DENSITY-FUNCTIONAL THEORY, AND DENSITY-FUNCTIONAL PRACTICE
Hartree-Fock Equations

\[
\begin{align*}
\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) &= \frac{1}{\sqrt{n!}} \\
\begin{bmatrix}
\phi_\alpha(\vec{r}_1) & \phi_\beta(\vec{r}_1) & \cdots & \phi_\nu(\vec{r}_1) \\
\phi_\alpha(\vec{r}_2) & \phi_\beta(\vec{r}_2) & \cdots & \phi_\nu(\vec{r}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_\alpha(\vec{r}_n) & \phi_\beta(\vec{r}_n) & \cdots & \phi_\nu(\vec{r}_n)
\end{bmatrix} & & \text{SLATER OET}
\end{align*}
\]

\[
\begin{align*}
\begin{bmatrix}
-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \phi_\lambda(\vec{r}_i) + \\
\sum_\mu \left[ \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\mu(\vec{r}_j) d\vec{r}_j \right] \phi_\lambda(\vec{r}_i) - \\
\sum_\mu \left[ \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\lambda(\vec{r}_j) d\vec{r}_j \right] \phi_\mu(\vec{r}_i) = \varepsilon \phi_\lambda(\vec{r}_i)
\end{bmatrix}
\end{align*}
\]
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Screenshot of online article.
http://focus.aps.org/story/v2/st19
The Thomas-Fermi approach

- Let’s try to find out an expression for the energy as a function of the charge density
- \( E = \text{kinetic} + \text{external} + \text{el.-el.} \)
- Kinetic is the tricky term: how do we get the curvature of a wavefunction from the charge density?
- Answer: local density approximation
Local Density Approximation

- We take the kinetic energy density at every point to correspond to the kinetic energy density of the homogenous electron gas.

\[ T(\vec{r}) = A \rho^3(\vec{r}) \]

\[ E_{Th-Fe}[\rho] = A \int \rho^3(\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \]
It’s a poor man Hartree…

- The idea of an energy functional is not justified.
- It does not include exchange effects - but Dirac proposed to add the LDA exchange energy:

\[-C \int \rho(\vec{r})^\frac{4}{3} d\vec{r}\]

- It scales linearly, and we deal with 1 function of three coordinates!
The Argon atom
Density-functional theory

• The external potential $V_{\text{ext}}$ and the number $N$ of electrons completely define the quantum problem

• The wavefunctions are – in principle! – uniquely determined, via the Schrödinger Equation

• All system properties follow from the wavefunctions

• The energy (and everything else) is thus a functional of $V_{\text{ext}}$ and $N$
The Hohenberg-Kohn theorems (1965)

- The density as the basic variable: the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential.
1st Theorem: the Density as the Basic Variable.

Image removed for copyright reasons.
The universal functional $F[\rho]$

- The ground state density determines the potential of the Schrödinger equation, and thus the wavefunctions

$$F[\rho(\vec{r})] = \left\langle \Psi \middle| \hat{T} + \hat{V}_{e-e} \right\rangle$$

- It’s an emotional moment…
Second Hohenberg-Kohn theorem

The variational principle – we have a new Schrödinger’s-like equation, expressed in terms of the charge density only

$$E_v[\rho'(\vec{r})] = F[\rho'(\vec{r})] + \int v_{\text{ext}}(\vec{r}) \rho'(\vec{r}) d\vec{r} \geq E_0$$

($\rho'$ determines it’s groundstate wavefunction, that can be taken as a trial wavefunction in this external potential)

$$< \Psi' | \hat{H} | \Psi' > = < \Psi' | \hat{T} + \hat{V}_{e-e} + v_{\text{ext}} | \Psi' > = \int \rho' v_{\text{ext}} + F[\rho']$$
The non-interacting unique mapping

• The Kohn-Sham system: a reference system is introduced (the Kohn-Sham electrons)

• These electrons do not interact, and live in an external potential (the Kohn-Sham potential) such that their ground-state charge density is IDENTICAL to the charge density of the interacting system
Though this be madness, yet there’s method in’t

• For a system of non-interacting electrons, the Slater determinant is the EXACT wavefunction (try it, with 2 orbitals)
• The kinetic energy of the non interacting system is well defined

\[
F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})],
\]

\[
E_H[n(\mathbf{r})] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2.
\]
Euler-Lagrange Equations

\[ \delta \left[ F[n(r)] + \int v(r)n(r) \, dr - \mu \left( \int n(r) \, dr - N \right) \right] = 0 \]

\[ \frac{\delta F[n(r)]}{\delta n(r)} + v(r) = \mu \Rightarrow \frac{\delta T_s[n(r)]}{\delta n(r)} + v_{KS}(r) = \mu \]

\[ v_{KS}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|} \, dr' + v_{xc}(r); \quad v_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]
The Kohn-Sham equations

\[
\begin{aligned}
\left[-\frac{1}{2} \nabla^2 + v_H(r) + v_{xc}(r) + v_{ext}(r)\right] \psi_i(r) &= \hat{H}_{KS} \psi_i(r) = \varepsilon_i \psi_i(r) \\
v_H(r) &= \int \frac{n(r')}{|r - r'|} dr' , \quad v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \\
n(r) &= \sum_{i=1}^{N} |\psi_i(r)|^2 .
\end{aligned}
\]
Electronic Total Energy

\[
E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \, d\mathbf{r} + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int \psi_{ext}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r}
\]

\[
\sum_{\mathbf{r}} E_H[n(\mathbf{r})] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2
\]
The Homogeneous Electron Gas

Ground State of the Electron Gas by a Stochastic Method
The Exchange-correlation Energy

\[ E_{XC}[n(r)] = \int d\mathbf{r} \, e_{XC}[n(r)] \, n(\mathbf{r}) \]

\[ \approx \int d\mathbf{r} \, [e^{\text{hom}}_X(n(\mathbf{r})) + e^{\text{hom}}_C(n(\mathbf{r}))] \, n(\mathbf{r}) \]

\[ e^{\text{hom}}_X(n) = -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r}) \]

\[ e^{\text{hom}}_C(n) = \begin{cases} 
-0.1423(1 + 1.0529\sqrt{r_s} + 0.3334r_s)^{-1} & \text{if } r_s \geq 1, \\
-0.0480 + 0.0311\ln r_s - 0.0116r_s + 0.002 & \text{if } r_s < 1.
\end{cases} \]

\[ r_s := (4\pi n(\mathbf{r})/3)^{-1/3} \quad \text{Wigner-Seitz radius} \]

[see, e.g. Perdew & Zunger, PRB 23 5048 (1981)]
The Phases of Silicon

1982
MARVIN COHEN

Feb 24 2005   3.320 Atomistic Modeling of Materials -- Gerbrand Ceder and Nicola Marzari
GGAs, meta-GGA, hybrids

- GGAs: generalized gradient approximations (gradients of the density are introduced, preserving analytical – scaling – features of the unknown exact xc functional)
- Hybrids: a certain amount of non-local Hartree-Fock exchange is weighed in
Density-functional theory in practice: the total-energy pseudopotential method

- Remove tightly bound core electrons: the pseudopotential approach
- Represent orbitals on a basis (plane waves)
- Calculate total energy for trial orbitals
  - Kinetic, hartree energy in reciprocal space
  - Exchange-correlation, ext. pot. in real space
  - FFTs!
  - Sum over all states: BZ integrations
- Iterate or minimize to self-consistency
References (theory)

• R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*
• W. Kohn, *Nobel lecture*
• F. Jensen, *Introduction to Computational Chemistry*
• J. M. Thijssen, *Computational Physics*
• B. H. Bransden and C. J. Joachim, *Physics of Atoms and Molecules*
References (practice)


• Lecture notes from

  http://www.FHI-Berlin.MPG.DE/th/Meetings/FHImd2001/program.html ,

  (L3 Pehlke, L2 Kratzer, L4 Fuchs)

Software

- Gaussian (http://www.gaussian.com) ($$) (chemistry, Hartree-Fock, DFT, correlated approaches)
- Gamess-UK (http://www.cse.clrc.ac.uk/qcg/gamess-uk/) ($) (chemistry, Hartree-Fock, DFT, correlated approaches)
- Materials Studio/Cerius (http://www.accelrys.com) ($$) (DFT, planewave, ultrasoft)
- Crystal (http://www.chimifm.unito.it/teorica/crystal) ($) (Hartree-Fock)
- VASP (http://cms.mpi.univie.ac.at/vasp) ($) (DFT, planewave, ultrasoft, PAW)
- ESPRESSO (http://www.pwscf.org) (free) (DFT, planewave, ultrasoft, linear-response theory, Car-Parrinello)
- ABINIT (http://www.abinit.org) (free) (DFT, planewave, linear-response theory, GW)
- CPMD (http://www.cpmd.org) (free) (DFT, planewave, Car-Parrinello, time-dependent DFT)
- CASINO (http://www.tcm.phy.cam.ac.uk/~mdt26/cqmc.html) (free) (Quantum Monte Carlo)