Electronic Structure of Condensed Matter
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Density Functional Theory (DFT) -I

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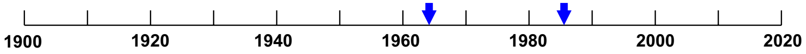
Basis of Most Modern Calculations Density Functional Theory

- Hohenberg-Kohn; Kohn-Sham – 1965
  - A new approach to the interacting electron problem
    - using independent electron methods!
  - Kohn & Sham proposed the LDA
    - the local density approximation - still widely used
- Improved approximations for the density functionals
  - Generalized Gradient Approximations, Orbital depndent functionals, van der Waals functionals, ...
- Evolution of computer power
- Car-Parrinello Method – 1985
- Nobel Prize for Chemistry, 1998, Walter Kohn



Basis of Most Modern Calculations Density Functional Theory

- Why is Density Functional Theory so widely used?
- A new approach to the many-body interacting electron problem
  - In principle DFT is exact
  - Kohn and Sham introduced the idea of an auxiliary system that in principle gives the exact ground state density and energy - but NOT other properties.
  - In practice, DFT allows useful approximations

First: What is needed to define the independent particle equation

- From previous lecture:

$$[\, -(\hbar^2/2m)\nabla^2 + V(\underline{\mathbf{r}})\,]\,\Psi\,(\underline{\mathbf{r}}) = E\,\Psi\,(\underline{\mathbf{r}})$$

- where

  m = mass of particle
  $V(\underline{r})$ = potential energy at point $\underline{r}^2$ = $(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$
  E = eigenvalue = energy of quantum state
  $\Psi(\underline{r})$ = wavefunction
  $n(\underline{r}) = |\Psi(\underline{r})|^2$ = probability density

- What is needed to specify the equation?

  m – fixed for electrons
  Boundary conditions
  $\boxed{\mathbf{V(r)}}$

- Consider m, boundary conditions to be given

First: What is needed to define the independent particle equation

- How would you find V(r)?

$$[\,-(\hbar^2/2m)\nabla^2 + V(\underline{\mathbf{r}})\,]\,\Psi(\underline{\mathbf{r}}) = E\,\Psi(\underline{\mathbf{r}})$$

- **This is the first problem - which V(r) corresponds to a given solid?**
- **Some estimate – like V(r) = sum of atomic potentials . . . .**

- Need a variational principle
- Must be based upon the energy of the system -- the real system including many-body interactions – to be relevant to the real problem

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The Fundamental Hamiltonian

Interacting electrons in an external potential

$$\boxed{\hat H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}$$

$$\cancel{-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- Only one small term: The kinetic energy of the nuclei
- If we omit this term, the nuclei are a fixed external potential acting on the electrons
- The final term is essential for charge neutrality – but is a classical term that is added to the electronic part

Not included in following derivations – must be added later

Many-Body Electron Problem

The many-electron wavefunction is a function in $3N$ dimensional space

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \qquad (2)$$

The total energy is the expectation value

$$E = \frac{\langle\Psi|\hat H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \equiv \langle\hat H\rangle = \langle\hat T\rangle + \langle\hat V_{int}\rangle + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}). \qquad (3)$$

electron-electron interactions

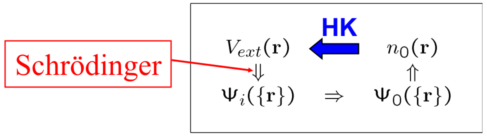
potential due to nuclei, other sources "external" to electrons

The ground state wavefunction Ψ_0 is the state with lowest energy *that obeys the symmetries of the particles and conservation laws.*

$$E_0 = min\frac{\langle\Psi|\hat H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \qquad (4)$$

The Hohenberg-Kohn Theorem – I

- Hohenberg-Kohn "theorem"(1964)



$$\begin{tikzcd} V_{ext}(\mathbf{r}) \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[l, "HK"'] \\ \Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] \end{tikzcd}$$

Schrödinger

- All properties of the many-body system are determined by the ground state density $n_0(r)$
- Each property is a functional of the ground state density $n_0(r)$ which is written as $f\,[n_0]$
- A functional F [f(r)] maps a function to a result: f(r) → F

The Hohenberg-Kohn Theorem – Ia
First Step – definition of functional

- What is a functional? A functional derivativative?
  Examples

$I[f] = \int dx \exp(f(x))$, for example, $I[f] = 1/a$ for $f(x) = -a^2 x^2$

- $H[f,g] = \int dx\, g(x) f(x))$, $\delta H/ \delta g(x) = \int dx\, \delta(x) f(x) = f(x)$

  δ = delta function

The Hohenberg-Kohn Theorem – Ib
Legendre Transformation - Example

- The "theorem" is really only a Legendre transformation
- Well-known example: thermodynamic equilibrium
  - Consider a classical liquid – many interacting atoms in thermal motion
  - Energy $E(V)$, V = volume (where n = density = N/V)
  - **What is the equilibrium volume under pressure?**

This problem has the classic form of a Legendre transformation:

Define the generalized function:

$F(P,V) = E(V) + PV + H(P)$

Minimization: $\partial F/ \partial V = dE/dV + P = 0 \Rightarrow$ P is the pressure $P = -dE/dV$

$\partial F/ \partial P = dH/dP + V = 0 \Rightarrow$ V is the volume $V = -dH/dP$

Thus the enthalpy $H(P) = E(V) + PV$ where P is the pressure $P = -dE/dV$

This is a Legendre transformation – a change of variables from V to P:

Question for you: Show that H is a function of P and NOT a function of V

The Hohenberg-Kohn Theorem – Ic
Example of Liquid continued

- So what is the functional for the classical liquid?
- We want to find the state of thermodynamic equilibrium for classical liquid:
  - The equilibrium state of the system at pressure P (an externally applied quantity) can be found by a two-step process
  - 1. Minimize the energy as a function of all internal variables (the many-body problem!) at fixed density $n = N/V \rightarrow$ function $E(n)$, Note: $E(n)$ is "universal" – it depends only on internal quantities
  - 2. Vary **$V \Rightarrow P(V)$** to find the **minimum enthalpy H** **for fixed applied P_{ap}**

    $\delta H/\delta P = 0 \Rightarrow H(P) = E(V_0) + P_{ap} V_0$ (where $V_0 = N/ n_0$)

    (really very simple interpretation) $P = -dE/dV = P_{ap}$
- Thus $P \rightarrow n_0$ and $n_0 \rightarrow P \rightarrow E$ and all properties!

The Hohenberg-Kohn Theorem – II
Density functional for electrons

- So what is the functional for electrons? More later on functional
- Consider the Hohenberg-Kohn functional for quantum electrons:

$$E = T[V_{ext}] + Vint[V_{ext}] + \int dr\, n(r)\, V(r) + F_{HK}[n]$$

T= KE, V_{int} = Expectation value of e-e interactions from Schr. Eq with V_{ext}

Hohenberg- Kohn functional

- **1. Minimize the energy as a function of density $n(r)$**
- **Function of internal variables -- internal variables - solving the many-body problem!) $\rightarrow V = V_{ext}(r)$**
- **2. Leads to HK functional $F[n(r)]$**

  Note: $F[n(r)]$ is "universal" – it depends only on internal quantities
- Thus $V_{ext}(r) \rightarrow n_0(r)$ and $n_0(r) \rightarrow V_{ext}(r) \rightarrow E$ and all properties!

A Nobel prize for a Legendre Transformation ??!!

- This the first step made by Hohenberg and Kohn sets up the next step – even if it is just a Legendre transformation

- **It appears that we have gained nothing! We still have to solve the many body Schrodinger Eq. to get the density functional!**

- It is the next step by Kohn &Sham that is truly ingenious :

The combination won the Nobel prize

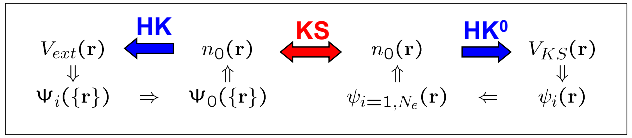
The Hohenberg-Kohn Theorem – III

- The Schrodinger Eq. gives all properties as functional of the potential.
- Why is it a good idea to make a functional of the density instead of a functional of the potential ?
- The hard part of the problem is the correlation energy
  - **Correlation means that the probability if finding two electrons at a distance r is reduced for small distances, since the interaction is repulsive**
  - **This is intrinsically a function of the density and only a secondary effect of the potential**
- Thus the first step made by Hohenberg and Kohn sets up the next step – even if it is just a Legendre ttansformation
- It is the next step by Kohn &Sham that makes DFT practical!

The Kohn-Sham Auxiliary System I

- Kohn-Sham (1965) – Replace original many-body problem with an independent electron problem – that can be solved!
- The ground state density is required to be the same as the exact density

$$n_0(\mathbf{r}) = \sum_\sigma \sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2,$$



$$\begin{tikzcd}
V_{ext}(\mathbf{r}) \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[l, "HK"'] \arrow[r, leftrightarrow, "KS"] & n_0(\mathbf{r}) \arrow[r, "HK^0"] & V_{KS}(\mathbf{r}) \arrow[d, Rightarrow] \\
\Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] & \psi_{i=1,N_e}(\mathbf{r}) \arrow[u, Rightarrow] & \psi_i(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

- Only the ground state density and energy are required to be the same as in the original many-body system

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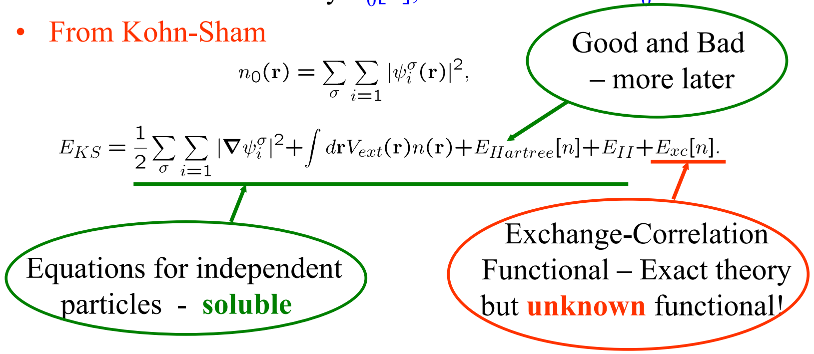
The Kohn-Sham Auxiliary System II

- From Hohenberg-Kohn the ground state energy is a functional of the density $E_0[n]$, minimum at $n = n_0$
- From Kohn-Sham

$$n_0(\mathbf{r}) = \sum_\sigma \sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2,$$



$$E_{KS} = \frac{1}{2}\sum_\sigma \sum_{i=1} |\nabla \psi_i^\sigma|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

Good and Bad – more later

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- **The new paradigm for many-body problems**

– Determine only the total energy and density, not other properties

- find useful, approximate functionals

The Kohn-Sham Auxiliary System III

- **Kohn-Sham is different from Hohenberg-Kohn**

$$E_{KS} = \frac{1}{2}\sum_{\sigma}\sum_{i=1} |\nabla\psi_i^\sigma|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

- **Kohn-Sham introduced the kinetic energy expressed as a functional of wavefunctions of the independent- particle auxiliary system –**
- **To be precise this is:**

  "Kohn-Sham Density Functional Theory"
- **This is one aspect makes KS-DFT practical :**

  The KE is very "non-local" --- Exc is much more local and it can be approximated much more easily the Hohenberg-Kohn functional F[n] which includes the total KE
- **The second is that KE, and Coulomb terms are all LARGE**

  These terms must be a good approximation or the method is useless

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The Kohn-Sham Equations I

- Assuming a form for $E_{xc}[n]$
- Minimizing energy (with constraints) → Kohn-Sham Eqs.

$$n_0(\mathbf{r}) = \sum_{\sigma}\sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2}\sum_{\sigma}\sum_{i=1} |\nabla\psi_i^\sigma|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

Variational principle

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma *}(\mathbf{r})} = 0, \qquad (1)$$

Constraint
Exclusion principle for
independent particles

$$\langle \psi_i^\sigma | \psi_j^{\sigma'} \rangle = \delta_{i,j}\delta_{\sigma,\sigma'}. \qquad (2)$$

$$(-\frac{1}{2}\nabla^2 + V_{KS}^\sigma(\mathbf{r}), -\varepsilon_i^\sigma)\psi_i^\sigma(\mathbf{r}) = 0 \qquad (3)$$

See Next Slide)

$$\begin{aligned} V_{KS}^\sigma(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r}) (4) \end{aligned}$$

The Kohn-Sham Equations II

- Kohn-Sham Self-Consistent Equations.
- Assuming a form for $E_{xc}[n]$

Eigenvalues are approximation to the energies to add or subtract electrons –electron bands
More later

$$\boxed{(-\frac{1}{2}\nabla^2 + V_{KS}^\sigma(\mathbf{r}), -\varepsilon_i^\sigma)\psi_i^\sigma(\mathbf{r}) = 0} \qquad (3)$$

$$\begin{aligned} V_{KS}^\sigma(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r}) (4) \end{aligned}$$

Kohn-Sham Potential
Function position **r**
Functional of density

Uses Chain rule
dE/dψ = (dE/dn) (dn/dψ)

Result
Density, Energy

$$n_0(\mathbf{r}) = \sum_{\sigma}\sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2,$$

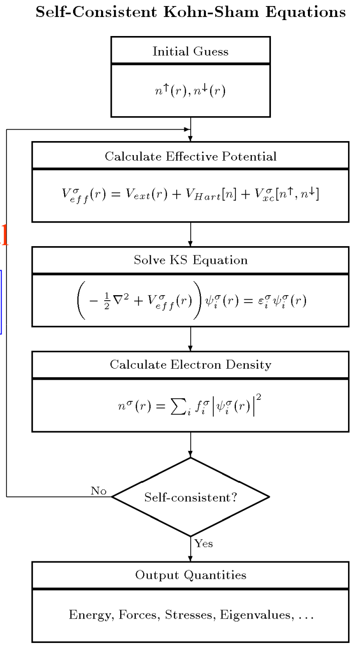
$$E_{KS} = \frac{1}{2}\sum_{\sigma}\sum_{i=1} |\nabla\psi_i^\sigma|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

Solving Kohn-Sham Equations

- Structure, types of atoms
- Guess for input density or potential
- Solve KS Eqs.

  This is the numerically intensive part
- New Density and Potential
- Self-consistent?
- Output:
  - **Total energy, force, stress, ...**

KS Eigenvalues - Only parameters - NOT eigenvalues of original man-body system



Why are forces and stresses given correctly ?

- The force on a nucleus **F = -dE/dR** is given by the “force theorem” also called the “Helmann-Feynman” theorem
  - For a small perturbation dR, you might think this requires expansion in the excited` states
  - **Exercise for you – Prove that F is given strictly by the density including all many-body terms**
- Stress σ = - dE/dε (generalization of virial theorem)
  - The same reasoning
- Perhaps most surprising – second derivatives (and higher) are also exact in principle.
  - Extension of above reasoning
  - Different from textbook perturbation theory – **Why?**