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FROM ___John Perdew___ NO. OF PAGES ___28___

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0.

BASICS OF GROUNDSTATE

DENSITY FUNCTIONAL THEORY

JOHN P. PERDEW
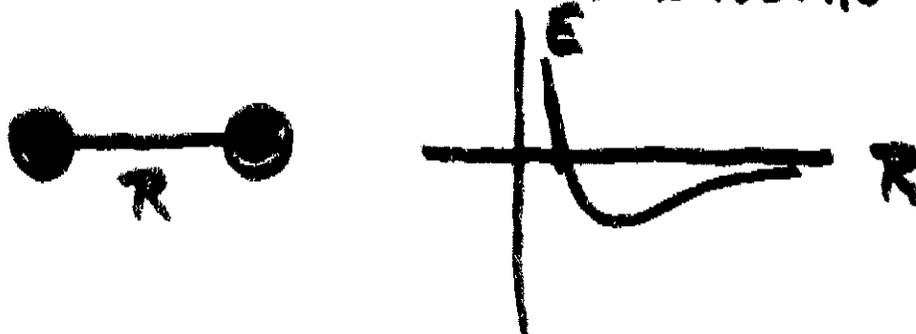### PHYSICS
TULANE UNIVERSITY
NEW ORLEANS

1.

ELECTRONIC STRUCTURE PROBLEM FOR ATOMS, MOLECULES, & SOLIDS

WHAT ATOMS, MOLECULES, & SOLIDS CAN EXIST, AND WITH WHAT PROPERTIES?

WHAT ARE THE GROUNDSTATE ENERGIES E AND ELECTRON DENSITIES $n(\vec{r})$?

WHAT ARE THE BOND LENGTHS & ANGLES?

WHAT ARE THE NUCLEAR VIBRATIONS?

HOW MUCH ENERGY IS NEEDED TO IONIZE THE SYSTEM, OR TO BREAK BONDS?

WAVEFUNCTION APPROACH

HAMILTONIAN FOR N ELECTRONS $(i=1...N)$
IN THE PRESENCE OF EXTERNAL POTENTIAL
$v(\vec{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i)$$

$$\hat{T} = \sum_i -\frac{1}{2} D_i^2$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} .$$

OFTEN $v(\vec{r}) = \sum_\beta \frac{-Z_\beta}{|\vec{r} - \vec{R}_\beta|}$

= ELECTRON-NUCLEUS ATTRACTION,
AND E INCLUDES ALSO

$$\frac{1}{2} \sum_\beta \sum_{\gamma \neq \beta} \frac{Z_\gamma Z_\gamma}{|\vec{R}_\beta - \vec{R}_\gamma|}$$

= NUCLEUS-NUCLEUS REPULSION.

3.

SCHRÖDINGER EQUATION FOR STATIONARY STATES $\hat{H}\Psi = E\Psi$

$$\Psi = \Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \ldots \vec{r}_N \sigma_N)$$

Ψ IS NORMALIZED: $\langle \Psi | \Psi \rangle = 1$,

AND ANTISYMMETRIC:

$$\Psi(\ldots \vec{r}_i \sigma_i \ldots \vec{r}_j \sigma_j \ldots)$$
$$= -\Psi(\ldots \vec{r}_j \sigma_j \ldots \vec{r}_i \sigma_i \ldots)$$

$$E \rightarrow \Delta E$$

$$n(\vec{r}) = N \sum_{\sigma_1} \ldots \sum_{\sigma_N} \int d^3 r_2 \ldots d^3 r_N$$
$$|\Psi(\vec{r}\sigma_1, \vec{r}_2 \sigma_2, \ldots \vec{r}_N \sigma_N)|^2$$

4.

$$h[\Psi] \equiv \langle \Psi | H | \Psi \rangle$$

IS A FUNCTIONAL:
A RULE THAT ASSIGNS A NUMBER h
TO EVERY FUNCTION Ψ.

WAVEFUNCTION VARIATIONAL PRINCIPLE:

THE EXTREMA OF $h[\Psi]$ ARE
THE STATIONARY STATES, AND
THE ABSOLUTE MINIMUM IS THE
GROUND STATE.

WAVEFUNCTIONS ARE NEVER USED
FOR LARGE ELECTRON NUMBER N!

5.

WHY NOT MANY-ELECTRON WAVE FUNCTIONS?

IMAGINE A GRID OF M POINTS IN POSITION SPACE FOR EACH ELECTRON. WE MUST THEN COMPUTE & STORE M^N VALUES OF Ψ.   (KOHN)

LET $M = 10^2$ (NOT REALLY ENOUGH).
FOR $N=2$, $M^N = 10^4$ IS OK.
FOR $N=10$, $M^N = 10^{20}$ IS NOT OK.

AVOIDING GRIDS, ONE CAN STUDY AT MOST (AND AT GREAT EXPENSE) 10 TO 100 ELECTRONS.

THE DENSITY $n(\vec{r})$ HOWEVER WOULD REQUIRE COMPUTING & STORING ONLY M VALUES.

6.

HOHENBERG-KOHN THEOREM 1964:
CENTRAL THEOREM OF DFT

(1) THERE EXISTS A FUNCTIONAL $F[n]$ OF THE ELECTRON DENSITY, SUCH THAT THE GS ENERGY AND DENSITY FOR N ELECTRONS IN THE PRESENCE OF EXTERNAL POTENTIAL $v(\vec{r})$ IS

$$E_{GS} = \min_{n} \left\{ F[n] + \int d^3r \, v(\vec{r}) \, n(\vec{r}) \right\}.$$

THE MINIMUM IS TAKEN OVER ALL POSITIVE $n(\vec{r})$ SUCH THAT $\int d^3r \, n(\vec{r}) = N$.

$F[n]$ IS UNIVERSAL (INDEPENDENT OF v)

THE PROBLEM IS TO FIND (APPROXIMATE) THE FUNCTIONAL $F[n]$.

7.

(2) THE EXTERNAL POTENTIAL $v(\vec{r})$ AND HENCE THE HAMILTONIAN $\hat{H}$ ARE DETERMINED TO WITHIN AN ADDITIVE CONSTANT BY $n(\vec{r})$.

PROOF BY LEVY CONSTRAINED SEARCH M79

$$E_{GS} = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i) | \Psi \rangle$$

$$= \min_n \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d\vec{r} \, v(\vec{r}) n(\vec{r}) \right\}$$

(1)
$$= \min_n \left\{ F[n] + \int d\vec{r} \, v(\vec{r}) n(\vec{r}) \right\}$$

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle$$

$\Psi_n =$ THAT WAVEFUNCTION YIELDING DENSITY $n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \hat{V}_{ee} \rangle$

8.

EULER EQUATION FOR $n(\vec{r})$:

$$\delta \left\{ F[n] + \int d\vec{r}\, n(\vec{r})\, v(\vec{r}) - \mu \int d^3r\, n(\vec{r}) \right\} = 0$$

$$\frac{\delta F}{\delta n(\vec{r})} + v(\vec{r}) - \mu = 0 \left.\right\} \quad \text{FOR GS}$$

$$\text{(2)} \quad v(\vec{r}) = \mu - \frac{\delta F}{\delta n(\vec{r})} \qquad n(\vec{r})$$

FUNCTIONAL DERIVATIVE $\frac{\delta F}{\delta n(\vec{r})}$:

$$\delta F \equiv \int d^3r \left(\frac{\delta F}{\delta n(\vec{r})} \right) \delta n(\vec{r}) .$$

EX: $\quad E_x^{LDA}[n] = -C \int d^3r\, n^{4/3}(\vec{r})$

$$\delta E_x^{LDA}[n] = -C \int d\vec{r}\, \frac{4}{3}\, n^{1/3}(\vec{r})\, \delta n(\vec{r})$$

$$\frac{\delta E_x^{LDA}}{\delta n(\vec{r})} = -\frac{4}{3} C\, n^{1/3}(\vec{r})$$

9.

THE CONSTRAINED SEARCH IS
FOR UNDERSTANDING, NOT FOR
CALCULATING!

THE EXACT $F[n]$ REQUIRES A CONSTRAINED
SEARCH OVER N-ELECTRON WAVEFUNCTIONS,
WHICH IS IMPRACTICAL.

APPROXIMATIONS FOR $F[n]$ THAT ARE
EXPLICIT FUNCTIONALS OF $n(\vec{r})$ ARE
TOO CRUDE TO BE VERY USEFUL.

1965: THE KOHN-SHAM SCHEME INTRODUCES
ORBITALS THAT ARE IMPLICIT
FUNCTIONALS OF THE DENSITY,
AND CALCULATES THE BIGGEST
PART OF $F[n]$ EXACTLY FROM
THESE ORBITALS.

KOHN-SHAM NON-INTERACTING SYSTEM :

A FICTIONAL NON INTERACTING GROUND STATE Φ_n (USUALLY A SINGLE SLATER DETERMINANT) WITH THE SAME DENSITY $n(\vec{r})$ AND CHEMICAL POTENTIAL AS THE PHYSICAL INTERACTING GROUND STATE Ψ_n.

$$\hat{H}_s = \hat{T} + \sum_i \upsilon_s(\vec{r}_i)$$

$$s = \text{single-particle}$$

$$\hat{H}_s \Phi_n = E_s \Phi_n$$

Φ_n = THAT NON INTERACTING WAVE FUNCTION YIELDING DENSITY $n(\vec{r})$ AND MINIMIZING $\langle \hat{T} \rangle$.

NON-INTERACTING KINETIC ENERGY

$$T_s[n] = \langle \Phi_n | \hat{T} | \Phi_n \rangle$$

$$F[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle$$

$$= \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle + E_c[n]$$

CORRELATION ENERGY

$$E_c[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle$$
$$\leq 0.$$

$$\langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle = U[n] + E_x[n]$$

HARTREE ELECTROSTATIC ENERGY

$$U[n] = \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

EXCHANGE ENERGY $E_x[n]$

$$F[n] = \underbrace{T_s[n] + U[n]}_{\text{TREATED EXACTLY}} + \underbrace{E_{xc}[n]}_{\substack{\text{SOME APPROX. FOR} \\ E_x + E_c}}$$

EULER EQUATIONS

$$\frac{\delta T_s}{\delta n(\vec{r})} + v_s(\vec{r}) = \mu$$

$$\frac{\delta T_s}{\delta n(\vec{r})} + \frac{\delta u}{\delta n(\vec{r})} + \frac{\delta E_{xc}}{\delta n(\vec{r})} + v(\vec{r}) = \mu$$

} SAME SOLUTION

$$v_s(\vec{r}) = v(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{xc}([n],\vec{r})$$

$$v_{xc}([n];\vec{r}) = \frac{\delta E_{xc}}{\delta n(\vec{r})}$$

SELF-CONSISTENT KOHN-SHAM SCHEME

$$\left[-\frac{1}{2}\nabla^2 + v(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}([n];\vec{r}) \right] \psi_\alpha(\vec{r}) = \varepsilon_\alpha \psi_\alpha$$

$$n(\vec{r}) = \sum_\alpha^{occ} |\psi_\alpha(\vec{r})|^2$$

$$T_s[n] = \sum_\alpha^{occ} \int d^3r\, \psi_\alpha^*(\vec{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_\alpha(\vec{r})$$

THE KOHN-SHAM ORBITALS $\psi_\alpha(\vec{r})$ ARE
IMPLICIT FUNCTIONALS OF $n(\vec{r})$.

COUPLING CONSTANT INTEGRAL FOR E_{xc}

LANGRETH + PERDEW 1975

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \sum_i \upsilon_\lambda(\vec{r}_i)$$

ADJUST $\upsilon_\lambda(\vec{r})$ TO HOLD THE GS DENSITY

FIXED AT ITS $\lambda = 1$ VALUE.

$\lambda = 1$: REAL INTERACTING SYSTEM

$$\upsilon_\lambda(\vec{r}) = \upsilon(\vec{r}).$$

$\lambda = 0$: KOHN-SHAM NON-INTERACTING SYSTEM

Ψ_n^λ = THAT WAVEFUNCTION YIELDING DENSITY

$n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$.

$$\Psi_n^1 = \Psi_n, \quad \Psi_n^0 = \Phi_n$$

$$E_{xc}[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle$$

$$- \langle \Phi_n | \hat{T} | \Phi_n \rangle - U[n]$$

$$= \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle \Big|_{\lambda=0}^{1} - U[n]$$

$$= \int_0^1 d\lambda \, \frac{d}{d\lambda} \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n]$$

$$= \int_0^1 d\lambda \, \langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n]$$

BY   HELLMANN-FEYNMAN

$$\langle \Psi_\lambda^\lambda | \hat{V}_{ee} | \Psi_\lambda^\lambda \rangle = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \, \frac{\rho_2^\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

WHERE

$$\rho_2^\lambda(\vec{r}, \vec{r}') = N(N-1) \sum_{\sigma_1} \cdots \sum_{\sigma_N} \int d\vec{r}_3 \cdots d\vec{r}_N$$

$$| \Psi_n^\lambda(\vec{r}\sigma_1, \vec{r}'\sigma_2, \vec{r}_3\sigma_3 \cdots \vec{r}_N \sigma_N) |^2$$

$$= \text{TWO-PARTICLE DENSITY MATRIX}$$

15.

$$\rho_2^2(\vec{r},\vec{r}') = \text{JOINT PROBABILITY DENSITY}$$

$$= n(\vec{r})\left[n(\vec{r}') + n_{xc}^2(\vec{r},\vec{r}') \right]$$

$$\int d^3r \int d^3r' \, \rho_2(\vec{r},\vec{r}') = N(N-1)$$

$$\int d^3r \int d^3r' \, n(\vec{r}) \, n(\vec{r}') = N(N)$$

$$\text{so} \quad \int d^3r' \, n_{xc}^2(\vec{r},\vec{r}') = -1 \qquad \text{SUM RULE}$$

$n_{xc}^2(\vec{r},\vec{r}') =$ DENSITY AT $\vec{r}'$ OF THE XC HOLE AROUND AN ELECTRON AT $\vec{r}$, AROUND AN ELECTRON AT $\vec{r}$, ONE ELECTRON IS MISSING FROM THE SPACE $\vec{r}' \neq \vec{r}$.

$$E_{xc}[n] = \int_0^1 d\lambda \, \frac{1}{2} \int d^3r \int d^3r' \, n(\vec{r}) \, \frac{n_{xc}^2(\vec{r},\vec{r}')}{|\vec{r} - \vec{r}'|}$$

16.

E_x CAN BE EXPRESSED AS A FOLK INTEGRAL OF OCCUPIED ORBITALS:

$$n_x(\vec{r},\vec{r}') = n_{x_c}^{\lambda=0}(\vec{r},\vec{r}')$$

$$= -\frac{1}{n(\vec{r})} \sum_{\sigma} |\rho_\sigma(\vec{r},\vec{r}')|^2$$

WHERE $\rho_\sigma(\vec{r},\vec{r}') = \sum_{\alpha}^{occup} \psi_{\alpha\sigma}^*(\vec{r}') \psi_{\alpha\sigma}(\vec{r})$

$$= \text{KOHN-SHAM ONE-PARTICLE}$$
$$\text{DENSITY MATRIX}$$

EXACT CONSTRAINTS: WE KNOW MANY EXACT CONSTRAINTS ON THE HOLE (SUCH AS THE SUM RULE) OR ON THE X_C ENERGY.

17.

EX: UNIFORM DENSITY SCALING OF $E_x[n]$

LEVY + PERDEW

FOR ANY POSITIVE SCALE PARAMETER λ,
DEFINE A SCALED DENSITY

$$n_\lambda(\vec{r}) = \lambda^3 n(\lambda\vec{r})$$

WHEN $n(\vec{r}) \to n_\lambda(\vec{r})$,

$$\not{\psi}_\alpha(\vec{r}) \to \lambda^{3/2} \not{\psi}_\alpha(\lambda\vec{r}),$$

SO

$$E_x[n_\lambda] = \lambda\, E_x[n]$$

HIGH-DENSITY LIMIT: $\lambda \to \infty$

$$E_c[n_\lambda] \to \text{CONSTANT} \quad \text{(NON-DEGEN)}$$

$$E_x \text{ DOMINATES } E_c$$

18.

MANY OTHER EXACT CONSTRAINTS
ON $n_{xc}^2(\vec{r}, \vec{r}')$ OR $E_{xc}[n]$
HAVE BEEN DERIVED. THESE
CONSTRAINTS HAVE BEEN USED
TO CONSTRUCT APPROXIMATIONS
TO $E_{xc}[n]$, WITHOUT (OR WITH)
FITTING TO DATA.

FULLY NONEMPIRICAL :

    LOCAL DENSITY APPROXIMATION

    PBE GENERALIZED GRADIENT APPROX.

    TPSS META-GENERALIZED GRADIENT
    APPROXIMATION

    PBEsol : MONDAY AFTERNOON
             DFT SYMPOSIUM

19.

WE CAN CONSTRUCT THE EXACT $E_x[n]$ FROM KOHN-SHAM ORBITALS (AS IN OEP), BUT BONDS ARE DESCRIBED BETTER WHEN WE MAKE THE SAME LOCAL OR SEMI-LOCAL APPROXIMATION FOR E_x AND FOR E_c. THAT IS BECAUSE $n_{xc}^2(\vec{r}, \vec{r}')$ IS TYPICALLY DEEPER, MORE SHORT-RANGED IN $|\vec{r}' - \vec{r}|$, AND THUS MORE SEMI-LOCAL THAN IS $n_x(\vec{r}, \vec{r}')$.

20.

SIMPLEST DENSITY FUNCTIONAL:
LOCAL DENSITY APPROXIMATION

$$E_{xc}^{LDA}[n] = \int d^3r \; n(\vec{r}) \; \varepsilon_{xc}^{unif}(n(\vec{r}))$$

$\varepsilon_{xc}^{unif}(n) = xc$ ENERGY PER ELECTRON
FOR AN ELECTRON GAS OF UNIFORM
DENSITY n.

EXACT FOR A UNIFORM DENSITY.
   CORRECTIONS FOR A SLOWLY-VARYING
DENSITY $\sim |\nabla n|^2$.

$$n_{xc}^{LDA}(\vec{r}, \vec{r}') = n_{xc}^{unif}(n(\vec{r}); |\vec{r}'-\vec{r}|)$$
   SATISFIES SUM RULE AND SEVERAL
OTHER EXACT CONSTRAINTS,
INCLUDING SCALING FOR x.

21.

JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

$$E_{xc} = \int d^3r \, f(n, Dn, \tau, \ldots)$$

$$\tau(\vec{r}) = \sum_{\alpha}^{occ} \frac{1}{2} |D\varphi_{\alpha}|^2 = \text{POSITIVE}$$

KE DENSITY

HEAVEN OF CHEMICAL ACCURACY

ALL $\varphi_{i}(\vec{r})$ ————————— GENERALIZED RPA

E_x^{exact} ————————— HYPER-GGA

τ ————————— META-GGA

Dn ————————— GGA

n ————————— LDA

SIMPLICITY ↓

ACCURACY ↑

HARTREE WORLD
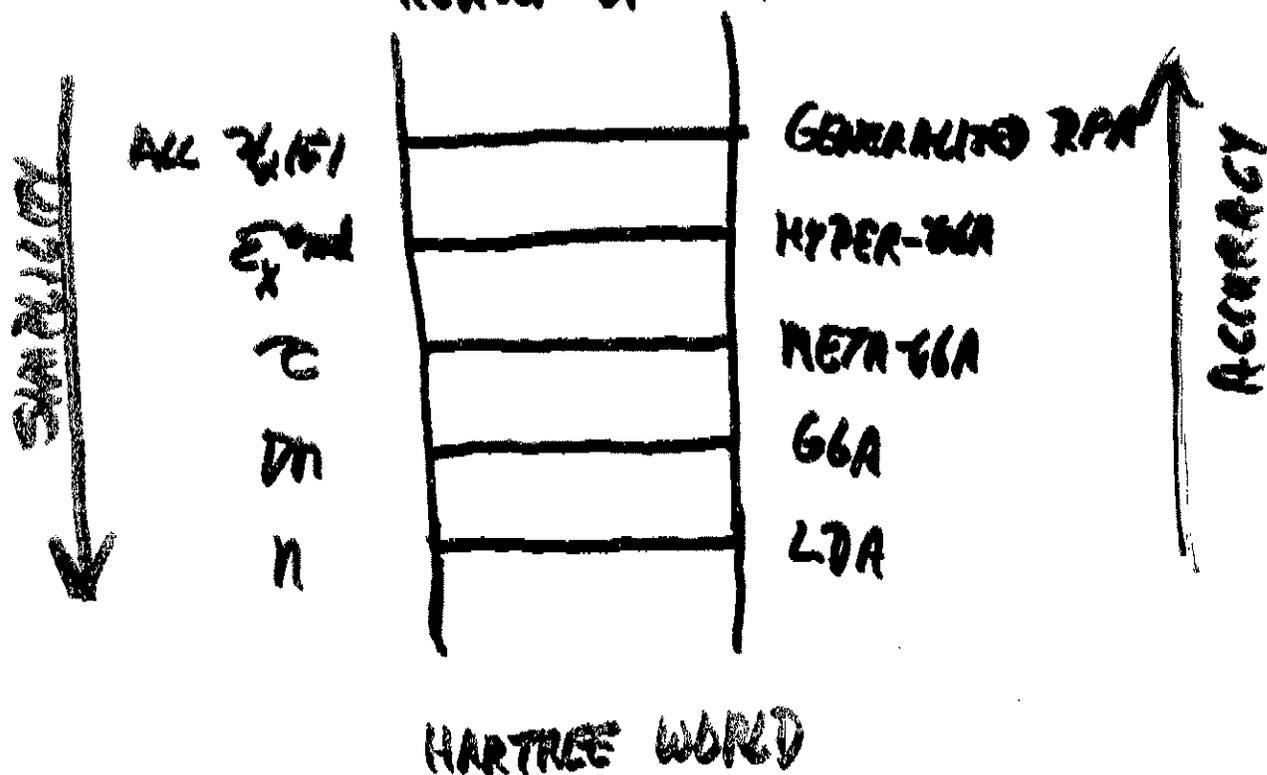
More basics of DFT

Kieron Burke and friends
UC Irvine Physics and Chemistry

3/23/2010   APS tutorial   1

References for ground-state DFT

- *ABC of DFT*, by KB and Rudy Magyar, http://dft.uci.edu
- *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003)
- *Density Functional Theory*, Dreizler and Gross, (Springer-Verlag, Berlin, 1990)
- *Density Functional Theory of Atoms and Molecules*, Parr and Yang (Oxford, New York, 1989)
- *A Chemist's Guide to Density Functional Theory*, Koch and Holthausen (Wiley-VCH, Weinheim,2000)
- *Which functional should I choose?* D. Rappoport et al, http://dft.uci.edu
- *Excited states from time-dependent density functional theory* P. Elliott, F. Furche, and K. Burke, in Reviews in Computational Chemistry, eds. K. B. Lipkowitz and T. R. Cundari, (Wiley, Hoboken, NJ, 2009) and http://dft.uci.edu

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Atomic units and particles in box

- In atomic units, all energies are in Hartree (1 H = 27.2 eV) and all distances in Bohr (1 a_0 = 0.529 Å)
- To write formulas in atomic units, set $e^2 = \hbar = m_e = 1$
- E.g., usual formula for energy levels of infinite well of width L:

$$\varepsilon_j = \frac{h^2 j^2}{8mL^2}, \quad j = 1,2,3,\ldots$$

- Atomic units, box length L=1:

$$\varepsilon_j = \frac{\pi^2 j^2}{2}, \quad j = 1,2,3,\ldots$$

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Constructing your very first density functional

- Let's look at the kinetic energy of spinless fermions in 1d: $T_s[n] = \frac{1}{2} \int_{-\infty}^{\infty} dx \sum_{j=1}^{N} \left| \frac{d\phi_j(x)}{dx} \right|^2$
- Is there some way to get T_s *without* evaluating all those damn orbitals? Yes!
- Write it as a *density* functional, i.e., an integral over some function of n(x).
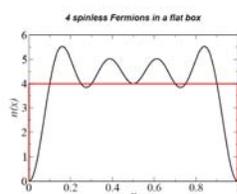- Simplest choice: a local approx:

$$T_s^{(0)}[n] = \frac{\pi^2}{6} \int_{-\infty}^{\infty} dx \, n^3(x)$$

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Particles in box

- Accuracy

N	$T_s^{[0]}$	T_s	%err
1	4.112	4.934	-17
2	21.79	24.67	-12
3	62.92	69.09	-9

Leading Corrections to the Local Density Approximation Attila Cangi, Donghyung Lee, Peter Elliott, and Kieron Burke, arXiv: 1002.1351 (2010).
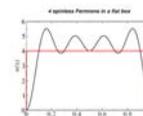
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What we've learned

- Density functionals are approximations for the energy of many particles
- Work best for large N, worst for small N
- Local approximations are crudely correct, but miss details

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Asymptotic exactness of E(N)

- As $N \rightarrow \infty$, LDA becomes relatively exact.
- Leading corrections dominate total energies of atoms, molecules, and solids, and X given correctly by popular functionals.
- PBEsol – ignores asymptotics and restores regular gradient expansion, improving bond lengths but worsening atomization energies.
- Why? See *Semiclassical Origins of Density Functionals* P. Elliott, D. Lee, A. Cangi, and K. Burke, Phys. Rev. Lett. 100, 256406 (2008).; and *Non-empirical 'derivation' of B88 exchange functional* P. Elliott and K. Burke, Can. J. Chem. 87, 1485 (2009)
- I'll talk for 10 mins on Weds 9am (P28.00004)

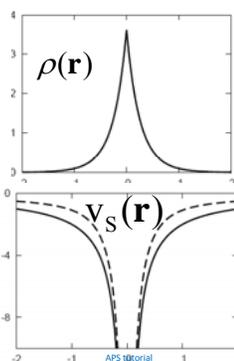3/23/2010   APS tutorial   7

Essence of Kohn-Sham DFT

- Even with exact $E_{xc}[n]$, only get E_0 and n(**r**) (and I). So other properties may not be right.
- Results only as good as functional used.
- Vast amount of information from E_0 alone, such as geometries, vibrations, bond energies…
- Well-fitted functionals are accurate for limited set
- Non-empirical functionals less so, but more reliable for a broader range, and errors understandable
- Although all properties (including excitations) are *in principle* functionals of the density, and even if we knew the exact ground-state energy functional, we still can't calculate them.

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He atom in Kohn-Sham DFT

$\rho(\mathbf{r})$

$v_S(\mathbf{r})$

Everything has (at most) one KS potential

Dashed-line: EXACT KS potential

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Functionals in common use today

- Local density approximation (LDA)
  - Uses only n(**r**) at a point. $E_{XC}^{(0)}[n] = \int d^3 r \, e_{XC}^{unif}(n(\mathbf{r}))$
- Generalized gradient approx (GGA)
  - Uses both n(**r**) and $|\nabla n(\mathbf{r})|$ $E_{XC}^{GGA}[n] = \int d^3 r \, e_{XC}(n, |\nabla n|)$
  - More accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP
- Hybrid:
  - Mixes some fraction of HF
  - Examples are B3LYP and PBE0

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The functional zoo

3/23/2010   KITP: Materials by design   11

Things users despise about DFT

- No simple rule for reliability
- No systematic route to improvement
- If your property turns out to be inaccurate, must wait several decades for solution
- Complete disconnect from other methods
- Full of arcane insider jargon
- Too many functionals to choose from
- Can only be learned from another DFT guru

Mar 24,09   ACS   12

Things developers love about DFT

- No simple rule for reliability
- No systematic route to improvement (except maybe semiclassical…wait and see)
- If a property turns out to be inaccurate, can take several decades for solution
- Wonderful disconnect from other methods
- Lots of lovely arcane insider jargon
- So many functionals to choose from
- Must be learned from another DFT guru

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New capabilities in many codes

- Many flavors of GW
- Exact exchange
- RPA (see recent work of Furche)
- Van der Waals functional of Langreth-Lundquist (plus Soler algorithm).
- But how to put them all together?

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Simple conditions for Coulomb systems

- Asymptotic decay of the density

$$\sqrt{n(\mathbf{r})} \rightarrow A r^{\beta} e^{-\sqrt{2I}r}$$

- Leads to severe constraint on KS potential

$$v_{xc}(\boldsymbol{r}) \rightarrow -1/r \qquad (r \rightarrow \infty)$$

- And determines KS HOMO: $\varepsilon_{HOMO} = -I$

- But $\varepsilon_{LUMO} \neq$ -A

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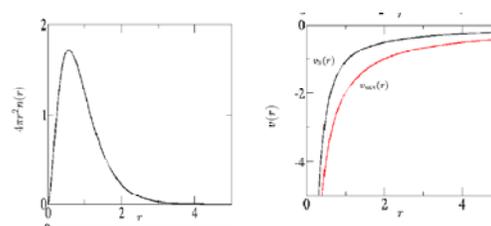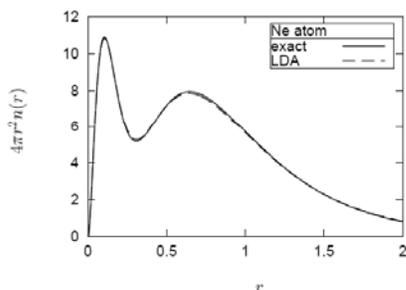
KS potential for He atom

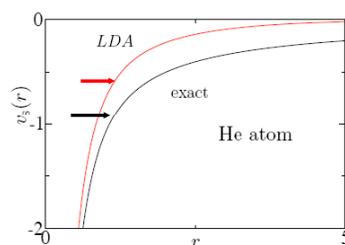3/23/2010   APS tutorial   16

Densities

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LDA potential

FIG. 7: Exact and LDA KS potentials for the He atom.

- Never calculate I from HOMO, but always from E(N)-E(N-1)

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Self interaction

- Violated by most semilocal functionals (unless built in)

  n: For any one-electron system,

  $$E_\mathrm{x}[n] = -E_\mathrm{H}[n], \quad E_\mathrm{c} = 0 \quad (N=1),$$

- Perdew-Zunger: SIC removes error for 1 electron, but non-invariant functional

Energy as function of N

From Dreizler + Gross
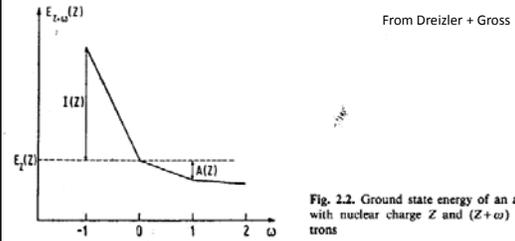
Fig. 2.2. Ground state energy of an atom with nuclear charge Z and (Z+ω) electrons
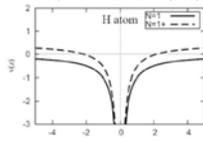
Derivative discontinuity

- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before, $\varepsilon_\mathrm{HOMO}$ (N)=-I, but now, $\varepsilon_\mathrm{HOMO}$ (N+δ)=-A
- Thus $v_s(r)$ must jump by Δ_xc=(I-A)- ($\varepsilon_\mathrm{HOMO}$-$\varepsilon_\mathrm{LUMO}$)

- PPLB, PRL 1982.

Ne Potentials
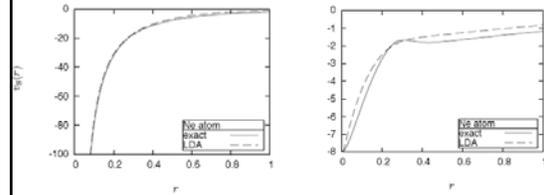
$$v_\mathrm{xc}(\boldsymbol{r}) \to -1/r \quad (r \to \infty)$$

$$\varepsilon_\mathrm{HOMO} = -I$$

Missing derivative discontinuity in LDA
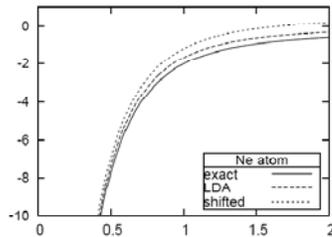
LDA looks like exact, shifted by about (I-A)/2

What ever happened to HF?

- We know E_x is just

  $$-\frac{1}{2}\sum_\sigma \sum_{i,j}^{occ} \int d^3r \int d^3r' \phi_{i\sigma}^*(\mathbf{r})\, \phi_{j\sigma}^*(\mathbf{r}')\, \phi_{i\sigma}(\mathbf{r}')\, \phi_{j\sigma}(\mathbf{r})/|\mathbf{r}-\mathbf{r}'|$$

- So why can't we just put that in KS equations?

- Because don't know $E_x[n]$, so must approximate

OEP   See RMP , Kuemmel and Kronik,2009

- Way to handle orbital-dependent functionals in KS scheme, i.e., with single multiplicative KS potential
- Still density functionals, since orbitals uniquely determined by density
- Often called OPM
- Several schemes to implement, all much more expensive than regular KS-DFT
- Can improve other properties:
  - No self-interaction error
  - Potentials and orbital energies much better
  - Approximates derivative discontinuity

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HF versus EXX

- HF minimizes $E_x[\{\phi_i\}]$ over all possible wavefunctions
- EXX includes additional constraint of common potential (i.e., KS)
- Yield almost identical total energies, with HF an eensty bit lower.
- Occupied orbital energies very similar, but big difference in unoccupied orbitals

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A tale of three gaps

- Fundamental gap:
  - $\Delta = I - A = 24.6eV$ for He
- Kohn-Sham gap:
  - $\Delta_s = \varepsilon_{HOMO} - \varepsilon_{LUMO} = 21.16$ eV
- Derivative discontinuity: $\Delta_{xc} = \Delta - \Delta_s$
- Lowest optical transition:
  - $\omega_{min} = E(1s,2p) - E(1s^2) = 21.22eV$
- NOTE: All same if non-interacting, all different when interacting
- Of course, $\varepsilon_{HOMO}(LDA) = 15.5$ eV, very bad.

- In solids: Fundamental gap ≠ KS gap
- In LDA and GGA, KS gap is about right
- If calculate I-A for finite sample in LDA, GGA, collapses to KS gap.
- With hybrid, depends on if you do OEP or HF.

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Partition DFT

- Partition theory (Wasserman et al):
  - Instead of replacing interacting electrons with effective non-interacting problem, replace interacting ATOMS with effective isolated fragments
- KS-PDFT: Perform an approximate KS treatment of fragments, reproducing the same approx KS treatment of molecule, precisely.
- Many, many implications:
  - O(N) methods of DFT
  - QM/MM partitioning of systems
  - Fixing dissociation limits of H_2 and H_2^+

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New Quiz

1. For a H atom, $E_{PBE} = -0.4999$. Is PBE self-interaction free?
2. Is there a route to systematic improvement of functionals?
3. True or false: You cannot calculate the exact gap of a semiconductor with the exact E_{XC}
4. The density of an LDA calculation is accurate everywhere except the far tail. What does this imply about the LDA XC potential?
5. The correlation energy in quantum chemistry is defined relative to HF, but in DFT it is defined relative to exchange on the exact KS orbitals. Which is more negative?

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New Quiz Answers

1. For a H atom, $E_{PBE} = -0.4999$. Is PBE self-interaction free?
   - NO, not true for other 1e sys.
2. Is there a route to systematic improvement of functionals?
   - YES, via semiclassics
3. True or false: You cannot calculate the exact gap of a semiconductor with the exact E_{XC}
   - False!
4. The density of an LDA calculation is accurate everywhere except the far tail. What does this imply about the LDA XC potential?
   - Must run parallel to exact one where density is noticeable.
5. The correlation energy in quantum chemistry is defined relative to HF, but in DFT it is defined relative to exchange on the exact KS orbitals. Which is more negative?
   - Because HF is an unrestricted minimum, the QC correlation energy is LESS negative than the DFT one.

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What we've learned, maybe

- Ground-state density determines all properties of system, *in principle*, but in practice, only really get energy and density (which is 90% of what you want).
- Local density functional theories give roughly correct answers, but are too inaccurate to be helpful in quantum chemistry.
- The commonly-used functionals in chemistry are well-founded and have few parameters.
- There are known exact properties of the density in real atoms.
- There are subtle and bizarre effects in the KS potential because real electrons do interact.
- Exact exchange is expensive, and we don't have a correlation functional to go with it, but it improves some properties.