Fullerenes: a workbench for many-body theories benchmarks

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OAK RIDGE National Laboratory

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Acknowledgements

- Support
  - DOE
- Codes
  - PWSCF PARSEC & RGWBS DFT, GW-BSE, TDLDA
  - CASINO QMC
- Computational support
  - NCCS at ORNL
  - NERSC
  - LLNL
  - TACC

•**Thanks A. J. Williamson, R. J. Needs, N. Drummond, M. Towler, J. Kim and M. Kalos**

Theoretical methods for as a function of the size of the electron system

$$H_{e-} = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

Minimum approximations

- Many body (everything)

Quantum Monte Carlo (QMC)
Configuration interaction (CI)
GW-BSE

$$H_{e-} \approx -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \mathrm{v}_{eff}(\rho(r)) - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

- Single particle approximation

Density Functional Theory (ab-initio)

$$H_{e-} \approx -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \mathrm{v}^*_{eff}(\rho(r))$$

- Empirical methods (fit to experiment)

$$H_{e-} \approx -\sum_i \frac{\hbar^2 \nabla_i^2}{2m^*}$$

- Effective mass of **k.p** methods

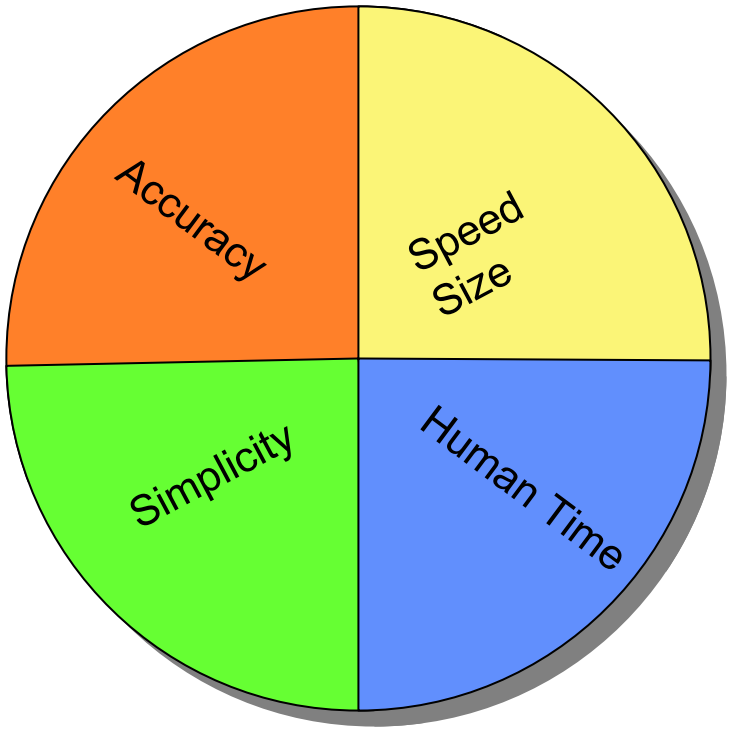
$$j(r), \rho(r)$$

- Hydrodynamical classical models

Stronger approximations

•**Thanks A. J. Williamson, R. J. Needs, N. Drummond, M. Towler, J. Kim and M. Kalos**

There is always a good reason to learn a new theory



Molecules-Solid State
Condensed Matter
Chemistry

NCCS Jaguar

CASINO 2.1 **Cambridge Quantum Monte Carlo Code**

When we should learn something new?

Calculations of Silicon Q-Dots

- B. Delley and E.F. Steigmeier, Phys. Rev. B 47, 1397 (1993).
- L.-W. Wang and Alex Zunger, J. Chem. Phys. 100, 2394 (1994).
- S. Ogut, J.R. Chelikowsky and S.G. Louie, Phys. Rev. Lett. 79, 1770 (1997).
- M. Rohlfing and S.G. Louie, Phys. Rev. Lett. 80, 3320 (1998).
- F.A. Reboredo, A. Franceschetti and A. Zunger, Appl. Phys. Lett. 75, 2972 (1999).
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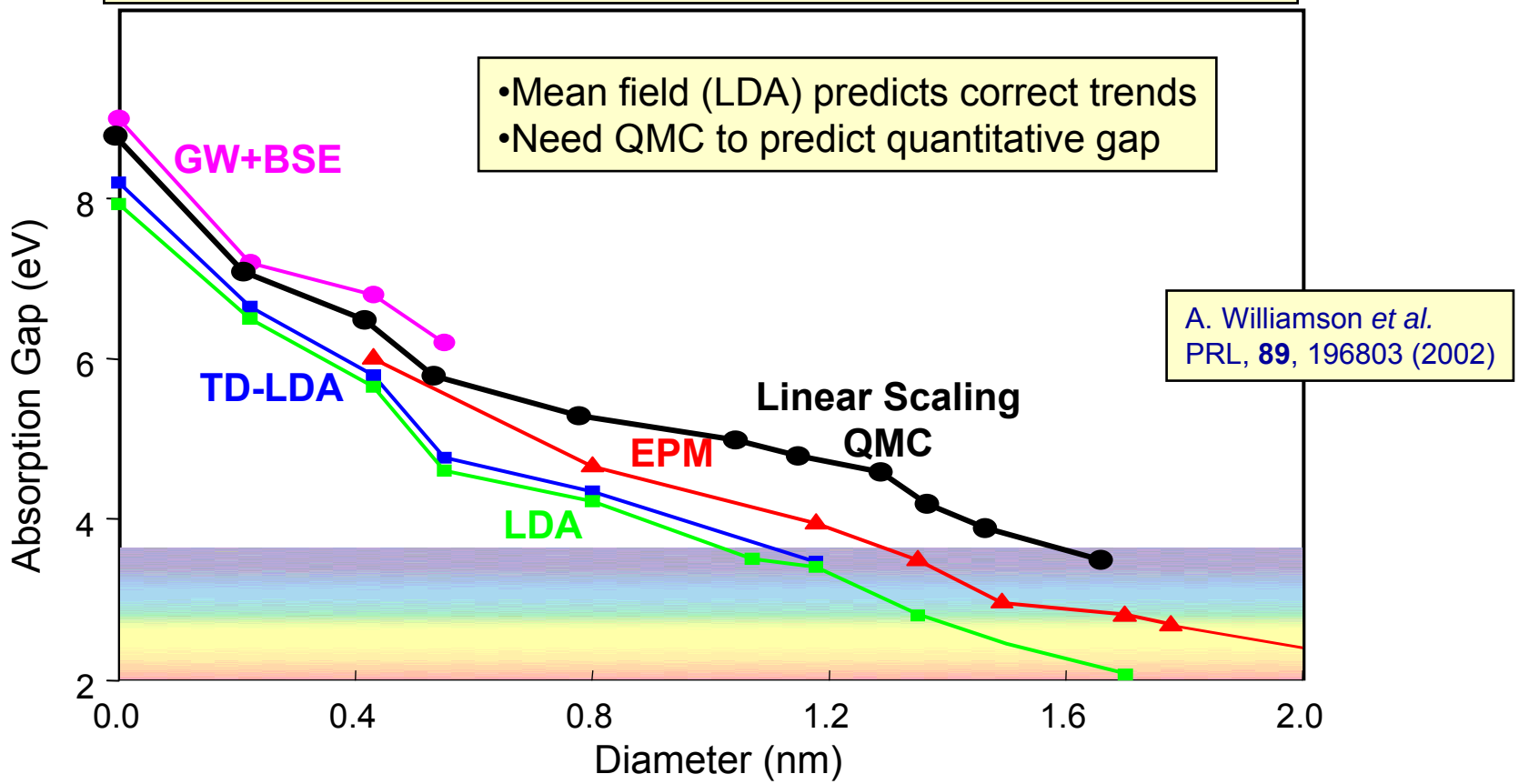
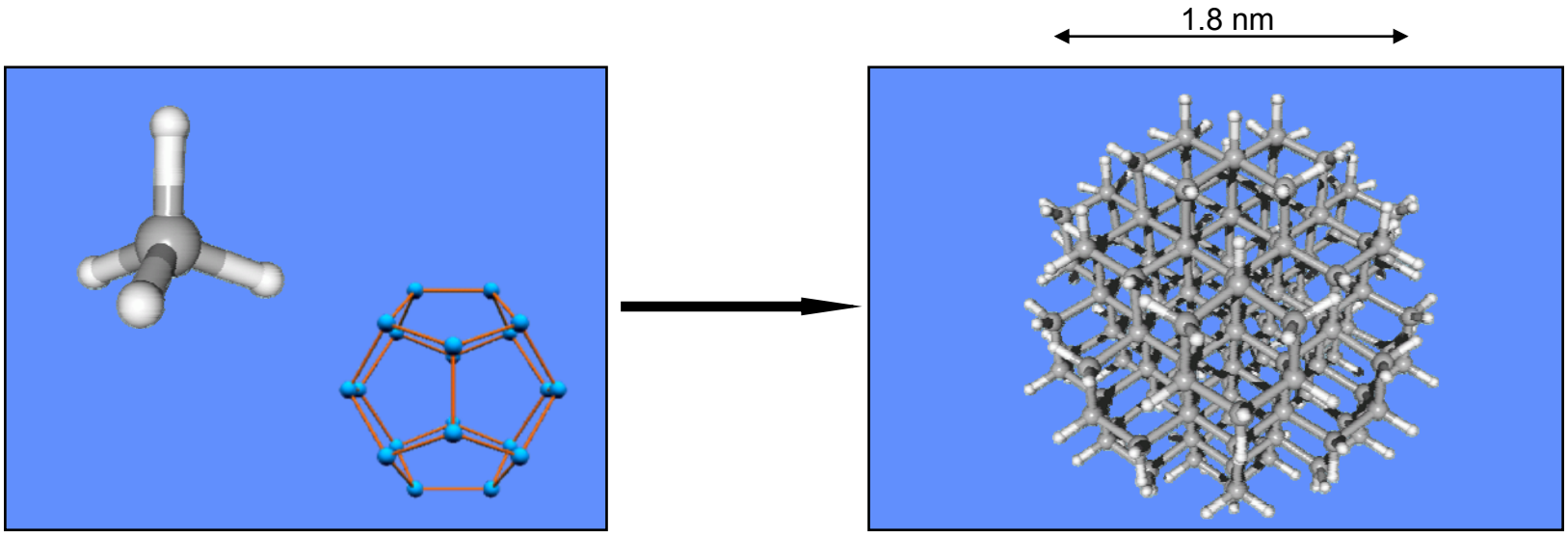
- C.S. Garoufalis, A.D. Zdetsis and S. Grimme, Phys. Rev. Lett. 87, 276402 (2001).



A. Williamson *et al.*
PRL, **89**, 196803 (2002)

Experimental characterization of Si Q-Dots is very difficult

QMC: From quantum Chemistry to Materials Science



SiH_4 , C_{20}

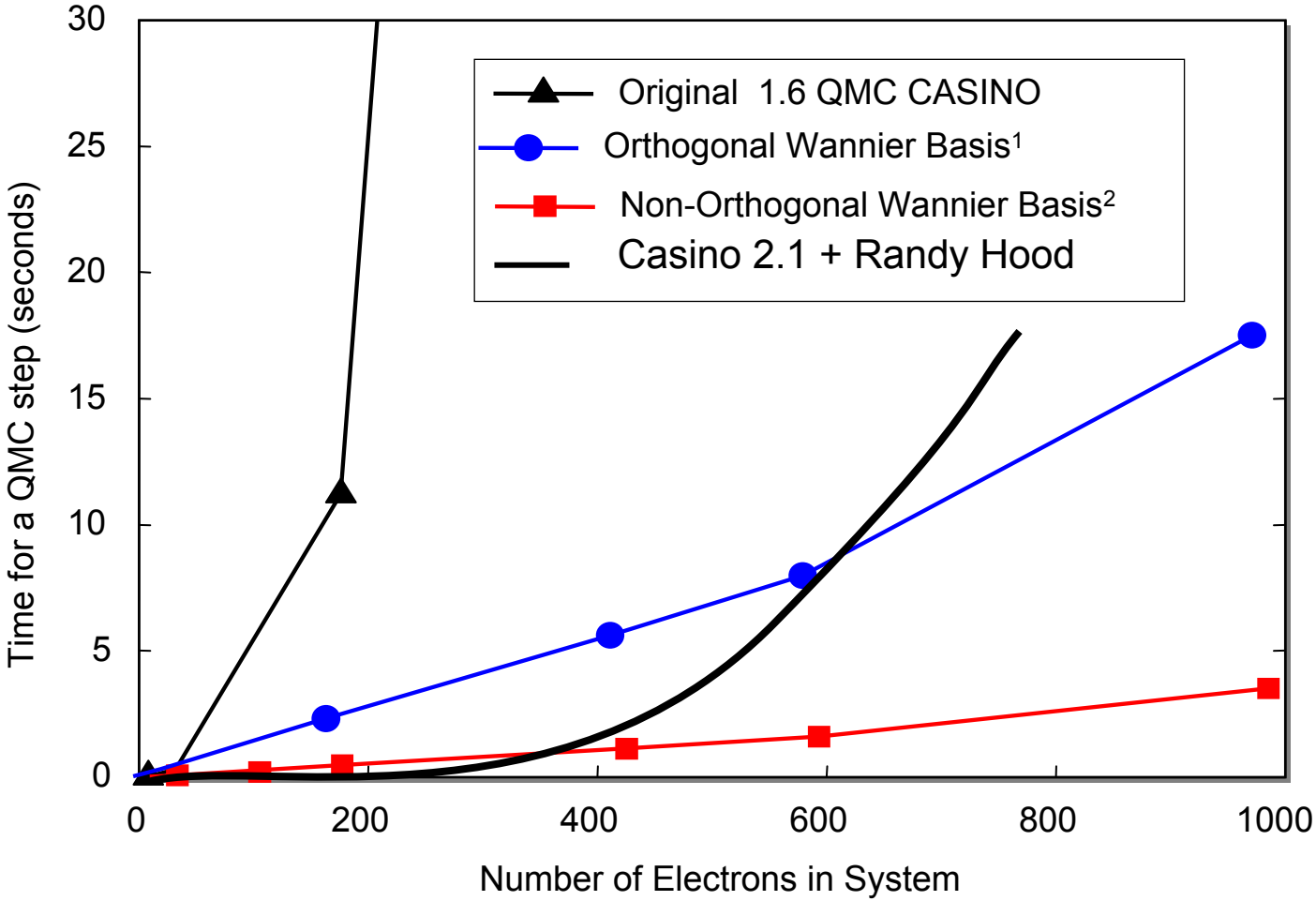
$Si_{148}H_{120}$

- Grossman *et al.* PRL **86** 472 (2001)
- Porter *et al.* PRB **64** 035320 (2001)
- Kent *et al.* PRB **62**, 15394 (2000)

- Williamson *et al.* PRL (2002)
- Reboredo and Williamson PRB (2005).
- Alfe and Gillan J. Phys. C (2004).

Similar progress in the GW-BSE area

Near Linear Scaling QMC for 0→1000 Electrons



[1] A.J. Williamson, R. Hood, and J. Grossman, Phys. Rev. Lett. **87**, 246406 (2001)

[2] F. A. Reboredo, A. J. Williamson, Phys. Rev. B (R) March 15 (2005)

Changes in CASINO

- Acceleration of blip evaluation routines
- Distribution wave function storage memory in different nodes
- Asynchronous transfer of data between different processors (elimination of mpi barriers). Reduction of waiting time

- Randy Q. Hood Lawrence Livermore National Laboratory

Calculations of Silicon Q-Dots

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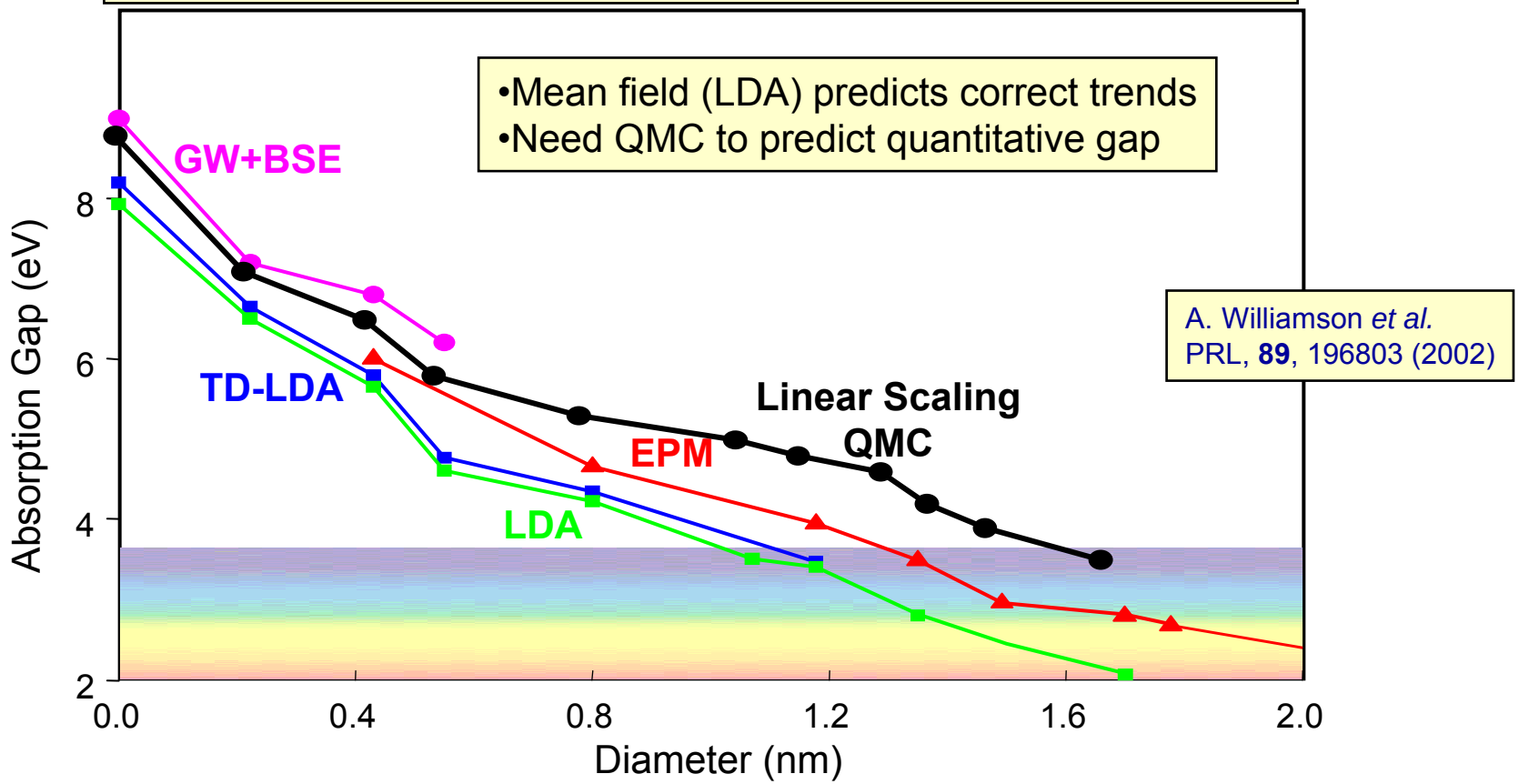

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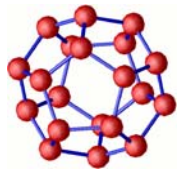
Experimental characterization of Si Q-Dots is very difficult

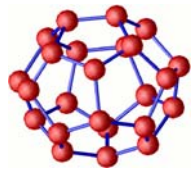
We calculated neutral and charged excitations of fullerenes

- Systematic analysis of accuracy involving various *ab initio* theories:
  - Time-dependent DTF-LDA.
  - GW and Bethe-Salpeter.
  - Quantum Monte Carlo.
  - Do QMC and GW-BSE always
  - agree
- Goals:
  - Benchmark methodologies.
  - Identify points of improvement.

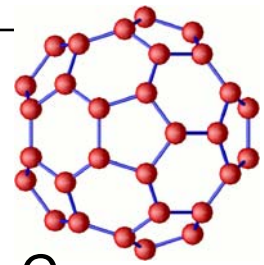
• Predictive power:
At first calculations were done in "clean conditions": (without knowing the experimental result).



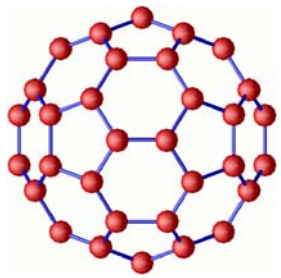
C_{20}



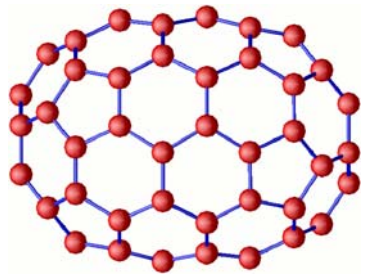
C_{24}



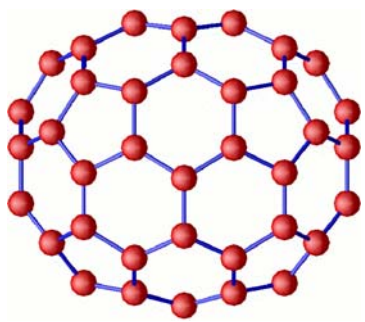
C_{50}



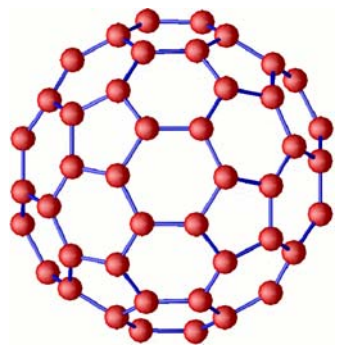
C_{60}



C_{70}



C_{80} ($D5_d$)



C_{80} (I_h)

Experimental information on fullerenes exists

Diffusion Quantum Monte Carlo (DMC)

$$H_{e-} = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

$$H_{e-} = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + V\{R_i\}$$

$$e^{iH_{e-}t}\psi_e(\{R\}) = \sum_n c_n \psi_n(\{R_j\}) e^{i\varepsilon_n t}$$

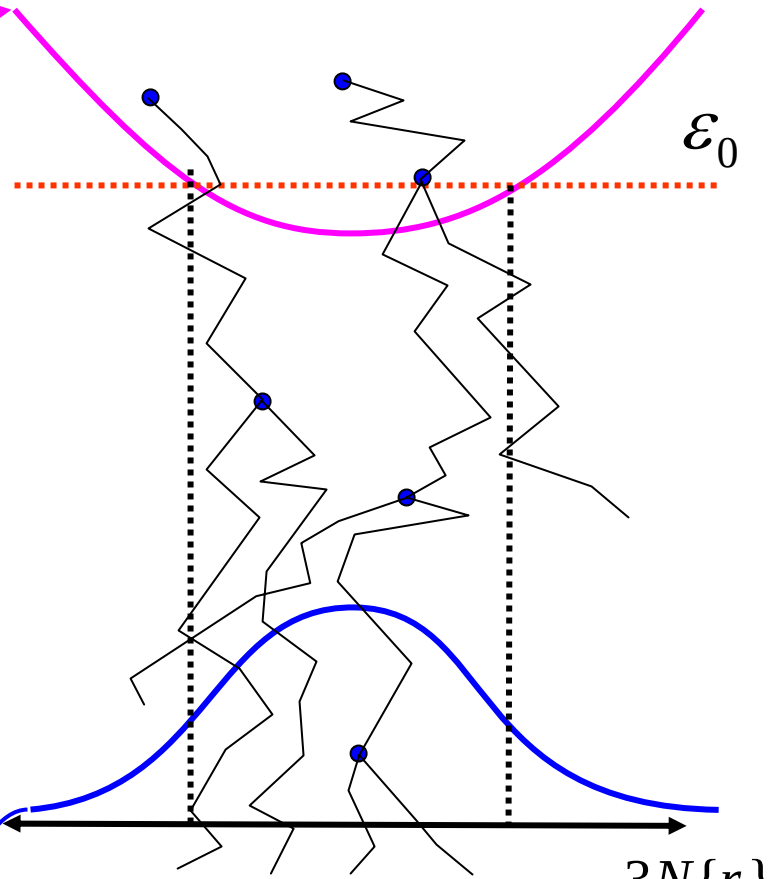
For imaginary time : $t = i\tau$

$$\lim_{\tau\to\infty} e^{-H_{e-}\tau}\psi_e(\{R_i\}) = c_0\psi_0(\{R_i\})e^{-\varepsilon_0\tau}$$

Diffusion term

Source or sink of walkers

$$\frac{d}{d\tau}\psi_e(\{R_i\}) = \left[-\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \left(V\{R_i\} - \varepsilon_0\right)\right]\psi_e(\{R_i\})$$



Equilibrium population

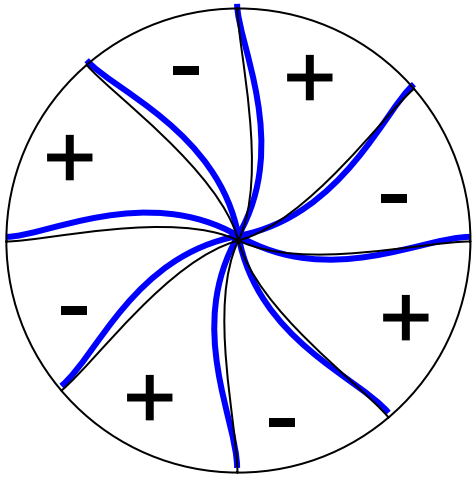
Fig. Foulkes, Mitas, Needs and Rajagopal RMP (2001).

(DMC) For fermions

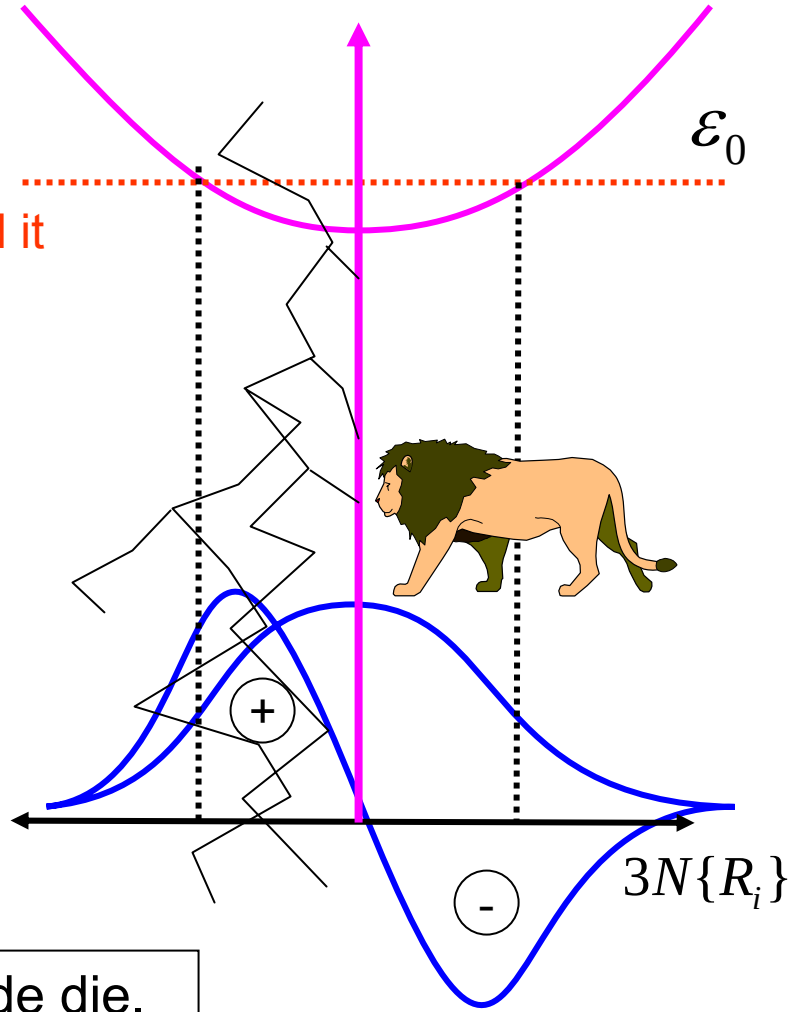
$$\lim_{\tau\to\infty} e^{-H_{e-}\tau}\psi_e(\{R_i\}) = c_0\psi_0(\{R_i\})e^{-\varepsilon_0\tau}$$

•The ground state of many body system is a symmetric (bosonic) wavefunction: DMC will find it

• For fermions we need to impose the symmetry with zero boundary conditions at the nodes of the trial wave function.



Since we do not know the nodes exactly there is a nodal error



For fermions all the trajectories that cross a node die. Many trajectories die at the node unstable

The symmetry of the wave function is enforced by the nodes of a trial wave function.
Often the trial wave-function is obtained from mean field or DFT.

DMC for fermions

$$\frac{\partial f}{\partial \tau} = \frac{\hbar^2}{2m}\left[\sum_{i=1}^{N}\nabla_i^2 f - \nabla_i\left(f\nabla_i \ln|\psi_T|^2\right)\right] - \left[\frac{H\psi_T}{\psi_T} - \varepsilon_0\right] f$$

Ceperley Alder PRL 1980

$$H = -\sum_i \frac{\hbar^2\nabla_i^2}{2m} + \sum_{i,j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I}\frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{J,I}\frac{Z_I Z_J e^2}{|\vec{R}_J - \vec{R}_I|}$$

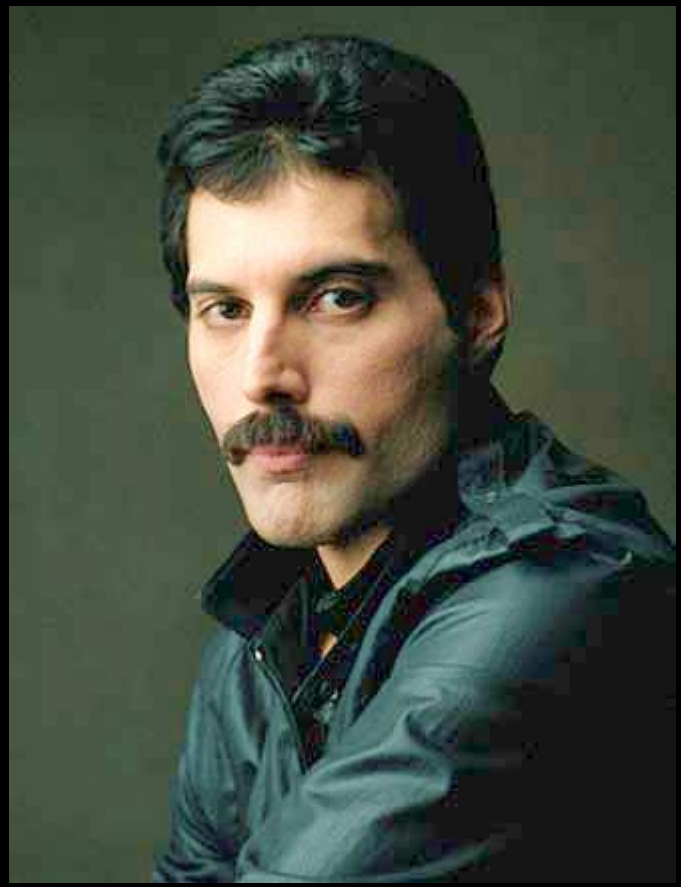
$$\Psi = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \\ \vdots & & \ddots \\ & & \phi_N(\mathbf{r}_N) \end{vmatrix} \cdot \exp\left[\sum_i^N \chi(\mathbf{r}_{iI}) - \sum_i^N u(\mathbf{r}_{ij})\right]$$

Slater Determinant
$O(N^3)$

Jastrow correlation function
$O(N^2)$

We use CASINO 2.1  **Cambridge Quantum Monte Carlo Code**

(1975)



Notation:

mama = DMC algorithm
man, boy = walker
landslide = trial wave function
monstrosity, nothing = node

DMC for poets

The Quantum Monte Carlo Song

Bohemian Rhapsody (1975)

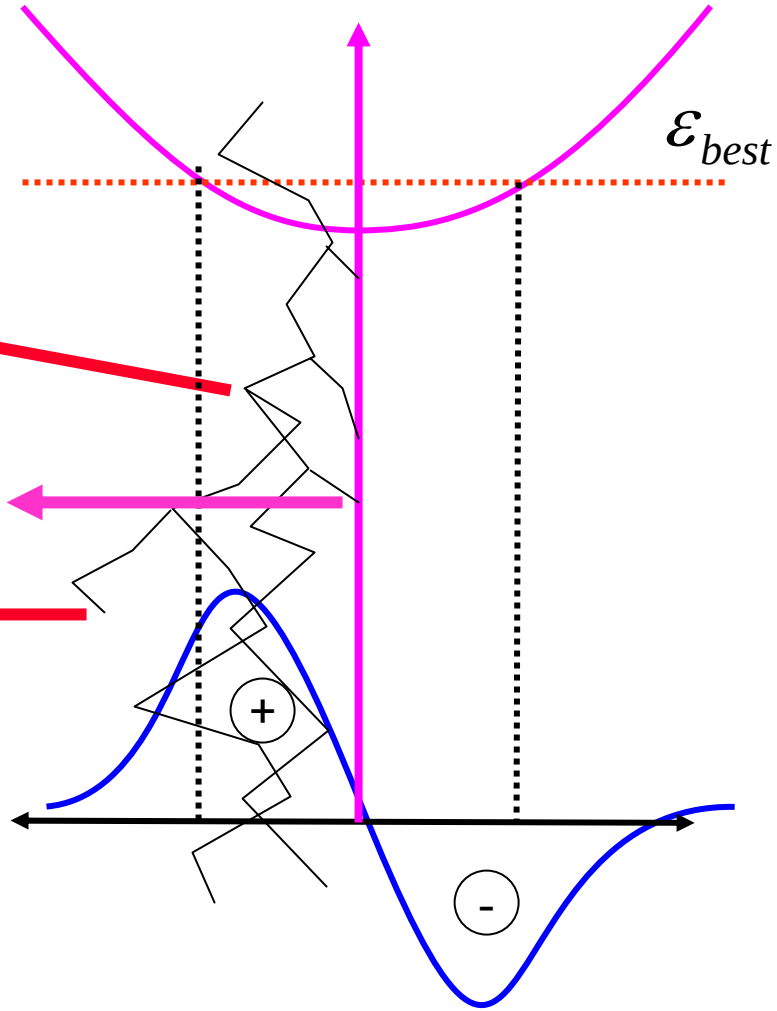
Is this the real life
Is this just fantasy
Caught in a wave function Nodal error
No escape from reality
Open your eyes
Look up to the skies and see
I'm just a walker, I need no sympathy
Because I'm easy come, easy go,
Little high, little low
Anyway the wind blows, doesn't really matter to me - to me

Anderson, Kalos,
Ceperey & Alder

The Quantum Monte Carlo Song

Mama, just killed a walker,
Put a gun against his head,
Pulled my trigger, now he's dead,
Mama, life had just begun,
But now I've gone and thrown it all away
Mama, ooo,
Didn't mean to make you cry
If I'm not back again this time tomorrow
Carry on, carry on, as if nothing really matters

Too late, my time has come,
Sends shivers down my spine
Body's aching all the time,
Goodbye everybody - I've got to go -
Gotta leave you all behind and face the truth
Mama, ooo -
I don't want to die,
I sometimes wish I'd never been born at all -



Fear experience by walker
with high local energy

The Quantum Monte Carlo Song

I see a little silhouetto of a man,
Scaramouch, scaramouch will you do the Fandango
Thunderbolt and Lightning - very very frightening me-
Gallileo, Gallileo,
Gallileo, gallileo,
Gallileo Figaro - Magnifico -
I'm just a poor boy nobody loves me
He's just a poor boy froma poor family
Spare him his life from this monstrosity
Easy come, easy go - will you let me go
Bismillah! No, - we will not let you go - let him go -
Bismillah! We will not let you go - Let him go
Bismillah! We will not let you go - Let him go
Will not let you go - Let me go
Will not let you go - Let me go
No, no, no, no, no, no, no-
Mama mia, mama mia, mama mia let me go -
Beelzebub has a devil put aside for me, for me, for me -

So you think you can stone me and spit in my eye
So you think you can love me and leave me to die
Oh Baby - Can't do this to me Baby
Just gotta get out- just gotta get right outta here -

Random walk over all lyrics space

Debate on whether a walker must be killed or rejected when crossing a node

Persistent or stack walker
solved by
C. Umrigar et al. JPC (1993)
M. Casula et al. PRL (2005)

Random walk over all Lyrics space continues

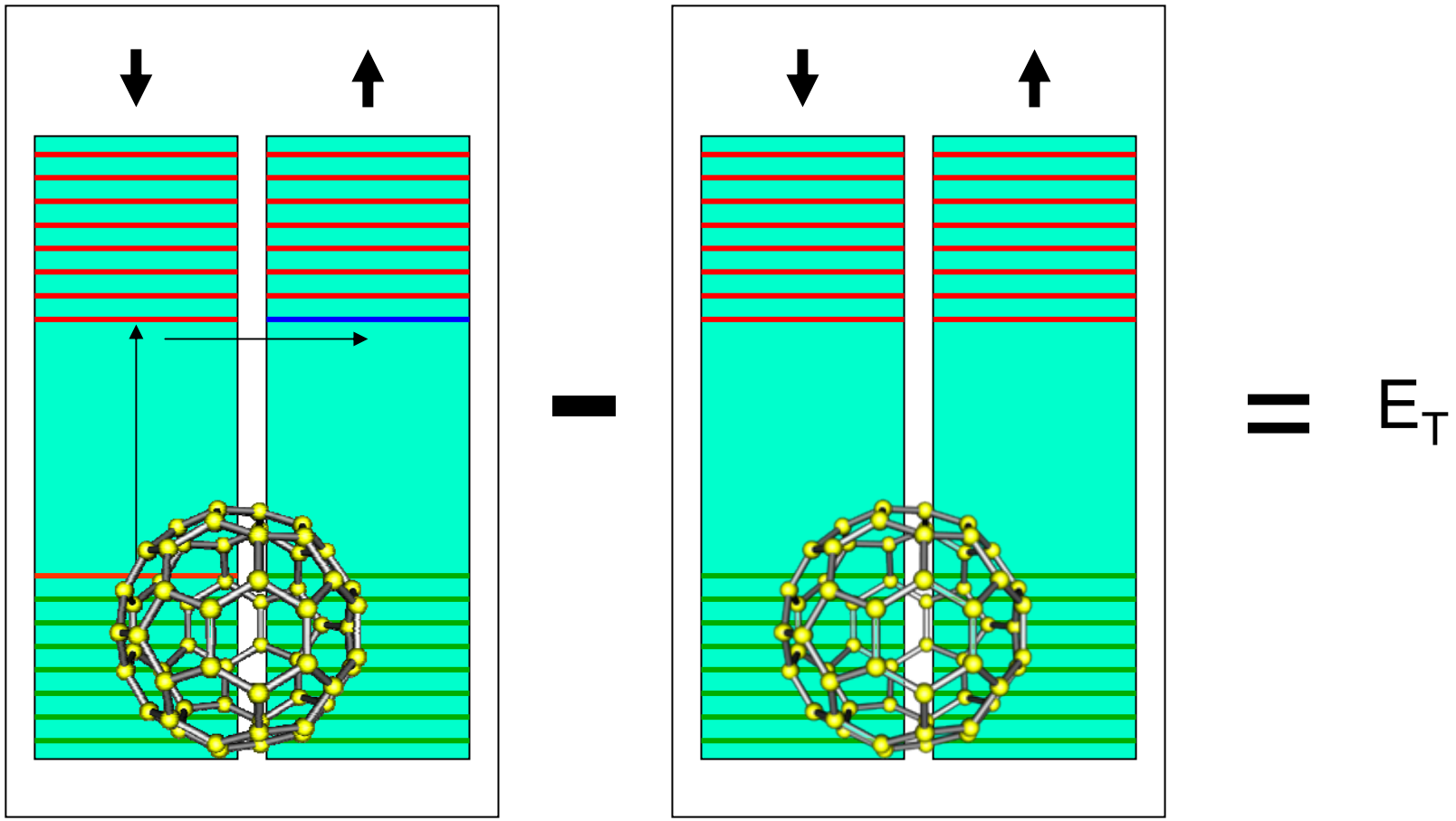
Quantum Monte Carlo Song

$$\psi_T(R) = 0$$

“Nothing really matters
Anyone can see
Nothing really matters, nothing really matters - to me”

Freddie Mercury **(see also M Kalos L Mitas, R Needs)**

Approximations (1) pseudopotentials, (2) Fix Node (3) DFT structure



This is a very demanding test for DMC
Total energy differences require cancelation of errors on 0.01% or more

Levels of approximation of GW methods:

"DFT"

$$\Sigma = V_{xc}$$

Hybertsen & Louie (1985)

$$G_0(\mathbf{r},\mathbf{r}';E) = \sum_n \frac{\psi_n(\mathbf{r})\psi_n^\star(\mathbf{r}')}{E - E_n}$$

$$W \approx \epsilon^{-1}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$$

G_0W_0 approximation

$$\Sigma = iG_0W_0$$

Del Sole et al. (1994)

Tiago et. al (2006)

G_0W_0 + vertex: G_0W_f approximation

$$\Sigma = iG_0W_0\Gamma_0$$

Self-consistent: GW approximation

$$\Sigma = iGW$$

Hedin's equations

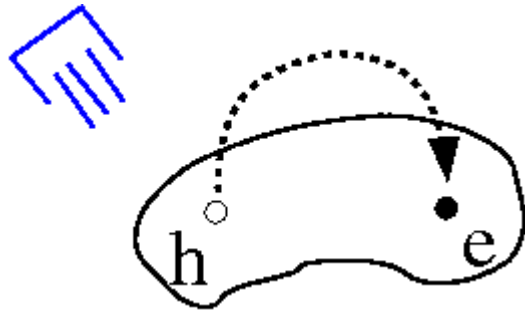
$$\begin{cases} W = V + VPW \\ P = -iGG\Gamma \\ \Sigma = iG\Gamma W \\ \Gamma = 1 + \frac{\delta\Sigma}{\delta G}GG\Gamma \end{cases}$$

G_0W_0 and G_0W_f approximations rely on DFT as a "good starting point".

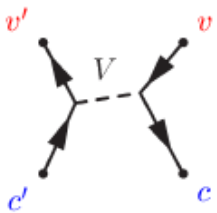
Optical Excitations: Bethe-Salpeter Equation

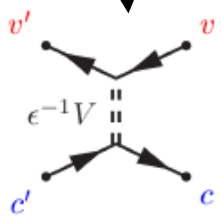
Eigenvalue problem:

$$\left(\varepsilon_c^{GW} - \varepsilon_v^{GW}\right) A_{cv}^S + \sum_{c'v'} \langle vc|K^{BSE}|c'v'\rangle A_{c'v'}^S = \Omega^S A_{cv}^S$$



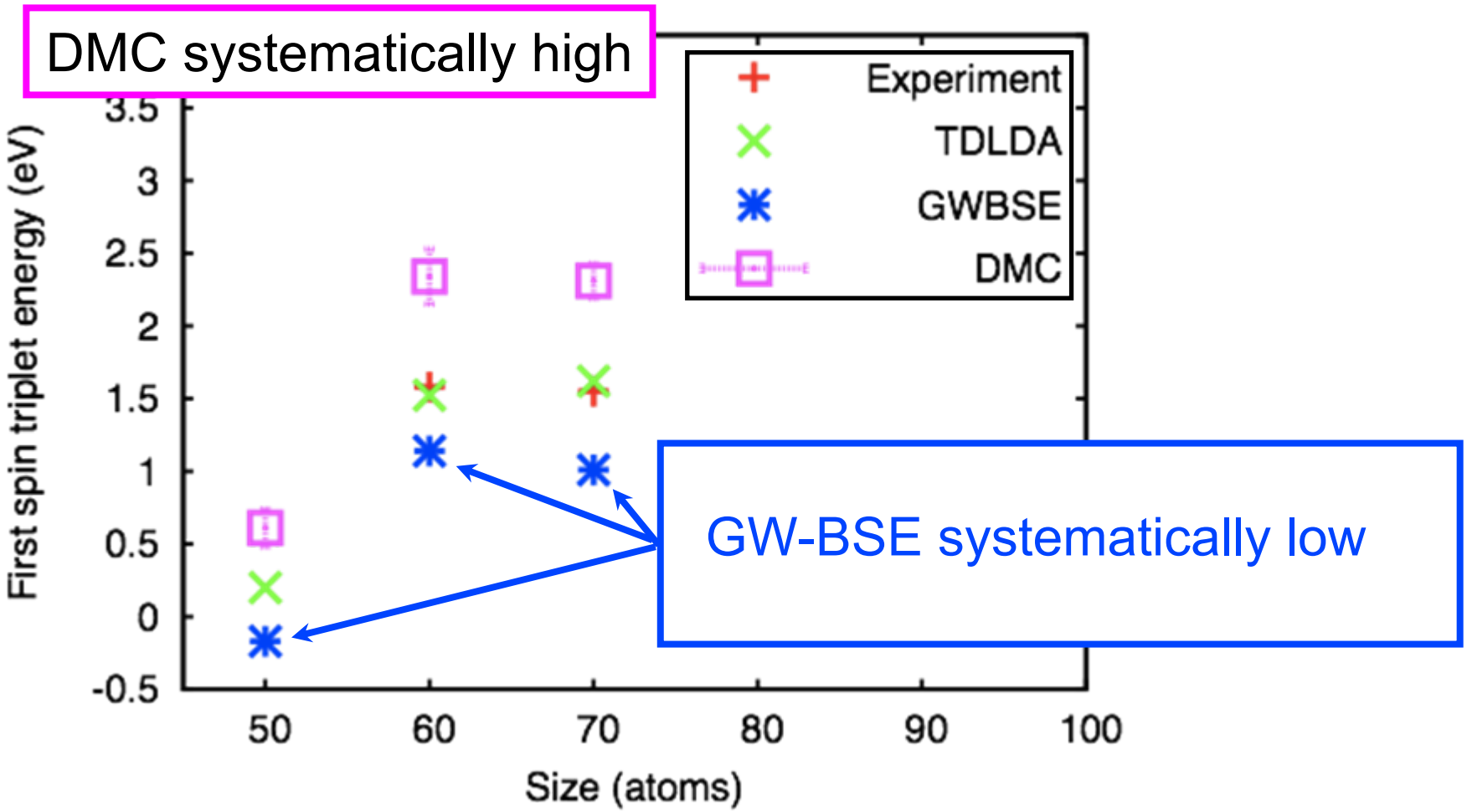
$$K^{BSE} = \frac{\delta}{\delta G}\left[1 \cdot V_{Coul} + \Sigma\right]$$





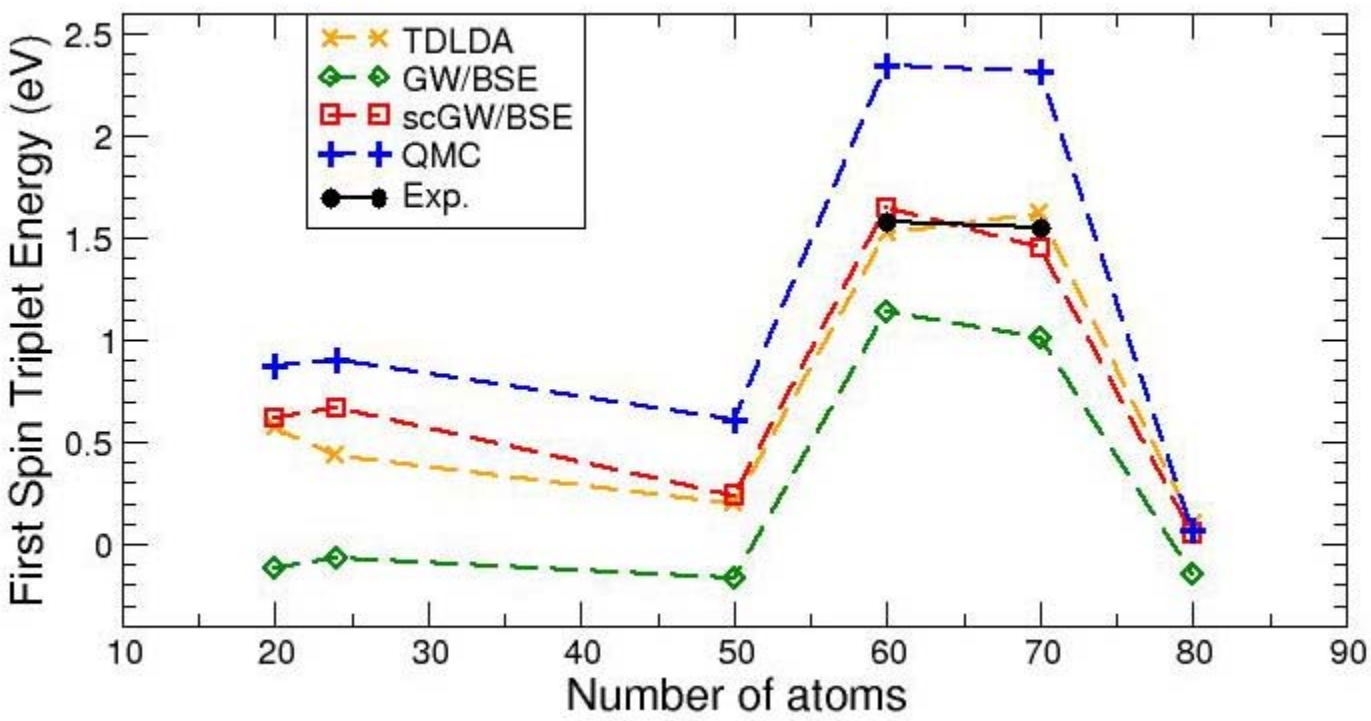
- Many-body expansion of the electron-hole propagator.
- Dynamics of electron-hole excitation obtained by solving the Bethe-Salpeter equation (BSE).
- Requires knowledge of quasiparticle orbitals (get from GW).

Results: First spin-triplet



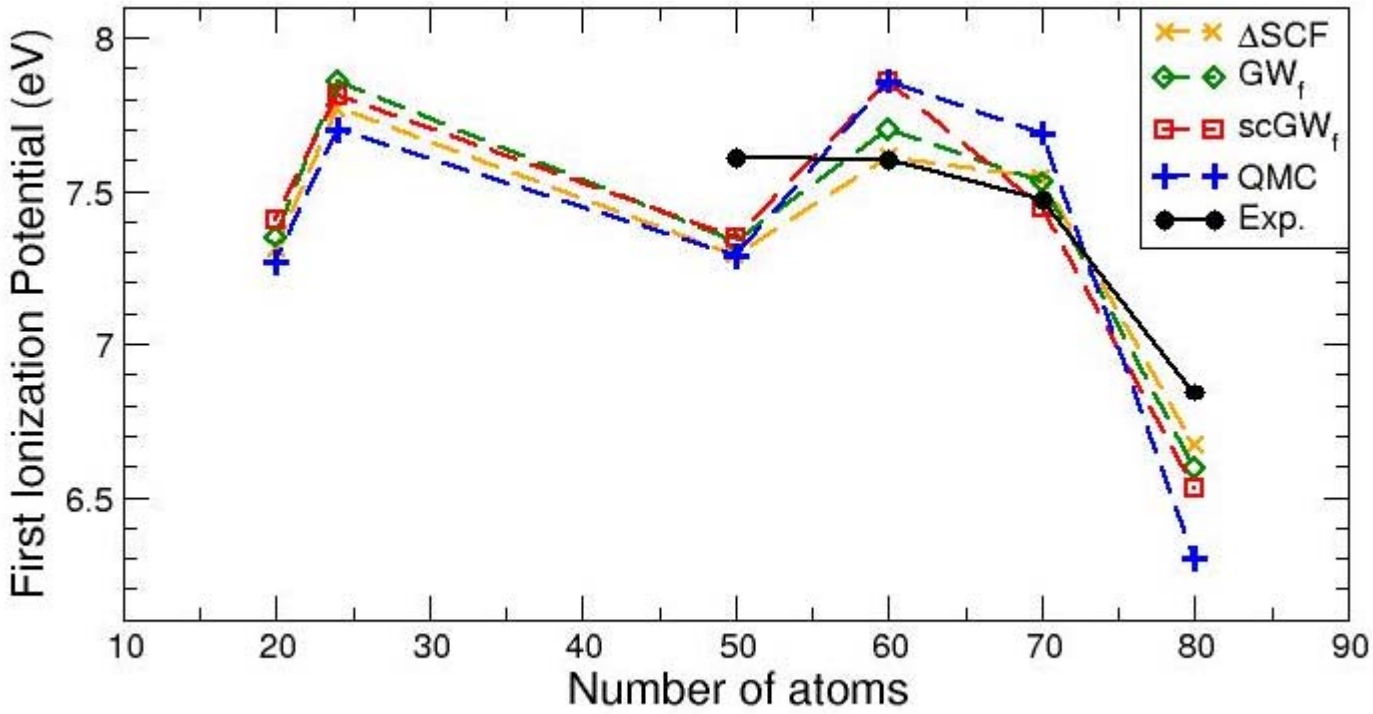
- Stoke's shifts estimated as max 0.2 eV from DFT not included in above data

Experimental data suggest incorporating self-consistency



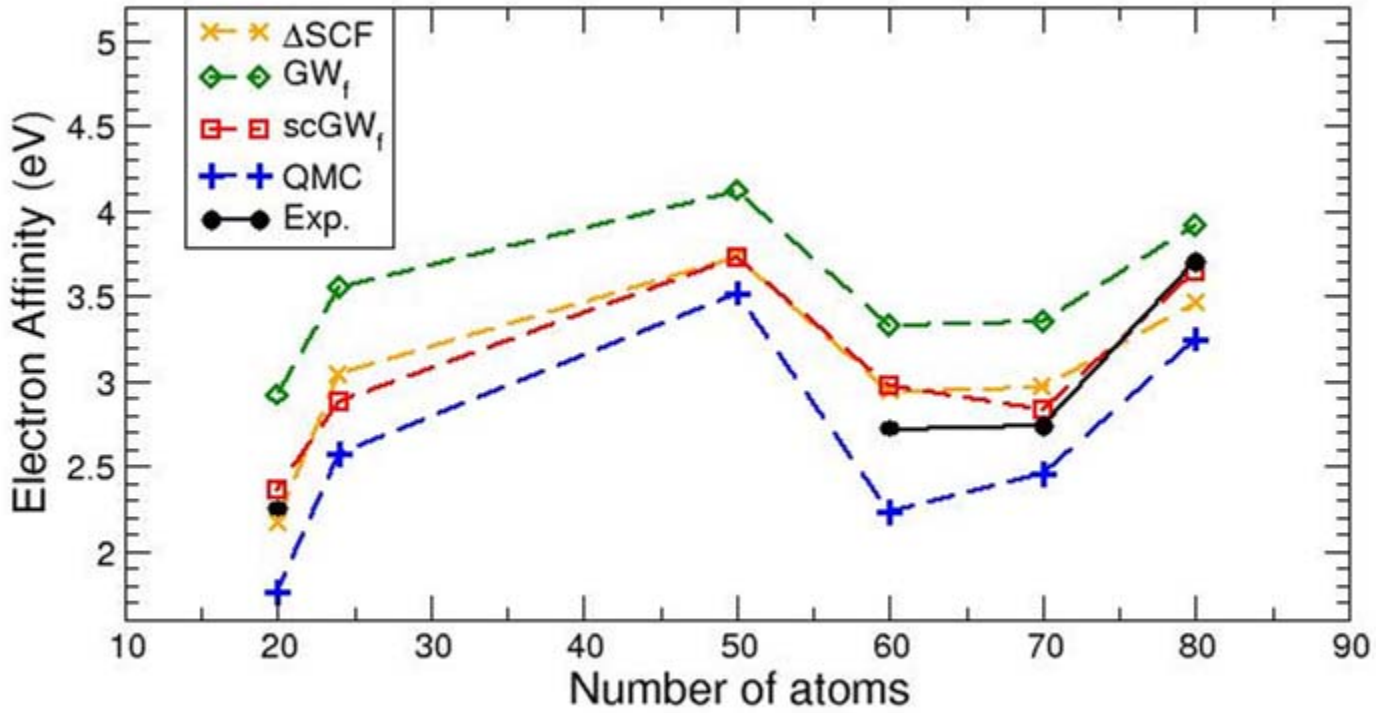
Scissors (eigen-values) self-consistency seems essential in GW/BSE.
DMC gives higher (~0.8 eV) triplet energies

First Ionization Potentials



We find good agreement for Ionization Potentials
ΔSCF (DFT) QMC and GW are similar.

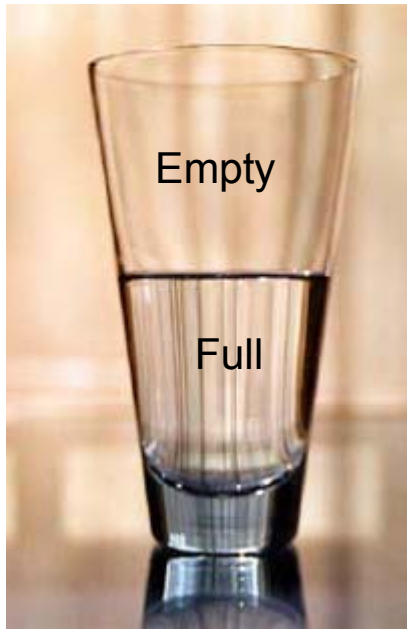
Electron Affinities



ΔSCF (DFT) is still not far from experimental data.
GW requires self-consistency
QMC systematically underestimates EA.

Is the glass full or empty?

- GW-BSE
  - Scissors self-consistent improves agreement with experiment
  - Has the approach predictive power in general?
- ΔSCF and TDLDA
  - Agree with experiment in fullerenes
  - They are known to disagree in carbon nanotubes
- QMC
  - Cancelations of the relative systematic errors < 10^{-5}
  - Need compact multiconfigurational expansions &/or orbital optimization for large systems
  - Pseudopotential evaluation related errors are small
- Experiment
  - Experiments in single molecules



http://arxiv.org/abs/0803.0560

Quantum Monte Carlo Song

$$\psi_T(R) = 0$$

“Nothing really matters
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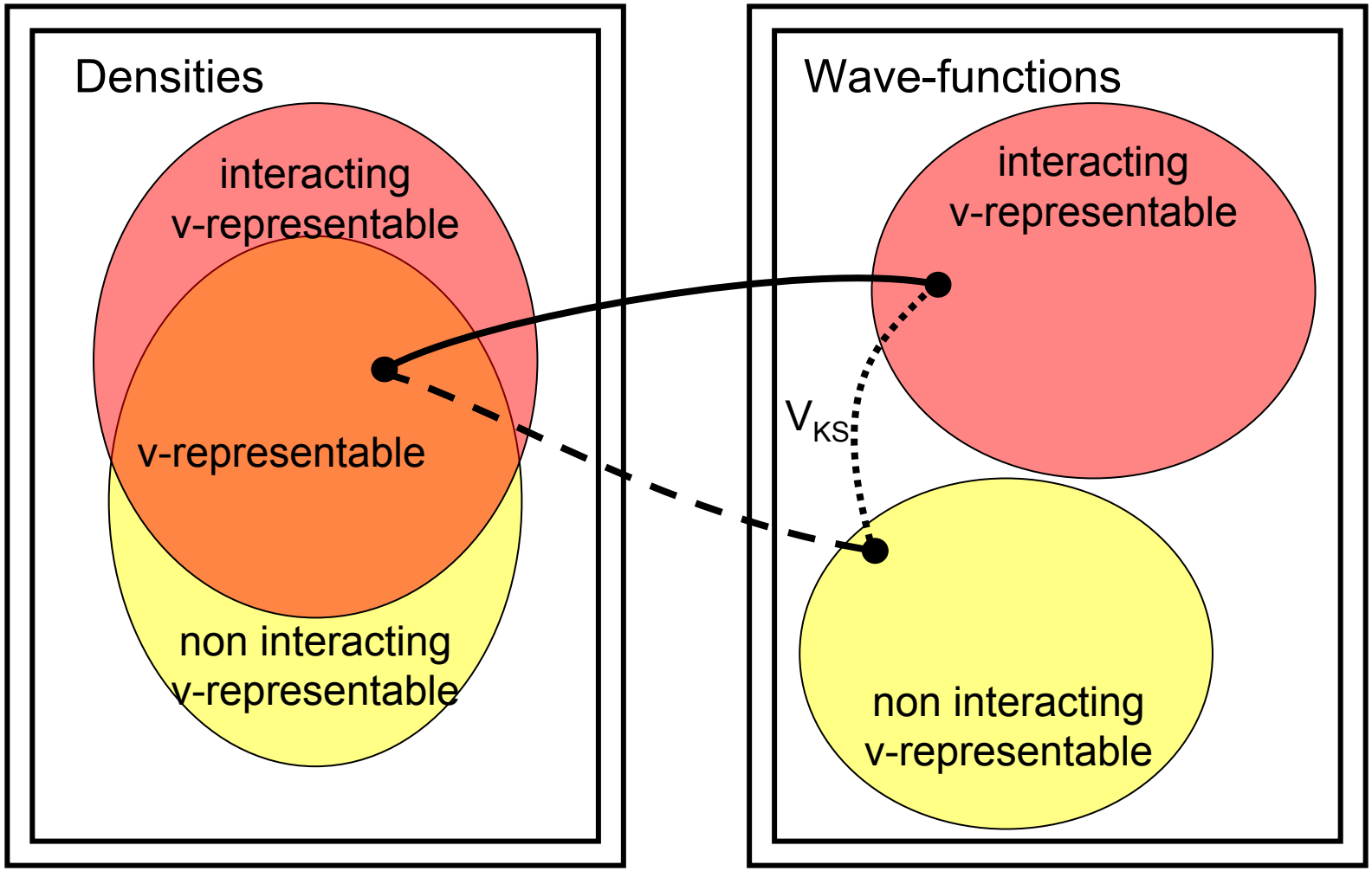
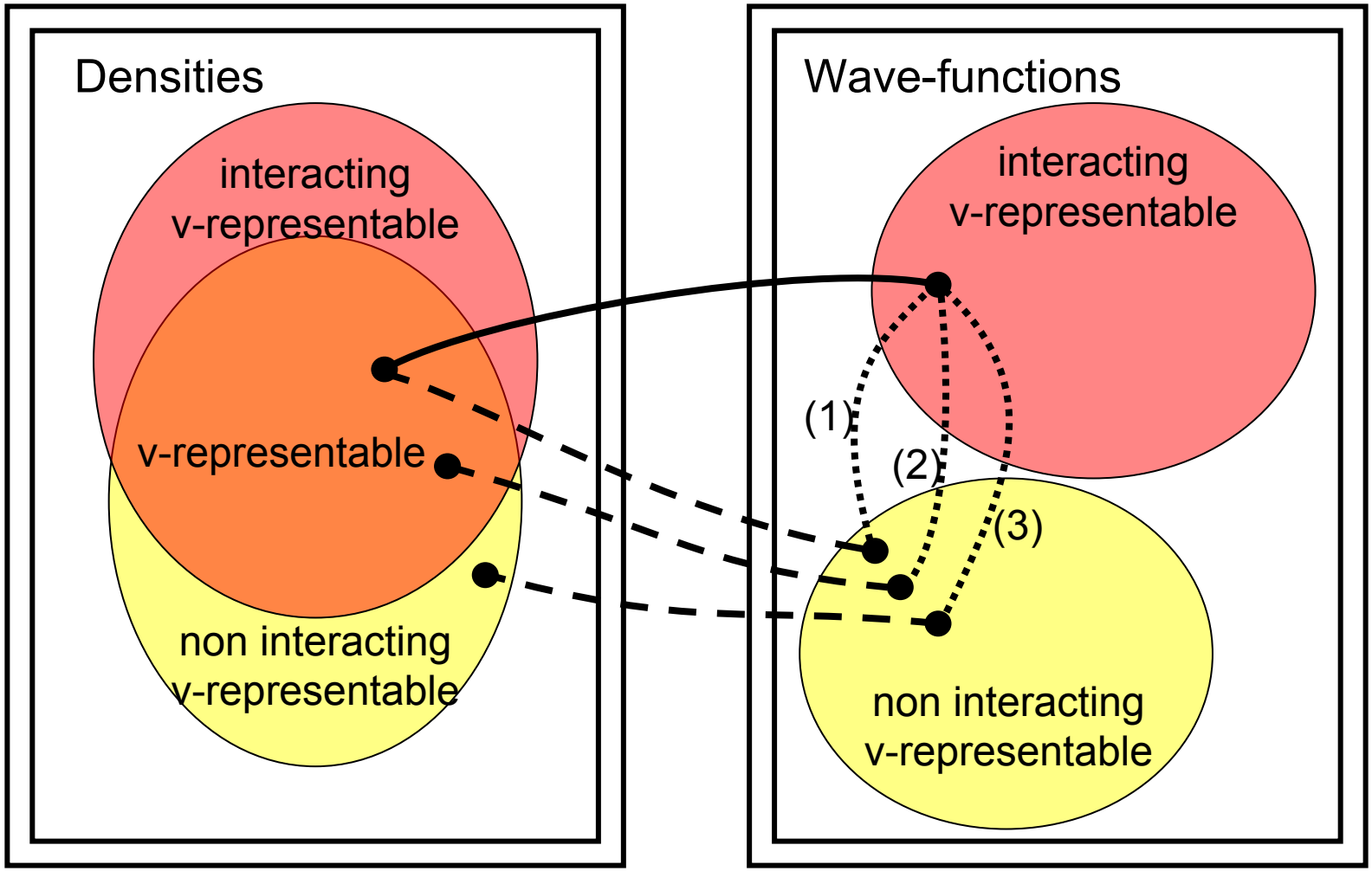
Freddie Mercury **(see also M Kalos L Mitas, R Needs)**

Kohn-Sham correspondence between interacting and non-interacting densities



For non-degenerate systems there is at most one Kohn-Sham wave-function with the interacting density

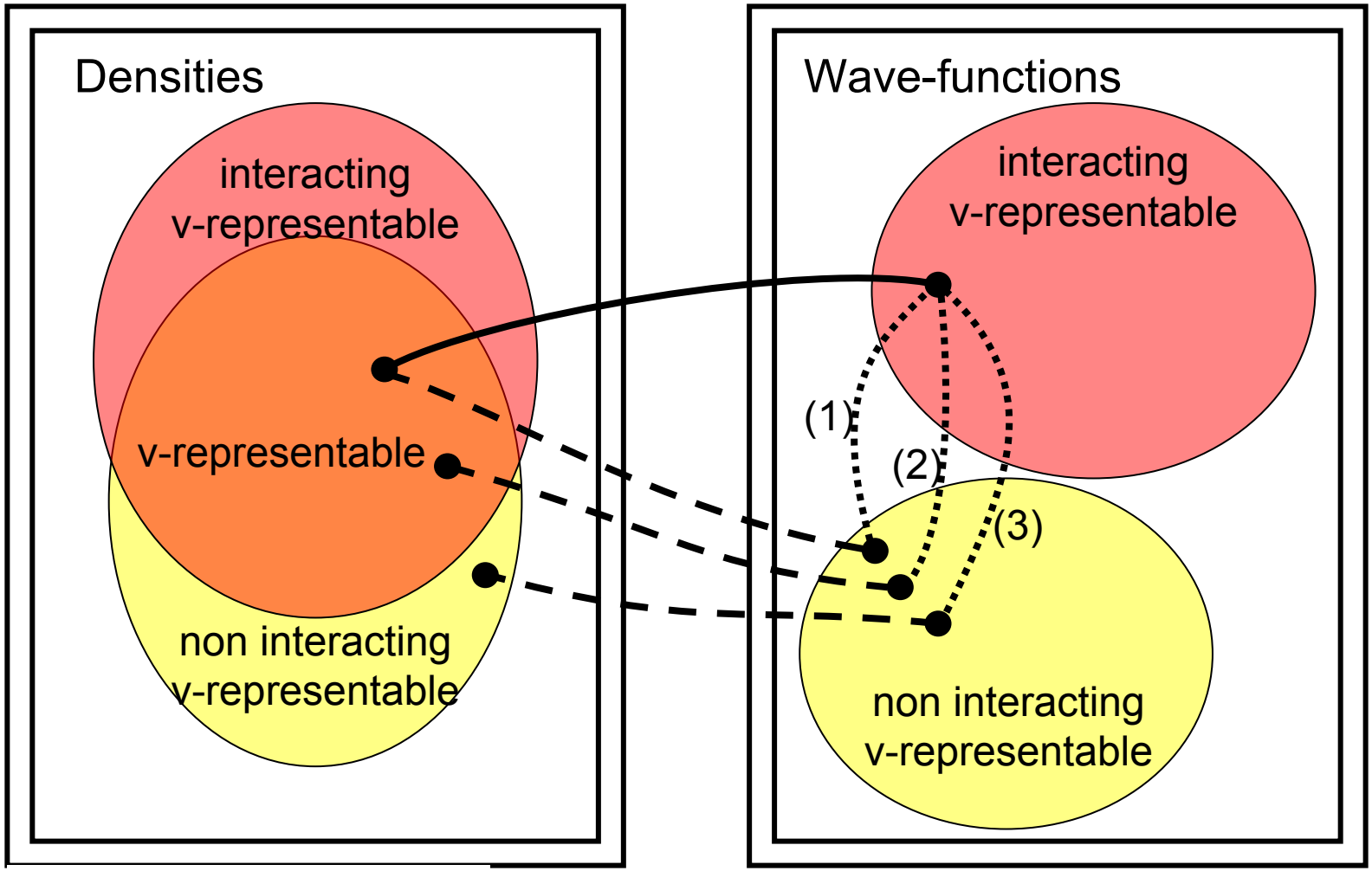
Retaining other properties of the interacting ground state in the non interacting wave-function



For non-degenerate systems there is at most one Kohn-Sham wave-function with the interacting density

Optimizing other properties thus requires to change the density

Retaining other properties of the interacting ground state
A density-density functional transformation must be found



$$\bar{\rho}_K(\mathbf{r}) = U_K\left[\rho(\mathbf{r})\right]$$

Reboredo & Kent PRB (2008)

Optimizing other properties thus requires to change the density

Minimization of cost functions in the v-representable set

$$\left[-\frac{1}{2}\nabla^2 + \bar{V}(\mathrm{r})\right]\phi_\nu(\mathrm{r}) = \varepsilon_\nu \phi_\nu(\mathrm{r})$$

$$K_\rho = \frac{1}{2}\int \mathrm{dr}\,[\bar{\rho}(\mathrm{r}) - \rho(\mathrm{r})]^2$$

Kohn-Sham DFT

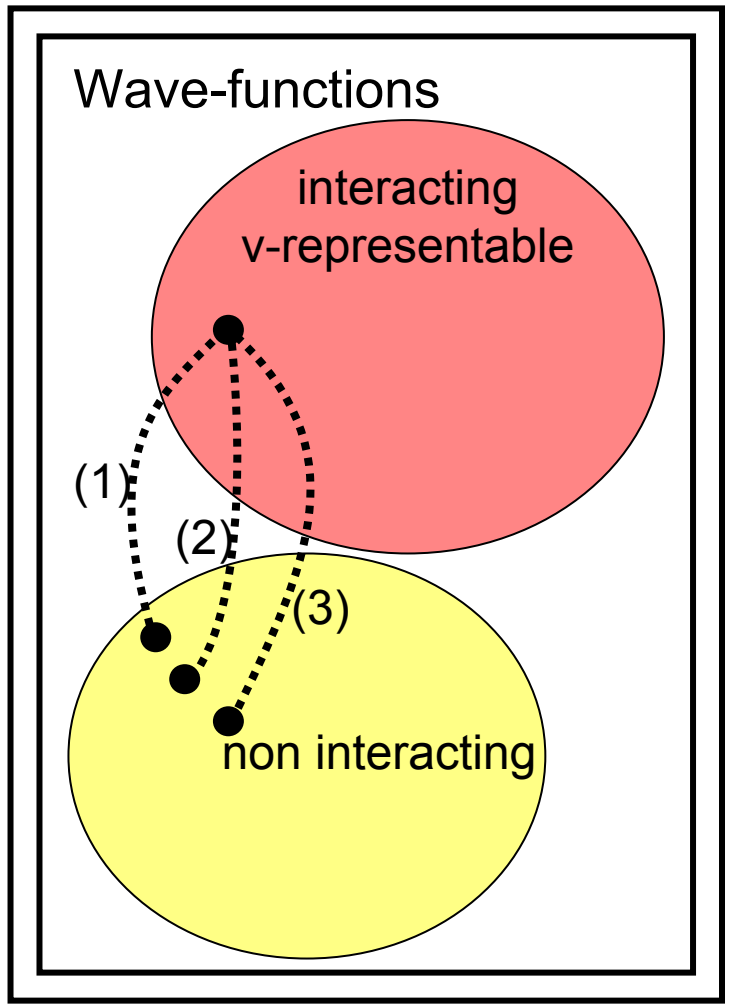
$$\Delta\bar{V}_{K_\rho}(\mathrm{r}) = \int \mathrm{dr}'\,[\rho(\mathrm{r}') - \bar{\rho}(\mathrm{r}')]\,\frac{\delta V(\mathrm{r}')}{\delta\rho(\mathrm{r})}$$

$$K_{Det} = -\left|\langle\Psi\,|\Phi_T\rangle\right|^2$$

$$\delta V_{K_{Det}}(\mathrm{r}) = \epsilon\,\langle\Psi\,|\Phi_T\rangle \sum_\nu^o \sum_n^u \langle\Psi|\,c_n^\dagger c_\nu\,|\Phi_T\rangle\,\frac{\phi_n(\mathrm{r})\phi_{nu}(\mathrm{r})}{\varepsilon_\nu - \varepsilon_n}$$

$$K_{S_0} = \int_{S_0} \mathrm{dS}\,|\Phi_T(\mathrm{R})|^2$$

$$\delta V_{K_{Det}}(\mathrm{r}) = \epsilon \sum_\nu^o \sum_n^u \int_{S_0} \mathrm{dS}\Phi_T^{n,\nu}(\mathrm{R})\Phi_T(\mathrm{R})\,\frac{\phi_n(\mathrm{r})\phi_{nu}(\mathrm{r})}{\varepsilon_\nu - \varepsilon_n}$$



Different properties imply different cost functions and different potentials

Effective potentials depend strongly on the many-body property retained

$$K_\rho = \frac{1}{2}\int \mathrm{dr}\,[\bar{\rho}(\mathrm{r}) - \rho(\mathrm{r})]^2$$

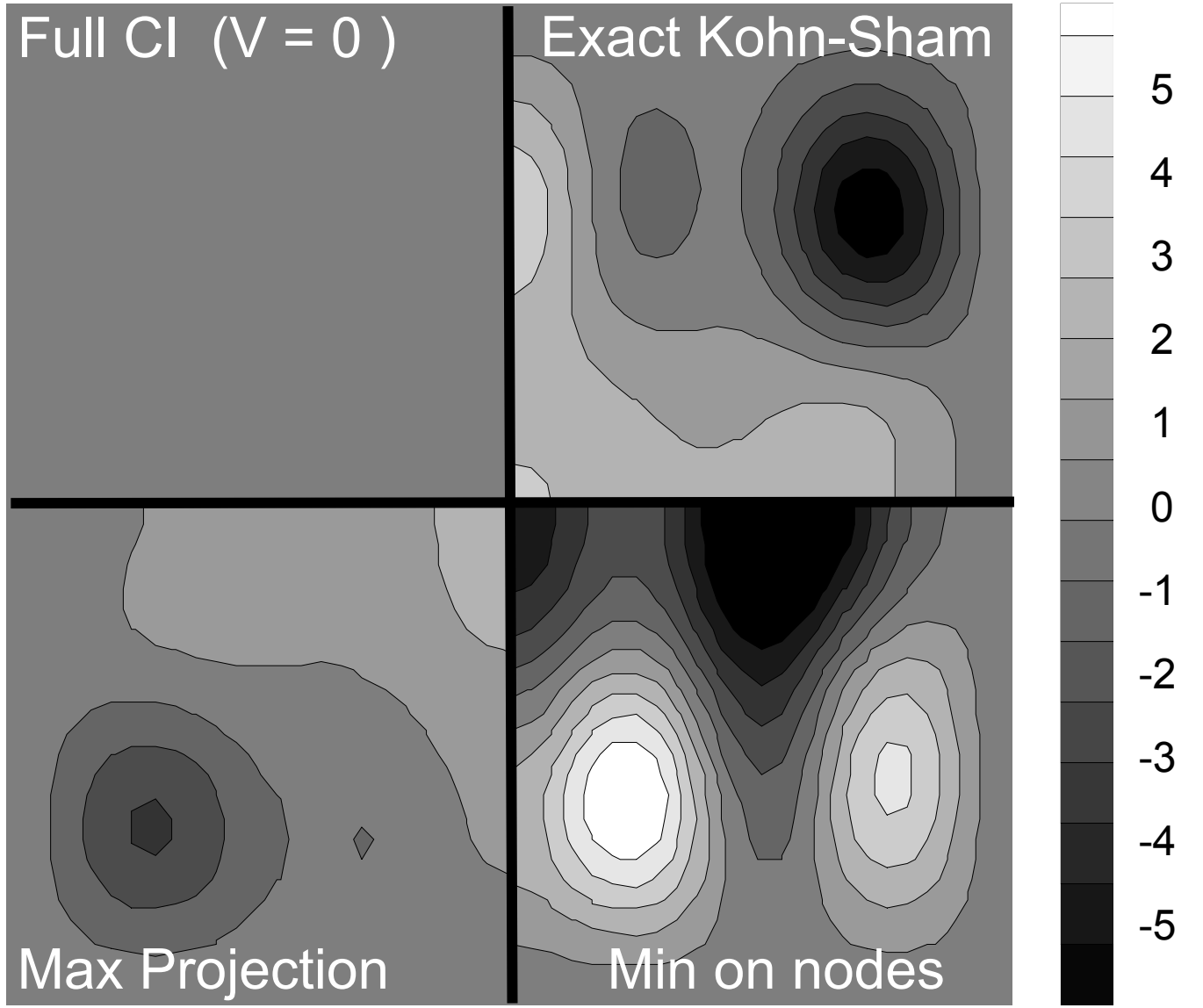
Exact Kohn-Sham

$$K_{Det} = -\left|\langle \Psi \,|\Phi_T\rangle\right|^2$$

Max Projection

$$K_{S_0} = \int_{S_0} \mathrm{dS}\,|\Phi_T(\mathrm{R})|^2$$

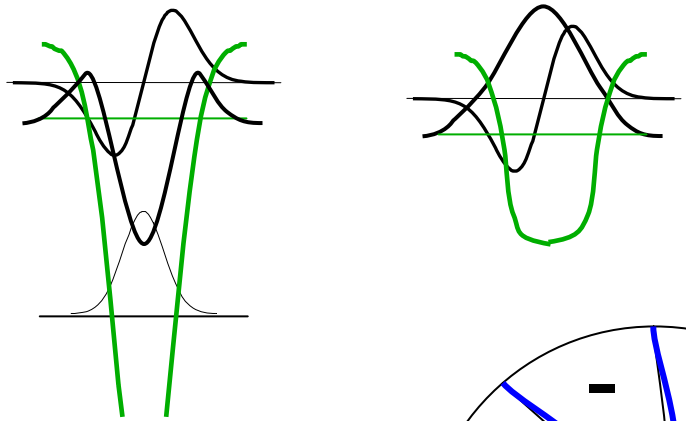
Min on nodes



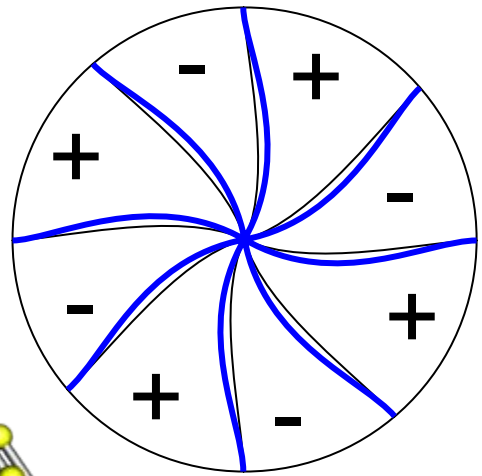
See details on Reboredo and Kent, Physical Review B **77** 245110 (2008).

DMC calculations independent of DFT input

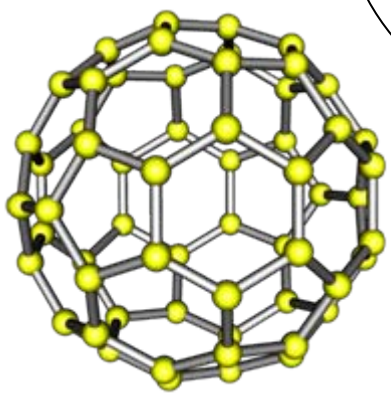
1) QMC Pseudopotentials



2) Trial wave function optimized in DMC
Elimination or control of the nodal error



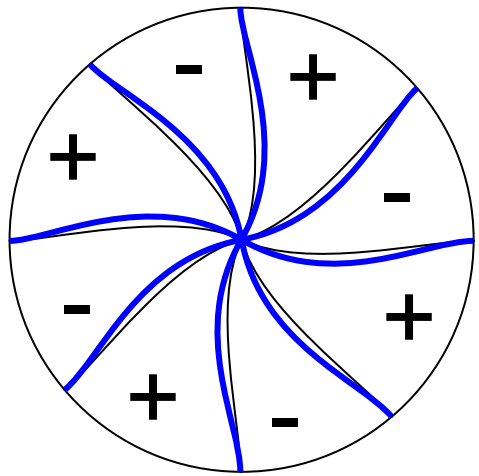
3) Structures relaxed in QMC



2) and 3) are currently possible in small systems

A Theoretical Blue Unicorn: finding the nodes

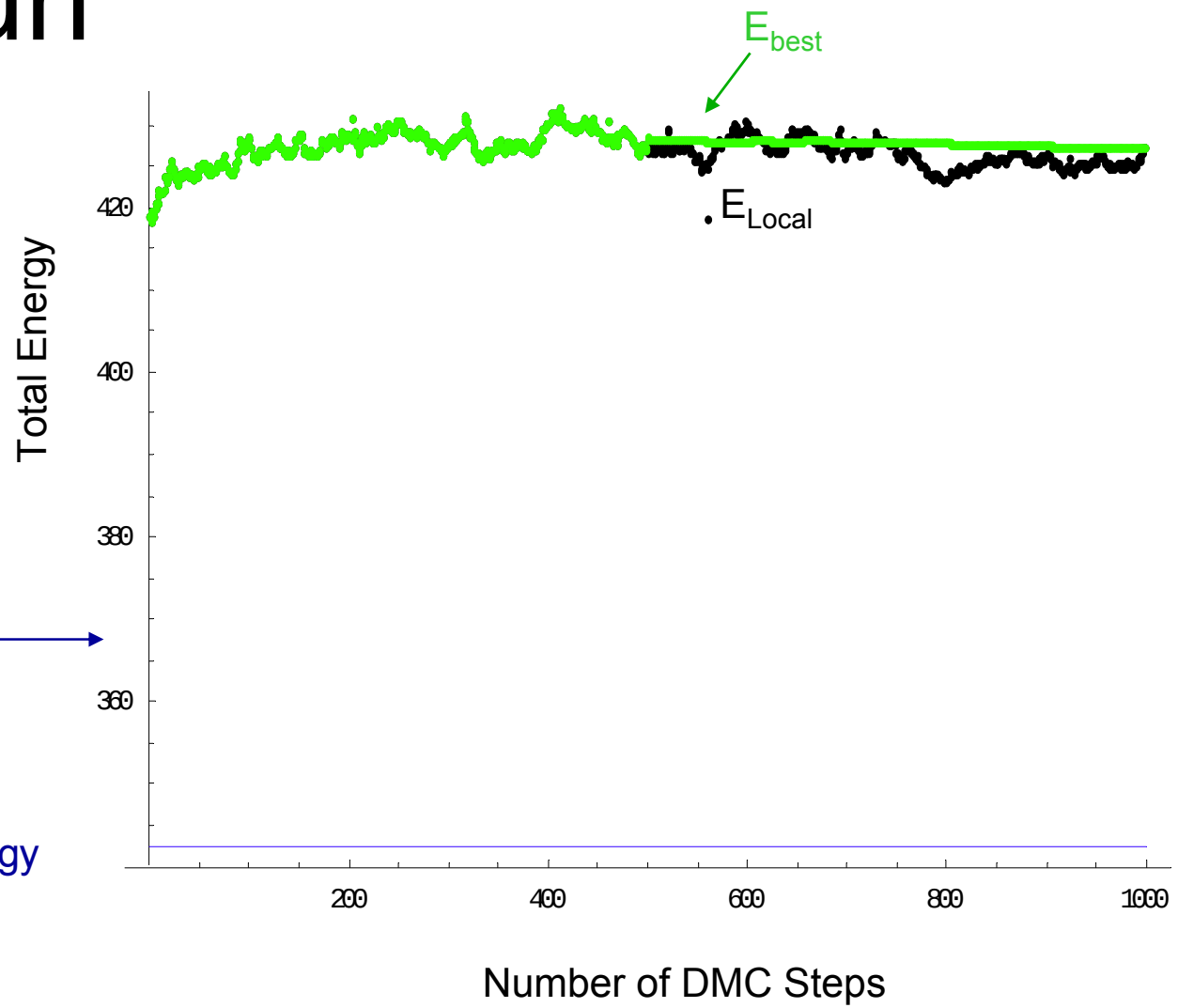
$$\psi_0(R) = 0$$



A Theoretical Blue Unicorn : finding the blue nodes

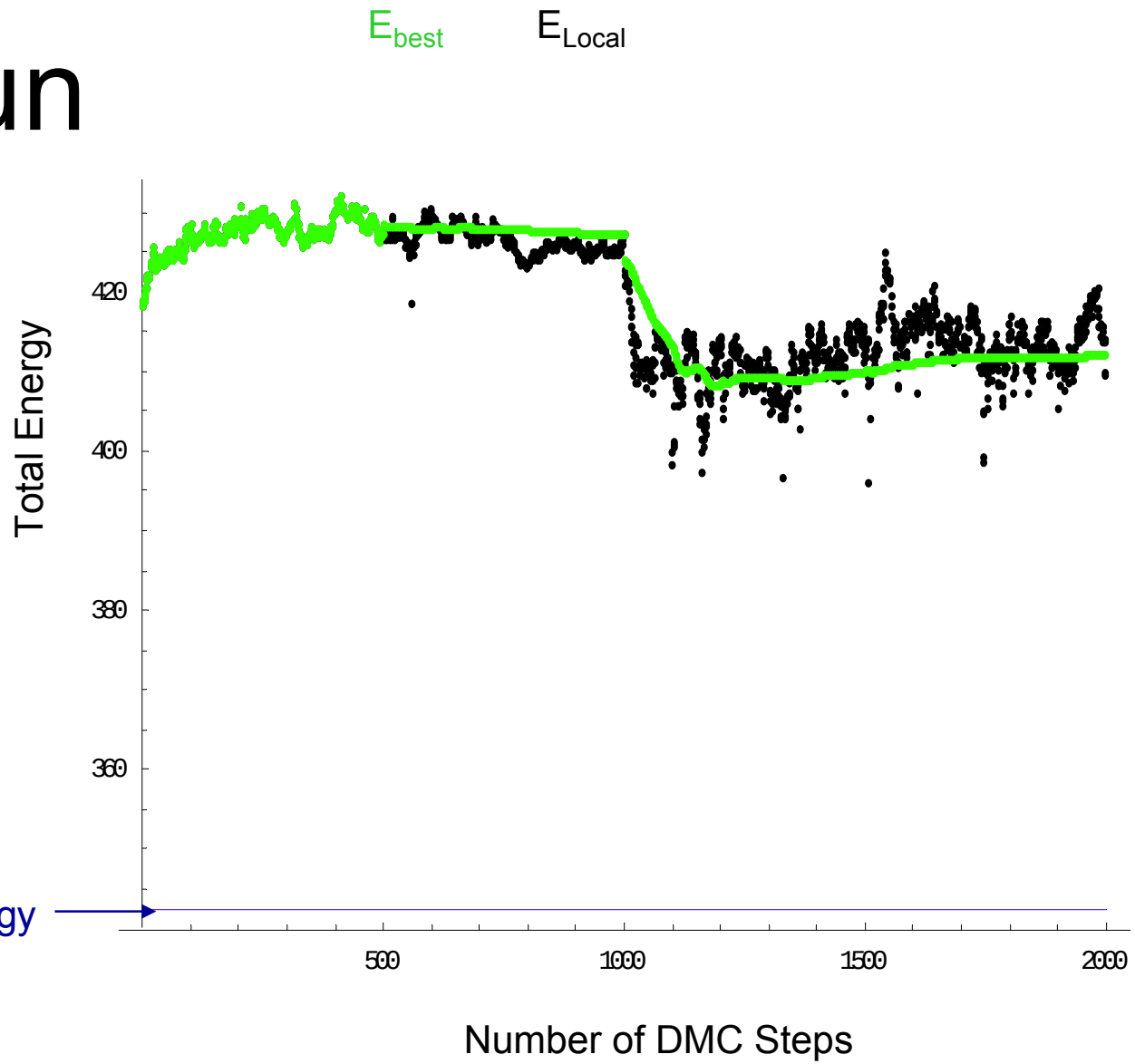
DMC run

Exact (Full CI) energy



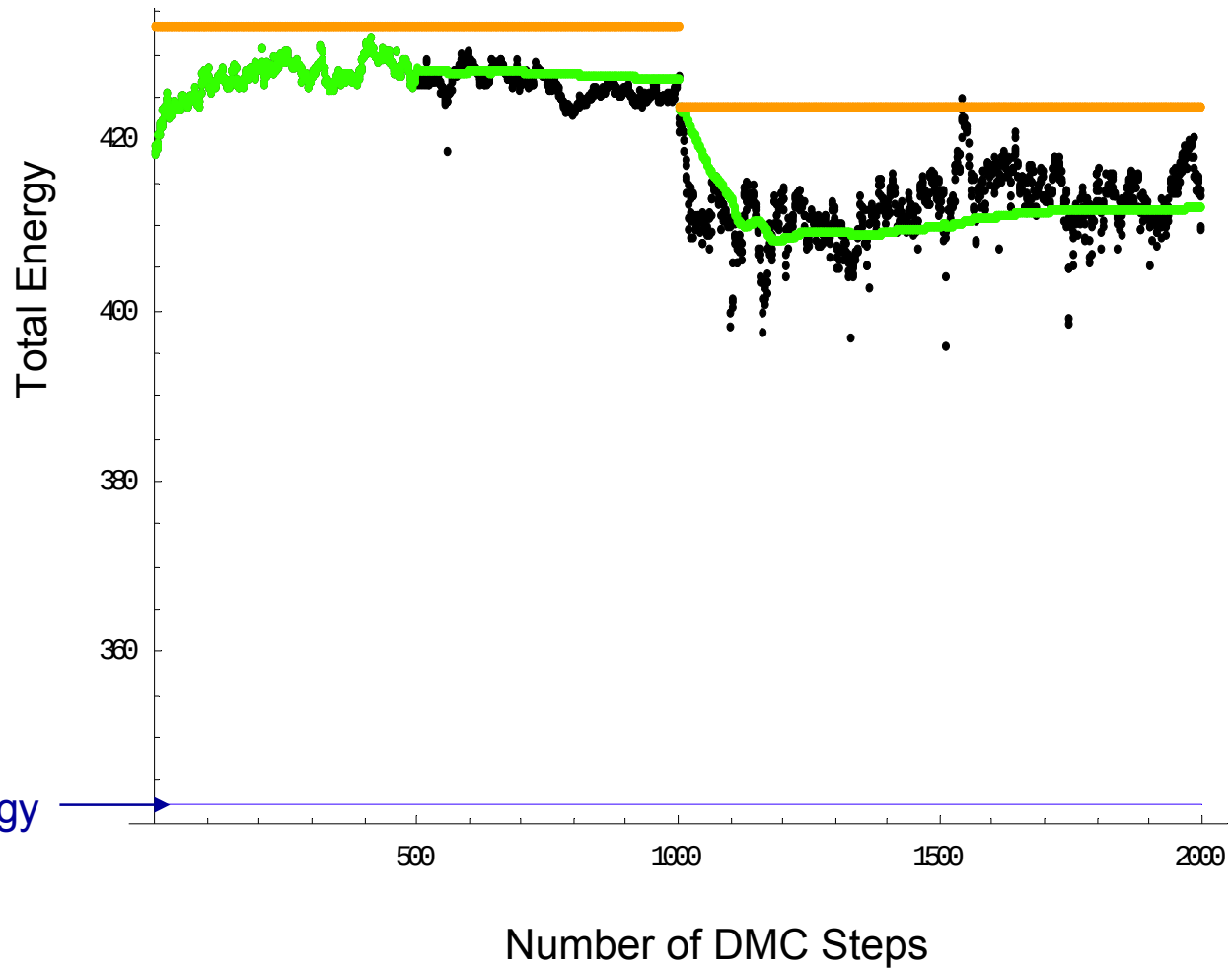
A Theoretical Blue Unicorn : finding the blue nodes

DMC run



A Theoretical Blue Unicorn : finding the nodes

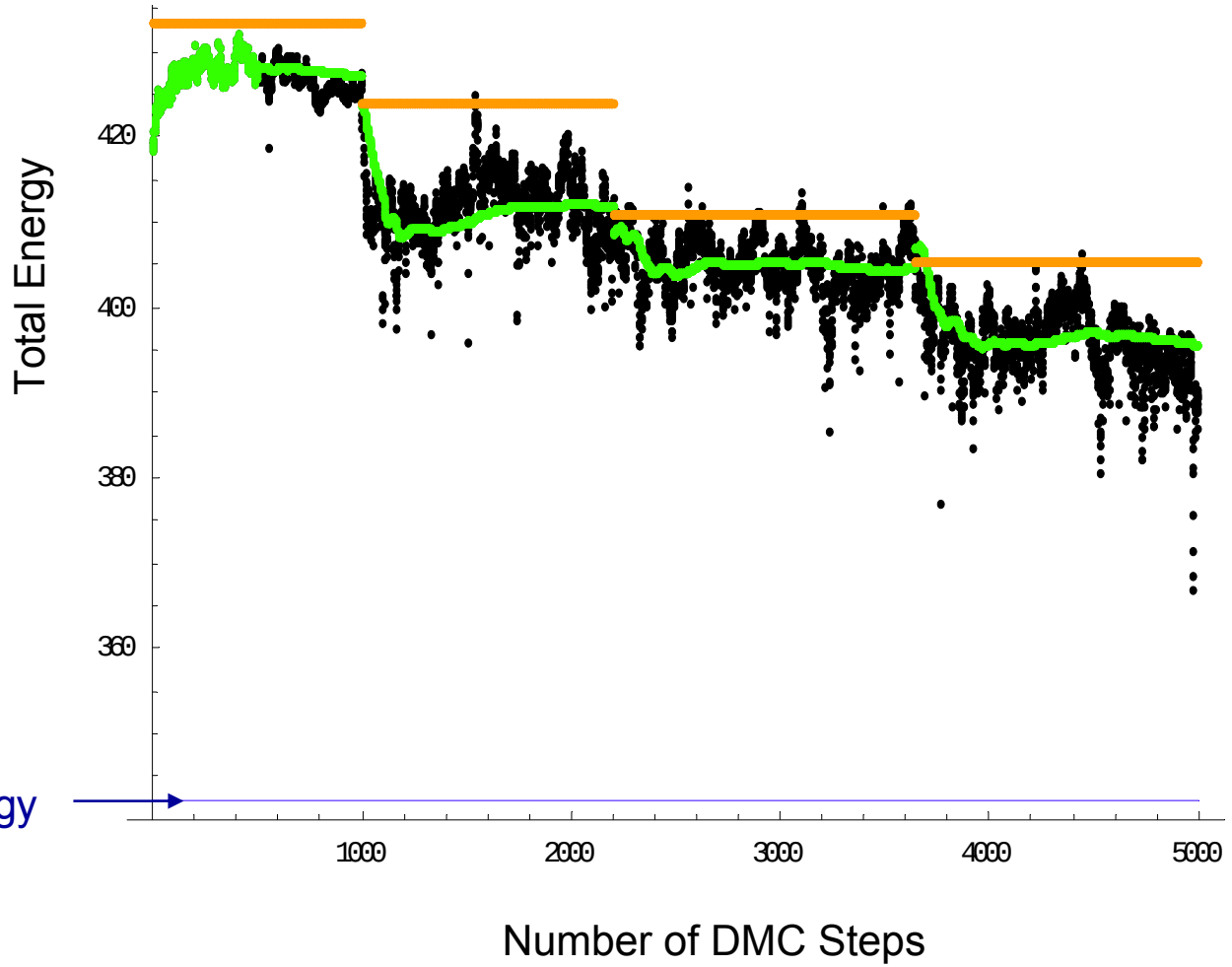
DMC run



DMC run

Exact (Full CI) energy

E_{best} E_{Local} $E= \langle \psi_T|H|\psi_T \rangle_I$



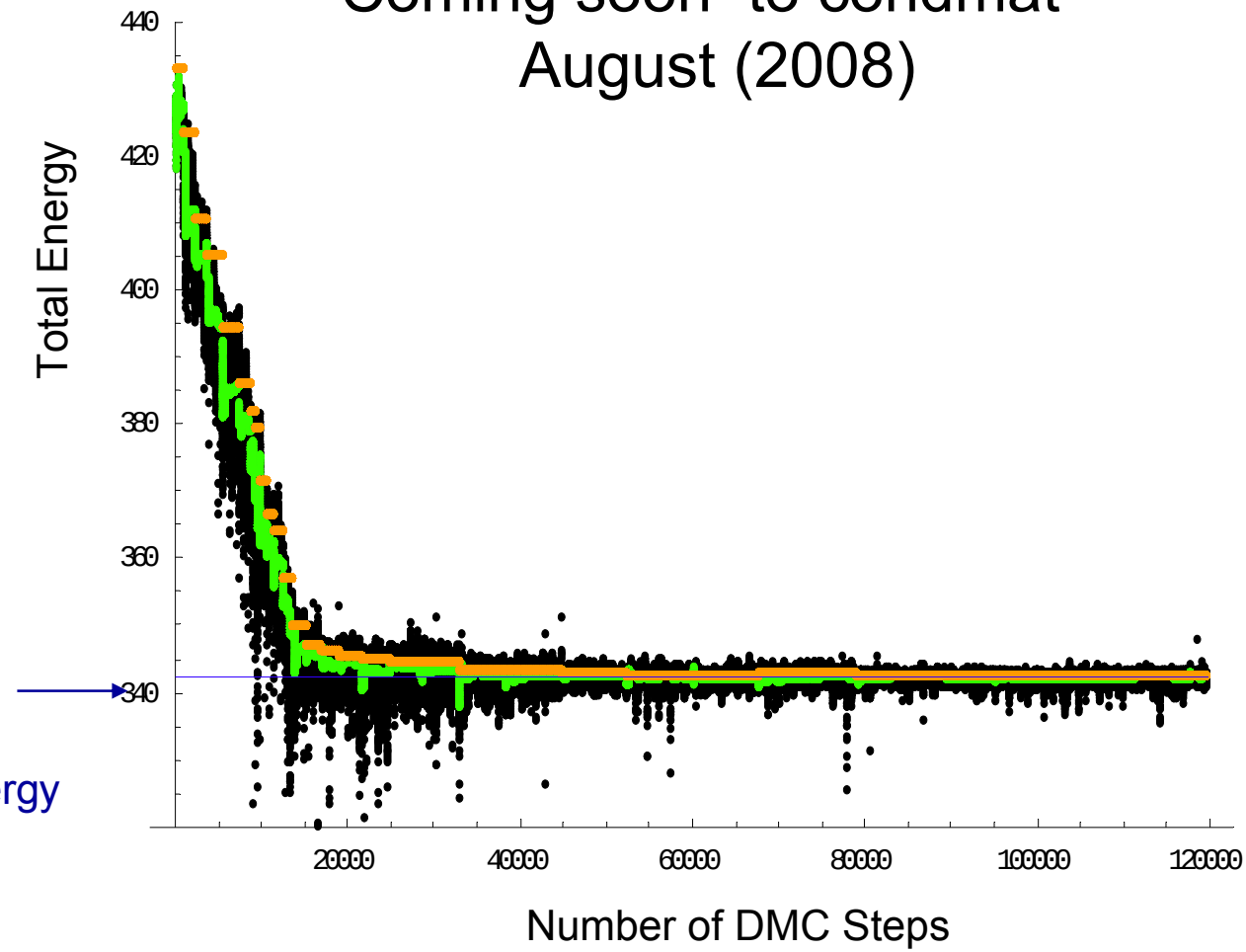
A Theoretical Blue Unicorn : finding the blue nodes

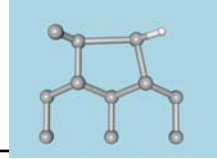
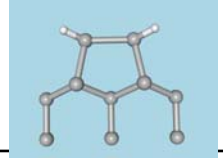
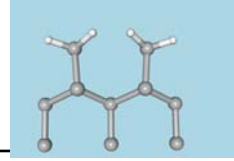
DMC run

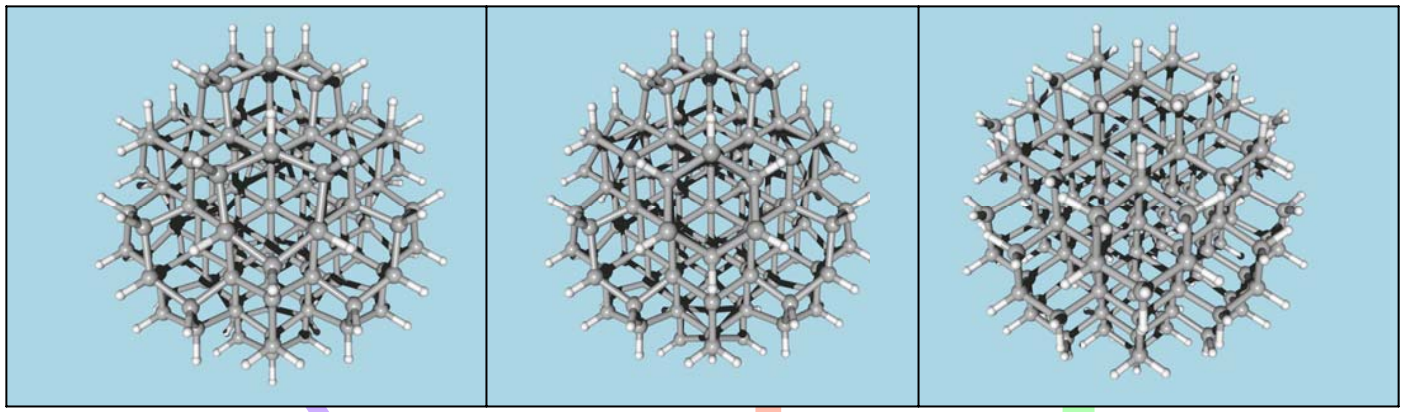
E_{best} E_{Local} $E= \langle \psi_T|H|\psi_T \rangle_I$

Coming soon to condmat
August (2008)

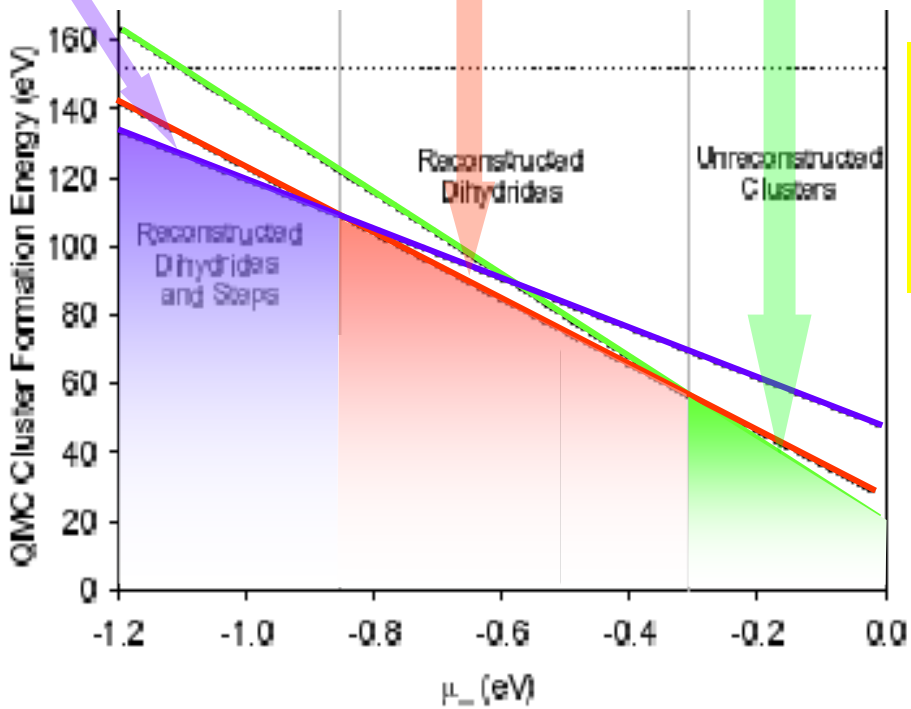
Exact (Full CI) energy





$Si_{148}H_{72}$ $Si_{148}H_{96}$ $Si_{148}H_{120}$

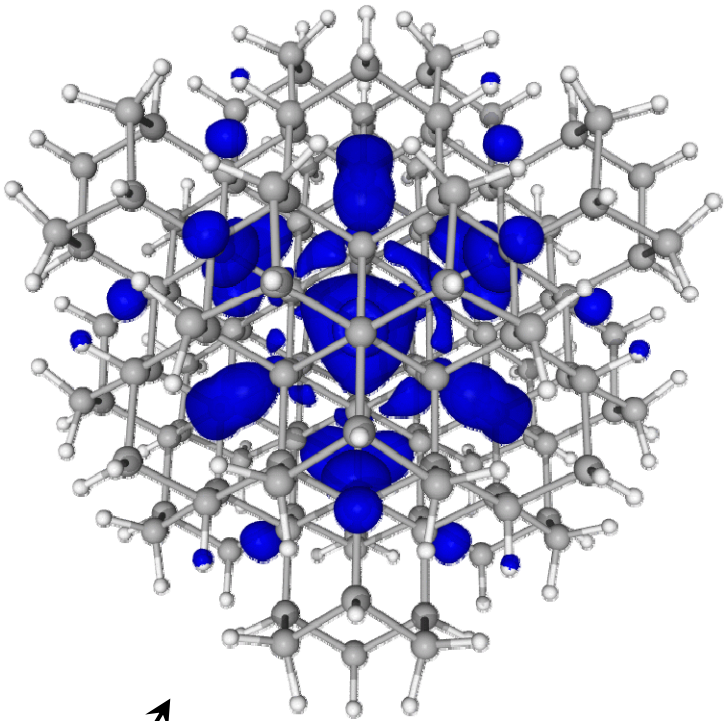


Phase diagram of reconstructed surfaces calculated with Diffusion QMC

Puzder, Williamson
Reboredo and Galli
PRL (2003)

Effect of Surface Reconstructions

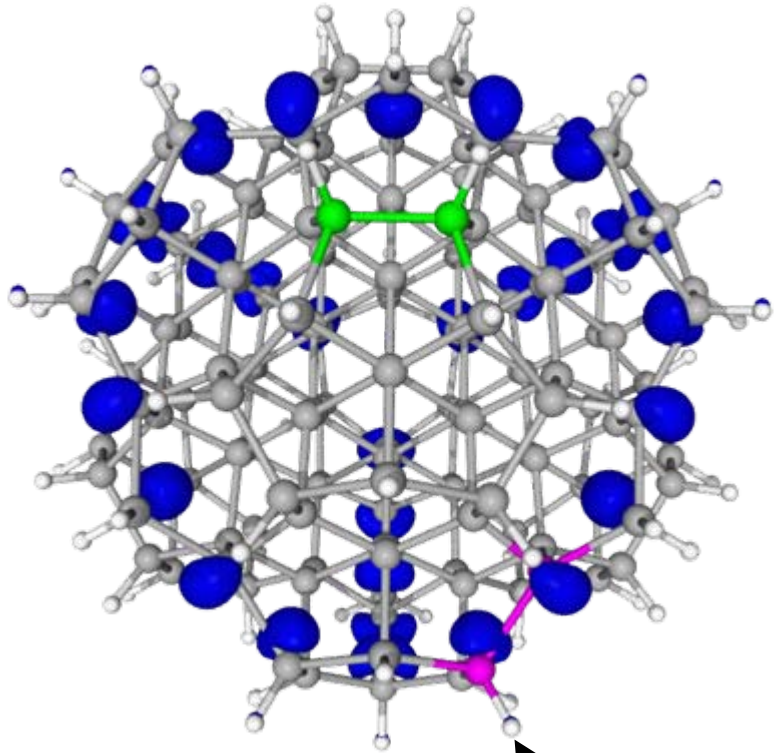
$Si_{148}H_{120}$



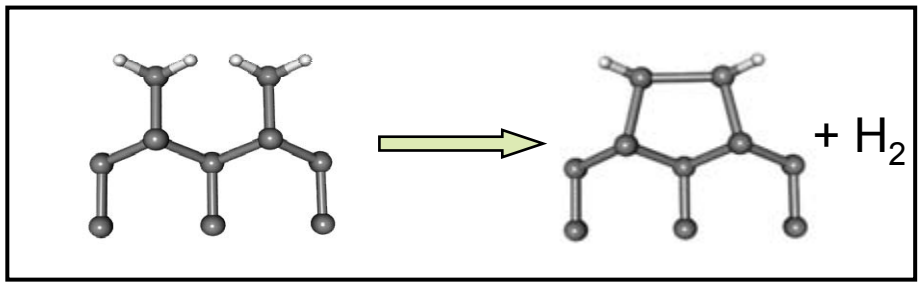
QMC Gap=3.5 eV

Reconstruct facets

$Si_{148}H_{72}$



QMC Gap=1.8 eV



- A. Puzder, A. Williamson, F. Reboredo and G. Galli, *PRL (2003)*