Tulane University | **Department of Physics**
and Engineering Physics

TO Professor Kieron Burke

DEPT./CO. Chemistry UC Irvine

DATE March 17, 2008 FAX 949 824 8571

TIME PHONE

FROM John Perdew NO. OF PAGES 23

PHONE FAX 504-862 8702

MESSAGE:

2001 PERCIVAL STERN HALL
6400 FRERET STREET,
NEW ORLEANS, LA 70118
PHONE: (504) 865-5520
FAX: (504) 862-8702

BASICS OF GROUNDSTATE DENSITY FUNCTIONAL THEORY

JOHN P. PERDEW
PHYSICS
TULANE UNIVERSITY
NEW ORLEANS

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

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

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

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

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

= ELECTRON-NUCLEUS ATTRACTION,

AND E INCLUDES ALSO

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

= NUCLEUS-NUCLEUS REPULSION.

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:

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

$E \to \Delta E$

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

$$h[\Psi] \equiv \langle \Psi | \hat{H} | \Psi \rangle$$

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!

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 <u>NOT</u> 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.

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 $F[n]$.

(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

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

$$= \min_{n} \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3r\, v(\vec{r}) n(\vec{r}) \right\}$$

$$(1) \qquad = \min_{n} \left\{ F[n] + \int d^3r\, v(\vec{r}) n(\vec{r}) \right\}$$

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

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

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

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

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

$$\left.\begin{aligned} &\frac{\delta F}{\delta n(\vec{r})} + v(\vec{r}) - \mu = 0 \\ (2) \quad &v(\vec{r}) = \mu - \frac{\delta F}{\delta n(\vec{r})} \end{aligned}\right\} \text{FOR GS } n(\vec{r})$$

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

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

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

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 NONINTERACTING 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.

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

s= single-particle

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

Φ_n = THAT NONINTERACTING 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 $E_x[n]$

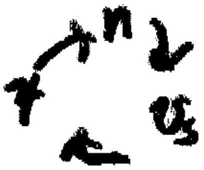
$$F[n] = \underbrace{T_s[n] + U[n]}_{\text{TREATED EXACTLY}} + \underbrace{E_{xc}[n]}_{\text{SOME APPROX. FOR } E_x + E_c}$$

EULER EQUATIONS

$$\left.\begin{aligned}
&\frac{\delta T_s}{\delta n(\vec{r})} + v_s(\vec{r}) = \mu \\
&\frac{\delta T_s}{\delta n(\vec{r})} + \frac{\delta U}{\delta n(\vec{r})} + \frac{\delta E_{xc}}{\delta n(\vec{r})} + v(\vec{r}) = \mu
\end{aligned}\right\} \text{SAME SOLUTION}$$

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

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



SELFCONSISTENT KOHN-SHAM SCHEME

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

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

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

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

COUPLING CONSTANT INTEGRAL FOR E_{xc}

LANGRETH + PERDEW 1975

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

ADJUST $v_\lambda(\vec{r})$ TO HOLD THE GS DENSITY FIXED AT ITS $\lambda = 1$ VALUE.

$\lambda = 1$: REAL INTERACTING SYSTEM

$$v_\lambda(\vec{r}) = v(\vec{r}).$$

$\lambda = 0$: 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

$$\langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho_2^\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

WHERE

$$\rho_2^\lambda(\vec{r}, \vec{r}') = N(N-1) \sum_{\sigma_1} \cdots \sum_{\sigma_N} \int d^3r_3 \cdots d^3r_N$$

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

= TWO-PARTICLE DENSITY MATRIX

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

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

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

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

SO $\int d^3r'\, n_{xc}^\lambda(\vec{r},\vec{r}\,') = -1$ SUM RULE

$n_{xc}^\lambda(\vec{r},\vec{r}\,')$ = 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 $\vec{r}\,' \neq \vec{r}$.

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

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

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

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

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

= KOHN-SHAM ONE-PARTICLE DENSITY MATRIX

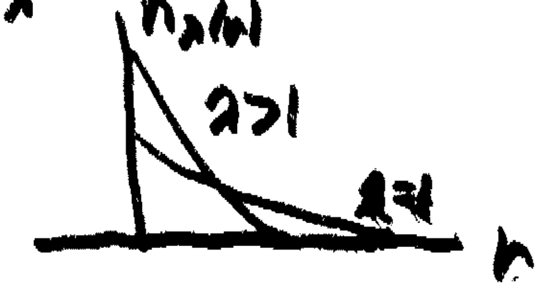
EXACT CONSTRAINTS: WE KNOW MANY EXACT CONSTRAINTS ON THE HOLE (SUCH AS THE SUM RULE) OR ON THE XC ENERGY.

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

$\psi_\alpha(\vec{r}) \to \lambda^{3/2} \psi_\alpha(\lambda \vec{r})$,

SO

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

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

$E_c[n_\lambda] \to$ CONSTANT (NON DEGEN

E_x DOMINATES E_c

MANY OTHER EXACT CONSTRAINTS ON $n_{xc}^{\lambda}(\vec{r}, \vec{r}')$ 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

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 $n_{xc}^{\lambda}(\vec{r}, \vec{r}')$ 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.

JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

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

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

KE DENSITY