Electronic Structure of Condensed Matter

David M. Ceperley
Richard M. Martin

- Goal: to solve THE many-body electronic structure problem in condensed matter

$$\hat{H} = \frac{-\hbar^2}{2}\sum_{i}^{N_e}\frac{1}{m_i}\vec{\nabla}_i^{\,2} + \frac{1}{\varepsilon}\sum_{i\neq j}\frac{e_i e_j}{r_{i,j}}$$

Nuclei
Electrons

- Electron Gas - Wigner Crystal
- Hydrogen
- Real Materials – Si, Al surface, molecules, ...
- Quantum Dots
- Theory of insulators – polarization and localization – metal-insulator transitions

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Nuclei
Electrons

- Special features of our work
  - Combine expertise and concepts of:
    Quantum Monte Carlo (QMC)
    Density Functional Theory (DFT)
    Analytic many-body theory

Theme of Recent Work
Advantage of Monte Carlo:

Averages are almost free.

Suppose we have an extra parameter "q" to sum over.

$$E(s) = \frac{1}{M}\sum_{i=1}^{M} E(s;q_i)$$

- Deterministic calculation: CPU time is multiplied by M.
- Monte Carlo calculation: almost no slow down since the calculation is just one more variable to average over.

  $3N \rightarrow 3N + 1$

- Especially adapted for parallel computers: Simply run M calculations on M separate processors for different values of q: they all serve to reduce the error bar.

The only slow down occurs comes from "start up" costs: e. g. Metropolis warm-up

Advantage of Monte Carlo:

Averages are almost free.

Examples of averages:

1. k-point sampling (integrate over Brillouin zone of supercell). Twist averaged boundary conditions converge much faster than periodic boundary conditions for metals. (M k-points)

2. Path Integrals for ions (particularly for protons or light ions) (M time slices to average over.)

3. Interactions of electrons in real complex quantum devices with different dielectric media and metal gates (M steps in the Dyson Green's function equation)

Recent Progress on Simulations of the Low Density Electron Gas

$$V(R) = \sum_{i<j} \frac{e^2}{r_{ij}} + background$$

- New Methods have led to progress in predicting the phase diagram
  - Path Integral Monte Carlo
  - Better wavefunctions (Kwon*, Holzmann)
  - Twisted Boundary conditions (Lin*, Zhang*)
- Wigner Crystal melting (Jones, Candido)
- Spin polarization (Lin*, Zong*)

*Supported by NSF Grant

3D electron gas
Brief History of Ferromagnetism

What is polarization state of fermi liquid at low density?

$$\zeta = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}}$$

- Bloch 1929 polarization from exchange interaction:
  - $r_s > 5.4$ 3D
  - $r_s > 2.0$ 2D
- Stoner 1939: include electron screening: contact interaction
- Herring 1960
- Ceperley-Alder 1980: $r_s > 20$
- Young-Fisk experiment on doped CaB_6 1999
- Ortiz-Balone 1999 : ferromagnetism of e gas.
- Our new work 2001: “twist averaged boundary conditions”

Twist averaged boundary conditions (or k-point sampling)

- Use a phase or twist as r $\rightarrow$ r+L. (Bloch boundary condition)

$$\psi(r+L) = e^{i\theta}\psi(r)$$

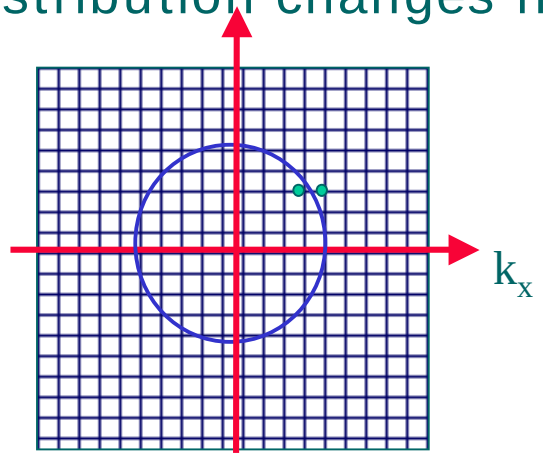
- For fermi liquid, one can eliminate single particle shell effects by averaging over the twist angle:

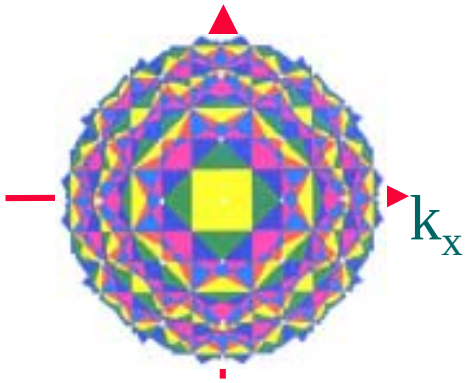
$$O = \frac{1}{(2\pi)^3}\int d\theta \left\langle \psi_\theta O \psi_\theta \right\rangle$$

- Gas: Momentum distribution changes from a lattice to a Fermi sea

$$\varphi = e^{ikr}$$

$$kL = 2\pi n + \theta$$

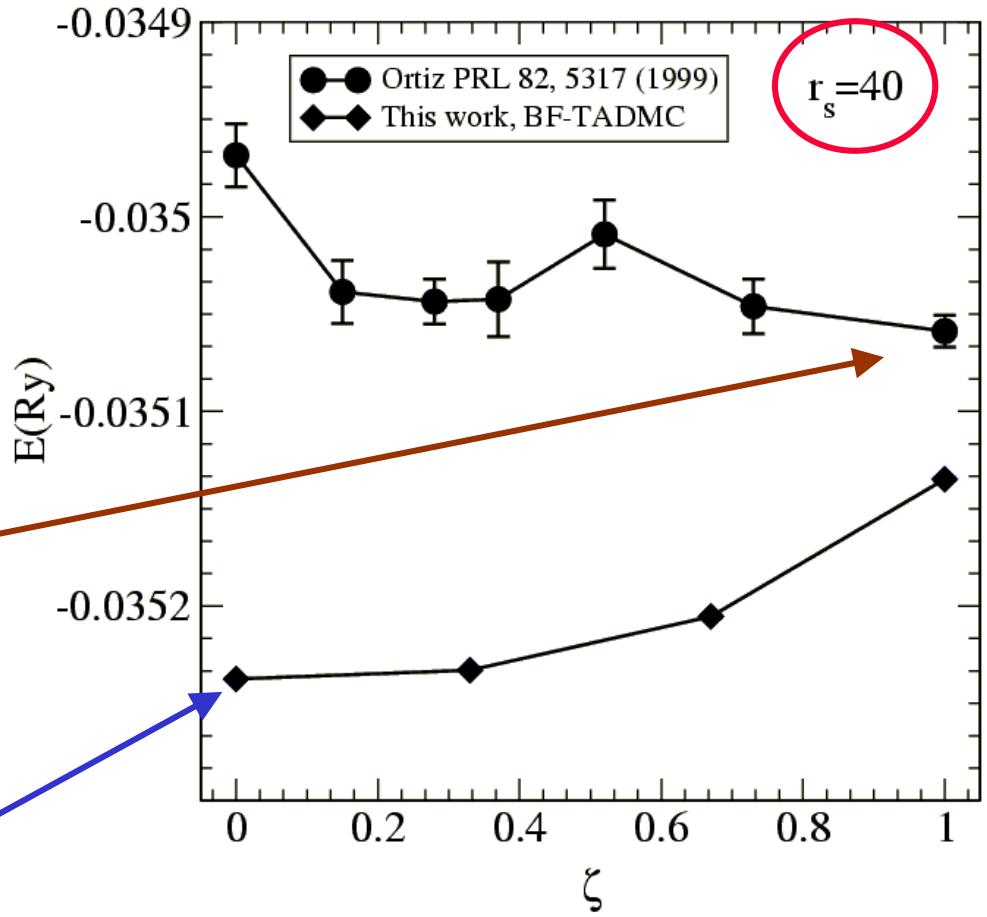




- No more shell effects!

Polarization with backflow

- Twist averaging allows calculation with small systems and high quality wavefunctions
- Polarization is sensitive to wavefunction
  - Jastrow wavefunctions favor the ferromagnetic phase.
  - Improved Backflow 3-body wavefunctions are more paramagnetic



- General rule: any approximation favors ferromagnetism

Coupled Ionic-Electronic Simulations (CIEMC)

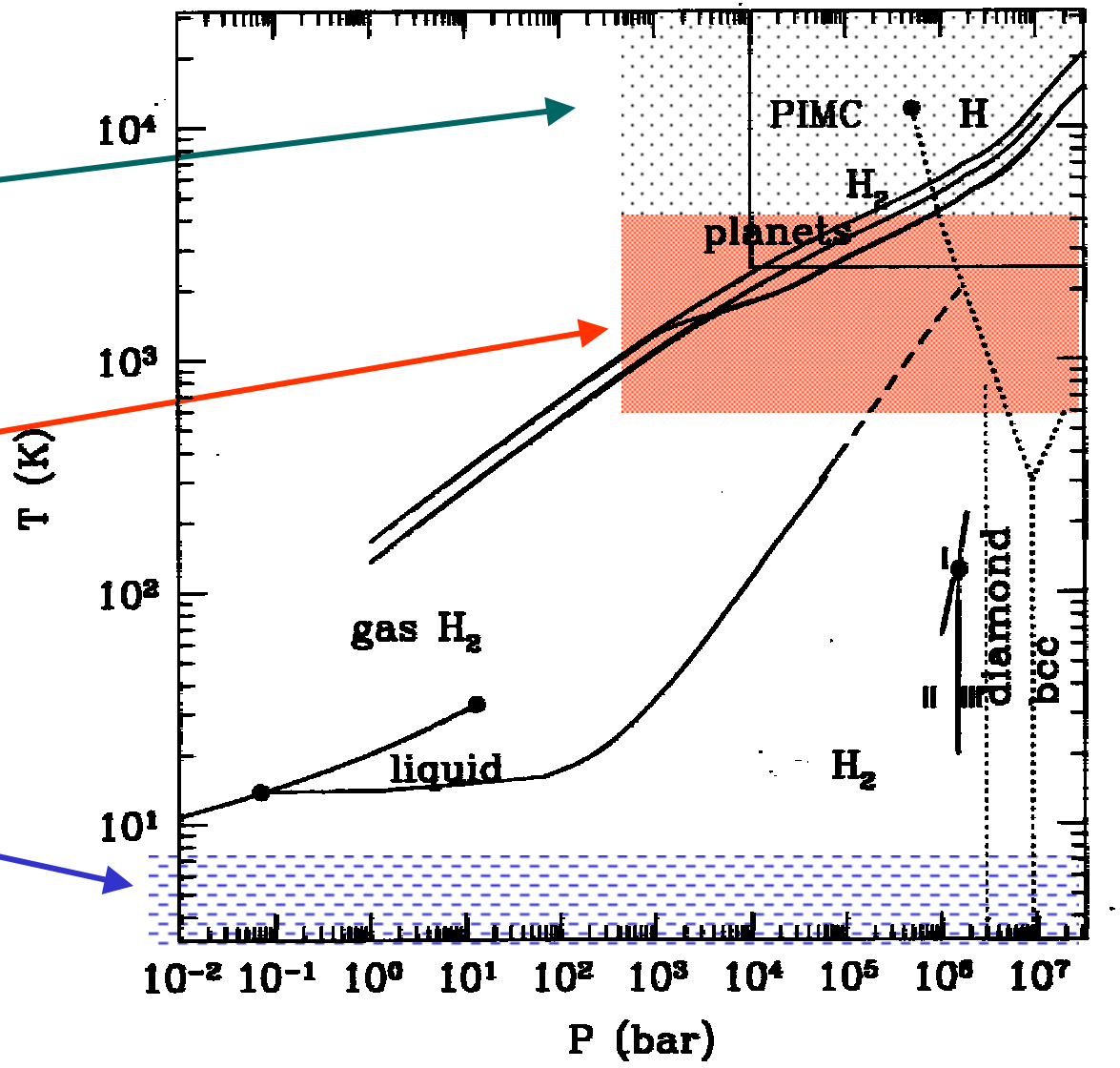
- Much progress in recent years with “ab initio” molecular dynamics simulations.
- However density functional theory is not always accurate enough.
- Is it possible to go to the next level of accuracy in description of the electronic structure?

accuracy ↓

- Hard sphere MD/MC ~1953
- Empirical potentials (e.g. Lennard-Jones) ~1960
- Local density functional theory
  Car-Parrinello MD simulations ~1985
- Quantum Monte Carlo

Phase Diagram of Hydrogen

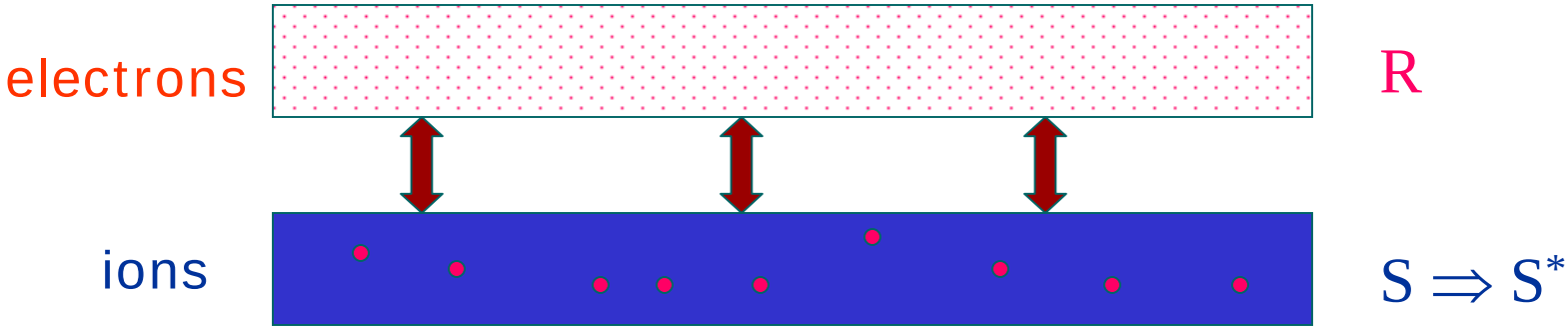
- Full PIMC works well at higher temperatures
  ($T > E_F/10$)
- We need a method for intermediate temperatures
- DMC works well at T=0
  (but time scale problem M_p/M_e)



A single CIEMC step

- Move ions from S to S*
- Pre-reject moves based on empirical potential
- Re-optimize trial function $\Psi_T(R|S^*;a)$ w.r.t. "a".
- Sample electron from $P(R,S,S^*)$
- Determine energy difference.
- Use penalty method to accept or reject

Problem – "Noise" from sampling electrons



The Penalty method

***J. Chem. Phys.* 110, 9812(1998).**

- **Assume** estimated energy difference Δe is **normally distributed*** with variance σ^2 **and the correct mean**.

$$< \Delta e > = \Delta E$$

$$< [\Delta e - \Delta E]^2 > = \sigma^2$$

*results from averaging according to central limit theorem if $\sigma < \infty$

- **Acceptance probability**:

$$a(x,\sigma) = \min [\ 1,\ \exp(-x - \sigma^2/2)]$$

- Simply add an additional "penalty" to the energy difference!
- The extra factor $\sigma^2/2$ is the penalty
- This exactly satisfies detailed balance and hence converges to the Boltzmann distribution independent of noise level.

Protons treated classically at present

CEIMC for Hydrogen

- Solved major problem: Improved “backflow” wavefunction involving electrons and protons allows reoptimization during the CEIMC run.
- No parameters, no LDA calculation needed at each step.
  An LDA/Jastrow trial function is too slow!
- Especially appropriate for liquid metallic hydrogen and disordered systems.

- ***The result is a very fast CEIMC code (faster (?) than Car-Parrinello-MD for metallic hydrogen) which treats electrons and protons by accurate QMC simulations.***

Correlated Electrons in Quantum Dots
Spin States, Charge Gaps
Quantum Monte Carlo Studies

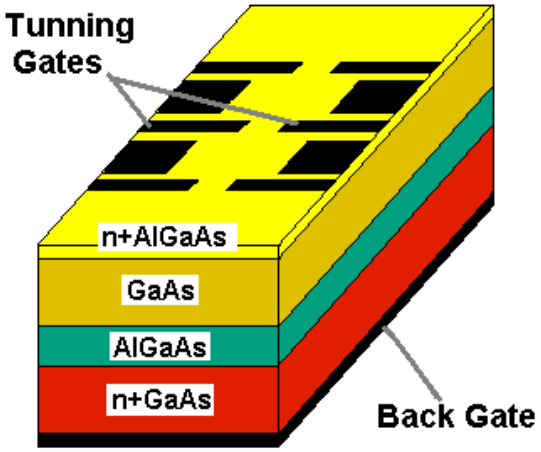
Tim Wilkens
Hoon Kim
Curry Taylor (undergrad)
Richard M. Martin
David M. Ceperley

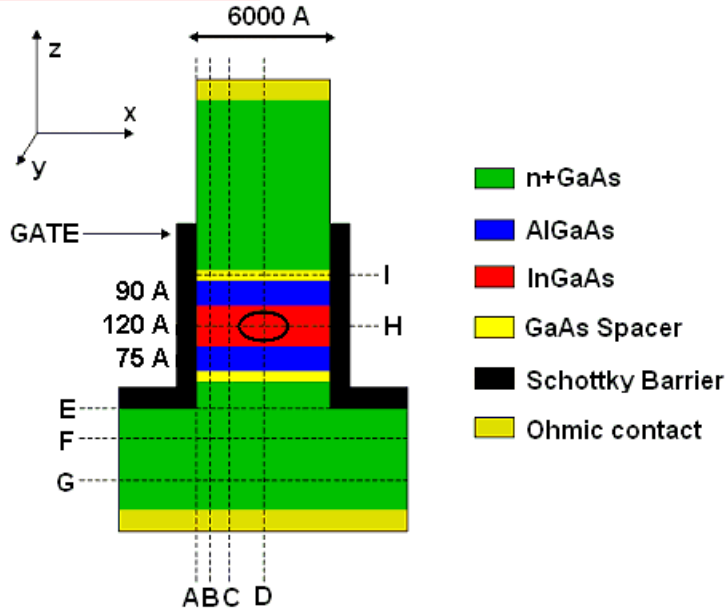
Philippe Matagne, J. P. Leburton
(Dept. of Electical Engineering)

- **Compare some results to coupled cluster methods (group of R. Bartlett, U. of Florida)**

Electrons in Quantum Dots

What type of dots?

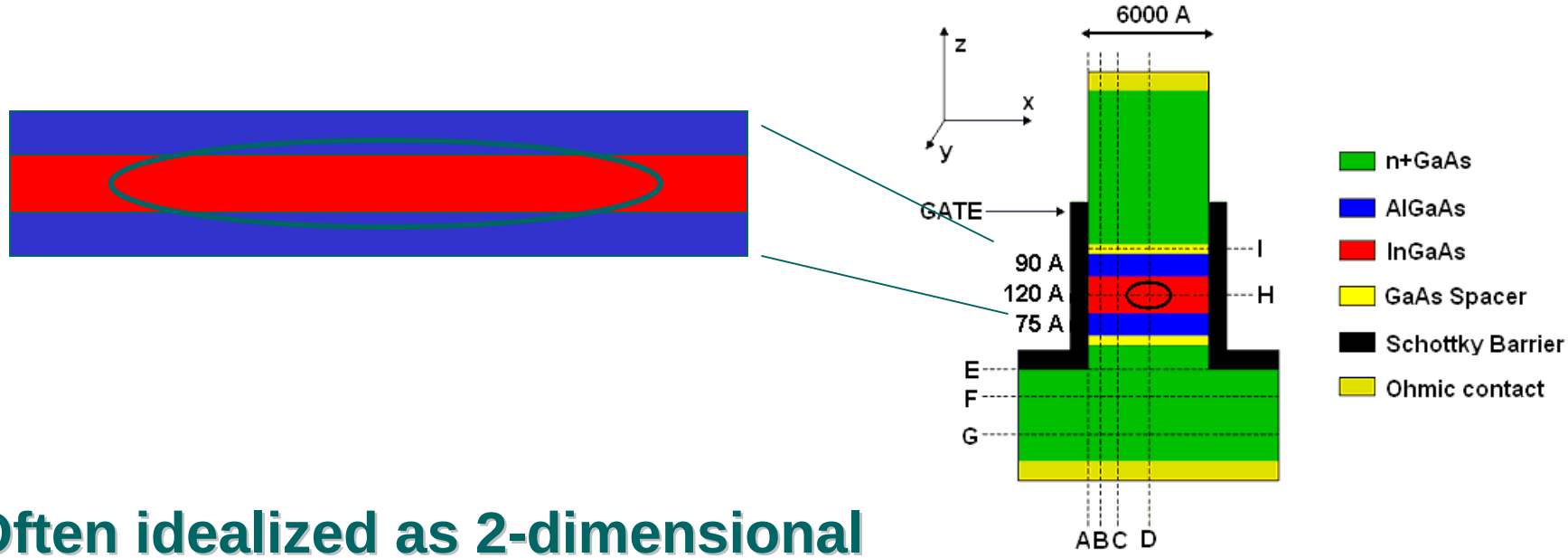




- Dots created by layered materials, applied potentials
- Effective mass approximation valid
- Idealized and realistic dots

Electrons in Quantum Dots

“Squashed” pancake shaped dot



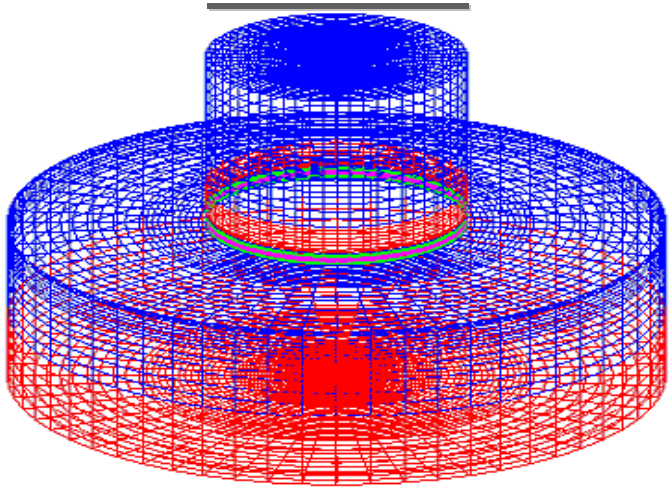
Often idealized as 2-dimensional

Our work: full 3-dimensional interacting electron problem

First QMC calculation for “real” system, m*(r) , …

N_e	$N_\uparrow$	SlatDet Orbital Type	LSDA(meV)	DMC(meV)
2	1	$\frac{[1s]_\uparrow}{[1s]_\downarrow}$	−14.90	−15.98(5)
3	2	$\frac{[1s,1p_x]_\uparrow}{[1s]_\downarrow}$	−28.55	−30.04(3)
4	3	$\frac{[1s,1p_x,1p_y]_\uparrow}{[1s]_\downarrow}$	−41.12	−43.12(6)
4	2	$\frac{[1s,2p_x]_\uparrow}{[1s,2p_y]_\downarrow}$	+1.11	+1.05(8)
5	3	$\frac{[1s,1p_x,1p_y]_\uparrow}{[1s,1p_y]_\downarrow}$	−48.43	−51.25(14)
6	3	$\frac{[1s,1p_x,1p_y]_\uparrow}{[1s,1p_y,1p_x]_\downarrow}$	−72.85	−75.85(12)
7	4	$\frac{[1s,1p_x,1p_y,1d_{x,y}]_\uparrow}{[1s,1p_y,1p_x]_\downarrow}$	−105.38	−109.09(15)
8	5	$\frac{[1s,1p_x,1p_y,1d_{x,y},1d_{x^2-y^2}]_\uparrow}{[1s,1p_y,1p_x]_\downarrow}$	−126.98	−130.71(21)
8	4	$\frac{[1s,1p_x,1p_y,1d_{x,y}]_\uparrow}{[1s,1p_y,1p_x,1d_{x^2-y^2}]_\downarrow}$	+0.76	+0.65(13)
9	6	$\frac{[1s,1p_x,1p_y,1d_{x,y},1d_{x^2-y^2},2s]_\uparrow}{[1s,1p_y,1p_x]_\downarrow}$	−154.45	−158.7(17)
9	5	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2}]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2}]_\downarrow}$	+0.38	+0.57(13)
10	6	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2}]_\downarrow}$	−180.25	−185.04(9)
10	5	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2}]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y}]_\downarrow}$	+0.07	+0.20(12)
10	6	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2}]_\downarrow}$	+0.37	+0.58(13)
11	6	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y}]_\downarrow}$	−208.00	−213.24(11)
11	6	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},2s]_\downarrow}$	−0.43	0.32(12)
12	6	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	−237.86	−243.26(14)
13	7	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	−277.41	−283.39(12)
13	7	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,2p_x]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	+0.65	+0.80(16)
14	8	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f,1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	−304.34	−310.63(15)
14	8	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f,2p_x]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	+0.71	+0.61(9)
14	7	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s,1f]_\downarrow}$	+0.44	+0.77(21)
14	8	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,2p_x,2p_y]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	+1.47	+1.56(13)
15	8	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f,1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s,1f]_\downarrow}$	−338.36	−345.26(17)
16	8	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f,1f]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s,1f,1f]_\downarrow}$	−367.46	−375.11(13)
16	10	$\frac{[1s,2p_x,2p_y,1d_{x,y},1d_{x^2-y^2},2s,1f,1f,2p_x,2p_y]_\uparrow}{[1s,2p_y,1p_x,1d_{x^2-y^2},1d_{x,y},2s]_\downarrow}$	+0.20	+0.54(17)

FEM GRID



- only center portion of **FEM** grid utilized:

X-Y: *51* pts {*–750*:*750* **A°**} ***Z****: 33 pts* {*–120*:*120* **A°**}

- *vertical confinement ratio ~* ***3***

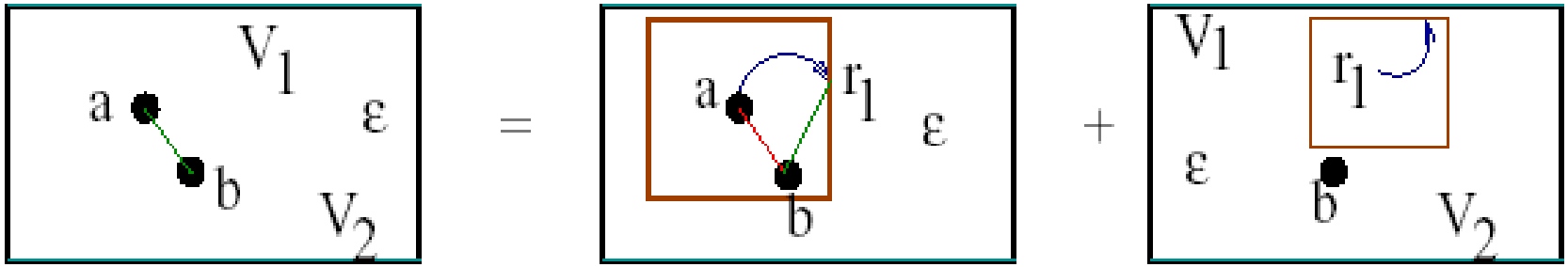
- **Hund's Rule** satisfied for all Cases of N_e

- **LDA** and **DMC** differ only for ***11*** electrons

MC simulation of full device?

- Poster – Das, Martin, Kalos , Ceperley
- Green's function Monte Carlo for Coulomb problem in complex geometry with gates, …..
- Example of Advantage of MC: $3N \rightarrow 3N + 3$
- In progress

The Random Walk for Coulomb Potentials



What is an insulator?
Brief History: Polarization & Localization

- Classical theory of E&M in matter:
  Free charge in metals - real currents
  Bound charge in insulators – polarization currents
- Kohn 1964 "Theory of the insulating state"
  - Localization
  - Due to Pauli principle, disorder, interactions
- Martin 1974 Problem in extended matter
  Polarization cannot be determined from the bulk density
- Kingsmith & Vanderbilt 1993
  Polarization determined by Berry's phase
- Ortiz & Martin 1994, 97
  Many-Body Berry's phase formulation
  Density-polarization theory
- Souza, Wilkens & Martin - 2001
  New formulation – rigorous definition of localization length

NSF

Lesson from statistics: Generating Functions

- Characteristic Function:

$$C(\alpha) = \int \exp(-i\,\alpha\,\mathbf{X})\; p(\mathbf{X})\; d\mathbf{X}$$

- Moments:

$$\langle X\,X\,\ldots\rangle_n = i^n\,(d/d\,\alpha)^n\,C(\alpha)\,\Big|_{\alpha=0}$$

- Cumulants:

$$\langle X\,X\,\ldots\rangle^c_n = i^n\,(d/d\,\alpha)^n\,\ln C(\alpha)\,\Big|_{\alpha=0}$$

- First Cumulant: $\langle X\rangle^c = \langle X\rangle$

- Advantage: Higher cumulants independent of origin, e.g.,

$$\langle X^2\rangle^c = -\,(d/d\,\alpha)^2\,\ln C(\alpha)\,\Big|_{\alpha=0}$$
$$= \langle X^2\rangle - \langle X\rangle^2 = \langle \Delta X^2\rangle$$

Moments of Polarization – Quantum Fluctuations

- Fluctuation-dissipation theorem for finite system:

$$< \Delta P^2 > = (e^2/V) < \Delta X^2 >$$

$$= (h/2\pi^2) \int \mathrm{Re}\, \sigma(\omega)\, d\omega / \omega$$

- And in the limit of large V

$< \Delta P^2 >$ = finite for insulators

$< \Delta P^2 >$ = infinite for metals

Measurable

- Souza (2001) – extension to infinite systems

$$C(\alpha) = < \Psi | \exp(-i \alpha \mathbf{X}) | \Psi >$$

- Cumulants of P:

$$< P\, P\, \ldots >^c_n = (e^n/V)\, i^n\, (d/d\alpha)^n \ln C(\alpha) \Big|_{\alpha=0}$$

- $< \Delta P^2 >^c$ defines localization length

Twisted boundary conditions & observables

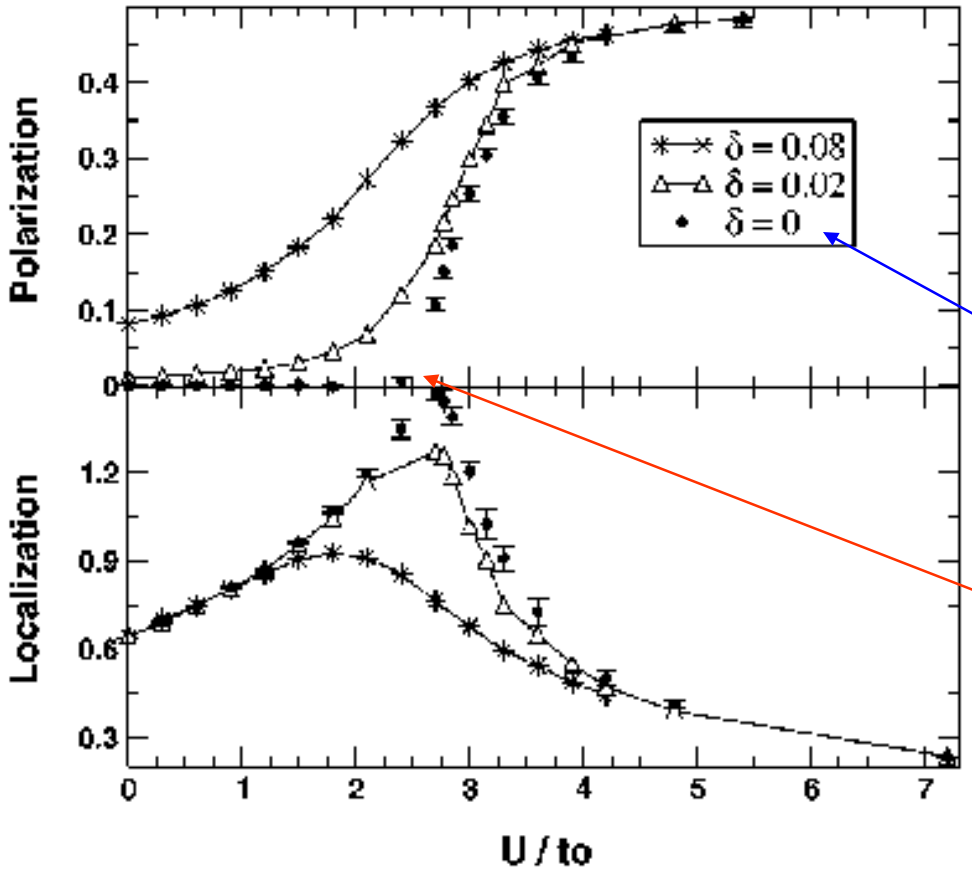
- Souza, et al., PRB 62, 1666(2000) -- Extends famous work of Kohn - 1964 - “Theory of the insulating state”

	Drude weight	Localization length
Formula in terms of twisted boundary conditions	$D_i = \frac{1}{2V} \frac{\partial^2 E(\mathbf{k})}{\partial k_i^2}\Big\|_{\mathbf{k}=0}$	$\xi_i^2(N) = -\frac{1}{N} \frac{\partial^2 \ln C(\boldsymbol{\alpha})}{\partial \alpha_i^2}\Big\|_{\boldsymbol{\alpha}=0}$
Relation to conductivity	$D_i = -\frac{1}{2} \lim_{\omega \to 0} \omega \, \mathrm{Im}\, \sigma_{ii}(\omega)$	$\xi_i^2(N) = \frac{\hbar}{\pi q_e^2 n_0} \int_0^\infty \frac{d\omega}{\omega} \mathrm{Re}\, \sigma_{ii}(\omega)$
Asymptotic value $(N, V \to \infty)$		
Insulators	Zero	Finite
Nonideal conductors	Zero	Infinite
Ideal conductors	Finite	Infinite

- Useful for insulators
  Approach to Metal-Insulator transition from insulating side

QMC calculation of Polarization, Localzation

- Ionic Hubbard Model in 1D – Wilkens - 2001
- Spontaneous symmetry breaking at transition



Symmetric lattice

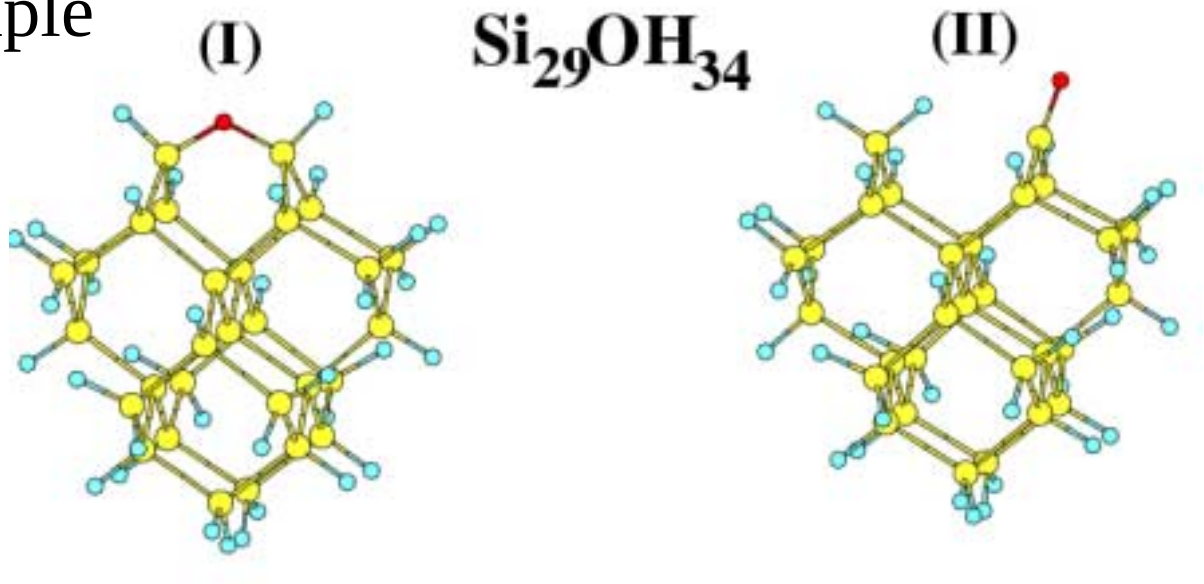
Gap vanishes

ζ diverges

Density Functional Calculations

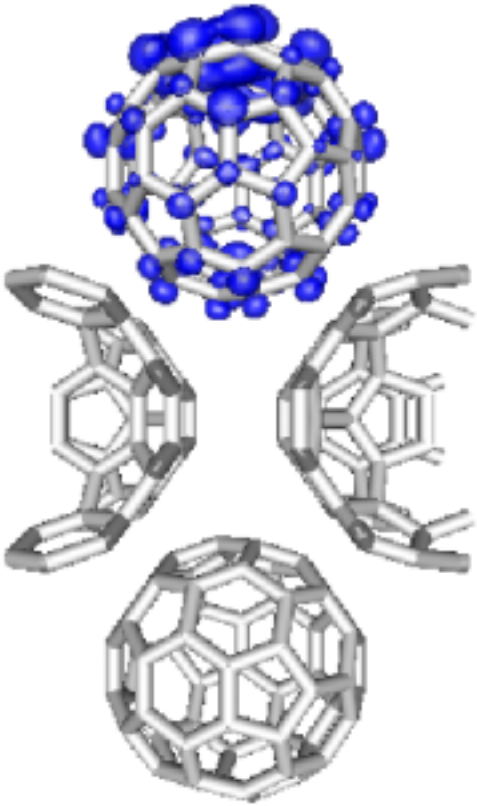
- Poster – Igor Vasiliev, Martin (Chelikowsky)
- Time dependent DFT for excitations
- Effect of Oxygen on Optical properties of Silicon Clusters

Example

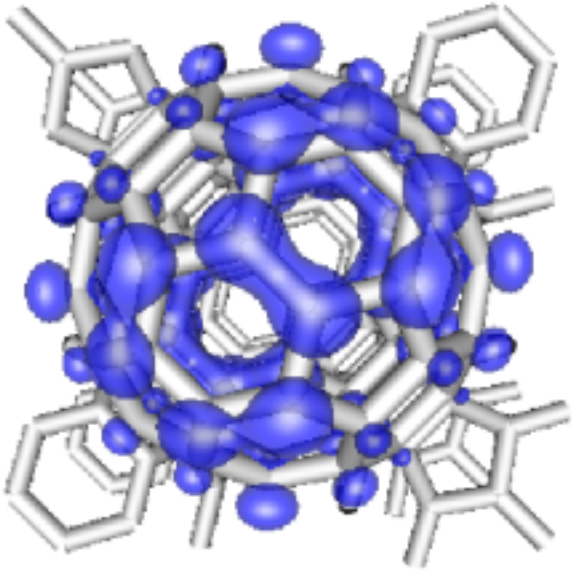


Density Functional Calculations

- Poster – Romero, Kim, Ordejon, Mozos, Martin
- FET's in C60?
- Nature of surface states - Superconductivity



Example: Added Holes



Electronic Structure of Condensed Matter
Summary

- Fundamental Advances toward the goal of solving THE many-body electronic structure problem in condensed matter
- Advantages of QMC
  - Many body method
  - Can use statistical sampling to advantage!
  - Electron gas, quantum dots, hydrogen, real materials
- Fundamental Advances in theory of insulators
  - Polarization & Localization
- Applications using DFT

Electronic Structure of Condensed Matter
Future

- QMC methods that:
  - Solve the real many-body problem
  - Compete with DFT in real applications
- New DFT approaches:
  - Develop Density-Polarization theory
  - Excitations
- Applications
  - Idealized and real systems - QMC and DFT

http://archive.ncsa.uiuc.edu/Apps/CMP/cmp-homepage.html
http://www.physics.uiuc.edu/research/ElectronicStructure/index.html