# 3.320: Lecture 7 (Feb 24 2005)

# DENSITY-FUNCTIONAL THEORY, AND DENSITY-FUNCTIONAL PRACTICE

# Hartree-Fock Equations

$$\psi(\vec r_1,\vec r_2,\ldots,\vec r_n)=\frac{1}{\sqrt{n!}}\begin{Vmatrix}\varphi_\alpha(\vec r_1) & \varphi_\beta(\vec r_1) & \cdots & \varphi_\nu(\vec r_1)\\ \varphi_\alpha(\vec r_2) & \varphi_\beta(\vec r_2) & \cdots & \varphi_\nu(\vec r_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_\alpha(\vec r_n) & \varphi_\beta(\vec r_n) & \cdots & \varphi_\nu(\vec r_n)\end{Vmatrix}$$

SLATER DET

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec R_I-\vec r_i)\right]\varphi_\lambda(\vec r_i)+$$

$$\left[\sum_\mu \int \varphi_\mu^*(\vec r_j)\frac{1}{|\vec r_j-\vec r_i|}\varphi_\mu(\vec r_j)\,d\vec r_j\right]\varphi_\lambda(\vec r_i)-$$

$$\sum_\mu\left[\int \varphi_\mu^*(\vec r_j)\frac{1}{|\vec r_j-\vec r_i|}\varphi_\lambda(\vec r_j)\,d\vec r_j\right]\varphi_\mu(\vec r_i)=\varepsilon\varphi_\lambda(\vec r_i)$$

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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

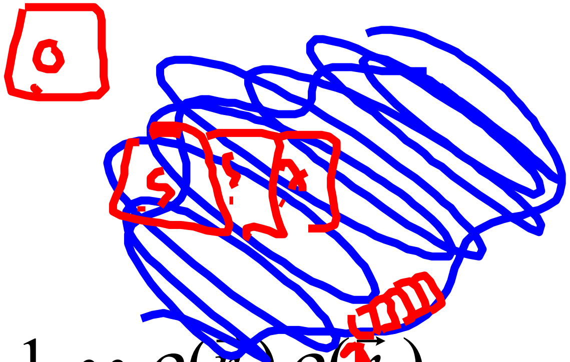
- Let’s try to find out an expression for the energy as a function of the charge density
- E=kinetic+external+el.-el.
- Kinetic is the tricky term: how do we get the curvature of a wavefunction from the charge density ?
- Answer: local density approximation

$e^{i\vec{k}\cdot\vec{r}}$

# Local Density Approximation

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

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

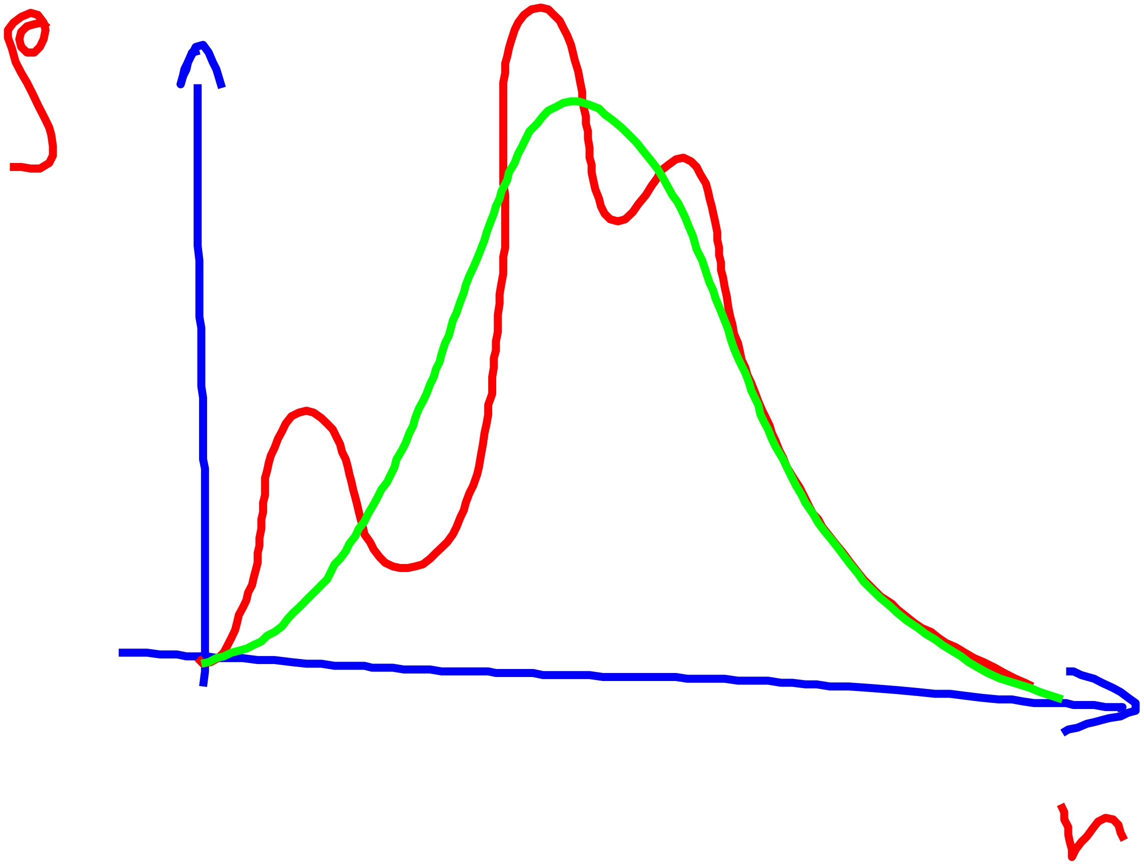


$$E_{Th-Fe}[\rho] = A\int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} + \int \rho(\vec{r})v_{ext}(\vec{r})d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d\vec{r}_1 d\vec{r}_2$$

# 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*[ρ]

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

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

- 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 it's groundstate wavefunction, that can be taken as a trial wavefunction in this external potential)

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

# 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

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

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

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

# The Kohn-Sham equations

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

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

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

# Electronic Total Energy

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \underline{\psi_i^\star(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\, d\mathbf{r}} + \underline{E_H[n(\mathbf{r})]} +$$

$$+\underline{E_{xc}[n(\mathbf{r})]} + \int \underline{v_{ext}(\mathbf{r})n(\mathbf{r})\, d\mathbf{r}}$$

$$\neq \sum \varepsilon_i$$

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

$$= \sum \langle \psi_i | \overset{\wedge}{T} + V_{KS} | \psi_i \rangle$$

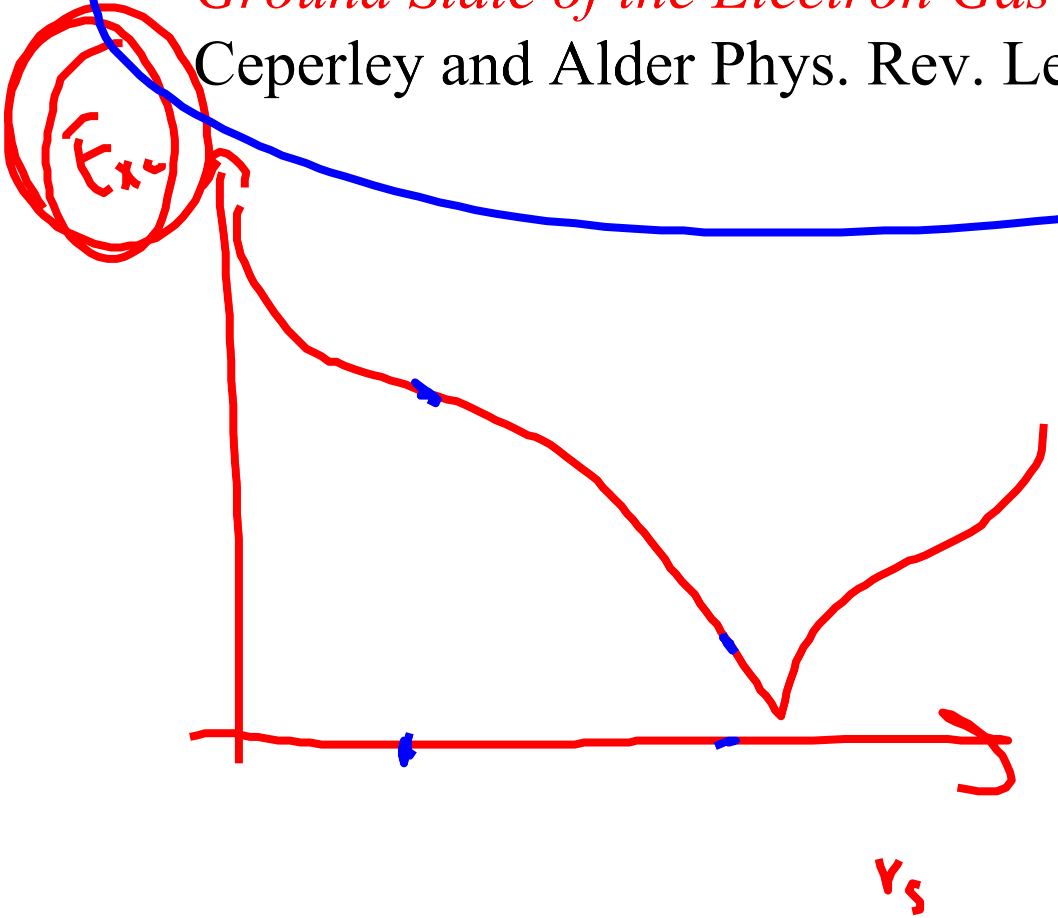
$$-\frac{1}{2}\nabla_i^2$$

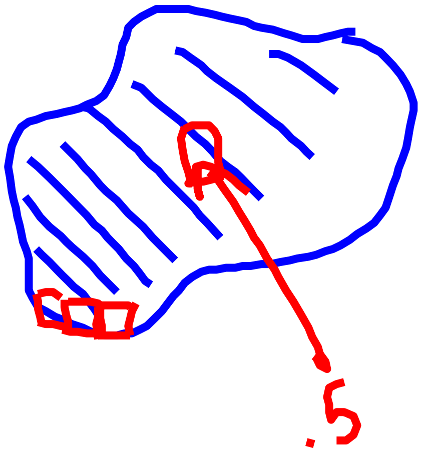
# The Homogeneous Electron Gas

*Ground State of the Electron Gas by a Stochastic Method*

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

$E_{xc}[n(\vec{r})]$





# The Exchange-correlation Energy

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

$$e_X^{hom}(n) = -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r})$$

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

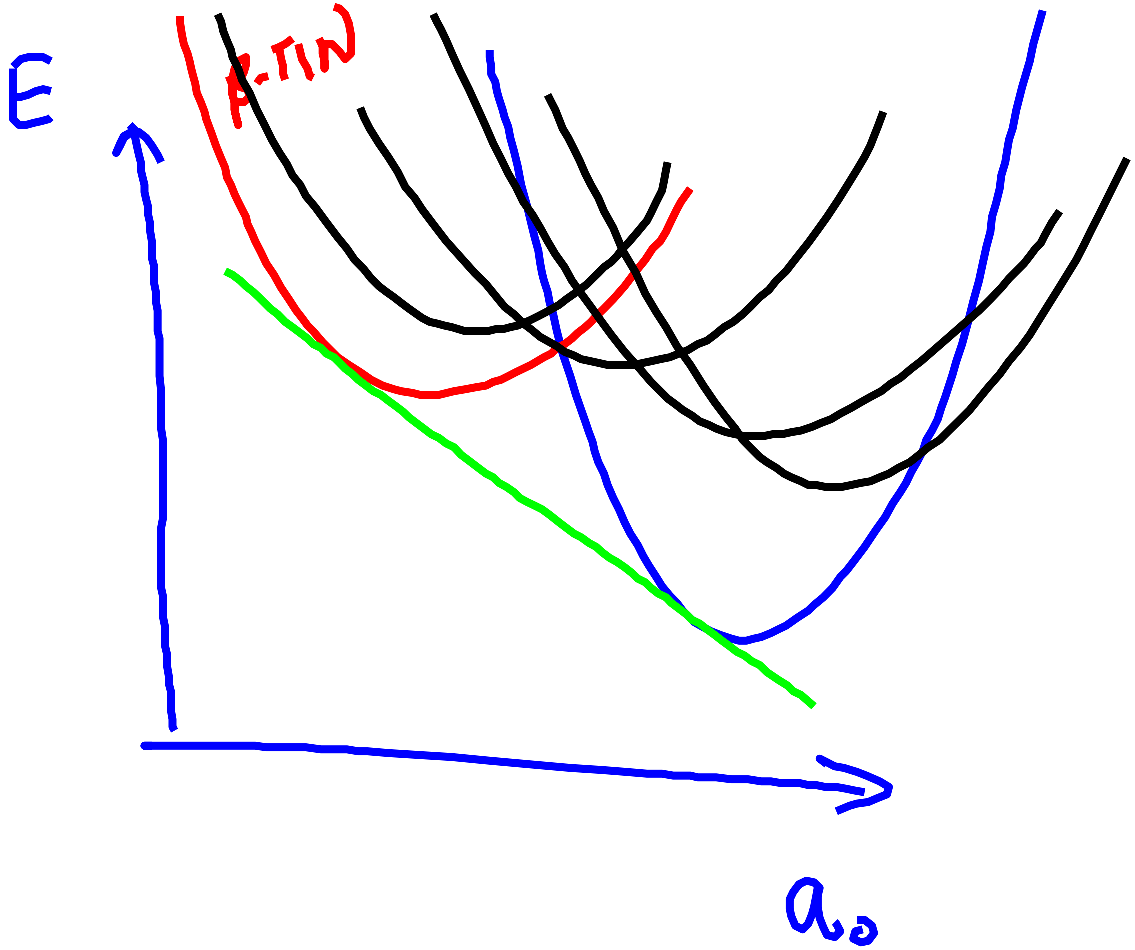
$r_s := (4\pi n(\mathbf{r})/3)^{-1/3}$ Wigner-Seitz radius

[see, e.g. Perdew & Zunger, PRB **23** 5048 (1981)]

# The Phases of Silicon

1982

MARVIN
COHEN



PBE-GGA

# 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/FHImd2001/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)