

Quantum Monte Carlo for electronic structure of materials

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Defense Advanced Research Projects Agency



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Motivation: electronic structure of variety of materials

New materials features:

- multi-component, complex
- 0-3D (dots, layers, interfaces)
- d and f elements
- nanoclusters and/or organics
- quantum effects important
- difficult to find unifying theory

Focus: $T=0$, continuous space

- interacting electrons and ions in continuous space

$$H\psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$$

- ground states
- excited states, optical props.
- responses to external fields, ...

Since many-body effects often hold the key it is worthwhile to explore (new) methods for efficient treatment of electron-electron correlation and other quantum many-body effects

One of the alternatives: quantum Monte Carlo (QMC)

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One- and two-particle quantities vs many-particle wave functions

Traditional approaches are based on one- or two-particle quantities:

- one-particle density (matrix)
- one-particle Green's function
- pair-correlation functions, etc

since these contain just the right amount of information necessary to describe the physics. We think and "understand" in terms of reduced quantities.

QMC, however, is based on wave functions: ... but

- in general, wave functions are intractable and contain too much of information most of which is irrelevant
- corresponding equations almost impossible to solve
- limit of large number of particles might not be straightforward
- difficult to understand the physics

Let's see how relevant are these arguments ...

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Slater-Jastrow trial (variational) wave functions

"Zero order" wave function: Slater determinant(s)

$$\psi_0(\mathbf{R}) = \sum_n \text{Det}_n[\phi_\alpha] \text{Det}_n[\phi_\beta]$$

one-particle orbitals from - Hartree-Fock, MCSCF

- Density Functional Theory (DFT)

- ...

Correlate the Slater wave function explicitly

$$\psi_T(\mathbf{R}) = \sum_n \text{Det}_n[\phi_\alpha] \text{Det}_n[\phi_\beta] \exp(U_{corr})$$

$$U_{corr} = \sum_{i,j} \sum_{k,l,m} c_{klm} a_k(r_{ij}) b_l(r_{il}) b_m(r_{jl})$$

electrons ions correlation basis expansion

e-e terms (e-e cusps), e-e-ions terms

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Stochastic method for the multi-D task: variational Monte Carlo (VMC)

Evaluate the expectation values by sampling electron configurations,
eg, variational energy

$$E_{VMC} = \frac{\int \psi_T^2 [H\psi_T / \psi_T] d\mathbf{R}}{\int \psi_T^2 d\mathbf{R}} = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{sample} \frac{H\psi(\mathbf{R}_{sample})}{\psi(\mathbf{R}_{sample})}$$

where samples are distributed as $\psi_T^2(\mathbf{R})$

Correlation variational parameters $\{c_{km}\}$ optimized
by minimization of the local energy variance

$$\sigma_{VMC}^2 \approx \frac{1}{N} \sum_{sample} \left[\frac{H\psi(\mathbf{R}_{sample})}{\psi(\mathbf{R}_{sample})} - E_{VMC} \right]^2$$

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Beyond VMC

VMC : straightforward, fast, efficient but not enough accuracy
and variational bias

Eliminate VMC bias by projecting out the (ground) state in
imaginary time

$$\psi(\mathbf{R}, t) = \exp(-tH)\psi_T(\mathbf{R})$$

$$-\partial_t \psi(\mathbf{R}, t) = H\psi(\mathbf{R}, t)$$

$$\psi(\mathbf{R}, t + \tau) = \int G(\mathbf{R}, \mathbf{R}', \tau) \psi(\mathbf{R}', t) d\mathbf{R}'$$

Wave function can be sampled and the equation solved by
interpreting the Green's functions as a transition probability density
However, the wavefunction is both + and -

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Fermion sign problem

Naïve approach for fermionic wave functions: decompose to + and -

$$\psi_{\tau}(\mathbf{R}) = \psi_{\tau}^{+}(\mathbf{R}) - \psi_{\tau}^{-}(\mathbf{R})$$

$$-\partial_t \psi_{\tau}^{+}(\mathbf{R}, t) = H \psi_{\tau}^{+}(\mathbf{R}, t)$$

$$-\partial_t \psi_{\tau}^{-}(\mathbf{R}, t) = H \psi_{\tau}^{-}(\mathbf{R}, t)$$

and + and - components decouple because the Sch. equation is linear. Therefore + and - components converge independently to the lowest energy solution (which is bosonic)

$$\lim_{t \rightarrow \infty} \psi^{+}(\mathbf{R}, t) - \lim_{t \rightarrow \infty} \psi^{-}(\mathbf{R}, t) \propto \exp[-(E_{0, \text{Fermi}} - E_{\text{Boson}})t]$$

Fermion "signal" decays exponentially quickly into the bosonic "noise"

Fixed-node diffusion Monte Carlo (DMC)

Introduce importance sampling with $\psi_{\tau}(\mathbf{R})$

$$f(\mathbf{R}, t + \tau) = \int G^*(\mathbf{R}, \mathbf{R}', \tau) f(\mathbf{R}', t) d\mathbf{R}'$$

$$\lim_{t \rightarrow \infty} f(\mathbf{R}, t) \propto \psi_{\tau}(\mathbf{R}) \phi_{\text{ground}}(\mathbf{R})$$

$$G^*(\mathbf{R}, \mathbf{R}', \tau) = \frac{\langle \mathbf{R} | \exp(-\tau H) | \mathbf{R}' \rangle}{\psi_{\tau}(\mathbf{R}') \psi_{\tau}^{-1}(\mathbf{R})}$$

Fixed-node approximation: fermion node (zero hypersurface) of the solution $\phi_0(\mathbf{R})$ is enforced to be identical to the fermion node of the trial function $\psi_{\tau}(\mathbf{R})$: then $f(\mathbf{R}, \tau) > 0$ everywhere

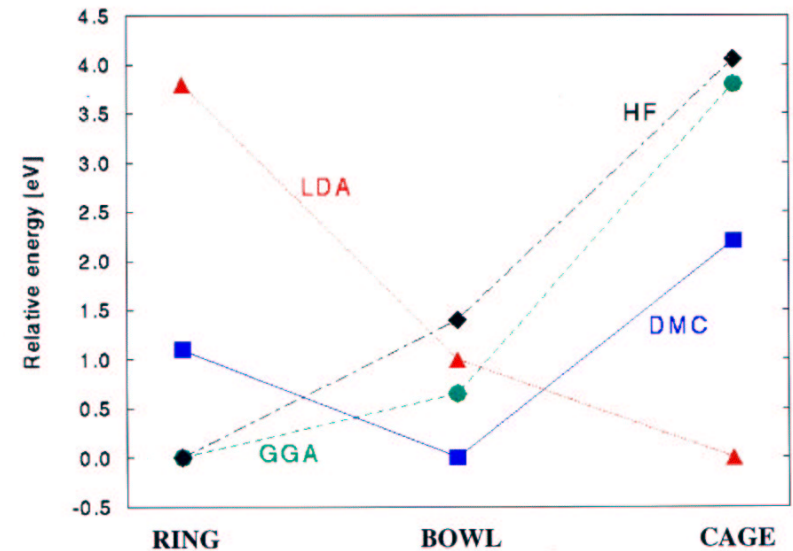
Symmetry condition (nonlocal) replaced by boundary cond. (local)

Key new features of QMC

- works **directly in the multi-dimensional space**, ie, in $3N$ -dimensions for N particles, using stochastic rather than basis function representation
- builds upon but goes beyond one-particle approaches: **genuine many-body method**
- computationally demanding but **feasible for realistic systems**

Applications follow ...

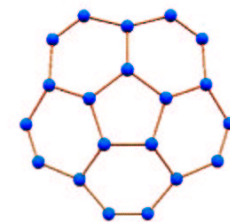
Relative energies [eV] of C₂₀ isomers



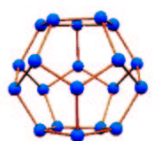
"1D"



"2D"



"3D"



Ring Inversion of Cyclooctatetraene

- Wenthold, Hrovat, Borden, Lineberger, *Science* 272, 1456 (1996)
- Hrovat, Borden, *JACS* 114, 5879 (1992)
- Trindle, Wolfskill, *J. Org. Chem.* 56, 5426 (1991)
- Dewar, Merz, *JPC* 89, 4739 (1985)



Energy difference (kcal/mol): D2d → D8h (singlet, triplet)

METHOD	SINGLET	TRIPLET
GVB (1 pair)	32.2	27.5
LSDA	21.8	15.4
BLYP	19.7	11.9
BPW91	20.2	11.6
DMC	14(2)	20(2)
EXP	14(2)	22(2)

- Accuracy comparable with experiment
- Confirmed non-Hund's rule transition state

Grossman and Mitas, '97

C_n ($n=4N+2$) – CARBON RINGS

Previous studies: K. Raghavachari '86, J.D. Watts & R.J. Bartlett '92, J.M.L. Martin & P.R. Taylor '96, G. Galli *et al.* '98, J.H. Weare *et al.* '98

- C_{4N} rings are acetylenic ($-C\equiv C-$); strong stabilization from bond alternation because of anti-aromatic character
- C_{4N+2} rings different: Huckel rule fulfilled, three competing isomers

angle alternation
(cumulenic)



full symmetry
(cumulenic)



bond alternation
(dimerized)

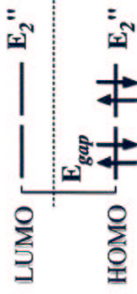


Competition of aromaticity vs. alternation (decrease of symmetry)

Electronic structure

small rings

cumulenic
closed shell + large gap



==>

large rings

two half-filled π bands
Peierls instability opens gap

σ band: doubly occupied
 π_x, π_y bands: singly occupied!

==>

Q: How does the gap develop as the ring size increases?

Strikingly different perspectives:

LDA/GGA results

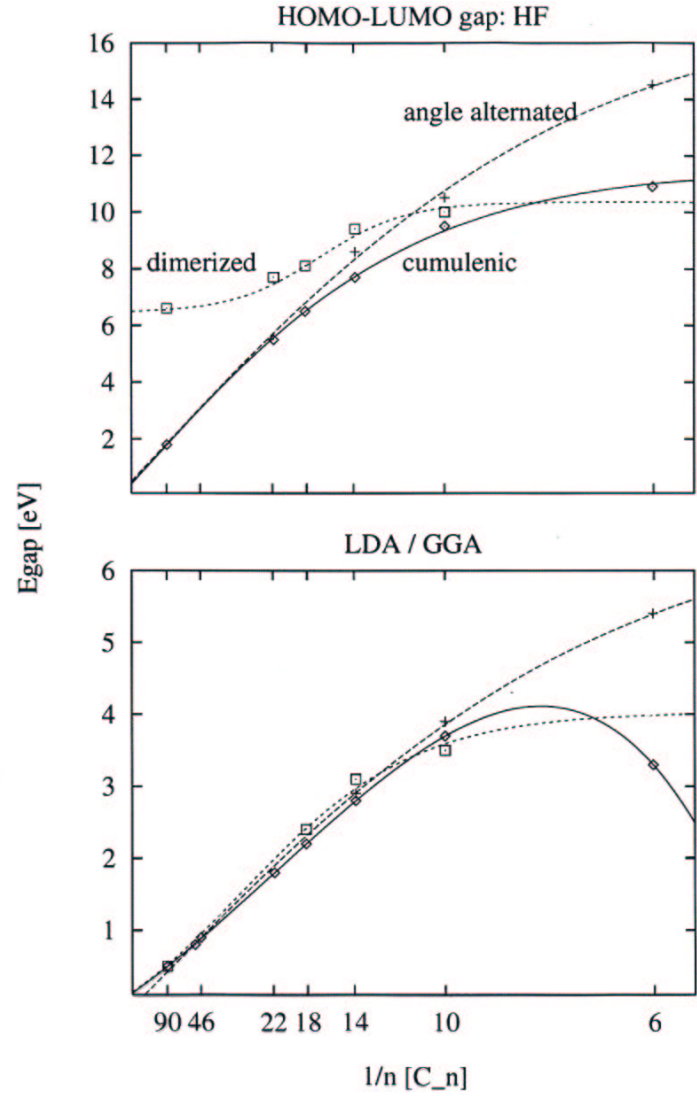
- ◆ no dimerization even for one hundred atoms
- ◆ very tiny for infinite length [Bylaska *et al.* PRB 58 (1998)]

Peierls mechanism

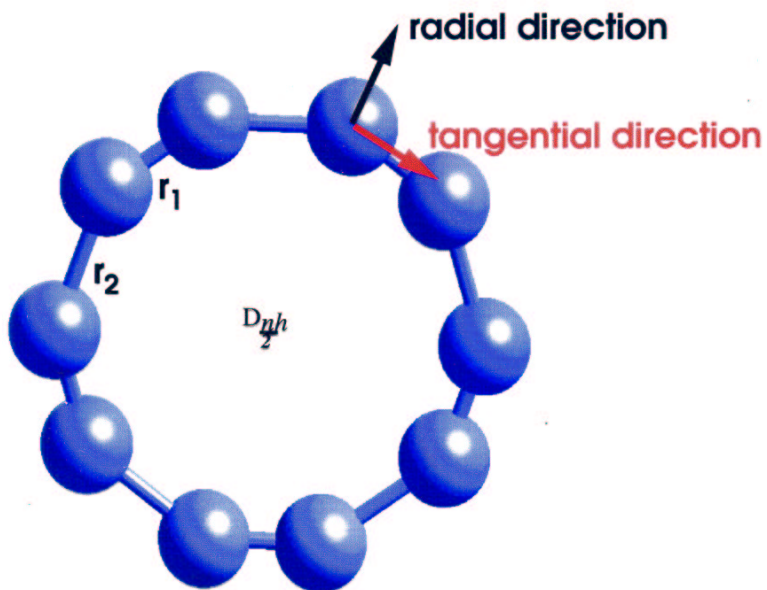
HF/MCSCF results

- ◆ strong tendency to dimerize
- ◆ large dimerization already for C_{18}

Second order Jahn–Teller



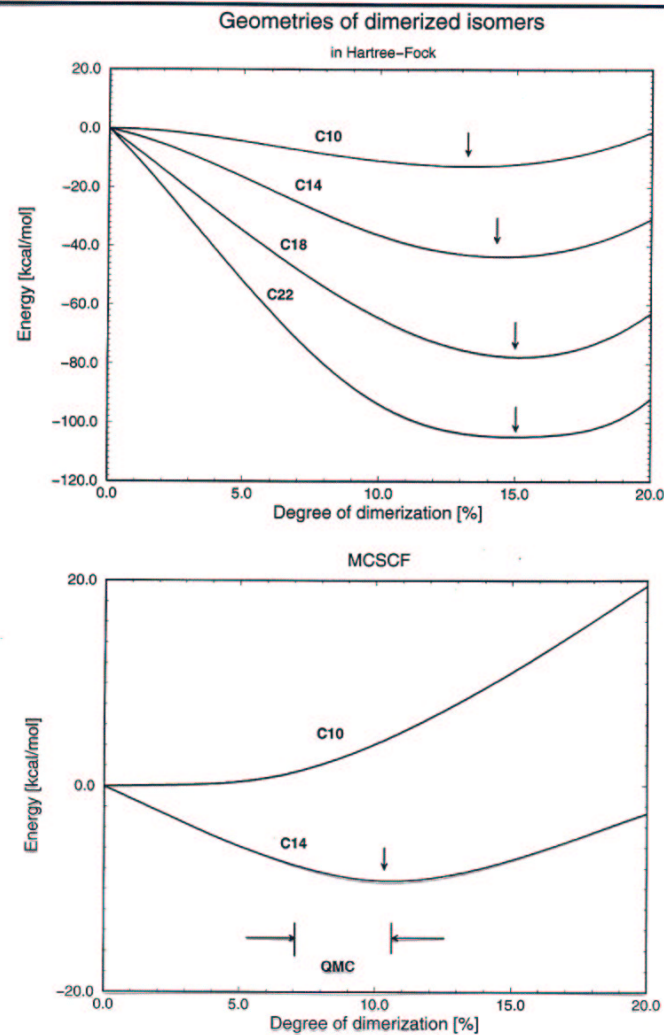
Forces for C_n

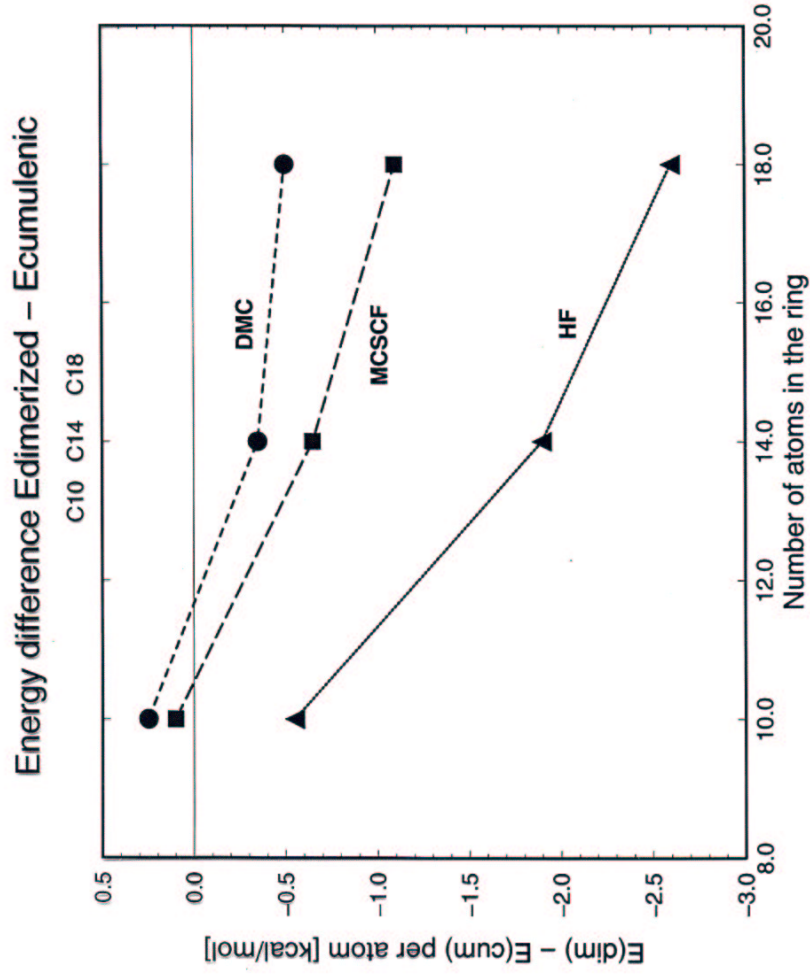


Radial direction: QMC force ~ 0

Tangential dir.: force towards smaller dimerization

Challenging to get the geometries right (no good mean-field available): forces helpful





C_{N+2} rings summary

Cumulenenic vs alternated:

- alternated geometries favored at all sizes
- cumulenenic isomer is a transition state

Angle alternated vs. bond length alternated (dimerized):

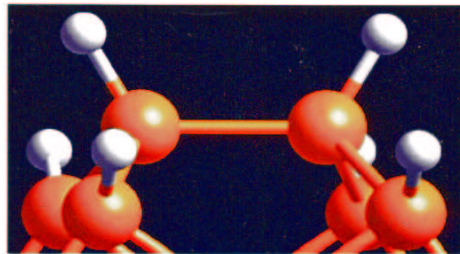
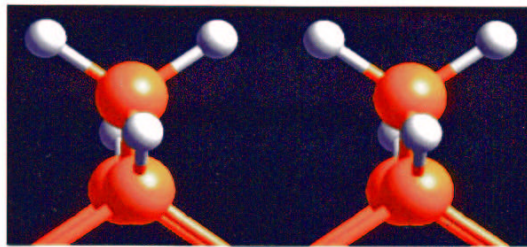
- crossover between C_{10} and C_{14}

Gap present at all sizes: smooth evolution from the second-order Jahn-Teller to the Peierls regime

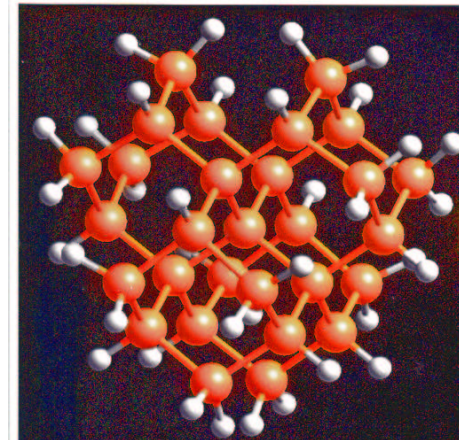
- for C_{10} difference between the isomers ~ 0.1 eV

Search for Structural Prototypes

- Cut an approximately spherical shape from crystalline silicon
- Saturate dangling bonds with hydrogen
- Possibly, reconstruct the "surface" bond pattern
- For example, dimer reconstruction:



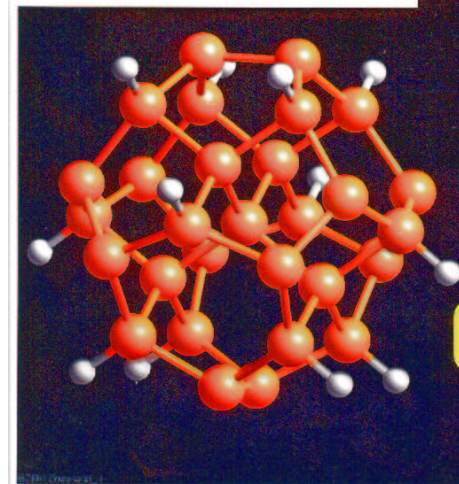
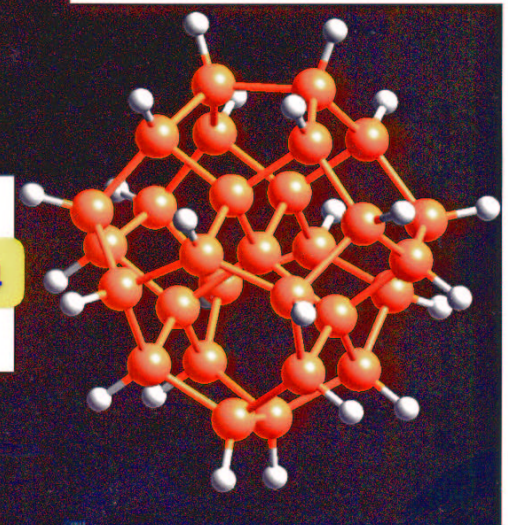
- Optimize the geometry in Density Functional Theory



Si₂₉ H₃₆

Si_nH_m clusters:
saturation vs.
reconstruction

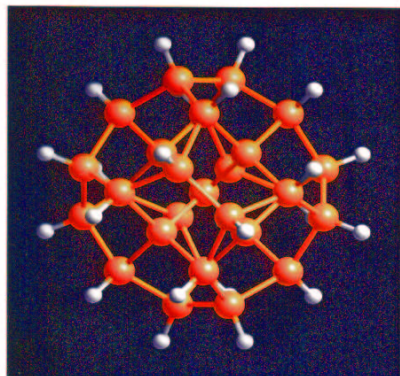
Si₂₉ H₂₄



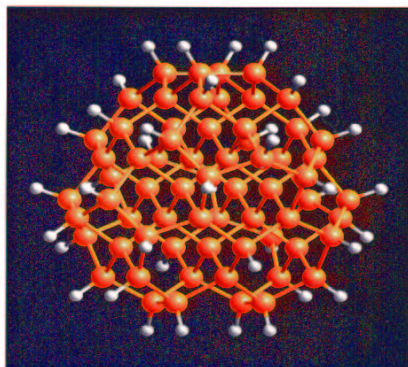
Si₂₉ H₁₂

L. Mitas, NCSU

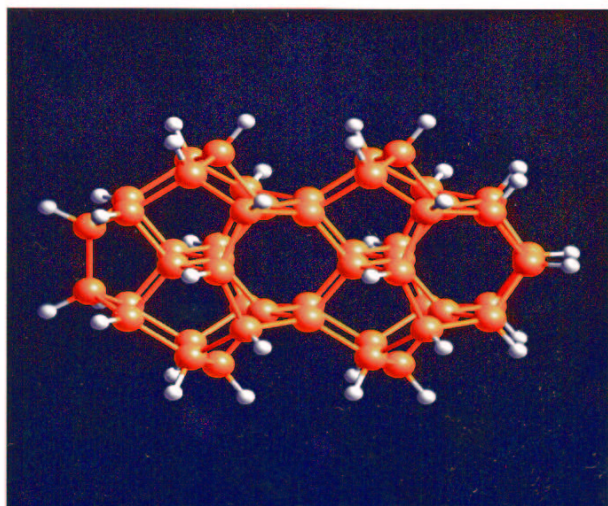
Structures with saturated bonds form magic sizes



$\text{Si}_{29}\text{H}_{24}$

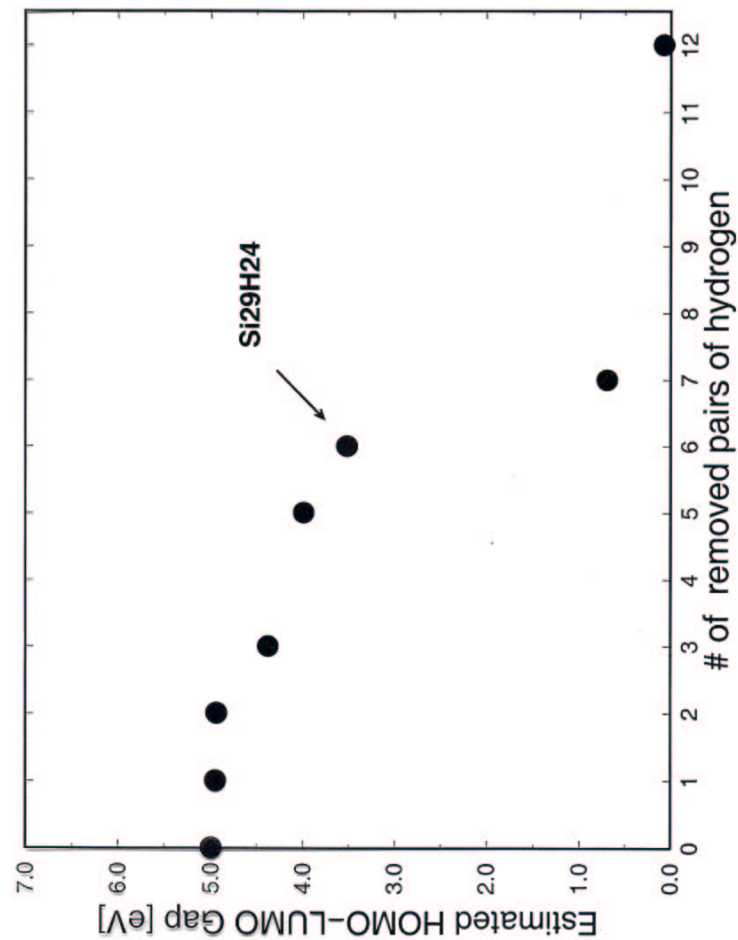


$\text{Si}_{66}\text{H}_{40}$

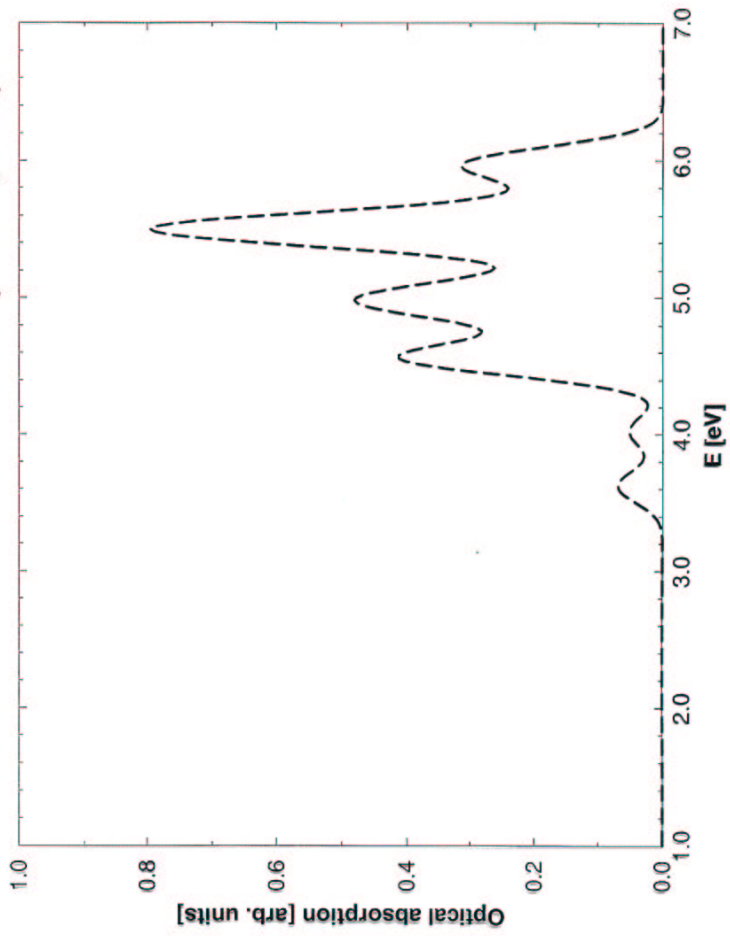


$\text{Si}_{50}\text{H}_{36}$ from elliptical cutout: "fused" $\text{Si}_{29}\text{H}_{24}$

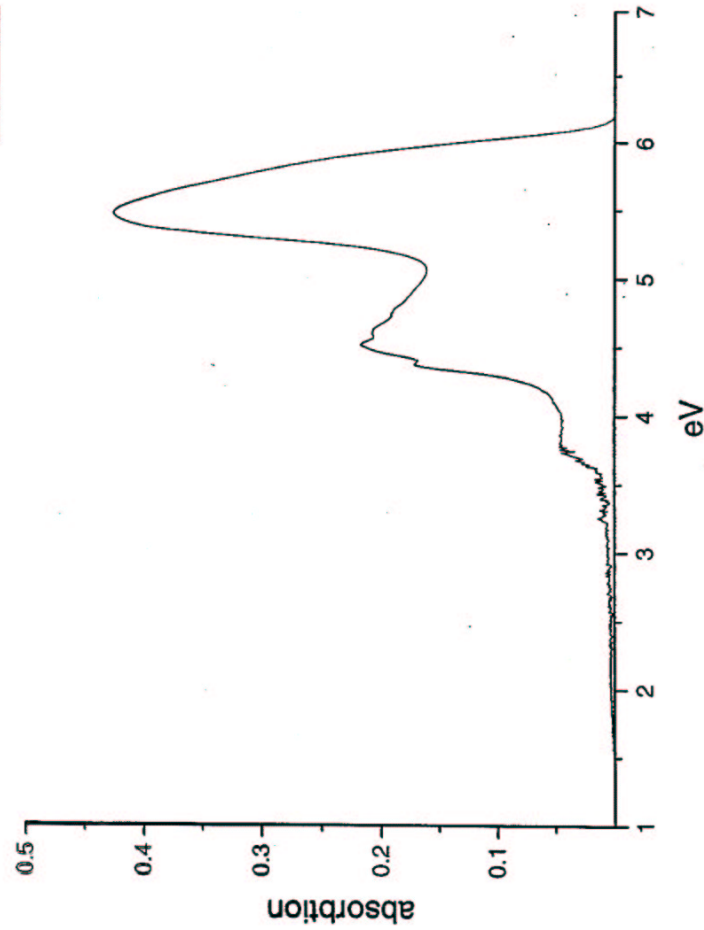
Gaps: Si29H36 to Si29H12



Si29H24, Optical absorption
 CIS with correction/broad. 0.12 eV (L. Mitas, UIUC)



D

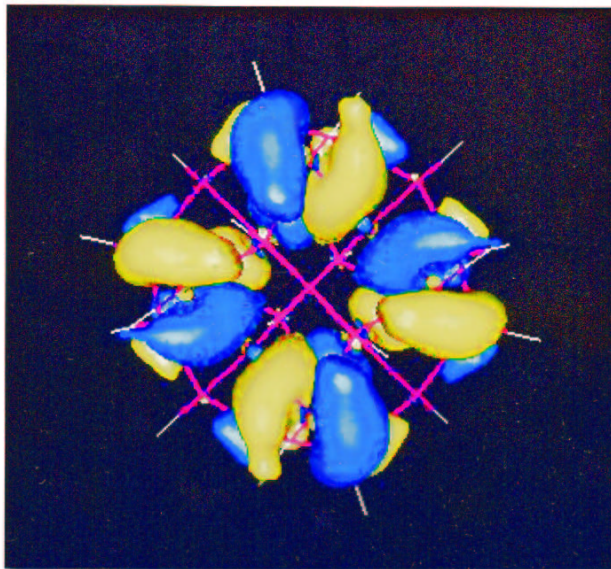


Previous models had assumed excitations were **localized** on a single bond.

We found:

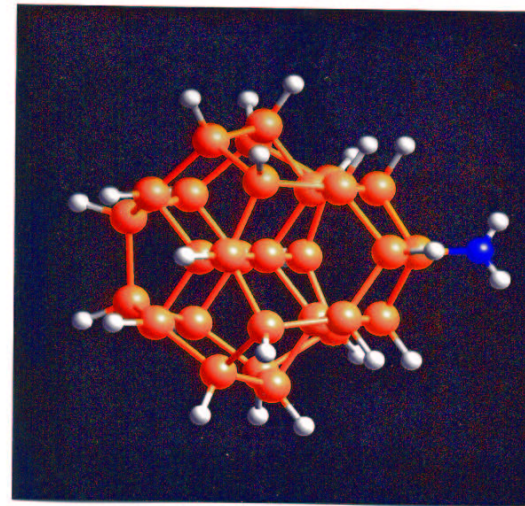
- no change in bonding pattern
- change in bond lengths ~ 0.01 angstrom
- slight distortions distributed across the whole system

Exciton is delocalized across the whole structure



Single particle state of excited electron

"Doping" with Nitrogen and Carbon



NH_2

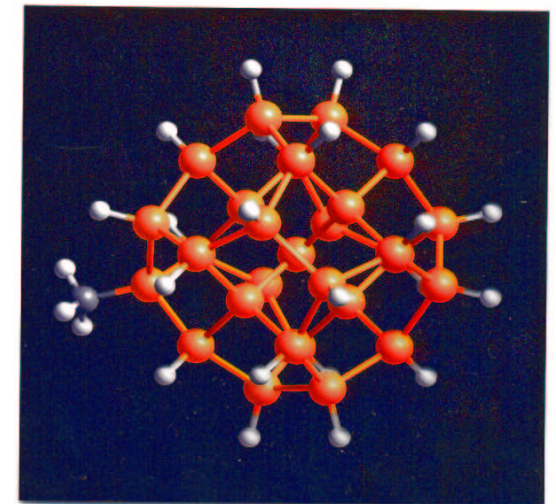
Emission energy lowered by .25 eV

Shift from violet to blue

CH_3

No shift

Can be bound to organic molecules



QMC for solids

- supercell + periodic boundary conditions

- Ewald sums

- finite size effects for:

kinetic energy ("k- points")
potential energy ("cell shape")

extrapolations to $N \rightarrow \infty$

- besides cohesive energies, lattice constants etc, possible to study **band structures** using excitons : "band structure scan"

Mitas and Martin, PRL 72, 2438 ('94)

- studies of Fermi surfaces feasible in future

Beyond cohesive energies

• QMC evaluation of band structures for insulators (band gaps, band widths)

- create an exciton (Mitas, Martin '94):
PRL 72, 2438 (1994)
 e^- from the valence \rightarrow conduction band

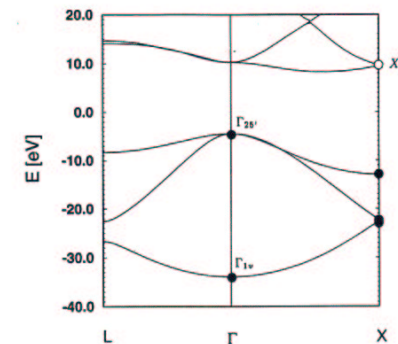


Fig. 3. Hartree-Fock band structure of diamond. The filled circles indicate states which are occupied in the 8-atom simulation supercell.

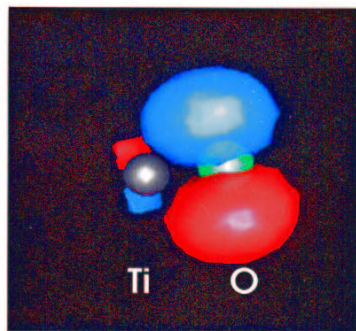
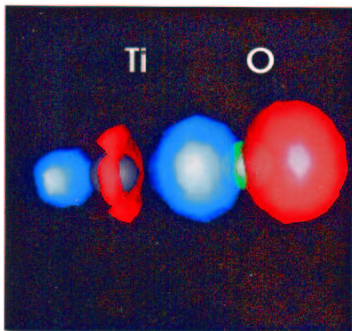
$$E_{\text{exciton}} - E_{\text{ground}} = E_{\text{gap}} + E_{e-h}$$

- alternatively: add/subtract an electron

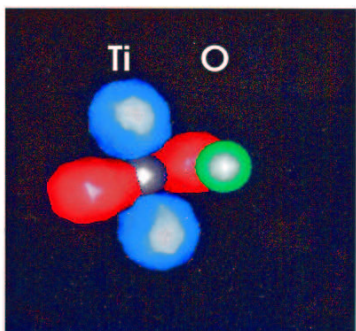
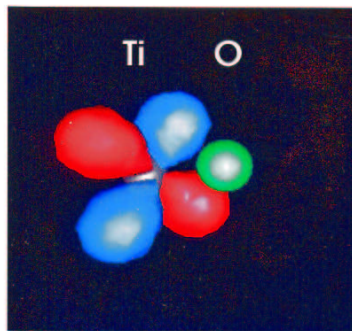
• challenge: Fermi surfaces for metals (very large supercells necessary)

Start with a molecule first:
TiO as a prototype

- qualitatively: $Ti^{++} O^{--}$, triplet with two unpaired d electrons on Ti



Doubly occupied orbitals



d_{xy} singly occupieds $d_{x^2-y^2}$

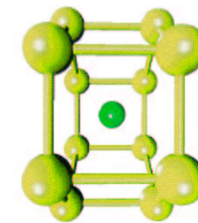
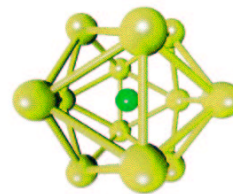
Magnetic nanomaterials: caged transition elements $Si_{12}X$ $X=Sc, Ti, \dots, 3d, 4d, 5d$ series

APS March Meeting in '94:

L. M.: Electronic structure of $Mn@Si_{12}$

Experiment in Japan in '01!

$W@Si_{12}$, later $Cr@Si_{12}$, etc

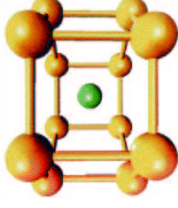


- attempt to predict caged d-spin syst.
- not successful, hybridized, unstable

Currently investigating the 3d-series: $X = Sc, Ti, \dots, Cu$

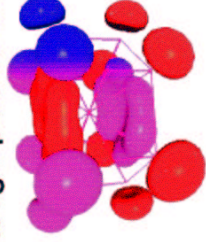
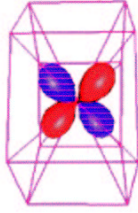
Magnetic nanomaterials ... caged TMs

- even number of e^- : singlets
- odd number of e^- : dublets
- spins localized inside, gaps up to 2.5 eV
- exception: Ti,Zr, singlet and triplet close



Competition between

localized d states on TM and less tight p states on Si



Difficult to get the ground state (probably beyond DFT capabilities)

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QMC: facts and performance

Fundamental:

- wave function-based
- wide range of applicability
- accuracy for sp-systems :
- VMC ~ 85 % of correlation
- DMC ~ 95 % of correlation
- fixed-node error ~ 5% of corr.
- within 1-2 % of experiments

$$(E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}})$$

Computational:

- robust algorithms
- easy to parallelize
- scaling in e^- : N^3 (or better)
- 100-200 valence electrons
- up to 1000 electrons tried
- 100 times slower than DFT

QMC is often the reference for testing other methods:
accuracy for energy differences ~ 0.1 eV or better

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Hartree-Fock (or MCSCF) nodes: why are they reasonable

- HF is a size-consistent theory (ie, HF energy is proportional to the number of particles)
- implies that the correlation energy remains the same as a percentage of the total energy
- implies that the HF fermion-nodes are size consistent (note that node is energetically very costly)
- implies that the fixed-node approximation (the best solution within the fixed boundary) is size consistent
- implies that the percentage of recovered correlation energy should be constant for any system: correct, for atom, clusters, solids essentially the same amount of correlation is recovered

Stationary Schrödinger equation

Suppose the correlation is decomposed into two parts

- fermion nodes, ie, boundary conditions
- often one or few determinants are very reasonable
- "non-dynamical" correlation, multi-reference wavefunctions
- can be obtained within mean-field/basis set methods
- "bosonic" correlations within the fermion node domains
- e-e cusps, multiple collision points, etc
- "dynamical" correlation, very difficult for other methods
- easy within QMC

The methods are complementary: together best of both, productive

One- and two-particle quantities vs many-particle wave functions (II)

QMC and wavefunctions:

- it seems that in a number of cases it is more efficient to do the many-particle calculations than to try to build a better mean-field
- let the machine to worry about reducing the unnecessary information
- combination of variational trial functions and stochastic methods is quite effective for getting high accuracy solutions of Schr. eq.
- physics and understanding can be built into and obtained from wave functions (sometimes the breakthrough *is* the wave function)
- limit of large number of particles is OK