Auxiliary-field quantum Monte Carlo calculations of excited states and strongly correlated systems

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Outline

- Formally simple -- a framework for going beyond 'DFT'?
  - Random walks in non-orthogonal Slater determinant (SD) space
  - Relation to other methods (quantum chemistry, DFT, QMC)
- Applications (**plane-wave+pseudopotential; Gaussian; lattice models**)
  - Accuracy of CCSD(T) at equilibrium; better in bond-breaking; N^3
- Recent efforts:
  - Excited states: band structure calculations
  - Systems of strong correlations; release constraint
  - Faster and larger: "down-folded" Hamiltonians; embedding in DFT

Collaborators:

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Fengjie Ma

Yudis Virgus

Henry Krakauer

Hao Shi

Support:

- NSF, DOE (ThChem, CMCSN), ARO, INCITE (jaguar)

Some references: (http://physics.wm.edu/~shiwei)

- Zhang & Krakauer, PRL '03
- Al-Saidi e*t. al*., JCP, '06
- Purwanto *et. al*., JCP '11
- Chang & Zhang, PRB '08; PRL '10

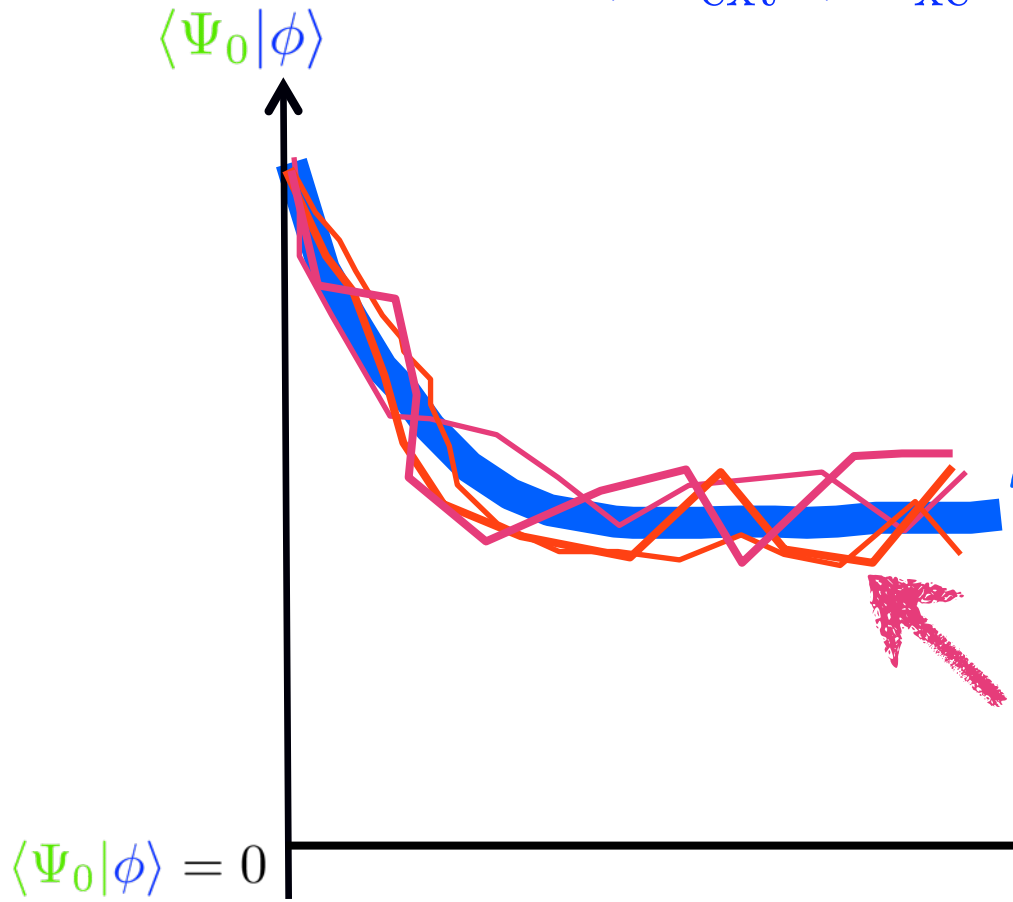
Overview - how does auxiliary-field QMC work?

Many-body effects as fluctuations around **mead-field**:

$$H_{\mathrm{MB}} = H_{\mathrm{LDA}} + \Delta V$$

$H_{\mathrm{LDA}} \rightarrow K + V_{\mathrm{ext}} + V_{\mathrm{xc}}$

$\Delta V \rightarrow V_{\mathrm{int}} - V_{\mathrm{xc}}$



$$|\phi^{(n+1)}\rangle = e^{-\tau H_{\mathrm{LDA}}(\rho^{(n)})} |\phi^{(n)}\rangle$$

$$e^{-\tau H_{\mathrm{MB}}} = e^{-\tau H_{\mathrm{LDA}}} e^{-\tau \Delta V}$$

HS

$$\int d\sigma\, p(\sigma)\, e^{\mathbf{v}(\sigma)}$$

next →

Overview - how does auxiliary-field QMC work?

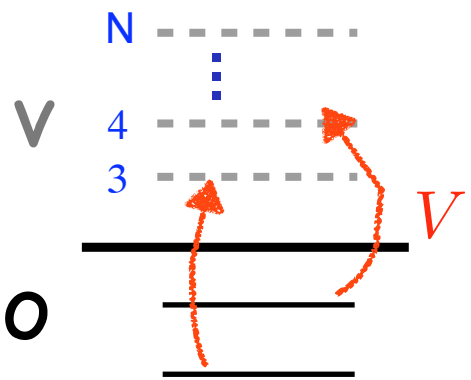
- Electronic Hamiltonian: (Born-Oppenheimer)

$$H = H_{1-\text{body}} + H_{2-\text{body}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{M}\nabla_i^2 + \sum_{i=1}^{M} V_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j}^{M} V_{\text{int}}(|\mathbf{r}_i - \mathbf{r}_j|)$$

can choose any single-particle basis $\{|\chi_i\rangle\}$

$$\hat{H} = \sum_{i,j}^{N} T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^{N} V_{ijlk} c_i^\dagger c_j^\dagger c_k c_l \qquad \int \chi_i^\star(\mathbf{r}_1)\chi_j^\star(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_1)\, d\mathbf{r}_1 d\mathbf{r}_2$$

- If we choose Kohn-Sham orbitals as $\{|\chi_i\rangle\}$



- FCIQMC (or 'diffusion' MC): apply $c - \hat{H}$

- Quantum chemistry: carry out excitations *systematically* to some order

Overview - how does auxiliary-field QMC work?

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- AFQMC uses Hubbard-Stratonivich transformation

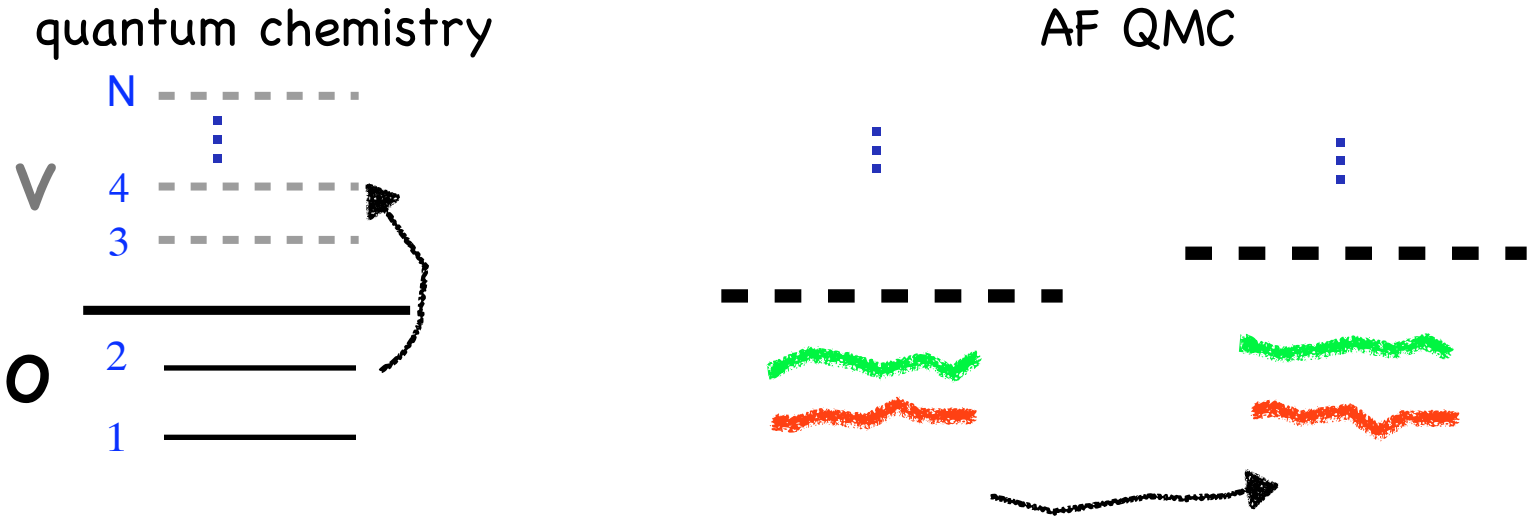
$$H_2 = \sum_\gamma \hat{v}_\gamma^2$$

$$e^{-\tau H_2} = \int e^{-\sigma^2/2}\, e^{\sigma\sqrt{\tau}\,\hat{v}}\, d\sigma$$

→ linear combination of 1-body systems in auxiliary-fields

Overview - how does auxiliary-field QMC work?

Random walks of non-orthogonal Slater determinants:

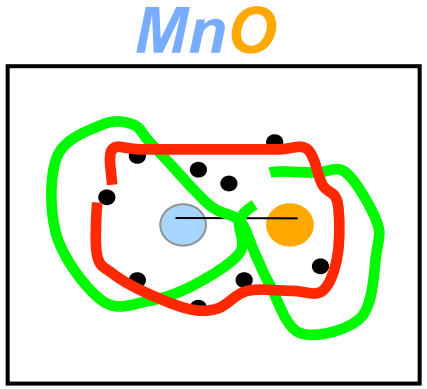


Walker in AF QMC:

$$\begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ . & . \\ . & . \\ \psi_N & \psi_N \end{pmatrix}$$

Slater det.

naturally multi-reference



In QC:

$\Psi_i = 1 \text{ or } 0$

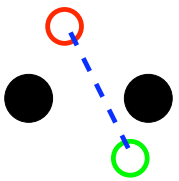
AFQMC:

continuous

How does auxiliary-field QMC work?

Toy problem -- Hubbard model:

H_2 molecule:

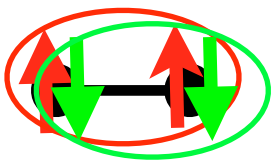


ion, fixed, +1 charge

electron, spin ↑

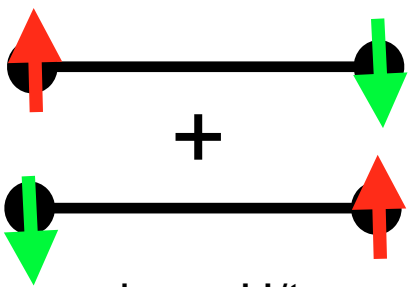
electron, spin ↓

tight binding/minimal basis => 1-band Hubbard model with U/t



small U/t

* 1 determinant



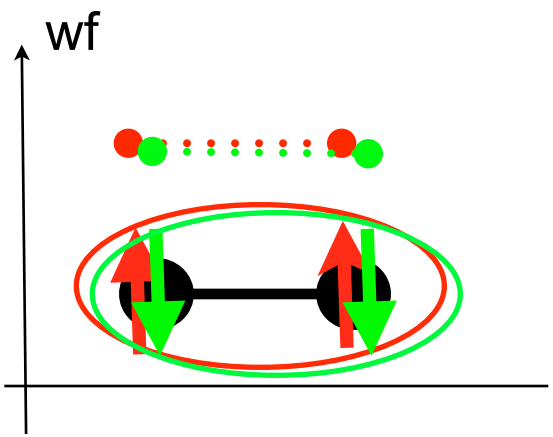
large U/t

* multi determinants
* correlation
* note 'antiferromagnetism'

Toy system: H_2 molecule

Illustration of how AFQMC works:

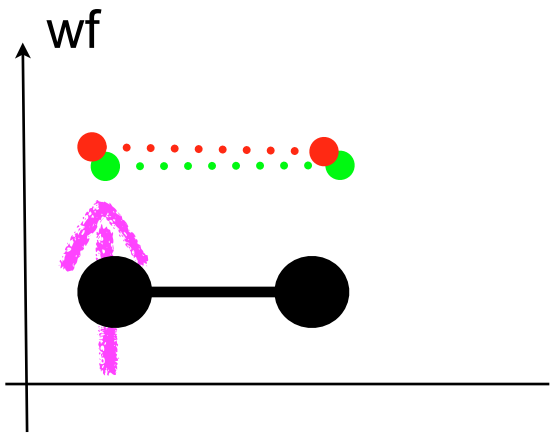
H2 molecule



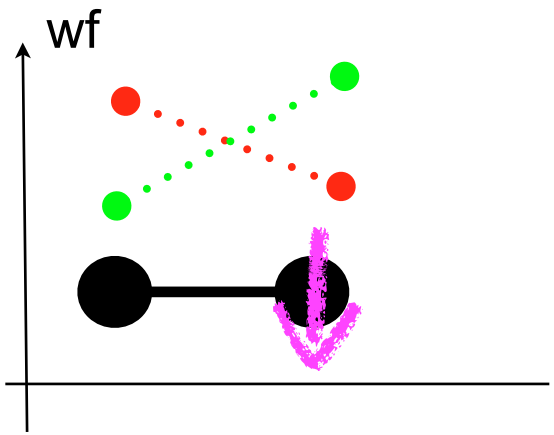
mean-field

- 'Sign problem' severe in most problems of interest (Koonin; Scalapino & White; Baroni, Car, Sorella; Fahy & Hamman; Baer et al)
- Reformulated into open-ended random walks

+



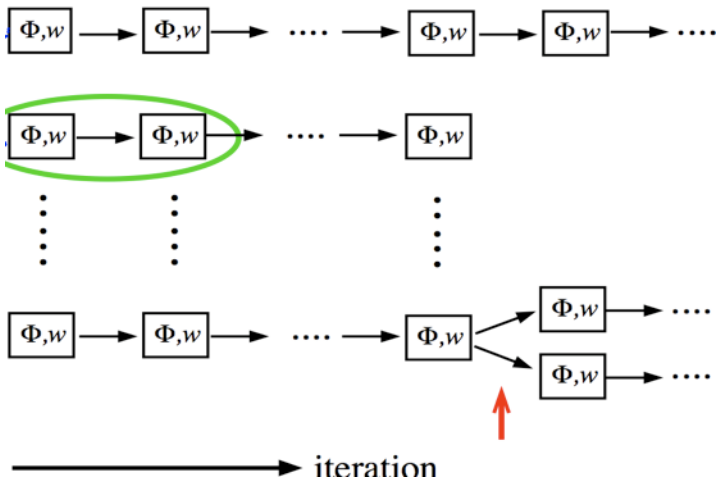
auxiliary-field QMC



+ ....

Overview - how does auxiliary-field QMC work?

Structure -- loosely coupled RWs of non-orthogonal SDs:



A **step** advances the SD by 'matrix multiplications'

$$e^{\sigma \hat{v}} \begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi_N & \psi_N \end{pmatrix} \rightarrow \begin{pmatrix} \psi'_1 & \psi'_1 \\ \psi'_2 & \psi'_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi'_N & \psi'_N \end{pmatrix}$$

NxN matrix

1-body op

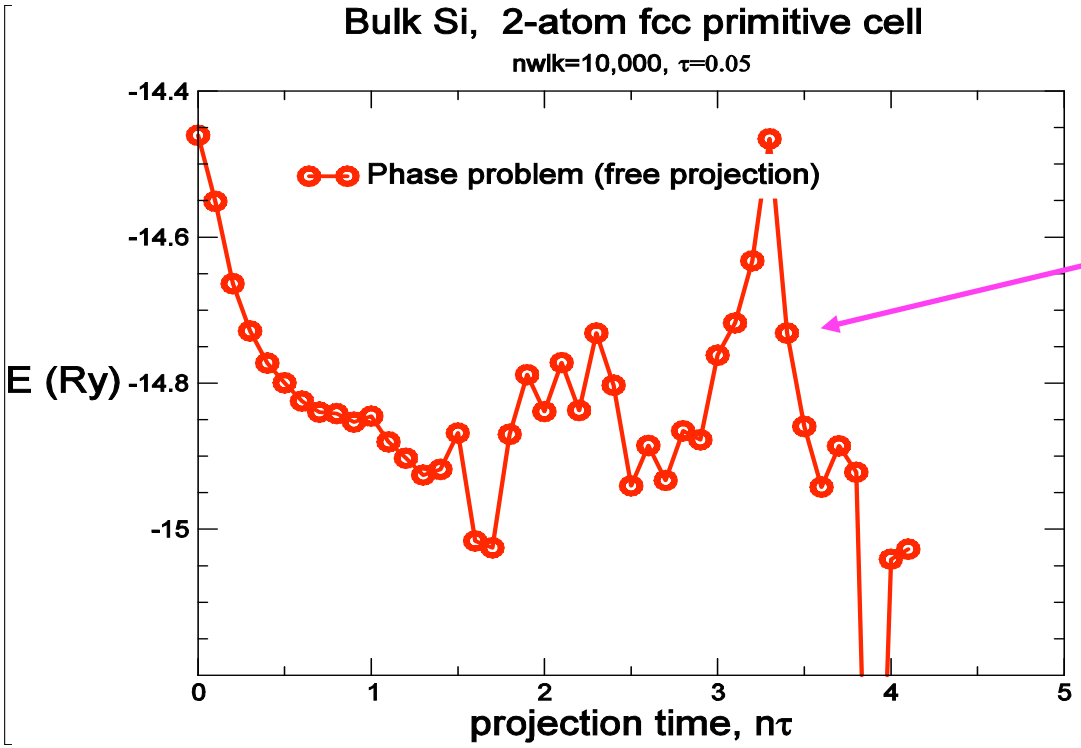
Gaussian, or 'Ising' variable

N is size of 'basis'

Importance sampling -> better efficiency (FB)

Overview - how does auxiliary-field QMC work?

Exact, ... but sign problem:



Exponential noise

In fact, for general (1/r) interaction,
a phase problem

$\hat{\mathbf{v}}(\sigma)$ is complex

1-body: $\sum_{i,j} v_{ij}(\sigma) c_i^\dagger c_j$

next →

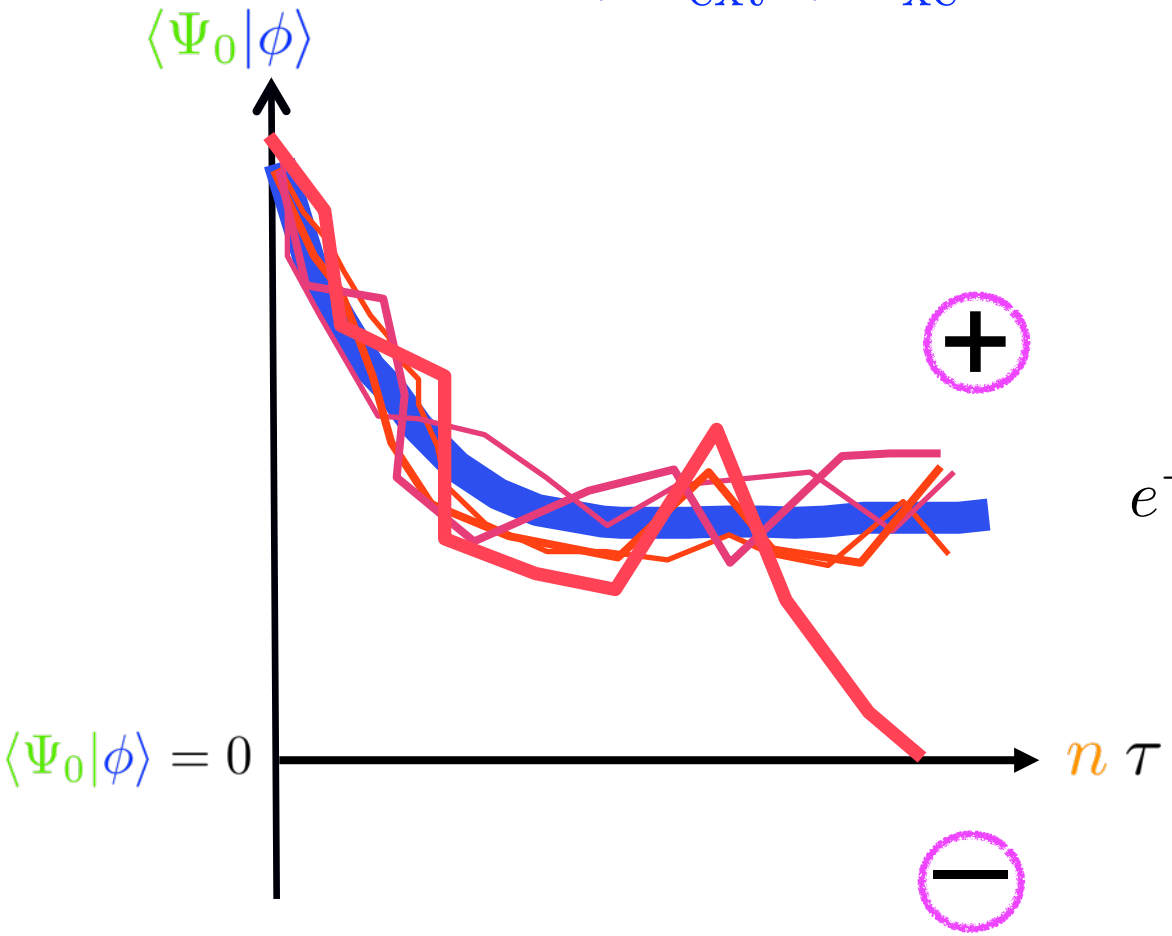
Sign problem in auxiliary-field QMC

Many-body effects as fluctuations around **mead-field**:

$$H_{\mathrm{MB}} = H_{\mathrm{LDA}} + \Delta V$$

$\Delta V \rightarrow V_{\mathrm{int}} - V_{\mathrm{xc}}$

$H_{\mathrm{LDA}} \rightarrow K + V_{\mathrm{ext}} + V_{\mathrm{xc}}$



$$e^{-\tau H_{\mathrm{MB}}} = e^{-\tau H_{\mathrm{LDA}}} e^{-\tau \Delta V}$$

Degeneracy between

$+|\phi\rangle$ and $-|\phi\rangle$

General: +/- $\rightarrow e^{i\theta}$

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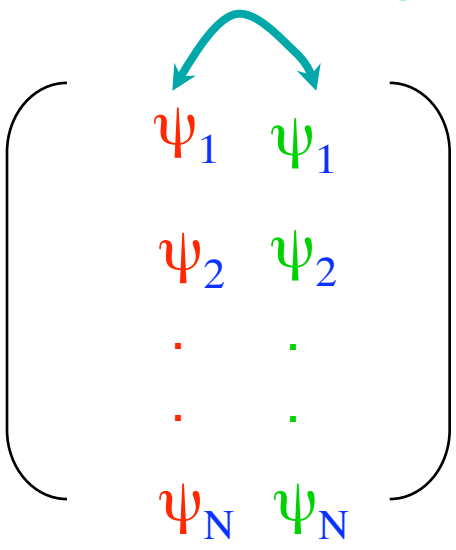
The sign problem

Sign/phase problem is due to --

"superexchange":



Slater det. - antisymmetric

To eliminate sign problem:

Use $\langle \Psi_T | \Psi \rangle = 0$ to determine if "superexchange" has occurred

Zhang, Carlson, Gubernatis, '97; Zhang, '00

To eliminate phase problem:

Generalize above with gauge transform --> "phaseless" constraint

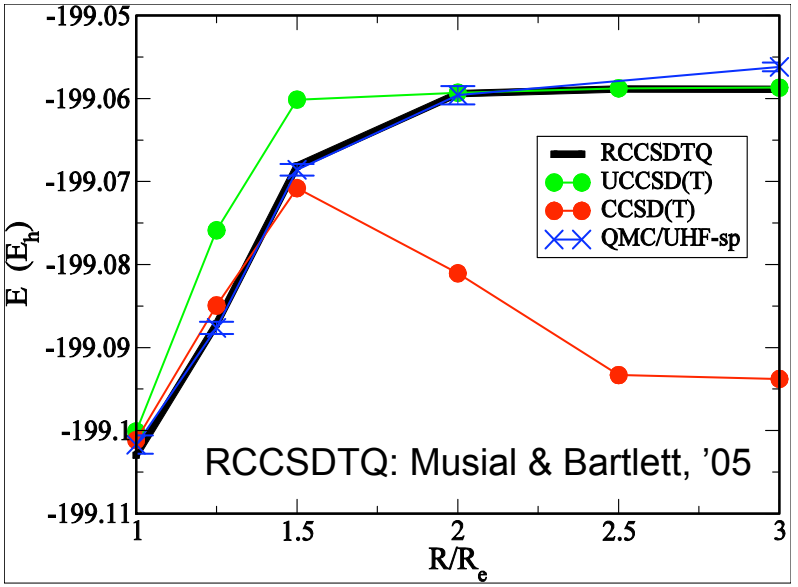
Zhang & Krakauer, '03; Chang & Zhang, '08

Benchmarks in electronic structure

F

Total energy calculations in ~100 systems -- atoms, molecules, solids: most with DFT or HF single determinant trial wavefunctions ==>

- accuracy comparable to CCSD(T) in molecules near equilibrium; better in bond-breaking
- N^3 scaling
- "automated" post-HF or post-DFT



Equilibrium → **Dissoc.**

* PW+psps
* Gaussian
* frozen-core

Benchmarks

Hydrogen lattice --- 2-D Hubbard:

- fundamental
- minimal model for CuO plane??

Largest relative error:

~ 0.5% for U/t = 4

~ 1.5% for U/t = 8

What does this mean?

at U/t=4 near n=1,

Ec~8%*E (after shift)

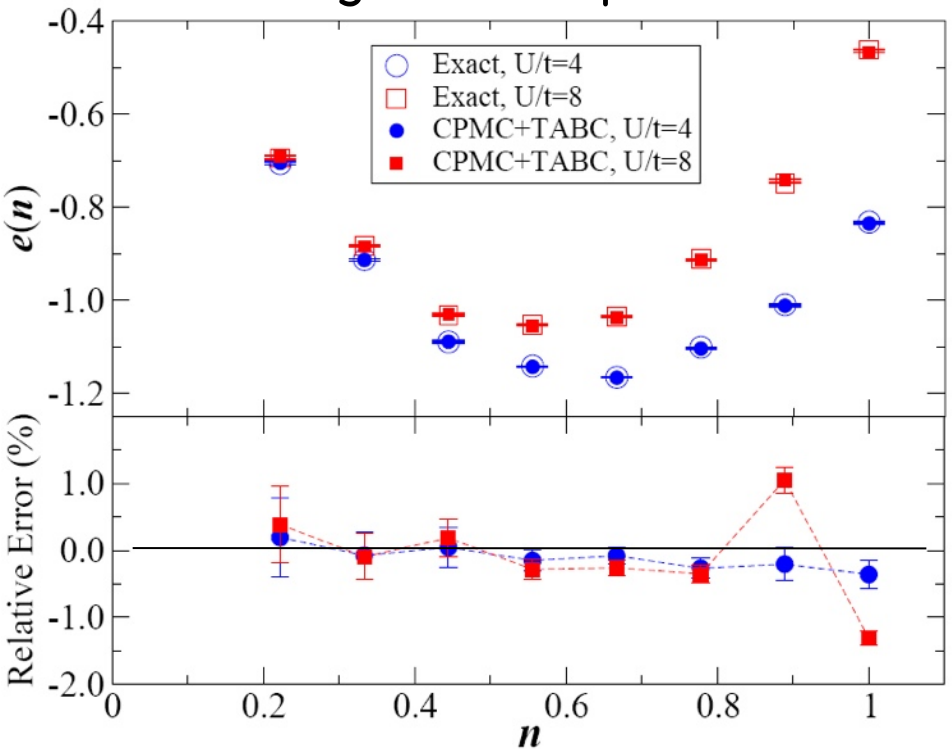
==> 'strongly correlated'

recall 'typical': 1-2%

AFQMC error ~ 2% Ec

Equation of state for 3x3

average 1000 k-points

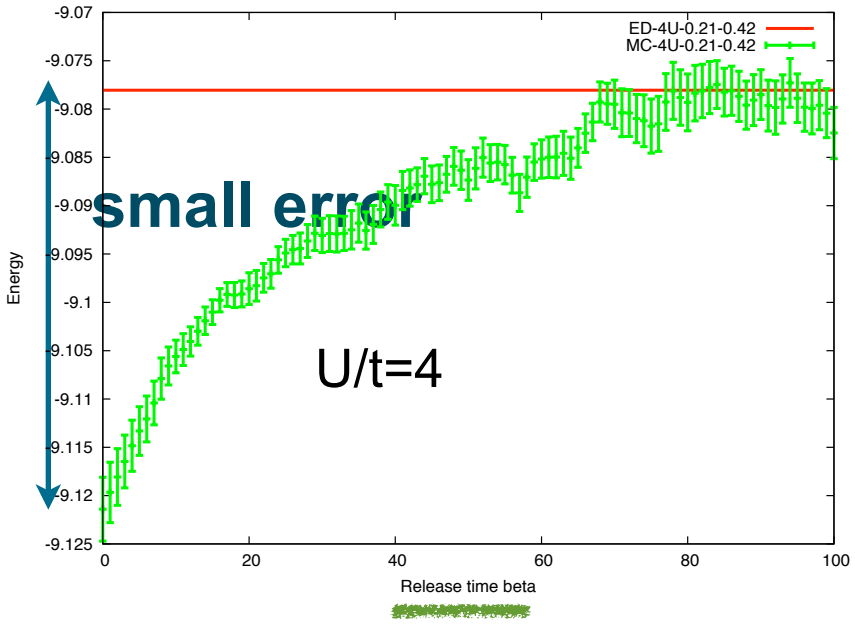


$$\text{Relative error}\% = \frac{e_{QMC}(n) - e_{Exact}(n)}{|e_{Exact}(n)|}$$

Chang & SZ, '08

Benchmark -- further reducing the error

Can release the constraint beyond constrained AFQMC:



Equation of state for 3x3

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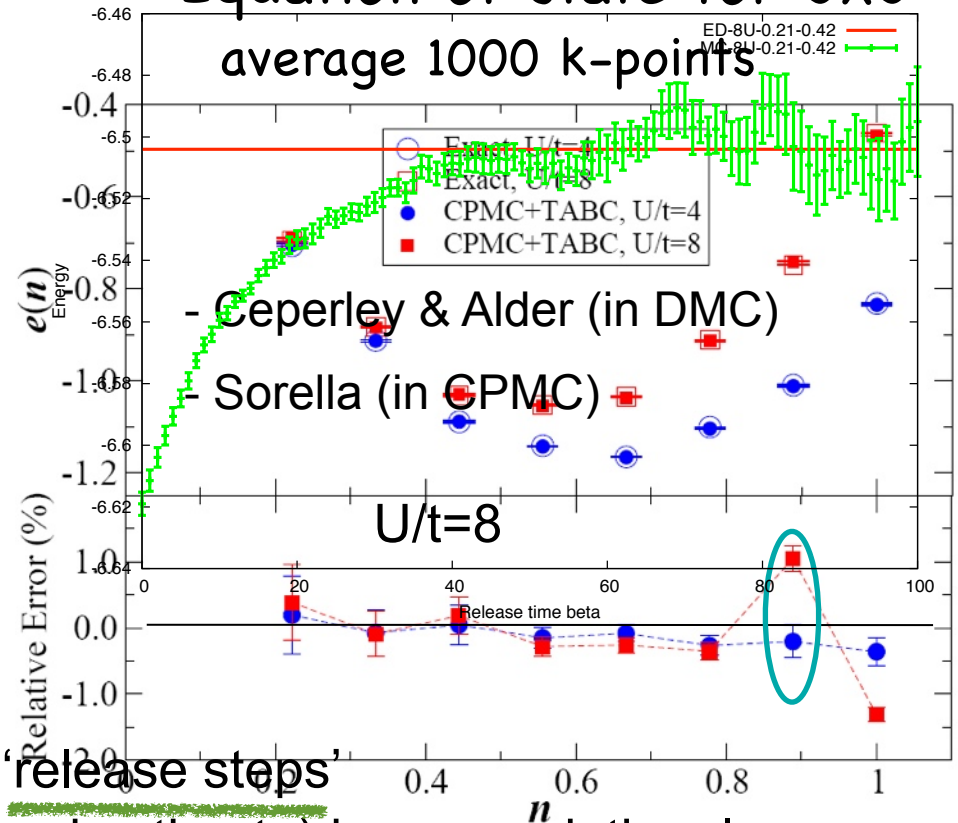


- Ceperley & Alder (in DMC)
- Sorella (in CPMC)

- Converges to **exact result** with 'release steps'
- Note energy from constraint (mixed estimate) is non-variational
- Sign/phase problem is back with release but useful info can be obtained in many systems

$$\text{Relative error}\% = \frac{|e_{MC}(n) - e_{Exact}(n)|}{|e_{Exact}(n)|}$$

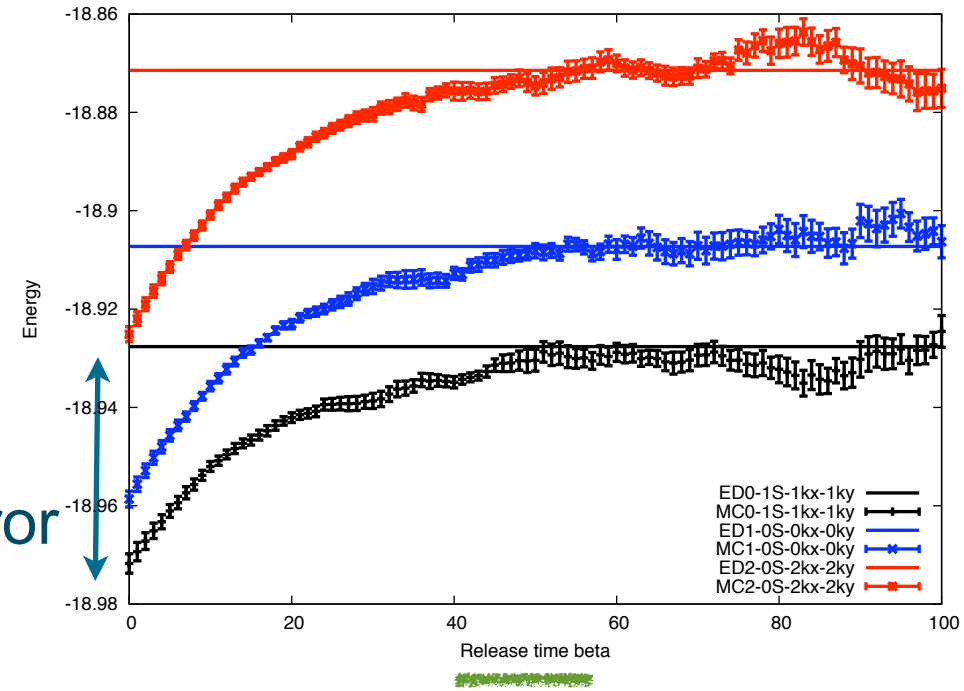
H. Shi & SZ

Releasing the phase constraint

Also excited states:

Explicitly impose symmetry in QMC propagation

H. Shi, SZ



S^2=0, k=(2,2)

S^2=0, k=(0,0)

GS, S^2=2, k=(1,1)

0.4%

CP error

4x4, 5u5d, (0.61,0.42)

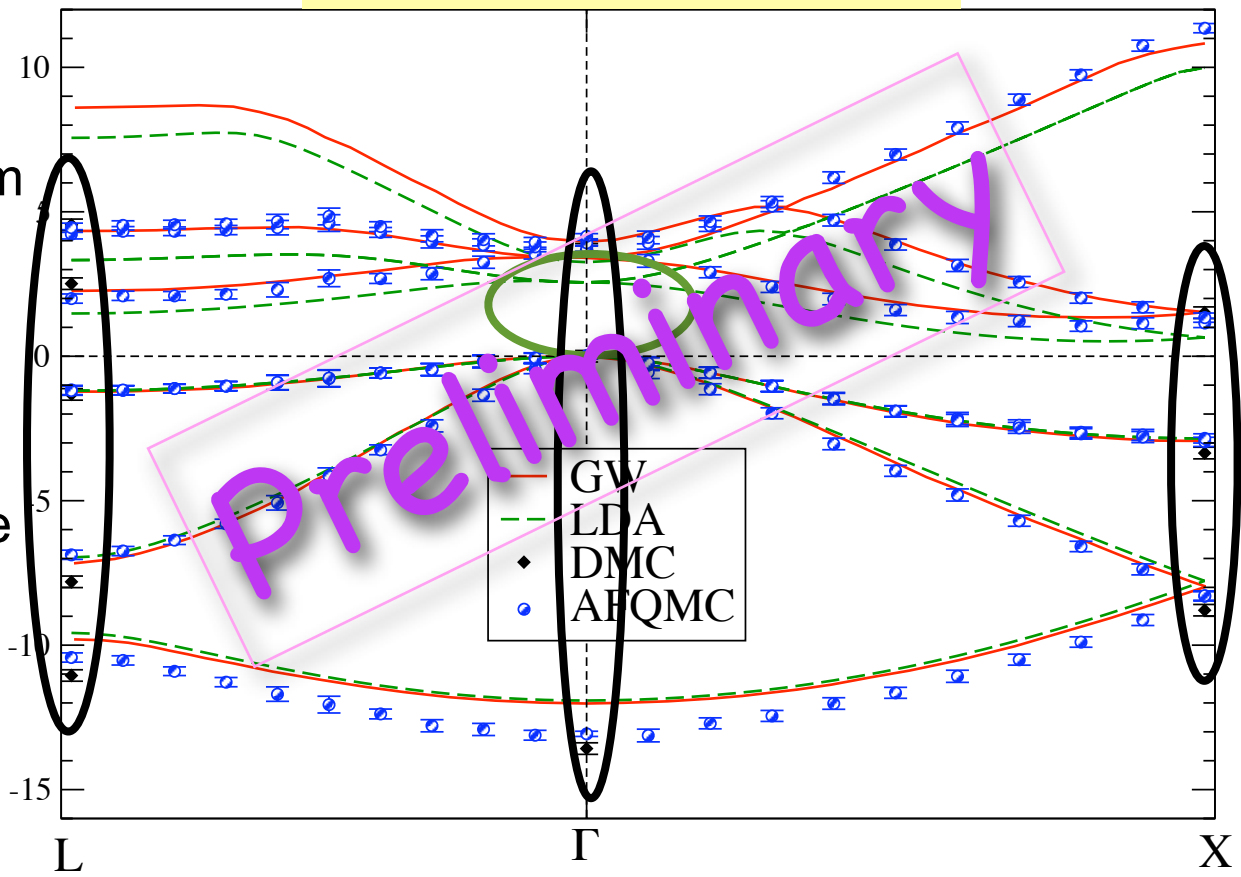
- Converges to exact results with 'release steps'
- Choice of HS transformations. Can preserve different symmetry properties. This allows fully unconstrained (exact) random walks to sample excited states without immediate collapse

Excited states: band structure

- Excited state (of same symmetry) can be calculated by constraint
- In C_2 molecule, very good results: multi-determinant trial wfs used
- First attempt in solids: ***preliminary results*** *F. Ma et al*

- **GW** (**Rohlfling et al, PRB '93**)
- **LDA** band gap problem
- DMC (**Williamson et al, PRB '98**)
- **AFQMC**: LDA trial wf; any k-point; primitive cell with new finite-size correction method

Band structure in silicon



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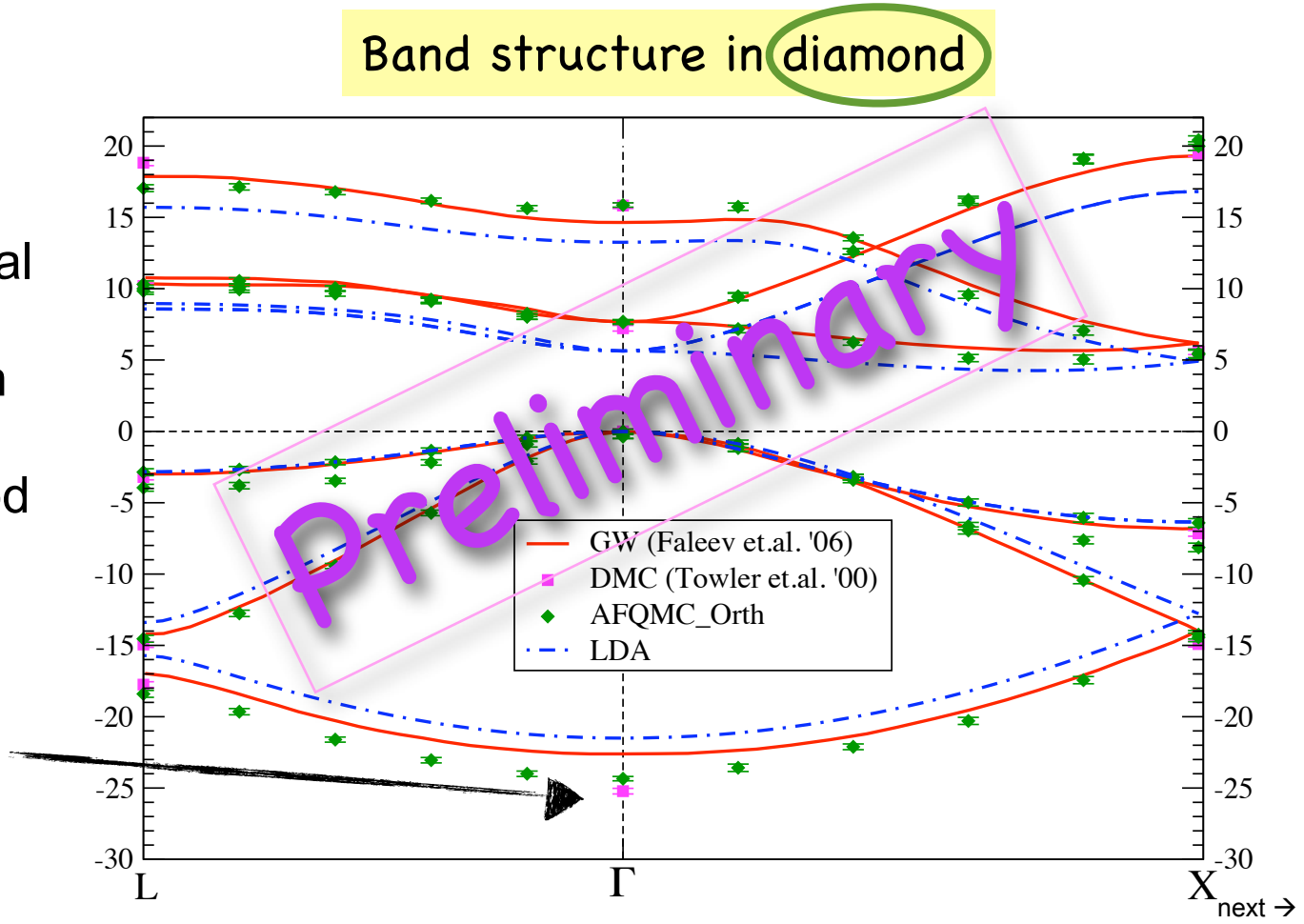
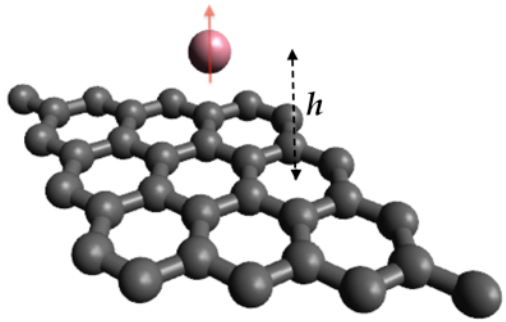
- **LDA** band gap problem
- **AFQMC:** LDA trial wf; any k-point; primitive cell with new finite-size correction method
- QMC has difficulties with high excitations: 'Orth' -- growing uncertainties



Co adsorption on graphene

- Spintronics applications of graphene --- adsorb transition metal atoms to induce local moments?
- Conflicting theoretical results:
  - GGA: min is Co low-spin, **h**~1.5
  - B3LYP: high-spin, **h**~1.8
  - GGA+U: high-spin, **h** ~ 1.9 (but global min is top site)



- We use AFQMC to study Co/benzene, then use embedding to correct for size effect for Co/graphene
  - Gaussian basis sets
  - frozen small core
  - hollow site; no relaxation
  - UHF trial wf

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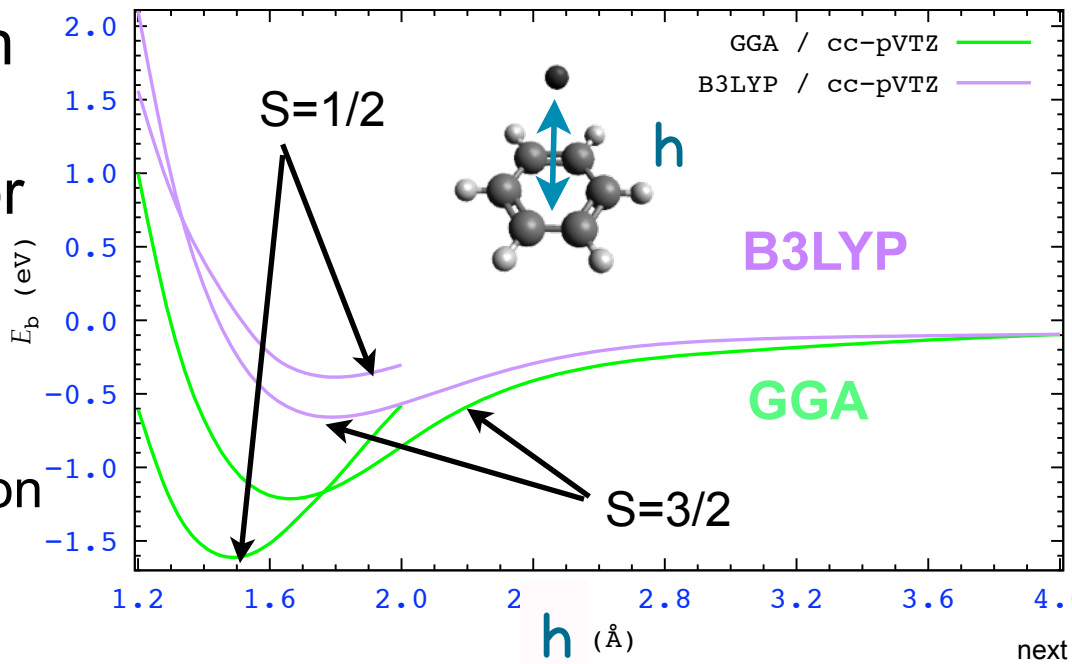
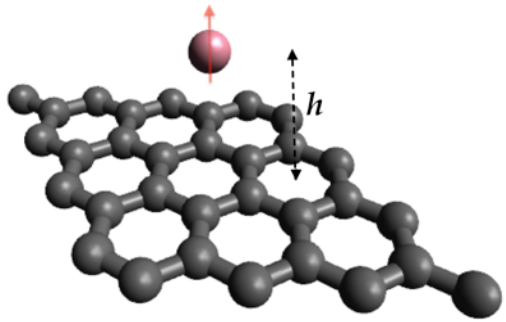


next →

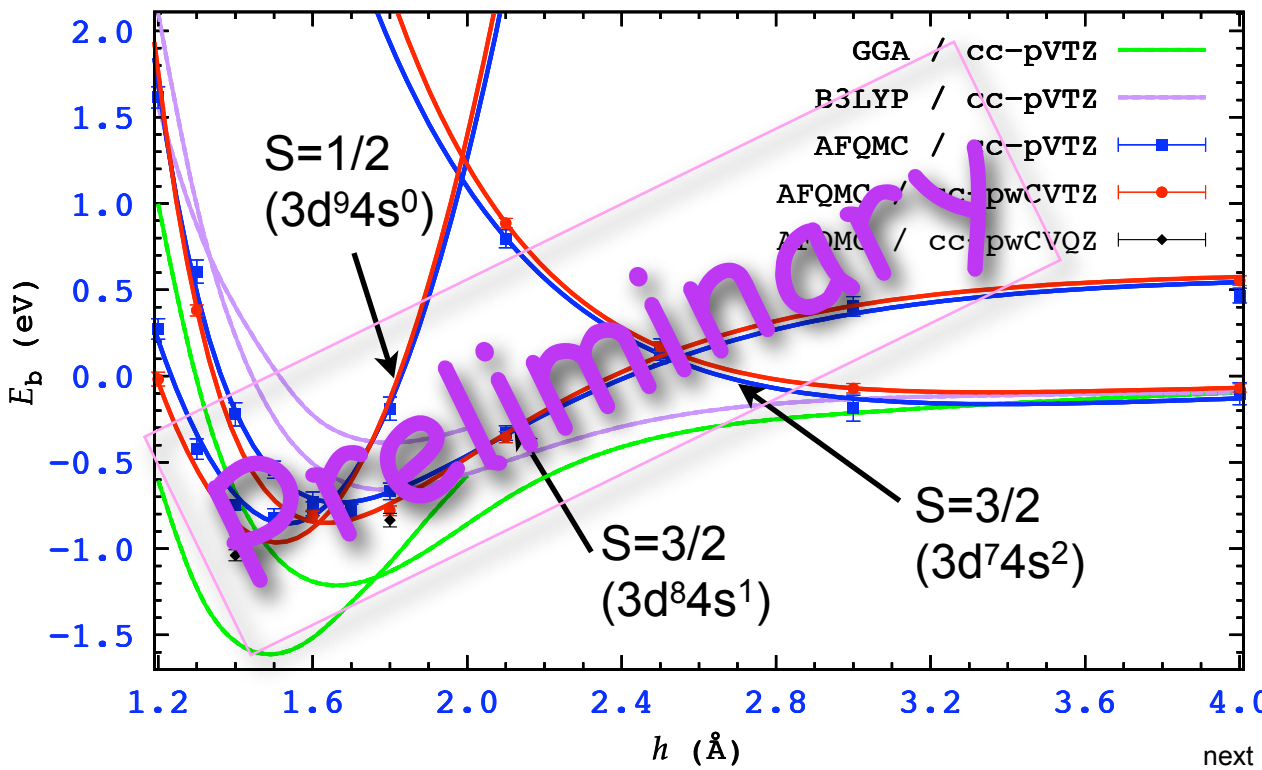
Co adsorption on graphene

- Co on benzene --- what are the states and what is the binding energy as a function of h?

  Preliminary (basis, more checks on wf, ...)



  - QMC: high -> high -> low h~1.5 (min)
  - double minima
  - reasonable basis set convergence
  - GGA and B3LYP: incorrect dissociation limit (vdW)
  - If shifted, GGA appears to capture correct physics



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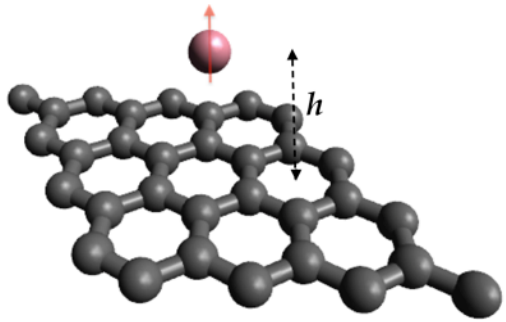
Co adsorption on graphene

Co/benzene --> Co/graphene by embedding size correction

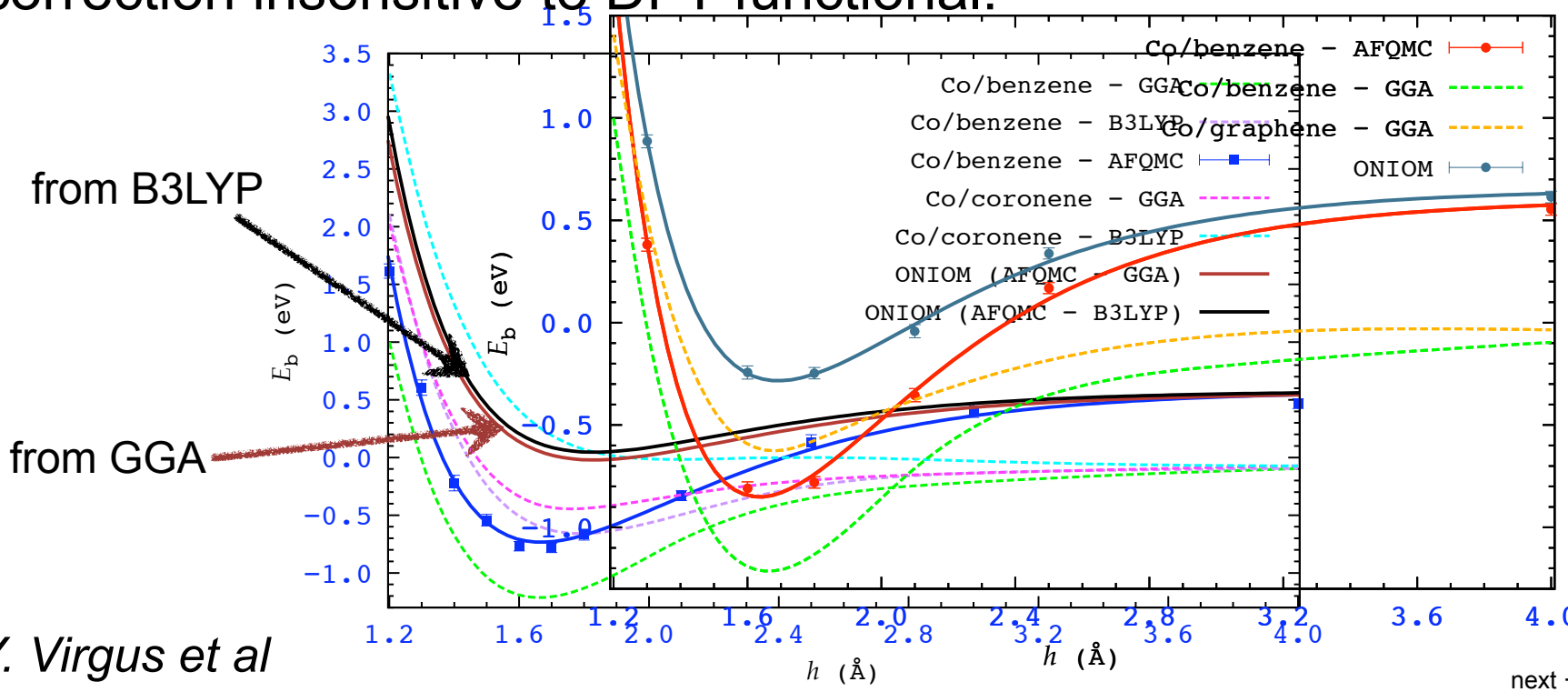
- treat “environment” at lower level of theory

$$E_b^{\mathrm{Co/g}} = E_{b,\mathrm{QMC}}^{\mathrm{Co/b}} + (E_{b,\mathrm{DFT}}^{\mathrm{Co/g}} - E_{b,\mathrm{DFT}}^{\mathrm{Co/b}})$$

ONIOM: Svensson et al. J. Phys Chem ’96



- correction insensitive to DFT functional:



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next →

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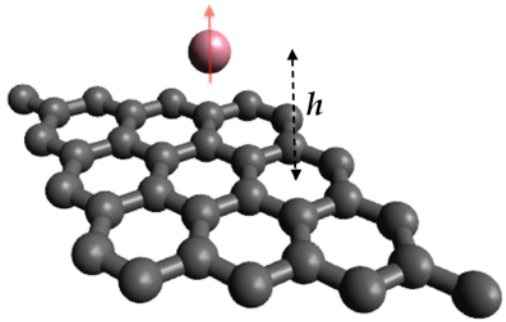
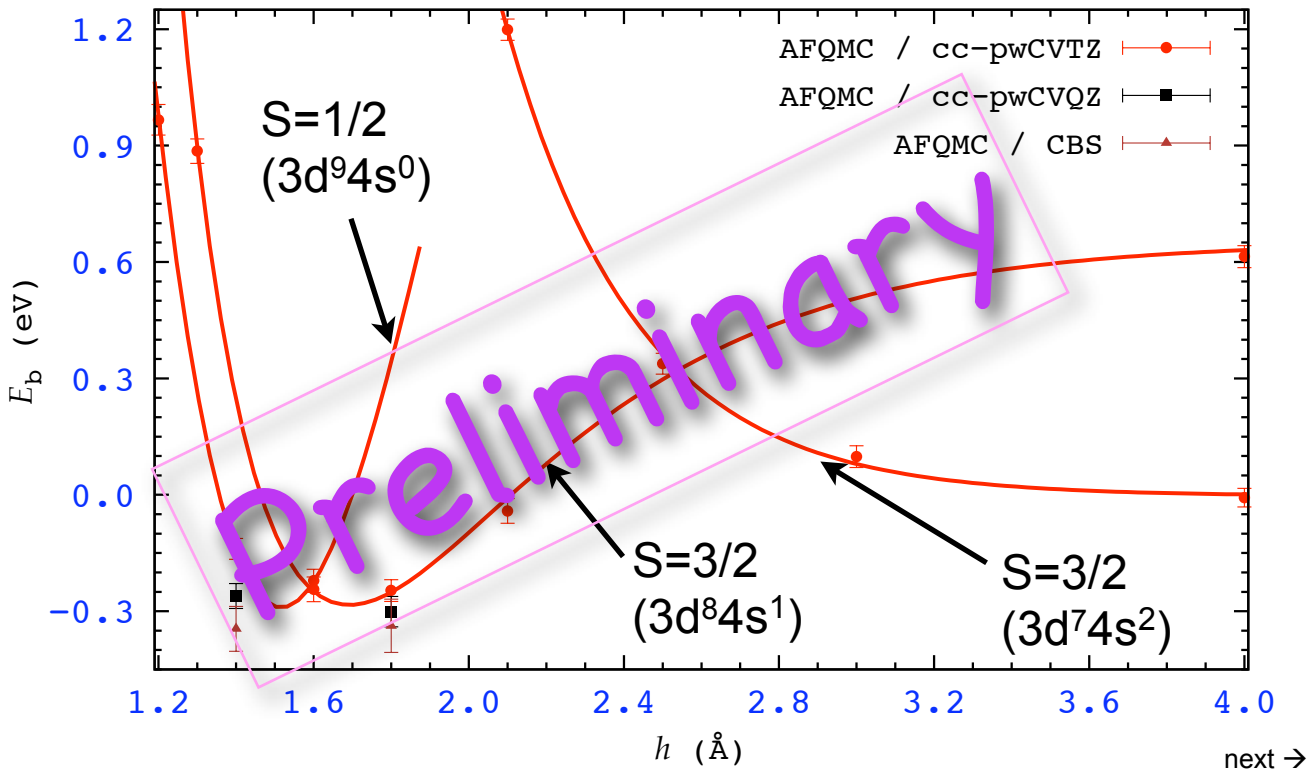
- Co on graphene --- what are the states and what is the binding energy as a function of h?

  Preliminary (basis, more checks on wf, ...)

  - QMC: high -> high -> low h~1.5 (min)
  - double well feature
  - comparable binding energies with small barrier





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Summary

- Auxiliary-field quantum Monte Carlo simulation method
  - Orbital-based, non-perturbative, many-body method
  - Comparable to CCSD(T) around equilibrium geometry, better for stronger correlation
  - Method to control the sign/phase problem:
    - much less sensitive to the trial wf -- can predict new phases
    - applicable to finite-temperature (lattice gauge? cluster solver)
  - Making QMC more accurate, more of a “blackbox”, for more problems; Petascale platforms can help make this a general tool
- Recent progress
  - Excited states and band structure
  - Release constraint; HFB trial wfs for strongly correlated systems
  - Downfolding; embedding?
  - Co adsorption on graphene