3.320: Lecture 6 (Feb 17 2005)

HARTREE-FOCK AND DFT

Photos of Hartree, Fock, Hohenberg, Kohn, and Sham
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Matrix Formulation and Variational Principle

$$\sum_{n=1,k} c_n \langle \varphi_m | \hat{H} | \varphi_n \rangle = E c_m$$

$$E[\Phi] = \frac{< \Phi | \hat{H} | \Phi >}{< \Phi | \Phi >} \geq E_0$$

Energy of an Hydrogen Atom

$$E_\alpha = \frac{\left\langle \Psi_\alpha \left| \hat{H} \right| \Psi_\alpha \right\rangle}{\left\langle \Psi_\alpha \middle| \Psi_\alpha \right\rangle}$$

$$\Psi_\alpha = C \exp\left(-\alpha r\right)$$

$$\left\langle \Psi_\alpha \middle| \Psi_\alpha \right\rangle = \pi \frac{C^2}{\alpha^3}, \qquad \left\langle \Psi_\alpha \left| -\frac{1}{2}\nabla^2 \right| \Psi_\alpha \right\rangle = \pi \frac{C^2}{2\alpha} \qquad \left\langle \Psi_\alpha \left| -\frac{1}{r} \right| \Psi_\alpha \right\rangle = -\pi \frac{C^2}{\alpha^2}$$

Two-electron atom

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right]\psi(\vec{r}_1,\vec{r}_2) = E_{el}\psi(\vec{r}_1,\vec{r}_2)$$

Many-electron atom

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1,...,\vec{r}_n) = E_{el}\psi(\vec{r}_1,...,\vec{r}_n)$$

Atomic Units and Conversion Factors (see handout)

1 a.u. = 2 Ry = 1 Ha

1 Ry = 13.6057 eV

1 eV = 23.05 kcal/mol

Molecules and Solids: Electrons and Nuclei

$$\hat{H}\psi(\vec{r}_1,...,\vec{r}_n,\vec{R}_1,...,\vec{R}_N) = E_{tot}\psi(\vec{r}_1,...,\vec{r}_n,\vec{R}_1,...,\vec{R}_N)$$

- We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying) nuclei

- This is generically called the adiabatic or Born-Oppenheimer approximation

- "Adiabatic" means that there is no coupling between different electronic surfaces; "B-O" implies there is no influence of the ionic motion on one electronic surface

Energy of a collection of atoms

$$\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-N} + V_{N-N}$$

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{V}_{e-N} = \sum_i \left[\sum_I V\left(\vec{R}_I - \vec{r}_i\right) \right] \qquad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- T_e: quantum kinetic energy of the electrons
- V_{e-e}: electron-electron interactions
- V_{e-N}: electrostatic electron-nucleus attraction (electrons in the field of all the nuclei)
- V_{N-N}: electrostatic nucleus-nucleus repulsion

Complexity of the many-body Ψ

"…Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of one variable requires a page, of two variables a volume and of three variables a library; but the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable at which to tabulate this function, but even so, full tabulation would require 10^{78} entries."

Mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons

- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons

Hartree Equations

The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written – as above – as the product of single orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1,...,\vec{r}_n) = \varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i}\int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|}d\vec{r}_j\right]\varphi_i(\vec{r}_i) = \varepsilon\varphi_i(\vec{r}_i)$$

The self-consistent field

- The single-particle Hartree operator is self-consistent ! It depends on the orbitals that are the solution of all other Hartree equations

- We have *n* simultaneous integro-differential equations for the *n* orbitals

- Solution is achieved iteratively

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j\neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon\varphi_i(\vec{r}_i)$$

Iterations to self-consistency

- Initial guess at the orbitals
- Construction of all the operators
- Solution of the single-particle pseudo-Schrodinger equations
- With this new set of orbitals, construct the Hartree operators again
- Iterate the procedure until it (hopefully) converges

Differential Analyzer
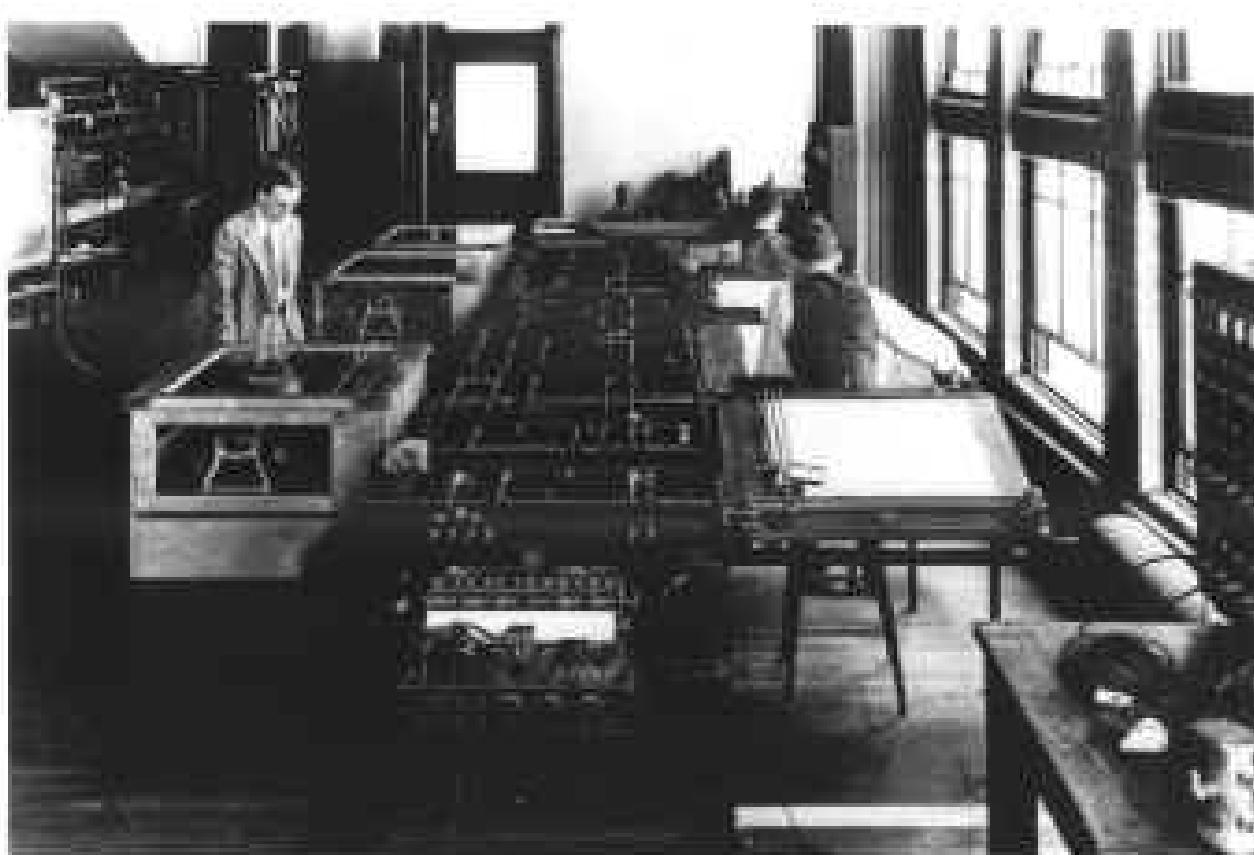
Vannevar Bush and the Differential Analyzer.
Courtesy of the MIT Museum. Used with permission.

What's missing

- It does not include correlation

- The wavefunction is not antisymmetric

- It does remove *nl* accidental degeneracy of the hydrogenoid atoms

Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)

- A set of identical (indistinguishable) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_j, ..., \vec{r}_k, ..., \vec{r}_n) = -\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_k, ..., \vec{r}_j, ..., \vec{r}_n)$$

- For bosons it is symmetric

Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

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

Pauli principle

- If two states are identical, the determinant vanishes (i.e. we can't have two electrons in the same quantum state)

Hartree-Fock Equations

The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schroedinger equation in the class of all wavefunctions that are written as a single Slater determinant

$$\psi(\vec{r}_1,...,\vec{r}_n) = \left\| Slater \right\|$$

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) +$$

$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) -$$

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

Shell structure of atoms

- Self-interaction free

- Good for atomic properties

- Start higher-order perturbation theory

- Exchange is in, correlation still out

Restricted vs. Unrestricted

- Spinorbitals in the Slater determinant: spatial orbital times a spin function

- Unrestricted: different orbitals for different spins

- Restricted: same orbital part

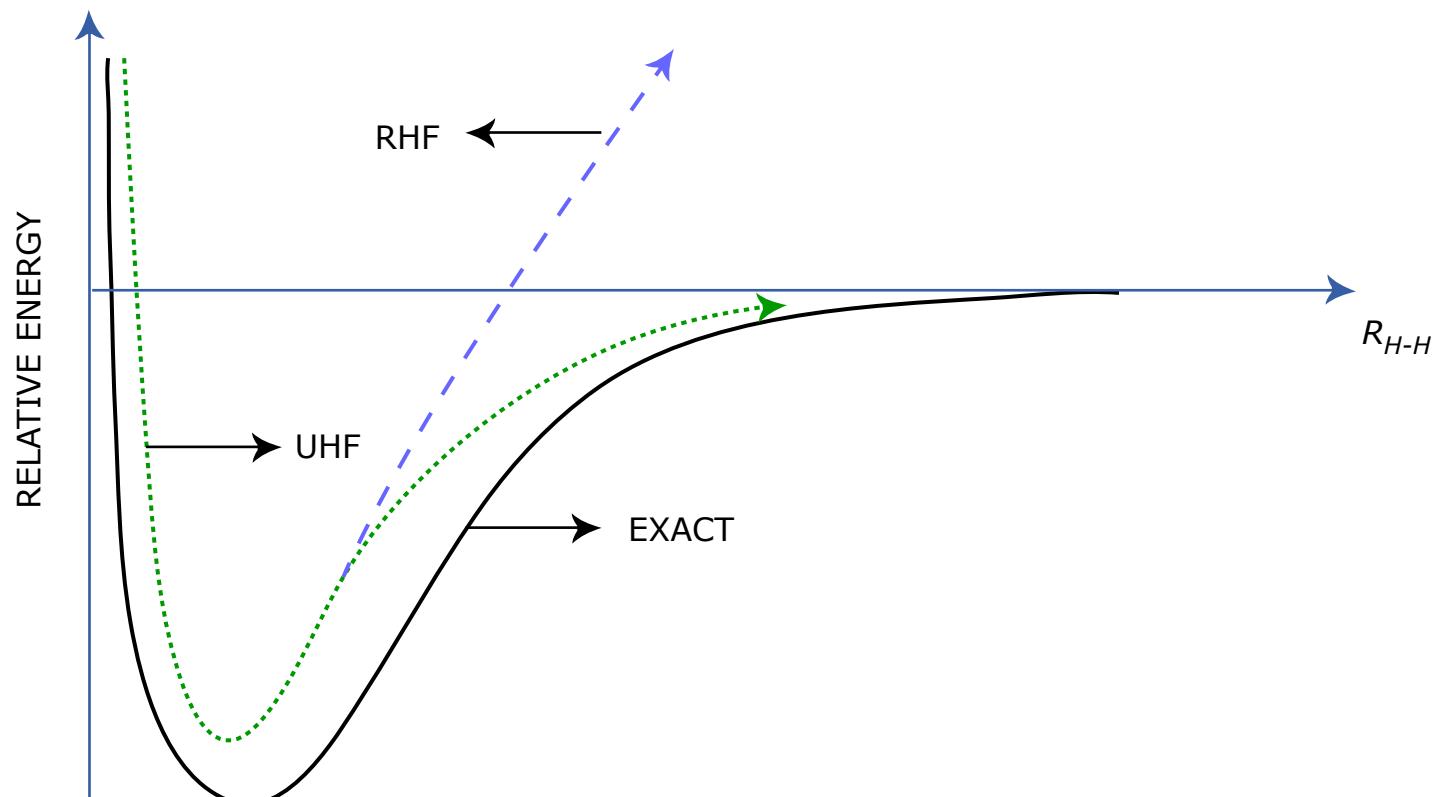# The Dissociation of H_2

Figure by MIT OCW.

Koopmans' Theorems

- Total energy is invariant under unitary transformations

- It is not the sum of the canonical MO orbital energies

- Ionization energy, electron affinity are given by the eigenvalue of the respective MO, in the frozen orbitals approximation

What is missing

- Correlations (by definition !)
  - Dynamical correlations: the electrons get too close to each other in H.-F.
  - Static correlations: a single determinant variational class in not good enough
- Spin contamination: even if the energy is correct (variational, quadratic) other properties might not (e.g. the UHF spin is an equal mixture of singlet and triplet)

Faster, or better

- The exchange integrals are the hidden cost (fourth power). Linear-scaling efforts underway

- Semi-empirical methods (ZDO, NDDO, INDO, CNDO, MINDO): neglect certain multi-center integrals

- Configuration interaction, Møller-Plesset

Configuration Interaction

In normal Hartree Fock, the HF determinant is built from the lowest energy single-electron states

N basis functions and K electrons -> fill up φ_i with K lowest energies

$$\Psi_{HF}^{0} = \left| \varphi_1 \; \varphi_2 \; ... \; \varphi_K \right|$$

IDEA of CI is to mix in "excited" states

e.g. exchange state i with K+1

$$\Psi_{HF}^{1} = \left| \varphi_1 \; \varphi_2 \; ... \; \varphi_{K+1} \; ... \; \varphi_K \right|$$

Issues:

Many possible excitations (combinatorial problem)

Time consuming (scaling N^7)

Define new variational wave function:

$$\Psi = c_0 \Psi_0 + c_1 \Psi_1 + c_2 \Psi_2 + ...$$

Image removed for copyright reasons.
Screenshot of online article.
"Nobel Focus: Chemistry by Computer." *Physical Review Focus*, 21 October 1998.
http://focus.aps.org/story/v2/st19

End of lecture

Background slides follow
(see next lecture)

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 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

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

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.

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

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

Euler-Lagrange equations

$$\delta\left[F[\rho(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r} - \mu\left(\int \rho(\vec{r})d\vec{r} - N\right)\right] = 0$$

$$\frac{\delta F[\rho(\vec{r})]}{\delta \rho(\vec{r})} + v_{ext}(\vec{r}) = \mu$$

References

- 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*

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)