Density Functional Theory for Electrons in Materials

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OUTLINE

- The many-body electron problem
- Hohenberg-Kohn Theorems
- Kohn-Sham Ansatz
- Functionals for Exchange and Correlation
  - LDA - Local Density Approximation
  - GGA - Generalized Gradient Approximations
- Solution of the Kohn-Sham "Schrodinger-like" Equations
- Results: H, He, H_2
- Results: Atomic examples
- Results: Solids
- Results: Molecules: GGA
- Failures!

The Fundamental Hamiltonian

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\vec{\mathbf{r}}_i - \vec{\mathbf{R}}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j|}$$
$$- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{\mathbf{R}}_I - \vec{\mathbf{R}}_J|} \qquad (1)$$

- 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
- The first line is the key problem for *ab initio* prediction of the properties of materials
- The ground state energy as a function of the positions of the nuclei determine:
  - Stable Structures – Phase transitions
  - Mechanical Deformations – Phonons, etc.
- The excited states determine "electronic" properties:
  - Electronic Bands, Optical properties, etc.

Many-Body Electron Problem

In atomic units ($\hbar = m_e = c = 1$) the electron Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + E_{II}, \tag{2}$$

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}_{ext}$ is the potential acting on the electrons due to the nuclei,

$$\hat{V}_{ext} = \sum_{i,I} V_I(|\vec{\mathbf{r}}_i - \vec{\mathbf{R}}_I|), \tag{3}$$

$\hat{V}_{int}$ is the many-body electron-electron interaction, and E_{II} is the classical ion-ion interaction.

The total energy is the expectation value

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle + \int d^3r V_{ext}(\vec{\mathbf{r}}) n(\vec{\mathbf{r}}). \tag{4}$$

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

Hohenberg-Kohn Theorems

- Theorem I: For any system of electrons in an external potential $V_{ext}(\vec{\mathbf{r}})$, that potential is determined uniquely, except for a constant, by the ground state density $n(\vec{\mathbf{r}})$.

  Corollary I: Since the Hamiltonian is thus fully determined, except for a constant shift of the energy, the full many-body wavefunction and all other properties of the system are also completely determined!

- Theorem II: A *universal functional* for the energy $E[n]$ of the density $n(\vec{\mathbf{r}})$ can be defined for all electron systems. The exact ground state energy is the global minimum for a given $V_{ext}(\vec{\mathbf{r}})$, and the density $n(\vec{\mathbf{r}})$ which minimizes this functional is the exact ground state density.

  Corollary II: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. Excited states of the electrons must be determined by other means.

- Comment: Functionals may be arbitrarily complex!

Proof of Hohenberg-Kohn Theorems

Proof of Theorem I:

Suppose that there were two different external potentials $V_{ext}^{(1)}(\vec{\mathbf{r}})$ and $V_{ext}^{(2)}(\vec{\mathbf{r}})$ with the same ground state density $n(\vec{\mathbf{r}})$. The two external potentials lead to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same density $n(\vec{\mathbf{r}})$. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \tag{5}$$

which leads to

$$E^{(1)} < E^{(2)} + \int d^3r \{ V_{ext}^{(1)}(\vec{\mathbf{r}}) - V_{ext}^{(2)}(\vec{\mathbf{r}}) \} n(\vec{\mathbf{r}}). \tag{6}$$

But changing the labels leads to

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{ext}^{(2)}(\vec{\mathbf{r}}) - V_{ext}^{(1)}(\vec{\mathbf{r}}) \} n(\vec{\mathbf{r}}). \tag{7}$$

which is a contradiction!

Theorem II (Not proved here) leads to

$$\begin{aligned} E_{HK}[n] &= T[n] + V_{int}[n] + \int d^3r V_{ext}(\vec{\mathbf{r}}) n(\vec{\mathbf{r}}) \\ &\equiv F_{HK}[n] + \int d^3r V_{ext}(\vec{\mathbf{r}}) n(\vec{\mathbf{r}}) \end{aligned} \tag{8}$$

The Kohn-Sham Ansatz

The Kohn-Sham approach is to replace the original difficult interacting-particle Hamiltonian with a *different* Hamiltonian which could be solved more easily.

Kohn-Sham Hamiltonian for *non-interacting "electrons"* **assumed** to have the same density as the true interacting system

$$H_{eff} = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\vec{\mathbf{r}}). \tag{9}$$

where

$$n_{eff}(\vec{\mathbf{r}}) = \sum_{i=1}^{N} |\psi_i(\vec{\mathbf{r}})|^2, \tag{10}$$

and the kinetic energy T_{eff} is given by

$$T_{eff} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\langle\psi_i|\nabla^2|\psi_i\rangle, \tag{11}$$

The Kohn-Sham energy is the sum

$$\tilde{E} = T_{eff} + \int V_{ext}(\vec{\mathbf{r}})n_{eff}(\vec{\mathbf{r}})dr + E_{Hartree}[n_{eff}] + E_{xc}[n_{eff}], \tag{12}$$

The Kohn-Sham Equations

The ground state can be found by minimizing with respect to the independent-electron wavefunctions $\psi_i(\vec{\mathbf{r}})$

$$\frac{\partial \tilde{E}[n]}{\partial \psi_i(\vec{\mathbf{r}})} = \frac{\partial T_{eff}}{\partial \psi_i(\vec{\mathbf{r}})} + \frac{\partial E_{other}}{\partial n_{eff}(\vec{\mathbf{r}})} \frac{\partial n_{eff}(\vec{\mathbf{r}})}{\partial \psi_i(\vec{\mathbf{r}})} = 0 \qquad (13)$$

subject to the orthonormalization constraints

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j} \qquad (14)$$

The Lagrange multiplier method constraints leads to the Kohn-Sham Schroedinger-like equations:

$$(H_{eff} - \epsilon_i)\psi_i(\vec{\mathbf{r}}) = 0 \qquad (15)$$

where the ϵ_i are the eigenvalues,

$$H_{eff}(\vec{\mathbf{r}}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\vec{\mathbf{r}}). \qquad (16)$$

and

$$\begin{aligned} V_{eff}(\vec{\mathbf{r}}) &= V_{ext}(\vec{\mathbf{r}}) + \frac{\partial E_{Hart}}{\partial n_{eff}(\vec{\mathbf{r}})} + \frac{\partial E_{xc}}{\partial n_{eff}(\vec{\mathbf{r}})} \qquad (17) \\ &= V_{ext}(\vec{\mathbf{r}}) + V_{Hart}[n_{eff}] + V_{xc}[n_{eff}]. \qquad (18) \end{aligned}$$

The total energy can be written

$$\tilde{E} = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2}\int V_{Hart}(\vec{\mathbf{r}}) n_{eff}(\vec{\mathbf{r}}) dr + (E_{xc}[n] - \int (V_{xc} n_{eff}(\vec{\mathbf{r}}) dr) \qquad (19)$$

Exchange-Correlation Functional $E_{xc}[n]$

The Exchange-Correlation energy is defined by

$$\begin{aligned} F_{HK}[n] &= T[n] + V_{int}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle \\ &\equiv T_{eff}[n] + E_{Hartree}[n] + E_{xc}[n] \end{aligned} \quad (20)$$

where

$$E_{Hartree}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(\vec{\mathbf{r}})n(\vec{\mathbf{r}}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} \quad (21)$$

Key points:

- T_{eff} is really calculated from the wavefunctions!
- $E_{xc}[n]$ contains all the difficult terms is a functional of n by the Hohenberg-Kohn Theorem.
- $E_{xc}[n]$ is reasonably approximated as approximately local – unlike $T_{eff}[n]$ and $E_{Hartree}[n]$

Exchange-Correlation Hole

(See, *e.g.,* *Many-Particle Physics* by Mahan)

Around each electron at point $\vec{\mathbf{r}}$ other electrons are excluded to form a hole at points $\vec{\mathbf{r}}'$, $n_{xc}(\vec{\mathbf{r}}, \vec{\mathbf{r}}')$.

- The Pauli principle (exchange) causes there to be a hole with ***exactly one missing electron*** compared to the average density of all electrons including the one under consideration.
- Correlation causes rearrangement but still ***exactly one missing electron.***
- The energy is given by the interaction with the hole $\overline{n}_{xc}$ ***averaged over all coupling constants*** e^2 (not proved here)

$$E_{xc}[n] = \int d^3r n(\vec{\mathbf{r}}) \int d^3r' \frac{\overline{n}_{xc}(\vec{\mathbf{r}}, \vec{\mathbf{r}}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} \qquad (22)$$

LDA - Local Density Approximation

Assume $E_{xc}[n]$ is a sum of contributions from each point in space *depending only upon the density at each point independent of other points.* Then

$$E_{xc}[n] = \int d^3 r n(\vec{\mathbf{r}}) \epsilon_{xc}(n(\vec{\mathbf{r}})) \tag{23}$$

where $\epsilon_{xc}(n)$ is the x-c energy per electron

- Since $\epsilon_{xc}(n)$ is assumed to be universal, ***must be the same as for homogeneous electrons of density*** n.
- Exchange (*e.g.,* Aschroft and Mermin, p. 411)

$$\epsilon_x(n) = -\frac{0.458}{r_s} \;\; Hartree, \tag{24}$$

  where r_s is the average distance between electrons given by $\frac{4\pi}{3} r_s^3 = \frac{1}{n}$.

- Correlation found by:
  - RPA approximation - good at high density
  - Interpolation between low and high density - Wigner (1934), Lindberg and Rosen (1970), ...
  - Essentially exact Monte Carlo Calculations done by Ceperley and Alder, 1980

Kohn-Sham Equations in the LDA

In the LDA the potential in Kohn-Sham equations is found as a simple derivative:

$$H_{eff}(\vec{\mathbf{r}}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\vec{\mathbf{r}}). \tag{25}$$

and

$$\begin{aligned} V_{eff}(\vec{\mathbf{r}}) &= V_{ext}(\vec{\mathbf{r}}) + \frac{\partial E_{Hart}}{\partial n_{eff}(\vec{\mathbf{r}})} + \frac{\partial E_{xc}}{\partial n_{eff}(\vec{\mathbf{r}})} &(26)\\ &= V_{ext}(\vec{\mathbf{r}}) + V_{Hart}[n_{eff}] + V_{xc}[n_{eff}]. &(27) \end{aligned}$$

where

$$V_{xc}(\vec{\mathbf{r}}) = \frac{\partial E_{xc}}{\partial n_{eff}(\vec{\mathbf{r}})} = \frac{\partial n_{eff}(\vec{\mathbf{r}})\epsilon_{xc}(n_{eff}(\vec{\mathbf{r}}))}{\partial n_{eff}(\vec{\mathbf{r}})} \tag{28}$$

The equations are solved self-consistently with the density which results from the eigenfunctions of the independent electron equations

$$n_{eff}(\vec{\mathbf{r}}) = \sum_{i=1}^{N} |\psi_i(\vec{\mathbf{r}})|^2, \tag{29}$$

LSD - Local Spin Density Approx.

- It is straightforward to generalize the Hohenberg-Kohn and Kohn-Sham approaches to functions of *two* densities $n_\uparrow$ and $n_\downarrow$.
- The exchange energy is easily generalized since exchange is always a sum of terms for $\uparrow$ and $\downarrow$ spins.
- Correlation involves both spins, so it must be parametrized in terms of both $n_\uparrow$ and $n_\downarrow$.
- Thus we are led to the *LSD* form $E_{xc}[n_\uparrow, n_\downarrow]$. All widely used forms are based upon fitting the energies found by Quantum Monte Carlo calculations for interacting electrons done by Ceperley and Alder.
- Parametrized forms given by Perdew and Zunger, 1981, and Vosko, Wilk, and Nusair, 1980.

GGA - Generalized Gradient Approx.

- Exchange and Correlation are ***not*** really local.
- Next approximation: consider $\epsilon_{xc}[n]$ a function of the density and the ***gradient of the density*** at each point
- The function is expressed in terms of the reduced density $s = \frac{|\nabla n|}{2k_F n}$, where $k_F = (3\pi^2 n)^{1/3}$.
- Now widely used especially in chemistry because the GGA improve the estimates of dissociation energies. The GGA lowers the energy of systems with larger gradients. It tends to lower the energy to dissociate a molecule into parts.
- Discussion of forms in paper:
  J. P. Perdew and Kieron Burke, "Comparison Shopping for a gradient-corrected density functional", Int. J. Quant. Chem. 57, 309 (1996).
- Programs for the LDA and various GGA's are available from:
  http://www.phy.tulane.edu/ kieron/dft.html

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