

# Density Functional Theory

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# Summary of QM

- There are probability waves associated with all particles
  - The **wave function ( $\Psi$ )** is used to represent probability wave
  - The state of the system is completely specified by  $\Psi$ .
  - $|\Psi(x, t)|^2 dx$  = probability of the particle being at  $x$  and  $x \pm dx$
- Operators are associated with dynamic variables
  - Average value (Expectation value) of an operator  $\hat{A}$  is given by

$$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx \rightarrow \langle \Psi | \hat{A} | \Psi \rangle$$

# Summary of QM

- Measurement of  $\hat{A}$  will yield one of the values  $a_i$ 
  - Each **eigen value**  $a_i$  has an **eigen state**  $\psi_i$  associated with it.

$$\hat{A}\psi_i = a_i\psi_i$$

- The state of the system can be expanded as

$$\Psi = \sum_i^n c_i \psi_i$$

- For particle in a time independent potential the Time independent Schrödinger equation can be used

$$\left[ \frac{\hbar^2}{2m} \frac{\partial^2}{\partial^2 x} + V \right] \psi(x) = E\psi(x)$$

$$H\psi_n(x) = E_n\psi_n(x)$$

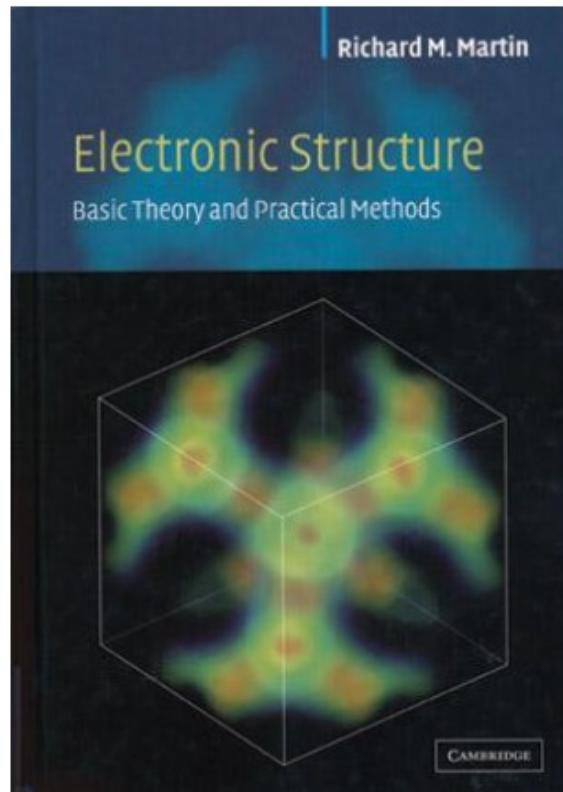
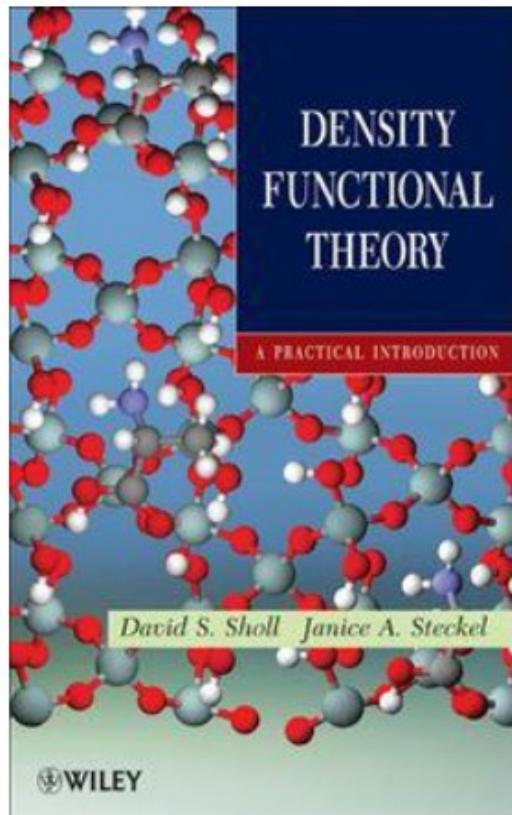
# Timeline

- 1927: Introduction of the Thomas-Fermi model (statistics of electrons).
- 1964: Hohenberg-Kohn paper proving existence of exact Density Function.
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA (local density approximation). DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello)  
(Now one of PRL's top 10 cited papers).
- 1988: Becke and LYP functionals. DFT useful for some chemistry.
- 1998: Nobel prize awarded to Walter Kohn in chemistry for development of DFT.

From many-body Hamiltonian to Kohn-Sham equations

## **THEORETICAL BACKGROUND**

# References



# References

**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*.

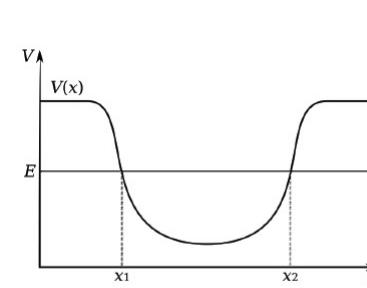
# Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

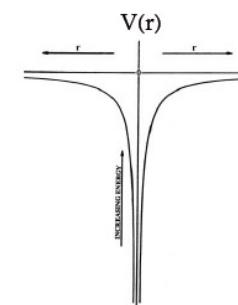


$$KE + PE = E_{Total}$$

- 1926 – Erwin Schrödinger develops wave mechanics
- Energy equation
- $\Psi$  - Wave function
  - Mathematical object that corresponds to de Broglie's wave
- There are NO physical assumptions available to "derive" the Schrödinger Equation



Arbitrary 1-D "Potential Well"



Potential an electron in a Hydrogen atom sees due to the Coulomb attraction of the Proton.

# Electronic n-body problem

- Materials are composed of nuclei  $\{Z_\alpha, M_\alpha, R_\alpha\}$  and electrons  $\{r_i\}$   
→ the interactions are known

$$H = -\sum_{\alpha} \frac{\hbar^2 \nabla_{\alpha}^2}{2M_{\alpha}} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{\alpha, \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} - \sum_{i, \alpha} \frac{Z_{\alpha} e^2}{|\vec{R}_{\alpha} - \vec{r}_i|} + \frac{1}{2} \sum_{i, j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy  
of nuclei

Kinetic energy  
of electrons

Nucleus-Nucleus  
interaction

Electron-Nucleus  
interaction

Electron-Electron  
interaction

$$H\Psi = E\Psi$$

$H$ : Hamiltonian operator

$E$ : total ground-state energy

$\Psi$ : a set of solutions (wave functions of electrons) of Hamiltonian

# Born-Oppenheimer Approximation I

- Hamiltonian of the coupled electron-ion system

$$\begin{aligned}\mathcal{H} &= T_I + T_e + V_{II} + V_{ee} + V_{eI} \\ &= - \sum_I \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{J \neq I} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}\end{aligned}$$

- Many-body Schrödinger equation

$$\mathcal{H}\Phi(\{\mathbf{r}_i; \mathbf{R}_I\}) = E\Phi(\{\mathbf{r}_i; \mathbf{R}_I\})$$

- Difference in time scales of ionic and electronic motions
  - Electrons respond instantaneously to slow ionic motion

$$\frac{m_N}{m_e} \geq \frac{m_p}{m_e} \approx 1839$$

# Born-Oppenheimer Approximation

- Decoupled wave function

$$\Phi(\{\mathbf{r}_i; \mathbf{R}_I\}) = \Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})\chi(\{\mathbf{R}_I\})$$

- Adiabatic approximation

- First, we solve, for fixed positions of the atomic nuclei, the equations that describe the electron motion.
- For a given set of electrons moving in the field of a set of nuclei, we find the lowest energy configuration – **ground state**
- For set of M nuclei the ground-state energy, E, as a function of the positions of these nuclei,  $E(R_1, \dots, R_M)$  - *adiabatic potential energy surface*.
- From the potential energy surface we can calculate how the energy change when atoms are moved around

# Key Points

- We need to know the energy and how energy changes if the atoms move around
- Electrons respond instantaneously to changes in their surroundings compared to nuclei
- If we have  $M$  nuclei at positions  $R_1, R_2, \dots, R_M$ , then we can express the ground-state energy,  $E$ , as a function of the positions of these nuclei,  $E(R_1, \dots, R_M)$ : “adiabatic potential energy surface”

# Hartree Approximation

- Hamiltonian for electrons

$$\mathcal{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \sum_i V_{\text{ion}}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

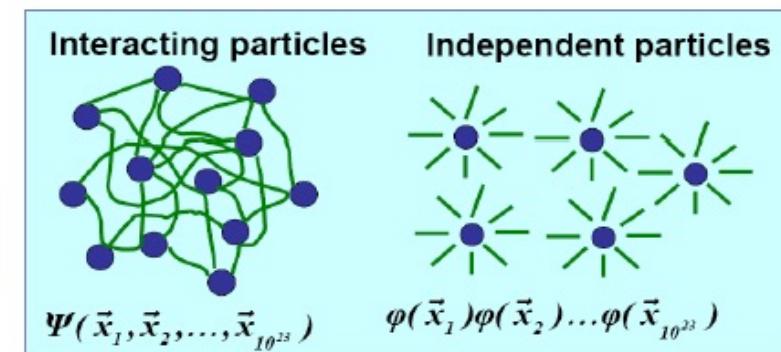
- Electronic wave function has  $3N$  variables

$$\psi = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

- Consider electrons as independent
  - Moving in an **effective potential** (of ions).

$$\psi^H(r_1, \dots, rN) = \psi_1(r_1)\psi_1(r_2) \dots \psi_N(rN)$$

- Hartree product*
- Still solving for the electronic wave function is a challenge
  - For  $\text{CO}_2$  the full wave function has 66 dimensions
  - For 100 Pt atom cluster 23,000 dimentions



Basically, approximate

# Some Helpful Points

- For ground state energy, the Schrodinger equation is time-independent
- It's possible to approximate  $\Psi$  as a product of individual electron wave functions (Hartree product):  
$$\Psi = \Psi_1(r)\Psi_2(r) \cdots \Psi_N(r)$$
- Electrons are identical particles

# Relevance of Charge Density

- Although solving the Schrödinger equation can be viewed as the fundamental problem of quantum mechanics
  - the wave function for any particular set of coordinates cannot be directly observed
- Quantity measured is the probability that the N electrons are at a particular set of coordinates  $\{\mathbf{r}_i\}$ .
- Do not care which electron in the material is labeled electron 1, electron 2 and so on.
  - A closely related quantity is the density of electrons  $n(\mathbf{r})$ .

$$n(\mathbf{r}) = 2 \sum_i |\psi_i|^2$$

- where  $\psi_i$  are single-electron wave functions.
- $n(\mathbf{r})$  is a function of only 3 variables.

# First Hohenberg-Kohn theorem

- The ground state density  $n(r)$  of a many-electron system determines uniquely the external potential  $V(r)$ .

Proof by contradiction

Recall : Expectation value of operator  $\hat{A}$

$$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx$$
$$\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle$$

Suppose two external potentials  $V(r)$  and  $V'(r)$  give the same density  $n(r)$ , and  $E = \langle \Psi | \mathcal{H} | \Psi \rangle$  and  $E' = \langle \Psi' | \mathcal{H}' | \Psi' \rangle$ .

txp\_fig

$$\begin{aligned} E &< \langle \Psi' | \mathcal{H} | \Psi' \rangle = \langle \Psi' | \mathcal{H}' + V - V' | \Psi' \rangle \\ &= E' + \langle \Psi' | V - V' | \Psi' \rangle = E' + \int dr n(r) [V(r) - V'(r)], \\ E' &< E - \langle \Psi | V - V' | \Psi \rangle = E - \int dr n(r) [V(r) - V'(r)], \end{aligned}$$

This leads to an obviously wrong relation,  $E + E' < E + E'$ .

# First Hohenberg-Kohn theorem

- The ground-state (GS) energy is a unique *functional* of the electron density.
- $n_{GS}(r)$  uniquely determines all properties, including the energy and wave function, of the ground state.
  - Problem with  $3N$  variables reduced to problem with 3 (i.e.:  $x,y,z$ ) variables
- A functional takes a function and defines a single number from the function.

$$F[f] = \int_{-1}^1 f(x) dx$$

- $f(x) = x^2 + 1$ , we get  $F[f] = \frac{8}{3}$
- $E_{GS}$  can be expressed as  $E[n_{GS}(r)]$
- What is  $E[n(r)]$ ?

# Second Hohenberg-Kohn theorem

- For a given  $V(\mathbf{r})$ , the correct  $n_{GS}(\mathbf{r})$  minimizes the energy functional  $E[n(\mathbf{r})]$  and this minimum  $E[n_{GS}(\mathbf{r})]$  is the ground state energy. The electron density ( $n_{GS}(\mathbf{r})$ ) that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation
- If the “true” functional form were known, then we could vary the electron density until the energy from the functional is minimized.

$$\begin{aligned} E[n'(\mathbf{r})] &= \langle \Psi' | \mathcal{H} | \Psi' \rangle & H = T_e + V_{int} + V_{ext} \\ &= F[n'(\mathbf{r})] + \int V_{ext}(\mathbf{r}) n'(\mathbf{r}) d\mathbf{r} \\ &> E[n_{GS}(\mathbf{r})] = \langle \Psi_{GS} | \mathcal{H} | \Psi_{GS} \rangle = F[n_{GS}(\mathbf{r})] + \int V_{ext}(\mathbf{r}) n_{GS}(\mathbf{r}) d\mathbf{r} \end{aligned}$$

- Where  $F[n(\mathbf{r})]$  must be a universal functional of the density, not known explicitly.

# Some Helpful Points

- “Density” “Functional” Theory:
  - “Density”: electron density
  - “Functional”: there exists a one-to-one mapping between energy and electron density
- A useful way to write down the functional is in terms of the single-electron wave functions

# Energy Functional

- In terms of the single-electron wave functions,  $\psi_i(\mathbf{r})$

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

- The “known” terms include four contributions

$$\begin{aligned} E_{\text{known}}[\{\psi_i\}] = & \frac{\hbar^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3 r + \int V(\mathbf{r}) n(\mathbf{r}) d^3 r \\ & + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{\text{ion}}. \end{aligned}$$

1. Kinetic energy
2. Coulomb interactions (electrons-nuclei)
3. Coulomb interactions (electron-electron)
4. Coulomb interactions (nucleus-nucleus)

- They are  $T_e, V_{Ie}, V_{ee}$  and  $V_{II}$ .
- $E_{\text{XC}}[\{\psi_i\}]$  - exchange–correlation functional

This is unknown and related to quantum mechanical effects that are not included in the “known”.

# Exchange-Correlation functional ( $E_{XC}$ )

- Exchange
  - Keeps electrons of same spin away from each other (Pauli exclusion)
- Correlation A measure of how much the movement of one electron is influenced by the presence of all other electrons
  - Keeps electrons away from each other due to Coulomb force  
To calculate this, total energy – exchange energy
- Finding exact  $E_{XC}$  is a great challenge – sure to win Nobel Prize
  - Approximate functionals work
    - LDA
    - GGA
    - meta-GGA
    - hyper-GGA
    - Hybrid
    - and dozens of other functionals

# 1965: Kohn-Sham Scheme

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

15 NOVEMBER 1965

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

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(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.

### I. INTRODUCTION

IN recent years a great deal of attention has been given to the problem of a homogeneous gas of interacting electrons and its properties have been established with a considerable degree of confidence over a wide range of densities. Of course, such a homogeneous gas represents only a mathematical model, since in all real systems (atoms, molecules, solids, etc.) the electronic density is nonuniform.

It is then a matter of interest to see how properties of the homogeneous gas can be utilized in theoretical studies of inhomogeneous systems. The well-known methods of Thomas-Fermi<sup>1</sup> and the Slater<sup>2</sup> exchange hole are in this spirit. In the present paper we use the formalism of Hohenberg and Kohn<sup>3</sup> to carry this approach further and we obtain a set of self-consistent equations which include, in an approximate way, ex-

In Secs. III and IV, we describe the necessary modifications to deal with the finite-temperature properties and with the spin paramagnetism of an inhomogeneous electron gas.

Of course, the simple methods which are here proposed in general involve errors. These are of two general origins<sup>4</sup>: a too rapid variation of density and, for finite systems, boundary effects. Refinements aimed at reducing the first type of error are briefly discussed in Appendix II.

### II. THE GROUND STATE

#### A. Local Effective Potential

It has been shown<sup>3</sup> that the ground-state energy of an interacting inhomogeneous electron gas in a static potential  $v(\mathbf{r})$  can be written in the form

# Kohn-Sham equations

- Map interacting system to non-interacting system
- $n_{GS}(\mathbf{r})$  can be found by solving a set of equations in which each equation only involves a single electron wave function (**KS orbital**).

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

- $V(\mathbf{r})$  - electron – nuclei interaction
- $V_H(\mathbf{r})$  - electron – electron density interaction

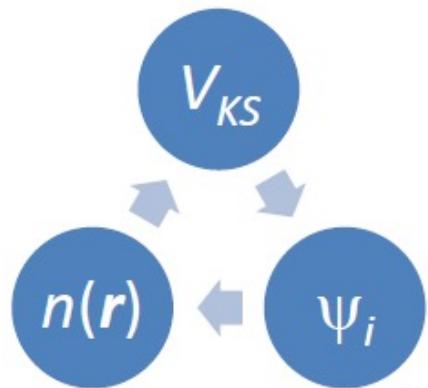
Hartree potential  $V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'$  Exchange-correlation potential  $V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}$

- Kohn – sham potential (Effective potential)

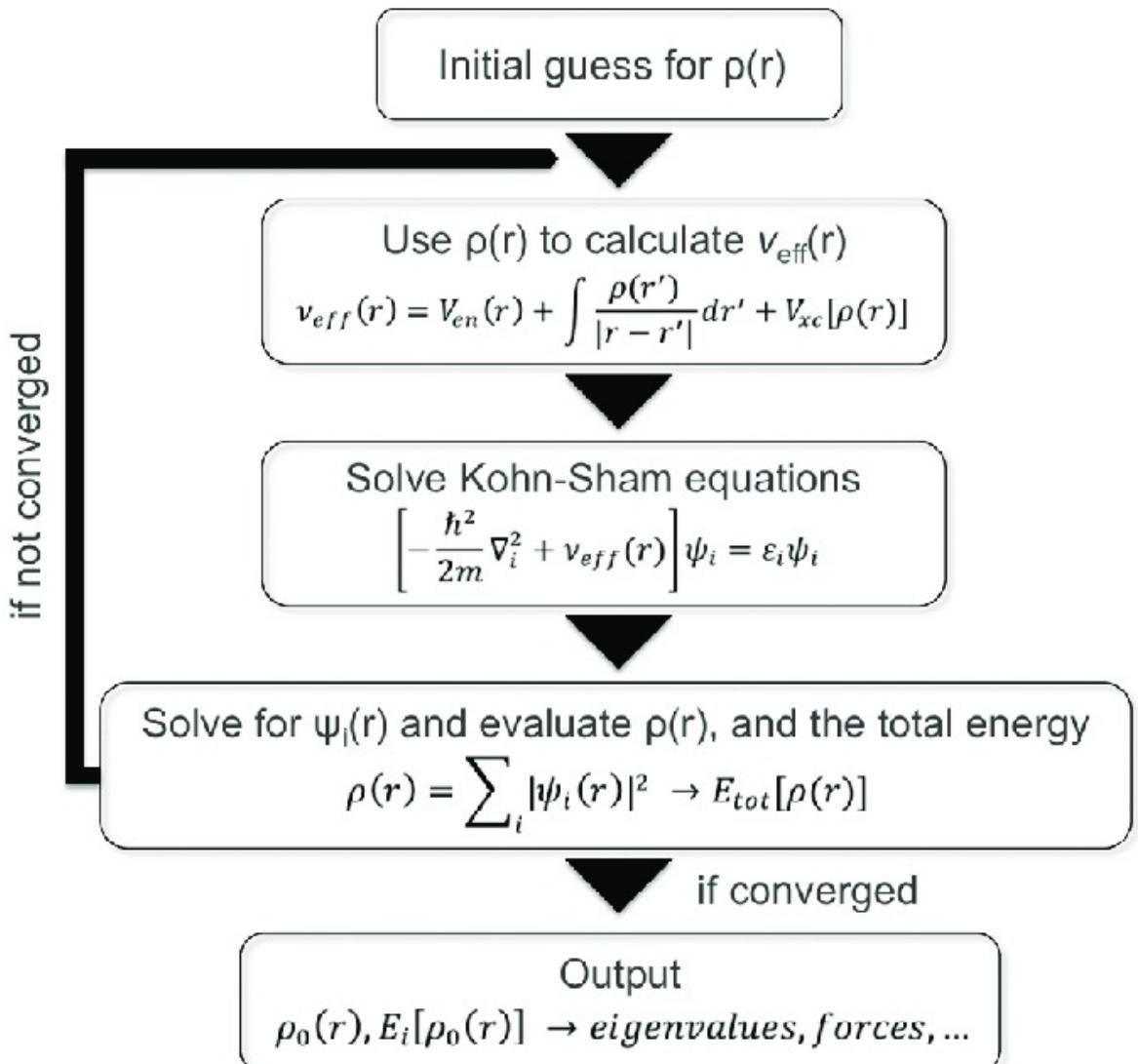
$$V_{KS} = V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$$

- $V_{KS}$  is such that  $n_{\text{non-int}}(\mathbf{r}) = n_{\text{int}}(\mathbf{r})$

# Self Consistent Field (SCF) method



- To solve KS eq.s need to define  $V_H$ ,
  - $n(\mathbf{r})$  is needed to define  $V_H$
  - To find  $n(\mathbf{r})$ , we need  $\psi_i(\mathbf{r})$
  - To find  $\psi_i(\mathbf{r})$  have to solve KS equations



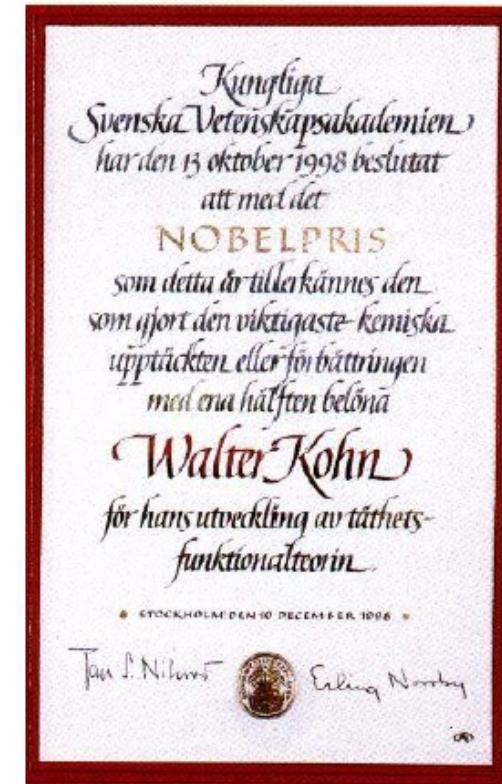
# Output from KS equations

- We have solved the Kohn-Sham equations and found the KS orbitals ( $\psi_i$ ) and respective energies ( $\varepsilon_i$ ), what next?
- We can obtain
  - Ground state total energy
  - Forces acting on atom
  - Charge density
- Kohn-Sham eigenvalues and orbitals have no physical meaning
  - Since they are of the equivalent non-interacting system
- Only the **ground state density** and **total energy** has relevance to the real system.

# Nobel Prize 1998 Chemistry



Walter Kohn



“Self-consistent Equations including Exchange and Correlation Effects”

**W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)**

Literal quote from Kohn and Sham's paper: "... We do not expect an accurate description of chemical binding."

# Local Density Approximation (LDA)

- The exchange-correlation energy at each point in the system is the same as that of an uniform electron gas of the same density
- Set the  $V_{XC}$  at each position to  $V_{XC}^{\text{electron gas}}$  for  $n(\mathbf{r})$  at that position

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

–  $\varepsilon(n)$  is the exchange-correlation energy per electron in homogenous electron gas at density  $n$ , which can be calculated

- Does not exactly solve the true Schrödinger equation

# Local Density Approximation (LDA)

$$E_{XC}^{LDA} = \int n(r) \varepsilon_{XC}(n) dr$$

$$V_{XC}^{LDA} = \frac{\partial E_{XC}^{LDA}}{\partial n(r)} = \varepsilon_{XC}(n) + n(r) \frac{\partial \varepsilon_{XC}^{LDA}}{\partial n(r)}$$

- LDA is the only case where XC functional can be derived exactly
- The LDA gives bond lengths and thus the geometries of molecules and solids typically with an astonishing accuracy of 1%

# Generalized Gradient Approximation (GGA)

- Uses information about the local electron density and the local gradient in the electron density
- Take the value of the density at each point as well as the magnitude of the gradient of the density

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \mathcal{E}_{xc}(n, \nabla n) d\mathbf{r}$$

- Improvement over LDA for many properties
  - Binding energies, lattice constants, bulk modulus etc.
- Many ways in which information from the gradient of the electron density can be included
  - Perdew–Wang functional (PW91)
  - Perdew–Burke–Ernzerhof functional (PBE)

# Hellmann-Feynman theorem: Forces

- Forces acting on atoms can be evaluated by

$$\mathbf{F}_I = -\left\langle \psi \left| \frac{\partial H}{\partial \mathbf{R}_I} \right| \psi \right\rangle$$

- Forces are **very sensitive** to errors in total energy; accuracy of ground state must be high.

# Advantages of DFT

- Works well for crystalline materials
  - Works best for metallic systems
- Not an empirical theory
  - Derived from first principles
  - No fitting of parameters
  - Underestimation/Overestimation of properties is consistent
- Accuracy
  - bond lengths are accurate to within 1-2%
  - LDA < GGA < hybrid
  - desired accuracy for hybrid functionals

# Limitations of DFT

- Overbinding
  - LDA gives large cohesive energies and high bulk moduli
  - GGA corrects overbinding to a large extent
- Neglect of van-der-Waals forces
  - Not included in any functional
- Limited no. of atoms due to computational complexity
  - Different codes can handle different no. of atoms
    - VASP ~100-150 atoms
    - SIESTA ~ Thousands of atoms

How to solve the quantum problem as accurately as possible?

# **CONVERGED DFT CALCULATION**

# What do we mean by convergence?

- The ground-state electron density of a configuration of atoms is defined by the solution to a complicated set of equations (**Kohn-Sham equations**)
- To actually solve this problem on a computer, we must make a series of numerical approximations.
  - integrals in multidimensional space must be evaluated by examining the function to be integrated at a finite collection of points
  - solutions that formally are expressed as infinite sums must be truncated to finite sums
- In each numerical approximation it is possible to find a solution that is closer and closer to the exact solution by using more and more computational resources.
- A “well-converged” calculation is one in which the numerically derived solution accurately approximates the true solution.

# **k-space**

- **Bloch's theorem**
  - For a periodic system the solutions to the Schrödinger equation can be expressed as a sum of terms with the form

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}).$$

- $u_{\mathbf{k}}(\mathbf{r})$  is periodic in space
$$u_{\mathbf{k}}(\mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) = u_{\mathbf{k}}(\mathbf{r})$$
- Where  $n_1, n_2, n_3$  are any integers
- can solve the Schrödinger equation for each value of  $\mathbf{k}$  independently
- functions  $\exp(i\mathbf{k} \cdot \mathbf{r})$  are called **plane waves**
- space of vectors  $\mathbf{r}$  is called **real space**
  - The smallest periodic unit of a crystal in real space – **primitive unit cell**
- space of vectors  $\mathbf{k}$  is called **reciprocal space ( $k$  space)**
  - Primitive cell in  $k$  space - **Brillouine zone**

# Integrals in $k$ -space

- Many quantities require integration over Brillouin zone (BZ), e.g. charge density, total energy, ...

$$n(\mathbf{r}) = \sum_n^{\text{occ}} \int_{\Omega_{\text{BZ}}} |\psi_n(\mathbf{k}, \mathbf{r})|^2 \frac{d^3 \mathbf{k}}{\Omega_{\text{BZ}}}$$

- Key features of the integral
  - defined in reciprocal space
  - integrates only over the possible values of  $\mathbf{k}$  in the Brillouin zone
- To evaluate computationally the integrals transform to weighted sum over special  $k$ -points

$$n(\mathbf{r}) \approx \sum_n^{\text{occ}} \sum_j w_j |\psi_n(\mathbf{k}_j, \mathbf{r})|^2$$

- **Sampling of  $k$ -space** within the BZ is crucial to the accuracy of the integration

# Choosing $k$ points in BZ

- Monkhorst-Pack scheme
  - One of the most popular schemes for generating  $k$ -points
  - Choose the no. of  $k$ -points in each direction of  $k$ -space
  - A uniform grid of  $k$ -points in BZ
- Perform  $k$ -point convergence test
  - Mention  $k$ -point grid when referring to your calculation

TABLE 3.2 Results from Computing the Total Energy of fcc Cu with  $M \times M \times M k$  Points Generated Using the Monkhorst-Pack Method

$M$	$E/\text{atom (eV)}$	No. of $k$ Points in IBZ	$\tau_M/\tau_1$
1	1.8061	1	1.0
2	3.0997	1	1.1
3	3.6352	4	2.3
4	3.7054	4	2.6
5	3.7301	10	5.2
6	3.7541	10	6.0
7	3.7676	20	10.4
8	3.7671	20	11.2
9	3.7680	35	16.9
10	3.7676	35	17.1
11	3.7662	56	31.2
12	3.7665	56	28.5
13	3.7661	84	40.0
14	3.7659	84	39.7

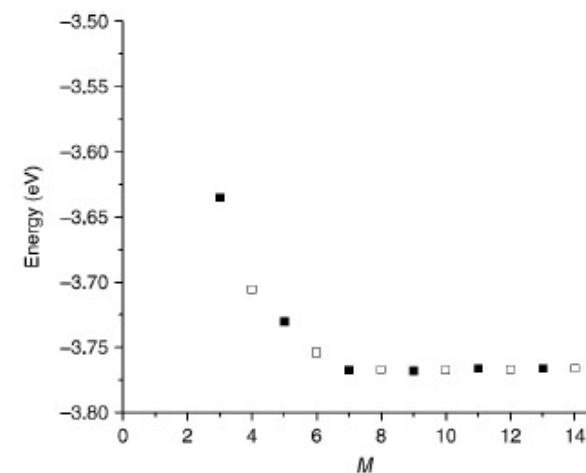
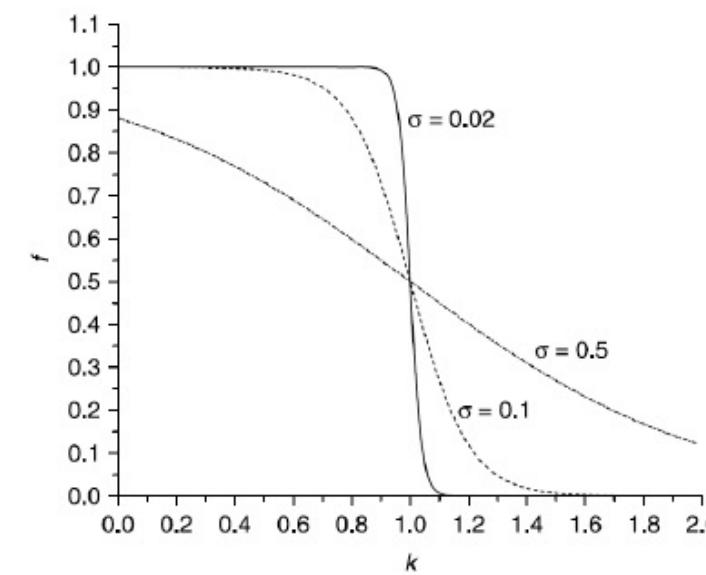


Figure 3.2 Total energies (per atom) for bulk Cu calculated as described in Table 3.2 as a function of  $M$  for calculations using  $M \times M \times M k$  points. Results with even (odd)  $M$  are shown with unfilled (filled) symbols.

# Metals – a special case for $k$ -points

- The BZ has regions both occupied and unoccupied by electrons.
- The surface that separates the two regions – *Fermi surface*
- For integral calculations –
  - Functions that are integrated change discontinuously from nonzero to zero values, at the *Fermi surface*
  - Solutions
    - **Tetrahedron method** – very accurate total energy
    - **Smearing techniques**
      - replace step function by a smoother function
      - Fermi-Dirac, Gaussian, Methfessel-Paxton



# Energy cutoffs

- Recall: Solutions to SE  $\rightarrow \phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r})$
- Where  $u_{\mathbf{k}}(\mathbf{r})$  is periodic
  - Therefore can be expanded as an infinite sum of plane waves
- To make the sum finite we have to limit the no. of plane waves used
- $E_{\text{cut}}$  is used for this purpose
  - Controls the completeness of the plane wave basis set
  - Truncation will cost accuracy
  - Reduce the error by increasing the value of cutoff energy
  - Mention  $E_{\text{cut}}$  when referring to calculation

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

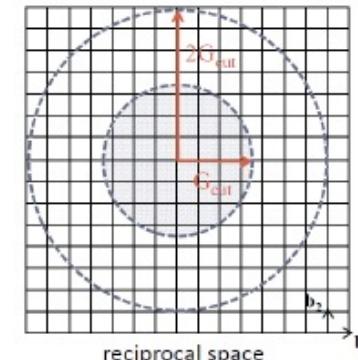
$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$$

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]$$

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2$$

$$E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2$$

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]$$

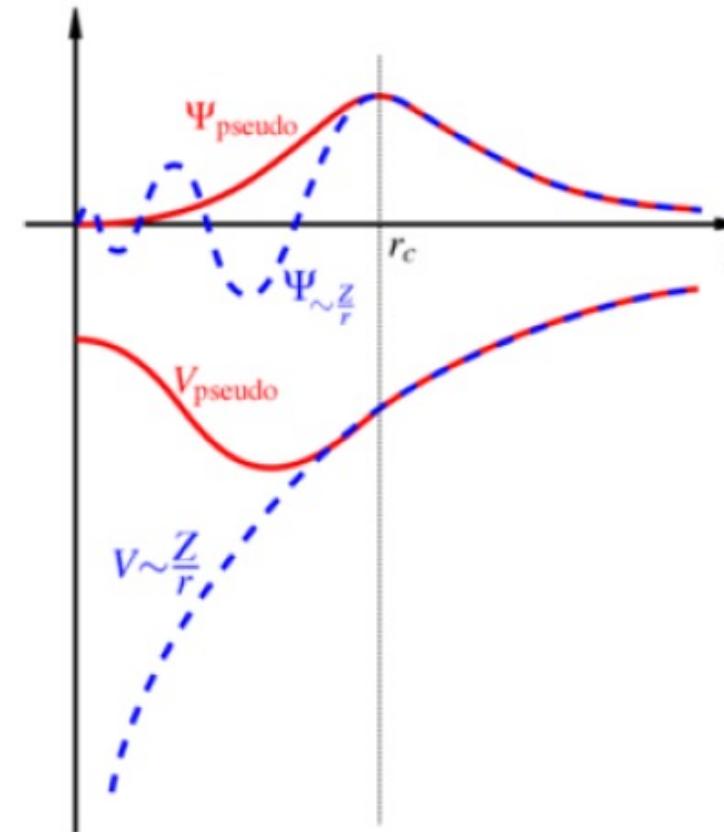


# Pseudopotential approximation

- Wave functions are written as sum of plane waves

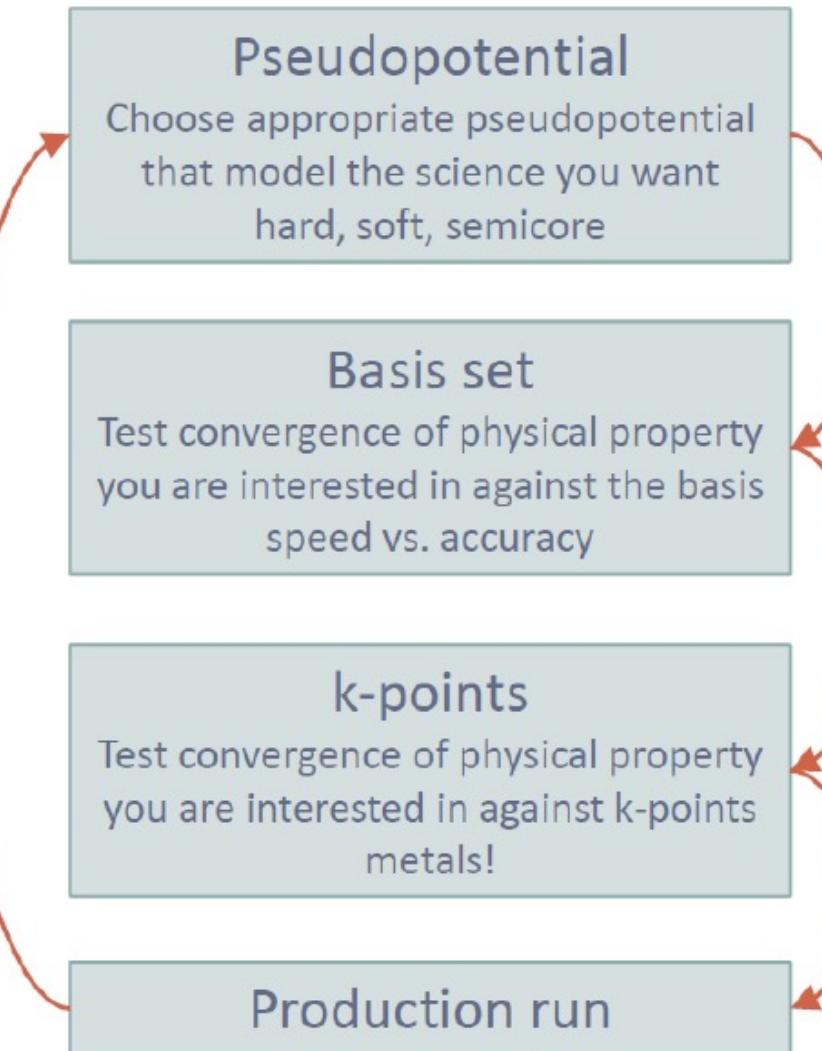
$$\psi_i(\mathbf{r}) = c_1 e^{i\mathbf{G}_1 \cdot \mathbf{r}} + c_2 e^{i\mathbf{G}_2 \cdot \mathbf{r}} + c_3 e^{i\mathbf{G}_3 \cdot \mathbf{r}} + \dots$$

- To represent all electron states
  - The number of plane waves would be very large ( $>10^6$ )
  - Replace nucleus and core electrons by a fixed effective potential
  - Only valence electrons are taken into account in the calculation
- Types of Pseudopotentials
  - Ultra-soft (US)
  - Projector augmented wave (PAW)



# Running a calculation

If your results are unphysical, then you may have to start again



The whole setup must be the same for comparison between calculations to be meaningful

# Optimization

- Ionic relaxation
  - Conditions for equilibrium
    - Forces on all atoms = 0
    - Stress = externally applied stress
  - Method
    - minimization algorithm (CG, BFGS)
    - by hand – minimum of total energy curve
- Geometric optimization
  - Number of plane waves may change discontinuously when cell size changed
  - Increase  $E_{\text{cut}}$  by 20-30% to get a smooth E-V curve

# Summary

- Total energy is a unique functional of electron density
- The functional  $E[n(r)]$  has its minimum when electron density is at ground state electron density
- The complete functional is not known
  - But good approximations exist (LDA,GGA )
- Convergence must be investigated in terms of
  - $k$  points
  - Energy cutoff