_2) \phi_3(r_3) dr_1 dr_2 dr_3$$

$$= \int \phi_1^*(r_1) h(r_1) \phi_1(r_1) dr_1 + \int \phi_2^*(r_2) h(r_2) \phi_2(r_2) dr_2$$

$$+ \int \phi_3^*(r_3) h(r_3) \phi_3(r_3) dr_3$$

$$+ \int \int \phi_1^*(r_1) \phi_2^*(r_2) \frac{1}{|r_1 - r_2|} \phi_1(r_1) \phi_2(r_2) dr_1 dr_2$$

$$+ \int \int \phi_1^*(r_1) \phi_3^*(r_3) \frac{1}{|r_1 - r_3|} \phi_1(r_1) \phi_3(r_3) dr_1 dr_3$$

$$+ \int \int \phi_2^*(r_2) \phi_3^*(r_3) \frac{1}{|r_2 - r_3|} \phi_2(r_2) \phi_3(r_3) dr_2 dr_3$$

$$\begin{aligned} & \langle \Psi(r_1, r_2, r_3) | H(r_1, r_2, r_3) | \Psi(r_1, r_2, r_3) \rangle \\ = & \int \phi_1^*(r) h(r) \phi_1(r) dr + \int \phi_2^*(r) h(r) \phi_2(r) dr + \int \phi_3^*(r) h(r) \phi_3(r) dr \\ & + \int \int \phi_1^*(r) \phi_2^*(r') \frac{1}{|r - r'|} \phi_1(r) \phi_2(r') dr dr' \\ & + \int \int \phi_1^*(r) \phi_3^*(r') \frac{1}{|r - r'|} \phi_1(r) \phi_3(r') dr dr' \\ & + \int \int \phi_2^*(r) \phi_3^*(r') \frac{1}{|r - r'|} \phi_2(r) \phi_3(r') dr dr' \\ = & \sum_i \int \phi_i^*(r) h(r) \phi_i(r) dr \\ & + \frac{1}{2} \sum_{j(\neq i)} \sum_i \int \int \phi_i^*(r) \phi_j^*(r') \frac{1}{|r - r'|} \phi_i(r) \phi_j(r') dr dr' \end{aligned}$$

# 用行列式波函数算平均值

若设哈密顿量为

$$H = H_0 + \frac{1}{|r_1 - r_2|}$$

$$H_0(\{r_i\}) = h(r_1) + h(r_2)$$

满足反对称性的波函数为

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} (\phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1)),$$

计算平均值

# 单体项的平均值

计算平均值

$$\langle \Psi(r_1, r_2) | H_0(r_1, r_2) | \Psi(r_1, r_2) \rangle$$

$$= \frac{1}{2} \langle \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1) | h(r_1)$$

$$+ h(r_2) | \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1) \rangle$$

$$= \frac{1}{2} \langle \phi_1(r_1)\phi_2(r_2) | h(r_1) + h(r_2) | \phi_1(r_1)\phi_2(r_2) \rangle$$

$$+ \frac{1}{2} \langle \phi_1(r_2)\phi_2(r_1) | h(r_1) + h(r_2) | \phi_1(r_2)\phi_2(r_1) \rangle$$

$$- \frac{1}{2} \langle \phi_1(r_2)\phi_2(r_1) | h(r_1) + h(r_2) | \phi_1(r_1)\phi_2(r_2) \rangle$$

$$- \frac{1}{2} \langle \phi_1(r_1)\phi_2(r_2) | h(r_1) + h(r_2) | \phi_1(r_2)\phi_2(r_1) \rangle$$

$$\begin{aligned} &= \frac{1}{2} \langle \phi_1(r_1) | h(r_1) | \phi_1(r_1) \rangle + \frac{1}{2} \langle \phi_2(r_2) | h(r_2) | \phi_2(r_2) \rangle \\ &+ \frac{1}{2} \langle \phi_2(r_1) | h(r_1) | \phi_2(r_1) \rangle + \frac{1}{2} \langle \phi_1(r_2) | h(r_2) | \phi_1(r_2) \rangle \\ &- \frac{1}{2} \langle \phi_1(r_2) \phi_2(r_1) | h(r_1) | \phi_1(r_1) \phi_2(r_2) \rangle \\ &- \frac{1}{2} \langle \phi_1(r_2) \phi_2(r_1) | h(r_2) | \phi_1(r_1) \phi_2(r_2) \rangle \\ &- \frac{1}{2} \langle \phi_1(r_1) \phi_2(r_2) | h(r_1) | \phi_1(r_2) \phi_2(r_1) \rangle \\ &- \frac{1}{2} \langle \phi_1(r_1) \phi_2(r_2) | h(r_2) | \phi_1(r_2) \phi_2(r_1) \rangle \end{aligned}$$

$$\begin{aligned} &= \langle \phi_1(r) | h(r) | \phi_1(r) \rangle + \langle \phi_2(r) | h(r) | \phi_2(r) \rangle \\ &\quad - \frac{1}{2} \langle \phi_1(r_2) | \phi_2(r_2) \rangle \langle \phi_2(r_1) | h(r_1) | \phi_1(r_1) \rangle \\ &\quad - \frac{1}{2} \langle \phi_2(r_1) | \phi_1(r_1) \rangle \langle \phi_1(r_2) | h(r_2) | \phi_2(r_2) \rangle \\ &\quad - \frac{1}{2} \langle \phi_2(r_2) | \phi_1(r_2) \rangle \langle \phi_1(r_1) | h(r_1) | \phi_2(r_1) \rangle \\ &\quad - \frac{1}{2} \langle \phi_1(r_1) | \phi_2(r_1) \rangle \langle \phi_2(r_2) | h(r_2) | \phi_1(r_2) \rangle \\ &= \sum_i \langle \phi_i(r) | h(r) | \phi_i(r) \rangle \end{aligned}$$

得到

$$\langle \Psi(r_1, r_2) | H_0(r_1, r_2) | \Psi(r_1, r_2) \rangle = \sum_i \langle \phi_i(r) | h(r) | \phi_i(r) \rangle$$

# 两体项的平均值

现在计算

$$\langle \Psi(r_1, r_2) | \frac{1}{|r_1 - r_2|} | \Psi(r_1, r_2) \rangle = ?$$

因为

$$\Psi(r_1, r_2) = -\frac{1}{\sqrt{2}} (\phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1)),$$

$$\begin{aligned} & \int \int \Psi^*(r_1, r_2) \frac{1}{|r_1 - r_2|} \Psi(r_1, r_2) dr_1 dr_2 \\ &= +\frac{1}{2} \int \int \phi_1^*(r_1)\phi_2^*(r_2) \frac{1}{|r_1 - r_2|} \phi_1(r_1)\phi_2(r_2) dr_1 dr_2 \\ &\quad - \frac{1}{2} \int \int \phi_1^*(r_1)\phi_2^*(r_2) \frac{1}{|r_1 - r_2|} \phi_1(r_2)\phi_2(r_1) dr_1 dr_2 \\ &\quad - \frac{1}{2} \int \int \phi_1^*(r_2)\phi_2^*(r_1) \frac{1}{|r_1 - r_2|} \phi_1(r_1)\phi_2(r_2) dr_1 dr_2 \\ &\quad + \frac{1}{2} \int \int \phi_1^*(r_2)\phi_2^*(r_1) \frac{1}{|r_1 - r_2|} \phi_1(r_2)\phi_2(r_1) dr_1 dr_2 \end{aligned}$$

$$\begin{aligned} &= + \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_1) \phi_2^*(r_2) \phi_2(r_2)}{|r_1 - r_2|} dr_1 dr_2 \\ &+ \frac{1}{2} \int \int \frac{\phi_1^*(r_2) \phi_1(r_2) \phi_2^*(r_1) \phi_2(r_1)}{|r_1 - r_2|} dr_1 dr_2 \\ &- \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_2) \phi_2^*(r_2) \phi_2(r_1)}{|r_1 - r_2|} dr_1 dr_2 \\ &- \frac{1}{2} \int \int \frac{\phi_1^*(r_2) \phi_1(r_1) \phi_2^*(r_1) \phi_2(r_2)}{|r_1 - r_2|} dr_1 dr_2 \end{aligned}$$

$$\begin{aligned} &= + \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_1) \phi_2^*(r_2) \phi_2(r_2)}{|r_1 - r_2|} dr_1 dr_2 \\ &\quad + \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_1) \phi_2^*(r_2) \phi_2(r_2)}{|r_2 - r_1|} dr_2 dr_1 \\ &\quad - \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_2) \phi_2^*(r_2) \phi_2(r_1)}{|r_1 - r_2|} dr_1 dr_2 \\ &\quad - \frac{1}{2} \int \int \frac{\phi_1^*(r_1) \phi_1(r_2) \phi_2^*(r_2) \phi_2(r_1)}{|r_2 - r_1|} dr_2 dr_1 \\ &= \int \int \frac{\phi_1^*(r) \phi_1(r) \phi_2^*(r') \phi_2(r')}{|r - r'|} dr dr' \quad \text{库仑积分} \\ &\quad - \int \int \frac{\phi_1^*(r) \phi_1(r') \phi_2^*(r') \phi_2(r)}{|r - r'|} dr dr' \quad \text{交换积分} \end{aligned}$$

# 定义库仑积分与交换积分

定义库仑积分

$$J_{ij} = \iint \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_i(r_1) \phi_j(r_2) dr_1 dr_2$$

定义交换积分

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

细节：态标记含自旋态标记，坐标含自旋变数

# 平均值的结果

设哈密顿量为

$$H = \sum_i h(r_i) + \frac{1}{2} \sum_{i,j(\neq i)} \frac{1}{|r_i - r_j|}$$

且在哈特里-福克近似下的波函数为 $\Psi$ .

平均值的计算结果是

$$\langle \Psi | H | \Psi \rangle = \sum_i^N H_i + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij})$$

其中交换积分和库仑积分如上，注意 $J_{ii} = K_{ii}$ ，可不记限制 $j \neq i$ ，而单体项为

$$H_i = \int \phi_i^*(r_1) h(r) \phi_i(r) dr.$$

# 构造含条件极值的泛函

构造带条件极值

$$\langle \phi_i | \phi_i \rangle = 1$$

的泛函  $\Omega$

$$\Omega = \sum_i^N H_i + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}) - \sum_i \epsilon_i (\langle \phi_i | \phi_i \rangle - 1)$$

考虑对  $\phi_a^*$  的变分，注意  $\{\phi_a^*\}$  与  $\{\phi_a\}$  是在不同的空间中，是独立的。

1) 对拉格朗日乘子项的变分导数为

$$\frac{\delta \sum_i \epsilon_i (\langle \phi_i | \phi_i \rangle - 1)}{\delta \phi_a^*(r)} = \epsilon_a \phi_a(r)$$

2) 对单体项的变分导数为

$$\frac{\delta \sum_i H_i}{\delta \phi_a^*(r)} = h(r) \phi_a(r) = [-\frac{1}{2} \nabla^2 + v(r)] \phi_a(r)$$

3) 对库仑积分项的变分导数为

$$\frac{\delta \frac{1}{2} \sum_{ij} J_{ij}}{\delta \phi_a^*} = ?$$

$$\begin{aligned} & \delta \frac{1}{2} \sum_{ij} J_{ij} \\ = & \delta \frac{1}{2} \sum_{ij} \int \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_i(r_1) \phi_j(r_2) dr_1 dr_2 \\ = & \frac{1}{2} \sum_j \int \int \delta \phi_a^*(r_1) \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_a(r_1) \phi_j(r_2) dr_1 dr_2 \\ & + \frac{1}{2} \sum_i \int \int \phi_i^*(r_1) \delta \phi_a^*(r_2) \frac{1}{|r_1 - r_2|} \phi_i(r_1) \phi_a(r_2) dr_1 dr_2 \\ = & \sum_j \int \int \delta \phi_a^*(r_1) \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_a(r_1) \phi_j(r_2) dr_1 dr_2 \end{aligned}$$

公式

$$\boxed{\delta F[\phi] = \int \frac{\delta F}{\delta \phi(r)} \delta \phi(r) dr}$$

T

利用公式

$$\delta F[\phi] = \int \frac{\delta F}{\delta \phi(r)} \delta \phi(r) dr$$

得到

$$\begin{aligned} \frac{\delta \frac{1}{2} \sum_{ij} J_{ij}}{\delta \phi_a^*} &= \sum_j \int \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_a(r_1) \phi_j(r_2) dr_2 \\ &= \sum_j \phi_a(r_1) \int \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_j(r_2) dr_2 \\ &= \sum_j \phi_a(r_1) \int \frac{\rho_j(r_2)}{|r_1 - r_2|} dr_2 \end{aligned}$$

4) 对交换积分项的变分导数为

$$\frac{\delta \frac{1}{2} \sum_{ij} K_{ij}}{\delta \phi_a^*} = ?$$

同库仑积分项的变分导数计算，结果为

$$\frac{\delta \frac{1}{2} \sum_{ij} K_{ij}}{\delta \phi_a^*} = \sum_j \int \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_j(r_1) \phi_a(r_2) dr_2$$

$$= \sum_j \phi_j(r_1) \int \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_a(r_2) dr_2$$

# 泛函的极值条件要求

$$\begin{aligned}
 \frac{\delta \Omega}{\delta \phi_a^*} &= \frac{\delta \sum_i H_i}{\delta \phi_a^*(r)} + \frac{\delta \frac{1}{2} \sum_{ij} J_{ij}}{\delta \phi_a^*} - \frac{\delta \frac{1}{2} \sum_{ij} K_{ij}}{\delta \phi_a^*} \\
 &\quad - \frac{\delta \sum_i \epsilon_i (\langle \phi_i | \phi_i \rangle - 1)}{\delta \phi_a^*(r)} \\
 &= 0
 \end{aligned}$$

有

$$\begin{aligned}
 &[-\frac{1}{2} \nabla^2 + v(r)] \phi_a(r) + \sum_j \phi_a(r) \int \frac{\rho_j(r_2)}{|r - r_2|} dr_2 \\
 &\quad - \sum_j \phi_j(r) \int \phi_j^*(r_2) \frac{1}{|r - r_2|} \phi_a(r_2) dr_2 \\
 &= \epsilon_a \phi_a(r)
 \end{aligned}$$

注意到

$$\rho(r_2) \equiv \sum_j \rho_j(r_2)$$

且定义

$$v_H(r) = \int \frac{\rho(r_2)}{|r - r_2|} dr_2$$

有简化形式

$$[-\frac{1}{2} \nabla^2 + v(r) + v_H] \phi_a(r)$$

$$- \sum_j \phi_j(r) \int \phi_j^*(r_2) \frac{1}{|r - r_2|} \phi_a(r_2) dr_2$$

$$= \epsilon_a \phi_a(r)$$

这是一个微分积分方程。 |

## 5e. 注释:

*Note 1.* 需要自洽计算;

*Note 2.* Lagrangian乘子应为  $\epsilon_{ij}$ 。但可证  $\epsilon_{ij}$  能对角化。

*Note 3:*  $E_i \approx \epsilon_i$  , 近似为单电子能量(Koopman's theory)。

*Note 4:*  $\langle H \rangle_{HF} \neq \sum_i \epsilon_i$ , 单粒子能量和不是总能量。

*Note 5:* 关联能定义为

$$E_c = \langle H \rangle - \langle H \rangle_{HF} \leq 0$$

由于近似的能量总是高于基态的能量，关联能只能为负。

i.e. for He atom:  $\langle H \rangle = -2.904$ ,

$\langle H \rangle_{HF} = -2.862$ ,  $E_c = -0.042$

for Be atom:  $\langle H \rangle = -14.667$ ,

$\langle H \rangle_{HF} = -14.571$ ,  $E_c = -0.096$

for Ne atom:  $\langle H \rangle = -128.938$ ,

$\langle H \rangle_{HF} = -128.555$ ,  $E_c = -0.383$

Hartree-Fock的最大问题是没有考虑关联，但重要的一步<sup>43</sup>

next

# 上一讲回顾

- 用到的一点数学
  - 什么情形可以分离变量，可分离变量解的一般形式？
  - 变分法，条件极值问题。
- 多电子体系的平均场概念：
  - Hatree-Fock近似，
  - Hatree-Fock方程

# 补充：泛函、变分、分离变量等

从多元函数到泛函：

泛函的类比定义：

$$F(\varphi_1, \varphi_2, \dots, \varphi_n) \rightarrow F[\varphi(x)]$$

泛函导数的类比定义：

$$dF(\varphi_1, \varphi_2, \dots, \varphi_n) = \sum_j \frac{\partial F}{\partial \varphi_j} d\varphi_j$$

$$\delta F[\varphi(x)] = \int \frac{\delta F}{\delta \varphi} \delta \varphi dx$$

# 泛函的变分：

设有泛函  $F[\varphi(x)]$ , 极值条件为  $\delta F[\varphi] = 0$ , 可推出

$$\delta F[\varphi] = \int \frac{\delta F[\varphi(x)]}{\delta \varphi(x)} \delta \varphi(x) dx = 0.$$

由于  $\delta \varphi$  的任意性, 取  $\delta \varphi(x) = \delta(x - x_0)$ , 极值条件变为

$$\frac{\delta F[\varphi(x)]}{\delta \varphi(x)}|_{x=x_0} = 0.$$

对有条件  $G[\varphi] = 0$  的极值问题, 利用拉格朗日乘子法, 定义

$$\Omega[\varphi] = F[\varphi] - \lambda G[\varphi]$$

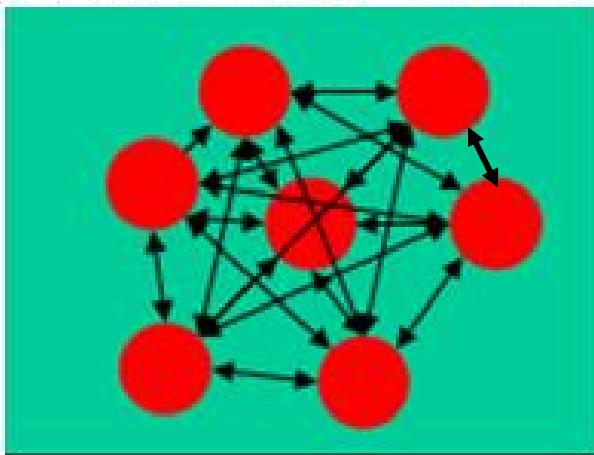
极值条件变为

$$\frac{\delta \Omega[\varphi]}{\delta \varphi} = 0.$$

薛定方程的变分求解基于此。

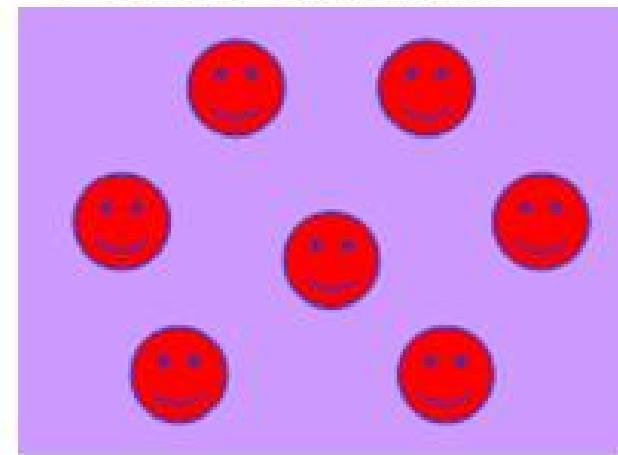
# 多电子体系的平均场概念

真实库仑相互作用：



相互作用的电子体系

平均场有效势：



非相互作用的准粒子体系

如何构造出较好的有效势?  
平均场的适用条件是什么?

## 如何构造有效势:

- 利用单行列式波函数作为变分波函数
- 用变分波函数计算总能量的平均值
- 构造一个总能量附加波函数归一化条件的泛函
- 对泛函取变分极小得到Hartree-Fock方程

平均场的适用条件:  $\hat{H} = \sum_{i=1}^n \left( -\frac{1}{2} \nabla_i^2 + \hat{\nu}_i \right) + \hat{U}_{ee}$

把电子间相互作用势作为微扰, 电子间相互作用不能太强。  $\hat{H} \approx \sum_{i=1}^n \left( -\frac{1}{2} \nabla_i^2 + \hat{\nu}_i + \hat{g}_i \right)$

思考题: 假如电子动能为meV, 求两个电子间库伦势能大于电子动能时两电子间的最大距离。

# Hartree-Fock方程是一个单粒子方程

$$\hat{f}(r_1)\phi_i(r_1) = \epsilon_i\phi_i(r_1)$$

where the Fock operator  $\hat{f}(r_1)$  is defined as:

$$\hat{f}(r_1) = \hat{h}(r_1) + \sum_a [\hat{j}_a(\mathbf{r}_1) - \hat{k}_a(\mathbf{r}_1)].$$

$$[-\frac{1}{2}\nabla^2 + v(r) + v_H]\phi_a(r)$$

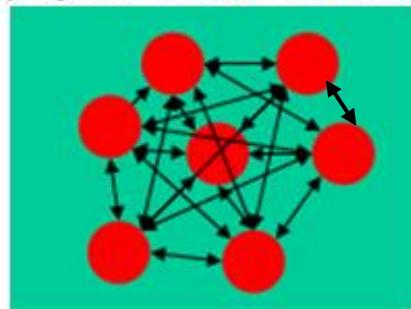
$$- \sum_j \phi_j(r) \int \phi_j^*(r_2) \frac{1}{|r - r_2|} \phi_a(r_2) dr_2$$

$$= \epsilon_a \phi_a(r)$$

要知道是如何推导出的  
150

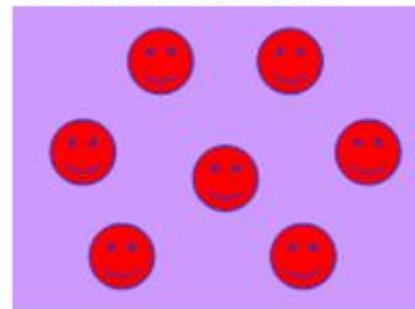
# 每个电子满足的HF方程相同

真实库仑相互作用:



相互作用的电子体系

平均场有效势:

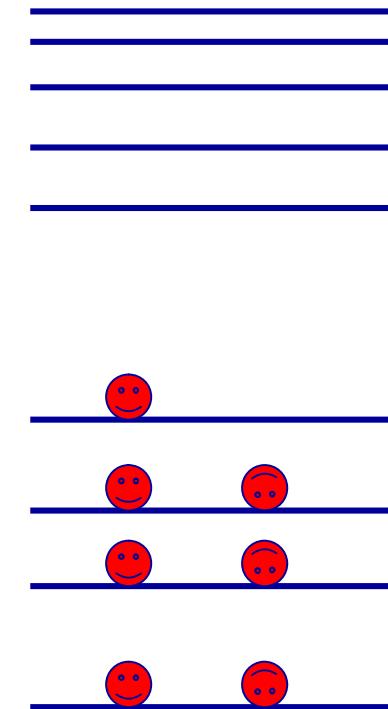


非相互作用的准粒子体系

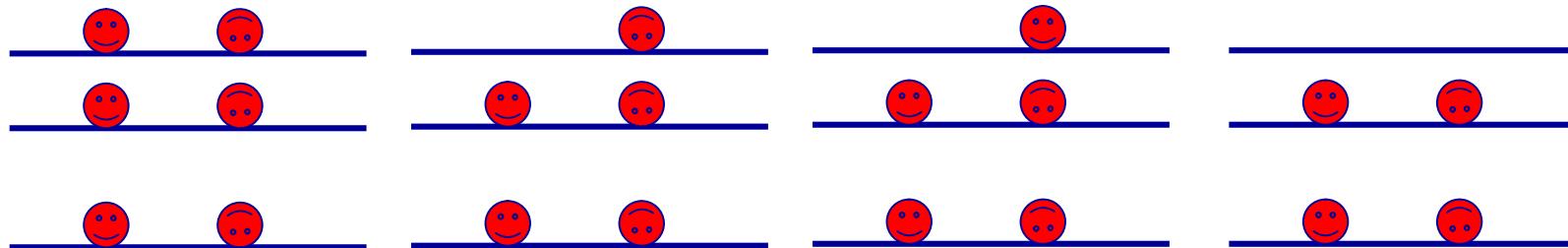
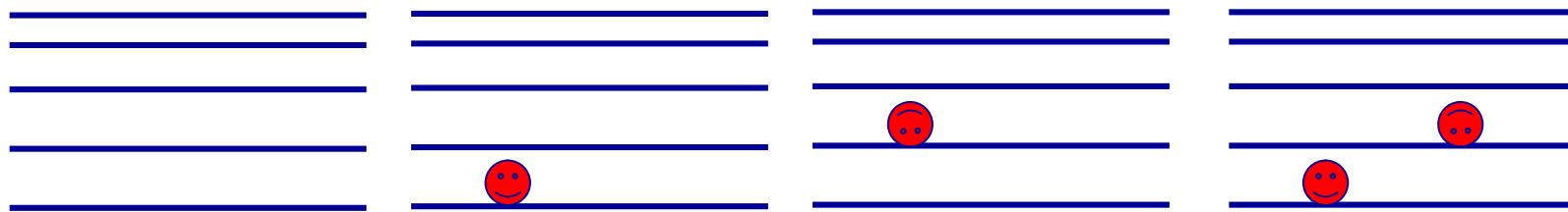
近似

• 对非相互作用体系，N个电子的每一个满足同样的薛定格方程。每一个电子都处于绝对平等的地位。不是求解N个电子联立方程。

• 解单粒子方程可得到足够多的单粒子态，所有N个电子按照量子力学逐次填充这些单粒子态。



# 行列式波函数是不唯一的



基态

单激发态1

单激发态2

双激发态1

有无穷多种行列式波函数！

# 关于Koopmans定理

电子离化能 = 电子轨道能量

利用  $E_N = \sum_i^N H_i + \frac{1}{2} \sum_{i,j}^N (J_{ij} - K_{ij})$  和  $\langle \phi_a | \hat{f}_a | \phi_a \rangle = \varepsilon_a$  可证：

$E_N - E_{N-1} = \varepsilon_a$ , Koopmans定理

$E_N \neq \sum_{a=1}^N \varepsilon_a$  总能量不是单粒子能量的和

对密度泛函情形有类似的关系，此处对HF情形不推导了，自己证明？ [需假定N-1电子波函数与N电子波函数中对应的N-1电子波函数相同]

# 证明：Koopmans定理

总能量可写为：

$$E_{HF}(N - 1) = \sum_i^{N-1} H_i + \frac{1}{2} \sum_{i,j}^{N-1} (J_{ij} - K_{ij})$$

$$E_{HF}(N) = \sum_i^N H_i + \frac{1}{2} \sum_{i,j}^N (J_{ij} - K_{ij})$$

$$E_{HF}(N + 1) = \sum_i^{N+1} H_i + \frac{1}{2} \sum_{i,j}^{N+1} (J_{ij} - K_{ij})$$

N电子体系拿走一个电子后的离化势IP(ionization potential)

$$IP = E_{HF}(N - 1) - E_{HF}(N) = ?$$

N电子体系加入一个电子后的电子亲和势EA(electron affinity)

$$EA = E_{HF}^0(N) - E_{HF}(N + 1) = ?$$

需要计算N电子体系拿走一个电子后的离化势IP(ionization potential)

$$\text{IP} = E_{HF}(N - 1) - E_{HF}(N) = ?$$

设前 $N - 1$ 个电子的能级和波函数都相同, 第 $N$ 个电子能级为 $\epsilon_a$ , 波函数为 $\phi_a(\mathbf{r})$ , 则

$$\begin{aligned} & E_{HF}(N - 1) - E_{HF}(N) \\ &= -H_a + \frac{1}{2} \sum_i^{N-1} \sum_j^{N-1} (J_{ij} - K_{ij}) - \frac{1}{2} \sum_i^N \sum_j^N (J_{ij} - K_{ij}) \end{aligned}$$

$$= - \int \phi_a^*(\mathbf{r}) \hat{h}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \sum_i^N (J_{ia} - K_{ia}) - \frac{1}{2} \sum_j^N (J_{aj} - K_{aj})$$

$$E_{HF}(N - 1) - E_{HF}(N) = - \int \phi_a^*(\mathbf{r}) \hat{h}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} - \sum_i^N (J_{ia} - K_{ia})$$

$$E_{HF}(N-1) - E_{HF}(N)$$

$$= - \int \phi_a^*(\mathbf{r}) \hat{h}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} - \sum_i^N \int \int \phi_a^*(\mathbf{r}_2) \frac{\rho_i(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_a(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$+ \sum_i^N \int \int \phi_i^*(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_2) \phi_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{HF}(N-1) - E_{HF}(N) = - \int \phi_a^*(\mathbf{r}) \hat{h}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} - \int \phi_a^*(\mathbf{r}_2) \hat{j}_a(\mathbf{r}_2) \phi_a(\mathbf{r}_2) d\mathbf{r}_2$$

$$+ \int \phi_a^*(\mathbf{r}_2) \hat{k}_a(\mathbf{r}_2) \phi_a(\mathbf{r}_2) d\mathbf{r}_2$$

$$= - \int \phi_a^*(\mathbf{r}) \hat{f}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r}$$

$$= -\epsilon_a$$

其中用到了

$$\hat{f}(\mathbf{r}) \phi_a(\mathbf{r}) = \hat{h}(\mathbf{r}) \phi_a(\mathbf{r}) + \hat{j}_a(\mathbf{r}) \phi_a(\mathbf{r}) - \hat{k}_a(\mathbf{r}) \phi_a(\mathbf{r}) = \epsilon_a \phi_a(\mathbf{r}).$$

即离化势为单粒子能量：

$$\text{IP} = E_{HF}(N - 1) - E_{HF}^0(N) = -\epsilon_a$$

若计算N电子体系加入一个电子后的电子亲和势EA(electron affinity)

$$\text{EA} = E_{HF}^0(N) - E_{HF}(N + 1) = ?$$

设前N个电子的能级和波函数都相同，第N + 1个电子能级为 $\epsilon_b$ ，波函数为 $\phi_b(\mathbf{r})$ ，同样可证明电子亲和势

$$\text{EA} = E_{HF}^0(N) - E_{HF}(N + 1) = -\epsilon_b$$

即Koopmans定理得证。注意推导没有做近似！

# 佳林·库普曼斯？



考证来源：

- Koopmans' theorem [wikipedia]
- 佳林·库普曼斯 [互动百科]
- Tjalling Koopmans [wikipedia]

# Tjalling C. Koopmans-佳林·库普曼斯

- 佳林·库普曼斯(1910年—1985年), 美国人, 1910年8月28日生于荷兰, 1940年离开荷兰移居美国。1975年, 他和康托罗维奇同时**获得诺贝尔经济学奖**。线性规划经济分析法的创立者。



库普曼斯于1910年8月28日生于荷兰, 自幼刻苦读书, 立志成为科学家。1933年, 毕业于乌德勒支大学的数理系。

次年, 库普曼斯写出了关于量子力学的论文, 获得了硕士学位。

1936年获得了荷兰莱顿大学的数理统计学博士学位。

1938年至1940年担任日内瓦国际联盟财政秘书, 在1940年移居美国, 在普林斯顿大学研究会研究经济并兼任纽约大学商学院特邀教师。

1941年, 转任宾夕法尼亚互助人寿保险公司经济员, 在英国航运协会任统计员。

1944年返回学术界, 在芝加哥大学柯尔斯委员会从事经济研究工作。

1946年, 他任芝加哥大学经济学副教授,

1948年升为教授并兼任柯尔斯委员会主任。

1955年, 他到耶鲁大学任教, 此后又受聘于哈佛大学。

# 证明： HF总能量不是单粒子能量的和

从HF方程出发

$$\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) = (\hat{h}(\mathbf{r}_1) + \sum_a [\hat{j}_a(\mathbf{r}_1) - \hat{k}_a(\mathbf{r}_1)])\phi_i(\mathbf{r}_1) = \epsilon_i\phi_i(\mathbf{r}_1)$$

$$\hat{h}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) + \sum_a \int \frac{\rho_a(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \phi_i(\mathbf{r}_1) - \sum_a \int \frac{\phi_a^*(\mathbf{r}_2)\phi_a(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 = \epsilon_i\phi_i(\mathbf{r}_1)$$

两边乘 $\phi_i^*(\mathbf{r}_1)$ 积分并对*i*求和：

$$\begin{aligned} & \sum_i \int \phi_i^*(\mathbf{r}_1) \hat{h}(\mathbf{r}_1) \phi_i(\mathbf{r}_1) d\mathbf{r}_1 + \sum_{a,i} \int \int \frac{\rho_a(\mathbf{r}_2)\rho_i(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1 \\ & - \sum_{a,i} \int \int \frac{\phi_a^*(\mathbf{r}_2)\phi_j^*(\mathbf{r}_1)\phi_a(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1 \\ & = \sum_i \epsilon_i \end{aligned}$$

$$\sum_i H_i + \sum_{a,i} (J_{ai} - K_{ai}) = \sum_i \epsilon_i$$

$$\sum_i H_i + \sum_{a,i} (J_{ai} - K_{ai}) = \sum_i \epsilon_i$$

总能量写法为

$$E_{HF} = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

$$= \sum_i \epsilon_i - \sum_{i,j} (J_{ij} - K_{ij}) + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

$$E_{HF} = \sum_i \epsilon_i - \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij})$$

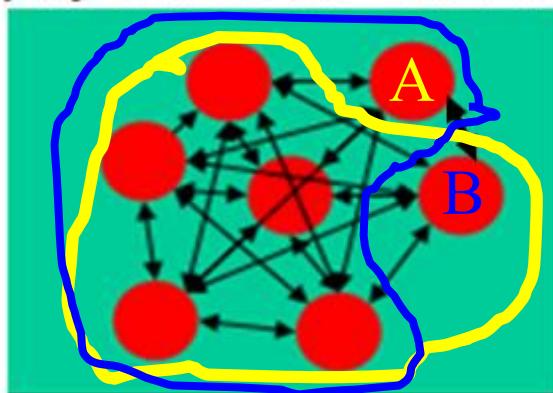
可见， HF总能量不是单粒子能量的和。<sub>161</sub>

# HF总能量不是单粒子能量的和

单粒子能量的和  
把电子间的相互  
作用重复计算了。

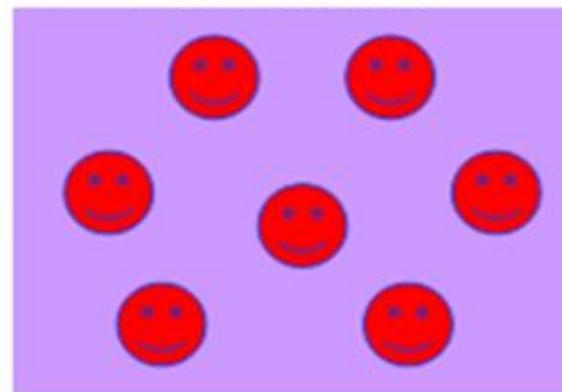
$$\sum_i \epsilon_i = \sum_i H_i + \sum_{a.i} (J_{ai} - K_{ai})$$
$$E_{HF} = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij})$$
$$E_{HF} = \sum_i \epsilon_i - \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij})$$

真实库仑相互作用：



相互作用的电子体系

平均场有效势：



非相互作用的准粒子体系

# 电子关联 (纠缠)

所谓的“关联”指波函数不能写为单粒子波函数的乘积形式：

$$\Phi(r_1, r_2, \dots, r_n) \neq \varphi(r_1)\varphi(r_2)\dots\varphi(r_n).$$

如何详尽的考虑关联是凝聚态物理最难的地方。

$$\hat{H}_{el} = T_e + V_{ext} + U_{ee} \equiv \sum_i \hat{h}_i + U_{ee}$$

$$\hat{H}_{el} = T_e + V_{ext} + U_{ee} \approx \sum_i \hat{h}_i + \sum_i \hat{g}_i$$

# 关联问题

简单讲：关联是指有相互作用的多粒子体系的波函数不是单粒子体系的波函数的乘积！

Hartree:  $\Psi_H = \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N)$

Slater:  $\Psi_D = \frac{1}{\sqrt{N}} \sum_{\sigma \in P} sign(\sigma) \psi_1(x_{\sigma(1)}) \psi_1(x_{\sigma(2)}) \dots \psi_1(x_{\sigma(N_e)})$

Slater-Jastrow:  $\Psi_T = [\text{Multi Slater}] \times [\text{All Correlation}]$

$$= \left( \sum_l d_l \Psi_{D_l} \right) \exp \sum_{i,j,\alpha} J(r_{i\alpha}, r_{j\alpha}, r_{ij}) \quad \begin{matrix} \text{Electron -} \\ \text{electron -} \\ \text{nucleus} \\ \text{correlation} \end{matrix}$$

$$J(r_{i\alpha}, r_{j\alpha}, r_{ij}) = \underbrace{\sum_{i\alpha} A(r_{i\alpha})}_{\text{electron - nucleus correlation}} + \underbrace{\sum_{i \neq j} B(r_{ij})}_{\text{electron - electron correlation}} + \underbrace{\sum_{i,j,\alpha} C(r_{i\alpha}, r_{j\alpha}, r_{ij})}_{\text{Electron - electron - nucleus correlation}}$$

猜出一个正确的关联  
波函数能得诺贝尔奖



R. B. Laughlin, PRL50,1395(1983):

$$\Psi_m = \prod_{1 \leq j < k \leq N} (z_j - z_k)^m \exp\left(-\alpha \sum_{j=1}^N |z_j|^2\right)$$

Jastrow-like, 用于量子霍尔效应理论

# 关联能

*Note 5:* 关联能定义为

$$E_c = \langle H \rangle - \langle H \rangle_{HF} \leq 0$$

由于近似的能量总是高于基态的能量，关联能只能为负。

i.e. for He atom:  $\langle H \rangle = -2.904$ ,  
 $\langle H \rangle_{HF} = -2.862$ ,  $E_c = -0.042$

for Be atom:  $\langle H \rangle = -14.667$ ,  
 $\langle H \rangle_{HF} = -14.571$ ,  $E_c = -0.096$

for Ne atom:  $\langle H \rangle = -128.938$ ,  
 $\langle H \rangle_{HF} = -128.555$ ,  $E_c = -0.383$

HF是单粒子波函数的积，完全没有考虑关联。如何考虑关联？

# 组态相互作用(CI): 考虑激发态

$$\Psi = \Psi_0 + \sum_{ia} t_i^a \Psi_i^a + \sum_{ijab} t_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijkabc} t_{ijk}^{abc} \Psi_{ijk}^{abc} + \dots$$

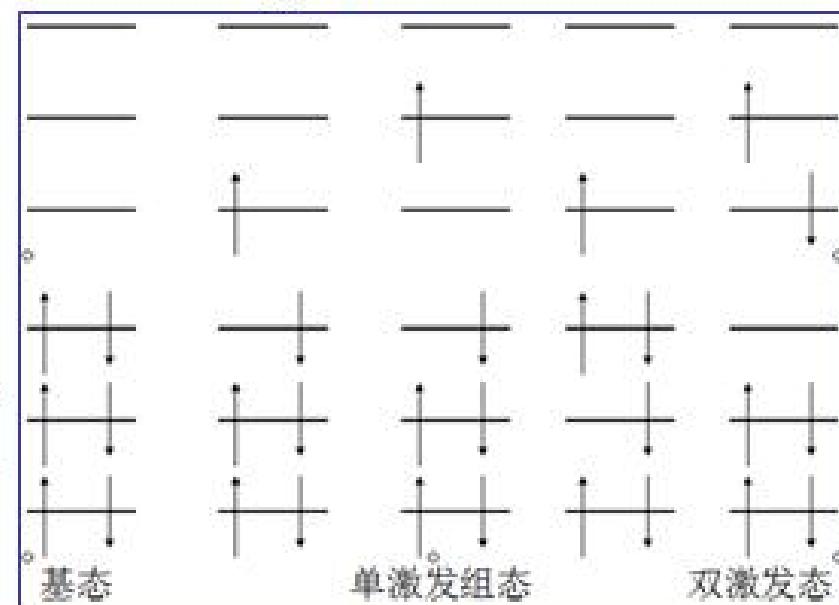
变分波函数

$$\Psi_0 = |\phi_1 \cdots \phi_n|$$

$$\Psi_i^a = |\phi_1 \cdots \phi_{i-1} \phi_a \phi_{i+1} \cdots \phi_n|$$

$$\Psi_{ij}^{ab} = |\phi_1 \cdots \phi_{i-1} \phi_a \phi_{i+1} \cdots \phi_{j-1} \phi_b \phi_{j+1} \cdots \phi_n|$$

$$(\phi_i \rightarrow \phi_a, \phi_j \rightarrow \phi_b)$$

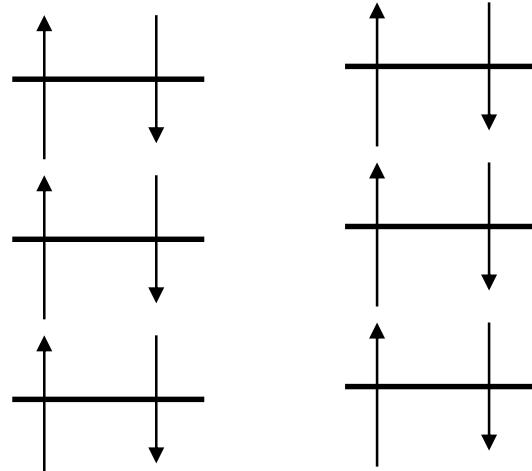
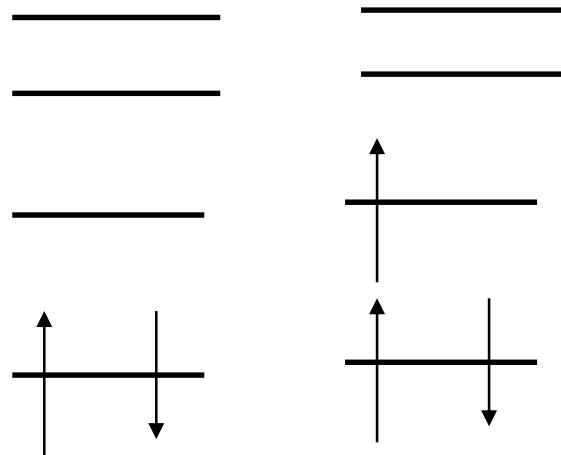


# 组态相互作用(CI)中的名词

- CIS – 包括所有单激发态
  - 用于激发态计算, 不是用于基态相关能
- CISD – 包括所有单激发和双激发态
  - 对计算基态的相关能非常有用
  - $O^2U^2$  个行列式 ( $O$ = 占据轨道的数目,  $U$ =未占据轨道的数目)
- CISDT – 单重, 双重和三重激发态
  - 仅限于小分子, 大概  $O^3U^3$  个行列式
- 完全 CI – 所有可能的激发态
  - $((O+U)!/O!U!)^2$  个行列式,  $O, U$ 大则计算量很大
  - 在基组给定的情况下, 得到精确的相关能
  - 大概限于14个轨道上分布14个电子

该方法计算量特别大, 只能用于原子和 小分子情形。  
168

# 化学家用概念：闭壳层与开壳层



闭壳层

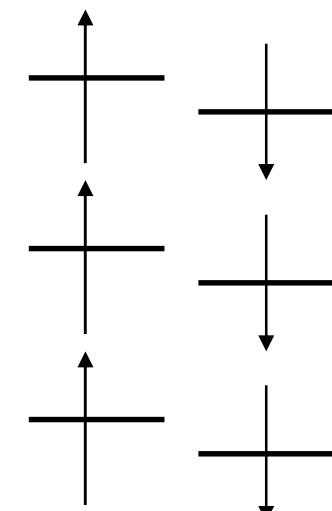
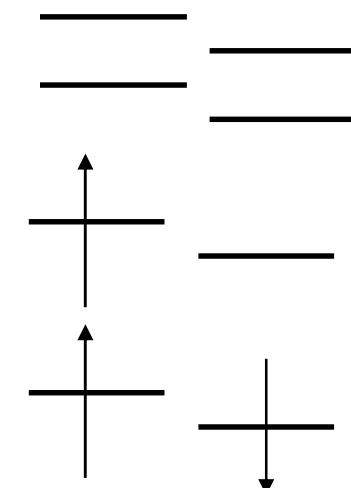
开壳层

哈密顿量

$$H = \begin{pmatrix} H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\ H_{\downarrow\uparrow} & H_{\downarrow\downarrow} \end{pmatrix}$$

—— 空间波函数

↑ 自旋波函数



一般情形

# Hartree-Fock波函数：

■ 闭壳层, RHF:

自旋限制 Hartree-Fock,

$\alpha$  和  $\beta$  自旋电子占据同一个空间轨道

■ 开壳层, UHF:

自旋非限制 Hartree-Fock,

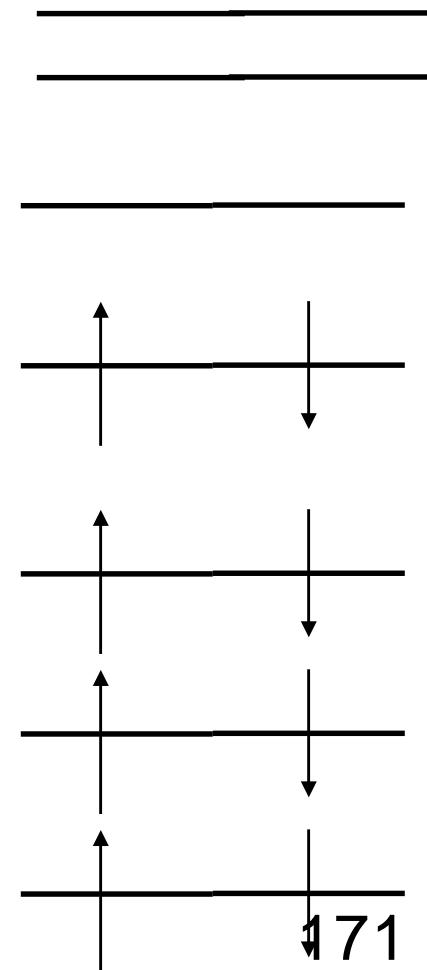
$\alpha$  和  $\beta$  自旋电子有不同的空间轨道

# 限制 Hartree-Fock 波函数, RHF

自旋限制 Hartree-Fock,  $\alpha$  和  $\beta$   
自旋电子占据同一个空间轨道

用 RHF 只有 4 个不同的空间轨道  
用 UHF 有 8 个不同的空间轨道

由于计算量的差别, 也常用 RHF  
但哈量一定是与自旋无关的才可以

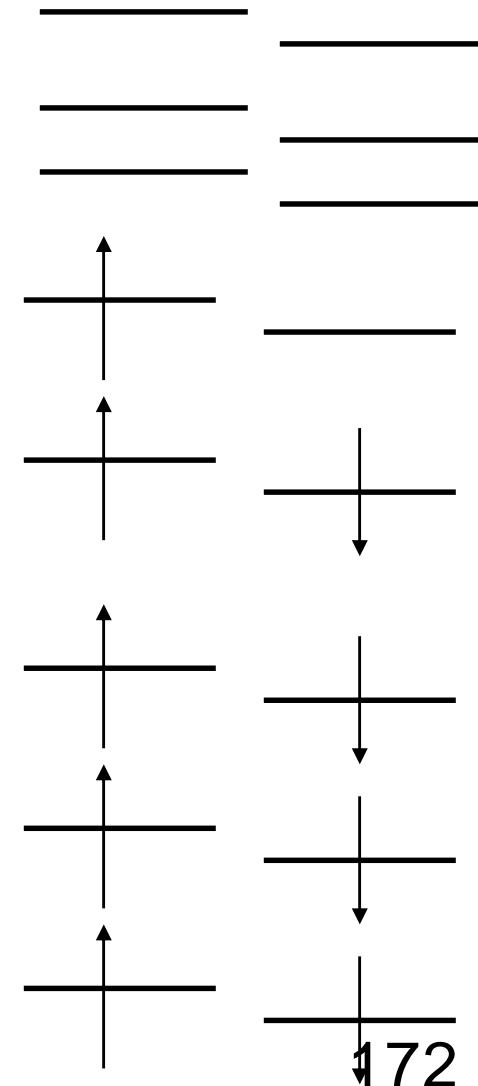


# 自旋非限制 Hartree-Fock 波函数：UHF

自旋非限制 Hartree-Fock,  $\alpha$  和  $\beta$   
自旋电子有不同的空间轨道，  
是最一般的情形，开壳层与闭壳  
层都可用该方法。

特别适合处理哈密顿量含自旋情  
形（比如自旋轨道相互作用），  
此时的哈密顿量是  $2 \times 2$  的算符。

$$H = \begin{pmatrix} H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\ H_{\downarrow\uparrow} & H_{\downarrow\downarrow} \end{pmatrix}$$



# 任意函数按正交完备函数集展开

参考：物理学中的数学方法 - 李政道著,吴顺唐译

郭敦仁及梁昆淼的‘数学物理方法’均提到了按正交完备函数集展开或广义富利叶级数展开，但都没有李政道的书单独一章讲授。

## 第三章 按正交函数系展开

§1	希尔伯特空间 .....	107
§2	函数系的完备性 .....	109
§3	完备正交系的例子。富里埃级数 .....	119
§4	富里埃积分 .....	129
§5	埃尔米特算子 .....	135
§6	勒让德多项式 .....	141
§7	多极展开式 .....	148
§8	球谐函数 .....	154

## 5f. 把求本征值的微分方程问题化为代数问题

为了把微分方程的本征值问题化为代数的本征值问题，需要把单粒子波函数用一组完备的基函数展开。如果取基底为  $\chi_k(r)$ ，可把单粒子波哈密  $\phi_i$  按基底展开为  $\phi_i(r) = \sum_{k=1}^n C_{ki} \chi_k(r)$ ，代入 Hartree-Fock 方程可得到：

$$\hat{f}(\mathbf{r}_1) \sum_{k=1}^n C_{ki} \chi_k(\mathbf{r}_1) = \epsilon_i \sum_{k=1}^n C_{ki} \chi_k(\mathbf{r}_1)$$

方程两边同乘  $\chi_l(r_1)$  并对  $r_1$  积分有：

$$\begin{aligned} & \sum_{k=1}^n C_{ki} \int \chi_l^*(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \chi_k(\mathbf{r}_1) d\mathbf{r}_1 \\ &= \epsilon_i \sum_{k=1}^n C_{ki} \int \chi_l^*(\mathbf{r}_1) \chi_k(\mathbf{r}_1) d\mathbf{r}_1 \end{aligned}$$

引入定义：

$$(\mathbf{F})_{lk} = F_{lk} = \int \chi_l^*(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \chi_k(\mathbf{r}_1) d\mathbf{r}_1$$

是  $n \times n$  Fock矩阵  $\mathbf{F}$  的矩阵元。还有定义

$$(\mathbf{S})_{lk} = S_{lk} = \int \chi_l^*(\mathbf{r}_1) \chi_k(\mathbf{r}_1) d\mathbf{r}_1$$

是  $n \times n$  重叠积分矩阵  $\mathbf{S}$ 。有  $n$  个方程 ( $n$  是基底的数目), 可写为矩阵形式:

$$\mathbf{FC} = \mathbf{SC}\epsilon.$$

在线性代数里, 求  $\mathbf{F}$  的本征值问题是标准的问题。第一步是找到矩阵  $\mathbf{X}$  对角化重叠积分矩阵  $\mathbf{S}$ , 这相当于把基底正交归一化:

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}.$$

得到

$$\mathbf{F}' \mathbf{C}' = \epsilon \mathbf{C}', \text{ 或 } \mathbf{C}'^\dagger \mathbf{F}' \mathbf{C}' = \epsilon$$

其中  $\mathbf{C} = \mathbf{X} \mathbf{C}'$  和  $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$ 。求  $\mathbf{C}'$  的方法是现成的。

是广义的本征值问题, 在矩阵维数不大时容易解出的。175

表面上看很简单，但实际上需要自洽计算的。因为  $F$  的矩阵元与待求解的轨道  $\phi$  有关。还有，由于库仑和交换算符导致方程为微分积分方程，化为代数方程时涉及大量的双电子积分：

$$\langle ij|kl \rangle = \int \int \chi_i^*(\mathbf{r}_1) \chi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_k(\mathbf{r}_1) \chi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2,$$

这是非常耗费计算时间的。

由于单行列式波函数的限制，Hartree-Fock方法也是一个没有考虑关联的近似方法。Hartree-Fock方法对结构的决定还可以，但涉及键的形成与断裂很差（化学精度）。若使用多行列式波函数则计算量太大，只能算小分子体系。

注1：求解用基底可以是Gauss型轨道(GTO)，也可以是Slater型轨道(STO)，激发态原子轨道，或平面波。常用前两种。

注2：不计计算矩阵元时的多中心积分，构成了物理上的或化学上的各种近似方法。

**化学精度：要求1kcal/mole~0.01eV/分子**

➤ Hartree-Fock, LDA,GGA均不能达到此精度

# Hartree-Fock方法

**Hartree-Fock**方法的单行列式波函数形式无法考虑关联。对结构的决定还可以，但涉及键的形成与断裂很差（化学精度）。若使用多行列式波函数则计算量太大，只能算小分子体系。

注1：求解用基底可以是Gauss型轨道(GTO)，也可以是Slater型轨道(STO)，激发态原子轨道，或平面波。常用前两种。

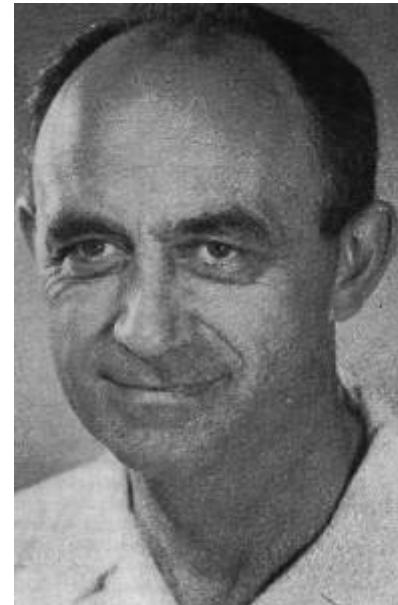
注2：不计计算矩阵元时的多中心积分，构成了物理上的或化学上的各种近似方法。

有没有更好的方法？ 密度泛函理论！

# 6. 密度泛函的雏形: Thomas-Fermi



L. H. Thomas



E. Fermi

原子的总能量是电子密度的泛函

# Thomas Femi Theory

## Thomas-Fermi Theory

Thomas-Fermi approximation: based on Hartree total energy

$$\langle H \rangle_{\text{hartree}}$$

$$= \sum_{i=1} \langle \phi_i(\mathbf{r}) | \hat{h}_i | \phi_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i \neq j} \langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle$$

$$= \sum_{i=1} \langle \phi_i(\mathbf{r}) | (-\frac{1}{2} \nabla_i^2) | \phi_i(\mathbf{r}) \rangle$$

$$+ \sum_{i=1} \int v(\mathbf{r}_1) \rho_i(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \sum_{i \neq j} \int \int \frac{\rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$= T_{TF}[\rho] + \int v(\mathbf{r}_1) \rho(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2,$$

计及交换时方可

注：托马斯-费米理论具有DFT理论的特点：总能量是密度的泛函

动能项由下式近似

$$T_{TF} = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r},$$

$$C_F = \frac{3}{10} (3\pi^2)^{2/3} = 2.871,$$

电子密度为  $\rho(r) = \sum_i \rho_i(r) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$ , 这样总能量可写为只是电子密度的泛函

$$\langle H \rangle_{TF} = C_F \int \rho^{5/3}(r_1) dr_1 + \int v(r_1) \rho(r_1) dr_1$$

$$+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 r_2.$$

# 均匀电子气的动能

如何得到  $T_{TF}$  ? 三维无穷深阱的能量为

$$\begin{aligned}\varepsilon(n_x, n_y, n_z) &= \frac{\hbar^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2) \\ &\equiv \frac{\hbar^2}{8ml^2} R^2.\end{aligned}$$

对于较大的  $R$ , 比  $\varepsilon$  小的能级的数目是半径为  $R$  的球的体积  $1/8$  (注:  $n_x, n_y, n_z \geq 0$ , 因此  $1/8$ ):

$$\Phi(\varepsilon) = \frac{1}{8} \frac{4\pi R^3}{3} = \frac{\pi}{6} \left( \frac{8ml^2\varepsilon}{\hbar^2} \right)^{3/2}.$$

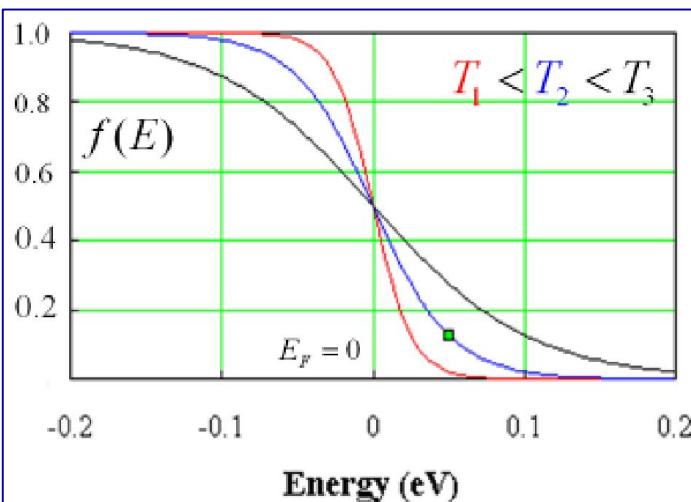
这样，态密度DOS  $g(\varepsilon)$ 可得到：

$$\begin{aligned} g(\varepsilon)\Delta\varepsilon &= \Phi(\varepsilon + \Delta\varepsilon) - \Phi(\varepsilon) \\ &= \frac{\pi}{4} \left( \frac{8ml^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon + O((\Delta\varepsilon)^2). \end{aligned}$$

在这个盒子中的总能量是

$$\Delta E = 2 \int \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon.$$

在零温



$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases} \quad \vdots$$

思考题：用不同的方法计算态密度

则,

$$\Delta E = 2 \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon = \frac{8\pi}{5} \left( \frac{2m}{h^2} \right)^{3/2} l^3 \varepsilon_F^{5/2}.$$

试图找到电子密度( $\rho = \frac{\Delta N}{\Delta V}$ ,  $\Delta V = l^3$ )  
与能量的关系. 先找到盒子中的电子数目,

$$\Delta N = 2 \int f(\varepsilon) g(\varepsilon) d\varepsilon$$

$$= 2 \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^{3/2} l^3 \varepsilon_F^{3/2}.$$

注意: 认为密度在小体积内为常数!

得到

$$\begin{aligned}\Delta E &= \frac{3}{5} \varepsilon_F \Delta N \\ &= \frac{3h^2}{10m} \left( \frac{3}{8\pi} \right)^{2/3} \left( \frac{\Delta N}{\Delta V} \right)^{5/3} \Delta V.\end{aligned}$$

注意  $\hbar = 2\pi\hbar$ , 取原子单位 ( $\hbar = 1, m = 1$ ), 得到,

$$\Delta E = C_F \rho^{5/3} \Delta V.$$

假设  $\Delta V = d\mathbf{r}$  非常小, 总动能是在整个空间的求和(能量可加性)

$$T_{TF} = \int \Delta E = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}.$$

注: 能量是广延量, 可以相加。在总能量上还可以加交换能。

# 思考题： Thomas-Fermi有发展吗？

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- 现代应用？ - J. Phys. B: At. Mol. Opt. Phys. 42 (2009) 145304, Finite temperature correction to the Thomas–Fermi approximation for a Bose–Einstein condensate

# 均匀电子气的交换积分与交换能

均匀自由电子气的交换能可如下得到。设自由电子气的波函数是平面波  $\phi_k = \frac{1}{\sqrt{V}} e^{ik \cdot r}$ . 交换积分是

$$\begin{aligned} K_{k_1 k_2} &= - \int \frac{\phi_{k_1}^*(\mathbf{r}_1) \phi_{k_2}^*(\mathbf{r}_2) \phi_{k_1}(\mathbf{r}_2) \phi_{k_2}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \\ &= - \frac{1}{V^2} \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-ik_1 r_1} e^{-ik_2 r_2} e^{ik_1 r_2} e^{ik_2 r_1} d\mathbf{r}_1 d\mathbf{r}_2, \\ &= - \frac{1}{V^2} \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{i(\mathbf{k}_2 - \mathbf{k}_1)(\mathbf{r}_1 - \mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= - \frac{1}{V} \int \frac{1}{|\mathbf{R}|} e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}} d\mathbf{R} = - \frac{1}{|\mathbf{k}_2 - \mathbf{k}_1|^2}. \end{aligned}$$

# 1/r的积分问题

$$\begin{aligned} & \int \frac{1}{|\mathbf{x}|} e^{-i\mathbf{G}\cdot\mathbf{x}} d\mathbf{x} \\ = & 2\pi \int \int -d \cos(\theta) x^2 dx \frac{1}{x} e^{-i|\mathbf{G}|x \cos(\theta)} e^{-ix} \\ = & 2\pi \int \int \frac{1}{i|\mathbf{G}|} d(-i|\mathbf{G}|x \cos(\theta)) e^{-i|\mathbf{G}|x \cos(\theta)} e^{-ix} dx \\ = & \frac{2\pi}{i|\mathbf{G}|} \int_0^\infty e^{-ix} (e^{i|\mathbf{G}|x} - e^{-i|\mathbf{G}|x}) dx \\ = & -\frac{2\pi}{i|\mathbf{G}|} \left( \frac{1}{i|\mathbf{G}|-\tau} - \frac{1}{-i|\mathbf{G}|-\tau} \right) = \frac{4\pi}{|\mathbf{G}|^2}. \end{aligned}$$

注：|G|不能为零，若为零则积分发散

自由电子气的交换能是交换积分的和

$$E_x = \sum_{k_1, k_2} K_{k_1 k_2} = - \sum_{k_1, k_2} \frac{1}{|\mathbf{k}_2 - \mathbf{k}_1|^2}$$

$$= - \int_0^{\mathbf{k}_F} d\mathbf{k}_1 \int_0^{\mathbf{k}_F} d\mathbf{k}_2 \frac{1}{|\mathbf{k}_2 - \mathbf{k}_1|^2}$$

$$= - \int \int \frac{1}{|\mathbf{k}_2 - \mathbf{k}_1|^2} \theta(\mathbf{k}_F - \mathbf{k}_1) \theta(\mathbf{k}_F - \mathbf{k}_2) d\mathbf{k}_1 d\mathbf{k}_2$$

定义  $\mathbf{k}_2 - \mathbf{k}_1 = \mathbf{q}$ ,

定义  $\mathbf{k}_2 - \mathbf{k}_1 = \mathbf{q}$ ,

$$\begin{aligned} E_x &= - \int \int \frac{1}{q^2} \theta(\mathbf{k}_F - \mathbf{k}_1) \theta(\mathbf{k}_F - \mathbf{k}_1 - \mathbf{q}) d\mathbf{k}_1 d\mathbf{q} \\ &= - \int \int \frac{1}{q^2} \theta(\mathbf{k}_F - \mathbf{k}) \theta(\mathbf{k}_F - \mathbf{k} - \mathbf{q}) k^2 dk q^2 dq d\Omega_q d\Omega_k \\ &= - \int \int \theta(\mathbf{k}_F - \mathbf{k}_1) \theta(\mathbf{k}_F - \mathbf{k}_1 - \mathbf{q}) k_1^2 dk_1 dq d\Omega_q d\Omega_k \\ &= -\alpha \int_0^{k_F} k^2 dk \int_0^{k_F - k} dq, \quad \text{对角度的积分不易做出,} \\ &= -\alpha \int_0^{k_F} k^2 (k_F - k) dk \quad \text{用常数代替} \\ &= -\alpha \left( k_F \frac{1}{3} k_F^3 - \frac{1}{4} k_F^4 \right) \\ &= -\frac{\alpha}{12} k_F^4. \end{aligned}$$

我们还知道

$$\epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3}{8\pi} \rho \right)^{2/3} = \frac{(2\pi)^2 \hbar^2}{2m} \left( \frac{3}{8\pi} \rho \right)^{2/3},$$

或  $k_F = 2\pi \left( \frac{3}{8\pi} \rho \right)^{1/3}$

可得到

$$\begin{aligned} E_x &= -\frac{\alpha}{12} (2\pi)^4 \left( \frac{3}{8\pi} \rho \right)^{4/3} \\ &= -\frac{\alpha (2\pi)^4}{12} \frac{3}{8\pi} \frac{1}{2} \left( \frac{3}{\pi} \right)^{1/3} (\rho)^{4/3} \\ &= -\alpha' \left( \frac{3}{\pi} \right)^{1/3} (\rho)^{4/3} \end{aligned}$$

Dirac修正：考虑交换能修正 $E_x(\rho)$

$$E_x[\rho] = -C_x \int \rho^{4/3}(\mathbf{r}_1) d\mathbf{r}_1,$$

$$C_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} = 0.7386$$

则

$$\langle H \rangle_{TFD} = \langle H \rangle_{TF} + E_x$$

如果引入两粒子密度矩阵，容易得到动能和交换能都是电子密度的泛函，请参阅参考文献Parr书。

# Thomas-Fermi-Dirac理论表明总能量近似为密度的泛函

$$\langle H \rangle_{TFD} = C_F \int \rho^{5/3}(r_1) dr_1$$

电子动能

$$+ \int v(r_1) \rho(r_1) dr_1$$

外势项

$$+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 dr_2$$

库伦能

$$- C_x \int \rho^{4/3}(\mathbf{r}_1) dr_1.$$

电子交换能

除对交换能修正外，还可对动能进行高阶修正。  
92

# von Weizsäcker梯度修正（动能修正）

von Weizsäcker's gradient correction

$$T_{vW} = \lambda \int \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}, \quad \frac{1}{9} \leq \lambda \leq 1.$$

$$\langle H \rangle_{TFDvW} = C_F \int \rho^{5/3}(r_1) dr_1 + \int v(r_1) \rho(r_1) dr_1$$

$$+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 r_2 - C_x \int \rho^{4/3}(\mathbf{r}_1) d\mathbf{r}_1.$$

$$+ \lambda \int \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}$$

实际上是把动能按密度做形式展开到二阶项，但是这个展开是不收敛的，到二阶有好的修正，到高阶反而更差。参见Page 193书。

注1: Local Density Approximation (**LDA**):  
动能是由均匀电子气的动能相加得到的。

注2: generalized gradient approximation (**GGA**):  
要考虑到动能的梯度修正。

注3: orbit-free approximation (无轨道近似) :  
由考虑von Weizsacker梯度修正的总能量，通过变分极小化，可得到电子密度的微分方程。  
可以用于计算几何结构，很快，较好。得不到电子波函数，完全不能用于电子结构的计算。

# 能否把总能量是密度的泛函的概念推广到所有可观测量都是密度的泛函？

- 在Thomas-Fermi 框架下，总能量是电子密度的泛函。外势项与库仑能是显然的，对动能项和交换能项取近似后是电子密度的泛函。关联能还无法考虑。
- 总能量可以写为电子密度的泛函是否是一般的结论？
- 所有物理可观测量是否都是密度的泛函？

## 密度泛函理论！

# Density Functional Theory

Hohenberg and Kohn theorems

Kohn-Sham Method

Kohn-Sham equations

$E_{xc}$ , LDA

Program Organization for SCF-KS equations

Performance of DFT

# 密度泛函理论的发展历史

- Thomas, Fermi, 1927
- Slater, X\_alpha交换能, 1951
- Hohenberg, Kohn, Phys. Rev, B13(1964)864.
- Kohn, Sham, Phys. Rev, A140(1965)1133.
- Tong, Sham, Phys. Rev, 144(1966)1-4. 第一次用于原子问题的求解并与HF比较。

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

## Inhomogeneous Electron Gas\*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France  
and

University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential  $v(\mathbf{r})$ . It is proved that there exists a universal functional of the density,  $F[n(\mathbf{r})]$ , independent of  $v(\mathbf{r})$ , such that the expression  $E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$  has as its minimum value the correct ground-state energy associated with  $v(\mathbf{r})$ . The functional  $F[n(\mathbf{r})]$  is then discussed for two situations: (1)  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ ,  $\tilde{n}/n_0 \ll 1$ , and (2)  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$  with  $\varphi$  arbitrary and  $r_0 \rightarrow \infty$ . In both cases  $F$  can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

15 NOVEMBER 1965

## Self-Consistent Equations Including Exchange and Correlation Effects\*

W. KOHN AND L. J. SHAM

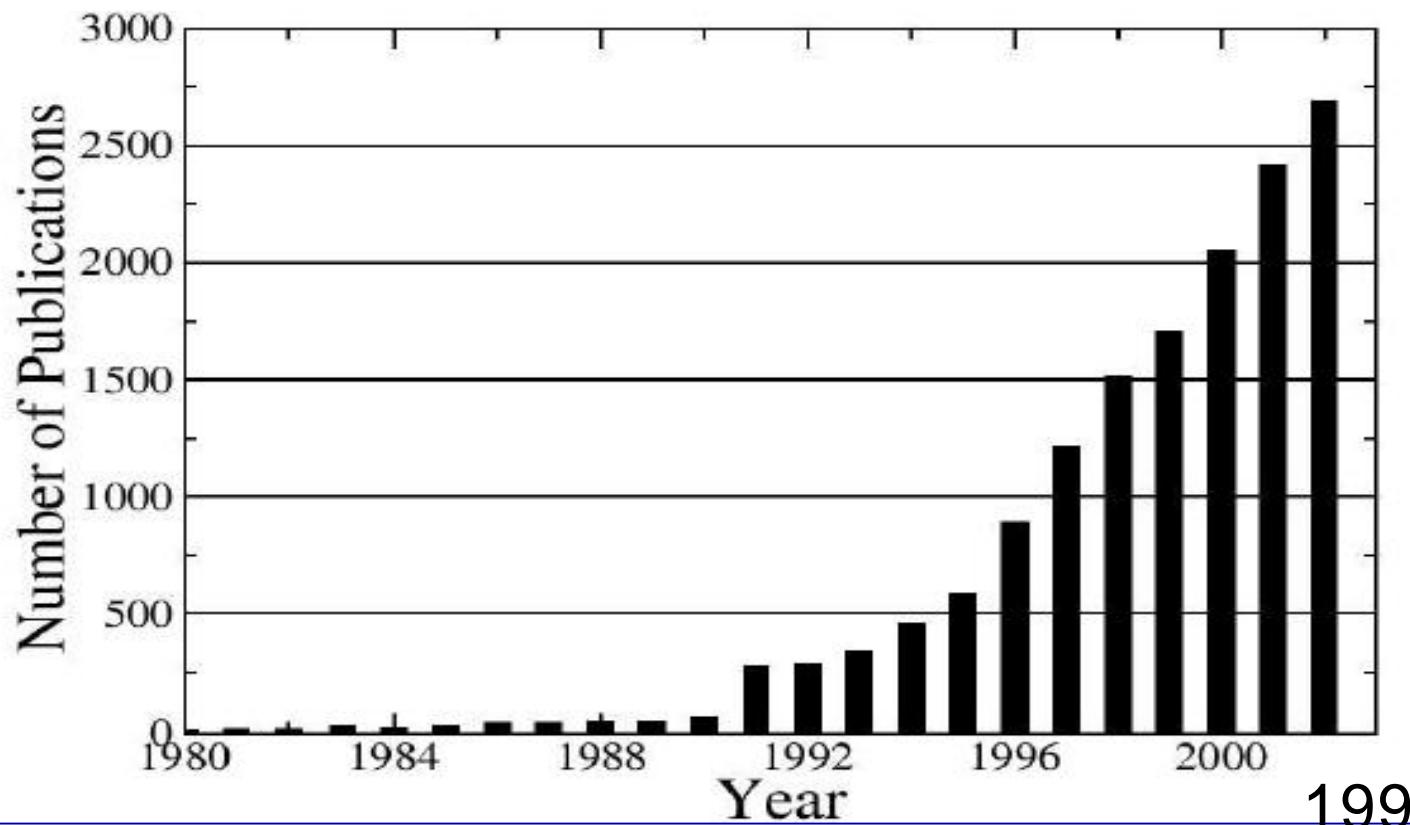
University of California, San Diego, La Jolla, California

(Received 21 June 1965)

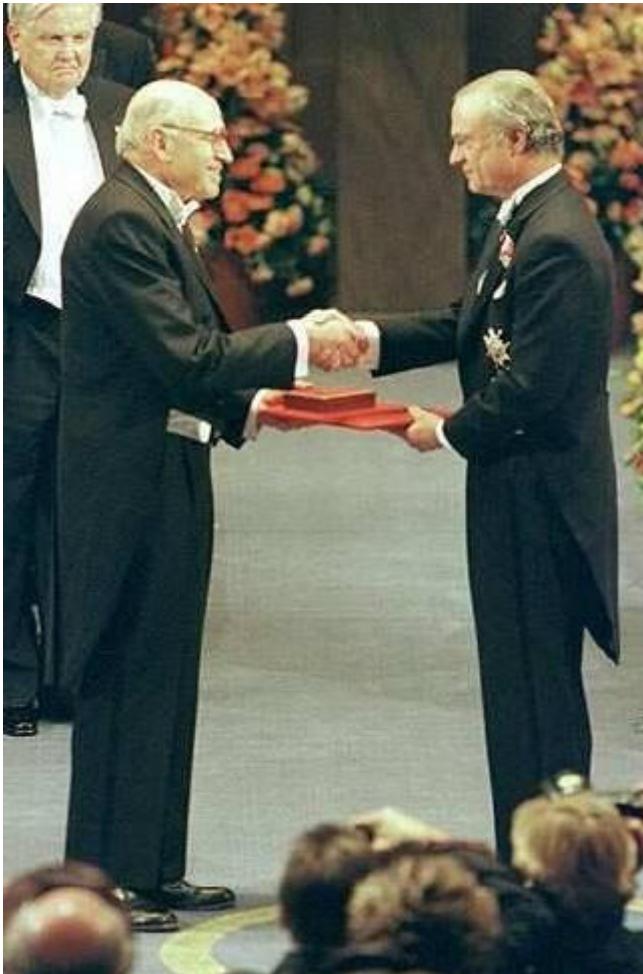
From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of  $\frac{2}{3}$ .) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

# 大规模应用：1990年代（硬件，数值极小化方法，更好的xc泛函）

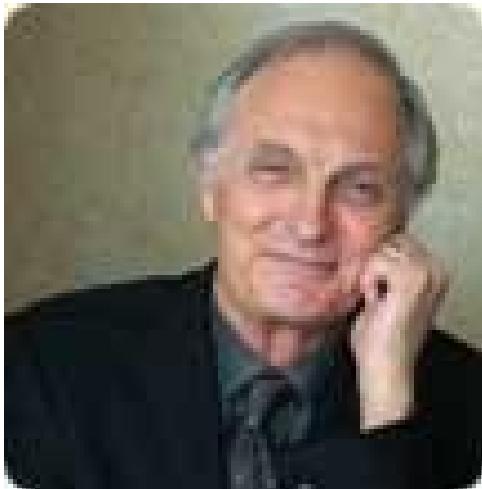
The following figure shows the number of publications where the phrase DFT appears in the title or abstract (taken from the ISI Web of Science).



# Walter Kohn 于1998年获 Nobel 化学奖



200

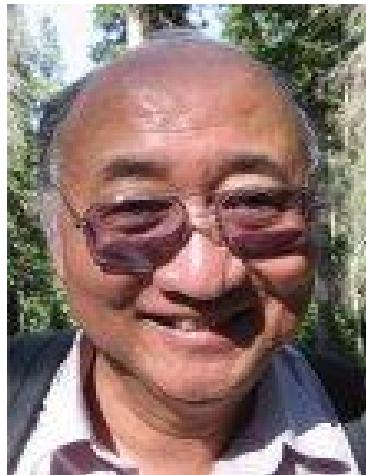


P. Hohenberg

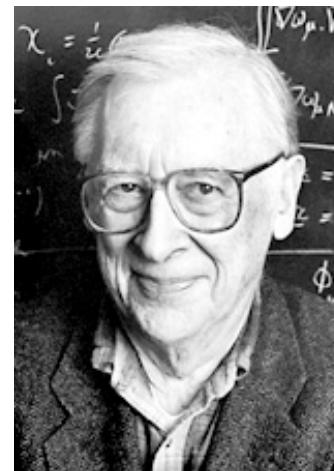


W. Kohn

# DFT的 先驱们



L. J. Sham



J. Pople

# 高斯公司和波普尔先生之间的不愉快

- Gaussian 03 还有John A. Pople 的名字
- 2004年John A. Pople 去世后， Gaussian09 已经把他的名字从软件中去掉了。
- 商业的胜利，科学的悲哀！

# Banned By Gaussian

<http://www.bannedbygaussian.org/>

## Who is banned?

- **By University/Institution:**
  - California Institute of Technology
  - Columbia University
  - University of Florida
  - University of Georgia
  - Georgia Institute of Technology
  - Iowa State University
  - Michigan State University
  - Northwestern University
  - South Carolina State University
  - State University of New York, Buffalo
  - University of California, Berkeley



- **By Individual:**

- Reinhart Ahlrichs (Karlsruhe)
- Rod J. Bartlett (Florida)
- Emily A. Carter (Princeton)
- Richard A. Friesner (Columbia)
- Tom R. Furlani (SUNY-Buffalo)
- Jurgen Gauss (Mainz)
- Peter M.W. Gill (Austr. Nat. Univ)
- William A. Goddard III (Caltech)
- Mark S. Gordon (Iowa State)
- Martin Head-Gordon (UC Berkeley)
- Anna I. Krylov (USC)
- Per Ake Malmqvist (Lund)
- Ajith Perera (Florida)
- Piotr Piecuch (Michigan State)
- **John A. Pople (Northwestern)**
- Mark A. Ratner (Northwestern)
- Vitaly A. Rassolov (South Carolina)
- H.F. Schaefer III (Georgia)
- George C. Schatz (Northwestern Univ.)
- C. David Sherrill (Georgia Tech)
- Michael W. Schmidt (Iowa State)
- John F. Stanton (Texas)
- Theresa L. Windus (PNNL)

# Who is Gaussian, Inc.?

- In the late 1960s and early 1970s, the Pople group at Carnegie-Mellon University began to develop a general purpose computer code, based on the use of gaussian basis functions, in order to enable molecular electronic structure calculations. The initial computer program, called **Gaussian70**, was made freely available to users via the Quantum Chemistry Program Exchange (QCPE). Subsequent versions, through **Gaussian80**, were distributed in the same manner. After 1980, in order to recoup development costs for the increasingly popular program, a small charge was implemented for subsequent versions of the Gaussian code. Professor Pople, the recipient of the **1998 Nobel Prize** in Chemistry, has not been associated with Gaussian, Inc. since **1991**.
- The departure (and subsequent "banning") of Professor Pople from the Gaussian project marked a sad day for science, a day in which commerce trumped science and loyalty.
- The goal of this site is to shed light on some practices of Gaussian, Inc. that can undermine basic scientific ideals.

# What is meant by "Banned By Gaussian"?

- Simply: **YOU CAN NOT USE THE GAUSSIAN PROGRAM!**
- Restricting access to the Gaussian program, a.k.a. "banning", has become **an increasingly common practice at Gaussian, Inc.**
- Banning occurs on different levels. Simple banning may consist of specific research groups at an institution that are prohibited from purchasing and/or using the latest versions of the Gaussian program. An extreme form of banning dictates that no single person at an institution can use any commercial version of Gaussian ever created.
- Take heart if you have been banned ...

It has been said that mimicry is the sincerest form of flattery. **It is also true that having your research group or your university banned by Gaussian is recognition of your outstanding scientific achievements!**

next

# 上一讲回顾

- Hartree-Fock方程，局限性，扩展，求解方法，困难
- 原子的Thomas-Fermi理论
- 密度泛函理论的发展历程简介

# 统计物理复习

- 经典多粒子体系几率分布
  - 哈密顿量, 运动方程, 几率密度
  - Liouville方程
  - 约化几率密度
- 量子多粒子体系密度矩阵
  - 哈密顿量, 运动方程, 密度矩阵, 几率密度
  - Liouville方程
  - 约化密度
- 参考书:
  - 王竹溪, 统计物理学导论, 第一章, 1964, 人民教育出版社
  - 林宗涵, 热力学与统计物理学, 第八章, 2007, 北大
  - Reichl, **Modern Course in Statistical Physics**, Univ. Texas Press, 1980 中译本: 雷克. 统计物理现代教程. 黄畇等译, 赵凯华校. 北大, 1983

# 经典多粒子体系

## 哈密顿量

经典保守体系:  $H(q, p)$ ,

其中  $q = \{q_1, q_2, q_3, \dots, q_N\}$ ,  $p = \{p_1, p_2, p_3, \dots, p_N\}$ .

运动方程: (牛顿定律)

$$\dot{q} = \frac{\partial H}{\partial p}, \dot{p} = -\frac{\partial H}{\partial q}$$

几率密度:  $\rho(q, p; t)$

令  $X = (q, p)$ , 也可写为  $\rho(X; t) = \sum_{\alpha} \delta(X - X_{\alpha})$ .

几率密度在相空间沿任何轨道运动都是常数:  $\frac{d\rho}{dt} \equiv 0$ .  
(几率流是不可压缩的流体)

# Liouville方程:

全微分  $\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^N (\frac{\partial\rho}{\partial q_i} \dot{q}_i + \frac{\partial\rho}{\partial p_i} \dot{p}_i)$

不可压缩  $\frac{d\rho}{dt} = 0,$

得到

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^N (\frac{\partial\rho}{\partial q_i} \dot{q}_i + \frac{\partial\rho}{\partial p_i} \dot{p}_i) = 0.$$

也可用变量 $\mathbf{X}$ 写为连续性方程形式

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^N (\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}) = 0$$

$$\frac{\partial\rho}{\partial t} + \nabla_{\mathbf{X}} \cdot (\rho \dot{\mathbf{X}}) = 0.$$

用运动方程改写Liouville方程

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^N \left[ \frac{\partial \rho}{\partial q_i} \left( \frac{\partial H}{\partial p_i} \right) + \frac{\partial \rho}{\partial p_i} \left( -\frac{\partial H}{\partial q_i} \right) \right] = 0$$

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^N \left[ \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0$$

$$\frac{\partial \rho}{\partial t} + \{ \rho, H \} = 0$$

其中定义了Poisson括号

$$\{ \rho, H \} = \sum_{i=1}^N \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \equiv \hat{\mathcal{H}}\rho.$$

定义Liouville算符  $\hat{\mathcal{L}} = -i\hat{\mathcal{H}}$  有标准的Liouville方程  $i \frac{\partial \rho}{\partial t} = \hat{\mathcal{L}}\rho$ .

与无碰撞项的Boltzmann方程的联系：3D空间  $p_i = m\dot{q}_i$ ,  $F_i = \dot{p}_i = m\ddot{q}_i$ ,

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^N \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0,$$

$$\frac{\partial \rho}{\partial t} + \frac{1}{m} \mathbf{p} \cdot \nabla_{\mathbf{q}} \rho + \mathbf{F} \cdot \nabla_{\mathbf{p}} \rho = 0.$$

# 约化几率密度

几率密度:  $\rho(\mathbf{q}, \mathbf{p}) = \rho(X)$

几率密度满足归一化条件 (在整个空间一定能找到这些粒子)  $\int \rho(\mathbf{X}) d\mathbf{X} = 1.$

定义位形几率密度  $\rho(\mathbf{q}) = \int \rho(\mathbf{q}, \mathbf{p}) d\mathbf{p}$ . 通常  $\rho(\mathbf{q})$  是  $N$  粒子体系的几率密度 (或分布函数), 但最重要的分布函数是单粒子分布函数与二粒子分布函数。

定义单粒子分布函数

$$f_1(q_1) \equiv N \int \cdots \int \rho(q_1, q_2, q_3, \dots, q_N) dq_2 \cdots dq_N$$

系数  $N$  是由单粒子分布函数的全空间积分应该得到总粒子数  $N$ , 即

$$\int f_1(q_1) dq_1 = N$$

但是  $\rho$  是归一化的, 故必须有系数  $N$ .

定义二粒子分布函数（即关联函数）

$$f_2(q_1, q_2) \equiv N(N - 1) \int \cdots \int \rho(q_1, q_2, q_3, \dots, q_N) dq_3 \cdots dq_N.$$

许多物理量都可用这些分布函数来表达。

还可定义 $s$ 粒子分布函数

$$f_s(q_1, \dots, q_s) \equiv \frac{N!}{(N - s)!} \int \cdots \int \rho(q_1, \dots, q_s, \dots, q_N) dq_{s+1} \cdots dq_N.$$

BBGKY级联 (Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy)

在特定情形，可以推出 $s$ 粒子分布函数的运动方程依赖于 $s + 1$ 粒子分布函数，如果要求解则需要截断。由此可以导出流体力学基本方程，**Boltzmann**方程等。

# 量子多粒子体系

## 哈密顿量

正则量子化:  $\hat{H}(\mathbf{q}, \mathbf{p})$ , 其中  $\mathbf{q} = \{q_1, q_2, q_3, \dots, q_N\}$ ,  $\mathbf{p} = \{p_1, p_2, p_3, \dots, p_N\}$ .

## 运动方程

(含时多粒子薛定格方程) :

$$i\hbar \frac{\partial \Phi(q_1, q_2, q_3, \dots, q_N; t)}{\partial t} = \hat{H}(\mathbf{q})\Phi(q_1, q_2, q_3, \dots, q_N; t)$$

## 几率密度:

$$\rho(\mathbf{q}; t) = \Phi^*(\mathbf{q}; t)\Phi(\mathbf{q}; t)$$

$$\rho(q_1, q_2, q_3, \dots, q_N; t) = \Phi^*(q_1, q_2, q_3, \dots, q_N; t)\Phi(q_1, q_2, q_3, \dots, q_N; t)$$

# 多粒子密度矩阵

设体系只有一个态，定义密度矩阵  $\rho(q, q'; t) = \Phi^*(q; t)\Phi(q'; t)$ ,

【纯态，算符形式  $\hat{\rho} = |n\rangle\langle n|$

混合态，算符形式  $\hat{\rho} = \sum_n P_n |n\rangle\langle n|$ ,  $P_n$  混合的几率，满足

$$\sum_n P_n = 1.$$
】

多粒子量子几率密度是多粒子密度矩阵的对角元：

$$\begin{aligned}\rho(\mathbf{q}; t) &= \lim_{q' \rightarrow q} \rho(q, q'; t) = \lim_{q' \rightarrow q} \Phi^*(q; t)\Phi(q'; t) \\ &= \Phi^*(\mathbf{q}; t)\Phi(\mathbf{q}; t)\end{aligned}$$

几率密度在相空间沿任何轨道运动都是常数：  $\frac{d\rho}{dt} \equiv 0$ . (几率流是不可压缩的流体)。

# 多粒子密度矩阵的Liouville方程:

考虑密度矩阵的时间演化

$$\begin{aligned}\frac{d\rho}{dt} &= \frac{\partial\rho(q, q'; t)}{\partial t} + (\dot{\Phi}^*(q; t) \frac{\partial\rho(q, q'; t)}{\partial\Phi^*(q; t)} + \frac{\partial\rho(q, q'; t)}{\partial\Phi(q'; t)} \dot{\Phi}(q'; t)) \\ &= 0\end{aligned}$$

$$\frac{\partial\rho}{\partial t} + (\dot{\Phi}^* \frac{\partial\rho}{\partial\Phi^*} + \frac{\partial\rho}{\partial\Phi} \dot{\Phi}) = 0$$

$$\frac{\partial\rho}{\partial t} + \frac{1}{-i\hbar} [\hat{H}\Phi^*(q; t)]\Phi(q'; t) + \Phi^*(\mathbf{q}; t) \frac{1}{i\hbar} \hat{H}\Phi(q'; t) = 0$$

$$i\hbar \frac{\partial\rho(q, q'; t)}{\partial t} = [\hat{H}(q)\Phi^*(q; t)]\Phi(q'; t) - \Phi^*(\mathbf{q}; t)\hat{H}(q')\Phi(q'; t)$$

$$i\hbar \frac{\partial\rho(q, q'; t)}{\partial t} = \hat{H}(q)\rho(q, q'; t) - \rho(q, q'; t)\hat{H}(q')$$

写为算符形式Liouville方程

$$i\hbar \frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \equiv \hat{\mathcal{L}}\hat{\rho}$$

验证, 设  $\hat{H}(q, q') = \hat{H}(q)\delta(q - q')$ , 有完备集  $\sum_{q''} |q''\rangle\langle q''| = 1$

$$i\hbar \frac{\partial}{\partial t} \langle q|\hat{\rho}|q'\rangle = \langle q|\hat{H}\hat{\rho}|q'\rangle - \langle q|\hat{\rho}\hat{H}|q'\rangle$$

$$i\hbar \frac{\partial}{\partial t} \langle q|\hat{\rho}|q'\rangle = \sum_{q''} \langle q|\hat{H}|q''\rangle\langle q''|\hat{\rho}|q'\rangle - \sum_{q''} \langle q|\hat{\rho}|q''\rangle\langle q''|\hat{H}|q'\rangle$$

$$i\hbar \frac{\partial \rho(q, q')}{\partial t} = \sum_{q''} \hat{H}(q, q'')\rho(q'', q') - \sum_{q''} \rho(q, q'')\hat{H}(q'', q')$$

$$= \hat{H}(q)\rho(q, q') - \rho(q, q')\hat{H}(q')$$

注意该式与算符的运动方程差一个符号(算符运动方程  $i\hbar \frac{\partial \hat{A}}{\partial t} = [\hat{A}, \hat{H}]$ )。

# 约化密度

定义单粒子分布函数即密度

$$f_1(q_1) \equiv N \int \cdots \int \rho(q_1, q_2, q_3, \dots, q_N) dq_2 \cdots dq_N$$

系数N是由单粒子分布函数的全空间积分应该得到总粒子数N,即

$$\int f_1(q_1) dq_1 = N$$

但是 $\rho$ 是归一化的，故必须有系数N.

定义二粒子分布函数（即关联函数）

$$f_2(q_1, q_2) \equiv N(N - 1) \int \cdots \int \rho(q_1, q_2, q_3, \dots, q_N) dq_3 \cdots dq_N.$$

许多物理量都可用这些分布函数来表达。

还可定义s粒子分布函数

$$f_s(q_1, \dots, q_s) \equiv \frac{N!}{(N - s)!} \int \cdots \int \rho(q_1, \dots, q_s, \dots, q_N) dq_{s+1} \cdots dq_N.$$

同样有量子力学的BBGKY方程。

# 平均场下單粒子密度公式

单粒子密度的定义为

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

其中波函数是真正的包含关联的多体波函数。

在平均场近似下，波函数是SLATER 行列式，

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \det |\phi_{i_1}(\mathbf{r}_1) \phi_{i_2}(\mathbf{r}_2) \cdots \phi_{i_N}(\mathbf{r}_N)|$$

此时的单粒子密度变为

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2.$$

在前面的课件中已经用到了此公式。

注意比较平均场近似的密度与没有近似的密度的巨大差别！

证明：考虑两粒子情形， 波函数为

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) \\ \phi_1(r_2) & \phi_2(r_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)),$$

波函数的模平方为

$$\Psi(\mathbf{r}_1, \mathbf{r}_2)\Psi^*(\mathbf{r}'_1, \mathbf{r}'_2) = \frac{1}{2} (\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2))(\phi_1^*(r'_1)\phi_2^*(r'_2) - \phi_2^*(r'_1)\phi_1^*(r'_2))$$

计算

$$\begin{aligned} \rho(r_1) &= N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \\ &= 2 \int \Psi(\mathbf{r}_1, \mathbf{r}_2)\Psi^*(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \phi_1(r_1)\phi_1^*(r_1) + \phi_2(r_1)\phi_2^*(r_1). \end{aligned}$$

注意求和包含自旋态指标。

一般有

$$\rho(r) = \sum_i \phi_i(r)\phi_i^*(r).$$

更一般形式:  $\rho(r) = \sum_i f_i |\phi_i(r)|^2$ ,  $f_i$  为占据几率

# 7a. 有关DFT的两个定理

## Hohenberg-Kohn Theorems

- I: 所有可观察量都是密度的泛函。
- II: 总能量对密度的变分极小就是总能量对波函数的变分极小，是体系的基态。

# DFT中定理I的证明思路

体系可观察量由H确定:  $H\Psi = E\Psi, \bar{O} = \langle \Psi | \hat{O} | \Psi \rangle$

H由V<sub>ext</sub>完全确定:  $H = T_e + U_{ee} + V_{ext}$  故体系总能量由外势确定

V<sub>ext</sub>由密度确定(密度由V确定):  $\rho \longleftrightarrow V_{ext}$



体系可观察量由密度确定(包括总能量):

$$E[\rho] = T_e[\rho] + U_{ee}[\rho] + V_{ext}[\rho]$$

但是: T<sub>e</sub> 和 U<sub>ee</sub> 与密度的泛函形式未知!

# DFT中定理II的证明思路

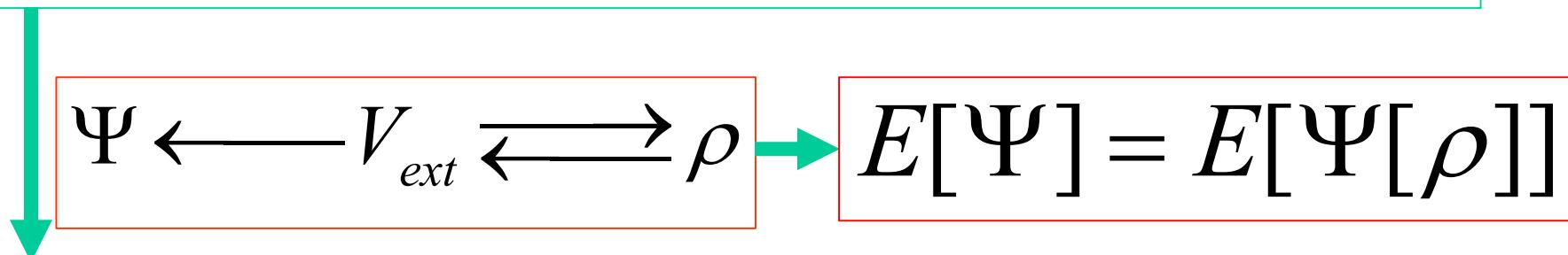
总能量可写为密度的泛函：

$$E[\rho] = T_e[\rho] + U_{ee}[\rho] + V_{ext}[\rho]$$

也可以写为波函数的泛函：

$$E[\Psi] = \langle \Psi | \hat{T}_e + \hat{U}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

在粒子数不变条件下由变分原理：  $E[\Psi]$  存在极小，为基态



在粒子数不变条件下由变分原理：  $E[\rho]$  存在极小，为基态

# Hohenberg-Kohn Theorems

## Hohenberg and Kohn theorems

They proved the following:

- I. Every observable of a stationary quantum mechanical system (including energy), can be calculated, in principle exactly, from the ground-state density alone, i.e., every observable can be written as a functional of the ground-state density.
- II. The ground state density can be calculated, in principle exactly, using the variational method involving only density.

最初的定理适合于时间无关的体系的基态。现在已经扩展到激发态、时间相关和多分量的情形。我们还是只考虑与时间无关的体系的基态问题。

在绝热近似框架下，电子系统的基态是由核的位置决定的。在电子的哈密顿量  $\hat{H}_{el}$  里面，电子的动能项( $\hat{T}_e$ )和电子-电子互作用项( $\hat{U}_{ee}$ )不断调节使得与(来自原子核的)外势  $\hat{V}_{ext}$  相适应，使得体系的总能量为最低。  
**一旦外势  $V_{ext}$  确定了，其它的量都确定了**，从而波函数，包括电子密度也确定了。这实际上是说当给定原子种类和原子的空间位置后，体系的特性是确定的。可见外势  $\hat{V}_{ext}$  是唯一可变的量，其它的量都间接依赖于它。

$V_{ext}$  决定了密度

Hohenberg - Kohn 提出了一个有趣的逻辑上的反问题：外势  $\hat{V}_{ext}$  是否可以由电子的密度  $\rho(r)$  唯一确定？如果我们知道了基态的电子密度  $\rho(\mathbf{r})$ ，原理上（可能不容易），我们能否找到原子核在什么地方及是什么样的原子核？是否存在一个从  $\rho(\mathbf{r})$  到  $\hat{V}_{ext}$  的精确映射？对这个问题的回答是肯定的！

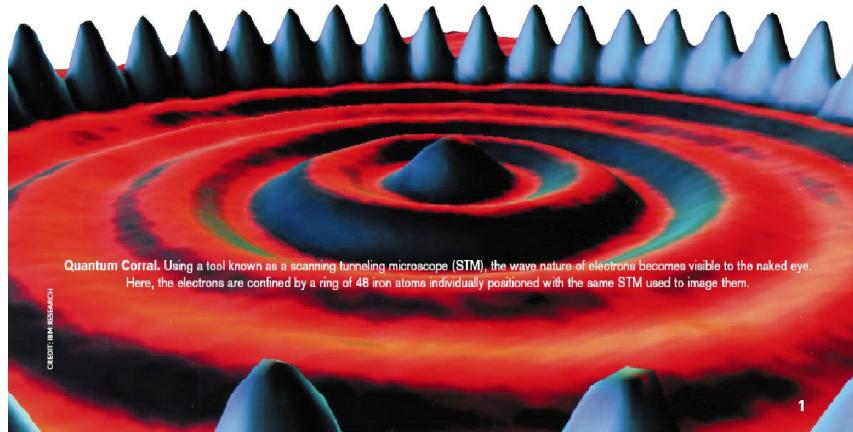
密 度  $\rho$  是 否 决 定 了  $V_{ext}$  ?

实际上该映射只能精确到一个常数（与势的零点选取有关）。都知道对 Schrödinger 方程， $\hat{H}_{el}$  和  $\hat{H}_{el} + const$  给出精确相同的本征函数(Schrödinger 方程是线性的)，能量或本征值会有一个 *const* 的移动。注意所有的能量都只能精确到一个常数（参考能量）。这样，电子密度的知识提供了系统的全部信息。形式上，如果我们知道了电子密度，我们就知道了所有该知道的东西。

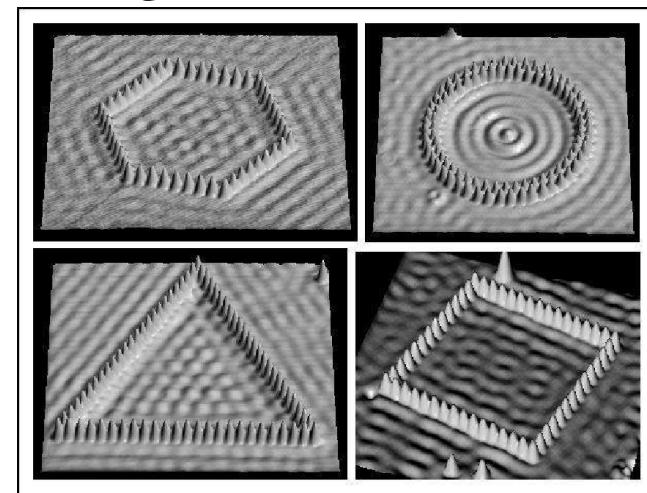
因为  $\rho(\mathbf{r})$  决定了电子的数目  $N: N = \int \rho(\mathbf{r}) d\mathbf{r}$ 。密度  $\rho$  还决定了外势  $\hat{V}_{ext}$ ，可见体系的密度和体系的波函数  $\Psi$  一样都可用于描述体系的状态。

# 现代STM实验给予的物理直觉：

48个铁原子的量子围栏



Quantum Corral



由STM可看到电子密度的分布，从而推断出原子核的位置，而原子核位置的确定可完全确定原子核与电子的相互作用势即外势，即实验上电子密度完全确定外势！可是1964年还没发明STM。

# Hohenberg Kohn定理一的证明

Hohenberg-Kohn利用反正法证明了定理一

- 设有一个精确的基态密度  $\rho(\mathbf{r})$ ,
- 设基态是非简并的(一个基态只有一个波函数 $\Psi$ ,可以扩展到简并情形).
- 设对一个密度  $\rho(\mathbf{r})$  有两个可能的外势:  $\hat{V}_{ext}$  和  $\hat{V}'_{ext}$ , 则有两个明显不同的哈密顿量:  $\hat{H}_{el}$  和  $\hat{H}'_{el}$ 。则对基态会有两个不同的波函数:  $\Psi$  和  $\Psi'$ 。对应的基态能量为:  $E_0 = \langle \Psi | H | \Psi \rangle$  和  $E'_0 = \langle \Psi' | H' | \Psi' \rangle$ 。

如果得到矛盾的结果, 则说明前提假设不正确。

# Hohenberg Kohn定理一的证明

反证法，设有一个密度  $\rho$  但对应有两个不同的外势  $V_{ext}, V'_{ext}$ 。则有两个不同的哈密顿量

$$H = H_0 + V_{ext},$$

$$H' = H_0 + V'_{ext},$$

从而有两个不同的精确解

$$H\Psi = E_0\Psi$$

$$H'\Psi' = E'_0\Psi'.$$

注意到 $\Psi$ 是 $H$ 的基态， $\Psi'$ 不是 $H$ 的基态，由于基态没有简并，且由基态是最低的能态，必有不等式

$$E_0 = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle$$

$$\begin{aligned} \langle \Psi' | H | \Psi' \rangle &= \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | (V_{ext} - V'_{ext}) | \Psi' \rangle \\ &= E'_0 + \langle \Psi' | (V_{ext} - V'_{ext}) | \Psi' \rangle \end{aligned}$$

$$E_0 < E'_0 + \langle \Psi' | (V_{ext} - V'_{ext}) | \Psi' \rangle$$

同理， $\Psi'$ 是 $H'$ 的基态， $\Psi$ 不是 $H'$ 的基态，由于基态没有简并，且由基态是最低的能态，必有不等式

$$E'_0 = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle$$

$$\begin{aligned} \langle \Psi | H' | \Psi \rangle &= \langle \Psi | H | \Psi \rangle + \langle \Psi | (V'_{ext} - V_{ext}) | \Psi \rangle \\ &= E_0 + \langle \Psi | (V'_{ext} - V_{ext}) | \Psi \rangle \end{aligned}$$

$$E'_0 < E_0 + \langle \Psi | (V'_{ext} - V_{ext}) | \Psi \rangle$$

两式相加有

$$\begin{aligned} E_0 + E'_0 &< E'_0 + E_0 \\ &+ \langle \Psi' | (V_{ext} - V'_{ext}) | \Psi' \rangle \\ &+ \langle \Psi | (V'_{ext} - V_{ext}) | \Psi \rangle \end{aligned}$$

可证最后两项抵消，故有矛盾的关系式

$$E_0 + E'_0 < E'_0 + E_0$$

即假设一个密度对应有两个不同的外势是不可能的。

证明：因为外势可写为  $V_{ext}(r_1, r_2, \dots, r_N) = \sum_i^N v_{ext}(r_i)$ , 有一般表达式

$$\langle \Psi | V_{ext} | \Psi \rangle = \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}, \quad \langle \Psi' | V'_{ext} | \Psi' \rangle = \int \rho(\mathbf{r}) v'_{ext}(\mathbf{r}) d\mathbf{r},$$

由于假定密度是唯一的（外势不唯一，波函数也不唯一），还有

$$\langle \Psi' | V_{ext} | \Psi' \rangle = \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}, \quad \langle \Psi' | V'_{ext} | \Psi' \rangle = \int \rho(\mathbf{r}) v'_{ext}(\mathbf{r}) d\mathbf{r},$$

从而

$$\langle \Psi' | (V_{ext} - V'_{ext}) | \Psi' \rangle + \langle \Psi | (V'_{ext} - V_{ext}) | \Psi \rangle$$

$$= \int \rho(\mathbf{r}) (v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r})) d\mathbf{r} + \int \rho(\mathbf{r}) (v'_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r})) d\mathbf{r}$$

$$= 0$$



# 多体单粒子密度

## 多电子体系的单粒子密度

$N$ 电子体系的波函数为 $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , 几率密度为 $|\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$ 。若不考虑自旋, 可定义单粒子密度

$$\begin{aligned}\rho(\mathbf{r}) &= N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \\ &= N \int \cdots \int |\Psi(\mathbf{r}_2, \cdots \mathbf{r}, \cdots \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N\end{aligned}$$

可以把任何一个电子坐标 $\mathbf{r}$ 都移到第一位, 反对称导致的符号不会出现。

$N$ 电子体系的外势为

$$V_{ext}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N v_{ext}(\mathbf{r}_i).$$

# 外势的平均值公式

## 计算外势的平均值

$$\begin{aligned}\langle \Psi | V_{ext} | \Psi \rangle &= \langle \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) | V_{ext}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) | \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rangle \\&= \sum_{i=1}^N \int \cdots \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 v_{ext}(\mathbf{r}_i) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \\&= \frac{1}{N} \int \rho(\mathbf{r}_1) v_{ext}(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{N} \int \rho(\mathbf{r}_2) v_{ext}(\mathbf{r}_2) d\mathbf{r}_2 + \cdots \\&\quad + \frac{1}{N} \int \rho(\mathbf{r}_N) v_{ext}(\mathbf{r}_N) d\mathbf{r}_N \\&= \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}\end{aligned}$$

可见在证明此定理时没有引入任何近似

# 总能量可写为密度的泛函

从现在起,我们知道  $\rho(\mathbf{r})$  决定了  $N$  和  $\hat{V}_{ext}$ , 这也决定了所有的基态特性, 包括  $T_e$  和  $U_{ee}$ , 即, 总的基态能量中的每一项都是密度的泛函:

$$\begin{aligned} E[\rho] &= T_e[\rho] + V_{ext}[\rho] + U_{ee}[\rho] \\ &\equiv V_{ext}[\rho] + F_{HK}[\rho], \end{aligned}$$

其中

$$V_{ext}[\rho] = \langle \Psi | \hat{V}_{ext} | \Psi \rangle = \int \rho(\mathbf{r}) \hat{v}_{ext}(\mathbf{r}) d\mathbf{r}$$

是唯一精确已知的项

真正的动能是

$$T_e[\rho] = \langle \Psi | \sum_{i=1} \left( -\frac{1}{2} \nabla_i^2 \right) | \Psi \rangle.$$

电子-电子相互作用能是

$$U_{ee} = \langle \Psi | \sum_{i < j} \left( \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) | \Psi \rangle.$$

(通常  $\Psi$  不是 Slater 行列式)。

这两项作为密度的泛函的精确形式是未知的！

# Thomas Fermi与DFT的本质差别

- 总能量都是密度的泛函，但是意义完全不同

$$\begin{aligned} \langle H \rangle_{TF} &= C_F \int \rho^{5/3}(r_1) dr_1 + \int v(r_1) \rho(r_1) dr_1 \\ &+ \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - C_x \int \rho^{4/3}(\mathbf{r}_1) d\mathbf{r}_1. \end{aligned}$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2.$$

TF近似

DFT精确

$$E[\rho] = T_e[\rho] + V_{ext}[\rho] + U_{ee}[\rho]$$

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

## 定理二的证明

第二HK定理提供了基于电子密度  $\rho(\mathbf{r})$  的变分原理。对一个试探密度  $\tilde{\rho}(\mathbf{r})$  满足  $\tilde{\rho}(\mathbf{r}) \geq 0$  及  $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$ , 则有

$$E_0 \leq E[\tilde{\rho}]$$

总能量存在一个极小!

其中  $E[\tilde{\rho}]$  是能量泛函。换言之, 如果有密度给出了正确的总电子数目  $N$ , 从这个密度计算的总能量不可能低于基态的真正能量。

对于这个定理的必要条件，就是密度的  
 $N$ 可表示性。

所谓的 $N$ 可表示性很容易通过试探密度  
 $\tilde{\rho}$ 的简单标度来满足密度的和是总电子数 $N$ 。  
如果把密度 $\rho(\mathbf{r})$ 映射为波函数，则 $N$ 可表示性  
是自动满足的。

肯定的说，试探密度的 $V_{ext}$ 可表示性不是  
很容易。 Levy和Lieb已经说明了，存在一些  
合理的试探密度，但他们不是任何外势 $V_{ext}$ 的  
基态密度，这样的密度不对应任何基态，变分  
绝不会收敛于任何真的基态密度。

Mel Levy , Phys. Rev. A 26, 1200 - 1208 (1982):Electron densities in  
search of Hamiltonians;

如果假定试探密度既是  $N$  也是  $\nu$  可表示的，可以证明密度的变分原理。

每一个试探密度  $\tilde{\rho}$  定义了一个  $\hat{H}_{el}$ 。从这个哈密顿量可得到对应的波函数  $\tilde{\Psi}$ 。遵照传统的变分原理，这个  $\tilde{\Psi}$  将不是真实系统  $\hat{H}_{el}$  的基态：

$$\tilde{\rho} \rightarrow \hat{H}_{el} \rightarrow \tilde{\Psi};$$

$$\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = E[\tilde{\rho}] \geq E[\rho_0] \equiv E_0$$

其中  $\rho_0(\mathbf{r})$  是真实体系的基态密度。

由于不等式的存在，总能量对密度变分也可以得到体系的基态。

另一个证明的写法，本质一样：

设有另一个密度  $\tilde{\rho}(r)$ , 粒子数与及态密度  $\rho_0(r)$  相同为  $N$ ，则

$$\begin{aligned} E[\tilde{\rho}(r)] &= \int v(r) \tilde{\rho}(r) dr + F[\tilde{\rho}(r)] \\ &= (\tilde{\Psi}, \hat{V} \tilde{\Psi}) + (\tilde{\Psi}, (\hat{T} + \hat{U}) \tilde{\Psi}) \\ &> (\Psi, \hat{V} \Psi) + (\Psi, (\hat{T} + \hat{U}) \Psi) = E[\rho_0(r)] \\ \therefore E[\rho_0(r)] &< E[\tilde{\rho}(r)] \end{aligned}$$

具体计算要利用变分原理，使系统能量达到最低。从而求出体系的真正电荷密度，并计算体系的各种基态性质。例如，能带结构，态密度，晶格常数，弹性模量等。

另一个证明方法：

已知：

在粒子数不变条件下由变分原理：  $E[\Psi]$  存在极小，为基态

又波函数依赖于密度  $\Psi \longleftrightarrow V_{ext} \longleftrightarrow \rho$   
或写为  $\Psi[\rho]$

则有  $E[\Psi] = E[\Psi[\rho]]$

则变分相等  $\delta E[\Psi] = \delta E[\Psi[\rho]] = 0$

对波函数的变分等同于对密度的变分

即在粒子数不变条件下由变分原理：  $E[\rho]$  存在极小，为基态

# 总能量对密度的变分

能量泛函的极小化条件:  $\delta E[\rho(\mathbf{r})] = 0$

必须附加限制条件密度的  $N$  可表示性。需要引入仪的待定的 Lagrange 乘子  $\mu$ 。其中  $N$  可表示性限制可写为:

$$\mu \left( \int \rho(\mathbf{r}) d\mathbf{r} - N \right) = 0.$$

我们可以极小化泛函:

$$E[\rho(\mathbf{r})] - \mu \left[ \int \rho(\mathbf{r}) d\mathbf{r} - N \right].$$

现在，我们寻求这个表达式的极小条件，即变分为零：

$$\delta \left\{ E[\rho(\mathbf{r})] - \mu \left[ \int \rho(\mathbf{r}) d\mathbf{r} - N \right] \right\} = 0$$

使用泛函的微分的定义：

$$F[f + \delta f] - F[f] = \delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx$$

及微分和积分符号可换的事实，我们得到了

$$\int \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r} - \mu \int \delta \rho(\mathbf{r}) d\mathbf{r} = 0.$$

可改写为：

$$\int \left\{ \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} - \mu \right\} \delta \rho(\mathbf{r}) d\mathbf{r} = 0$$

利用外势，可得到：

$$\mu = \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \hat{v}_{ext}(\mathbf{r}) + \frac{\delta F_{HK}(\rho(\mathbf{r}))}{\delta \rho(\mathbf{r})}$$

密度泛函给出了化学势 $\mu$ 的坚实定义，这将导致几个重要的一般结论，参见文献。

# 总能量对密度的变分的例子

## Thomas-Fermi总能量对密度的变分

Thomas-Fermi 总能量:

$$\begin{aligned} E_{TF} = & C_F \int \rho^{5/3}(r) dr + \int v(r)\rho(r)dr \\ & + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 r_2. \end{aligned}$$

对密度的限制条件为

$$N = \int \rho(\mathbf{r}) d\mathbf{r}.$$

定义变分问题:

$$\delta \{E_{TF}[\rho] - \mu(\int \rho(\mathbf{r}) d\mathbf{r} - N)\} = 0.$$

注意变分的定义

$$\begin{aligned}\delta F &= \int \frac{\delta F}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r}, \\ \delta \left\{ \int \rho(\mathbf{r}) d\mathbf{r} \right\} &= \int \delta \rho(\mathbf{r}) d\mathbf{r}, \\ \delta(\mu N) &= 0,\end{aligned}$$

有

$$\begin{aligned}&\int \frac{\delta E_{TF}[\rho]}{\delta \rho} \delta \rho d\mathbf{r} - \mu \int \delta \rho(\mathbf{r}) d\mathbf{r} = 0 \\ \mu &= \frac{\delta E_{TF}}{\delta \rho} \\ &= \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &\equiv \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r}).\end{aligned}$$

注意已定义了核及电子的静电势为

$$\phi(\mathbf{r}) = -v(\mathbf{r}) - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

边界条件：对电中性体系，

$$\lim_{\mathbf{r} \rightarrow \infty} \phi(\mathbf{r}) = 0, \text{ 无穷远处静电势为零}$$

$$\lim_{\mathbf{r} \rightarrow \infty} \rho(\mathbf{r}) = 0, \text{ 无穷远处没有电荷分布}$$

则拉格朗日乘子  $\mu$  对所有  $\mathbf{r}$  成立的值恒为零，可得到方程

$$\mu = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r}) = 0.$$

可通过联立求解方程组（自洽迭代求解）

$$\left\{ \begin{array}{l} \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r}) = 0, \\ \phi(\mathbf{r}) = -v(\mathbf{r}) - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \end{array} \right.$$

得到体系的密度，从而由总能量是密度的泛函得到体系的总能量。

注意，通过对密度的变分不能得到体系的波函数和能级。|

# 有关DFT的两个定理

## Hohenberg-Kohn Theorems

- I: 所有可观察量都是密度的泛函。
- II: 总能量对密度的变分极小就是总能量对波函数的变分极小，是体系的基态。

# DFT中定理I的证明思路

体系可观察量由H确定:  $H\Psi = E\Psi, \bar{O} = \langle \Psi | \hat{O} | \Psi \rangle$

H由 $V_{ext}$ 完全确定:  $H = T_e + U_{ee} + V_{ext}$

$V_{ext}$ 由密度确定(密度由V确定):  $\rho \rightleftharpoons V_{ext}$



体系可观察量由密度确定(包括总能量):

$$E[\rho] = T_e[\rho] + U_{ee}[\rho] + V_{ext}[\rho]$$

但是: **Te 和Uee 与密度的泛函形式未知!**

# DFT中定理II的证明思路

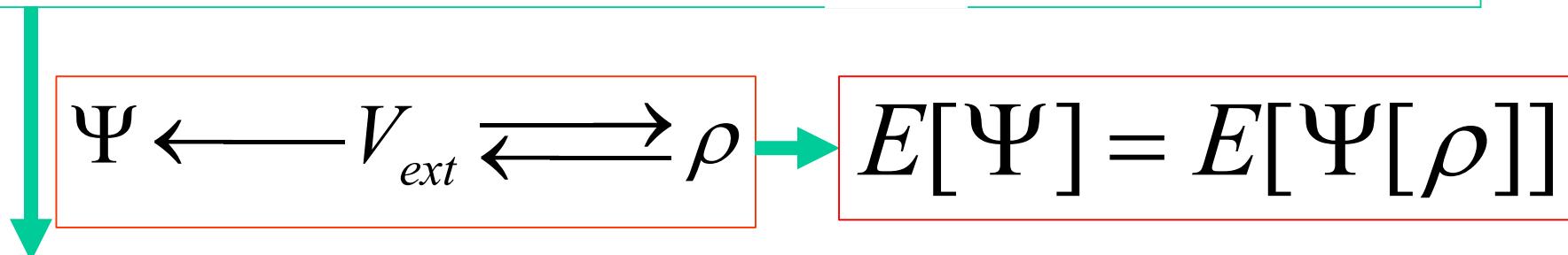
总能量可写为密度的泛函：

$$E[\rho] = T_e[\rho] + U_{ee}[\rho] + V_{ext}[\rho]$$

也可以写为波函数的泛函：

$$E[\Psi] = \langle \Psi | \hat{T}_e + \hat{U}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

在粒子数不变条件下由变分原理：  $E[\Psi]$  存在极小，为基态



在粒子数不变条件下由变分原理：  $E[\rho]$  存在极小，为基态

# DFT的两个注释

- DFT理论是精确的：可观察量一定是电子密度的泛函是精确证明了的，没有任何近似；
- 精确的DFT是无法实际使用的：动能项及电子-电子互作用项没有已知的精确的密度泛函表达式。只有外势项的密度泛函表达式精确已知。

# Walter Kohn 简历：

- 沃尔特·科恩于1923年3月9日出生于奥地利名城维也纳的一个犹太家庭，早年其父母均在纳粹集中营中被杀害，16岁的科恩从纳粹统治的奥地利逃亡加拿大，并入伍参加了第二次世界大战；
- 战后的科恩进入加拿大的多伦多大学深造，并于1945年获数学和物理学学士学位；
- 1946年再次于多伦多大学获应用数学硕士学位；
- 1948年在哈佛大学获物理学博士学位

Walter Kohn 没有学过任何化学课程（视频）

## 7b. Kohn-Sham Method

### Kohn-Sham Method

动能和密度的关系表达式没有精确的表达式。即使那些在原来的托马斯-费米理论基础上做出了很大改进的表达式，对于原子分子问题仍然非常粗糙。然而，另一方面，动能用波函数计算非常容易非常精确，当然前提是知道波函数。基于这个原因，Kohn和Sham在1965年提出了一个天才的把波函数与密度近似结合在一起的方法。

动能用密度不能准确表达,但用波函数算动能很准确。

# Thomas-Fermi动能计算的不准确性

考虑边长为  $L$  三维方盒子中的自由电子问题, 能量为

$$E = \frac{\hbar^2}{2m} \left[ \left( \frac{n_x}{L} \right)^2 + \left( \frac{n_y}{L} \right)^2 + \left( \frac{n_z}{L} \right)^2 \right],$$

其基态能量为基态动能(取  $(n_x, n_y, n_z) = (1, 0, 0)$ )

$$E_0 = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 = \frac{1}{2} \left( \frac{\pi}{L} \right)^2 \text{ a.u.}$$

这等于用波函数来计算的基态动能。

另一方面, 利用 Thomas-Fermi 理论, 动能项可写为

$$E_{TF} = 2.871 \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \text{ a.u.}$$

另一方面，利用Thomas-Fermi理论，动能项可写为

$$E_{TF} = 2.871 \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \text{ a.u.}$$

为使计算简化，近似取盒子内的波函数为

$$\varphi = \frac{1}{\sqrt{L^3}} \exp(i \frac{n_x \pi}{L} x) \exp(i \frac{n_y \pi}{L} y) \exp(i \frac{n_z \pi}{L} z)$$

基态波函数为

$$\varphi_0 = \frac{1}{\sqrt{L^3}} \exp(i \frac{\pi}{L} x)$$

电子密度可以用波函数来表示

$$\rho \equiv |\varphi_0|^2 = \frac{1}{L^3}$$

则

$$E_{TF} = 2.871 \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} = \frac{2.871}{L^5} \int d\mathbf{r} = \frac{2.871}{L^2}$$

能量差为

$$\begin{aligned} E_0 - E_{TF} &= \frac{1}{2} \left( \frac{\pi}{L} \right)^2 - \frac{2.871}{L^2} \\ &\approx \frac{2.2}{L^2} \end{aligned}$$

可见动能项的密度泛函形式未知会导致较大的动能项误差！

可见用波函数最准确,但精确波函数未知,  
该如何办呢?

Kohn-Sham方法

## 7c. 总能量

我们把总能量泛函写为如下的形式

$$\begin{aligned} E[\rho] &= T_e[\rho] + V_{ext}[\rho] + U_{ee}[\rho] \\ &\equiv V_{ext}[\rho] + F_{HK}[\rho], \end{aligned}$$

其中

$$V_{ext}[\rho] = \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

且  $\hat{v}_{ext}(\mathbf{r})$  是外势, 即, 核与电子相互作用部分:

$$\hat{v}_{ext}(\mathbf{r}) = \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|}.$$

如果使用类似于Hartree-Fock的试探波函数，近似动能为

$$T_0[\rho] = \sum_{i=1} \langle \phi_i | (-\frac{1}{2} \nabla^2) | \phi_i \rangle.$$

$$T_e[\rho] - T_0[\rho] = ?$$

$$E_{cl}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}'$$

(一些地方也称为  $J[\rho]$ ).

$$U_{ee}[\rho] - E_{cl}[\rho] = ?$$

The true kinetic energy is

$$T_e[\rho] = \langle \Psi | \sum_{i=1} \left( -\frac{1}{2} \nabla_i^2 \right) | \Psi \rangle.$$

$\Psi$  is not a Slater determinant

the approximate kinetic energy is

$$T_0[\rho] = \sum_{i=1} \langle \phi_i | \left( -\frac{1}{2} \nabla^2 \right) | \phi_i \rangle.$$

$$T_e[\rho] - T_0[\rho] = ?$$

The electron-electron interaction energy is

$$U_{ee} = \langle \Psi | \sum_{i < j} \left( \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) | \Psi \rangle.$$

$\Psi$  is not a Slater determinant

$$E_{cl}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}d\mathbf{r}'$$

$$U_{ee}[\rho] - E_{cl}[\rho] = ?$$

注意：密度表达式有区别了

定义

$$\begin{aligned} F_{HK}[\rho] &= T_e[\rho] + U_{ee}[\rho] \\ &\equiv T_0[\rho] + E_{cl}[\rho] + E_{xc}[\rho], \end{aligned}$$

其中

$$E_{xc}[\rho] \equiv T_e[\rho] - T_0[\rho] + U_{ee}[\rho] - E_{cl}[\rho].$$

泛函  $E_{xc}[\rho]$ , 称为交换关联能, 由这个方程本身定义(不能精确表达的部分)。

其中  $T_0[\rho]$  和  $T_e[\rho]$  分别是非相互作用电子体系的动能和有相互作用电子体系的动能。而  $E_{cl}[\rho]$  包含了明确的电子自相互作用能。

这种表达法是否合理?

革命性的一步, 对总能量贡献大的部分可较精确算出!  
263

# Kohn-Sham *Ansatz*(猜想、假说)

- Kohn-Sham辅助体系：  
一个“非相互作用”电子”体系(平均场意义)
- 假定“非相互作用”电子”体系与相互作用电子体系有相同的基态电子密度。
- 把原来的相互作用粒子问题换为容易求解的近似等价的非相互作用问题。

交换关联能  $E_{xc}[\rho]$  包含了总能量表达式前几项不能精确表达的部分，包含了：

- 电子交换能  $K_{ij}$
- 电子关联能
- 电子动能的不准确部分 ( $T_0[\rho]$  不同于真实动能  $T_e[\rho]$ )
- 库伦势导致的自相互作用修正(在HF中,仅当  $K_{ii} = J_{ii}$ , 自相互作用抵消)。

# 密度泛函：多电子问题化为单电子问题

电子总能量是电子密度的泛函：

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

Kohn-Sham方法：

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

$$\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho]$$

---

交换关联能包含：

1. 动能不精确:  $T_e[\rho] \neq T_0[\rho]$

2. 交换能和自相互作用纠正:  $U_{ee} = E_{cl} + \dots$

3. 关联能:  $\Psi(\vec{r}_1, \dots, \vec{r}_n) \neq \prod_P \phi_{p_1}(\vec{r}_1) \dots \phi_{p_n}(\vec{r}_n)$

# 总能量对密度的变分计算

实际上，如果精确知道  $E_{xc}[\rho]$ ，则 Kohn-Sham 泛函是精确的。然而，所有困难的事都集中到了计算关联能  $E_{xc}[\rho]$  上。假如我们对能量泛函知道的足够好，可以利用变分原理得到：

$$\begin{aligned}\mu &= \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T_0[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + \hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})},\end{aligned}$$

其中  $\hat{U}_{cl}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$ .

可仿照 Thomas-Fermi 情形求出总能量极小。

# 总能量的变分

$$\begin{aligned}\delta E[\rho(\mathbf{r})] &= \delta T_0 + \delta V_{ext} + \delta E_{cl} + \delta E_{xc} \\ &= \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{V}_{ext} + \hat{U}_{cl} + \hat{V}_{xc} \right\} \delta \rho d\mathbf{r} \\ &\equiv \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{V}_{eff} \right\} \delta \rho d\mathbf{r}\end{aligned}$$

# 库伦项的变分计算

Notice that

$$\begin{aligned}\delta E_{cl}[\rho] &= \frac{1}{2} \iiint \frac{\delta \rho(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' \\ &\quad + \frac{1}{2} \iiint \frac{\rho(\mathbf{r}') \delta \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' \\ &= \iint \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \delta \rho(\mathbf{r}) d\mathbf{r} \\ &= \int \hat{U}_{cl}(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r}.\end{aligned}$$

其中：

$$\hat{U}_{cl}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$

# 单粒子有效势

化学势可写为：

$$\mu = \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{\delta T_0[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + \hat{V}_{eff}(\mathbf{r}),$$

除了非相互作用电子动能项，其它项都统一称为有效势：

$$\hat{V}_{eff}(\mathbf{r}) = \hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})$$

其中  $\hat{V}_{xc}(\mathbf{r})$  定义为：

$$\hat{V}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}.$$

V<sub>xc</sub>是定义的

$$\delta E_{xc}[\rho] = \int \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r}$$

$$\equiv \int \hat{V}_{xc}(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r}$$

# 小结

$$\begin{aligned} E[\rho] &= T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho] \\ &\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho] \end{aligned}$$

$$\begin{aligned} \delta E[\rho(\mathbf{r})] &= \delta T_0 + \delta V_{ext} + \delta E_{cl} + \delta E_{xc} \\ &= \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{v}_{ext} + \hat{U}_{cl} + \hat{V}_{xc} \right\} \delta \rho d\mathbf{r} \\ &\equiv \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{V}_{eff} \right\} \delta \rho d\mathbf{r} \end{aligned}$$

问题：动能不能精确计算，交换关联能不能精确表达。

next

# 上一节回顾

- 两个定理：观测量是密度的泛函，总能量对密度变分的基态就是总能量对波函数变分的基态：关键 is  $\rho \longleftrightarrow V_{ext}$
- 总能量的改写：

$$\begin{aligned} E[\rho] &= T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho] \\ &\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho] \end{aligned}$$

- XC能包含哪些因素？交换，关联，自相互作用等
- 动能的LDA近似的不准确
- 引入波函数可得到Kohn-Sham方程

# 问题解答

- 第二定理的证明：已知有些密度不能对应可能的外势，为何DFT理论还成立？

对于**基态**密度与外势对应正确无疑。但在变分过程中，**未达到基态时的密度与外势的对应可能有问题**。要求实际变分时密度不能乱选，否则无V可表示。

- 改写总能量时，需要Kohn-Sham猜想，猜测**基态密度既可用真实波函数表达也可用无相互作用的波函数表达**。对非基态情形，该猜想还成立吗？结论是不知道。

# 密度泛函：多电子问题化为单电子问题

总能量是电子密度的泛函： $E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$

Kohn-Sham方法：

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

革命性的一步！

$$\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho]$$

交换关联能包含：

1. 动能不精确： $T_e[\rho] \neq T_0[\rho]$

2. 交换能和自相互作用纠正： $U_{ee} = E_{cl} + \dots$

3. 关联能： $\Psi(\vec{r}_1, \dots, \vec{r}_n) \neq \prod_P \phi_{p_1}(\vec{r}_1) \dots \phi_{p_n}(\vec{r}_n)$

# 关于单电子密度的再讨论

注意：密度表达式有区别了

$$F_{HF}[\rho] = T_e[\rho] + U_{ee}[\rho] \equiv T_0[\rho] + E_{cl}[\rho] + E_{xc}[\rho],$$

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \quad \leftrightarrow \quad \rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

怀疑：两边的密度定义不一样，  
总能量还能否相等？

# Kohn-Sham *Ansatz*(猜想、假说)

- Kohn-Sham辅助体系：  
一个“非相互作用”电子”体系(平均场意义)
- 假定“非相互作用”电子”体系与相互作用电子体系有相同的基态电子密度。
- 把原来的相互作用粒子问题换为容易求解的近似等价的非相互作用问题。

# 总能量对密度的变分计算

实际上，如果精确知道  $E_{xc}[\rho]$ ，则 Kohn-Sham 泛函是精确的。然而，所有困难的事都集中到了减缓关联能  $E_{xc}[\rho]$  上。假如我们队能量泛函知道的足够好，可以利用变分原理得到：

$$\begin{aligned}\mu &= \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T_0[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + \hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})},\end{aligned}$$

其中  $\hat{U}_{cl}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$ .

可仿照 Thomas-Fermi 情形求出总能量极小。

# 总能量的变分

$$\begin{aligned}\delta E[\rho(\mathbf{r})] &= \delta T_0 + \delta V_{ext} + \delta E_{cl} + \delta E_{xc} \\ &= \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{v}_{ext} + \hat{U}_{cl} + \hat{V}_{xc} \right\} \delta \rho d\mathbf{r} \\ &\equiv \int \left\{ \frac{\delta T_0}{\delta \rho} + \hat{V}_{eff} \right\} \delta \rho d\mathbf{r}\end{aligned}$$

# 其中：外势的变分

外势为

$$V_{ext}[\rho] = \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

其变分为

$$\delta V_{ext}[\rho] = \delta \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \int \hat{v}_{ext}(\mathbf{r})\delta\rho(\mathbf{r})d\mathbf{r}$$

对比

$$\delta V_{ext}[\rho] = \int \frac{\delta V_{ext}[\rho]}{\delta\rho} \delta\rho(\mathbf{r})d\mathbf{r}$$

得到

$$\frac{\delta V_{ext}[\rho]}{\delta\rho} = \hat{v}_{ext}(\mathbf{r})$$

# 其中：交换关联势的定义

$\hat{V}_{xc}(\mathbf{r})$  定义为：

$$\hat{V}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}.$$

$$\delta E_{xc}[\rho] = \int \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r}$$

$$\equiv \int \hat{V}_{xc}(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r}$$

# 其中：库伦项的变分计算

Notice that

$$\begin{aligned}\delta E_{cl}[\rho] &= \frac{1}{2} \iiint \frac{\delta \rho(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' \\ &\quad + \frac{1}{2} \iiint \frac{\rho(\mathbf{r}') \delta \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' \\ &= \iint \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \delta \rho(\mathbf{r}) d\mathbf{r} \\ &= \int \hat{U}_{cl}(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r}.\end{aligned}$$

其中：

$$\hat{U}_{cl}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$

# 定义：单粒子有效势

化学势可写为：

$$\mu = \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{\delta T_0[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + \hat{V}_{eff}(\mathbf{r}),$$

除了非相互作用电子动能项，其它项都统一称为有效势：

$$\hat{V}_{eff}(\mathbf{r}) = \hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})$$

其中  $\hat{V}_{xc}(\mathbf{r})$  定义为：

V<sub>xc</sub>是定义的

$$\hat{V}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}.$$

$$\delta E_{xc}[\rho] = \int \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r}$$

$$\equiv \int \hat{V}_{xc}(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r}$$

# 总能量的改写

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

$$E[\rho] \equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho]$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

XC能对总能量的贡献较小

改写后总能量可写为单粒子波函数的泛函

思考题：这样改写的合法性？是否恰当？是否改变了总能量？

# 对波函数变分

我们由变分原理可导出所谓的Kohn-Sham方程，这是一个非相互作用电子的 Schrödinger 方程：

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

注意势  $\hat{V}_{eff}(\mathbf{r})$  是非局域的。其解称为 Kohn-Sham 轨道  $\phi_i^{KS}(\mathbf{r})$ ，可用来计算总的电子密度：

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{KS}(\mathbf{r})|^2.$$

为了导出Kohn-Sham方程，总能量中动能要用波函数计算，密度也用波函数表示

密度可用于计算总能量。而动能  $T_0[\rho]$  的计算用波函数而不是密度本身：

$$T_0[\rho] = \frac{1}{2} \sum_{i=1}^N \langle \phi_i^{KS} | \nabla_i^2 | \phi_i^{KS} \rangle$$

能带能量的其余部分用密度计算：

$$V_{eff}[\rho] = \int \hat{V}_{eff}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}.$$

如果最终计算达到了自洽，我们置  $\phi_i \equiv \phi_i^{KS}$ 。

Kohn-Sham轨道 $\phi_i^{KS}(\mathbf{r})$ , 可用来计算总的电子密度:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{KS}(\mathbf{r})|^2.$$

电子密度 $\rho(\mathbf{r})$ 又可用于计算改进的有效势 $\hat{V}_{eff}(\mathbf{r})$ , 这样导致了一个自洽计算:

$$\rho_0(\mathbf{r}) \rightarrow \hat{V}_{eff}(\mathbf{r}) \rightarrow \phi_i^{KS}(\mathbf{r})$$

↖                    ↓ .

$$\rho(\mathbf{r})$$

问题：总能量已经是密度的泛函，对密度的变分还能得到系统的基态，那为什么还要采用总能量对波函数变分并且还引入Kohn-Sham方程？

1. 改进对动能的计算精度，要用波函数；
2. 许多物理量的计算需要能级和波函数(态密度，能带)，而密度又可从波函数获得；
3. 总能量对密度变分只能得到电子密度分布，总能量及其与几何结构相关的力学特性和声子特性等。
4. Kohn-Sham猜想确保了基态密度可由无相互作用电子波函数得到。

## 7d. Kohn-Sham方程的导出

总能量泛函在Kohn-Sham框架下写为

$$\begin{aligned} E[\rho] &= T_0[\rho] + \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho] \\ &= \sum_{i=1} \int \phi_i^*(\mathbf{r})(-\frac{1}{2}\nabla^2)\phi_i(\mathbf{r})d\mathbf{r} \\ &\quad + \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho]. \end{aligned}$$

其中,  $\rho(\mathbf{r}) = \sum_{i=1} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$ 。

# 构造变分函数：波函数正交归一

构造一个单粒子波函数 $\{\phi_i(\mathbf{r})\}$ 的泛函  
 $\Omega[\{\phi_i(\mathbf{r})\}]$ ,

$$\Omega = E[\rho] - \sum_{i,j} \varepsilon_{ij} \left( \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right).$$

这个泛函 $\Omega$ 相对于 $\phi_i^*(\mathbf{r})$ 的变分取极值，满足

$$\delta \Omega[\{\phi_i(\mathbf{r})\}] = 0.$$

注意： $\phi_i, \phi_i^*$ 是独立的变数

# 拉式乘子项及动能项的变分

拉式乘子项的变分：

$$\delta \sum_{i,j} \varepsilon_{ij} \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \sum_{i,j} \varepsilon_{ij} \int \delta \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r}$$

动能项的变分：

$$\begin{aligned} \delta T_0[\rho(\mathbf{r})] &= \delta \sum_i \int \phi_i^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(\mathbf{r}) d\mathbf{r} \\ &= \sum_i \int \delta \phi_i^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(\mathbf{r}) d\mathbf{r} \end{aligned}$$

# 外势项的变分

$$\begin{aligned} \delta \int v_{ext}(r) \rho(r) dr &= \int v_{ext}(r) \delta \rho(r) dr \\ &= \int v_{ext}(r) \sum_i \delta \phi_i^*(r) \phi_i(r) dr \\ &= \sum_i \int v_{ext}(r) \phi_i(r) \delta \phi_i^*(r) dr \end{aligned}$$

$$V_{ext}[\rho] = \int \hat{v}_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

其中：

$$\hat{v}_{ext}(\mathbf{r}) = \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|}.$$

# 库仑能的变分

$$E_{cl} = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr'$$

$$\delta E_{cl} = \int [\int \frac{\rho(r')}{|r-r'|} dr'] \delta\rho(r) dr = \int U_{cl}(r) \delta\rho(r) dr$$

$$\delta E_{cl} = \sum_i \int U_{cl}(r) \phi_i(r) \delta\phi_i^*(r) dr$$

其中：

$$\hat{U}_{cl}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}'$$

# 交换关联项的变分

$$\begin{aligned}\delta E_{xc}[\rho] &= \sum_i \int \frac{\delta E_{xc}[\rho]}{\delta \rho} \frac{\delta \rho}{\delta \phi_i^*(\mathbf{r})} \delta \phi_i^*(\mathbf{r}) d\mathbf{r} \\ &= \sum_i \int \hat{V}_{xc}(\mathbf{r}) \phi_i(\mathbf{r}) \delta \phi_i^*(\mathbf{r}) d\mathbf{r}.\end{aligned}$$

其中：

$$\hat{V}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}.$$

We have

$$\sum_i \int \delta\phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \phi_i(\mathbf{r}) d\mathbf{r}$$

$$+ \int [\hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r})] \sum_i \delta\phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r}$$

$$+ \delta E_{xc}[\rho] - \sum_{ij} \varepsilon_{ij} \int \delta\phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \mathbf{0}.$$

注意：利用了

$$\text{由 } \rho = \sum_i \phi_i^* \phi_i, \quad \text{有 } \delta\rho = \sum_i \delta\phi_i^* \phi_i$$

# 要求变分取极小

因为  $\{\phi_i(\mathbf{r}), i = 1, 2, \dots\}$  是完备集合，  
可令求和  $i$  的每一项为零，  
由变分  $\delta\Omega = 0$  得到

$$\begin{aligned} & \int \left\{ \left[ -\frac{1}{2} \nabla^2 + \hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \right. \right. \\ & \quad \left. \left. \hat{V}_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) \right\} \delta \phi_i^*(\mathbf{r}) d\mathbf{r} \\ &= \int \sum_j \epsilon_{ij} \phi_j(\mathbf{r}) \delta \phi_i^*(\mathbf{r}) d\mathbf{r}. \end{aligned}$$

# 导出K-S方程

由于 $\delta\phi_i^*(\mathbf{r})$ 是任意的,

$$\left[ -\frac{1}{2} \nabla^2 + \underbrace{\hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})}_{\hat{V}_{eff}(\mathbf{r})} \right] \phi_i(\mathbf{r})$$

$$= \sum_j \epsilon_{ij} \phi_j(\mathbf{r}),$$

或

$$H^{KS} \phi_i(\mathbf{r}) \equiv \left[ -\frac{1}{2} \nabla^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r})$$

$$= \sum_j \epsilon_{ij} \phi_j(\mathbf{r})$$

# 基底重组得标准K-S方程

由于 $\epsilon_{ij}$ 可以类似于Hartree-Fock情形对角化( $H^{KS}$ 是厄密的), 我们得到Kohn-Sham方程

$$\left[ -\frac{1}{2} \nabla^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}).$$

现在, 我们需要利用 $\epsilon_i$ 来计算总能量。

# 总能量的计算

从Kohn-Sham方程两边乘波函数并积分,

$$\sum_i \int \phi_i^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) d\mathbf{r}$$

两边同乘  $\phi_i^*(r)$  并对  $r$  积分

$$= \sum_i \int \epsilon_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r},$$

$$T_0 + \int (\hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r} = \sum_i \epsilon_i,$$

其中

$$\int \hat{U}_{cl}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = \iint \frac{\rho(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r}.$$

总能量中动能部分用单粒子能量和表达：

$$E[\rho] = T_0[\rho] + \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho]$$

$$E[\rho] = \sum_i \epsilon_i - \int (\hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$
$$+ \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho],$$

$$E[\rho] = \sum_i \epsilon_i - \int (\hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$
$$+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho].$$

$$T_0 + \int (\hat{v}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r} = \sum_i \epsilon_i$$

最终得到，使用轨道能量 $\epsilon_i$ 的总能量计算方式是：

$$\begin{aligned} E[\rho] = & \sum_{i=1}^N \epsilon_i - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\ & - \int \hat{V}_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho] \end{aligned}$$

**注1**:很清楚电子总能量不是单粒子能量的和。

**注2**: 在上面的Kohn-Sham方程推导中，使用的是非极化的电子密度(自旋上下简并的)，且Kohn-Sham轨道的占据数假定为1。这些都可推广到自旋极化的密度，及在(0, 1)之间的非整数占据。

**注3**: Kohn-Sham轨道和能量是什么？形式上只是参数，他们没有真实的物理意义。然而他们被用于表达电子轨道和能量，原因是这些值非常接近Hartree-Fock轨道和能量。

总能量非单粒子的能量和，与Hartree-Fock情形相似。

# Kohn-Sham轨道能量的含义

原则上，Kohn-Sham轨道的能量，或Kohn-Sham方程的本征值没有精确的物理含义，但是在近似下，该本征值与单粒子能量有关。

Kohn-Sham近似下密度的定义为：

$$N - 1\text{-electrons: } \rho(r) = \sum_i^{N-1} |\phi_i(r)|^2$$

$$N\text{-electrons: } \rho(r) + \delta\rho(r) = \sum_i^{N-1} |\phi_i(r)|^2 + |\phi_a(r)|^2$$

$$\text{difference: } \delta\rho(r) = |\phi_a(r)|^2$$

N电子体系的总能量：

$$E_{tot}^N[\rho + \delta\rho] = T_0[\rho + \delta\rho]$$

$$+ \int \hat{v}_{ext}(\mathbf{r})(\rho(\mathbf{r}) + \delta\rho)d\mathbf{r} + E_{cl}[\rho + \delta\rho] + E_{xc}[\rho + \delta\rho]$$

N-1电子体系的总能量：

$$E_{tot}^{N-1}[\rho] = T_0[\rho] + \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho]$$

# 类似于Hartree-Fock近似下的Koopman定理

N电子体系与N-1电子体系的总能量差为:

$$\Delta E = E_{tot}^N[\rho + \delta\rho] - E_{tot}^{N-1}[\rho] \approx \int \frac{\delta E_{tot}}{\delta\rho} \delta\rho(\mathbf{r}) d\mathbf{r}, \text{ 近似到一阶密度改变}$$

注意到:

$$\frac{\delta}{\delta\rho} \left\{ \int \hat{v}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{cl} + E_{xc}[\rho] \right\} = V_{eff}$$

$$\begin{aligned} T_0[\rho + \delta\rho] - T_0[\rho] &= \sum_i^N \left\langle \phi_i \left| -\frac{\nabla^2}{2} \right| \phi_i \right\rangle - \sum_i^{N-1} \left\langle \phi_i \left| -\frac{\nabla^2}{2} \right| \phi_i \right\rangle \\ &= \left\langle \phi_a \left| -\frac{\nabla^2}{2} \right| \phi_a \right\rangle \end{aligned}$$

因此有

$$\Delta E = \int \phi_a^*(\mathbf{r}) \frac{\delta E_{tot}}{\delta\rho} \phi_a(\mathbf{r}) d\mathbf{r} = \left\langle \phi_a \left| \frac{\delta E_{tot}}{\delta\rho} \right| \phi_a \right\rangle = \left\langle \phi_a \left| \left( -\frac{\nabla^2}{2} + V_{eff} \right) \right| \phi_a \right\rangle = \epsilon_a.$$

类似于Hartree-Fock近似下的Koopman定理。

## 7e. Kohn-Sham方程中的交换关联能

$$\begin{aligned} E[\rho] &= T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho] \\ &\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho] \end{aligned}$$

- 唯一不知道的项是交换关联能 $E_{xc}$ 。
- 如果 $E_{xc}$ 可以精确写出，在满足Kohn-Sham猜测下，Kohn-Sham方程是精确的方程。
- 但事与愿违，知道 $E_{xc}$ 不可精确写出，故从现在起要引入近似，而Kohn-Sham方程不再是精确的方程。  
304

# 交换关联能Exc

## 在Kohn-Sham方程中的 $E_{xc}$

Kohn-Sham方法的第一个移植使用的是LDA交换关联能。相应的泛函取自均匀电子气的数据。

交换关联能(XC能)可分为两部分：

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

即，交换能 $E_x[\rho]$ 和关联能 $E_c[\rho]$ 。注意这个分法是完全任意的。

# 交换关联能的一般形式

一般形式：

$$E_{xc}[\rho] = \int d\vec{r} \varepsilon_{xc}[\rho, \nabla\rho, \nabla^2\rho, \dots] \rho(\vec{r})$$

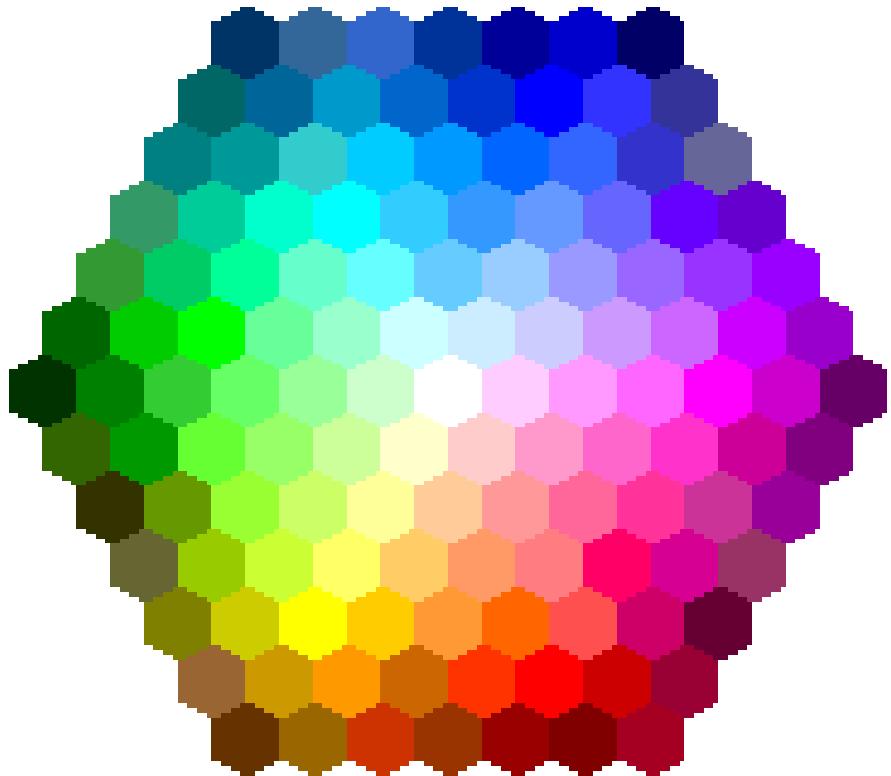
广义梯度近似（GGA）：

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

局域密度近似（LDA）：

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

# 局部密度近似(LDA) 的图示



1. 每一个小区域内的电子密度是常数，可以用均匀电子气描述
2. 均匀电子气的交换关联能可以算出
3. 整个体系的交换关联能是各个小区域的交换关联能的代数和。

如果有划分:  $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$ :

交换能近似为

$$E_x^{LDA}[\rho] = \int \epsilon_x[\rho(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r}.$$

其中  $\epsilon_x[\rho(\mathbf{r})]$  是密度为  $\rho(\mathbf{r})$  的电子气中单个电子的交换能。所谓的  $X\alpha$  方法就是在  $\epsilon_x$  中引入一个经验参数  $\alpha$ 。

关联能表达为:

$$E_c^{LDA}[\rho] = \int \rho(\mathbf{r})\epsilon_c[\rho(\mathbf{r})]d\mathbf{r}$$

其中  $\epsilon_c[\rho(\mathbf{r})]$  是在密度为  $\rho(\mathbf{r})$  的电子气中单个电子的关联能。

# LDA下的交换关联势

对于LDA,

$$\begin{aligned} E_{xc}^{LDA}[\rho] &= \int \rho(\mathbf{r})\epsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r} \\ &= \int \rho(\mathbf{r})(\epsilon_x + \epsilon_c)d\mathbf{r}. \end{aligned}$$

则  $E_{xc}[\rho]$  的变分可明确写出

$$\begin{aligned} \hat{V}_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}^{LDA}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{\delta \int \rho(\mathbf{r})\epsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r}}{\delta \rho(\mathbf{r})} \\ &= \epsilon_{xc} + \rho \frac{\partial \epsilon_{xc}}{\partial \rho}. \end{aligned}$$

# 总能量表达式中与交换关联相关 的一项的计算

$$E[\rho] = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\ - \int \hat{V}_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho]$$

$$-\int V_{xc}(r)\rho(r)dr + E_{xc} = -\int V_{xc}(r)\rho(r)dr + \int \varepsilon_{xc}\rho(r)dr \\ = \int (\varepsilon_{xc} - V_{xc})\rho(r)dr = \int [\varepsilon_{xc} - \varepsilon_{xc} - \rho \frac{\partial \varepsilon_{xc}}{\partial \rho}] \rho(r)dr \\ = -\int \rho \frac{\partial \varepsilon_{xc}}{\partial \rho} \rho dr$$

DFT可扩展到自旋相关(或自旋非共线)的情形。对于自旋极化情形的局域自旋密度近似(LSDA)是

$$\begin{aligned}\rho &= \rho_{\uparrow} + \rho_{\downarrow} \\ m &= \rho_{\uparrow} - \rho_{\downarrow}\end{aligned}$$

$$E_{xc}^{LSD}[\rho_{\uparrow}, \rho_{\downarrow}] = E_x[\rho_{\uparrow}, \rho_{\downarrow}] + E_c[\rho_{\uparrow}, \rho_{\downarrow}].$$

其中函数 $E_{xc}$ 不能解析得到，但能通过量子蒙特卡罗计算的不断改进，并拟合为解析表达式。

对于时间相关的DFT，交换关联能 $E_{xc}$ 更复杂与这里不相同。

从电子气导出的局域密度泛函实际应用中非常好。但是他低估交换能 $E_x$ 大约15%，高估关联能 $E_c$ 100%。

已知LDA过分束缚正常原子间键长，对于氢键又太弱了。GGA (Generalized Gradient Approximation)利用展开 $E_{xc}[\rho]$ 使得相对LDA有了很大改进。

现今最广泛使用的局域势是：

- For exchange: B88 (Becke, 1988), PW91(Perdew & Wang, 1991)
- For correlation: P86 (Perdew, 1986), LYP (Lee *et al.*, 1988)。

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**Dr. John Perdew**

Thus the density functional theory of Kohn and Sham 1965 has emerged as the most widely-used method of electronic structure calculation in both quantum chemistry and condensed matter physics. In this theory, one solves an exact-in-principle problem of non-interacting electrons in a self-consistent effective potential. **In practice, only the exchange-correlation energy has to be approximated.** The research of the Perdew group is primarily directed toward understanding this functional and improving the approximations to it.

# 交换关联能Exc的例子

- Ceperley-Alder plus Pedew-Zunger parameterization
- Teter's Pade fitting reproduces Perdew-Wang 1992 results
- References about: LDA, LSDA, GGA

不同的交换关联能选取，计算结果可能有区别，对研究某体系时，常要求取一样的交换关联能，以利于结果的比较和分析。

# Ceperley-Alder + PZ81

1. Ceperley-Alder XC: MC results of homogeneous electron gas.  
Perdew-Zunger 1981 parameterization.



D.M. Ceperley

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c,$$

交换能与关联能  
是分开的。

$$\varepsilon_x(r_s) = -\frac{0.9164}{r_s}$$

$$\varepsilon_c = \begin{cases} \frac{-0.2846}{1 + 1.0529 \sqrt{r_s} + 0.3334 r_s}, & r_s \geq 1 \\ -0.0960 + 0.0622 \ln r_s - \\ 0.0232 r_s + 0.0040 r_s \ln r_s, & r_s \leq 1 \end{cases}$$

where

D. M. Ceperley and B. J.  
Alder, PRB23, 5048(1981).

$$\rho^{-1} = \frac{4\pi}{3} r_s^3.$$

# Teter's Pade fitting

2. Teter's Pade approximation: It reproduces Perdew-Wang 1992 results but much faster.

$$\varepsilon_{xc} = -\frac{a_0(\xi) + a_1(\xi)r_s + a_2(\xi)r_s^2 + a_3(\xi)r_s^3}{b_1(\xi)r_s + b_2(\xi)r_s^2 + b_3(\xi)r_s^3 + b_4(\xi)r_s^4},$$

where  $\xi = \frac{\rho_\uparrow - \rho_\downarrow}{\rho_\uparrow + \rho_\downarrow}$ , and  $\frac{1}{\rho} = \frac{4\pi}{3} r_s^3$

$$a_i(\xi) = a_i + \delta a_i f_x(\xi),$$

$$b_i(\xi) = b_i + \delta b_i f_x(\xi)$$

不一定要把  
交换能与关  
联能分开。

$$f_x(\xi) = \frac{(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2}{2(2^{1/3} - 1)},$$

and  $a_i, \delta a_i, b_i, \delta b_i$  are parameters. See appendix in Goedecker, Teter and Hunter, Phys. Rev. B54, 1703(1996).

# Teter's Pade fitting parameters

Goedecker, Teter and Hunter, Phys. Rev. B54, 1703(1996)

a0 = 0.4581652932831429d0

a1 = 2.217058676663745d0

a2 = 0.7405551735357053d0

a3 = 0.01968227878617998d0

b1 = 1.0000000000000000d0

b2 = 4.504130959426697d0

b3 = 1.110667363742916d0

b4 = 0.02359291751427506d0

da0 = 0.119086804055547d0

da1 = 0.6157402568883345d0

da2 = 0.1574201515892867d0

da3 = 0.003532336663397157d0

db1 = 0.0000000000000000d0

db2 = 0.2673612973836267d0

db3 = 0.2052004607777787d0

db4 = 0.004200005045691381d0

# LSDA references I

1. von Barth - Hedin polarization applied to Wigner interpolation,  
Phys. Rev. 46, 1002 (1934)
2. Hedin - Lundqvist,  
J. Phys. C, 4, 2064 (1971)
3. Vosko - Wilk - Nusair,  
Can. J. Phys. 58, 1200 (1980), Phys. Rev. B 22, 3812 (1980)
4. Perdew-Wang 92,  
Phys. Rev. B 45 13244 (1992)
5. Macdonald-Vosko correction for the high density limit in the exchange, J. Phys. C, 12, 2977 (1979)
6. Perdew-Burke-Ernzerh(PBE) of GGA,  
Phys Rev Lett 77, 3865 (1996)
7. Lee-Yang-Parr correlation energy functional,  
Phys Rev B 37, 785 (1988)

# LSDA references II

- 8.** Becke exchange for a spin-unpolarized electronic system and Gradient-corrected exchange energy,  
J.Chem.Phys.96, 2155, 1992
- 9.** Wigner interpolation formula,  
E. Wigner, Phys. Rev. 46, 1002 (1934),  
W.E. Pickett, Comp.Phys.Rep. 9, 115 (1989)
- 10.** Ceperley - Alder exchange-correlation potential as parameterized by Perdew and Zunger,  
Phys. Rev. B23, 5048 (1981)
- 11.** LDA - scaled Wigner exchange-correlation,  
Q. Zhao, R.G. Parr, PRA 46, R5320 (1992)
- 12.** MacDonald et al. relativistic correction to lda exchange ,  
J Phys C 12 , 2977 (1979)

# 交换关联程序库LibXC

<http://www.tddft.org/programs/octopus/wiki/index.php/Libxc>

 octopus

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## Libxc

Libxc is a library of exchange-correlation functionals for density-functional theory. The aim is to provide a portable, well tested library of functionals that can be used by all the ETSF codes and also other codes.

In libxc you can find different types of functionals: LDA, GGA, hybrids, and mGGA (experimental). These functionals depend on the density at a given point depends only on the values of the density -- and the gradient of the density and the kinetic energy at that point:

$$E_{\text{xc}}^{\text{LDA}} = E_{\text{xc}}^{\text{LDA}}[n(\vec{r})],$$
$$E_{\text{xc}}^{\text{GGA}} = E_{\text{xc}}^{\text{GGA}}[n(\vec{r}), \vec{\nabla}n(\vec{r})],$$
$$E_{\text{xc}}^{\text{Hyb}} = a_x E^{\text{EXX}} + E_{\text{xc}}^{\text{GGA}}[n(\vec{r}), \vec{\nabla}n(\vec{r})],$$
$$E_{\text{xc}}^{\text{mGGA}} = E_{\text{xc}}^{\text{mGGA}}[n(\vec{r}), \vec{\nabla}n(\vec{r}), \nabla^2 n(\vec{r}), \tau(\vec{r})],$$

It can calculate the functional itself and its derivative; for some functionals, higher-order derivatives are available.

Libxc is written in C and has Fortran bindings. It is released under the LGPL license (v. 3.0). Contributions are welcome.

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其中有几百种交换关联泛函！

320

# 关于自相互作用修正(SIC)

J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

在HF情形  $J_{ii}=K_{ii}$ , 但是对DFT任何XC泛函均有

$$E_{SI} [\rho_{\sigma,i}] = \frac{1}{2} \iint \frac{\rho_{\sigma,i}(\mathbf{r}) \rho_{\sigma,i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc} [\rho_{\sigma,i}, 0] \neq 0$$

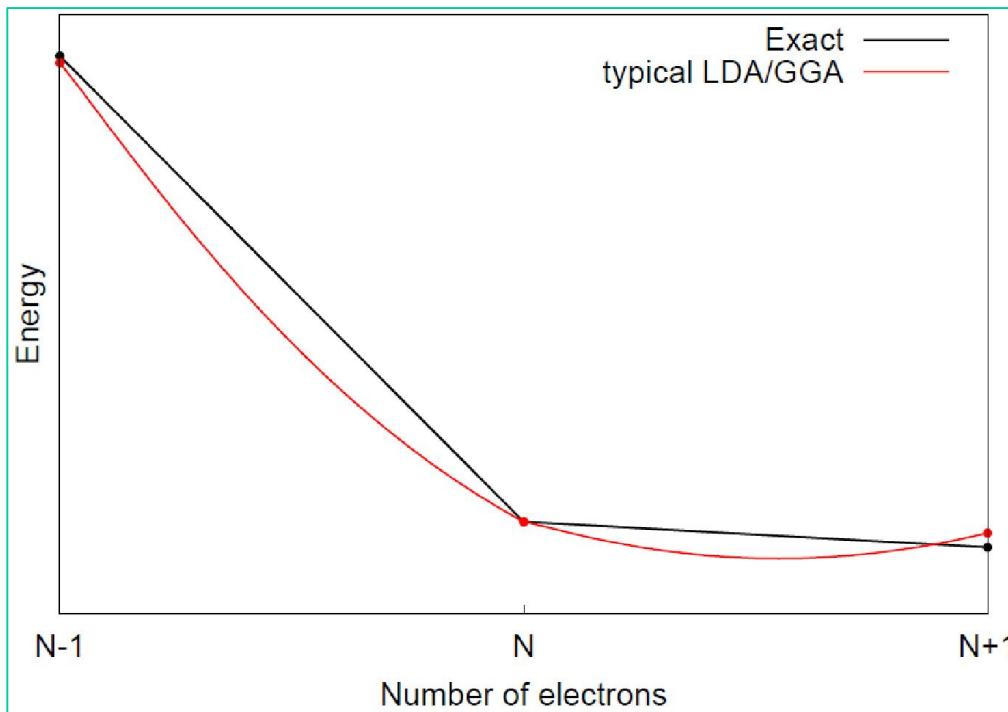
导致非物理的结果。

Perdew&Zunger self-interaction correction(SIC) 最直接简单:

$$E_{DFT-SIC} [\{\rho_{\sigma,i}\}] = E_{DFT} [\rho(\mathbf{r})] - \underbrace{\sum_{\sigma,i} \left\{ \frac{1}{2} \int \frac{\rho_{\sigma,i}(\mathbf{r}) \rho_{\sigma,i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc} [\rho_{\sigma,i}, 0] \right\}}_{E_{SIC}}$$

# 交换关联泛函导数的不连续性

- Perdew et al., Phys Rev Lett, 49, 1691 (1982)
- P. GORI-GIORGI , Int. J. of Quantum Chem., 109, 2410–2415 (2009)



总能量泛函及交换关联泛函相对电子数导数不连续(精确的，电荷的离散特性): 导致了与密度的变分计算相关的许多问题，比如能隙的计算。现在是密度泛函理论的重点研究方向。

- 回顾部分内容

- 验证：

$|库仑能| > |交换能| > |关联能|$

- KS方程的典型自洽求解过程

# 密度泛函：多电子问题化为单电子问题

电子总能量是电子密度的泛函：

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

Kohn-Sham方法：

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho]$$

$$\equiv T_0[\rho] + U_{ext}[\rho] + E_{cl}[\rho] + E_{xc}[\rho]$$

---

交换关联能包含：

1. 动能不精确:  $T_e[\rho] \neq T_0[\rho]$

2. 交换能和自相互作用纠正:  $U_{ee} = E_{cl} + \dots$

3. 关联能:  $\Psi(\vec{r}_1, \dots, \vec{r}_n) \neq \prod_P \phi_{p_1}(\vec{r}_1) \dots \phi_{p_n}(\vec{r}_n)$

# Kohn-Sham方程：单粒子方程

对总能量变分：

$$\delta\Omega[\{\phi_i(\mathbf{r})\}] = 0$$

$$\Omega[\{\phi_i(\mathbf{r})\}] = E[\rho] - \sum_{i,j} \varepsilon_{ij} \left( \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right)$$
$$\rho(\mathbf{r}) = \sum_{i=1} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

Kohn-Sham方程：

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

$$\hat{V}_{eff}(\mathbf{r}) = \hat{V}_{ext}(\mathbf{r}) + \hat{U}_{cl}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})$$

# 自洽求解图示

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

$$\rho_0(\mathbf{r}) \rightarrow \hat{V}_{eff}(\mathbf{r}) \rightarrow \phi_i^{KS}(\mathbf{r})$$

$$\rho_{in} = \omega \rho_{new} + (1-\omega) \rho_{old}$$

$$\rho(\mathbf{r})$$

326

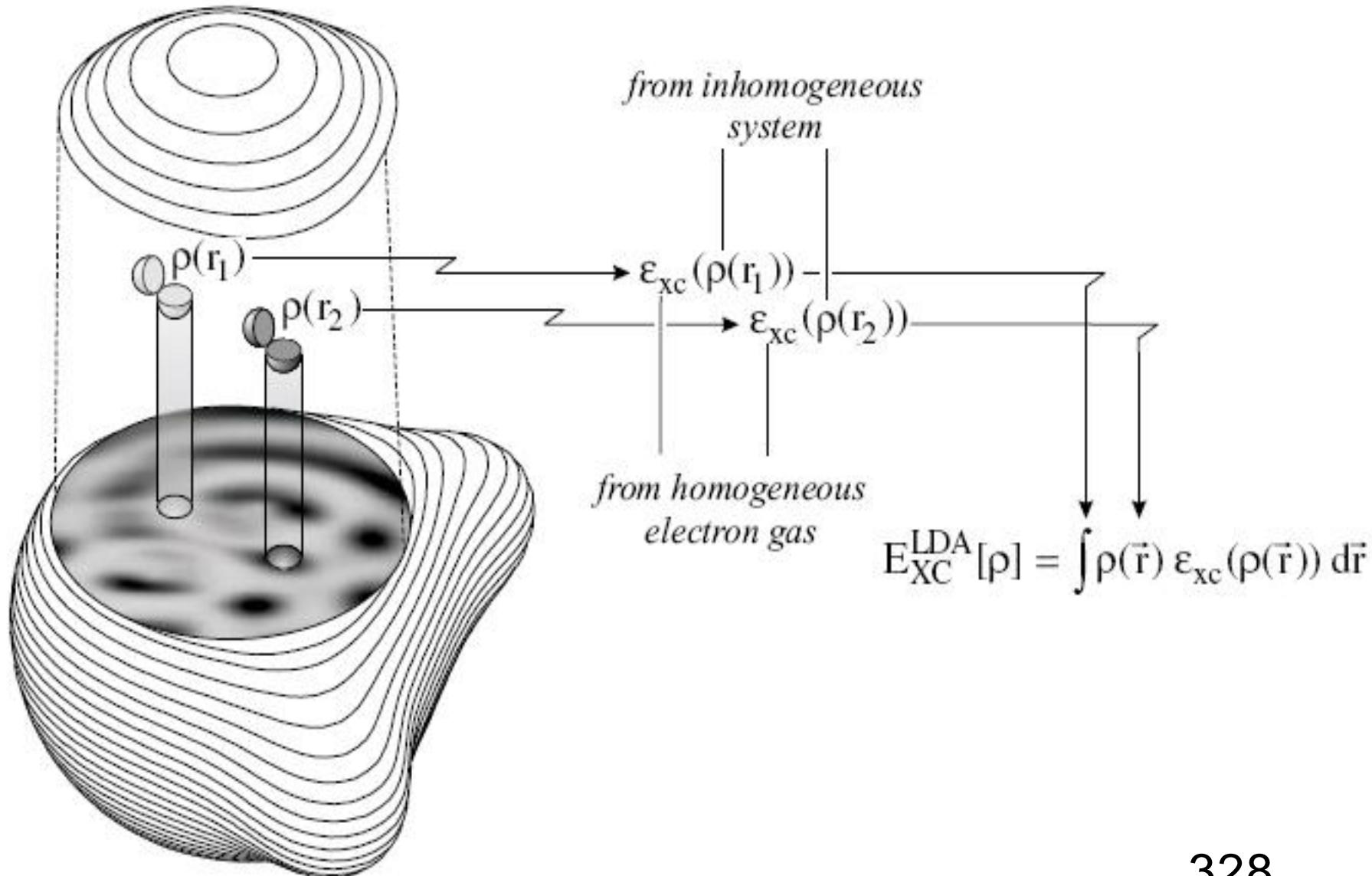
# Kohn-Sham方法下的总能量

$$E[\rho] = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$
$$- \int \hat{V}_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho]$$

能带能量不是总能量！

$$\hat{V}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$

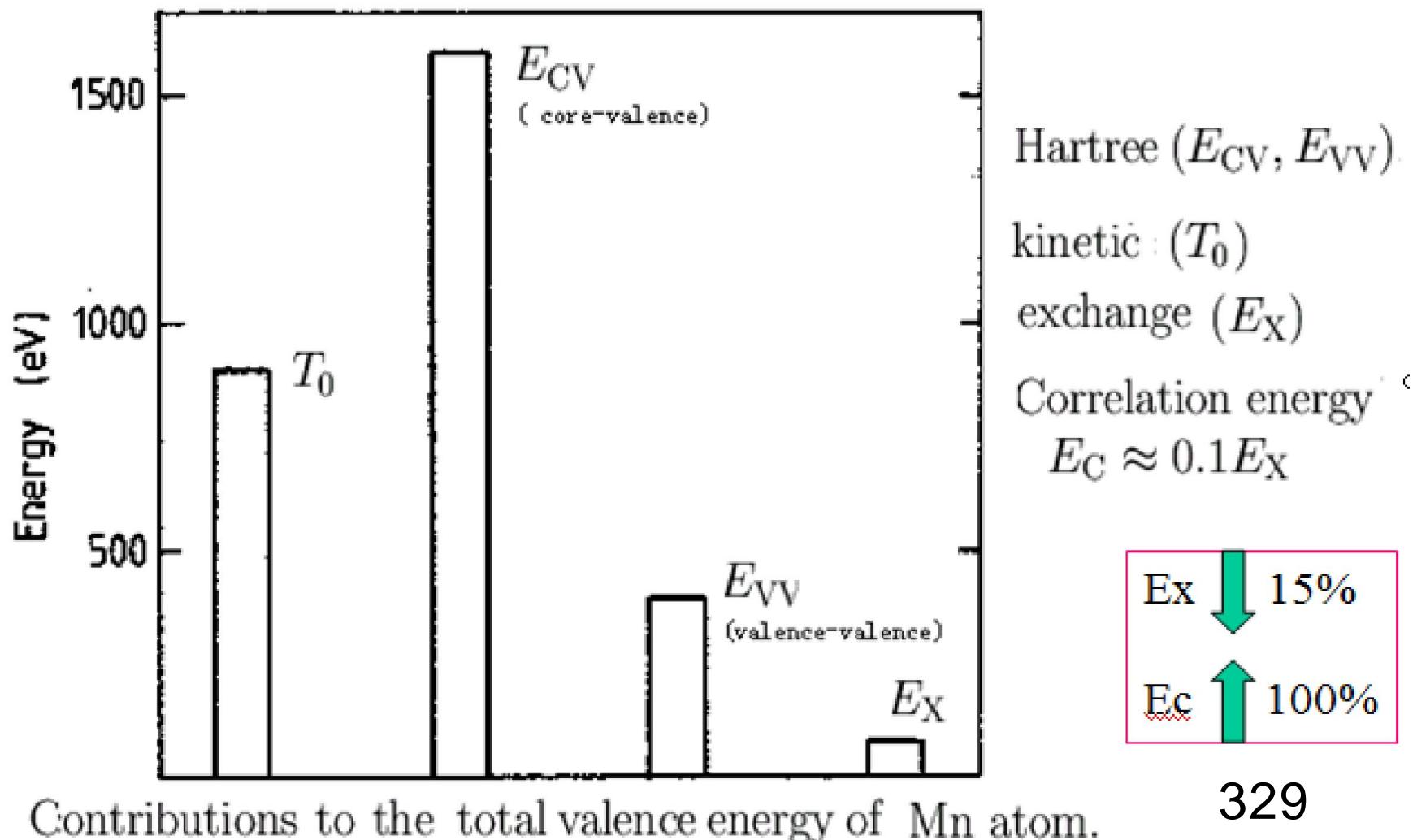
## (局域密度近似)LDA图解



# Why LDA works?

The Local Density Approximation works since ...

Only a small part of the total energy is approximated.



# 例：Si-fcc by siesta code

Si-Fcc

siesta:	Kinetic =	108.209594	电子动能
siesta:	Hartree =	21.437235	电子库仑能
siesta:	Ext. field =	0.000000	外场
siesta:	Exch.-corr. =	-67.999339	交换关联能
siesta:	Ion-electron =	-114.118626	离子电子库仑能
siesta:	Ion-ion =	-145.144457	离子离子库仑能
siesta:	Ekinion =	0.000000	离子动能
siesta:	Total =	-197.615592	总能量（内能）

$|库仑能| > |交换能| > |关联能|$

- 例:  $|交换能|$  大于  $|关联能|$
- 例:  $|库仑能|$  大于  $|交换能|$

Example:  
 $|交换能| > |关联能|$

# LDA,

$$\begin{aligned} E_{xc}^{LDA}[\rho] &= \int \rho(\mathbf{r}) \epsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r} \\ &= \int \rho(\mathbf{r}) (\epsilon_x + \epsilon_c) d\mathbf{r}. \end{aligned}$$

- 取密度为常数
- 取积分的体积为单位体积
- 考虑Ceperley-Alder + Perdew-Zunger交换关联
- 可以估计交换能与关联能的大小

# Ceperley-Alder + PZ81

1. Ceperley-Alder XC: MC results of homogeneous electron gas.  
Perdew-Zunger 1981 parameterization.

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c,$$

$$\varepsilon_x(r_s) = -\frac{0.9164}{r_s}$$

$$\varepsilon_c = \begin{cases} \frac{-0.2846}{1 + 1.0529 \sqrt{r_s} + 0.3334 r_s}, & r_s \geq 1 \\ -0.0960 + 0.0622 \ln r_s - \\ 0.0232 r_s + 0.0040 r_s \ln r_s, & r_s \leq 1 \end{cases}$$

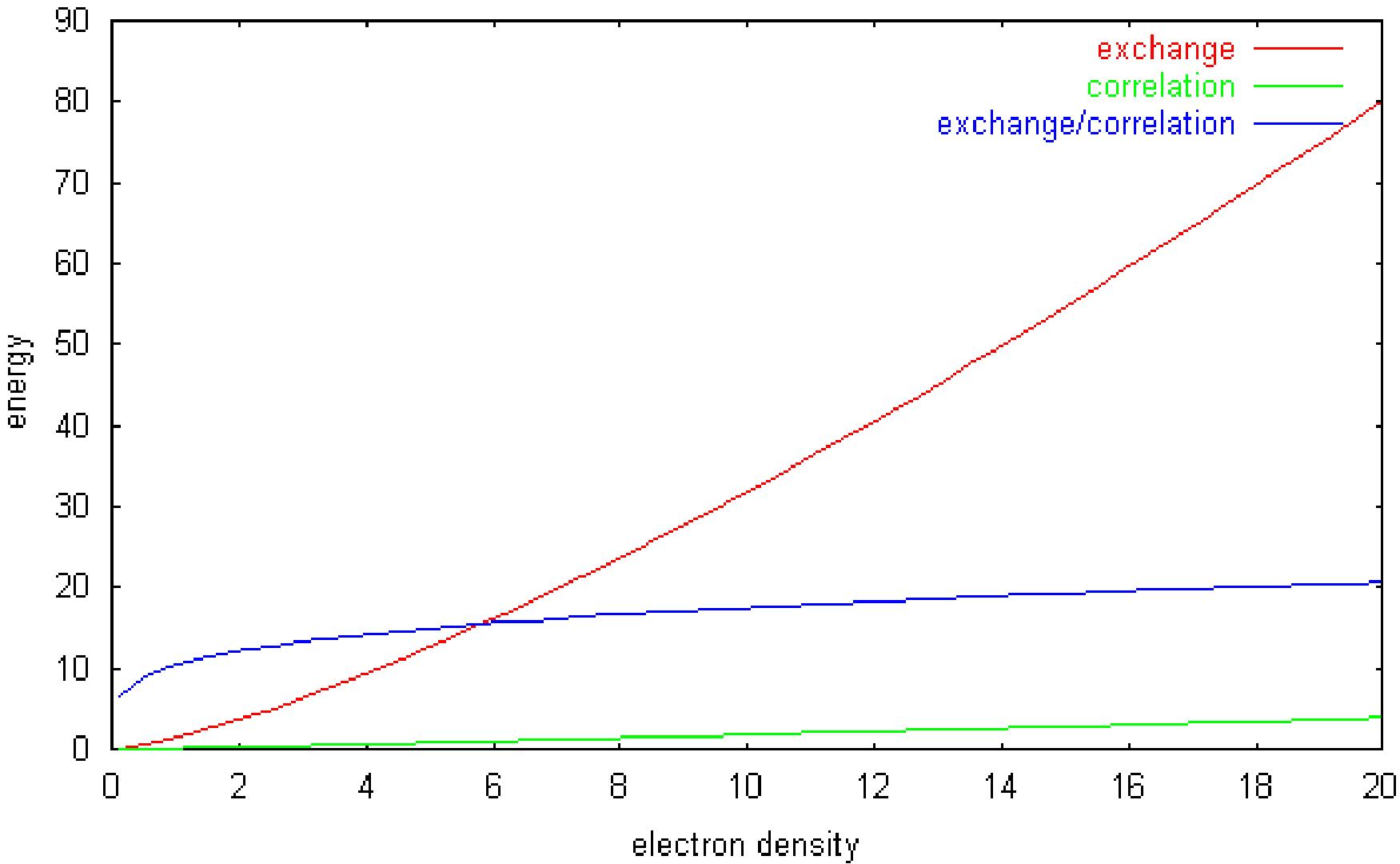
where

$$\rho^{-1} = \frac{4\pi}{3} r_s^3.$$

## c Ceperley-Alder,

```
nn=50
a0=0.1
b0=20.0
stp=(b0-a0)/(nn-1)
do j=1,nn
x=a0+(j-1)*stp
pi=4.d0*atan(1.d0)
third=1.d0/3.d0
rs=(3.0/(4.0*pi*x))**third
ex=-0.9164/rs
if(rs.gt.1.0)then
  ec=-0.2846/(1+1.0529*sqrt(rs)+0.3334*rs)
else
ec=-0.0960+0.0622*log(rs)-0.0232*rs+0.0040*rs*log(rs)
endif
eex=ex**x
eec=ec**x
write(6,*)x,abs(eex),abs(eec),abs(eex)/abs(eec)
enddo
stop
end
```

ABS(exchange) >> ABS(correlation) for high density



Example:  $|库仑能| > |交换能|$

Integration method: Take

取两个不同的单粒子态，  
用它们来计算库仑积分与  
交换积分

$$\phi_1(\mathbf{r}) = R_{10}(r)Y_{00},$$

$$\phi_2(\mathbf{r}) = R_{20}(r)Y_{00}.$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}},$$

$$R_{10}(r) = 2e^{-r},$$

$$R_{20}(r) = 2^{-3/2}(2-r)e^{-r/2}.$$

Coulomb energy and Exchange energy:

$$E_{Coulomb} = \frac{1}{2} \sum_{i \neq j} J_{ij} = J_{12} = \iint \frac{\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2,$$

$$E_{Exchange} = \frac{1}{2} \sum_{i \neq j} K_{ij} = K_{12} = \iint \frac{\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2.$$

Considering the expansion

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r'_<^l}{r'_>^{l+1}} Y_{lm}(\Omega_{r'}) Y_{lm}^*(\Omega_r).$$

Therefore,

$$E_{Coulomb} = \int \int dr_1 dr_2 \frac{1}{2} \frac{e^{-2r_1-r_2}(2-r_2)^2 r_1^2 r_2^2}{r_>}$$

$$E_{Exchange} = \int \int dr_1 dr_2 \frac{1}{2} \frac{e^{-3(r_1+r_2)/2}(2-r_1)(2-r_2) r_1^2 r_2^2}{r_>}$$

rr,exchange,coulomb

5. 0.0221349206 0.114381574

10. 0.0218205042 0.203431576

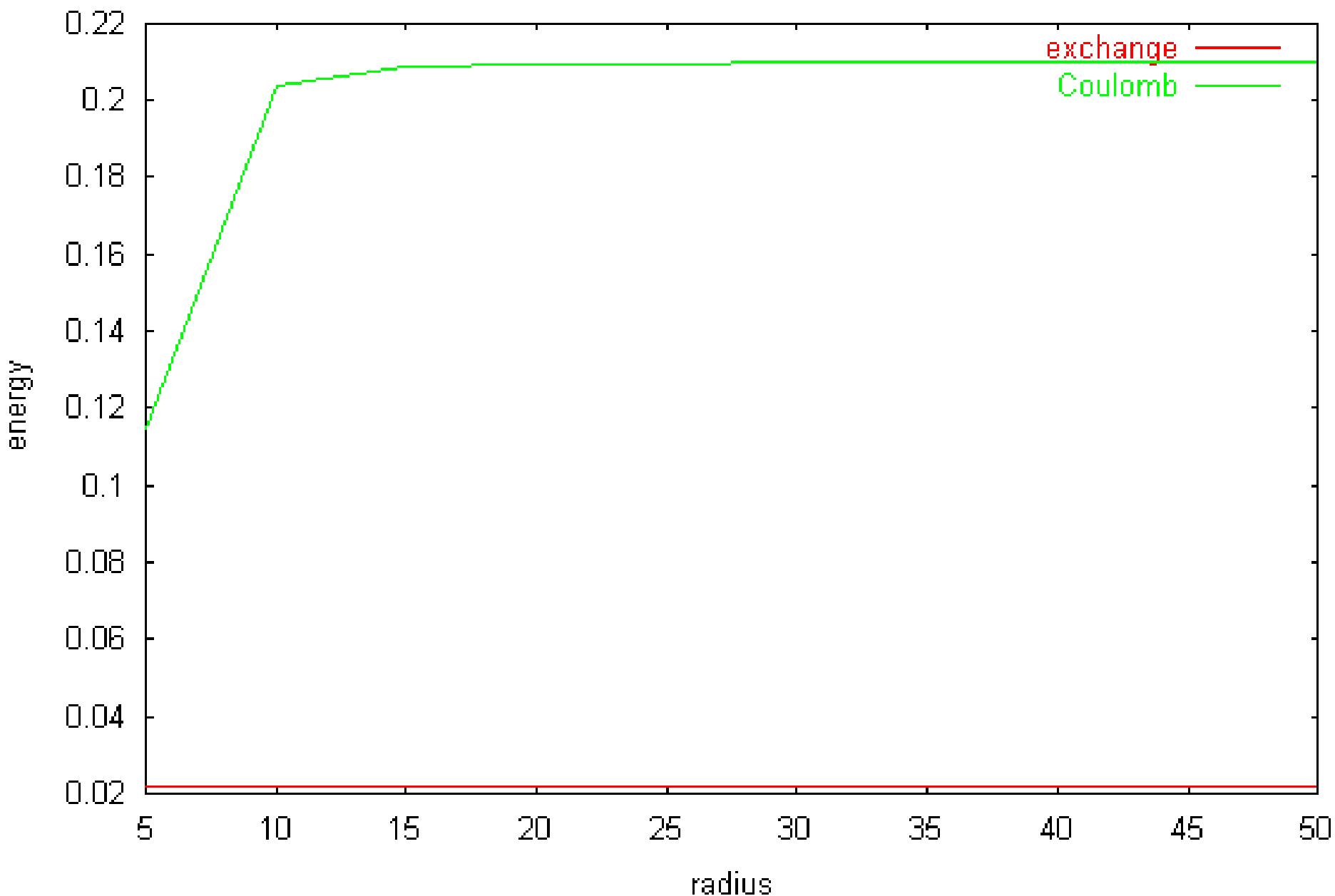
15. 0.0218861401 0.208890125

20. 0.0219105296 0.209314793

25. 0.0219234303 0.209506199

```
      integer nn
      parameter (nn=2000)
      real w(nn)

      write(6,*)'rr,exchange,coulomb'
      do i=1,10
      ar=0.0
      br=5*i
      rstp=(br-ar)/(nn-1)
      do j=2,nn-1
      w(j)=rstp
      enddo
      w(1)=0.5*rstp
      w(nn)=0.5*rstp
      eex=0.0
      eco=0.0
      do j=1,nn
      rj=ar+(j-1)*rstp
      do k=1,nn
      rk=ar+(k-1)*rstp
      if(j.gt.k)then
      rr=rj*rk*rk
      else
      rr=rj*rj*rk
      endif
      eex=eex+0.5*rr*(2-rj)*(2-rk)*exp(-3.0*(rj+rk)/2)*w(j)*w(k)
      eco=eco+0.5*rr*(2-rk)**2*exp(-(2*rj+rk))*w(j)*w(k)
      enddo
      enddo
      write(6,*)br,eex,eco
      enddo
      stop
      end
```



# 终于知道了LDA为什么有效了

## The Local Density Approximation works since ...

- Errors in the approximation of exchange and correlation cancel (e.g., in atoms: 10% error in  $E_x$  partially compensated by 100-200% error in  $E_c$ ).
- The exchange-correlation energy depends only on the angle-averaged exchange-correlation hole which is well described in LDA.

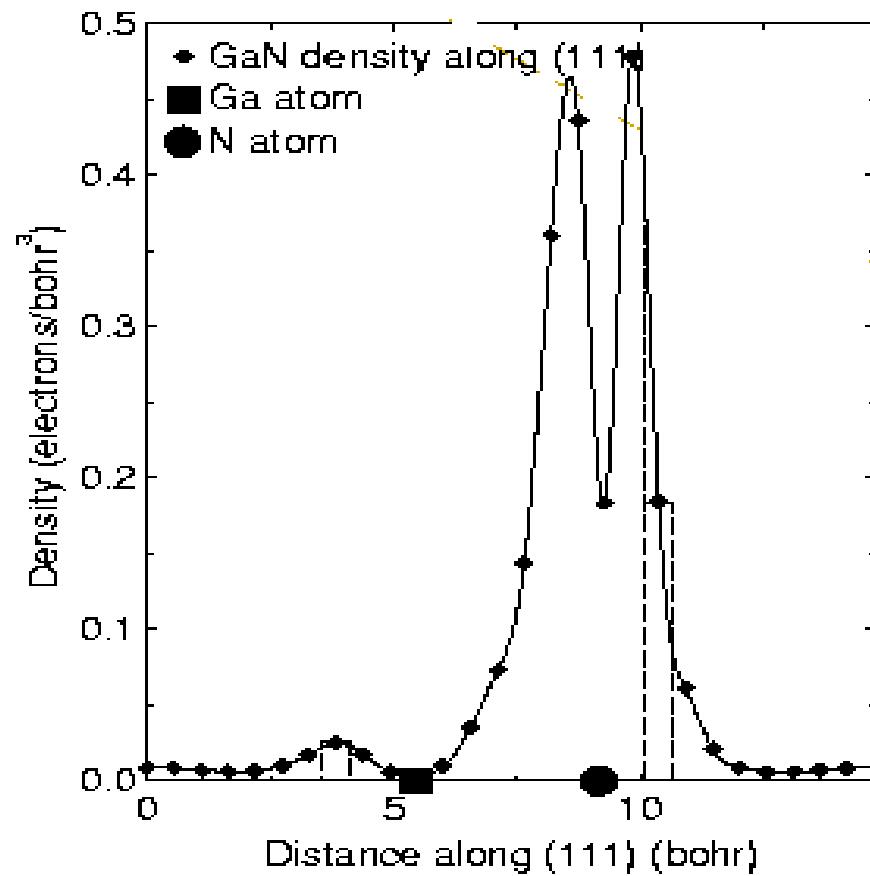
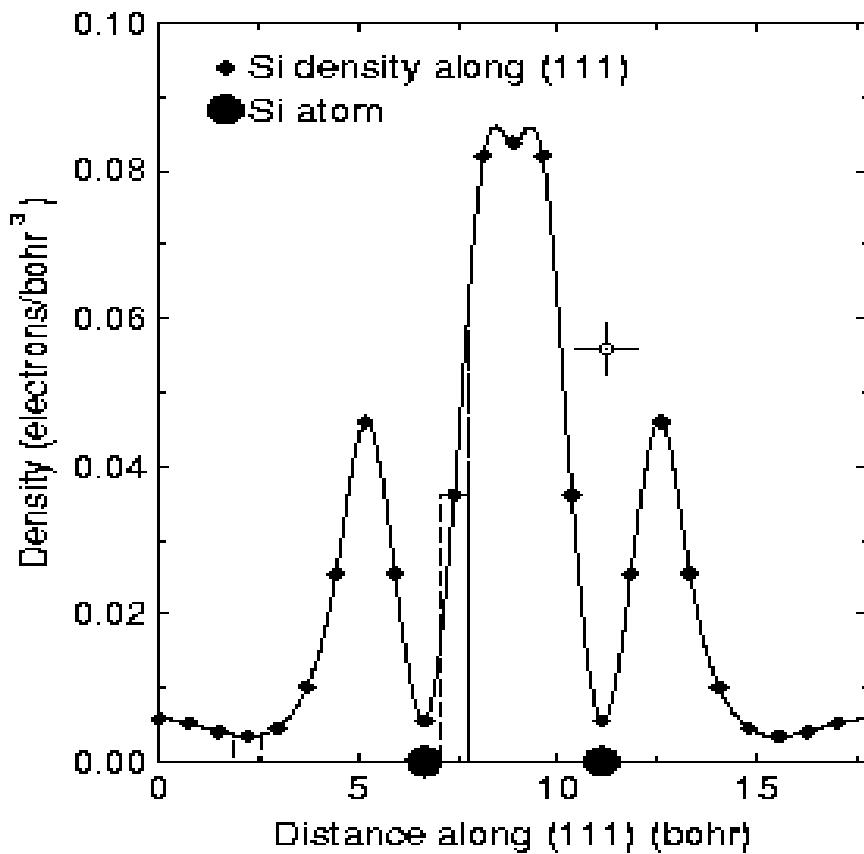
Ex : 设量级为100, 低估 10%~15%

Ec : 量级应为10, 高估100%~200%

两者误差有偶然部分相消的利好!

# 电子密度不必是慢变的

Does the density have to be slowly varying?



- The LDA works even if densities vary rapidly!
- The LDA is the most used approximation in DFT.

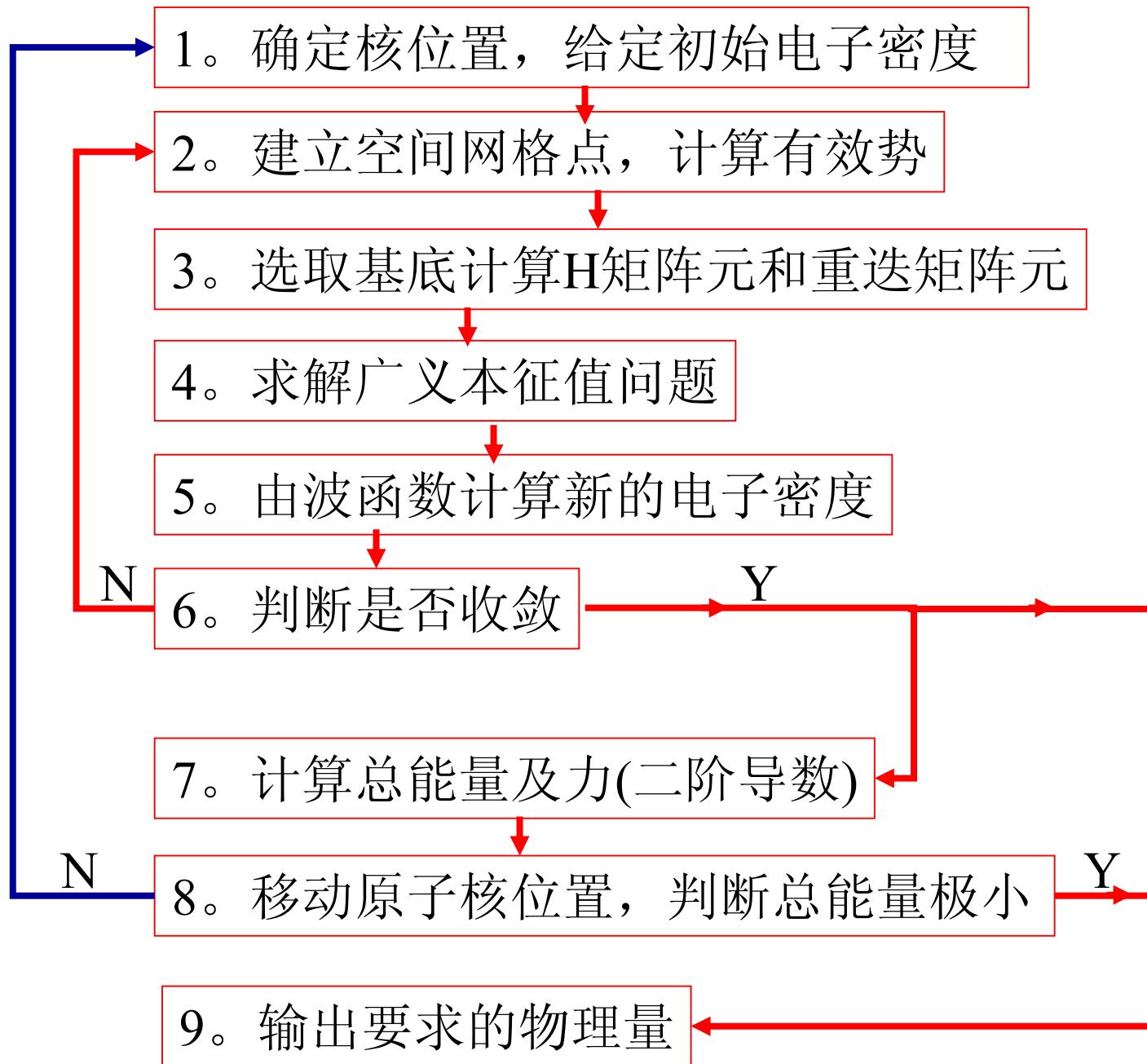
# KS方程的典型自洽求解过程

单个几何自洽循环或几何最佳化涉及如下步骤:

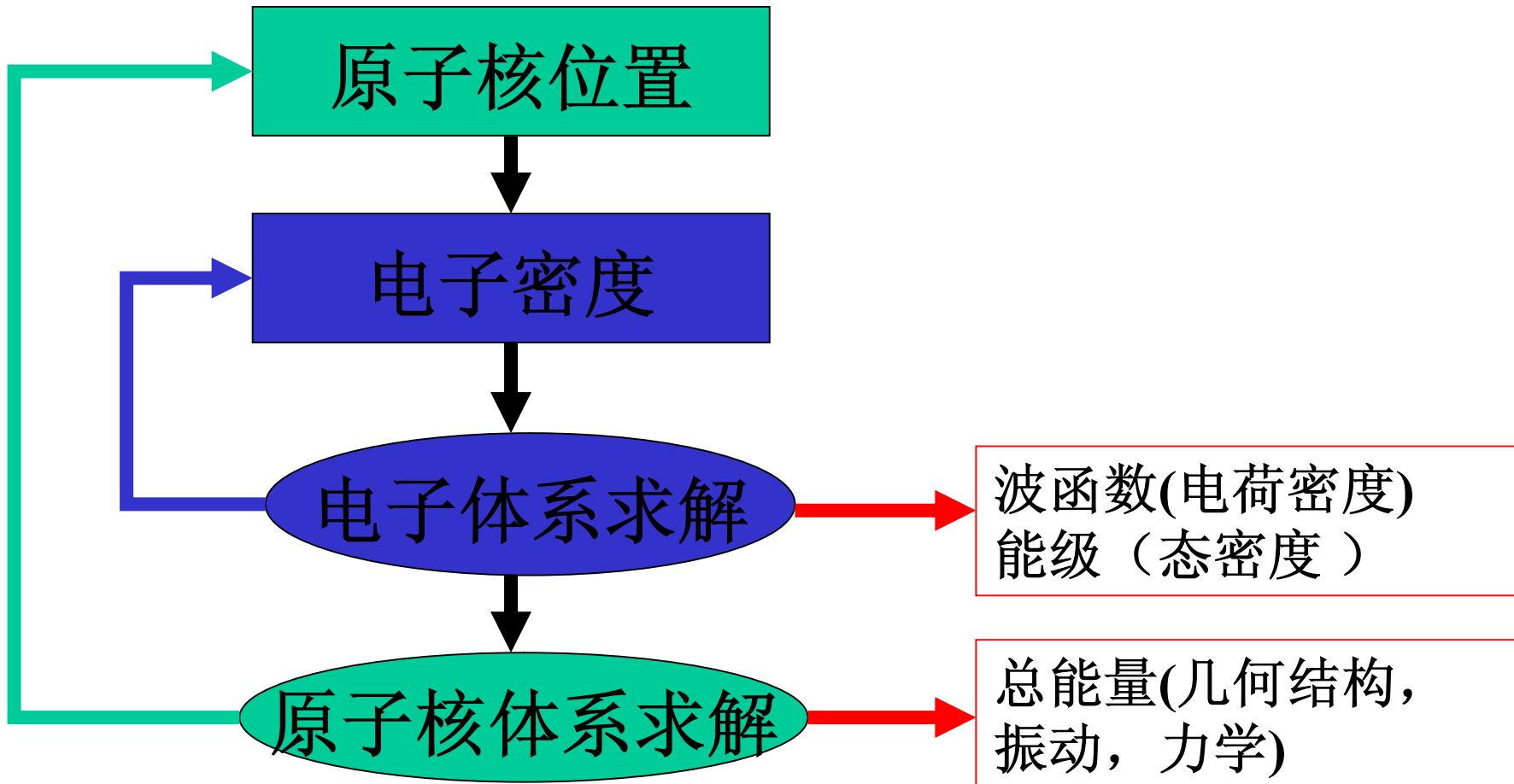
1. 给出一个初始密度(第一次迭代, 由原子密度叠加给出)
2. 建立电荷密度和交换关联势的空间网格
3. 计算KS矩阵元和重叠积分矩阵元
4. 解波函数展开系数的方程得到KS轨道
5. 计算新的密度  $\rho = \sum_{i=occ} |\phi_i(\mathbf{r})|^2$
6. 如果密度或能量有大的改变, 回到第1步
7. 如果自洽循环收敛且不要求几何优化, 前进到第10步
8. 计算总能量对于原子坐标的导数, 根据力更新原子坐标, 需要较密的积分用空间格点计算库伦势和交换关联势。
9. 如果力很大, 或原子核坐标显著运动, 回到第1步
10. 计算物理特性, 打印结果

当然, 还有许多这个方法的变种, 还有许多技术细节。

# 自洽求解图示



# 简化的自洽求解图



next

# 第2章：密度泛函理论

- 原子单位，
- 多粒子体系，
- 绝热近似，
- 哈特里近似， 哈特里-福克近似，
- 托马斯-费米理论，
- Hohenberg和Kohn的定理， Kohn-Sham 方法，  
Kohn-Sham方程，
- 交换关联能与LDA近似，
- Kohn-Sham方程的自洽求解，
- 密度泛函理论的优缺点。

# DFT与凝聚态物质特性列表

- **基态:**结合能, 平衡几何结构, 结构相变, 弹性常数, 电荷密度, 磁有序, 静态电极化率, 静态磁化率, 晶格振动, 态密度, ..., 等等。
- **激发态:**各种低能激发, 比热、Pauli自旋磁化率, 输运等; 各种较高能量激发, 能隙, 光特性, 增减电子的谱特性, ..., 等等。

# DFT与物质电子结构理论基础

当代物质电子结构理论与计算方法最重要的研究基础是：

- 电子基态和激发态的**密度泛函理论**；
- 可直接涉及电子与核的多体相互作用的**量子蒙特卡洛方法**；
- 电子系统激发谱的**多体微扰方法**；
- 能够进行真实体系模拟的计算进展，进一步影响理论与实验的进展。

# DFT与凝聚态物质特性计算方法

- 对于基态特性计算研究：包括几何结构，能谱等。
- 最广泛使用的方法是**密度泛函理论**；
- 最精确的方法是**量子蒙特卡洛方法**。
- 对于激发态特性计算研究：包括输运现象，电子-声子耦合现象等。
- 由于绝大多数激发态是在基态的小扰动，
- 微扰论方法会经常在计算中使用。

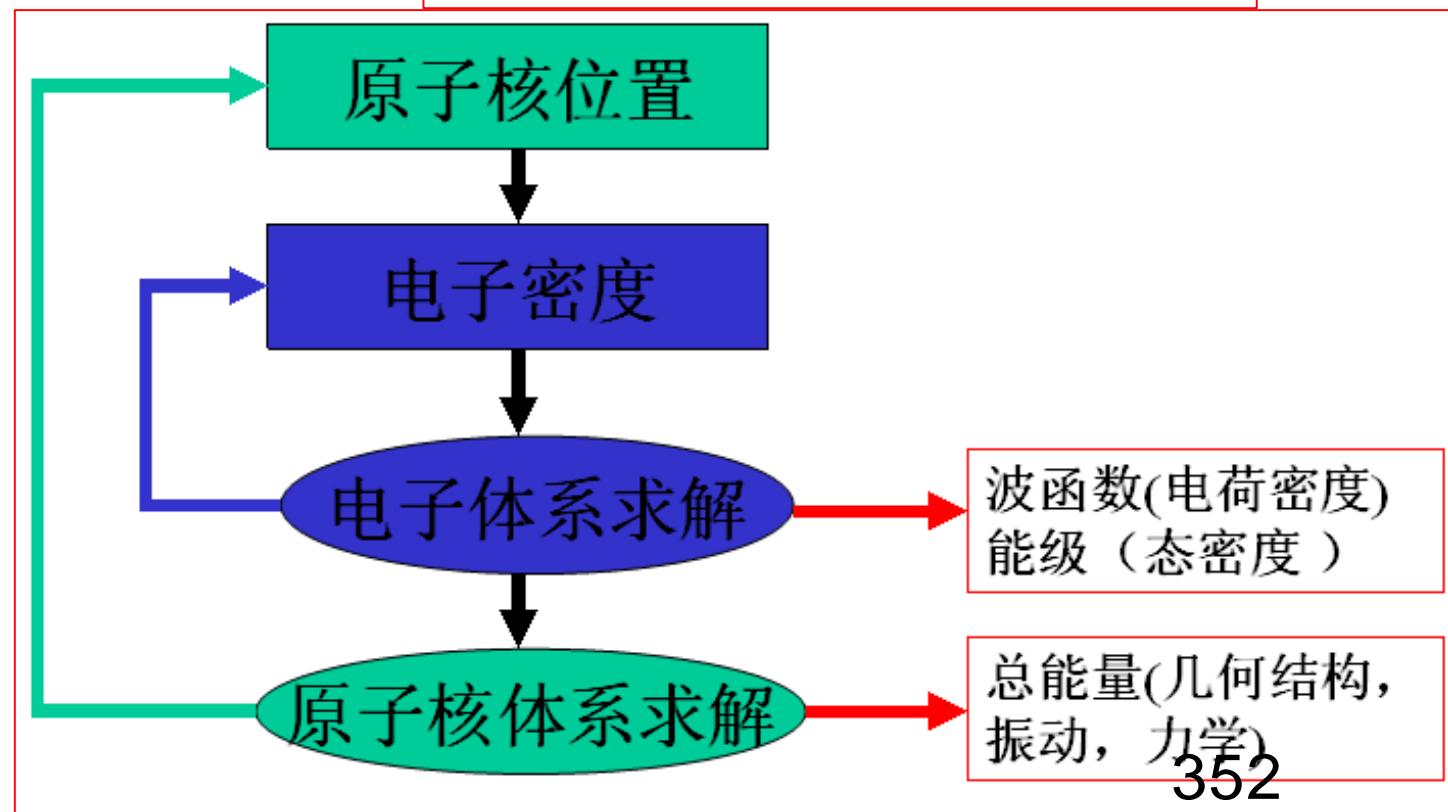
# 上一讲回顾

- Kohn-Sham方程的推导
- XC能的近似选取,LDA
- 能量的相对大小
- 自洽迭代

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

$$E_{xc}[\rho] = \int d\mathbf{r} \varepsilon_{xc}[\rho, \nabla\rho, \nabla^2\rho, \dots] \rho(\mathbf{r})$$

库仑能 | 交换能 | 关联能



# Performance of DFT(DFT的性能)

## • DFT的成功

- 原子总能量与原子离解能,
- 偶极矩和键离解能对比,
- 几何结构,
- 振动频谱,
- 原子和分子的电离能偏差,
- 电子亲和能误差,
- 极化率

## • DFT的失败

- 氢键问题
- 能隙问题

## • DFT理论的扩展

# 原子总能量与原子离解能

• The performance of a family of density functional methods

B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. 98 (7), (1993)5612

• 在包含多种分子的数据库中，原子离解能(atomization energies)实验值误差是在1kcal/mol内。Becke (1993)利用GGA泛函计算结果的平均误差是2.4kcal/mol。显然，这个误差是相对于绝对离解能的，通常这样的高精度计算难度是非常大的。采用DFT方法，其相对误差与实验值吻合的非常好。

TABLE I. Absolute total energies of neutral atoms (hartrees). Theoretical values were obtained with the 6-31G\* basis.

Atom	HF	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	MP2	QCISD	Exact <sup>a</sup>
H	0.4982	0.4540	0.4760	0.4540	0.4954	0.5178	0.4954	0.4982	0.4982	0.5000
He	2.8552	2.7146	2.8267	2.7582	2.8540	2.9671	2.8978	2.8664	2.8702	2.9037
Li	7.4314	7.1896	7.3410	7.2433	7.4264	7.5781	7.4801	7.4319	7.4319	7.4781
Be	14.5669	14.2164	14.4420	14.3119	14.5606	14.7869	14.6563	14.5964	14.6165	14.6674
B	24.5220	24.0532	24.3441	24.1798	24.5145	24.8061	24.6413	24.5625	24.5826	24.6539
C	37.6809	37.0950	37.4537	37.2527	37.6723	38.0318	37.8320	37.7365	37.7552	37.8450
N	54.3854	53.6840	54.1125	53.8760	54.3761	54.8053	54.5684	54.4595	54.4754	54.5893
O	74.7839	73.9544	74.4884	74.2105	74.7890	75.3238	75.0470	74.8820	74.8977	75.067
F	99.3650	98.4097	99.0490	98.7290	99.3803	100.0220	99.7021	99.4890	99.4995	99.734
Ne	128.4744	127.3950	128.1419	127.7777	128.4964	129.2442	128.8796	128.6262	128.6285	128.939

# 符号说明

- The functionals = Exchange + Correlation;
- Exchange: Slater LDA = (S);
- Exchange: Becke GGA = (B) ;
- Correlation: ignored = (null, X\_alpha);
- Correlation: Vosko, Wilk, and Nusair (VWN);
- Correlation: Lee, Yang, and Parr (LYP);
- B-null, S-VWN = LDA;
- B-VWN, S-LYP, and B-LYP = GGA;
- HF = Hartree-Fock;
- MP2 = second order Merller-Plesset Perturbation;
- QCISD = quadratic CI with single and double states;

TABLE V. Theoretical and experimental atomization energies (kcal/mol). Theoretical values were obtained with the 6-31G\* basis.

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. <sup>a</sup>
H <sub>2</sub>	76.8	107.5	100.2	79.5	110.8	103.2	75.9	86.6	91.2	103.3
LiH	31.4	57.5	52.5	33.6	60.3	54.9	30.4	39.8	44.1	56.0
BeH	46.4	57.7	54.4	46.1	57.6	53.9	48.8	45.3	38.3	46.9
CH	61.0	86.7	85.4	56.6	82.4	79.9	50.0	63.6	66.6	79.9
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	163.8	201.0	198.1	144.7	181.8	177.7	142.9	161.7	160.7	179.6
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	135.6	185.1	181.7	121.0	170.8	166.1	112.3	141.2	145.0	170.6
CH <sub>3</sub>	255.2	320.5	316.7	227.2	292.5	287.3	223.3	259.4	259.4	289.2
CH <sub>4</sub>	347.5	436.8	432.1	306.6	396.0	389.9	300.4	354.2	353.9	392.5
NH	58.8	87.7	86.2	54.4	83.3	81.8	43.0	60.6	62.5	79.0
NH <sub>2</sub>	133.2	189.1	186.6	117.6	173.4	170.8	98.8	137.8	139.0	170.0
NH <sub>3</sub>	224.9	306.0	302.6	192.7	273.5	270.1	170.2	232.4	230.7	276.7
OH	85.5	112.9	112.8	72.4	99.7	98.6	57.7	84.7	83.9	101.3
OH <sub>2</sub>	188.1	240.8	239.9	156.6	209.1	207.3	131.7	188.8	183.7	219.3
FH	119.3	146.2	145.6	99.5	125.3	124.4	82.1	118.2	114.0	135.2
Li <sub>2</sub>	5.6	22.5	21.8	3.4	20.5	19.8	2.2	14.1	20.9	24.0
LiF	125.9	151.3	152.6	110.5	134.9	135.6	85.2	129.5	123.5	137.6
HCCH	363.9	438.6	444.0	305.5	380.1	383.4	271.9	365.6	351.2	388.9
H <sub>2</sub> CCH <sub>2</sub>	489.8	600.9	603.0	417.5	528.5	528.1	394.2	489.4	481.7	531.9
H <sub>3</sub> CCH <sub>3</sub>	604.7	752.1	751.2	517.7	664.9	660.9	506.0	608.5	603.1	666.3
CN	172.9	213.5	221.5	138.8	179.1	186.0	84.4	150.6	155.4	176.6
HCN	281.6	346.5	352.6	236.5	301.2	306.2	184.9	287.3	269.7	301.8
CO	258.2	293.4	301.9	215.9	250.9	257.4	168.3	254.3	237.4	256.2
HCO	273.1	323.4	331.4	222.4	272.4	278.3	170.6	258.0	243.6	270.3
H <sub>2</sub> CO	345.1	417.6	423.3	286.0	358.4	361.8	237.8	335.5	321.9	357.2
H <sub>3</sub> COH	441.4	551.2	554.2	365.7	475.0	475.3	331.5	434.8	425.3	480.8
N <sub>2</sub>	202.6	257.3	264.3	169.9	224.3	231.3	105.1	212.1	192.3	225.1
H <sub>2</sub> NNH <sub>2</sub>	340.8	470.6	472.7	272.4	400.9	402.4	222.0	339.9	332.5	405.4
NO	153.5	193.8	202.8	114.9	154.8	162.8	46.4	134.8	124.8	150.1
O <sub>2</sub>	149.0	174.6	185.8	102.7	127.6	136.8	28.9	117.6	99.0	118.0
HOOH	240.6	310.4	317.3	179.6	248.2	252.8	109.4	219.6	206.8	252.3
F <sub>2</sub>	68.8	83.6	91.8	35.3	47.4	54.4	-34.3	36.8	27.9	36.9
CO <sub>2</sub>	406.3	464.3	481.0	321.8	379.2	392.9	234.7	381.0	347.8	381.9
Mean deviation	-19.1	35.6	37.7	-54.2	0.1	1.0	-85.8	-22.4	-28.8	
Mean absolute deviation	25.0	35.7	38.3	54.2	4.4	5.6	85.9	22.4	28.8	

# 原子离解能的平均绝对偏差

**Table 9-5.** Compilation of mean absolute and maximum absolute deviations (in parentheses) for atomization energies [kcal/mol] of small main group molecules from different sources.

## 32 1<sup>st</sup> row species, 6-31G(d) basis set, Johnson, Gill, and Pople, 1993

HF	85.9	SVWN	LSDA	35.7
MP2	22.4	BVWN		4.4
QCISD	28.8	BLYP		5.6

## 33 1<sup>st</sup> and 2<sup>nd</sup> row diatomic molecules, TZ2P basis, Laming, Termath, and Handy, 1993

LDA	43.6	(18.3)	CAM(A)-LYP	21.9	(14.5)
BLYP	9.5	(9.3)	CAM(B)-LYP	6.5	(12.0)

## G2 set, B1 = 6-31G(d), B2 = 6-311+G(3df,2p), Bauschlicher, 1995

HF/B1	80.5	(184.3)	HF/B2	74.5	(170.0)
MP2/B1	16.0	(40.3)	MP2/B2	7.3	(25.4)
BLYP/B1	5.3	(18.8)	BLYP/B2	5.0	(15.8)
BP86/B1	7.2	(24.0)	BP86/B2	10.3	(25.4)
B3LYP/B1	5.2	(31.5)	BP86/B2	2.2	(8.4)
B3P86/B1	5.9	(22.6)	BP86/B2	7.8	(22.7)

# 偶极矩和键离解能对比

- 使用GGA, DFT对于键的离解能(bond dissociation energies)远好于Hartree-Fock。通常HF不容易成键(underbinds), DFT容易成键 (overbinding)。

**Table 9.** Mean Unsigned Errors (MUEs) in DFT and HF Dipole Moment for Eight Zinc–Ligand Complexes (Nonrelativistic)<sup>a</sup>

functional	MUE (D)	functional	MUE (D)
M05-2X	0.19	OV5LYP	0.47
B97-2	0.26	OLYP	0.51
M05	0.27	TPSS	0.54
mPW1PW	0.28	TPSSVWN5	0.57
MPW1B95	0.29	MPW1KCIS	0.61
PBEh	0.29	VSXC	0.63
PW6B95	0.33	G96VWN5	0.63
O3LYP	0.36	G96HLYP	0.70
M06-2X	0.37	G96HLYP1M	0.70
TPSSh	0.38	mPWVWN5	0.72
TPSS1KCIS	0.39	BP86	0.73
B1LYP	0.39	MPWLYP1M	0.75
OVWN5	0.39	PBEVWN5	0.75
OPWL	0.39	PBELYP	0.81
MOHLYP	0.40	BVWN5	0.82
$\tau$ -HCTH	0.41	BLYP	0.85
X3LYP	0.43	mPWLYP	0.85
M06-L	0.43	HF	0.87
B3LYP	0.44	SVWN5	0.89
M06	0.45	G96LYP	0.90

<sup>a</sup> Nonrelativistic DFT/B1 tested against nonrelativistic CCSD/B2.

**Table 11.** Mean Unsigned Errors (MUEs) in DFT and HF Bond Dissociation Energy (BDE) for Twelve Zinc–Ligand Complexes (Nonrelativistic)<sup>a</sup>

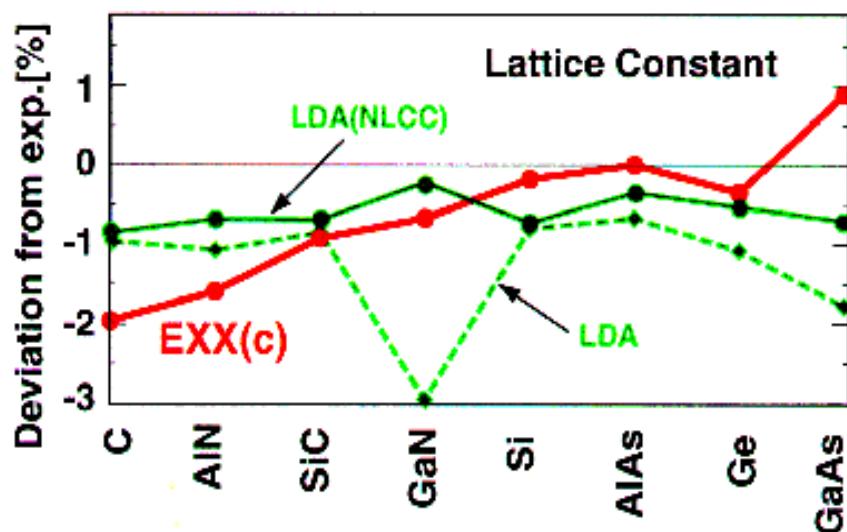
functional	MUE (kcal/mol)	functional	MUE (kcal/mol)
M06-2X	3.30	G96HLYP	7.27
M05	3.34	TPSSh	7.28
M06	3.80	G96LYP1M	7.33
B97-2	3.94	OV5LYP	7.47
B1LYP	4.26	mPWVWN5	7.50
M05-2X	4.30	OLYP	7.74
MPW1B95	5.16	OVWN5	7.87
mPW1PW	5.24	OPWL	7.88
PW6B95	5.26	PBEVWN5	7.90
M06-L	5.40	VSXC	8.04
B3LYP	5.41	TPSS	8.41
O3LYP	5.51	MPWLYP1M	8.49
X3LYP	5.64	BLYP	8.67
TPSSVWN5	5.97	PBELYP	8.89
PBEh	5.99	BP86	9.06
TPSS1KCIS	6.51	mPWLYP	9.49
MPW1KCIS	6.59	G96LYP	9.50
G96VWNS	6.66	MOHLYP	13.04
$\tau$ -HCTH	6.73	HF	15.02
BVWN5	6.99	SVWN5	22.06

<sup>a</sup> Nonrelativistic DFT/B1 tested against nonrelativistic CCSD(T).

# DFT给出满意的几何结构

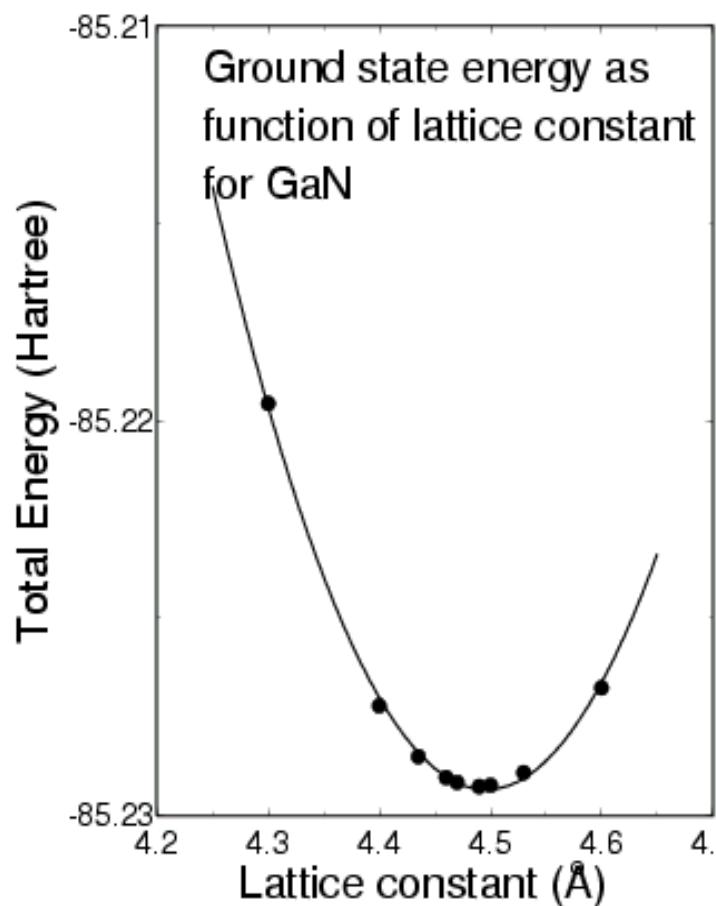
The Local Density Approximation works for structural properties.

- Lattice constants to within  $\sim 1\%$ .



LDA(NLCC) = approximate treatment  
of core electrons.

LDA = core electrons not treated.



# 键长DFT好于HF

- 分子的几何结构即使使用LSD也要远好于对应的HF结果。

**Table 8-5.** Computed bond lengths [Å] for the Cr(CO)<sub>6</sub> complex in O<sub>h</sub> symmetry. Experimental values: R<sub>Cr-C</sub> = 1.918 Å, R<sub>C-O</sub> = 1.141 Å (see ref. 70 in Jonas and Thiel 1995).

Bond	HF	MP2	CCSD(T)	SVWN	BP86	BLYP	B3P86	B3LYP
R <sub>Cr-C</sub>	2.010 <sup>a</sup>	1.862 <sup>a</sup>	1.939 <sup>c</sup>	1.865 <sup>d</sup>	1.911 <sup>d</sup>	1.942 <sup>f</sup>	1.901 <sup>d</sup>	1.927 <sup>d</sup>
	2.017 <sup>b</sup>	1.874 <sup>b</sup>		1.866 <sup>e</sup>	1.910 <sup>c</sup>	1.937 <sup>g</sup>		1.929 <sup>g</sup>
	1.970 <sup>c</sup>				1.908 <sup>f</sup>			1.921 <sup>h</sup>
R <sub>C-O</sub>	1.111 <sup>a</sup>	1.154 <sup>a</sup>	1.178 <sup>c</sup>	1.145 <sup>d</sup>	1.156 <sup>d</sup>	1.157 <sup>f</sup>	1.141 <sup>d</sup>	1.142 <sup>d</sup>
	1.111 <sup>b</sup>	1.154 <sup>b</sup>		1.145 <sup>c</sup>	1.153 <sup>e</sup>	1.164 <sup>g</sup>		1.150 <sup>g</sup>
	1.118 <sup>c</sup>				1.154 <sup>f</sup>			1.155 <sup>h</sup>

<sup>a</sup> Doubly polarized triple-zeta basis on C and O, ECP/triple-zeta basis on Cr (Jonas and Thiel, 1995); <sup>b</sup> doubly polarized triple-zeta basis on C and O, Wachters basis on Cr (Jonas and Thiel, 1995); <sup>c</sup> Wachters basis on Cr, triple-zeta basis on C and O (Barnes, Liu, and Lindh, 1993); <sup>d</sup> 6-311+G(d) basis as implemented in Gaussian (viz., modified Wachters basis on Cr) (Spears, 1997); <sup>e</sup> triple-zeta STO on Cr, polarized double-zeta STO on C and O (Ziegler, 1995); <sup>f</sup> double numerical basis as implemented in DMol (Delley, 1994); <sup>g</sup> Wachters basis on Cr, 6-31G(d) basis on C and O (Hamprecht *et al.*, 1998); <sup>h</sup> extended Wachters basis on Cr, polarized double-zeta basis (D95\*) on C and O (Koch and Hertwig, 1998).

# 一类材料的计算键长误差

- LDA与HF相当
- GGA好于HF，有些泛函的误差小一个量级

**Table 7.** Mean Unsigned Errors (MUEs) in DFT and HF Zn–Ligand Bond Distance for Ten Zinc–Ligand Complexes (Nonrelativistic)<sup>a</sup>

functional	MUE ( $\text{\AA}$ )	functional	MUE ( $\text{\AA}$ )
X3LYP	0.0069	M06-2X	0.0169
PW6B95	0.0072	MPWLYP1M	0.0175
M05-2X	0.0078	G96LYP	0.0177
B3LYP	0.0080	mPWLYP	0.0205
MPW1KCIS	0.0080	OLYP	0.0215
B1LYP	0.0084	BLYP	0.0223
mPW1PW	0.0089	HF	0.0224
PBEh	0.0089	G96LYP1M	0.0236
PB86	0.0090	G96HLYP	0.0241
B97-2	0.0090	OV5LYP	0.0244
TPSSh	0.0094	PBELYP	0.0291
TPSS1KCIS	0.0097	TPSSVWN5	0.0309
MPW1B95	0.0105	G96VWN5	0.0318
M06-L	0.0109	OVWN5	0.0355
TPSS	0.0113	OPWL	0.0358
$\tau$ -HCTH	0.0133	mPWVWN5	0.0359
O3LYP	0.0139	PBEVWN5	0.0368
M05	0.0147	BVWNS	0.0377
M06	0.0147	SVWN5	0.0410
VSXC	0.0151	MOHLYP	0.0769

<sup>a</sup> Nonrelativistic DFT/B1 tested against nonrelativistic CCSD(T)

# 键长键角的平均绝对偏差

- DFT总体好于HF
- 其中DFT的大部分偏差还与基底的完备性有关，采用好的基底可减小DFT计算的误差

**Table 8-4.** Compilation of mean absolute deviations for bond lengths [Å] / bond angles [degrees] for small main group molecules from different sources.

32 1 <sup>st</sup> row species, 6-31G(d) basis, Johnson, Gill, and Pople, 1993			
HF	0.020 / 2.0	SVWN	0.021 / 1.9
MP2	0.014 / 1.8	BLYP	0.020 / 2.3
QCISD	0.013 / 1.8		
33 1 <sup>st</sup> row species, TZ2P basis, Laming, Termath, and Handy, 1993			
SVWN	0.090 / 1.9	CAM(A)LYP	0.007 / 1.7
BLYP	0.013 / 1.7	CAM(B)LYP	0.009 / 1.5
13 species, Martin, El-Yazal, and François, 1995a			
CCSD(T)/cc-pVDZ	0.018 / 2.2	B3LYP/cc-pVDZ	0.009 / 1.7
CCSD(T)/cc-pVTZ	0.014 / 0.6	B3LYP/cc-pVTZ	0.004 / 0.3
CCSD(T)/cc-pVQZ	0.002 / 0.4	B3LYP/cc-pVQZ	0.004 / 0.3
20 organic molecules, Rauhut and Pulay, 1995			
BLYP/6-31G(d)	0.012 / 0.6	B3LYP/6-31G(d)	0.003 / 0.5
108 1 <sup>st</sup> and 2 <sup>nd</sup> row species, Scheiner, Baker, and Andzelm, 1997			
	6-31G(d,p)	DZVP	TZVP
HF	0.021		
MP2	0.014		
SVWN	0.016	0.016	0.014
BLYP	0.021	0.024	0.020
BPW91	0.017	0.019	0.016
ACM	0.011	0.011	0.009
			TZ2P
			UCC <sup>a</sup>
			0.013
			0.016
			0.012
			0.009
40 species cont. 3 <sup>rd</sup> row elements, 6-31G(d) basis, Redfern, Blaudeau and Curtiss, 1997			
MP2	0.022 / 0.4	B3LYP	0.030 / 0.5
BLYP	0.048 / 1.0	B3PW91	0.020 / 0.5
BPW91	0.020 / 0.5		
32 1 <sup>st</sup> row species, 6-311G(d,p) basis, Adamo and Barone, 1997, 1998, 1999			
BLYP	0.014	B3LYP	0.004
BPW91	0.014	B1LYP	0.005
PWPW91	0.012	B3PW91	0.008
mPWPW91	0.012	B1PW91	0.005
PBEPBE	0.012	mPW3PW91	0.008
BHLYP	0.015	mPW1PW91	0.010
		PBE1PBE	0.010
40 first and 2 <sup>nd</sup> row species, TZ2P basis, Hamprecht <i>et al.</i> , 1998			
BLYP	0.019 / 0.4	B3LYP	0.008 / 0.2
HTCH	0.013 / 0.7		

<sup>a</sup> uncontracted aug-cc-pVTZ basis.

# 氢键问题

- 但是LSD不能正确的处理氢键。如果使用GGA泛函，这个缺陷可基本被修复。对于金属有机反应中的过渡态的研究，传统的HF方法是一个典型的难题，但DFT提供了非常好的结果。

**Table 12-1.** Deviation in the computed  $R_{O-O}$  distance of the water dimer [ $\text{\AA}$ ] from the ‘experimental’  $R_c$  value of 2.952  $\text{\AA}$ .

Basis Set	HF	MP2	CCSD(T)	SVWN	BLYP	SLYP	BVWN	B3LYP
6-31++G(d,p)	0.035	-0.038	-0.030	-0.256	-0.040	-0.301	0.061	-0.066
6-311++G(d,p)	0.082	-0.042	-0.028	-0.244	-0.025	-0.291	0.082	-0.052
aug-cc-pVDZ	0.080	-0.034 <sup>a</sup>	-0.033 <sup>b</sup>	-	-0.012	-0.290	0.117	-0.041
aug-cc-pVTZ	0.086	-0.044 <sup>a</sup>	-0.057 <sup>b</sup>	-0.241	-0.004	-0.288	0.124	-0.034
aug-cc-pVQZ	0.086	-0.057 <sup>b</sup>	-	-0.238	-0.003	-0.286	0.119	-0.033

<sup>a</sup> Taken from Kim and Jordan, 1994. <sup>b</sup> Only  $R_{O-O}$  optimized, Halkier et al., 1997. <sup>c</sup> No  $C_2$ -*trans* minimum structure.

水分子二聚物的氧原子间距与氢键有关：LDA很差，杂化泛函也不好

# 振动频谱

- LSD可基本重复振动频谱。而GGA与实验吻合的更好。

**Table 8-7.** Frequency scaling factors, rms deviation, proportion outside a 10 % error range and listings of problematic cases [ $\text{cm}^{-1}$ ] for several methods employing the 6-31G(d) basis set. Taken from Scott and Radom, 1996.

Method	f <sup>a</sup>	RMS <sup>b</sup>	10 % <sup>c</sup>	Problematic Cases (Deviations larger than 100 $\text{cm}^{-1}$ )
HF	0.8953	50	10	233( $\text{O}_2$ ), 221( $\text{O}_3$ , $\text{F}_2$ ), 180( $^1\text{A}_1$ -CH <sub>2</sub> ), 164( $\text{F}_2\text{O}$ ), 139( $\text{N}_2$ ), 120( $\text{N}_2\text{F}_2$ ), 115(HOF, NF <sub>3</sub> ), 103(NClF <sub>2</sub> )
MP2	0.9434	63	10	660( $\text{O}_3$ ), 304( $\text{NO}_2$ ), 277( $\text{N}_2$ ), 225( $\text{O}_2$ ), 150(HF), 149( $^1\text{A}_1$ -CH <sub>2</sub> ), 142(HC <sub>2</sub> H), 136(HC <sub>4</sub> H), 131(CINS), 120(ClC <sub>2</sub> H), 117(H <sub>2</sub> ), 115( $^3\text{B}_2$ -CH <sub>2</sub> ), 111(C <sub>2</sub> N <sub>2</sub> ), 101(FCN)
QCISD	0.9537	37	6	202( $^1\text{A}_1$ -CH <sub>2</sub> ), 129(HF), 117(C <sub>2</sub> H <sub>2</sub> ), 101( $\text{O}_3$ )
BLYP	0.9945	45	10	224( $^1\text{A}_1$ -CH <sub>2</sub> ), 189(H <sub>2</sub> ), 165(HF), 116(OH), 113(SO <sub>3</sub> ), 112( $^3\text{B}_1$ -CH <sub>2</sub> ), 111(SO <sub>2</sub> ), 109(C <sub>2</sub> H <sub>2</sub> )
BP86	0.9914	41	6	229( $^1\text{A}_1$ -CH <sub>2</sub> ), 142(H <sub>2</sub> ), 115(HF), 114( $^3\text{B}_2$ -CH <sub>2</sub> ), 106(F <sub>2</sub> )
B3LYP	0.9614	34	6	204( $^1\text{A}_1$ -CH <sub>2</sub> ), 132(HF), 125(F <sub>2</sub> ), 121(H <sub>2</sub> ), 110( $\text{O}_3$ )
B3P86	0.9558	38	4	204 ( $^1\text{A}_1$ -CH <sub>2</sub> ), 146(F <sub>2</sub> ), 139( $\text{O}_3$ )
B3PW91	0.9573	34	4	204 ( $^1\text{A}_1$ -CH <sub>2</sub> ), 140(F <sub>2</sub> ), 137( $\text{O}_3$ )

<sup>a</sup> Scale factor; <sup>b</sup> root mean square error after scaling in  $\text{cm}^{-1}$ ; <sup>c</sup> percentage of frequencies that fall outside by more than 10 % of the experimentally observed fundamentals.

# From Jensen's book, p256

Jensen F.- Introduction to Computational Chemistry (2007)

- In general, it is found that DFT methods often give geometries and vibrational frequencies for stable molecules of the **same or better quality than MP2**, at a computational cost similar to HF.
- For systems containing multi-reference character, where MP2 usually fails badly, DFT methods are often found to generate results of a quality comparable to those obtained with coupled cluster methods

# 原子和分子的电离能偏差

- 采用GGA的DFT，其电离能、电子亲和能、质子亲和能(Ionization energy, electron affinities, and proton affinities)都能很好的重复实验结果。

**Table 9-12.** Compilation of mean absolute (maximum) deviations for ionization energies [eV] of small main group molecules from different sources.

• 电离能：拿走一个电子需要的能量

• HF低估电离能：在中性原子中的关联比在离子中的关联要多。

42 atoms and molecules, numerical, basis set free, Becke, 1992b and 1993b			
LDA	0.23 (0.62)	BPW91	0.15 (0.44)
BVWN	0.41 (1.26)	B3PW91	0.14 (0.41)
38 atoms and molecules, De Proft and Geerlings, 1997			
SVWN, aug-cc-pVTZ	0.69	BLYP, aug-cc-pVTZ	0.19
BP86, aug-cc-pVTZ	0.17	B3LYP, cc-pVDZ	0.18
B3LYP, aug-cc-pVTZ	0.15	B3PW91, cc-pVDZ	0.20
B3PW91, aug-cc-pVTZ	0.15		
83 atoms and molecules, Curtiss et al., 1998			
SVWN, 6-311+G(3df,2p)	0.59 (1.74)	B3LYP, 6-31+G(d)	0.18
BLYP, 6-311+G(3df,2p)	0.26 (1.02)	B3LYP, 6-311+G(2df,p)	0.18
BPW91, 6-311+G(3df,2p)	0.22 (1.17)	B3LYP, 6-311+G(3df,2p)	0.18 (1.65)
BP86, 6-311+G(3df,2p)	0.20 (1.20)	B3PW91, 6-311+G(3df,2p)	0.19 (1.67)
B3P86, 6-311+G(3df,2p)	0.57 (2.22)	G2	0.06 (0.32)
38 atoms and molecules, 6-311+G(3df,2p) basis, Ernzerhof and Scuseria, 1999			
SVWN	0.69 (1.2)	PBE	0.16 (0.5)
SVWN5	0.22 (0.6)	PBE1PBE	0.16 (0.7)
BLYP	0.20 (0.6)	VSXC	0.13 (0.4)
B3LYP	0.17 (0.8)		

# 电子亲和能误差

- 亲和能：额外添加一个电子需要的能量
- 需要考虑更多关联，任何HF方法都比较差
- DFT给出比较合理的结果

**Table 9-13.** Compilation of mean absolute deviations (maximum deviation in parenthesis) for electron affinities [eV] of small main group molecules from different sources.

27 atoms and molecules, De Proft and Geerlings, 1997			
SVWN, aug-cc-pVTZ	0.77	BLYP, aug-cc-pVTZ	0.14
BP86, aug-cc-pVTZ	0.23	B3LYP, aug-cc-pVDZ	0.15
B3LYP, aug-cc-pVTZ	0.12	B3PW91, aug-cc-pVDZ	0.13
B3PW91, aug-cc-pVTZ	0.11		

58 atoms and molecules, Curtiss et al., 1998			
SVWN, 6-311+G(3df,2p)	0.70 (1.31)	B3LYP, 6-31+G(d)	0.16
BLYP, 6-311+G(3df,2p)	0.11 (0.69)	B3LYP, 6-311+G(2df,p)	0.14
BPW91, 6-311+G(3df,2p)	0.12 (0.77)	B3LYP, 6-311+G(3df,2p)	0.13 (1.08)
BP86, 6-311+G(3df,2p)	0.19 (0.88)	B3PW91, 6-311+G(3df,2p)	0.15 (1.06)
B3P86, 6-311+G(3df,2p)	0.60 (1.61)		

25 atoms and molecules, 6-311+G(3df,2p) basis, Ernzerhof and Scuseria, 1999			
SVWN	0.74 (1.2)	PBE	0.11 (0.3)
SVWN5	0.30 (0.7)	PBE1PBE	0.13 (0.3)
BLYP	0.11 (0.4)	B3LYP	0.11 (0.5)

# GGA给出比较合理的极化率

- 极化率反比于单粒子轨道能量差
- LDA高估了极化率， HF低估了极化率
- GGA给出比较合理的值

Table 10-2. Average Polarizabilities  $\langle\alpha\rangle$  for selected molecules [a.u., 1 a.u. = 0.1482 Å<sup>3</sup>].

Molecule	HF POL <sup>a</sup>	MP2 POL <sup>a</sup>	SVWN numerical <sup>b</sup>	SVWN POL <sup>a</sup>	SVWN TZVP-FIP <sup>c</sup>	BLYP POL <sup>a</sup>	BLYP TZVP-FIP <sup>c</sup>	B3LYP POL <sup>a</sup>	B3LYP d-augTZ <sup>d</sup>	HCTH(AC) POL <sup>e</sup>	PBE1PBE POL <sup>f</sup>	Exp. <sup>ad</sup>
HF	4.88	5.67	6.23	6.17	5.94	6.26	6.00	5.83	5.79	5.60	5.67	5.60
HCl	16.67	17.37		18.43		18.54		17.90	17.99	17.77	17.58	17.39
F <sub>2</sub>	8.58	8.22		8.82		8.96		8.69	8.46	8.43	8.37	8.38
Cl <sub>2</sub>	29.89	30.56		31.70		31.97		31.16	31.27	30.84	31.05	30.35
CH <sub>4</sub>	15.91	16.54	17.70	18.01		17.59		17.03	17.25	16.51	16.86	17.27
SiH <sub>4</sub>	29.97	31.04		34.28		33.14		32.25	32.13			31.90
NH <sub>3</sub>	12.94	14.42	15.54	15.57	14.96	15.62	14.94	14.73	14.73	14.25	14.34	14.56
PH <sub>3</sub>	29.93	30.69		32.52		32.13		31.35	31.32	31.07	31.03	30.93
H <sub>2</sub> O	8.51	9.80	10.60	10.54	10.20	10.64	10.26	9.96	10.01	9.67	9.69	9.64
H <sub>2</sub> S	23.77	24.70		26.13	24.95	26.07	24.72	25.24	25.19	24.99	24.60	24.71
CO	12.23	13.09	13.70	13.62	13.39	13.66	13.43	13.18		13.03		13.08

<sup>a</sup> Cohen and Tantirungrotechai, 1999 and McDowell, Amos and Handy, 1995; <sup>b</sup> Dickson and Becke, 1996; <sup>c</sup> Calaminici, Jug and Köster, 1998; <sup>d</sup> van Caillie and Amos, 1998; <sup>e</sup> Tozer and Handy, 1998; <sup>f</sup> Adamo et al., 1999.

# DFT的成功之处

## Surface chemistry and heterogeneous catalysis

- Adsorbate structure and energetics
- Metals, ceramics, semiconductors, zeolites, etc.
- Reaction pathways and transition states

## Materials science

- Bulk, surface, interface, defects
- Electronic structure
- Mechanical properties
- Magnetic properties

# DFT的失败之处

## □ Failures of DFT – physics missing or incorrect:

- Strongly correlated systems (late transition metal oxides, sulfides, actinides, etc.)
- Van der Waals interactions
- Excited states
- Band gaps
- Open shell systems

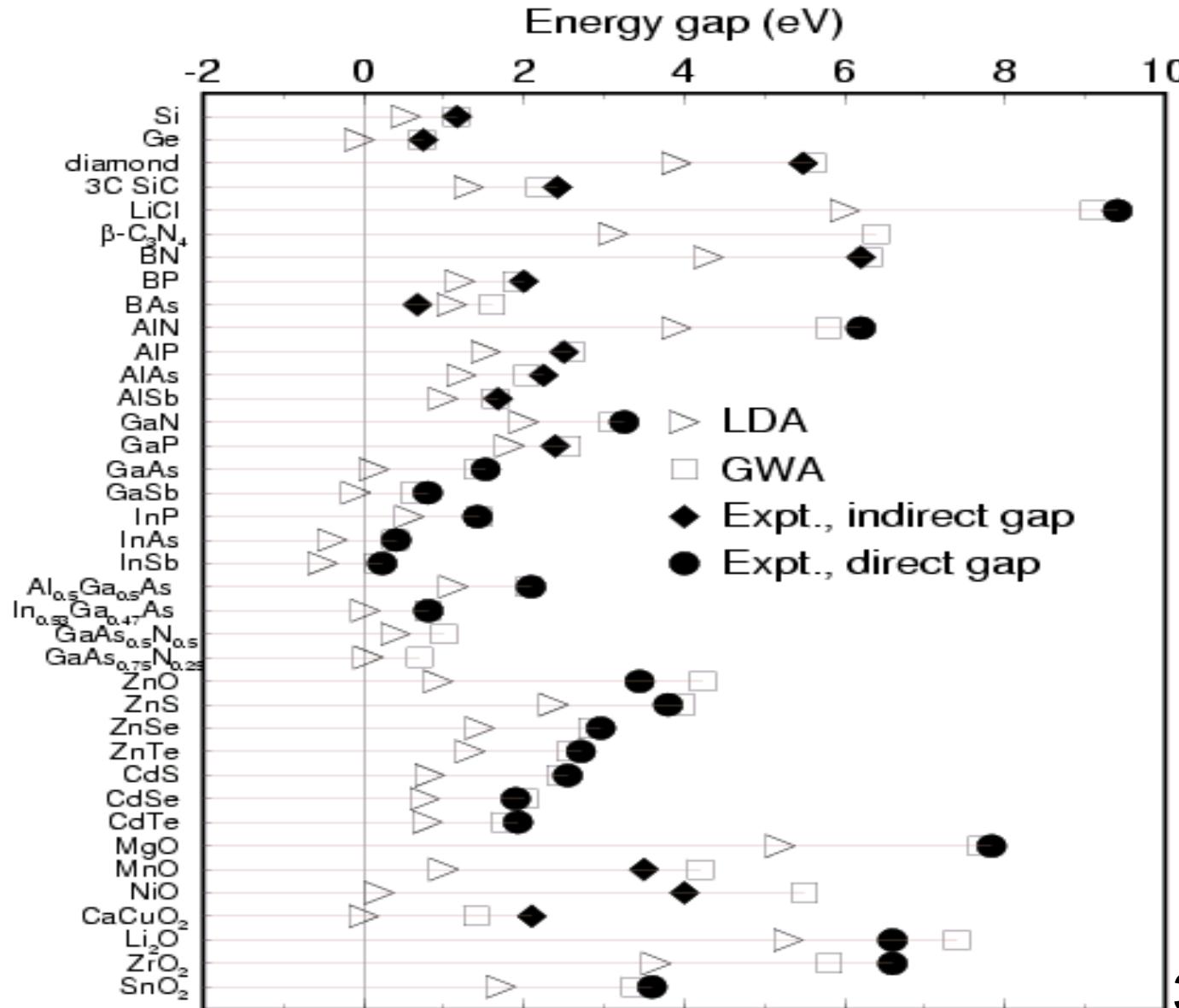
But...often works exceedingly well:  
depends on property and material  
of interest!

# DFT是基态理论

- 必须记住，DFT本质上是一个面向基态的理论。因此，采用LDA及GGA的DFT框架对于半导体的带隙的预测非常差。采用GW方法后，才得到了合理的结果(最近采用metaGGA泛函的DFT，对于绝缘体和半导体的带隙预言已GGA的计算量达到了GW的精度)。在激发态的计算中，采用LDA的DFT还不足以与半经验的、及修正的HF方法竞争(新近发展的TDDFT，及采用求解Bethe-Salpter Equation的方法可以很好地计算光吸收谱)。

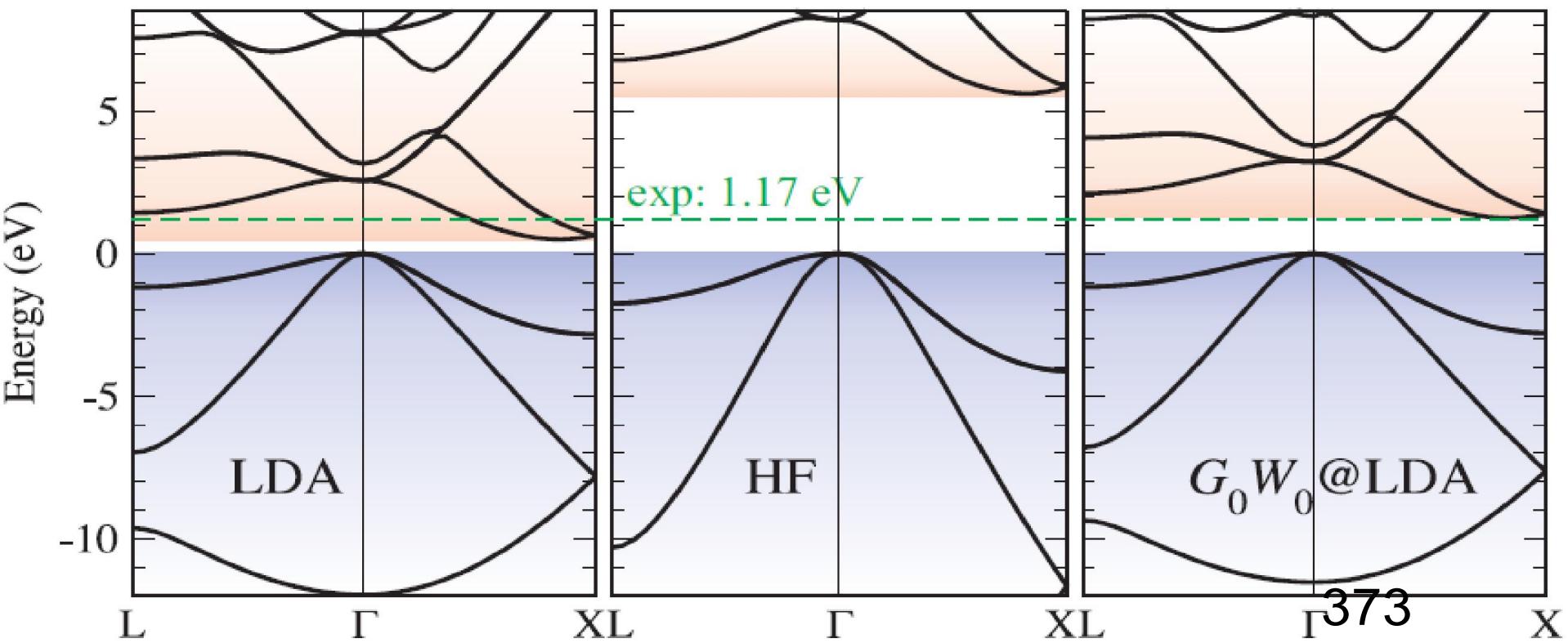
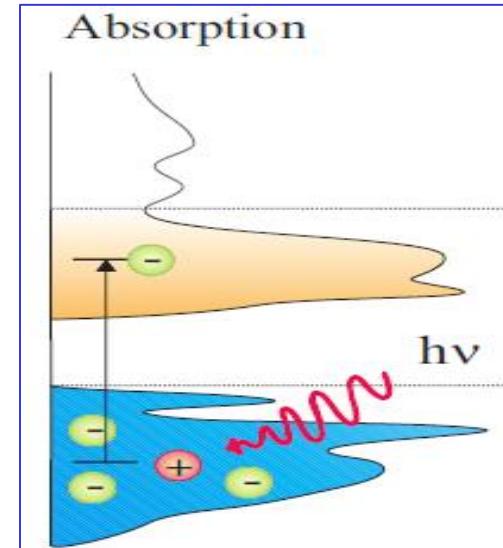
## The Local Density Approximation fails for excited state properties.

- Band gaps in insulators are 0.5 to 2 eV too small (dispersion often ok).

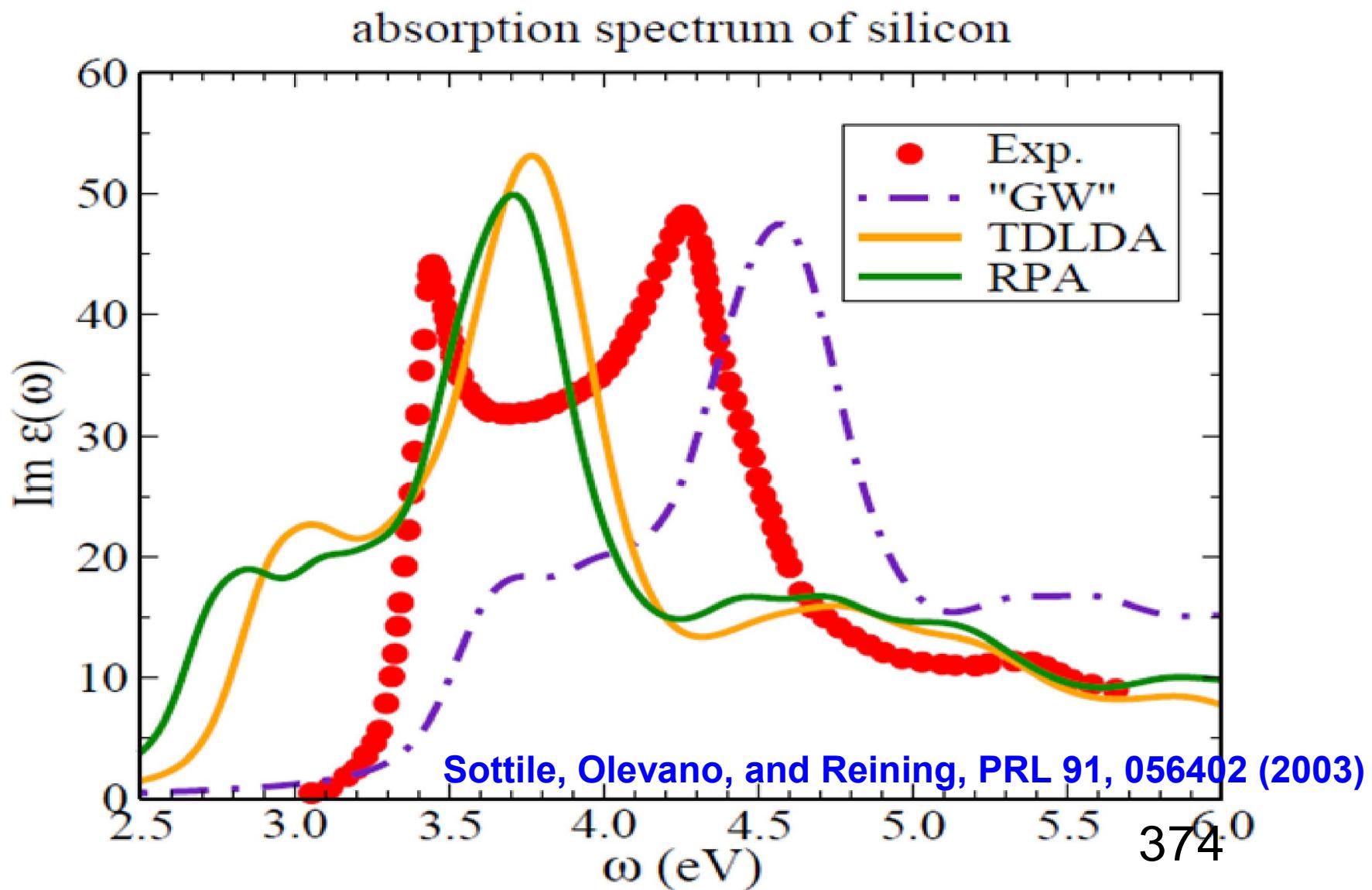


# 多体效应：激子，光吸收

能隙不是影响光吸收的唯一因数



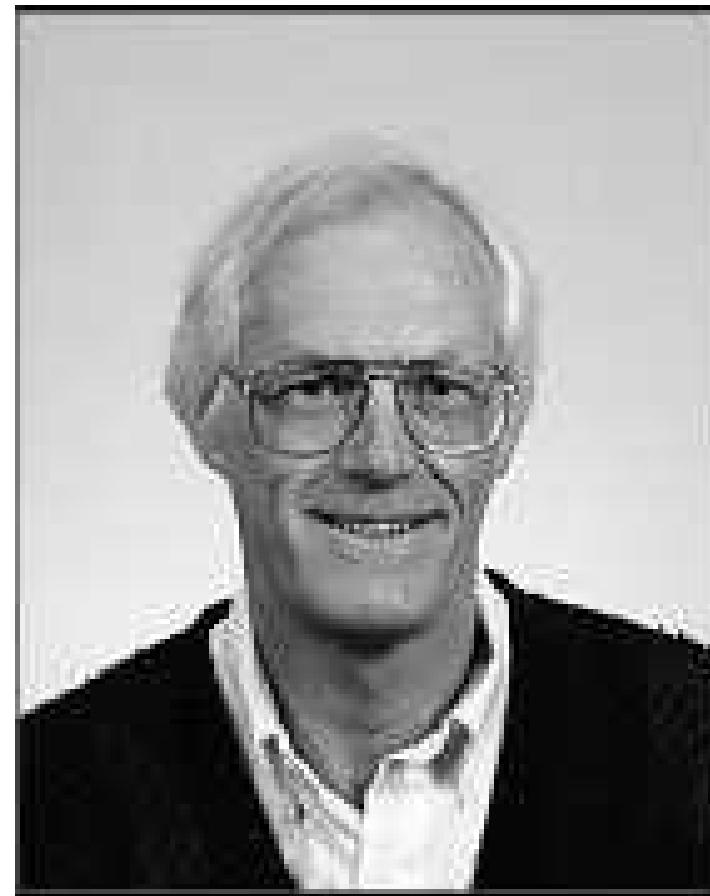
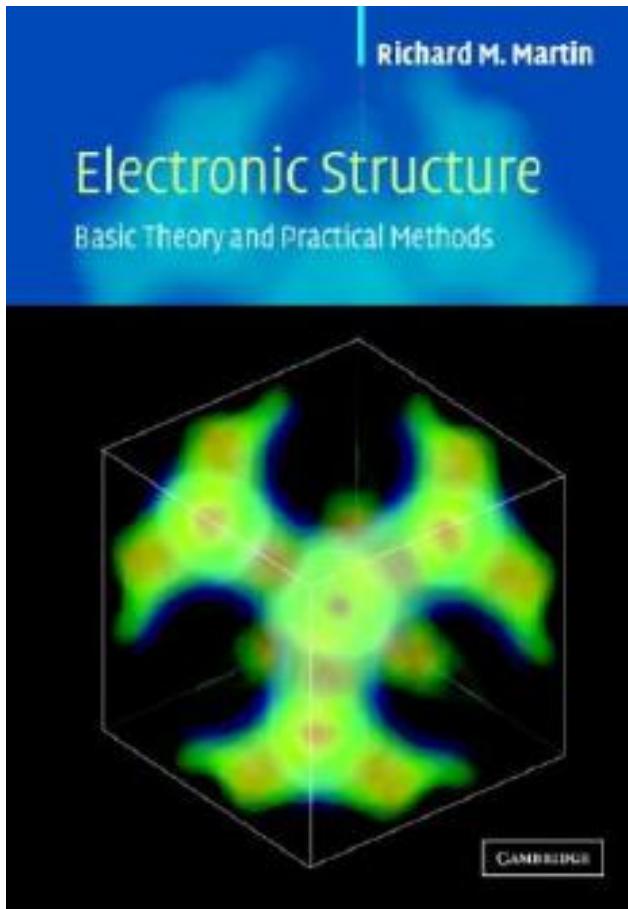
# 光吸收谱：GW计算与实验差距大



# 更多密度泛函理论：参考书目

1. J. Kohanoff, Electronic Structure Calculations for Solids and Molecules, Cambridge Univ. Press, 2006
2. **R. M. Martin, Electronic Structure, Cambridge Univ. Press, 2004**
3. R. G. Parr, W.T. Yang, Density Functional Theory of Atoms and Molecules, Oxford Univ. Press, 1989.
4. Topics in Current Chemistry, Density Functional Theory, Vol.180, 181, 182, 183, Springer-Verlag, Berlin, 1996.
5. 谢希德, 陆栋, 固体能带理论, 复旦大学出版社, 1998

# R. Martin, 2004



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University of Illinois, Urbana-Champaign Phys.  
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# DFT's Future

- Long range dispersion forces: van der Waals DFT
- Strongly correlated electrons: DMFT+DFT,  
Gutzwiller+DFT
- Exited states: GW+DFT, TDDFT, etc
- Linear Scaling:  $O(N)$
- Relativistic: RDFT
- Superconductivity:
- Nonequilibrium transport: DFT+NEGF
- Nonequilibrium transport: TDDFT+NEGF
- .....

# DFT理论的扩展

## 含时、相对论、流密度泛函等

部分资料在《密度泛函理论与应用讨论班》课程网站的资源项目下：文献.rar。

- 密度泛函的应用范围在迅速地不断扩大。这些扩展应用包括NMR和ESR谱，抗磁特性，极化率，相对论体系，非共线自旋体系，纳米尺度输运，超冷费米原子系统等等。
- 有许多的DFT扩展，包括但不限于：相对论的，时间相关的，有限温度的，依赖于流密度和电子密度的，等等。然而，DFT方法远没有成熟，还在不断的发展中。

# XC能的改进

## Adiabatic Connection for Strictly-Correlated Electrons

Zhen-Fei Liu and Kieron Burke

*Department of Chemistry, University of California, Irvine, California, 92697-2025, USA*

(Dated: July 17, 2009)

Modern density functional theory (DFT) calculations employ the Kohn-Sham (KS) system of non-interacting electrons as a reference, with all complications buried in the exchange-correlation energy ( $E_{XC}$ ). The adiabatic connection formula gives an exact expression for  $E_{XC}$ . We consider DFT calculations that instead employ a reference of strictly-correlated electrons. We define a “decorrelation energy” that relates this reference to the real system, and derive the corresponding adiabatic connection formula. We illustrate this theory in three situations, namely the uniform electron gas, Hooke’s atom, and the stretched hydrogen molecule. The adiabatic connection for strictly-correlated electrons provides an alternative perspective for understanding density functional theory and constructing approximate functionals.

arXiv:0907.2736v1

379

# XC能的改进

REVIEWS OF MODERN PHYSICS, VOLUME 80, JANUARY–MARCH 2008

## Orbital-dependent density functionals: Theory and applications

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(Published 2 January 2008)

This review provides a perspective on the use of orbital-dependent functionals, which is currently considered one of the most promising avenues in modern density-functional theory. The focus here is on four major themes: the motivation for orbital-dependent functionals in terms of limitations of semilocal functionals; the optimized effective potential as a rigorous approach to incorporating orbital-dependent functionals within the Kohn-Sham framework; the rationale behind and advantages and limitations of four popular classes of orbital-dependent functionals; and the use of orbital-dependent functionals for predicting excited-state properties. For each of these issues, both formal and practical aspects are assessed.

# XC能的Lieb-Oxford Bound

交换关联能满足 关系式  $E_{xc}[n] \geq \lambda E_x^{LDA}[n]$ ,

*Lieb-Oxford* :  $\lambda = 2.27$

有计算机模拟确定  $\lambda \approx 2$

一篇较近的文献：

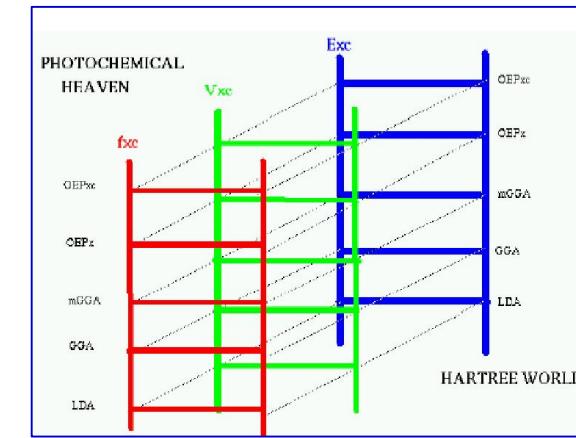
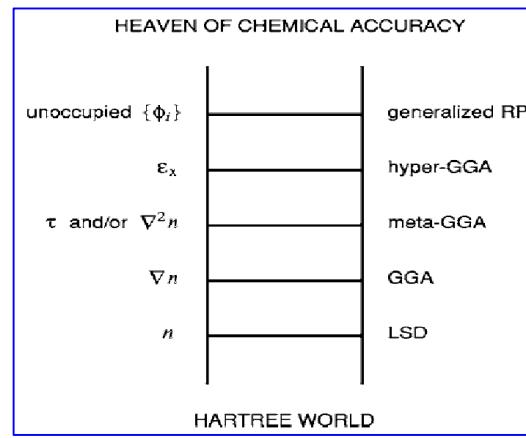
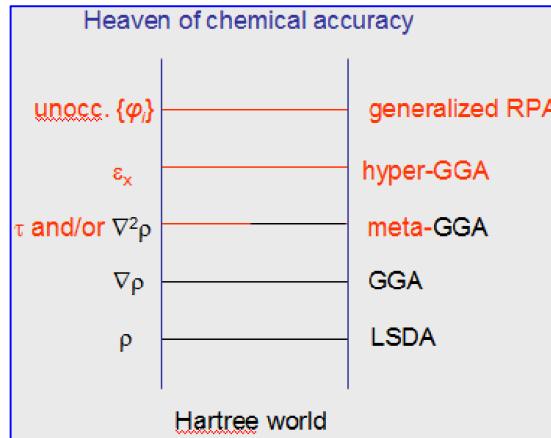
**Mariana M. Odashima, K. Capelle , Phys. Rev. A 79, p. 062515 (2009) : Non-empirical hyper-generalized-gradient functionals constructed from the Lieb-Oxford bound**

XC的不断改进：



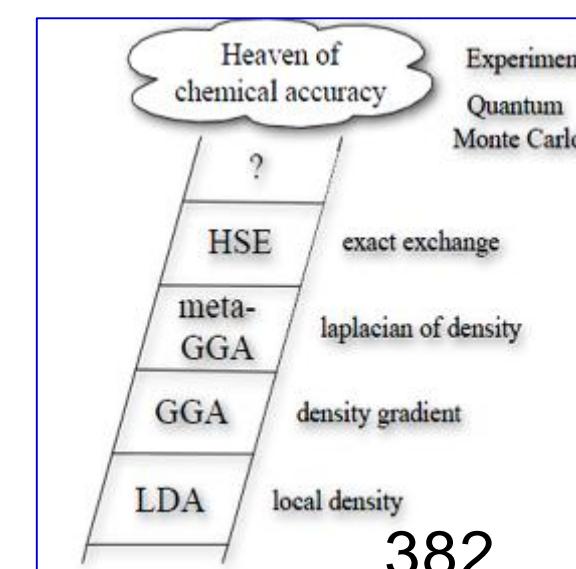
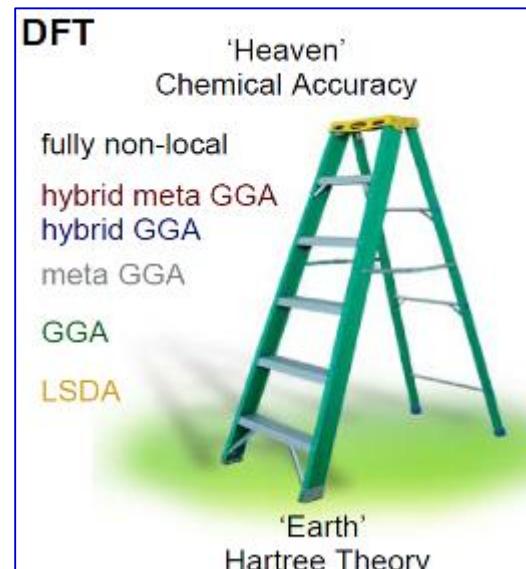
# 密度泛函的通天梯(Jacob's Ladder)

(J. P. Perdew and K. Schmidt, in: Density Functional Theory and its Application to Materials, V. Van Doren, C. Van Alsenoy, and P. Geerlings, Eds., AIP, Melville, New York, 2001.)

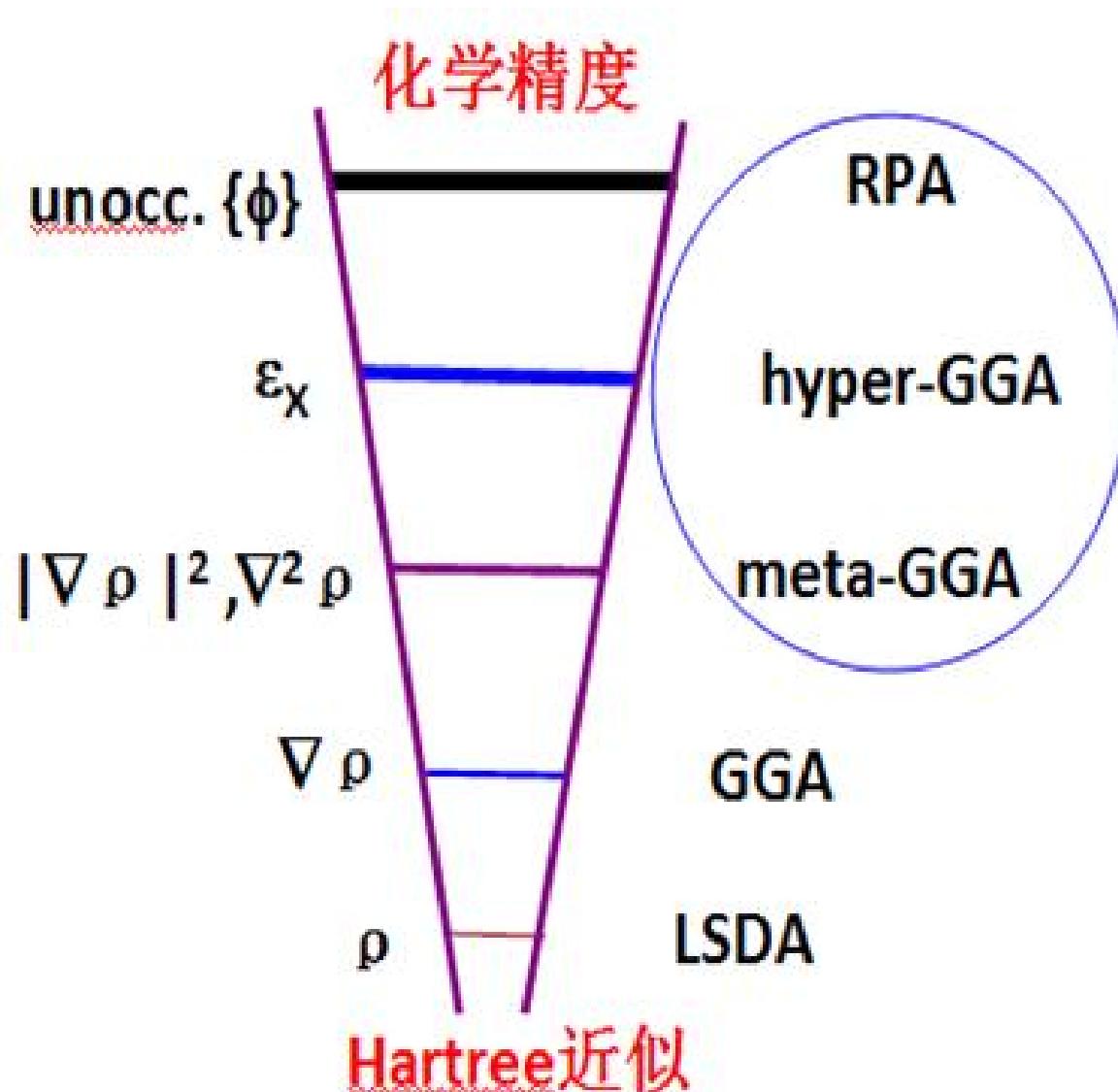


JACOBS LADDER OF DFT

QUANTUM MECHANICAL HEAVEN	
$H\Psi = E\Psi$	
$E(\rho, \nabla\rho, \nabla^2\rho) + HF$	Hyper-GGA
$E(\rho, \nabla\rho, \nabla^2\rho)$	Meta-GGA
$E(\rho, \nabla\rho)$	GGA
$E(\rho)$	LDA



# 密度泛函的通天梯(Jacob's Ladder)



- 加入新的成分, DMC等
- 精确交换+一阶梯度
- 含密度的二阶梯度
- 含密度的一阶梯度
- 局域密度, 不含梯度

# LibXC交换关联库

<http://www.tddft.org/programs/octopus/wiki/index.php/Libxc>

- Libxc is the library of exchange-correlation functionals.
- Libxc is written in C and has Fortran bindings. It is released under the LGPL license (v. 3.0).
- types of functionals: LDA, GGA, hybrids, mGGA (experimental) and LCA (local current appr) (not working)

# LDA, GGA 比较成熟

1	Symbol	#	Exc	Vxc	Fxc	Kxc
2	<hr/>					
3	LDA_X	1	OK	OK	OK	OK
4	<hr/>					
5	LDA_C_WIGNER	2	OK	OK	OK	OK
6	LDA_C_RPA	3	OK	OK	OK	OK
7	LDA_C_HL	4	OK	OK	OK	OK
8	LDA_C_GL	5	OK	OK	OK	OK
9	LDA_C_XALPHA	6	OK	OK	OK	
10	LDA_C_VWN	7	OK	OK	OK	OK
11	LDA_C_VWN_RPA	8	OK	OK	OK	OK
12	LDA_C_PZ	9	OK	OK	OK	OK
13	LDA_C_PZ_MOD	10	OK	OK	OK	OK
14	LDA_C_OB_PZ	11	OK	OK	OK	OK
15	LDA_C_PW	12	OK	OK	OK	OK
16	LDA_C_PW_MOD	13	OK	OK	OK	OK
17	LDA_C_OB_PW	14	OK	OK	OK	OK
18	LDA_TETER93	20	OK	OK	OK	OK
19	<hr/>					
20	LDA_X_2D	19	OK	OK	OK	OK
21	LDA_C_2D_AMGB	15	OK	OK	OK	OK
22	LDA_C_2D_PRM	16	OK	OK		
23	<hr/>					
24	LDA_C_1D_CSC	18				
25	<hr/>					
26	<hr/>					
27	GGA_X_PBE	101	OK	OK	OK	
28	GGA_X_PBE_R	102	OK	OK	OK	
29	GGA_X_B86	103	OK	OK	OK	
30	GGA_X_B86_R	104	OK	OK	OK	
31	GGA_X_B86_MGC	105	OK	OK	OK	
32	GGA_X_B88	106	OK	OK	OK	
33	GGA_X_G96	107	OK	OK	OK	
34	GGA_X_PW86	108	OK	OK	OK	

35	GGA_X_PW91	109	OK	OK	OK	
36	GGA_X_OPTX	110	OK	OK	OK	
37	GGA_X_DK87_R1	111	OK	OK	OK	
38	GGA_X_DK87_R2	112	OK	OK	OK	
39	GGA_X_LG93	113	OK	OK	OK	
40	GGA_X_FT97_A	114	OK	OK	OK	
41	GGA_X_FT97_B	115	OK	OK	OK	
42	GGA_X_PBE_SOL	116	OK	OK	OK	
43	GGA_X_RPBE	117	OK	OK	OK	
44	GGA_X_WC	118	OK	OK	OK	
45	GGA_X_mPW91	119	OK	OK	OK	
46	GGA_X_AM05	120	OK	OK	OK	
47	GGA_X_PBEA	121	OK	OK	OK	
48	GGA_X_MPBE	122	OK	OK	OK	
49	GGA_X_XPBE	123	OK	OK	OK	
50	<hr/>					
51	GGA_C_PBE	130	OK	OK	OK	
52	GGA_C_LYP	131				
53	GGA_C_P86	132				
54	GGA_C_PBE_SOL	133	OK	OK	OK	
55	GGA_C_PW91	134				
56	GGA_C_AM05	135				
57	GGA_C_XPBE	136	OK	OK	OK	
58	GGA_C_LM	137	OK	OK	OK	
59	<hr/>					
60	GGA_LB	160				
61	GGA_HCTH_93	161	OK	OK	OK	
62	GGA_HCTH_120	162	OK	OK	OK	
63	GGA_HCTH_147	163	OK	OK	OK	
64	GGA_HCTH_407	164	OK	OK	OK	
65	GGA_EDF1	165				
66	GGA_XLYP	166				
67	GGA_XC_B97	167	OK	OK	OK	
68	GGA_XC_B97_1	168	OK	OK	OK	
69	GGA_XC_B97_2	169	OK	OK	OK	
70	GGA_XC_B97_D	170	OK	OK	OK	
71	GGA_XC_B97_K	171	OK	OK	OK	
72	GGA_XC_B97_3	172	OK	OK	OK	

# Hyb-GGA, Meta-GGA待发展和验证

在Octopus - v3.2中已有许多新的XC泛函的实现，包括能很好地计算半导体和绝缘体带隙的修正Becke—Johnson类XC(MBJLDA).  
metaGGA的计算量与LDA相当,计算精度与GW相当

~~mgga\_x\_lta);  
mgga\_x\_tpss);  
mgga\_x\_m06);  
mgga\_x\_gvt4);  
mgga\_x\_tau\_hcth);  
mgga\_x\_br89);  
mgga\_x\_bj06);  
mgga\_x\_tb09);  
mgga\_x\_rpp09);  
mgga\_c\_tpss);  
mgga\_c\_vsxc);~~

Solid	LDA	MBJLDA	HSE	$G_0W_0$	GW	Expt.
Ne (A1)	11.42	22.72		19.59 <sup>e</sup>	22.1 <sup>g</sup>	21.70
Ar (A1)	8.16	13.91	10.34 <sup>a</sup>	13.28 <sup>e</sup>	14.9 <sup>g</sup>	14.20
Kr (A1)	6.76	10.83				11.6
Xe (A1)	5.78	8.52				9.8
C (A4)	4.11	4.93	5.49 <sup>b</sup>	5.50 <sup>e</sup>	6.18 <sup>g</sup>	5.48
Si (A4)	0.47	1.17	1.28 <sup>b</sup>	1.12 <sup>e</sup>	1.41 <sup>g</sup>	1.17
Ge (A4)	0.00	0.85	0.83 <sup>b</sup>	0.66 <sup>f</sup>	0.95 <sup>g</sup>	0.74
LiF (B1)	8.94	12.94		13.27 <sup>e</sup>	15.9 <sup>g</sup>	14.20
LiCl (B1)	6.06	8.64				9.4
MgO (B1)	4.70	7.17	6.67 <sup>b</sup>	7.25 <sup>e</sup>	9.16 <sup>g</sup>	7.83
ScN (B1)	-0.14	0.90		0.95 <sup>f</sup>	1.4 <sup>h</sup>	~0.9
MnO (B1)	0.76	2.95	2.8 <sup>c</sup>		3.5 <sup>i</sup>	3.9 ± 0.4
FeO (B1)	-0.35	1.82	2.2 <sup>c</sup>			2.4
NiO (B1)	0.42	4.16	4.2 <sup>c</sup>	1.1 <sup>f</sup>	4.8 <sup>i</sup>	4.0, 4.3
SiC (B3)	1.35	2.28	2.40 <sup>b</sup>	2.27 <sup>e</sup>	2.88 <sup>g</sup>	2.40
BN (B3)	4.39	5.85	5.99 <sup>b</sup>	6.10 <sup>e</sup>	7.14 <sup>g</sup>	~6.25
GaN (B3)	1.63	2.81	3.14 <sup>b</sup>	2.80 <sup>e</sup>	3.82 <sup>g</sup>	3.20
GaAs (B3)	0.30	1.64	1.12 <sup>b</sup>	1.30 <sup>e</sup>	1.85 <sup>g</sup>	1.52
AlP (B3)	1.46	2.32	2.51 <sup>b</sup>	2.44 <sup>e</sup>	2.90 <sup>g</sup>	2.45
ZnS (B3)	1.84	3.66	3.49 <sup>b</sup>	3.29 <sup>e</sup>	4.15 <sup>g</sup>	3.91
CdS (B3)	0.86	2.66	2.25 <sup>b</sup>	2.06 <sup>e</sup>	2.87 <sup>g</sup>	2.42
AlN (B4)	4.17	5.55	5.81 <sup>b</sup>	5.83 <sup>f</sup>		6.28
ZnO (B4)	0.75	2.68	2.49 <sup>d</sup>	2.51 <sup>f</sup>	3.3 <sup>g</sup>	3.44

# 杂化泛函(Hybrid functional)简介

[http://en.wikipedia.org/wiki/Hybrid\\_functional](http://en.wikipedia.org/wiki/Hybrid_functional)

## Method [edit]

A hybrid exchange-correlation functional is usually constructed as a [linear combination](#) of the Hartree–Fock exact exchange functional,  $E_x^{\text{HF}}$ :

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j} \int \int \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2,$$

and any number of exchange and correlation explicit density functionals. The parameters determining the weight of each individual functional are typically specified by fitting the functional's predictions to experimental or accurately calculated thermochemical data.

## B3LYP [edit]

For example, the popular B3LYP (Becke, three-parameter, Lee-Yang-Parr)<sup>[3][4]</sup> exchange-correlation functional is:

$$E_{xc}^{\text{B3LYP}} = E_x^{\text{LDA}} + a_0(E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_x(E_x^{\text{GGA}} - E_x^{\text{LDA}}) + E_c^{\text{LDA}} + a_c(E_c^{\text{GGA}} - E_c^{\text{LDA}}),$$

where  $a_0 = 0.20$ ,  $a_x = 0.72$ , and  $a_c = 0.81$ .  $E_x^{\text{GGA}}$  and  $E_c^{\text{GGA}}$  are [generalized gradient approximations](#): the Becke 88 exchange functional<sup>[5]</sup> and the correlation functional of Lee, Yang and Parr<sup>[6]</sup> for B3LYP, and  $E_c^{\text{LDA}}$  is the VWN [local-density approximation](#) to the correlation functional.<sup>[7]</sup>

Contrary to popular belief, B3LYP was not fit to experimental data. The three parameters defining B3LYP have been taken without modification from Becke's original fitting of the analogous B3PW91 functional to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies.<sup>[8]</sup>

## HSE [edit]

The HSE (Heyd-Scuseria-Ernzerhof)<sup>[9]</sup> exchange-correlation functional uses an [error function](#) screened [Coulomb potential](#) to calculate the exchange portion of the energy in order to improve computational efficiency, especially for metallic systems.

$$E_{xc}^{\omega\text{PBEh}} = a E_x^{\text{HF},\text{SR}}(\omega) + (1-a) E_x^{\text{PBE},\text{SR}}(\omega) + E_x^{\text{PBE},\text{LR}}(\omega) + E_c^{\text{PBE}},$$

where  $a$  is the mixing parameter and  $\omega$  is an adjustable parameter controlling the short-rangeness of the interaction. Standard values of  $a = \frac{1}{4}$  and

$\omega = 0.2$  (usually referred to as HSE06) have been shown to give good results for most of systems. The HSE exchange-correlation functional degenerates to the PBE0 hybrid functional for  $\omega = 0$ .  $E_x^{\text{HF},\text{SR}}(\omega)$  is the short range Hartree–Fock exact exchange functional,  $E_x^{\text{PBE},\text{SR}}(\omega)$  and  $E_x^{\text{PBE},\text{LR}}(\omega)$  are the short and long range components of the PBE exchange functional, and  $E_c^{\text{PBE}}(\omega)$  is the PBE<sup>[10]</sup> correlation functional.

# 关于XC的使用注意事项

需要仔细阅读文献，确保正确使用。例如：

- 修正Becke—Johnson类XC对绝缘体及半导体的能隙计算很准确，但不能用于优化结构。
- 有部分杂化泛函算分子等较好，但用于金属不好等。
- 计算层间化合物，需要考虑范德瓦尔斯泛函。

。 。 。

例如：科学网 - 博客 - 高斯计算方法的选择，[经验需要积累]  
<http://blog.science.net.cn/blog-346982-820651.html>

非双杂化泛函的最佳选择：

计算碳团簇用B3LYP

计算硼团簇用TPSS

计算双核金属用PBE、BP86，勿用杂化(see JCTC,8,908)

计算NMR用KT2, M06-L, VSXC, OPBE, PBE0

计算普通价层垂直激发用PBE0（误差约在0.25eV），M06-2X也凑合

计算电荷转移、里德堡垂直激发，以及各种绝热激发能用wB97XD、CAM-B3LYP、M06-2X

计算极化率、超极化率追求稳妥用PBE0，追求精度用CAM-B3LYP、HCTC(AC)

计算双光子吸收截面用CAM-B3LYP

# CASTEP软件建议的XC泛函选择：

- LDA: 共价系统, 简单金属
- DFT+U: Mott绝缘体, 强关联材料
- GGA: 分子, 氢键材料, 密度变化大的d态及f态, 大多数磁性材料, 特殊的金属
- Non-local hybrids and sX: 带隙, 特殊的磁性材料
- van der Waals: 层状材料等

对VASP软件, 有类似建议, 需要经验积累。

# DFT理论的改进：强相互作用体系

Density functional theory for strongly interacting electrons

Paola Gori-Giorgi,<sup>1,2</sup> Michael Seidl,<sup>3</sup> and G. Vignale<sup>4</sup>

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<sup>3</sup>Institute of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany

<sup>4</sup>Department of Physics and Astronomy, University of Missouri, Columbia, Missouri 65211, USA

(Dated: August 10, 2009)

We present an alternative to the Kohn-Sham formulation of density functional theory for the ground-state properties of strongly interacting electronic systems. The idea is to start from the limit of zero kinetic energy and systematically expand the universal energy functional of the density in powers of a “coupling constant” that controls the magnitude of the kinetic energy. The problem of minimizing the energy is reduced to the solution of a strictly correlated electron problem in the presence of an effective potential, which plays in our theory the same role that the Kohn-Sham potential plays in the traditional formulation. We discuss several schemes for approximating the energy functional, and report preliminary results for low-density quantum dots.

<http://cn.arxiv.org/abs/0908.0669v2>

# V-可表示问题

## An Interpretation of Naïve Density Functional Theory

Paul E. Lammert\*

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Pennsylvania State University  
University Park, PA 16802-6300*  
(Dated: July 29, 2009)

A coarse-grained quantum density functional theory is shown to model “naïve” DFT, meaning that all densities are (ensemble)-V-representable, the intrinsic (internal) energy functional and the external potential are continuous functions of the density and the external potential is the functional derivative of the intrinsic energy, in appropriate senses. These properties are proven with explanation of the “appropriate senses.” This coarse-grained interpretation of naïve DFT might be a suitable mathematical foundation for actual Kohn-Sham-based practice.

<http://cn.arxiv.org/abs/0908.1263v1>

# 交换关联泛函导数不连续性的改进

## The derivative discontinuity of the exchange–correlation functional

Cite this: *Phys. Chem. Chem. Phys.*,

2014, 16, 14378

Paula Mori-Sánchez<sup>\*a</sup> and Aron J. Cohen<sup>\*b</sup>

Piecewise Linearity of Approximate Density Functionals Revisited: Implications for Frontier Orbital Energies

Phys. Rev. Lett. **110**, 126403 – Published 19 March 2013

Eli Kraisler and Leeor Kronik

PRL **110**, 033002 (2013)

PHYSICAL REVIEW LETTERS

week end  
18 JANUAR'

## Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction

Jeng-Da Chai<sup>1,2,\*</sup> and Po-Ta Chen<sup>1</sup>

<sup>1</sup>Department of Physics, National Taiwan University, Taipei 10617, Taiwan

# LSDA+U

## Anisotropy and Magnetism in the LSDA+U Method

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Klaus Koepernik

*IFW Dresden, P O Box 270116, D-01171 Dresden, Germany*

(Dated: October 28, 2008)

Consequences of anisotropy (variation of orbital occupation) and magnetism, and their coupling, are analyzed for LSDA+U functionals, both the commonly used ones as well as less commonly applied functionals. After reviewing and extending some earlier observations for an isotropic interaction, the anisotropies are examined more fully and related to use with the local density (LDA) or local spin density (LSDA) approximations. The total energies of all possible integer configurations of an open  $f$  shell are presented for three functionals, where some differences are found to be dramatic. Differences in how the commonly used “around mean field” (AMF) and “fully localized limit” (FLL) functionals perform are traced to such differences. The LSDA+U interaction term, applied self-consistently, usually enhances spin magnetic moments and orbital polarization, and the double-counting terms of both functionals provide an opposing, moderating tendency (“suppressing the magnetic moment”). The AMF double counting term gives magnetic states a significantly larger energy penalty than does the FLL counterpart.

# DFT+Van der Waals

PRL 102, 206411 (2009)

PHYSICAL REVIEW LETTERS

## *Ab initio Calculation of van der Waals Bonded Molecular Crystals*

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(Received 23 March 2009; published 22 May 2009)

Intermolecular interactions in the van der Waals bonded benzene crystal are studied from first principles, by combining exact exchange energies with correlation energies defined by the adiabatic connection fluctuation-dissipation theorem, within the random phase approximation. Correlation energies are evaluated using an iterative procedure to compute the eigenvalues of dielectric matrices, which eliminates the computation of unoccupied electronic states. Our results for the structural and binding properties of solid benzene are in very good agreement with experimental results and show that the framework adopted here is a very promising one to investigate molecular crystals and other condensed systems bound by dispersion forces.

# 超导的DFT

## *Ab initio theory of superconductivity. I. Density functional formalism and approximate functionals*

M. Lüders,<sup>1,2</sup> M. A. L. Marques,<sup>2,3</sup> N. N. Lathiotakis,<sup>2,3</sup> A. Floris,<sup>3,4</sup> G. Profeta,<sup>5</sup> L. Fast,<sup>2,6</sup> A. Continenza,<sup>5</sup> S. Massidda,<sup>4,\*</sup> and E. K. U. Gross<sup>2,3</sup>

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<sup>2</sup>Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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<sup>4</sup>INFM SLACS, Sardinian Laboratory for Computational Materials Science and Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari, S. P. Monserrato-Sestu km 0.700, I-09124 Monserrato (Cagliari), Italy

<sup>5</sup>CASTI—Istituto Nazionale Fisica della Materia (INFM) and Dipartimento di Fisica, Università degli studi dell’Aquila, I-67010 Coppito (L’Aquila) Italy

<sup>6</sup>SP Swedish National Testing and Research Institute, P. O. Box 857, S-501 15 Borås, Sweden

(Received 1 June 2004; revised manuscript received 25 February 2005; published 29 July 2005)

An approach to the description of superconductors in thermal equilibrium is developed within a formally exact density functional framework. The theory is formulated in terms of three “densities:” the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear  $N$ -body density matrix. The electron density and the order parameter are determined by Kohn-Sham equations that resemble the Bogoliubov–de Gennes equations. The nuclear density matrix follows from a Schrödinger equation with an effective  $N$ -body interaction. These equations are coupled to each other via exchange-correlation potentials which are universal functionals of the three densities. Approximations of these exchange-correlation functionals are derived using the diagrammatic techniques of many-body perturbation theory. The bare Coulomb repulsion between the electrons and the electron-phonon interaction enter this perturbative treatment on the same footing. In this way, a truly *ab initio* description is achieved which does not contain any empirical parameters.

# DFT+DMFT

Rev. Mod. Phys. 78, 865 (2006)

## Electronic Structure Calculations with Dynamical Mean-Field Theory: A Spectral Density Functional Approach

G. Kotliar<sup>1,6</sup>, S. Y. Savrasov<sup>2</sup>, K. Haule<sup>1,4</sup>, V. S. Oudovenko<sup>1,3</sup>, O. Parcollet<sup>5</sup> and C.A. Marianetti<sup>1</sup>

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<sup>4</sup>*Jozef Stefan Institute, SI-1000 Ljubljana, Slovenia*

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<sup>6</sup>*Centre de Physique Theorique, Ecole Polytechnique 91128 Palaiseau Cedex, France*

(Dated: June 9, 2006)

We present a review of the basic ideas and techniques of the spectral density functional theory which are currently used in electronic structure calculations of strongly-correlated materials where the one-electron description breaks down. We illustrate the method with several examples where interactions play a dominant role: systems near metal-insulator transition, systems near volume collapse transition, and systems with local moments.

# DFT+Gutzwiller变换

PRL 101, 066403 (2008)

PHYSICAL REVIEW LETTERS

week 8 AUGU

## Phase Diagram of $\text{Na}_x\text{CoO}_2$ Studied By Gutzwiller Density-Functional Theory

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Beijing 100190, China*

(Received 30 January 2008; published 6 August 2008)

The ground state of  $\text{Na}_x\text{CoO}_2$  ( $0.0 < x < 1.0$ ) is studied by the local density approximation plus the Gutzwiller approach, where charge transfer and orbital fluctuations are all self-consistently treated *ab initio*. In contrast to previous studies, which are parameter-dependent, we characterized the phase diagram as (1) Stoner magnetic metal for  $x > 0.6$  due to  $a_{1g}$  van Hove singularity near the band top, (2) correlated nonmagnetic metal without  $e_g'$  pockets for  $0.3 < x < 0.6$ , and (3)  $e_g'$  pockets appear for  $x < 0.3$ , and additional magnetic instability is revealed. Experimental quasiparticle properties are well explained, and the  $a_{1g}$ - $e_g'$  anticrossing is attributed to spin-orbital coupling.

# DFT+DMRG or TN

- S.Sharma, G.Kin-Lic Chan, K.Sivalingam, F.Neese, Low-energy spectrum of iron-sulfur clusters directly from many-particle quantum mechanics, arXiv:1408.5080v1 【nature chemistry 2014】
- 把DFT与DMRG或张量网格(TN)结合，低能态的计算可达到化学精度。

# DFT与SO耦合

## On-site approximation for spin-orbit coupling in LCAO density functional methods

L Fernández-Seivane,<sup>1,\*</sup> M A Oliveira,<sup>2</sup> S Sanvito<sup>2</sup> and J Ferrer<sup>1</sup>

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<sup>2</sup> Department of Physics, Trinity College, Dublin 2, Ireland

E-mail: \* quevedin@condmat.uniovi.es

**Abstract.** We propose a computational method that simplifies drastically the inclusion of spin-orbit interaction in density functional theory when implemented over localised atomic orbital basis sets. Our method is based on a well-known procedure for obtaining pseudopotentials from atomic relativistic *ab initio* calculations and on an on-site approximation for the spin-orbit matrix elements. We have implemented the technique in the SIESTA[34] code, and show that it provides accurate results for the overall band structure and splittings of group IV and III-IV semiconductors as well as for 5d metals.

<http://arxiv.org/abs/cond-mat/0601093v399>

# DFT与非共线磁性

PHYSICAL REVIEW B 75, 134408 (2007)

## Potential in spin-density-functional theory of noncollinear magnetism determined by the many-electron ground state

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(Received 29 September 2006; revised manuscript received 8 February 2007; published 11 April 2007)

Since spin-density-functional theory was first proposed, but also recently, examples were constructed to show that a spin potential may share its ground state with other spin potentials. In fact, for collinear magnetic fields and systems with fixed magnetization, the mapping between potentials and ground states is invertible, provided the magnetization is not saturated and that spin potentials are determined within a spin constant. We complete the proof that the mapping is invertible also for noncollinear magnetic fields and systems with more than one electron. We then discuss the noncollinear exchange and correlation energy functional in the local-spin-density approximation and suggest improvements.

# 相对论的流密度泛函

THE JOURNAL OF CHEMICAL PHYSICS 127, 174111 (2007)

## Relativistic two-component formulation of time-dependent current-density functional theory: Application to the linear response of solids

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(Received 23 February 2007; accepted 14 August 2007; published online 7 November 2007)

In this paper we derive the relativistic two-component formulation of time-dependent current-density-functional theory. To arrive at a two-component current-density formulation we apply a Foldy-Wouthuysen-type transformation to the time-dependent four-component Dirac-Kohn-Sham equations of relativistic density-functional theory. The two-component Hamiltonian is obtained as a regular expansion which is gauge invariant at each order of approximation, and to zeroth order it represents the time-dependent version of the relativistic zeroth order regular Hamiltonian obtained by van Lenthe *et al.*, for the ground state [J. Chem. Phys. **99**, 4597 (1993)]. The corresponding zeroth order regular expression for the density is unchanged,

# 时间相关的流密度泛函

Pina Romaniello,

Time-Dependent Current-Density-Functional Theory for Metals,

Proefschrift Rijksuniversiteit Groningen.

© P. Romaniello, 2006

**PhD thesis 2006**

# 开放量子体系的时间相关DFT

## Time-Dependent Density Functional Theory for Open Quantum Systems using Closed Systems

Joel Yuen-Zhou,<sup>1</sup> César Rodríguez-Rosario,<sup>1</sup> and Alán Aspuru-Guzik<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, 02138, Cambridge, MA* <sup>\*</sup>

Time-Dependent Density Functional Theory has recently been extended to the domain of open quantum systems by Car, Gebauer, and Burke [Phys. Rev. Lett. **94**, 146805 (2005)]. The authors suggested a Kohn-Sham scheme that exploits an open non-interacting quantum system to reproduce the particle density of an original open interacting system. In this letter, we develop a construction where we prove the existence of their scheme and also extend it to the non-Markovian regime. By taking the appropriate limit in our proof, we propose an interesting scheme where the auxiliary Kohn-Sham system is taken to be both *closed* and *non-interacting*. Finally, we discuss this proposal in the context of previous work.

PACS numbers: 31.15ec, 71.15Mb, 02.70.-c, 71.15.-m, 31.10+z

# DFT+NEGF

Density functional method for nonequilibrium electron transport

J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 121104R(2001).

J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 245407(2001).

# NEGF+TDDFT方法

J. Phys.: Condens. Matter 20, 083203 (2008)

Density functional calculations of nanoscale conductance

Max Koentopp and Connie Chang

Kieron Burke

Roberto Car

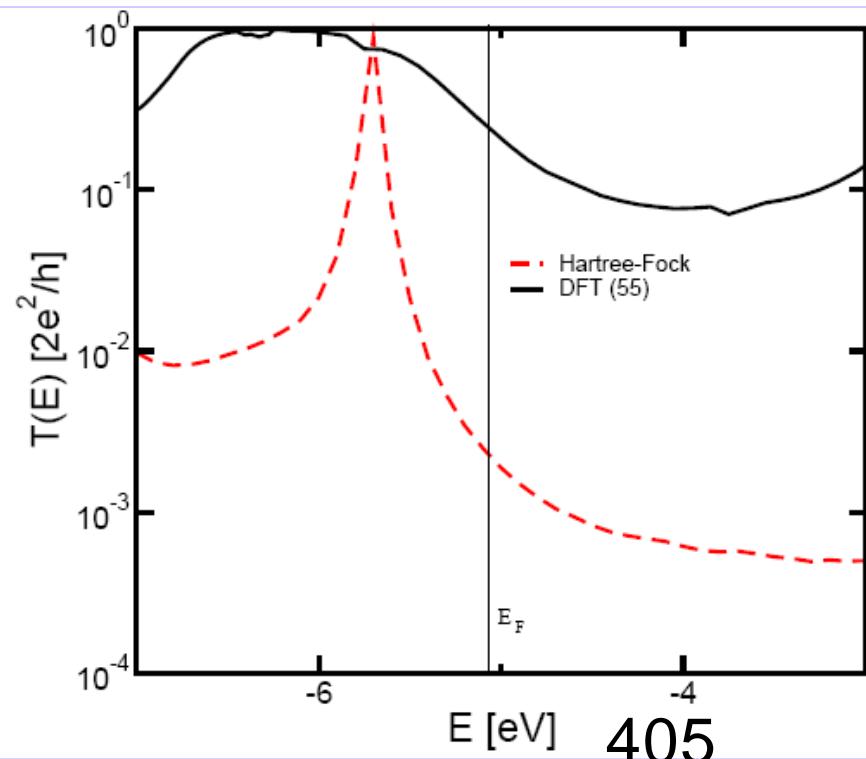
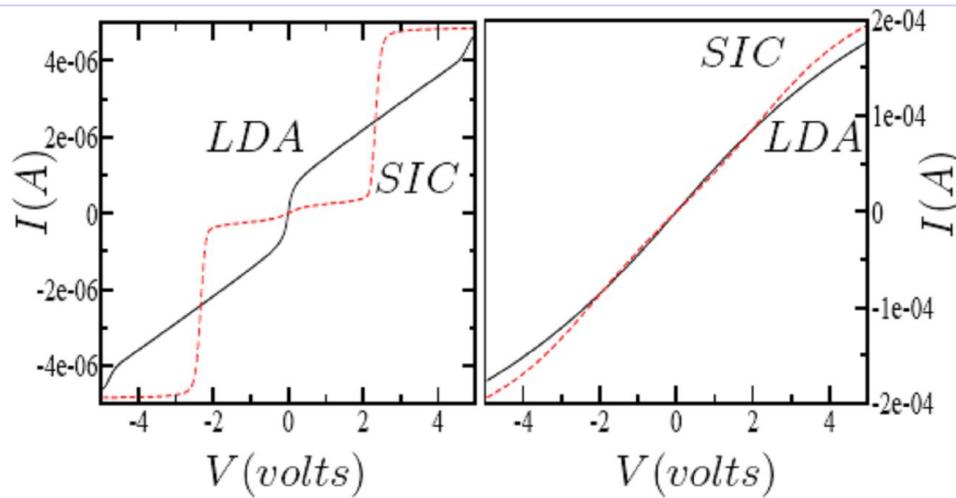


FIG. 11: Current of a single energy level coupled to two metallic leads as a function of bias. Left figure corresponds to the case of weak coupling and right figure corresponds to the case of strong coupling. Solid lines are results for LDA and the dotted lines are results using self-interaction corrected LDA (LDA-SIC). From Ref. [68].

# TB-LMTO+NEGF

PHYSICAL REVIEW B 71, 195422 (2005)

## *Ab initio* tight-binding LMTO method for nonequilibrium electron transport in nanosystems

Sergey V. Faleev,<sup>1,\*</sup> François Léonard,<sup>1</sup> Derek A. Stewart,<sup>1,†</sup> and Mark van Schilfgaarde<sup>2</sup>

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<sup>2</sup>*Department of Chemical and Materials Engineering, Arizona State University, Tempe, Arizona 85284, USA*

(Received 4 January 2005; revised manuscript received 25 February 2005; published 31 May 2005)

We present an *ab initio* method for calculation of the electronic structure and electronic transport of nanoscale systems coupled to electrodes with applied voltage bias. The method is based on the local density approximation of density functional theory and implemented in the framework of the tight-binding linear muffin-tin orbital approach in its atomic sphere approximation. A fully atomistic description of the electrodes and the nanosystem is used, and the self-consistent charge and electrostatic potential for the system under applied bias is calculated using the nonequilibrium Green's function (NEGF) approach. General expressions for the lesser Green's function and transmission coefficient obtained within NEGF theory are rewritten using auxiliary Green's functions that are defined by the inverse of the short-ranged structural constants. This reformulation of the theory with auxiliary Green's functions allows the use of very effective and well-developed tight-binding techniques. The method is applied to three systems: a single benzene di-thiol molecule coupled to (111) gold electrodes, a single gold atom coupled to (100) gold electrodes, and a single platinum

# 非弹性输运的DFT计算

Inelastic transport theory from first-principles:  
methodology and applications for nanoscale devices

Thomas Frederiksen,\* Magnus Paulsson, Mads Brandbyge, and Antti-Pekka Jauho

Phys. Rev. B 75,  
205413 (2007)

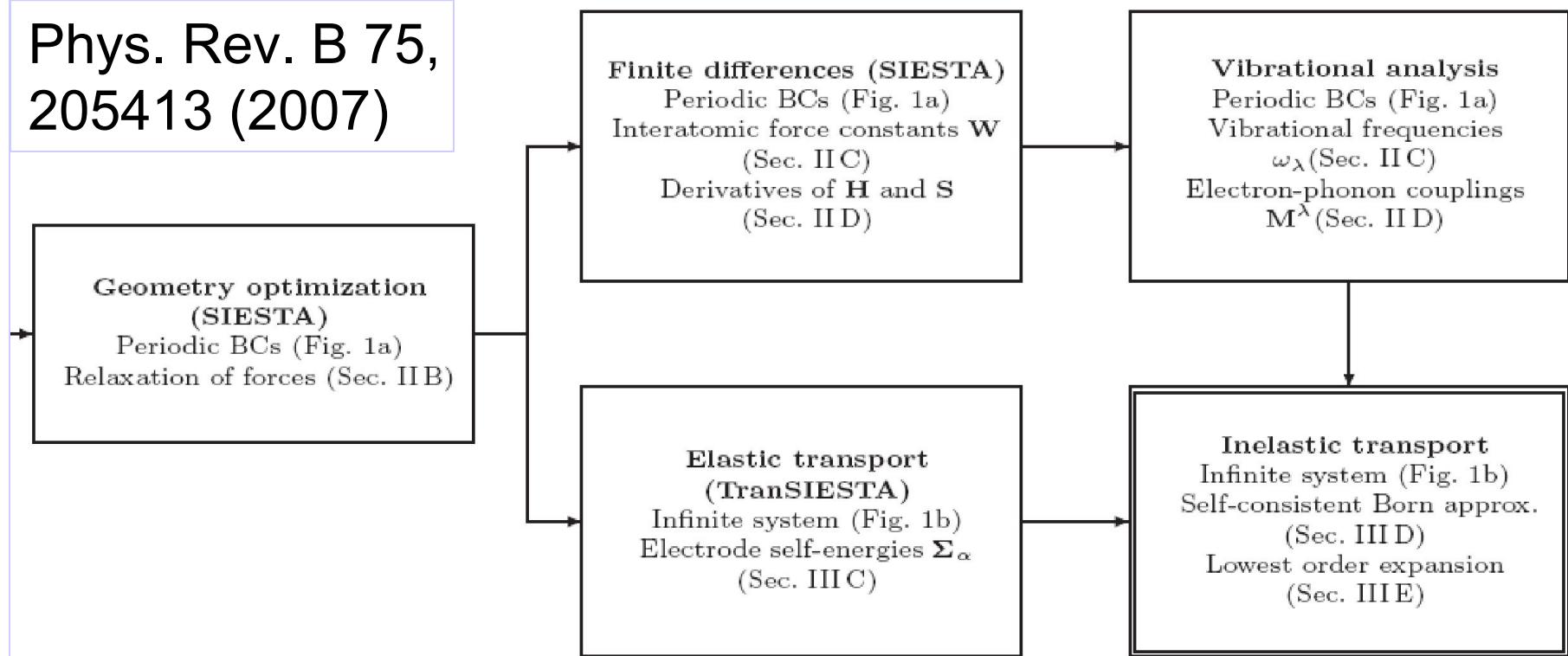
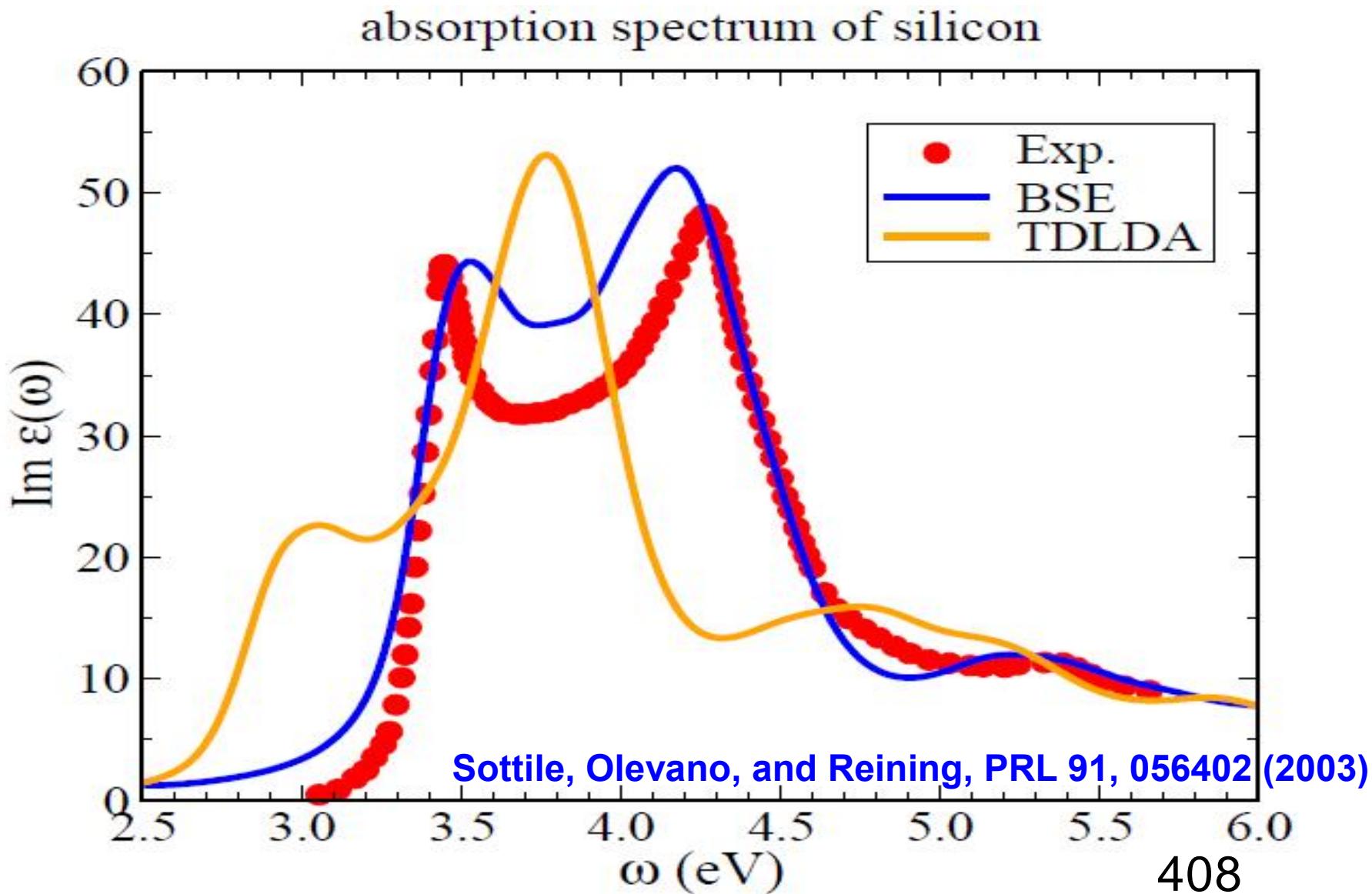


FIG. 2: Flow diagram for the complete analysis of the inelastic transport properties of an atomic structure

# 光吸收的计算改进：Bethe-Salpter方程



# 多电子体系的约化密度矩阵 泛函理论(rDMFT)

Is reduced-density-matrix functional theory a suitable vehicle to import explicit correlations into density-functional calculations?  
By Peter E. Bloechl etc. <http://arxiv.org/abs/1107.4780v1>

- T. Gilbert Phys. Rev. B 12, 2111 (1975)
- A. Muller, Phys. Lett. A 105, 446 (1984);
- S. Goedecker, C. J. Umrigar, Phys. Rev. Lett. 81, 866 (1998)
- M. A. Buijse, E. J. Baerends, Mol. Phys. 100, 401 (2002)
- S. Sharma et al, PRB, 78, 201103(R) (2008)
- Piris, et al, JCP 134, 164102 (2011)

rDMFT is implemented in the Elk code: <http://elk.sourceforge.net/>

已经有文章推广到含时情形, EPL, 92 (2010) 23001, 其它情形?

# 有限温度约化密度矩阵泛函理论(rDMFT)

Reduced density matrix functional theory at finite temperature,  
T. Baldsiefen and E. K. U. Gross, <http://arxiv.org/abs/1208.4707v1>

## Reduced density matrix functional theory at finite temperature. III. Application to the electron gas: Correlation effects

Tim Baldsiefen<sup>1,2</sup> and E. K. U. Gross<sup>2</sup>

<sup>1</sup>*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

<sup>2</sup>*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06112 Halle, Germany*

(Dated: August 24, 2012)

Based on our derivation of finite temperature reduced density matrix functional theory [1] and the discussion of the performance of its first-order functional [2] this work presents several different correlation-energy functionals and applies them to the homogeneous electron gas. The zero temperature limits of the correlation-energy and the momentum distributions are investigated and the magnetic phase diagrams in collinear spin configuration are discussed.

还在不断发展中：比如推广到相对论情形，含流密度情形，..., 等等。

难度不小，但确实还在不断变化与检验过程中。

# DFT应用于电化学

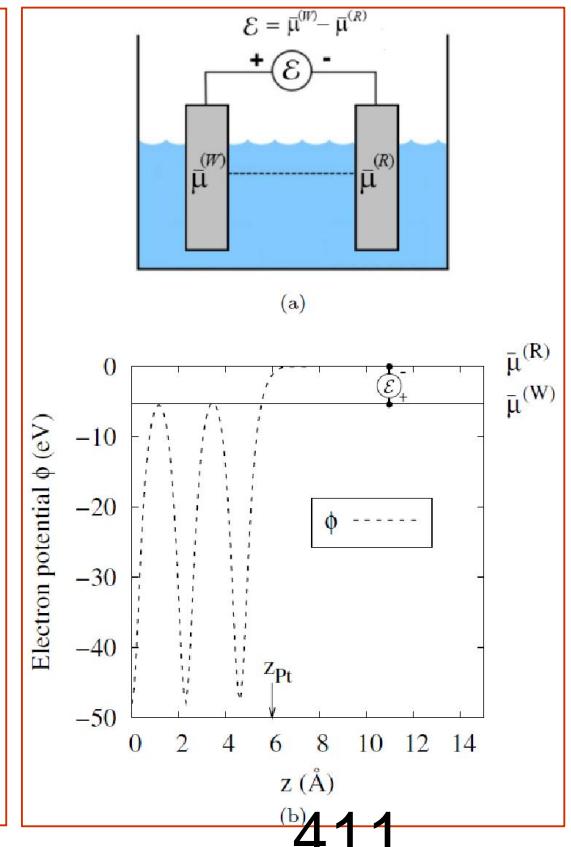
Joint Density-Functional Theory of the Electrode-Electrolyte Interface: Application to Fixed Electrode Potentials, Interfacial Capacitances, and Potentials of Zero Charge

Kendra Letchworth-Weaver and T.A. Arias

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

(Dated: May 3, 2012)

- JDFTx is a plane-wave density functional code designed for Joint Density Functional Theory (JDFT), a framework for *ab initio* calculations of **electronic systems in contact with liquid environments**.
- <http://cn.arxiv.org/abs/1205.0526v1>
- <http://jdftx.sourceforge.net/>
- Towards First-principles Electrochemistry  
<http://arxiv.org/abs/0901.0096v3>
- Phys. Rev. B 77, 245417 (2008), Phys. Rev. B 75, 205105 (2007), etc.



# 聚合物体系的DFT

## Density Functional Theory of Model Systems with the Biaxial Nematic Phase

Piotr Grzybowski

(PhD thesis 2008)

<http://cn.arxiv.org/abs/0907.1044v1>

# 经典流体的密度泛函理论

PHYSICAL REVIEW A

VOLUME 14, NUMBER 6

DECEMBER 1976

## Density-functional theory of simple classical fluids. I. Surfaces\*

C. Ebner

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and Battelle Memorial Institute, Columbus, Ohio 43201*

W. F. Saam

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D. Stroud

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(Received 27 May 1976)

A density-functional theory appropriate to nonuniform simple classical fluids is developed. Unlike most previous theories, the theory is in principle exact in the linear-response regime. For practical applications a small number of well-defined approximations, including that of Percus and Yevick, are made. Given only the Lennard-Jones 6-12 potential as input, the theory yields surface tensions and profiles in very good agreement with the results of Monte Carlo calculations. For a liquid pressed against a hard wall the expected oscillations in density in the vicinity of the wall are obtained. Comparisons with previous theories are made, and points of possible improvement in the formalism are discussed.

# 非均匀液体的密度泛函理论

THE JOURNAL OF CHEMICAL PHYSICS 134, 164501 (2011)

## Density functional theory of inhomogeneous liquids. IV. Squared-gradient approximation and classical nucleation theory

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(Received 2 February 2011; accepted 6 April 2011; published online 25 April 2011)

The squared-gradient approximation to the modified-core Van der Waals density functional theory model is developed. A simple, explicit expression for the SGA coefficient involving only the bulk equation of state and the interaction potential is given. The model is solved for planar interfaces and spherical clusters and is shown to be quantitatively accurate in comparison to computer simulations. An approximate technique for solving the SGA based on piecewise-linear density profiles is introduced and is shown to give reasonable zeroth-order approximations to the numerical solution of the model. The piecewise-linear models of spherical clusters are shown to be a natural extension of classical nucleation theory and serve to clarify some of the nonclassical effects previously observed in liquid–vapor nucleation. Nucleation pathways are investigated using both constrained energy-minimization and steepest-descent techniques. © 2011 American Institute of Physics.

# 分子密度泛函理论

J. Chem. Phys. 134, 194102 (2011)

THE JOURNAL OF CHEMICAL PHYSICS 134, 194102 (2011)

## Molecular density functional theory of solvation: From polar solvents to water

Shuangliang Zhao,<sup>1,a)</sup> Rosa Ramirez,<sup>2</sup> Rodolphe Vuilleumier,<sup>1</sup> and Daniel Borgis<sup>1,2,b)</sup>

<sup>1</sup>*École Normale Supérieure, Département de Chimie, UMR 8640 CNRS-ENS-UPMC, 24, rue Lhomond, 75005 Paris, France*

<sup>2</sup>*Laboratoire LAMBE, UMR 8547 CNRS-UEVE, Université Evry-Val-d'Essonne, Bd François Mitterrand, 91025 Evry, France*

(Received 15 February 2011; accepted 18 April 2011; published online 16 May 2011)

分子数密度满足的泛函：

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ext}[\rho] + \mathcal{F}_{exc}[\rho]$$

同样要求泛函变分取极小：

$$\frac{\delta \mathcal{F}}{\delta \rho} = \beta^{-1} \ln \left( \frac{\rho(\mathbf{r}, \Omega)}{\rho_0} \right) + V_{ext}(\mathbf{r}, \Omega) + V_{exc}(\mathbf{r}, \Omega) = 0$$

# 超冷原子系统的DFT

nature  
physics

LETTERS

PUBLISHED ONLINE: 17 JUNE 2012 | DOI: 10.1038/NPHYS2348

## Density functional theory for atomic Fermi gases

Ping Nang Ma<sup>1</sup>, Sebastiano Pilati<sup>1,2</sup>, Matthias Troyer<sup>1\*</sup> and Xi Dai<sup>3</sup>

- 中科院物理研究所理论室戴希研究员与瑞士联邦理工学院M. Troyer教授领导的研究小组合作，成功地将密度泛函理论推广到了超冷费米原子系统，并利用这一方法得到了光晶格中超冷费米原子体系的磁性相图。跟相互作用电子体系不同，中性的费米原子之间只存在着非常短程的碰撞相互作用，可以利用散射长度很好地描写。因此，在这一工作中，他们首先利用Fix-Node量子蒙特卡洛方法，得到了空间均匀体系的函数关系。然后，他们利用这种冷原子交换关联势，对光晶格里的费米原子体系进行局域密度近似，得到了这一真实体系的铁磁相图。

# 例子说明：求解Kohn-Sham 方程很重要

- 如何求解？简要答案
- 为什么要求解？目的
  - 从能谱可得到什么物理量？
  - 从总能量可得到什么？

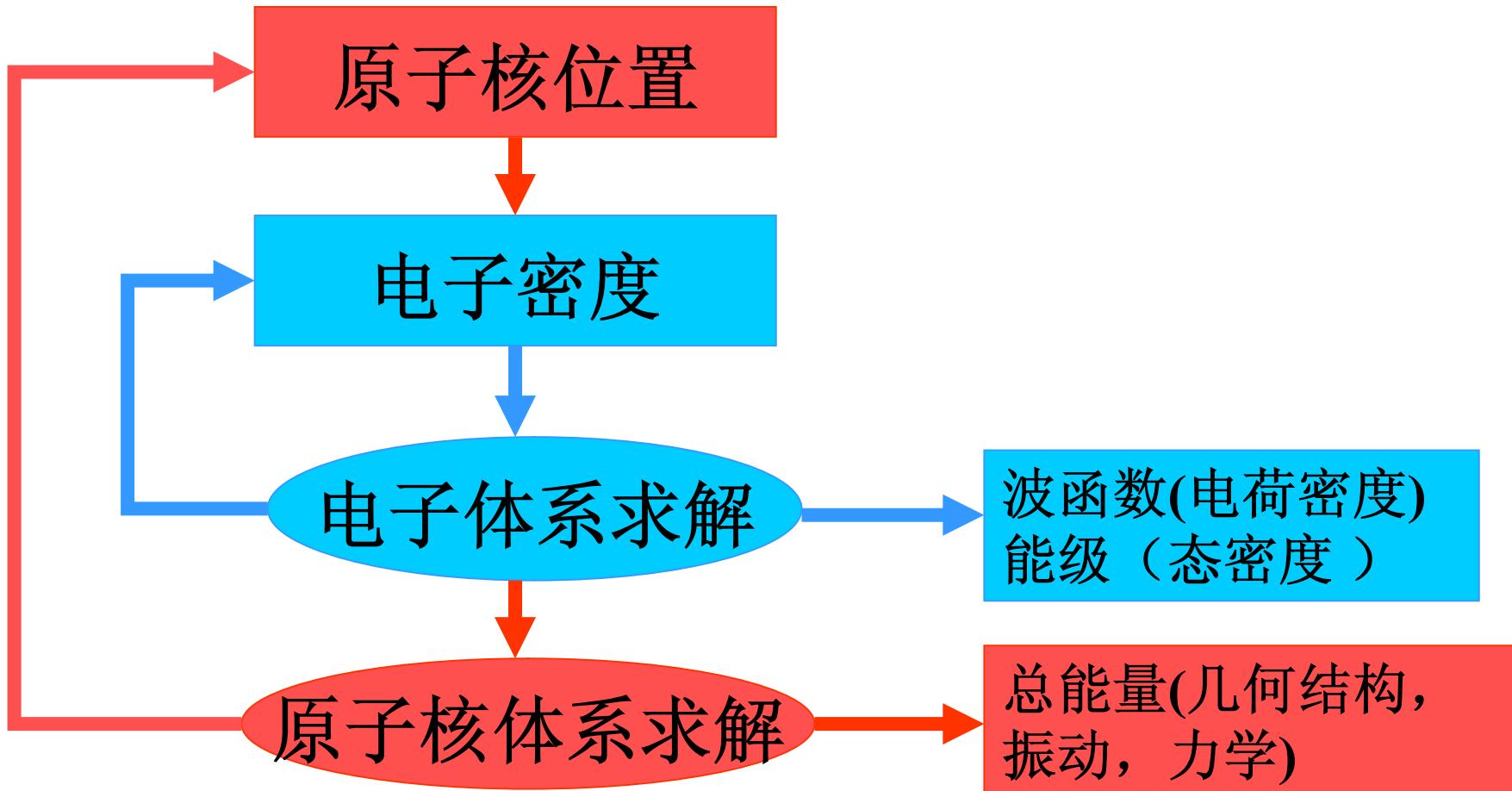
# 如何求解？为什么求解？

- Kohn-Sham 方程是单粒子方程。在固体物理学中学过的方法均可使用。
- 除关心能谱与波函数外，还关心体系的总能量。

首要的问题是为什么要解？

解这些较复杂的方程可得到哪些物理量？

# 简化的自洽求解图



# 如何求解？简要答案

如何求解电子体系的Kohn-Sham 方程？

选取基底展开单电子波函数自洽求解

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

如何求解原子核体系的牛顿运动方程？

直接解微分方程组，或求零温极小总能量

$$m_i \frac{d^2 R_i}{dt^2} = F_i = -\nabla_{R_i} E_{tot}(\{R_j\})$$

求解的细节还是较多，需要进一步讲解

# 为什么要求解?

通过求解KS方程， 我们能得到哪些物理量？

$$\left[ -\frac{1}{2} \nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r})$$

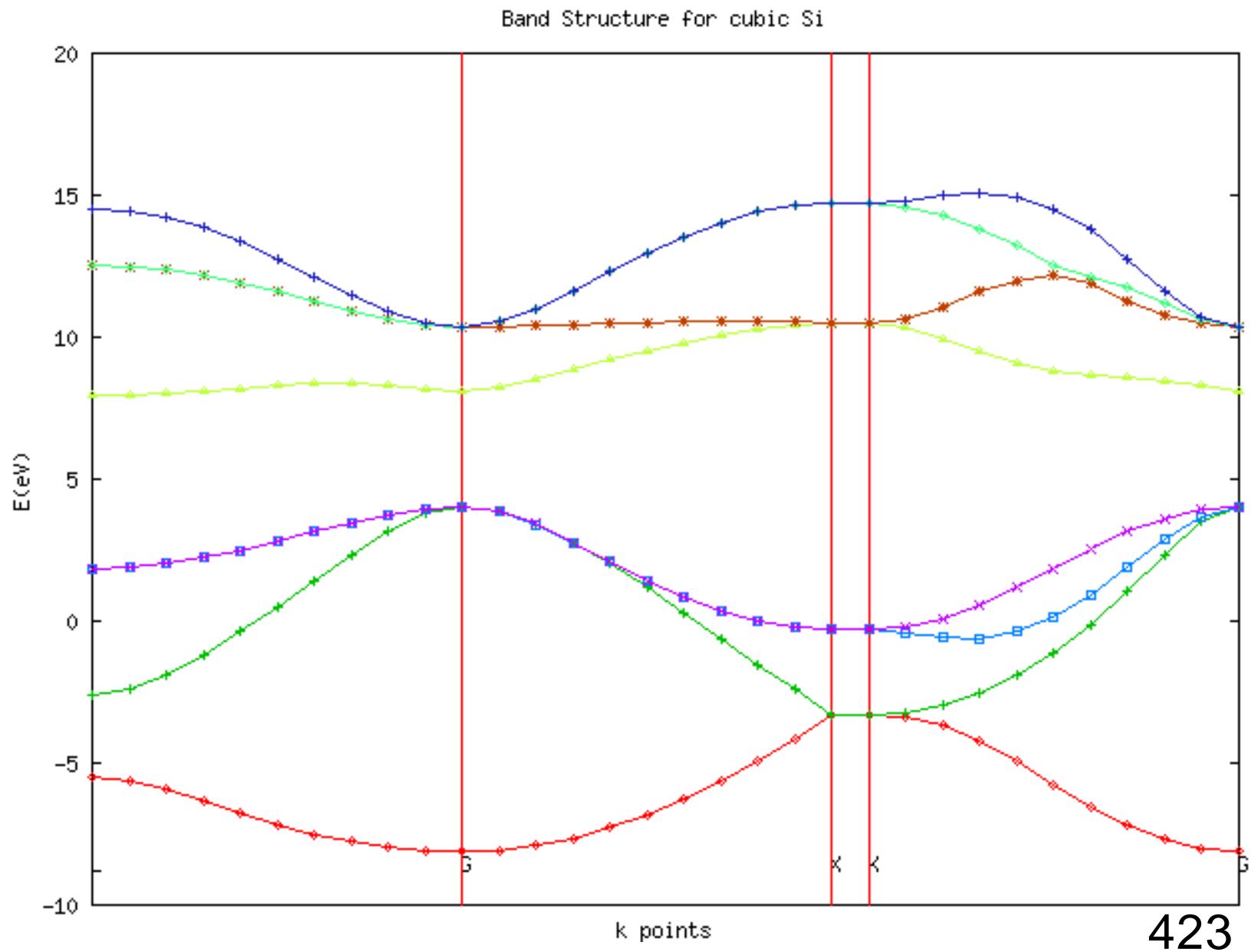
求解总能量能得到什么？

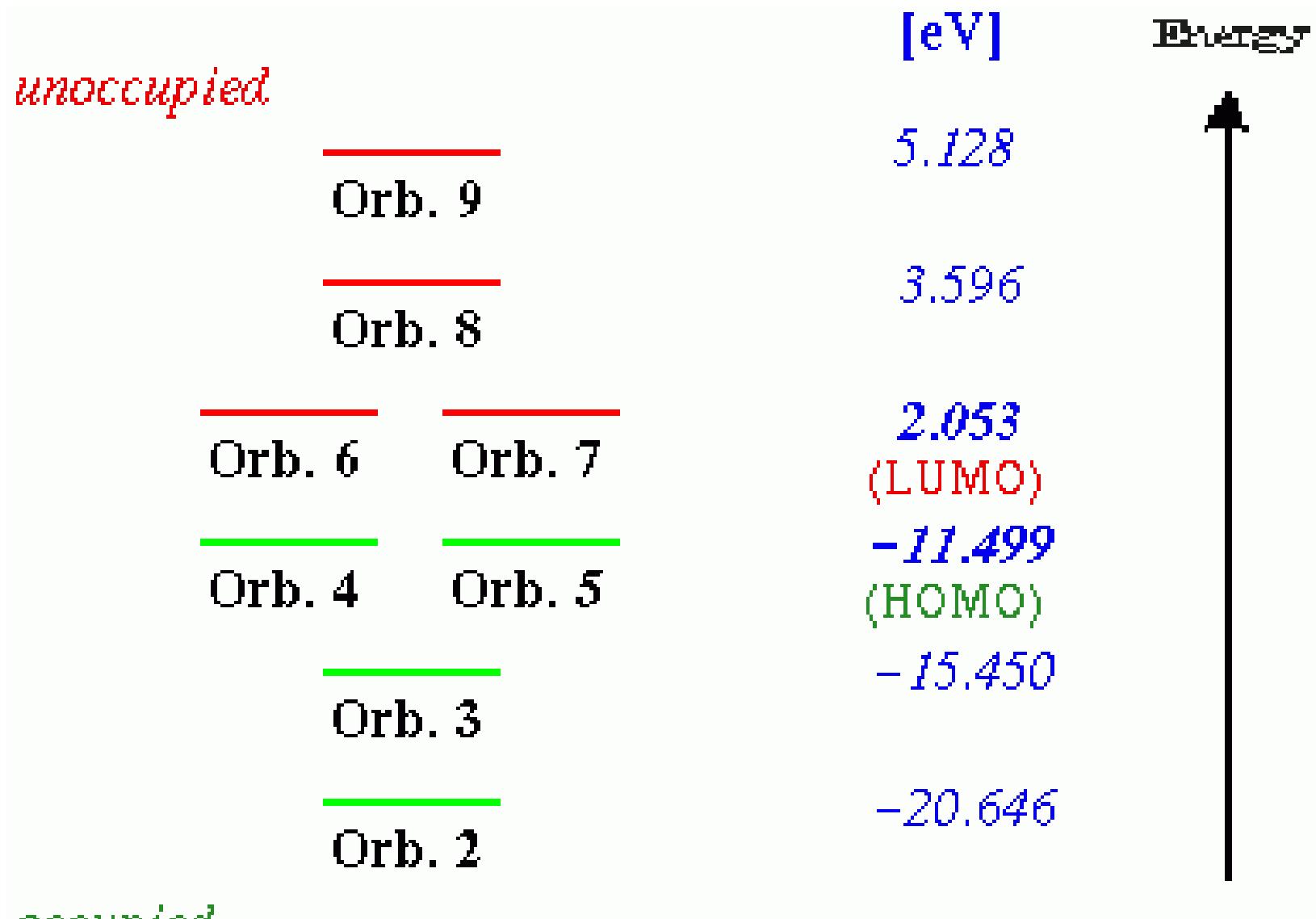
总势能:  $E_{tot}(\{R_j\}) = \frac{1}{2} \sum_{i \neq j}^m \frac{Z_i Z_j}{|R_i - R_j|} + E(R_1, R_2, \dots, R_m)$

如果了解能得到什么，会觉得掌握细节不太繁琐

# 从能谱可得到什么物理量？

- 对周期体系：
  - 态密度(DOS),
  - 费米能, 能隙,
  - 电子密度, ..., 等等。
- 对分子体系：
  - 能级,
  - 最低未占据分子轨道 (LUMO),
  - 最高占据分子轨道 (HOMO),
  - 电子密度, 电荷分布, ..., 等等。

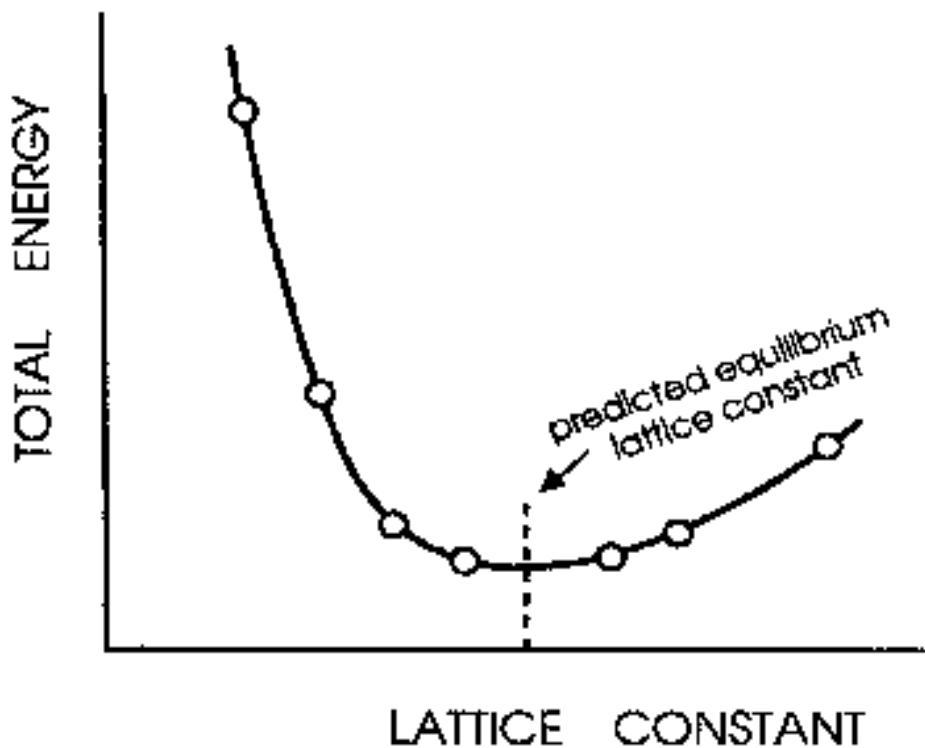


*occupied*

# 从总能量可得到什么？

从总能量可得到：

- 声子谱，
- 结合能 (cohesive energy)，
- 晶格常数，
- 弹性特性，
- 平衡几何构型
- 。     。     。



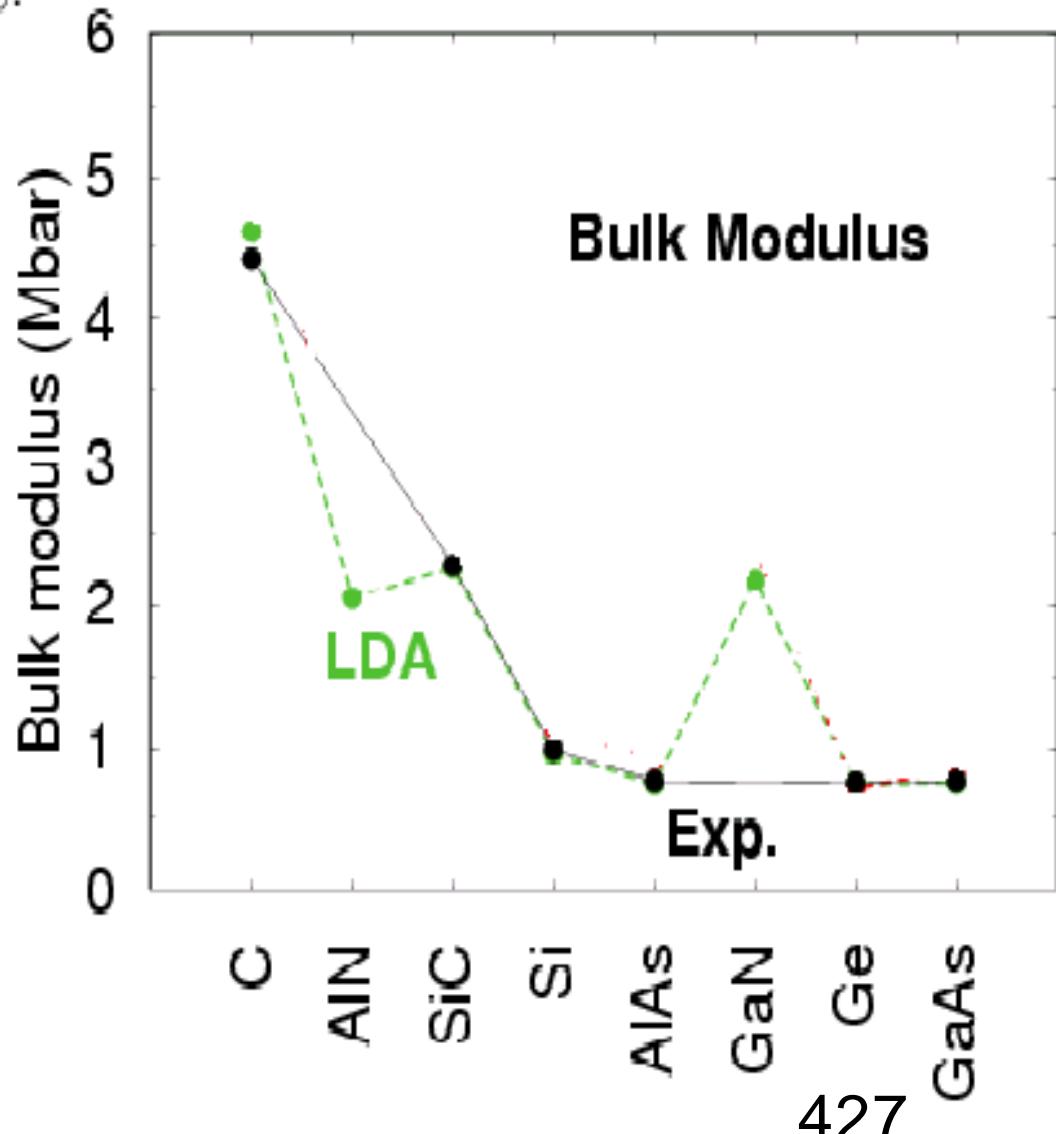
Theoretical determination of an equilibrium lattice constant. Calculations (open circles) at various possible lattice constants are performed and a smooth function is fitted through the points. The predicted lattice constant is determined by the minimum in the curve.

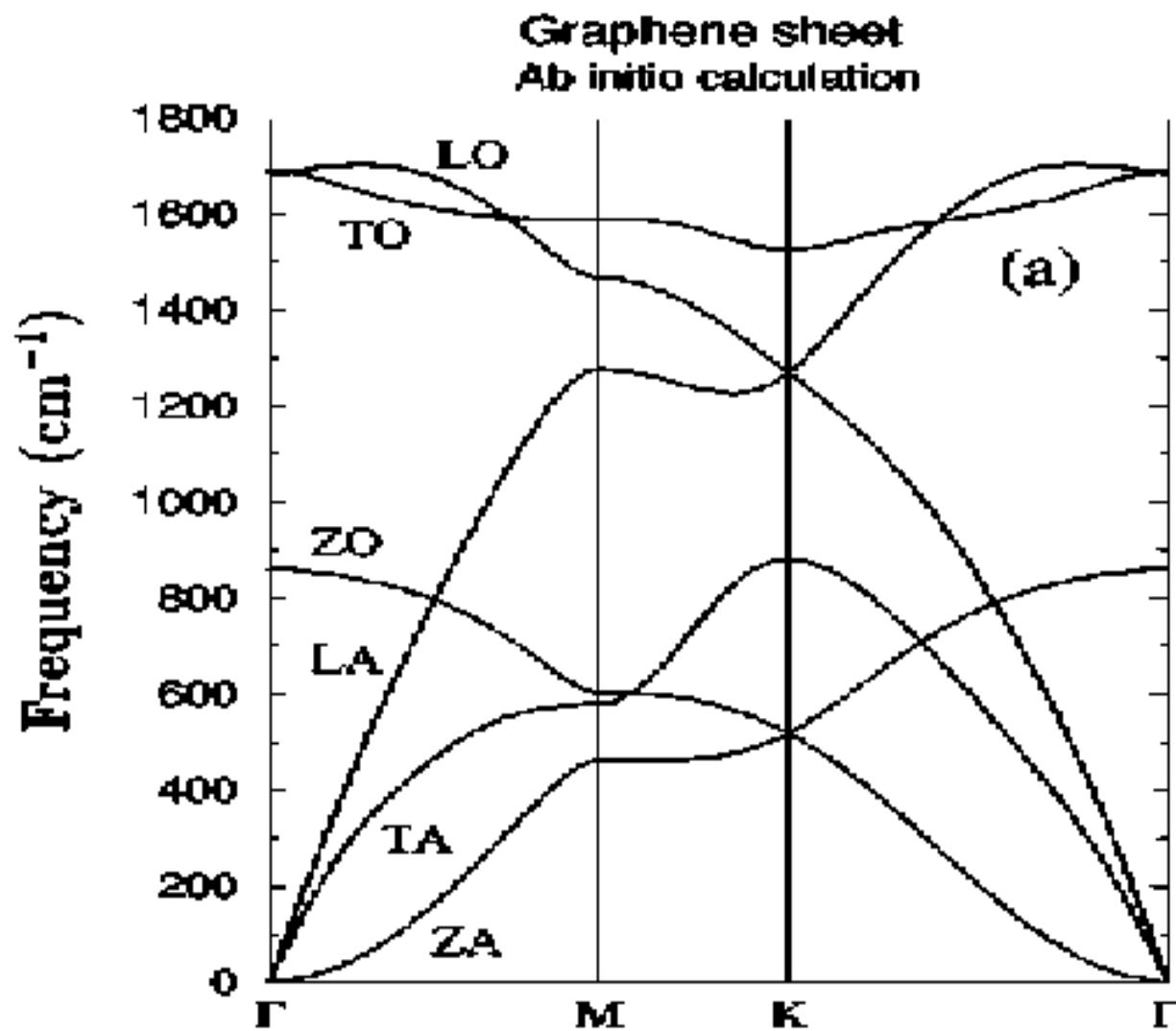
Bulk moduli  $B$  to within  $\pm 10\%$ .

$$B = -V \frac{\partial P}{\partial V} \Big|_{V_0} = -V \frac{\partial^2 E}{\partial V^2} \Big|_{V_0}$$

$V$  – crystal volume,

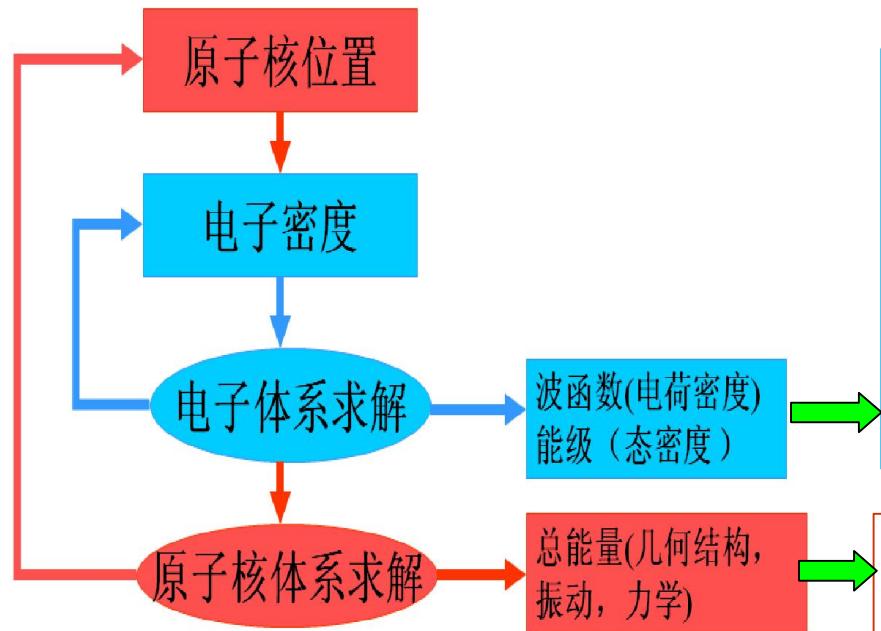
$P = \partial E / \partial V$  = pressure.





Calculated phonon structure

# 小结： 求解Kohn-Sham方程及总能量的重要性



1. 能带:  $E(k)$  图, (能级)  
2. 态密度(DOS): 单位能量间隔内的能级(能态)数目  
3. 费米能: 填满电子后的最后一个能级的能量  
4. 费米面: 当能量是费米能时的  $k$  空间等能面  
5. 电荷密度分布, 电荷转移多少  
6. 平衡输运特性(电导等), X射线谱, 光特性等

1. 结合能: 总能量+原子核零点能-孤立原子能量  
2. 力学特性:  
$$E_{tot} = E_{tot}(V) \quad B = \frac{\partial^2 E_{tot}(V)}{\partial V^2}$$
  
3. 振动特性: 动力学矩阵  
$$D_{i\alpha,j\beta} \propto \frac{\partial^2 E_{tot}(\{R_{i\alpha}\})}{\partial R_{i\alpha} \partial R_{j\beta}}$$
  
4. 自由能: 可计算各种热力学性质  
$$F = E_{tot} - TS$$

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