

3.320: Lecture 7 (Feb 24 2005)

DENSITY-FUNCTIONAL THEORY, AND DENSITY-FUNCTIONAL PRACTICE

Hartree-Fock Equations

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{vmatrix}$$

$$\begin{aligned} & \left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) + \\ & \left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \\ & \sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i) \end{aligned}$$

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Screenshot of online article.

"Nobel Focus: Chemistry by Computer." *Physical Review Focus*, 21 October 1998.

<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

$$T(\vec{r}) = A\rho^{\frac{5}{3}}(\vec{r})$$

$$E_{Th-Fe}[\rho] = A \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

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_{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_{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.

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The universal functional $F[\rho]$

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

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

- 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

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

(ρ' determines its groundstate wavefunction, that can be taken as a trial wavefunction in this external potential)

$$\langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{T} + \hat{V}_{e-e} + v_{ext} | \Psi' \rangle = \int \rho' v_{ext} + F[\rho']$$

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

$$\delta \left[F[n(\mathbf{r})] + \int v(\mathbf{r})n(\mathbf{r}) d\mathbf{r} - \mu \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) \right] = 0$$

$$\frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu. \quad \longrightarrow \quad \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{KS}(\mathbf{r}) = \mu.$$

$$v_{KS}(\mathbf{r}) \equiv v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}); \quad v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

The Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \hat{H}_{KS} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

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

Electronic Total Energy

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

$$E_H[n(\vec{r})] = \frac{1}{2} \iint \frac{n(\vec{r}_1) n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

The Homogeneous Electron Gas

Ground State of the Electron Gas by a Stochastic Method

Ceperley and Alder Phys. Rev. Lett. (1980)

The Exchange-correlation Energy

$$\begin{aligned} E_{XC}[n(\mathbf{r})] &= \int d\mathbf{r} e_{XC}[n(\mathbf{r})] n(\mathbf{r}) \\ &\approx \int d\mathbf{r} [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))] n(\mathbf{r}) \end{aligned}$$

$$\begin{aligned} e_X^{hom}(n) &= -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r}) \\ e_C^{hom}(n) &= \begin{cases} -0.1423(1 + 1.0529\sqrt{r_s} + 0.3334r_s)^{-1} & \text{if } r_s \geq 1, \\ -0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.002 & \text{if } r_s < 1. \end{cases} \end{aligned}$$

$r_s := (4\pi n(\mathbf{r})/\mathbf{3})^{-1/3}$ Wigner-Seitz radius
[see, e.g. Perdew & Zunger, PRB **23** 5048 (1981)]

The Phases of Silicon

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)

- W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional 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)

- Payne, Teter, Allan, Arias, Joannopoulos, *Review of Modern Physics* **64**, 1045 (1992).
- Lecture notes from <http://www.FHI-Berlin.MPG.DE/th/Meetings/FHIImd2001/program.html> ,
(L3 Pehlke, L2 Kratzer, L4 Fuchs)
- Hartree-Fock for solids, Dovesi *et al.*, *Physica Status Solidi (b)* **217**, 63 (2000).

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)