Expectation values in QMC

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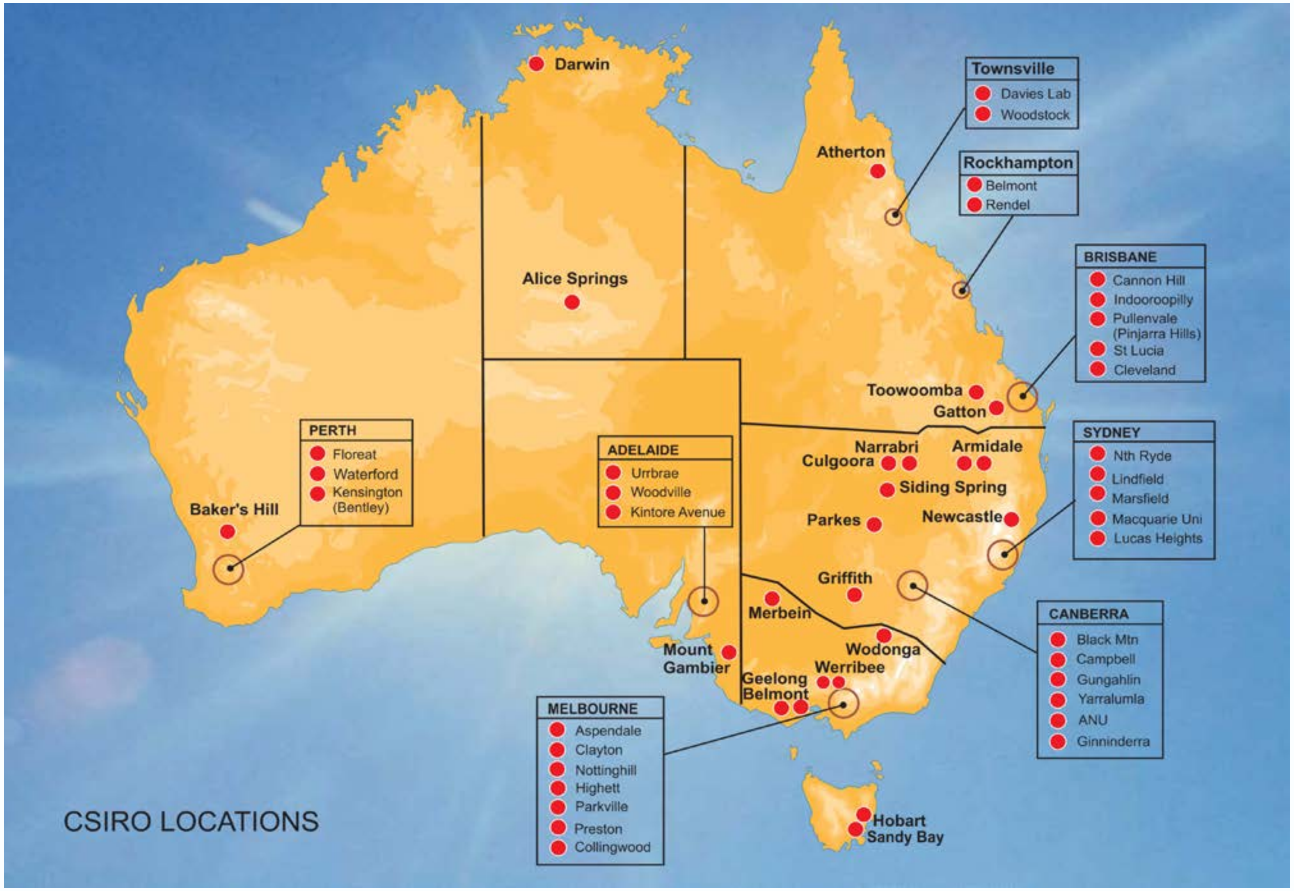
CSIRO labs



- Astronomy, Earth Science, Marine & Atmospheric, Energy Tech, Materials Science & Engineering

  - Wireless LAN
  - Relenza ('flu drug)
  - Ultrabattery

QMC Estimators

- Few estimators compared to DFT,quantum chem.
  - Geometries, Vibrations, Multipole moments, Densities, Electrostatic potentials, (Hyper)Polarizabilities, Hyperfine terms (Fermi contact, Anisotropic, Nuclear electric quadrupole constants, Electronic g-tensors)
- 'Simple' estimators $$\frac{\int \Psi_0 \hat{A} \Psi_0 d\mathbf{r}}{\int \Psi_0 \Psi_0 d\mathbf{r}}$$
- Systematic bias
- Large statistical variance

Bias in DMC

- DMC samples mixed distribution $\Psi_0 \Psi_T$

$$\frac{\int \Psi_0 \Psi_T \frac{\hat{A}\Psi_T}{\Psi_T} d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} \neq \frac{\int \Psi_0 \hat{A} \Psi_0 d\mathbf{r}}{\int \Psi_0 \Psi_0 d\mathbf{r}}$$

- Some methods for removing bias:
    - Extrapolation
    - Forward walking
    - Zero-Bias DMC
    - Hellmann-Feynman sampling
    - Reptation, PIGS

Extrapolation

- Write $\Psi_0 = \Psi_T + \delta\phi$
- Write DMC and Exact expectations in terms of VMC, e.g.

$$\langle A \rangle_{\mathrm{DMC}} = \langle A \rangle_{\mathrm{VMC}} + \delta \left[\frac{\int \phi A \Psi_T d\mathbf{r}}{\int \Psi_T^2 d\mathbf{r}} - \frac{\int \phi \Psi_T d\mathbf{r}}{\int \Psi_T^2 d\mathbf{r}} \frac{\int \Psi_T A \phi d\mathbf{r}}{\int \Psi_T^2 d\mathbf{r}} \right] + O(\delta^2)$$

$$\langle A \rangle_{\mathrm{Exact}} = 2\langle A \rangle_{\mathrm{DMC}} - \langle A \rangle_{\mathrm{VMC}} + O(\delta^2)$$

- Simple
- Approximate

Exact Methods

$$\frac{\int \Psi_0 \Psi_0 \hat{A} dr}{\int \Psi_0 \Psi_0 dr} = \frac{\int \Psi_0 \Psi_T \frac{\Psi_0}{\Psi_T} \hat{A} dr}{\int \Psi_0 \Psi_T \frac{\Psi_0}{\Psi_T} dr}$$

- DMC branching weight transforms $\Psi_T^2 \to \Psi_0 \Psi_T$

- *Average* of weights at given point:

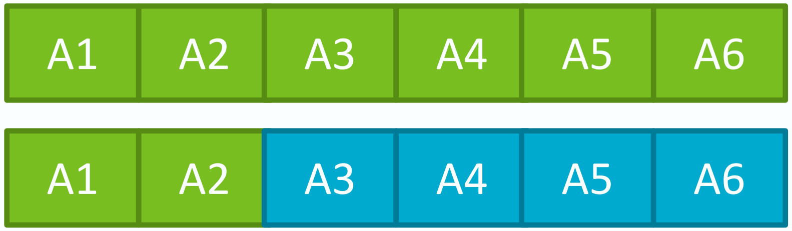
$$\frac{\Psi_0(\mathbf{r})}{\Psi_T(\mathbf{r})} = \langle w \rangle_{\text{walks ending at } \mathbf{r}}$$

- $\frac{\Psi_0(\mathbf{r})}{\Psi_T(\mathbf{r})}$ also given by asymptotic progeny of walker at r

Forward Walking

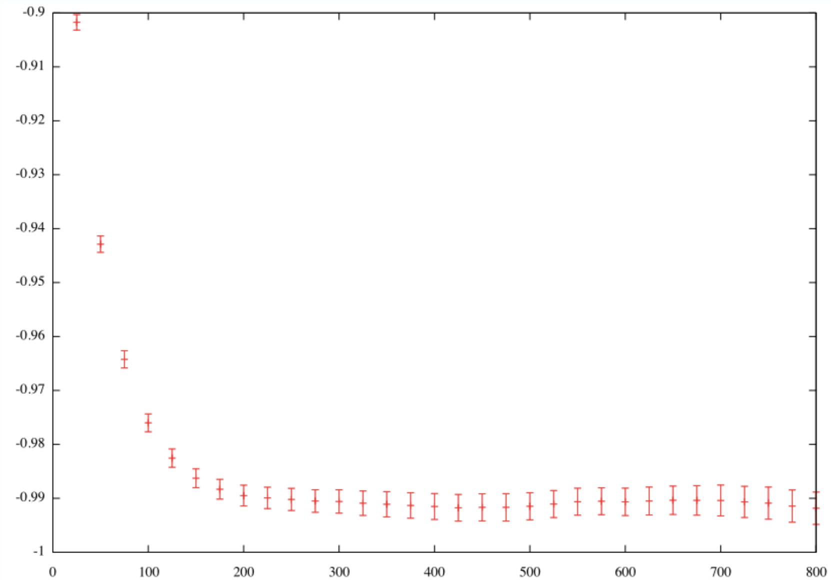
- Want $\frac{\Psi_0(\mathbf{r})}{\Psi_T(\mathbf{r})} A(\mathbf{r})$
- Vector on each walker holds samples of observable A at successive time steps

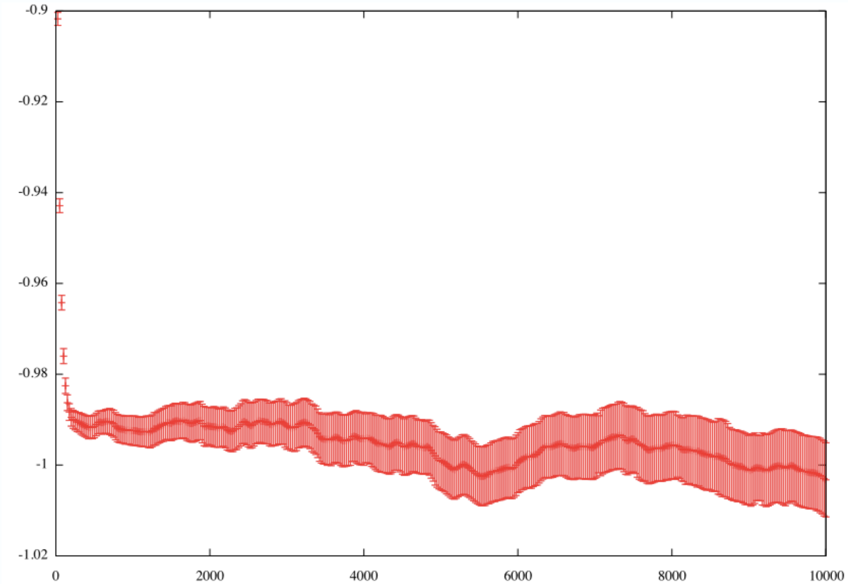
- At step t, sum values from step t-M. Automatically includes weight.



Forward Walking

Asymptotically unstable:





Can't do differential operators:

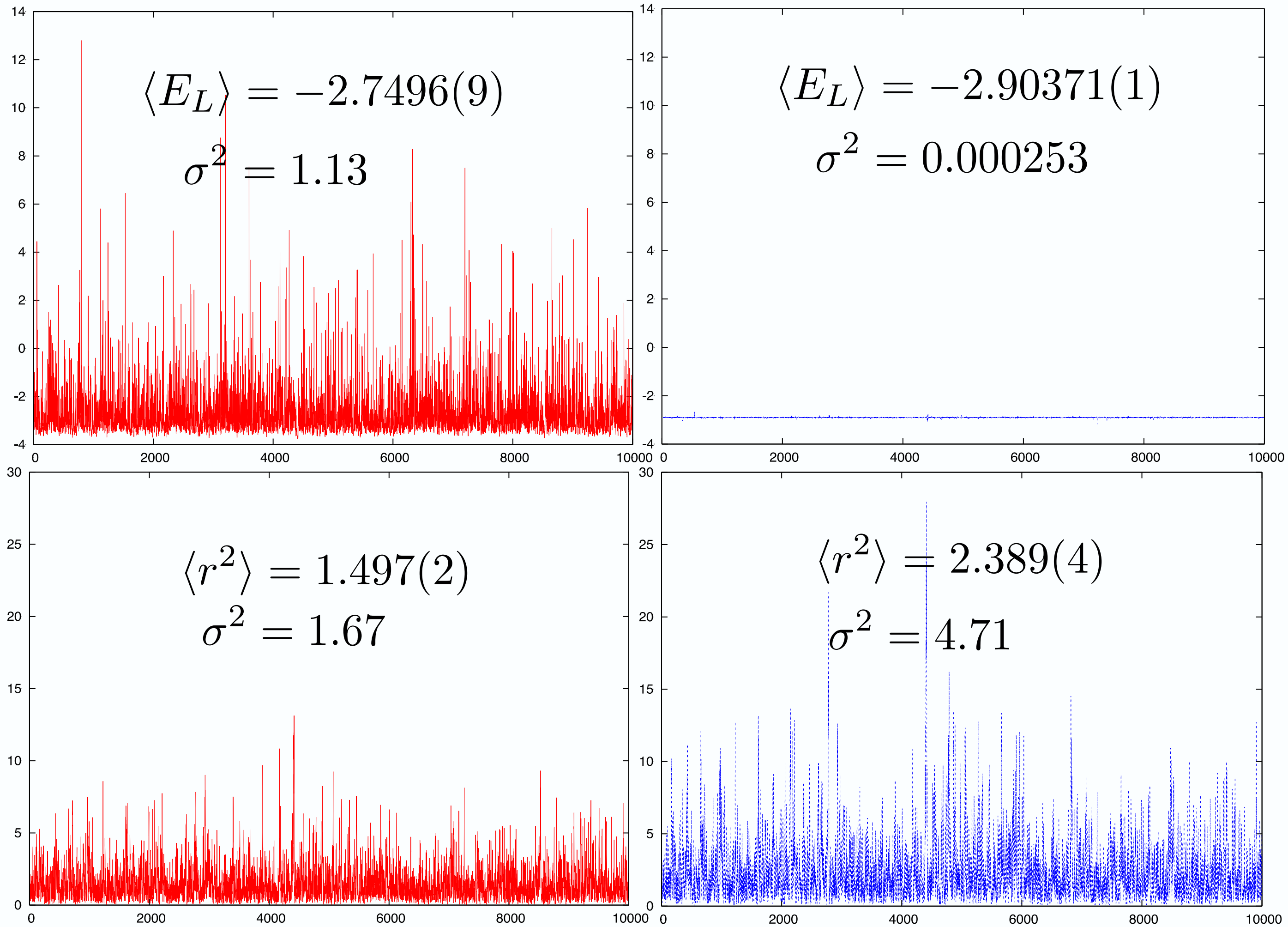
$$\frac{\int \Psi_0 \Psi_T \frac{\Psi_0}{\Psi_T} \frac{\hat{A}\Psi_T}{\Psi_T} d\mathbf{r}}{\int \Psi_0 \Psi_T \frac{\Psi_0}{\Psi_T} d\mathbf{r}} = \frac{\int \Psi_0 \Psi_0 \frac{\hat{A}\Psi_T}{\Psi_T} d\mathbf{r}}{\int \Psi_0 \Psi_0 d\mathbf{r}}$$

Variance

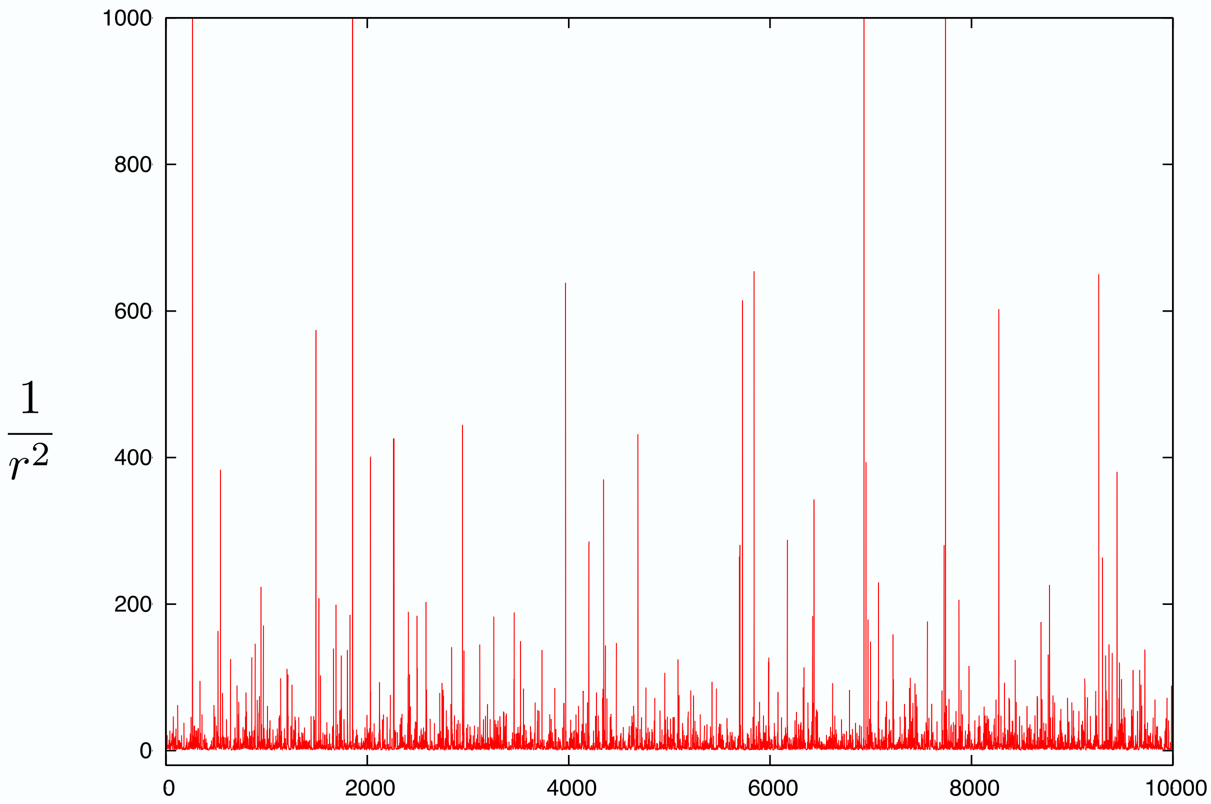
Poor Ψ_T Good Ψ_T

$$\langle E_L \rangle_{\text{exact}} = -2.903724...$$

$$\langle r^2 \rangle_{\text{exact}} = 2.3869...$$



Infinite variance



- Different causes:
  - "Algebraic singularity"
  - Nodal surfaces

Perturbation Theory in QMC

$$\frac{\int \Psi_0 \Psi_T E_L d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} = \frac{\int \Psi_0^2 E_L d\mathbf{r}}{\int \Psi_0^2 d\mathbf{r}}$$

- Perturb $H \to H + \lambda A$ $\quad E_{\text{mixed}}(\lambda) = E_{\text{pure}}(\lambda)$
- Differentiate: $\partial_\lambda E_{\text{mixed}} = \partial_\lambda E_{\text{pure}}$

$$\partial_\lambda E_{\text{pure}} = \frac{\int \Psi_0 A \Psi_0 d\mathbf{r}}{\int \Psi_0 \Psi_0 d\mathbf{r}} + h[\Psi_0] \partial_\lambda \Psi_0(\mathbf{r} = \mathbf{r}_N)$$

$$\partial_\lambda E_{\text{mixed}} = \frac{\int \Psi_0 \Psi_T \partial_\lambda E_L d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} + \frac{\int \partial_\lambda (\Psi_0 \Psi_T)(E_L - E_{\text{mixed}}) d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}}$$

Zero Variance Principle

- $E_L = \frac{H\Psi_T}{\Psi_T}$ can have ZV because $\frac{H\Psi_0}{\Psi_0} = E_0$

- Consider $\partial_\lambda E_L = \frac{\partial_\lambda H\Psi_T}{\Psi_T} + \frac{(H - E_L)\partial_\lambda \Psi_T}{\Psi_T}$

- Derivative of eigenvalue Eq. gives:

$$\partial_\lambda E_0 = \frac{\partial_\lambda H\Psi_0}{\Psi_0} + \frac{(H - E_0)\partial_\lambda \Psi_0}{\Psi_0}$$

- ZV if $\Psi_T, \partial_\lambda \Psi_T$ exact

Role of $\partial_\lambda \Psi_T$

$$\frac{\int \Psi_0 \Psi_T \partial_\lambda E_L d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} + \frac{\int \partial_\lambda(\Psi_0 \Psi_T)(E_L - E_{\text{mixed}})d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} = \frac{\int \Psi_0 A \Psi_0 d\mathbf{r}}{\int \Psi_0 \Psi_0 d\mathbf{r}} + h[\Psi_0]\partial_\lambda \Psi_0(\mathbf{r} = \mathbf{r}_N)$$

- $\partial_\lambda \Psi_T$ effects
  - Variance
  - Nodal Response
- Can think $\partial_\lambda \Psi_T = (\partial_\lambda \Psi)_T$
- Frozen Nodes $\partial_\lambda \Psi_T(\mathbf{r} = \mathbf{r}_N) = 0$
- Define Q: $\partial_\lambda \Psi_T = Q \Psi_T$

Zero Variance Estimators

- All-electron forces in molecules

(Assaraf & Caffarel, J. Chem. Phys 113, 4028 (2000))

$$F(\mathbf{x}) = \frac{Z_A Z_B}{R^2} - Z_A \sum_{i=1}^{N_{\text{elect}}} \frac{(x_i - R)}{|\mathbf{r}_i - \mathbf{R}|^3}$$

$$Q = Z_A \sum_{i=1}^{N_{\text{elect}}} \frac{(x_i - R)}{|\mathbf{r}_i - \mathbf{R}|}.$$

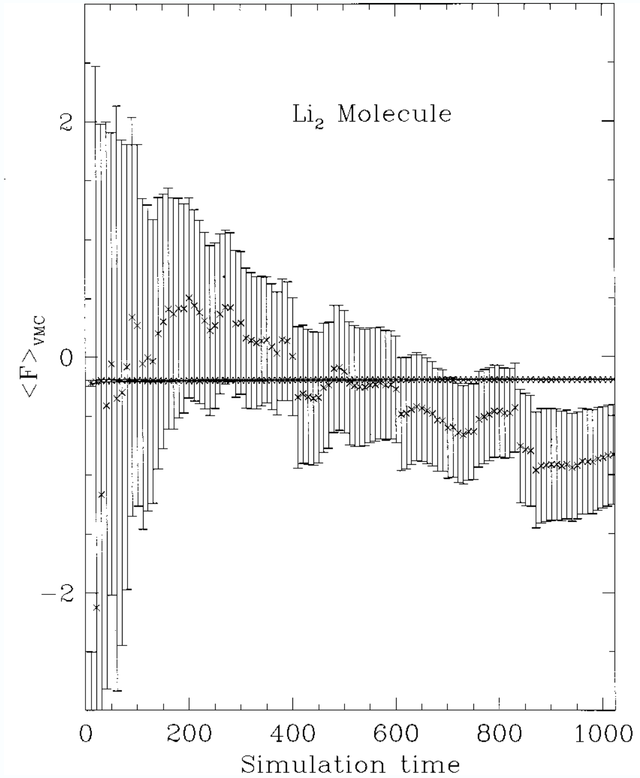


FIG. 1. Convergence of $\langle F\rangle_{\text{VMC}}$ and $\langle \tilde{F}\rangle_{\text{VMC}}$ as a function of the simulation time (proportional to the number of Monte Carlo steps) for the Li_2 molecule at the equilibrium geometry, $R=3.015$.

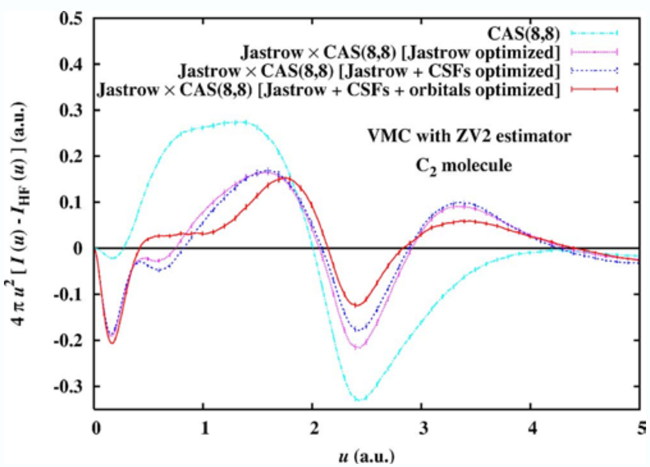
ZV Estimators

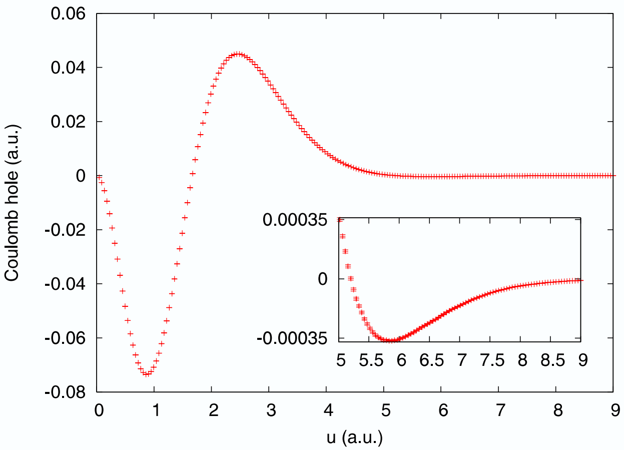
- Intracules: (Toulouse, Assaraf, Umrigar, J. Chem. Phys 126, 244112 (2007)

$$I(u) = \int \frac{d\Omega_{\mathbf{u}}}{4\pi} I(\mathbf{u}) \qquad I(\mathbf{u}) = \frac{1}{2}\sum_{i\neq j} \int d\mathbf{R}\Psi(\mathbf{R})^2 \delta(\mathbf{r}_{ij} - \mathbf{u})$$

- No discretisation error.

$$Q_2(u,\mathbf{R}) = -\frac{1}{8\pi}\sum_{i\neq j} \int \frac{d\Omega_{\mathbf{u}}}{4\pi} \frac{g(\mathbf{r}_{ij},\mathbf{u})}{|\mathbf{r}_{ij} - \mathbf{u}|} \qquad g(\mathbf{r}_{ij},\mathbf{u}) = e^{-\zeta|\mathbf{r}_{ij}-\mathbf{u}|}$$





JCP 130, 134103 (2009)

ZV Estimators

- Contact densities (J. Chem. Phys 135, 134112 (2011))

$$n(\mathbf{R}_A) = \frac{\langle \Psi_0 | \sum_i^N \delta(\mathbf{r}_i - \mathbf{R}_A) | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

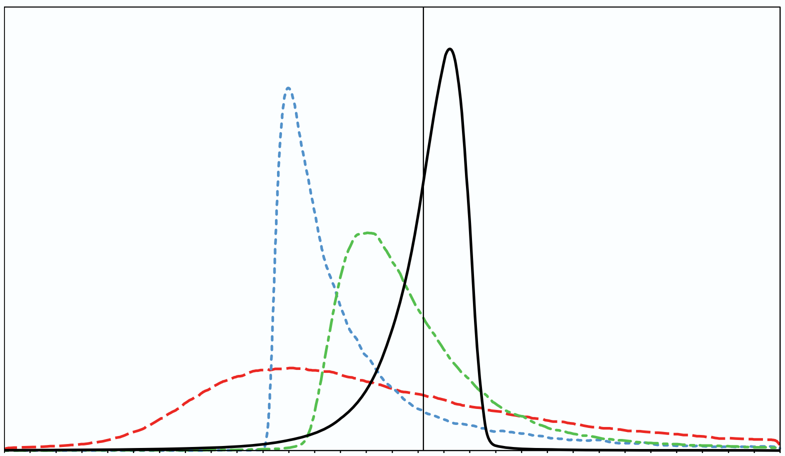
- Start from: $\delta(\mathbf{r}) = -\frac{1}{4\pi} \nabla^2 \left(\frac{1}{r} \right)$

$$\partial_\lambda E_L = \frac{\hat{A}\Psi_T}{\Psi_T} - \frac{1}{2} \sum_i \nabla_i^2 Q - \sum_i \nabla_i Q \cdot \frac{\nabla_i \Psi_T}{\Psi_T}$$

$$Q_1 = -\frac{1}{2\pi} \sum_i \frac{1}{r_{iA}}$$

Constructing ZV estimators

- Better estimators



$$Q_1 = -\frac{1}{2\pi}\sum_i \frac{1}{r_{iA}}$$

$$Q_2 = Q_1 + \frac{Z_A}{\pi}\sum_i \ln(r_{iA})$$

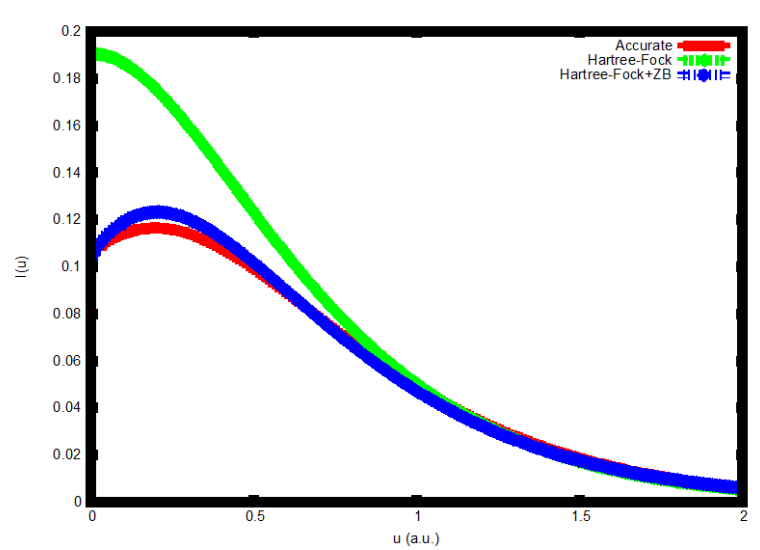
$$Q_3 = Q_2 + \frac{Z_A^2}{\pi}\sum_i r_{iA}$$

Back to Zero Bias

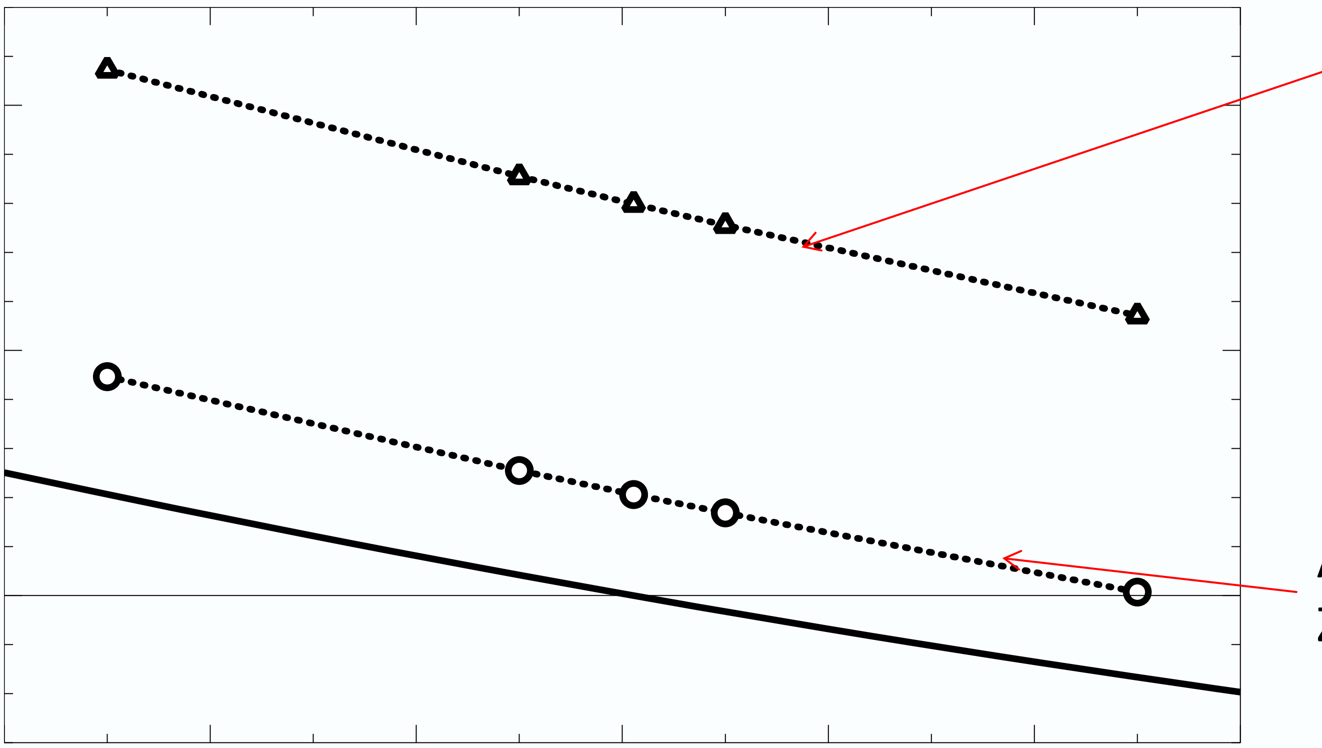
$$\partial_\lambda E_{\rm DMC} = \frac{\int \Psi_0 \Psi_T \partial_\lambda \left(\frac{H\Psi_T}{\Psi_T}\right) d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} + \frac{\int \partial_\lambda (\Psi_0 \Psi_T)(E_L - E_{\rm DMC}) d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}}$$

- Need $\partial_\lambda (\Psi_0 \Psi_T)$

- Approximations:
  - $\partial_\lambda \Psi_0 = 0$: gives DMC result (with ZV)
  - Approx. ZB : $\frac{\partial_\lambda \Psi_0}{\Psi_0} = \frac{\partial_\lambda \Psi_T}{\Psi_T}$



Force in H2 – poor wave function

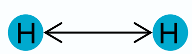


ZV DMC

$$\partial_\lambda \Psi_0 = 0$$

Approximate Zero-Bias

$$\frac{\partial_\lambda \Psi_0}{\Psi_0} = \frac{\partial_\lambda \Psi_T}{\Psi_T}$$



Exact Zero Bias DMC

- DMC evolution:

$$\lim_{\tau\to\infty} f(\mathbf{r}', t+\tau) = \lim_{\tau\to\infty} \Psi_0(\mathbf{r}')\Psi_T(\mathbf{r}')e^{-\tau(E_0-E_T)}C$$

- Derivative gives

$$\lim_{\tau\to\infty} \partial_\lambda f(\mathbf{r}', t+\tau) = \lim_{\tau\to\infty} \partial_\lambda \left(\Psi_0(\mathbf{r}')\Psi_T(\mathbf{r}')\right) e^{-\tau(E_0-E_T)}C +$$
$$\lim_{\tau\to\infty} \Psi_0(\mathbf{r}')\Psi_T(\mathbf{r}')e^{-\tau(E_0-E_T)}\left[\partial_\lambda C - \tau\left(\partial_\lambda E_0 - \partial_\lambda E_T\right)C\right]$$

- Contamination doesn't effect our answer:

$$\frac{\int \partial_\lambda(\Psi_0\Psi_T + \alpha\Psi_0\Psi_T)(E_L - E_0)d\mathbf{r}}{\int \Psi_0\Psi_T d\mathbf{r}} = \frac{\int \partial_\lambda(\Psi_0\Psi_T)(E_L - E_0)d\mathbf{r}}{\int \Psi_0\Psi_T d\mathbf{r}}$$

Source of Contamination

- First-order Schrodinger Eq:

$$(H - E_0)\partial_\lambda \Psi_0 = (\partial_\lambda E_0 - \partial_\lambda H)\Psi_0$$

$(H - E_0)\Psi_0 = 0$ so $\partial_\lambda \Psi_0 + \alpha \Psi_0$ also a solution

Practical Zero-Bias DMC

- Evolution equation:

$$f(\mathbf{r}_M, t + M\tau) = \int \prod_{i=0}^{M-1} G(\mathbf{r}_i, \mathbf{r}_{i+1}; \tau) f(\mathbf{r}_0, t) d\mathbf{r}_0 \ldots d\mathbf{r}_{M-1}$$

- Derivative:

$$\partial_\lambda f(\mathbf{r}_M, t + M\tau) = \int \sum_{j=0}^{M-1} \frac{\partial_\lambda G(\mathbf{r}_j, \mathbf{r}_{j+1}; \tau)}{G(\mathbf{r}_j, \mathbf{r}_{j+1}; \tau)} \prod_{i=0}^{M-1} G(\mathbf{r}_i, \mathbf{r}_{i+1}; \tau) f(\mathbf{r}_0, t) d\mathbf{r}_0 \ldots d\mathbf{r}_{M-1}$$

- Practical expression:

$$\frac{\int \partial_\lambda (\Psi_0 \Psi_T)(E_L - E_{\mathrm{DMC}}) d\mathbf{r}}{\int \Psi_0 \Psi_T d\mathbf{r}} = \lim_{n \to \infty} \frac{\sum_{i=1}^{n} w_i W_i (E_L - E_{\mathrm{DMC}})}{\sum_i w_i}$$

Derivative of Green's function

$$G(\mathbf{r},\mathbf{r}';\tau) = \underbrace{\exp\left(-\frac{1}{2\tau}(\mathbf{r}'-\mathbf{r}-\tau\mathbf{v}(\mathbf{r}))^2\right)}_{G_{dd}} \underbrace{\exp\left(-\frac{\tau}{2}(E_L(\mathbf{r}')+E_L(\mathbf{r})-2E_T)\right)}_{G_b}$$

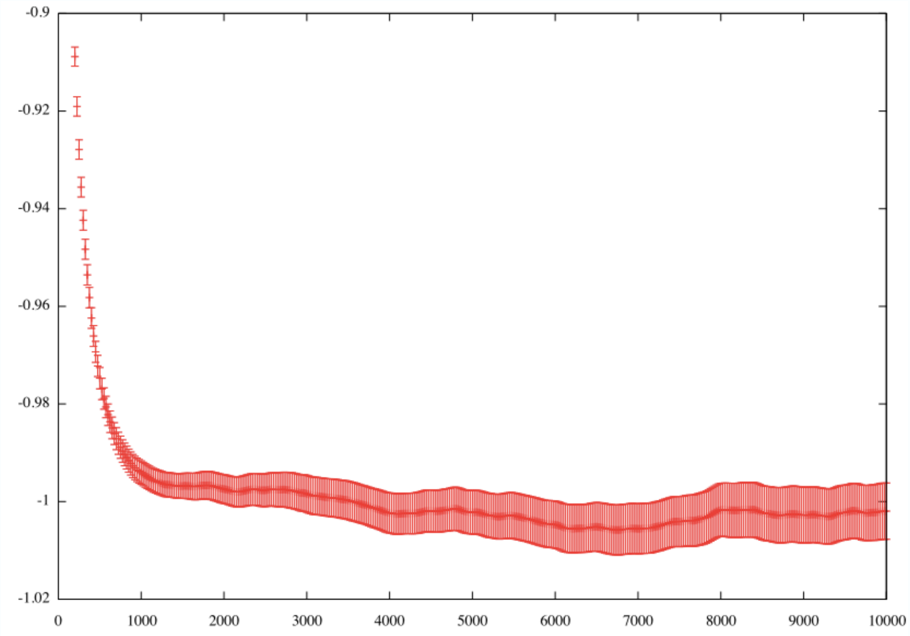
$$\frac{\partial_\lambda G_{dd}}{G_{dd}} = (\mathbf{r}'-\mathbf{r}-\tau\mathbf{v}(\mathbf{r}))\cdot\nabla Q$$

$$\frac{\partial_\lambda G_b}{G_b} = -\frac{\tau}{2}\left(\partial_\lambda E_L(\mathbf{r}')+\partial_\lambda E_L(\mathbf{r})-2\partial_\lambda E_T\right)$$

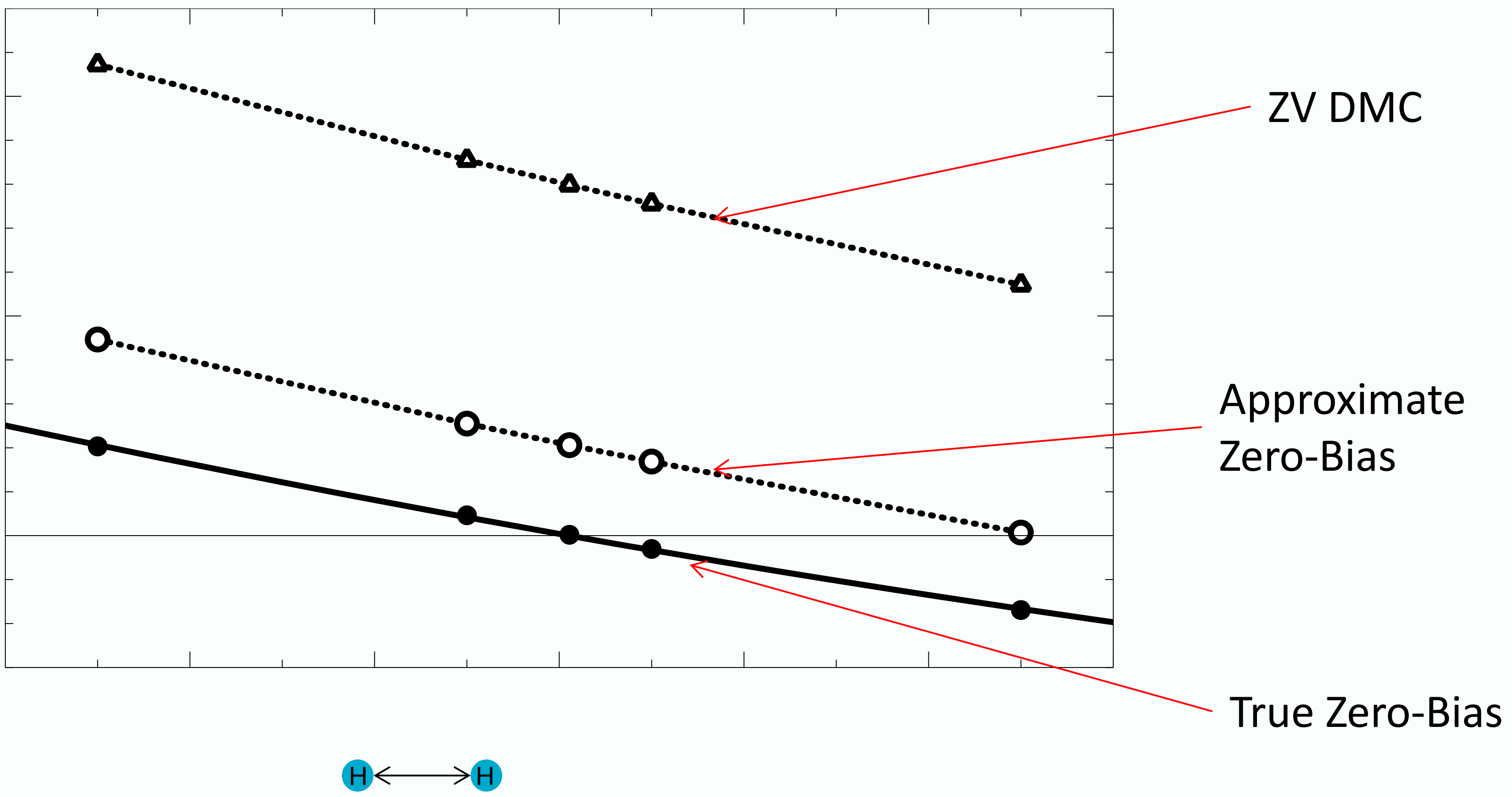
ZB Implementation

- Vector and scalar for each walker

$\left(\frac{\partial_\lambda G}{G}\right)_1$	$\left(\frac{\partial_\lambda G}{G}\right)_2$	$\left(\frac{\partial_\lambda G}{G}\right)_3$	$\left(\frac{\partial_\lambda G}{G}\right)_4$	$\left(\frac{\partial_\lambda G}{G}\right)_5$	$\left(\frac{\partial_\lambda G}{G}\right)_6$

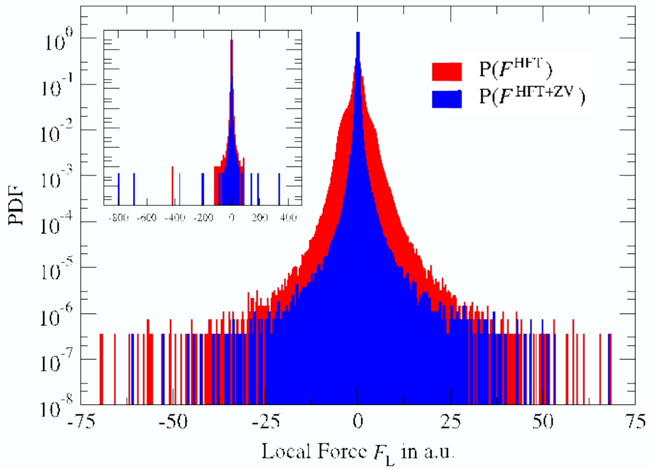


Exact forces in H2



Zero Bias Forces: Nodal response

- 'Nodal' infinite variance: $\partial_\lambda E_L = \frac{\partial_\lambda H \Psi_T}{\Psi_T} + \frac{H \partial_\lambda \Psi_T}{\Psi_T} - \frac{H\Psi_T}{\Psi_T}\frac{\partial_\lambda \Psi_T}{\Psi_T}$



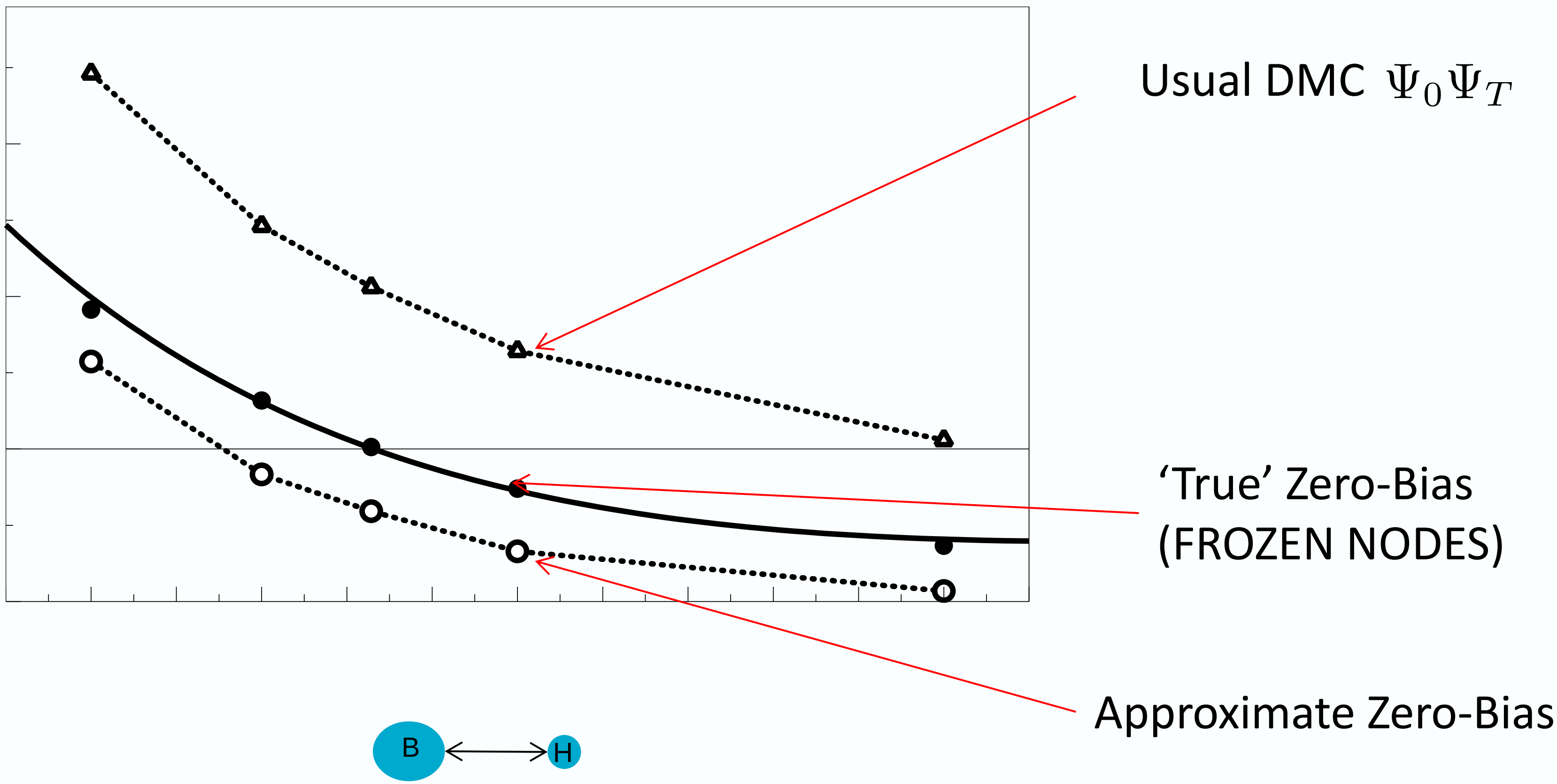
J. Phys.: Condens. Matter 22 074202 (2010)

- One solution: Ignore nodal response. Frozen nodes approx.

$$\partial_\lambda \Psi_T(\mathbf{r} = \mathbf{r}_N) = 0$$

DMC forces : BH

Works for many-fermion systems in the fixed-node approximation



Relation to Hellmann-Feynman Sampling

Gaudoin & Pitarke, PRL 99 126406 (2007)

- Consider $\partial_\lambda \Psi_T = 0$, i.e. no Zero Variance improvement

- Only contribution from branching term:

$$\frac{\partial_\lambda G}{G} = -\frac{\tau}{2}\left(A(\mathbf{r}') + A(\mathbf{r}) - 2\partial_\lambda E_T\right)$$ (same as HFS)

- Compare with full ZVZB branching term:

$$\frac{\partial_\lambda G_b}{G_b} = -\frac{\tau}{2}\left(\partial_\lambda E_L(\mathbf{r}') + \partial_\lambda E_L(\mathbf{r}) - 2\partial_\lambda E_T\right)$$

- HFS is ZBDMC without importance sampling.

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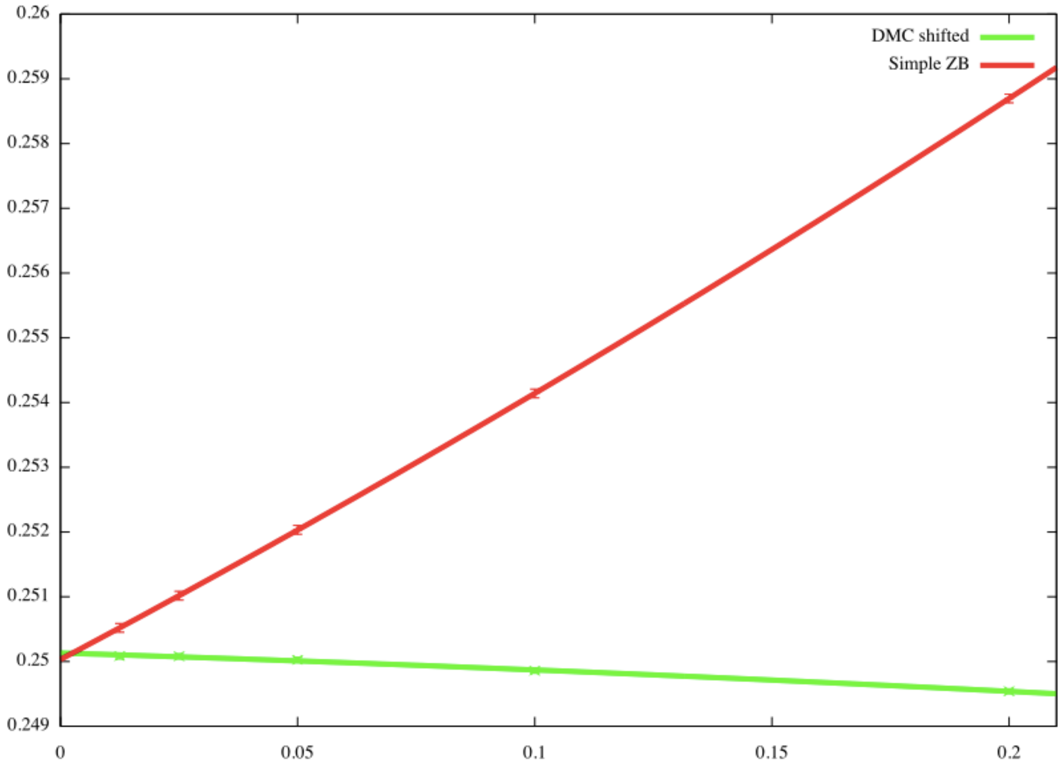
Finite time-step Bias

- We don't *really* do

$$f(\mathbf{r}_M, t + M\tau) = \int \prod_{i=0}^{M-1} G(\mathbf{r}_i, \mathbf{r}_{i+1}; \tau) f(\mathbf{r}_0, t) d\mathbf{r}_0 \ldots d\mathbf{r}_{M-1}$$



Metropolis DMC

$$G_b(\mathbf{r},\mathbf{r}')G_{dd}(\mathbf{r},\mathbf{r}') \to G_b(\mathbf{r},\mathbf{r}')K(\mathbf{r}'|\mathbf{r})$$

- Metropolis Hastings expression

$$K(\mathbf{r}'|\mathbf{r}) = G_{dd}(\mathbf{r},\mathbf{r}')\alpha(\mathbf{r},\mathbf{r}') + R(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

$$R(\mathbf{r}) = 1 - \int G_{dd}(\mathbf{r},\mathbf{y})\alpha(\mathbf{r},\mathbf{y})d\mathbf{y} \qquad \alpha(\mathbf{r},\mathbf{y}) = \min\left[1, \frac{\Psi_T^2(\mathbf{y})}{\Psi_T^2(\mathbf{r})}\frac{G_{dd}(\mathbf{y},\mathbf{r})}{G_{dd}(\mathbf{r},\mathbf{y})}\right]$$

- Re-write in terms of a single step

$$K(\mathbf{r}'|\mathbf{r}) = \int G_{dd}(\mathbf{r},\mathbf{y})\left\{\alpha(\mathbf{r},\mathbf{y})\delta(\mathbf{y}-\mathbf{r}') + [1-\alpha(\mathbf{r},\mathbf{y})]\delta(\mathbf{r}-\mathbf{r}')\right\}d\mathbf{y}$$

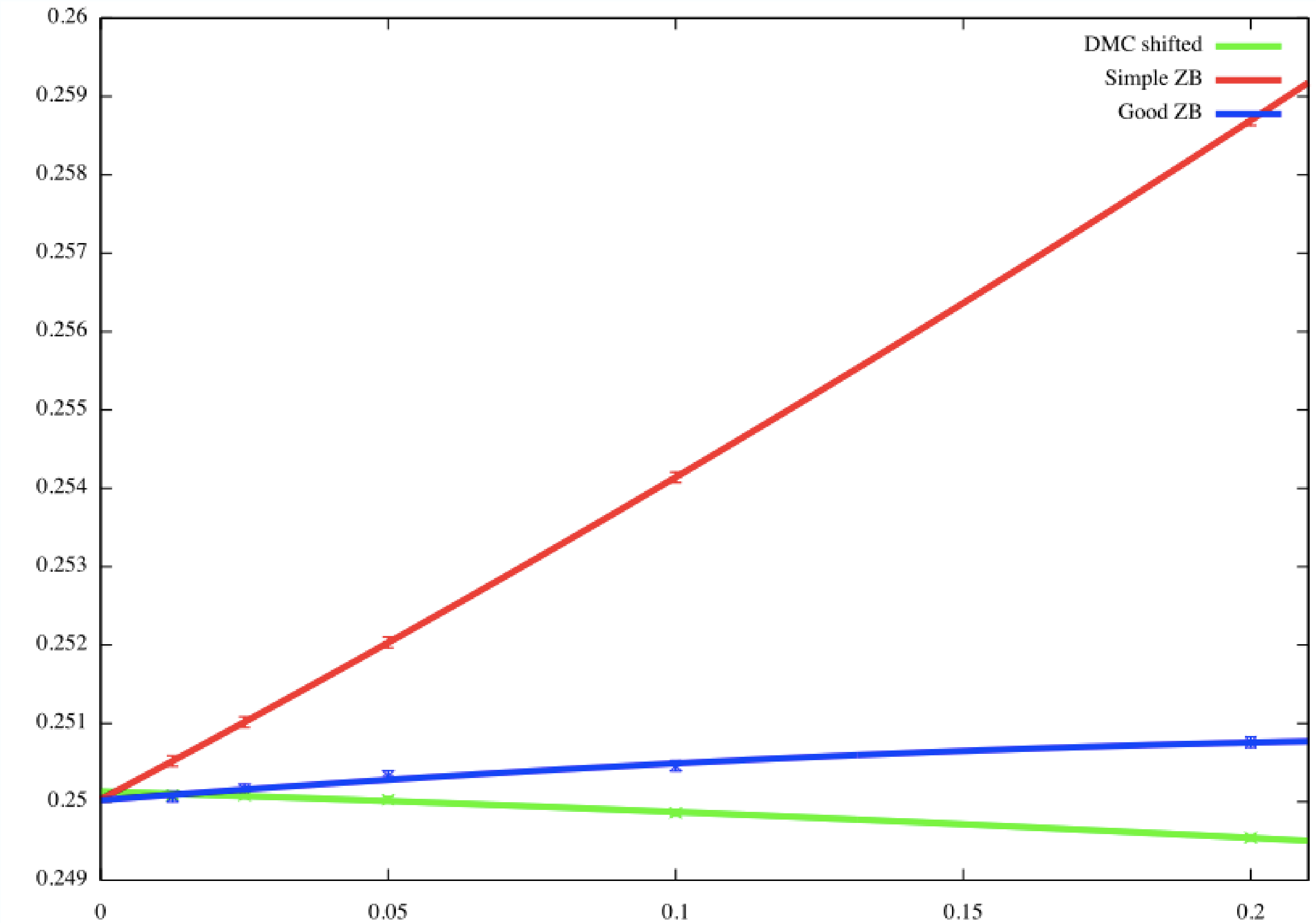
Metropolis ZBDMC

- Differentiate the complete weighted transition:

$$\partial_\lambda \left[G_b(\mathbf{r},\mathbf{r}')K(\mathbf{r}'|\mathbf{r})\right] = G_b(\mathbf{r},\mathbf{r}') \int G_{dd}(\mathbf{r},\mathbf{r}')\Bigg\{\alpha(\mathbf{r},\mathbf{y})\left(\frac{\partial_\lambda G_b(\mathbf{r},\mathbf{r}')}{G_b(\mathbf{r},\mathbf{r}')} + \frac{\partial_\lambda G_{dd}(\mathbf{r},\mathbf{y})}{G_{dd}(\mathbf{r},\mathbf{y})} + \frac{\partial_\lambda \alpha(\mathbf{r},\mathbf{y})}{\alpha(\mathbf{r},\mathbf{y})}\right)\delta(\mathbf{y}-\mathbf{r}') + [1-\alpha(\mathbf{r},\mathbf{y})]\left(\frac{\partial_\lambda G_b(\mathbf{r},\mathbf{r}')}{G_b(\mathbf{r},\mathbf{r}')} + \frac{\partial_\lambda G_{dd}(\mathbf{r},\mathbf{y})}{G_{dd}(\mathbf{r},\mathbf{y})} - \frac{\partial_\lambda \alpha(\mathbf{r},\mathbf{y})}{1-\alpha(\mathbf{r},\mathbf{y})}\right)\delta(\mathbf{r}-\mathbf{r}')\Bigg\} d\mathbf{y}$$

- Blue: Weight for accepted step
- Red: Weight for rejected step
- In practice, use complete expression weighted by accept/reject probability

Metropolis ZBDMC result



A quick experiment: Differential Operators

- Can't do differential operators with Forward-Walking.
- In principle, can with ZBDMC.

$$-\frac{\partial \Phi}{\partial \tau} = \left[-D\nabla^2 + V - E_T\right]\Phi \qquad -\frac{\partial f}{\partial \tau} = -D\nabla^2 f + 2D\nabla\cdot(f\mathbf{v}) + (E_L - E_T)f$$

$$D \to D(1+\lambda)$$

$$G_{dd,\lambda}(\mathbf{r}',\mathbf{r};\tau) = \frac{1}{(4\pi D(1+\lambda)\tau)^{d/2}} \exp\left[-\frac{1}{4D(1+\lambda)\tau}(\mathbf{r}'-\mathbf{r}-2D(1+\lambda)\tau\mathbf{v}(\mathbf{r}))^2\right]$$

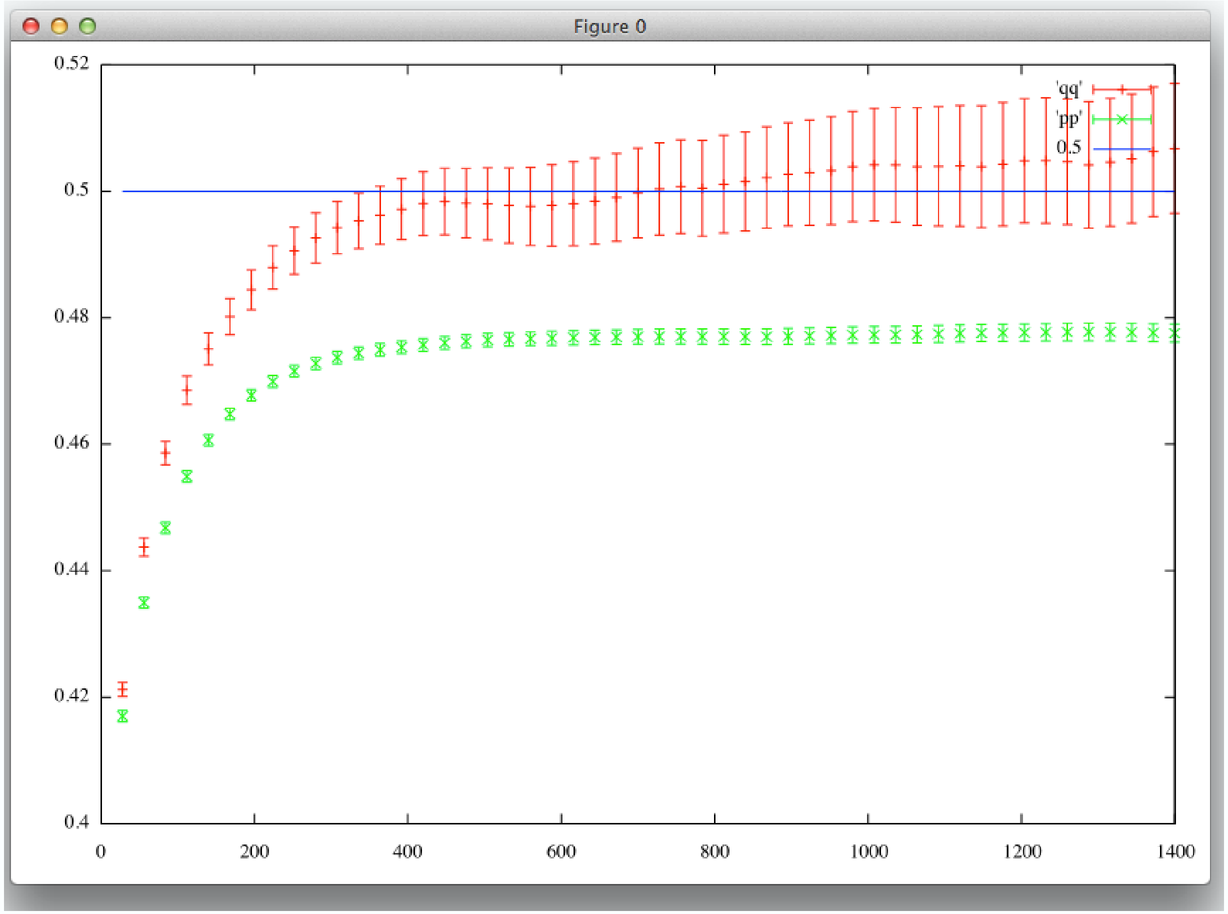
Kinetic

- Differentiate G

$$\left.\frac{\partial_\lambda G_{dd}}{G_{dd}}\right|_{\lambda=0} = -\frac{d}{2} + \frac{(\mathbf{r}' - \mathbf{r} - 2D\tau\mathbf{v}(\mathbf{r}))^2}{4D\tau} + \mathbf{v}\cdot(\mathbf{r}' - \mathbf{r} - 2D\tau\mathbf{v}(\mathbf{r})) + \nabla Q\cdot(\mathbf{r}' - \mathbf{r} - 2D\tau\mathbf{v}(\mathbf{r}))$$

- Drift-diffusion contributions even when Q=0.
- Constant unimportant.
- Major problems near nodes?
- Could some choice of Q improve it?

Example



- If just branch: get FW result, $\frac{T\Psi_T}{\Psi_T}$
- EXACT value, but large variance.