ITP, UCSB Kohn Science Symposium 12/08/2016

The Importance of Density

From Kohn's Obsession to Many-body Theory of Real Systems

Lu J. Sham

Emeritus, Physics and ECE, University of California San Diego

- Walter Kohn the mensh
- Density for a random choice of DFT topics unifying the finite N systems and macro systems $N \rightarrow \infty$

Walter

- Deep thinker and deliberate speaker
  - His pipe.
  - Throat clearing.
- Impish Humor – when least expected, examples later.
- Reckless athlete (in contrast to his usual staidness)
  - Skiing in June Mountain – Mogul for ski jump. Broke shoulder. Missed APS March Meeting 1966.
  - Sailfish off La Jolla Shores. Took Marilyn and me sailing on a blustery day. Capsized in by a squall. Lectured by life guard.
- Passionate advocate for banning nuclear weapons
  - Lecturing me on LANL and holding up the luncheon
- Environmentalist
  - Tree rescuing
  - His calling card as a movie producer

Density Obsession – Its manifestation of the quantum effects

Friedel Oscillations (1954) r space

Kohn Anomaly (1959) k space

Langer & Vosko (1959)

Impurity effect on electron density

Dielectric response at $q=2k_f$ log derivative

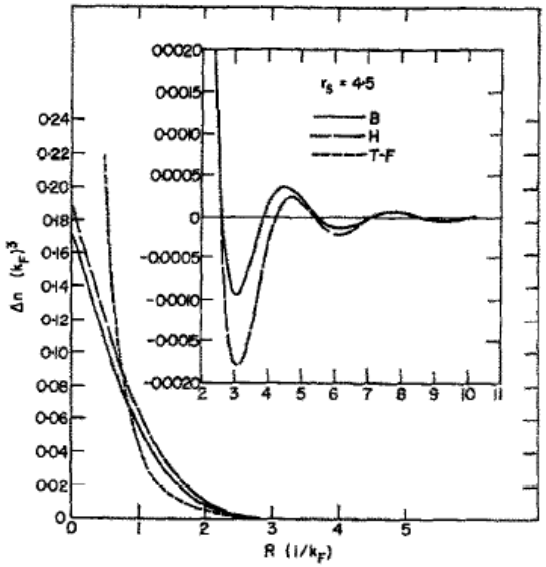
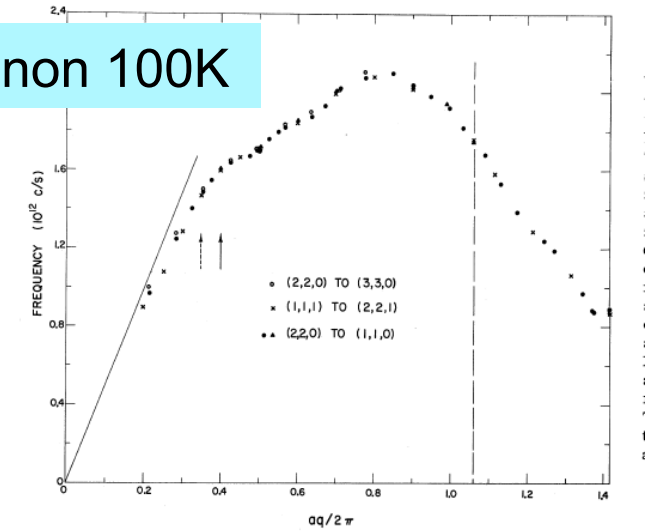


FIG. 5. The displaced electron density for $r_s = 4{\cdot}5$ vs. the distance from the inserted charge.

Pb phonon 100K



Brockhouse et al (1961)

Kohn & Vosko (1959)

Nuclear spin resonance in Cu/imp

Na phonon with el-ph at $2k_f$ too weak

Sham (1963,1965)

Den Obs II – Density as Road to high concentration alloys

Hohenberg, Kohn, Sham (1990)

25th Anniversary, Ed. S. Trickey

- Contains an account of the origin of the HK theorem
- And serves as a sample of Kohn's humor, as promised.

"A breezy account"

- … we have had a lot of fun with density functional theory, both doing it and watching other partisans (and even "enemies") …
- We trust that the editor will tactfully suppress failures.
- .. . We do not want to be relics of the past …
- … drawing on our vast experience (beware!) to suggest .. [future directions]

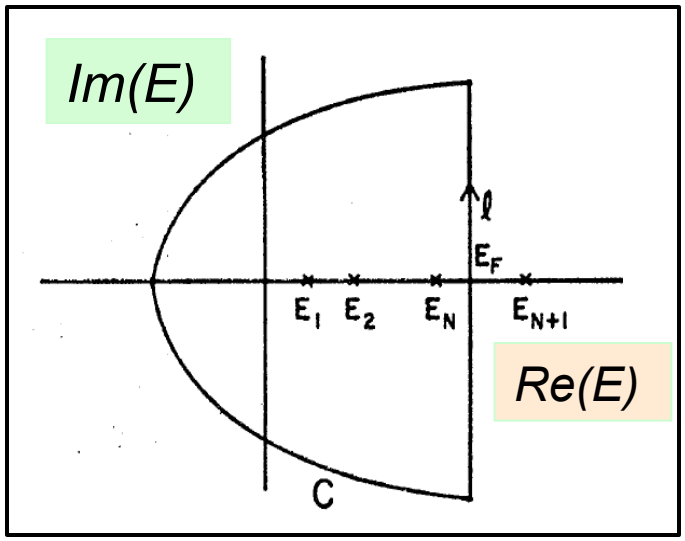
Den Obs III – Quantum Density Oscillations

Kohn-Sham-I (1965) – relatively unknown. (Unknown ratio: 100 to 1)

Quantum Density Oscillations in an Inhomogeneous Electron Gas

Find the Source of oscillations

To test the gradient series (HK)



One-electron Green's function

- Contour integration along ℓ.
- Oscillations from close to Im(E) =0
- In semi-classical approx, WKB phase leading to density oscillations is better than Thomas-Fermi.

Relation between the classical and the quantum regimes!

H = T + V; [T,V] $\neq$ 0, quantum

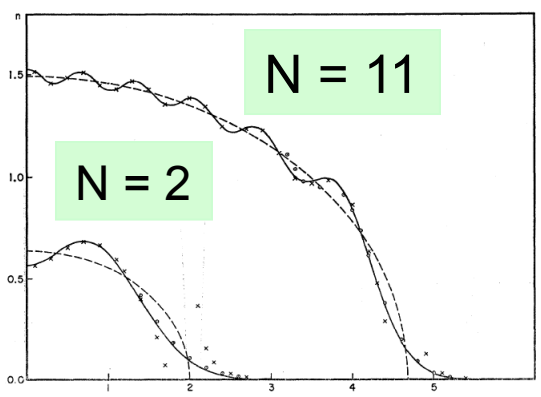
[T,V] = 0 (TF), classical

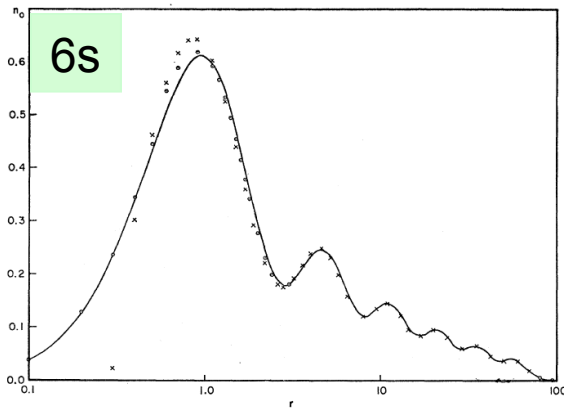
Den Obs III – Quantum Density Oscillations

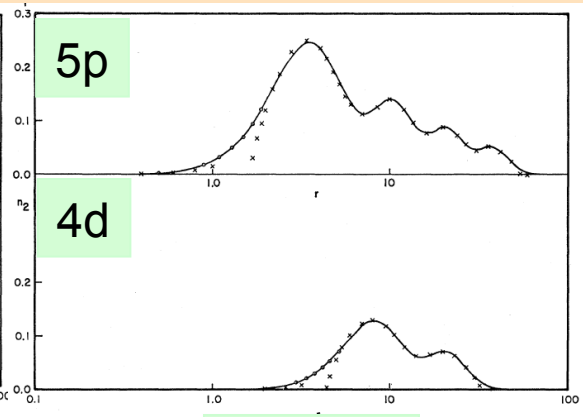
KS-I: Method of computation for finite systems

- Non-interacting particle approx.
- WKB turning point connection by Airy function (R.E. Langer 1937)
- 1D – Green's fn solved exactly in terms of wave fns at same E

- Oscillations – quantum confinement in r or k space.
- Slowly varying approx works quite well.







SHO —— Exact --- TF xxx WKB ••• Langer Atom Z

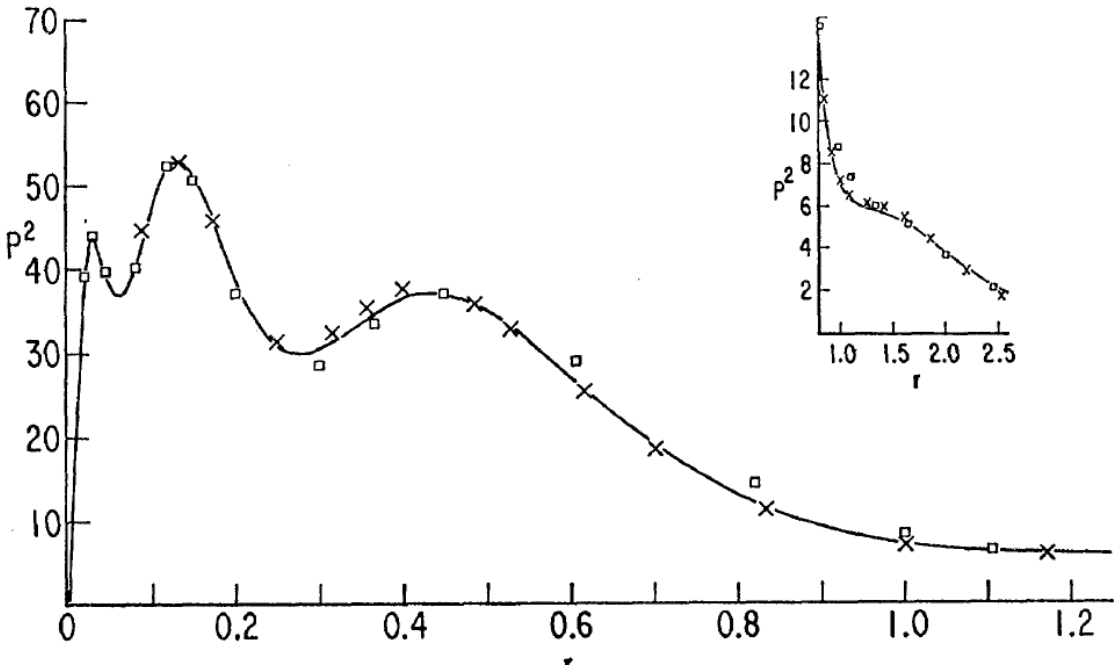
Applied to nucleus – David Thouless (private comm) use the method for Ca^{40}. [Nuc. Phys. (1965); Thorpe and Thouless, ibid (1970).]

First Application of DFT-LDA

Tong and Sham (1966) Noble atoms.

$\varepsilon_c(n)$ Interpolation between Wigner and Gellmann-Brueckner

Kr



Solid curve – KS-LDA, □-Old HF, X- Slater exchange

Deviation from Old HF worse than Ar. Agreed better with LANL group HF.

Density Functional Theory for Computation

Situation in the sixties – my impression, not rigorous history

- Electron gas (homogeneous) interaction theory RPA (Brueckner)
  - Exchange and correlation energy.
- Band structure theory in solids
  - Computation methods flourished.
  - One-particle potential.
  - Most in the Hartree approximation if at all.
  - A few Hartree-Fock calculations for insulating crystals.
  - John Ziman on band calculations: “Teaching elephants how to dance”.
- Never the twain shall meet.

Density Functional Theory for Computation

Letter from the Editor of PRL, S. A. Goudsmit

PHYSICAL REVIEW LETTERS

(PUBLISHED FOR THE AMERICAN PHYSICAL SOCIETY)

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The Physical Review
S. PASTERNACK, Editor
A. HERSCHMAN, ~~Assistant~~ Editor

Physical Review Letters
S.A. GOUDSMIT, Editor
G.L. TRIGG, Assistant Editor
M. J. FLEMING, Publication Manager

28 May 1965

Dr. L. J. Sham
Department of Physics
University of California, San Diego
PO Box 109
La Jolla, California 92038

Dear Dr. Sham:

For the reasons discussed in the enclosed memorandum, we are still finding it necessary to restrict the number of papers published

We have carefully considered the following manuscript:

"Exchange and Correlation Effects in an Inhomogeneous Gas" -- Kohn and Sham

Density Functional Theory for Computation

Letter - second half

Our judgment is that while it deserves publication it is not

Our judgment is that while it deserves publication it is not of such urgency as to warrant the speedy publication of a Letter.

notice to the physics community of the existence of the work.

We request, therefore, that you add an abstract to the above paper so that it may be published as an Article in The Physical Review. Please note that the abstract must be submitted in duplicate, with the exact title and byline typed above it, so that one copy may be used for Physical Review Letters.

We are holding the manuscript in this office pending receipt of the abstract, and will then transfer the paper to The Physical Review.

Yours sincerely,

S. A. Goudsmit

S. A. Goudsmit
Editor

lm
Encl.

One Particle Excitation Energy

Sham and Kohn (1966)

- Self energy Σ(r,r',E) short-ranged (λ_F, λ_{TF}) and depends on the density at the mean of r and r' (Wigner rep).
  - Proof for lattice to first order in v for an electron gas.
  - Separate Σ into the local φ (r) δ(r-r') and nonlocal, M(r,r',E).
  - M is shown short-ranged by
    - $1/r^3$ amplitude of quantum oscillation
    - two Ward identities, connecting the one-particle M to the two-particle vertex (linear response to v), leads to the screening of the long range part of M and the neighborhood density dependence.
  - An example of "nearsightedness", Kohn (1996), which led to O(N) computation. Unifies validity for finite and infinite N
- LDA for the self-energy in the Dyson equation to produce quasi-particle energy M(r,r',E).
- Application to metals.

$$M_h[r - r'; E - \mu + \mu_h(n(\bar{r})); n(\bar{r})]$$

Insulator Band Gap Problem – Solution Beyond LDA

Sham and Schlüter (1983)

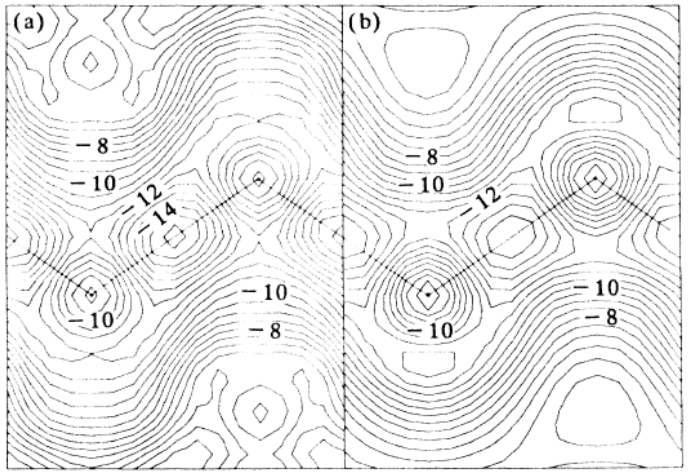
- $T_s[n]$ and $E_{xc}[n]$ have a derivative discontinuity in insulators.
- Formulation of the $E_{xc}[n]$ discontinuity contribution to the band gap, denoted by Δ, in terms of the self energy.
- A two-band model to demonstrate explicit .

Perdew, Parr, Levy, Balduz (1982), Perdew, Levy (1983)

$E_{xc}[n]$ discontinuity in finite atoms from fractional occupation in 1982. Then extend it to insulators in 1983.

Godby, Schlüter, Sham (1985-88)

- $v_{xc}(r, [n])$ computed in RPA, cf LDA. Difference in bond area.
- Calculated Δ solved the band gap problem (LDA gap too small by 50%).
- Si, GaAs, AlAs, Diamond.



Si: RPA LDA

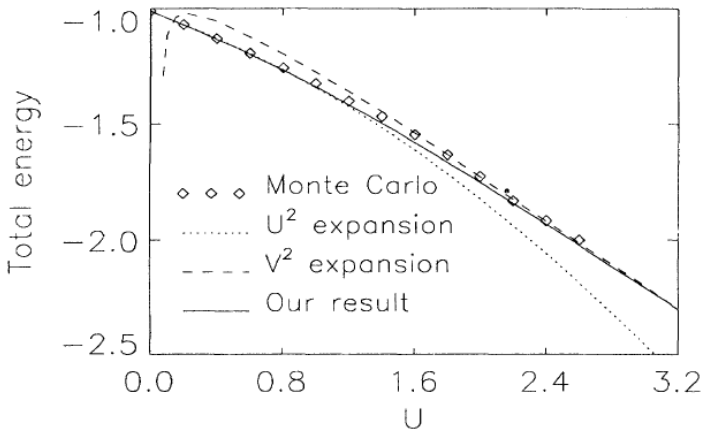
Strongly Correlated Electron System – I. Model Test

Steiner, Albers, Scalapino, Sham (1991).

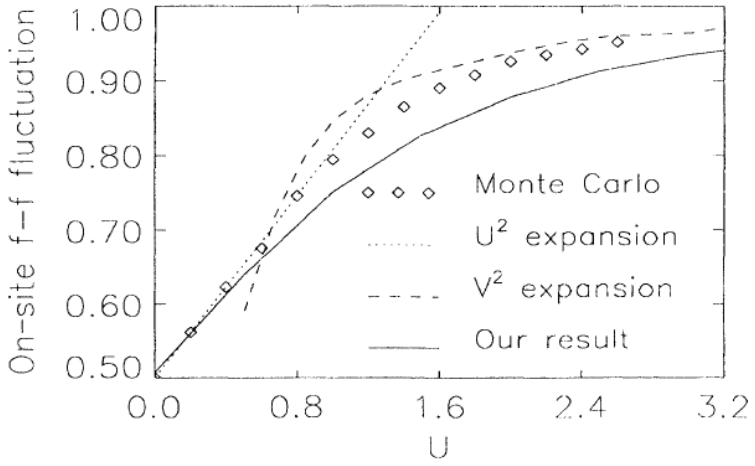
Methodology

- Essential ingredients from Anderson's model: onsite interaction U, and d-band/f-level hybridization V.
- Fluctuation around the MFT (not E) given in second order in U.

A test against QMC



Total energy

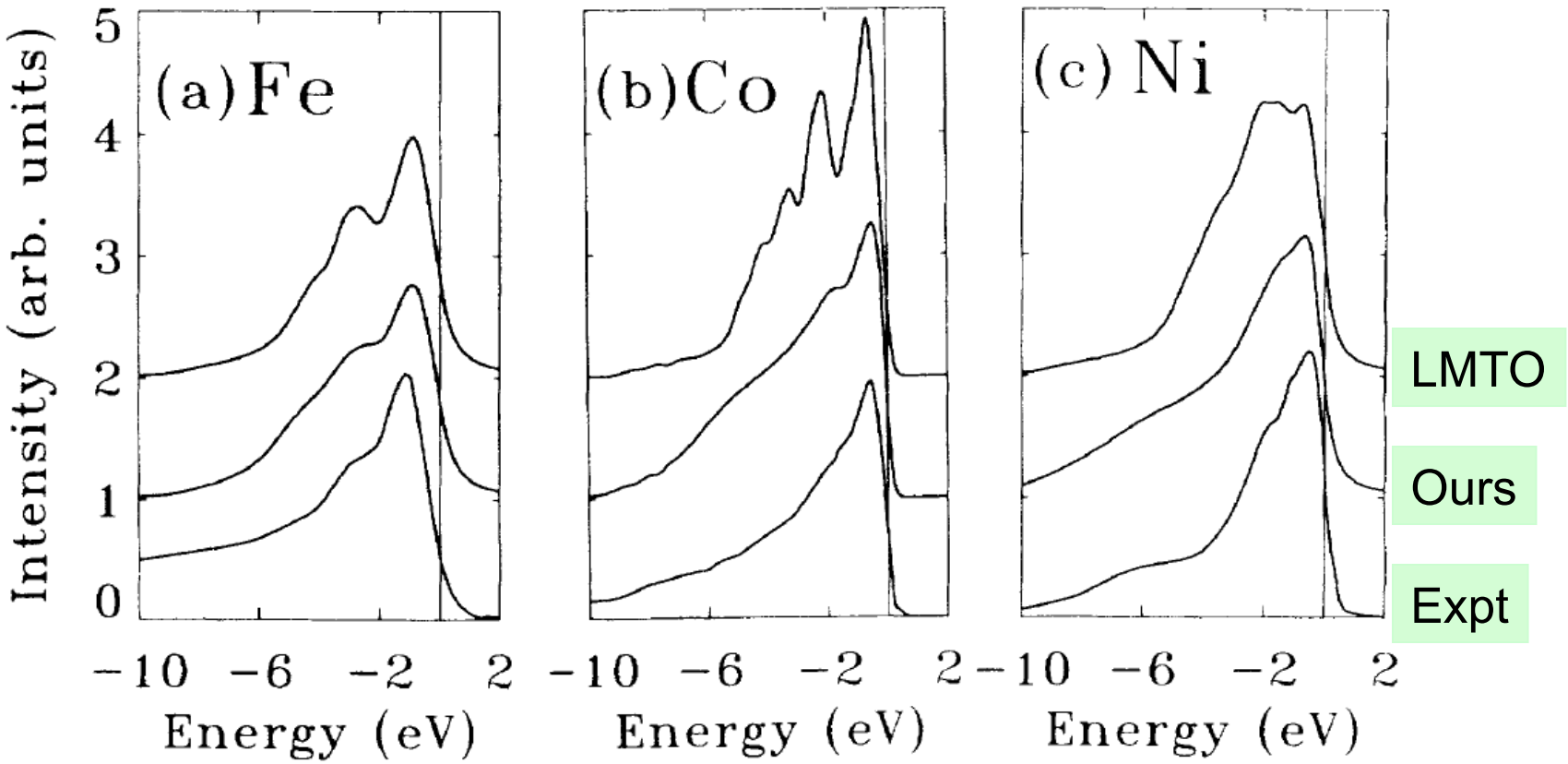


RMS magnetic moment on f site

Strongly Correlated Electron System – II Ferromagnets

Steiner, Albers, Sham (1992) Fe, Co, Ni

LDA & U fluctuations



XPS satellites for occupied DOS (theory results broadened).
Expt by Kirby, Kisker, King, Garwin (1985).

Strongly Correlated Electron System – III Heavy Fermions

Steiner, Albers, Sham (1994)

LDA bands & second order U fluctuations

To explain the variation in specific mass of UIr_3, UPt_3, UAu_3

mJ/K^2	UIr_3	UPt_3	"UAu_3"
γ^{expt}	19.5	452	260
$N^{LDA}(E_F)$	13.1	25.9	28.1
$\gamma^{(2)}$	17	475	243

Expt by Ott et al. (1987).

- The U and exchange effect of the localized electrons are essential. Dependence on the Hubbard U alone is insufficient.
- This theory expresses the varying contribution of Ir, Pt, Au.

Extension of DFT in [v(r), n(r)]

L.-A. Wu, M. S. Sarandy, D. A. Lidar, and L. J. Sham (2006)

Spin Hamiltonian $\hat{H} = \hat{F} + \int dr\ v(r)\hat{n}(r) \rightarrow \hat{H}_0 + \sum_l \lambda_l \hat{A}_l$

Micro Legendre Transformation: $v(r) \rightarrow n(r)$

Generalization: $\lambda_l \rightarrow a_l$

ground-state expectations of $\hat{A}_l$ $a_l = \langle \hat{A}_l \rangle$

Condition: Local observables $[\hat{A}_i , \hat{A}_k] = 0$

Some freedom to include interaction in the V term

$\hat{A}_i = \hat{B}_i \hat{B}_{i+k}$ is "local" for a fixed k for inter-site interaction

Quantum effects stem from non-commutative F and V

Quantum Phase Transition

Example

Transverse-field Ising model

$$H = -J\left(\sum_i \sigma_i^x \sigma_{i+1}^x + \lambda \sum_i \sigma_i^z\right)$$

field parameter

Phase transformation as a function of λ

Non-commutating terms in H make it quantum.

An Example of Transverse-Field Ising Model + Dipolar

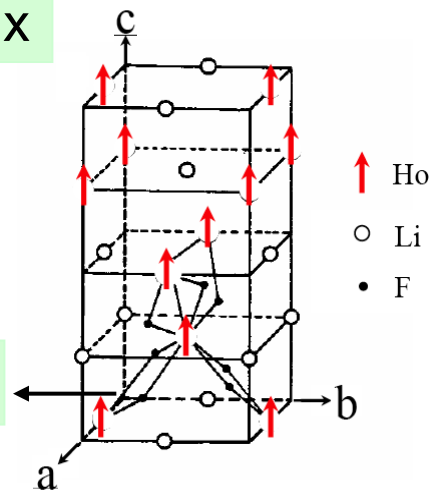
Bitko, Rosenbaum & Aeppli, PRL **77**, 940 (1996)

x

y

z, H_t

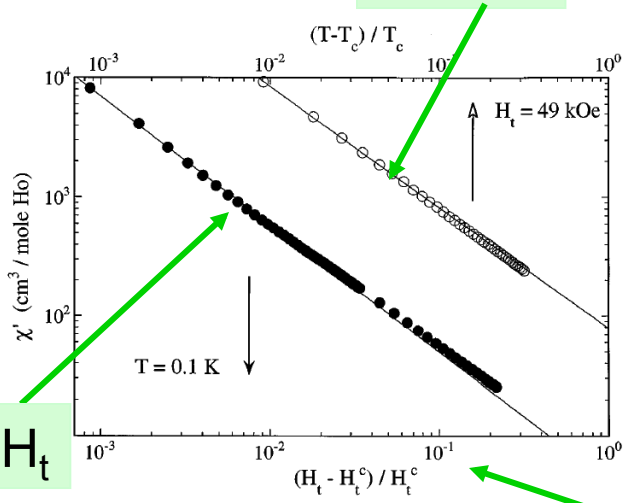
χ'

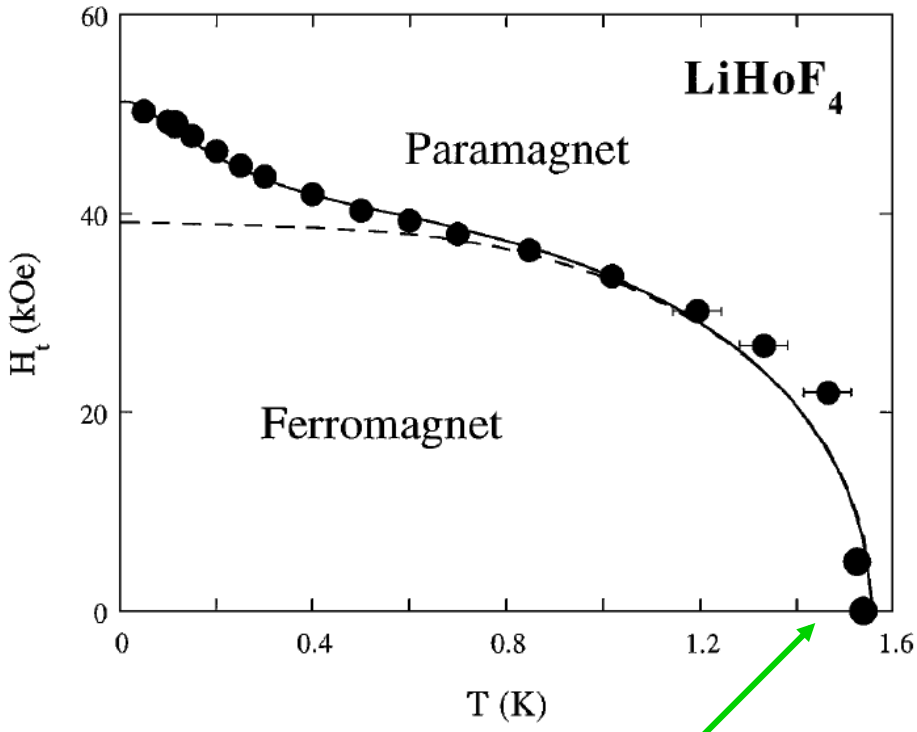


$LiHoF_4$

Fn of T

Fn of H_t





Behavior mean-field like

Critical behavior from susceptibility meas

DFT for Quantum Phase Transition

To find the quantum critical point and scaling

Correlation length scaling with coupling, $\xi \propto |\lambda - \lambda_c|^{-\nu}$

Entanglement is a pure quantum correlation.
Use it instead of the mixed correlation.

DFT to compute entanglement content by $a \rightarrow \lambda$**:**

$$\frac{\partial E}{\partial \lambda_l} = \langle \psi | \frac{\partial H}{\partial \lambda_l} | \psi \rangle = \langle \psi | \hat{A}_l | \psi \rangle = a_l$$

Entanglement measures by

- Reduced density matrix ρ_{ij}
- Bipartite systems
- Extremely case of 1 spin against the rest

DFT for Spin Systems

Valid "local" terms for V with larger scope including interaction

Transverse field Ising model

$H = -J\left(\sum_i \sigma_i^x \sigma_{i+1}^x + \lambda \sum_i \sigma_i^z\right)$

XXZ

$$H(\Delta) = \sum_l \left[\sigma_l^x \sigma_{l+1}^x + \sigma_l^y \sigma_{l+1}^y + \Delta \sigma_l^z \sigma_{l+1}^z\right]$$

field parameter

XYX(z): non-Abelian V?

$$H = \sum_{\langle ij \rangle} \left[S_i^x S_j^x + \Delta S_i^y S_j^y + S_i^z S_j^z\right] - h \sum_i S_i^z$$

Infinite-ranged interaction

Hartree-Fock exact

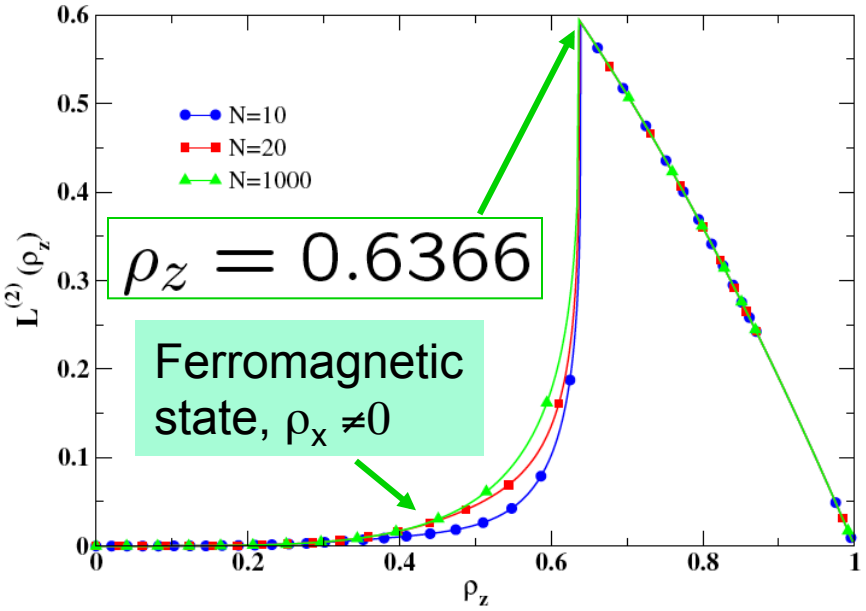
QPT of disordered systems

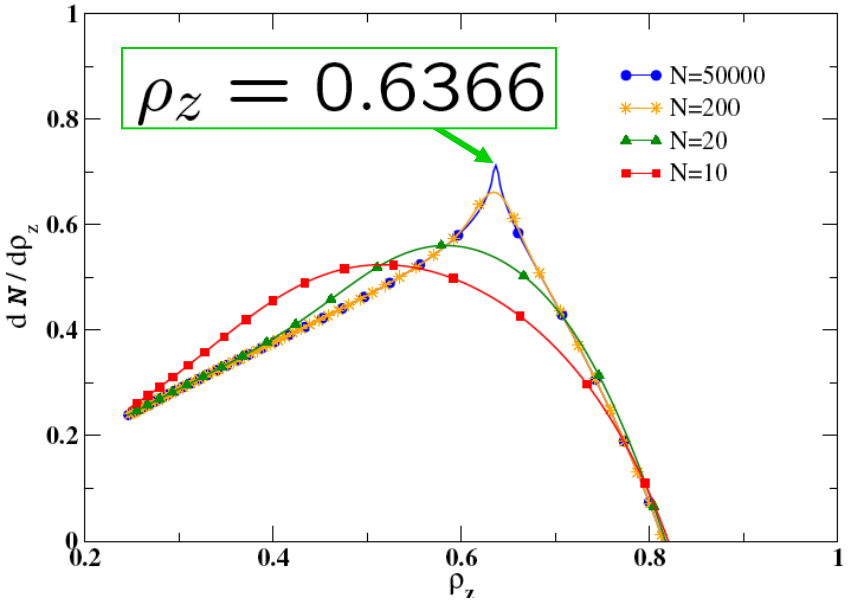
Spin liquid?

Application of DFT to the Transverse-field Ising Model

Spin polarization as variable

$$\rho_z = \langle \psi | \sigma^z | \psi \rangle$$





Bipartite entanglement of one spin and the rest: Linear entropy

$$L_i^{(2)} = 1 - |\vec{\rho}_i|^2$$

Bloch vector

n.n. spins entanglement measure:

Negativity $\mathcal{N}(\rho) \equiv \dfrac{\|\rho^{T_A}\|_1 - 1}{2}$

Sum of eigenvalue magnitudes

$$\langle i_A, j_B | \rho^{T_A} | k_A, \ell_B \rangle = \langle k_A, j_B | \rho | i_A, \ell_B \rangle$$

Future for DFT – Blind guesses

- Technological applications
  - More ab initial computation of technologically important systems, cf. Giulia Gulli
  - Beyond simple models, to study functionalities and noise.
  - Macro-systems needed for quantum information processing.
- Adding real material features to the model spin systems
  - It might alter the resultant phenomena.
- Validation of theory and computation
  - More imaginative and wide ranging tests by experiments and/or numerical analysis
  - Blind tests a la DeCarlos E Taylor, et al.
- Big Data simulations and studies

DFT – Find simple ways to solve complex systems