Energy derivatives in fixed-node QMC: unbiased estimates with finite variance

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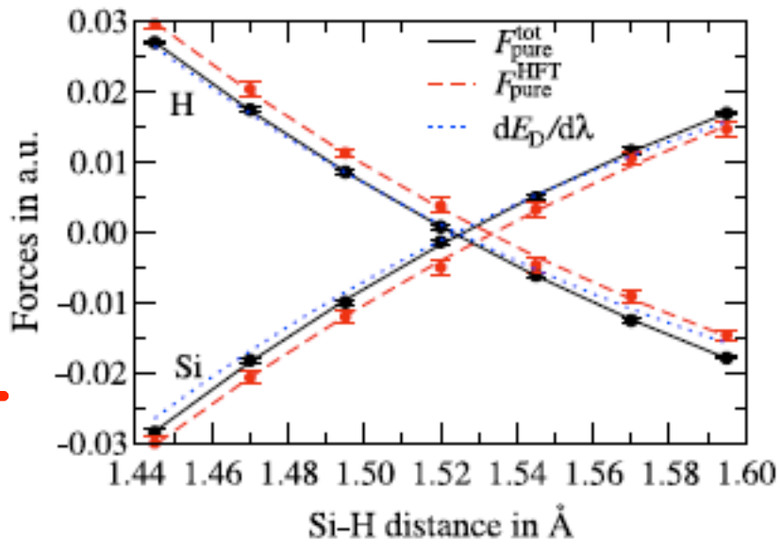
The forces evaluated using equation (21) yield bond lengths for the SiH molecule with an error (with respect to DMC energy calculations) of much less than 0.01 Å, which is acceptable for most purposes. Of course, before claiming that the problem of calculating DMC forces is 'solved', accurate results for heavier atoms and larger systems are required. To this we should add the issues of efficient generation of the pure probability distribution for large systems, overcoming the 'infinite variance' described in section 7, obtaining accurate forms for Ψ_T and $d\Psi_T/d\lambda$, and (hopefully) removing the second approximation in equation (21). Notwithstanding these



A.Badinski, P.D.Haynes, J.R.Trail and R.J.Needs (2010)

We want an estimator of the derivatives of E_{FN}
- with finite variance
- fully consistent with E_{FN}
- to second order

Energy derivatives in QMC

$$E = \int E_L P dX/Z = \langle E_L \rangle$$

$$E' = \langle E'_L + (E_L - E)(\ln P)' \rangle$$

$$E'' = \langle E''_L + (E_L - E)(\ln P)''$$

$$+(E_L - E)(\ln P)'(\ln P)' + 2(E'_L - E')(\ln P)' \rangle$$

$P = \Psi^2$	Variational Monte Carlo
$P = \Psi\Phi_{FN}$	Fixed-node QMC

these estimators have the zero-variance property
but their variance is actually infinite...

Fixed-node calculation by a Metropolis algorithm

- project a trial function in imaginary time

$$\Psi_\beta = e^{-\beta H/2}\Psi = (e^{-\tau H})^{P/2}\Psi \;\rightarrow \Psi_0 \qquad\qquad \tau = \beta/P$$

- $G(R, R'; \tau)$ short-time approximation of $\langle R|e^{-\tau H}|R'\rangle$

- express physical quantities as discretized path integrals

$$Z_\beta = \langle\Psi_\beta|\Psi_\beta\rangle = \int \Psi(R_0)\prod G(R_i, R_{i+1};\tau)\Psi(R_P)dX$$

$$= \int P(X)dX; \quad X = \{R_0, \ldots, R_P\}$$

$$E_\beta = \frac{1}{Z_\beta}\langle\Psi_\beta|H|\Psi_\beta\rangle = \frac{1}{Z_\beta}\int E_L(R_0)P(X)dX \geq E_0$$

- use a Metropolis algorithm (e.g. RQMC) to sample paths

a toy problem

1D particle in a box: $H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \gamma x, \qquad -L < x < L$

trial function (wrong on purpose): $\Psi(x) = \cos(kx)(1+\alpha x)$

sampling probability: $P(X) = \Psi(x_0)\prod G(x_i, x_{i+1}; \tau)\Psi(x_M)$

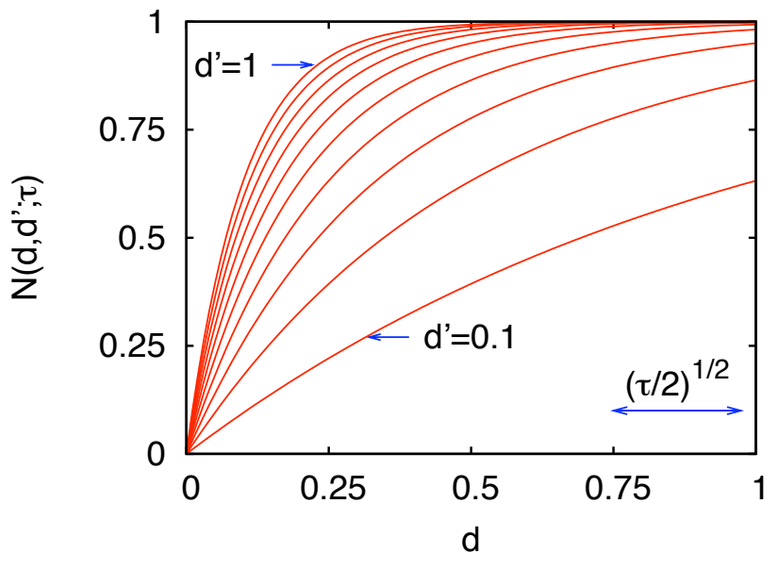
short time approximation:

$$G(x_i, x_j : \tau) = e^{-(x_i - x_j)^2/2\tau} e^{-\gamma(x_i + x_j)}\, N(x_i, x_j; \tau)$$

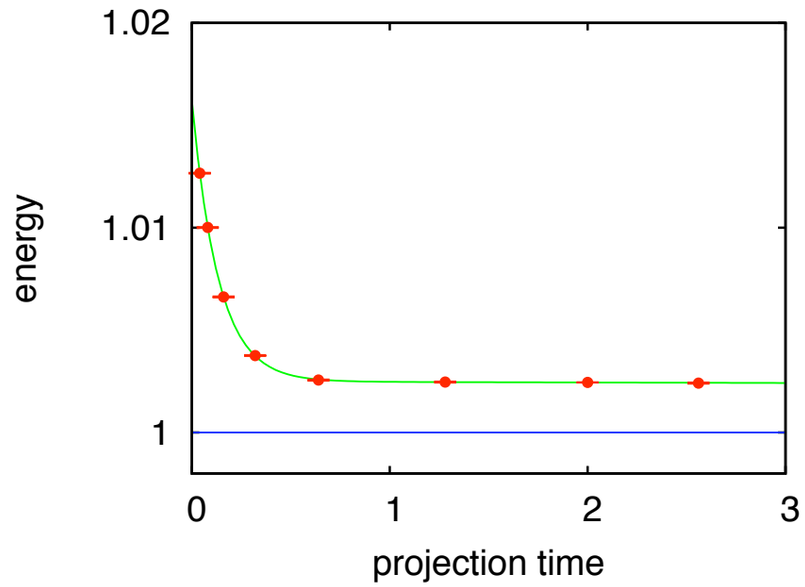
primitive nodal (Ceperley, 1996)

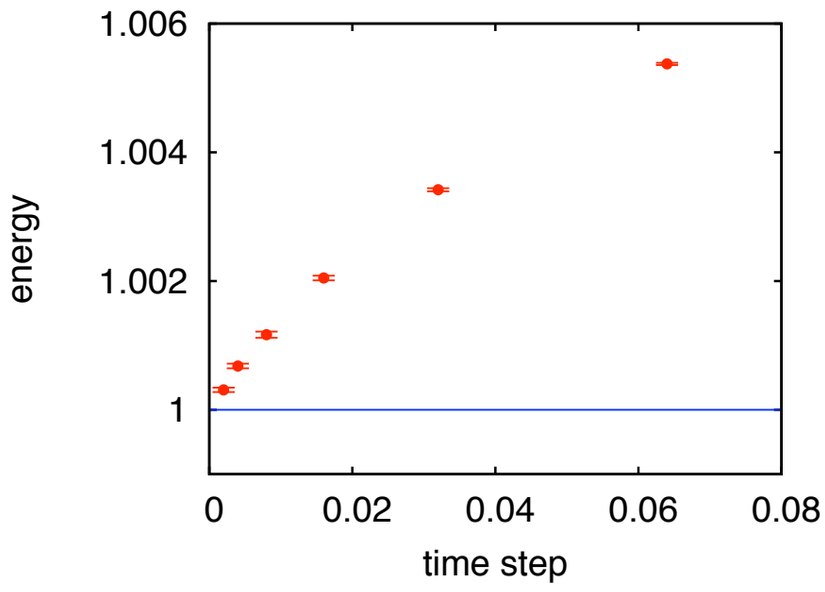
$$N(x_i, x_j; \tau) = 1 - e^{-2d(x_i)d(x_j)/\tau}$$

$$d(x_i) = \left| \frac{\Psi(x_i)}{\partial_x \Psi(x_i)} \right|$$

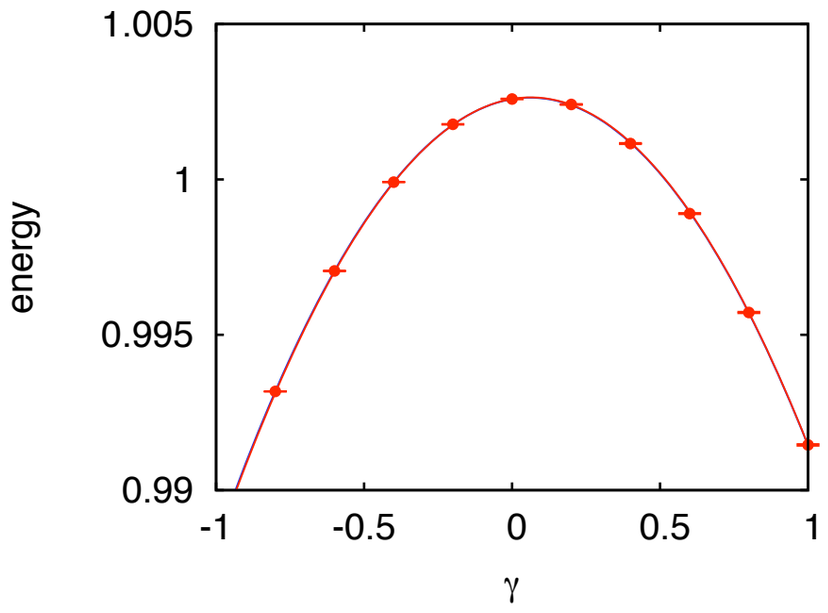


energy vs. projection time and time step





energy vs. γ



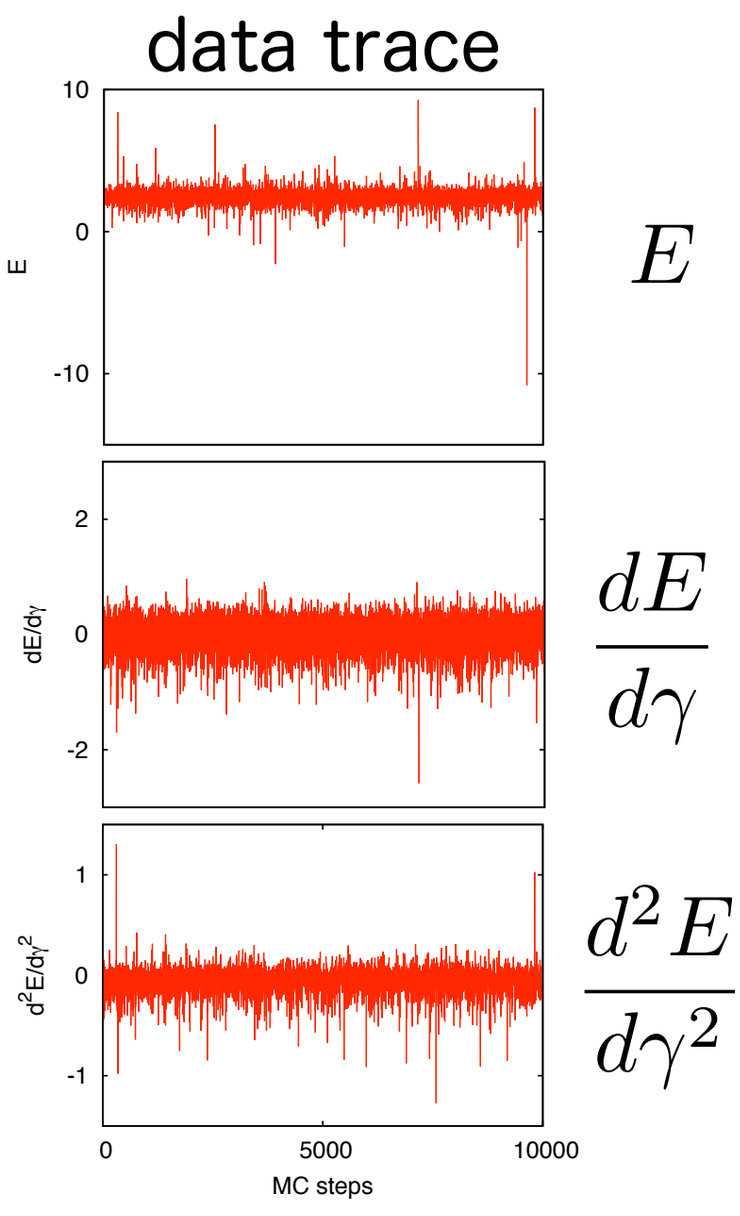
points: calculated for different γ's

line 1: from $E(0), E'(0), E''(0)$

line 2: fit to points

E', E'' consistent with E

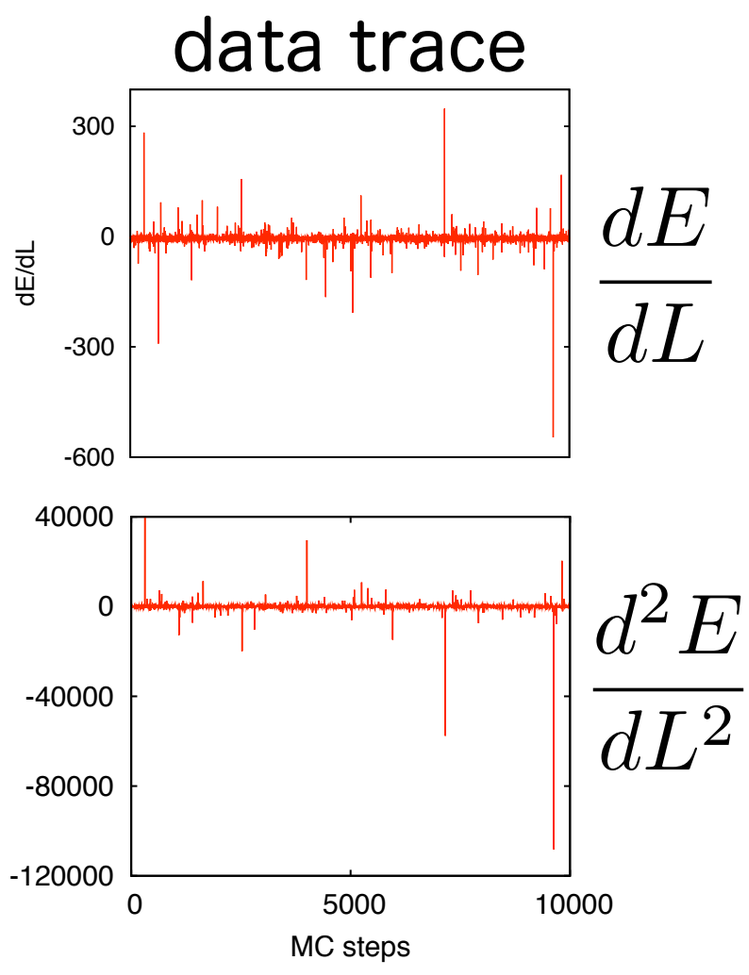
derivatives: $\frac{dE}{d\gamma}, \frac{d^2E}{d\gamma^2}$ “bosonic”, $\frac{dE}{dL}, \frac{d^2E}{dL^2}$ “fixed node”



E

$\frac{dE}{d\gamma}$

$\frac{d^2E}{d\gamma^2}$



$\frac{dE}{dL}$

$\frac{d^2E}{dL^2}$

infinite variance

$\frac{dE}{dL}, \frac{d^2E}{dL^2}$ have infinite variance:

$$\frac{dE}{dL} = \langle \frac{dE_L}{dL} + (E_L - E)\frac{d\ln P}{dL} \rangle$$

$$E_L(x) = \frac{1}{2}\left(\frac{\pi}{L}\right)^2 + \frac{\alpha}{1+\alpha x}\frac{\pi}{L}\tan\frac{\pi}{L}x$$

$$P(X) = \Psi(x_0)(1 - e^{-2d_0 d_1/\tau})(1 - e^{-2d_1 d_2/\tau}) \times \cdots$$

near a node:

$$E_L \sim 1/d \qquad P(x_i) \sim d^2(x_i)$$

$$dE_L/dL \sim 1/d^2 \qquad d\ln P/dL \sim 1/d$$

the integral of PE'_L is bounded, but the integral of $P(E'_L)^2$ is not (likewise for $E_L(\ln P)'$)

as the walls are displaced, $L_0 \to L$, we change variable:

$$E(L) = \frac{\int dx E_L(L, y(L,x)) P(L, y(L,x)) J}{\int dx P(L, y(L,x)) J}$$

$x \to y(L,x) = xL/L_0$

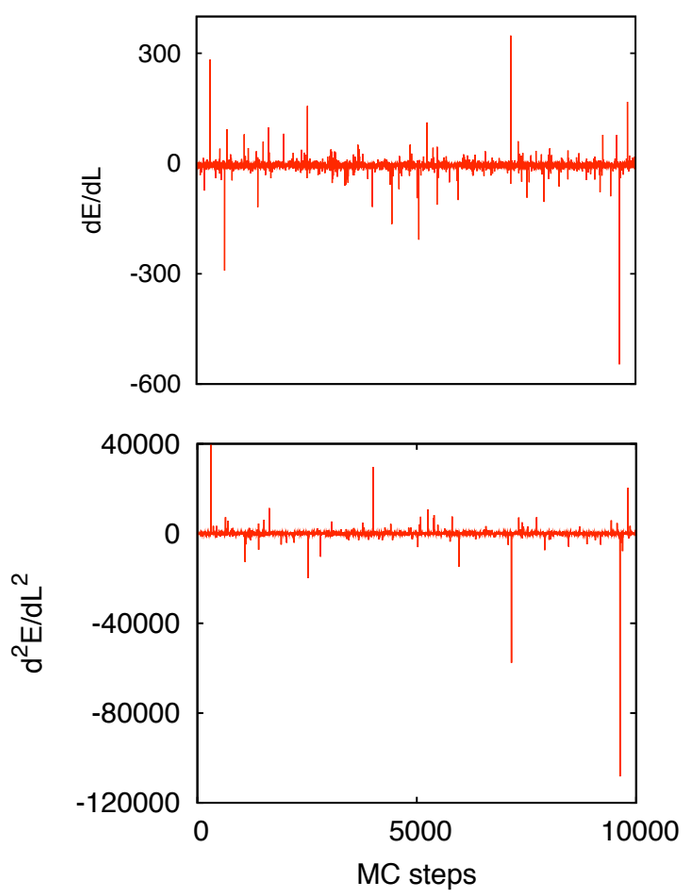
Jacobian $J = L/L_0$

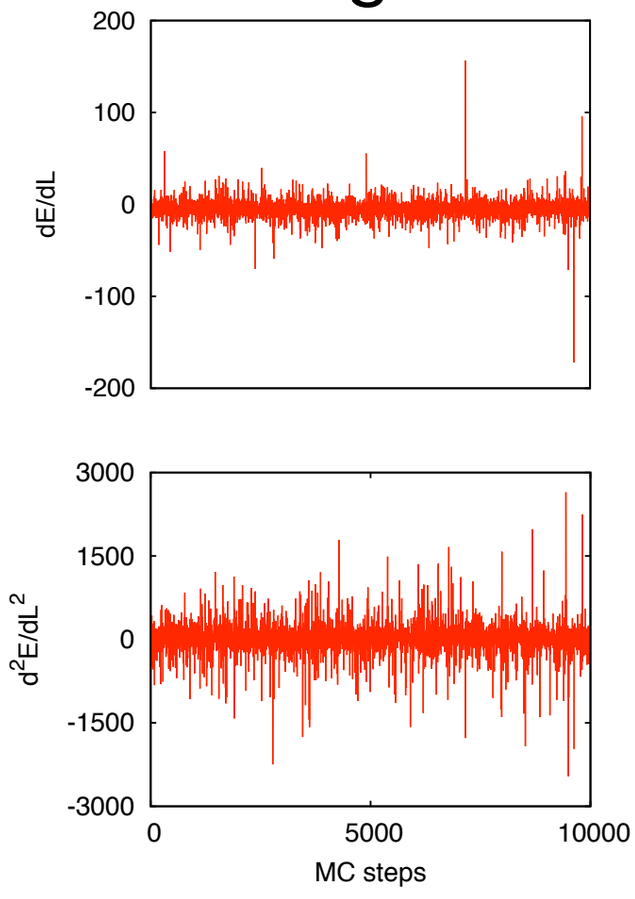
near the nodes, d remains unchanged upon displacing L:

$d(L_0, x) \sim d(L, y(L,x))$ ⟶ derivatives have finite variance.

(trade-off: change of variable puts some noise elsewhere,
e.g. in the free-particle action)

data trace without / with change of variable





estimators of E', E'' have finite variance

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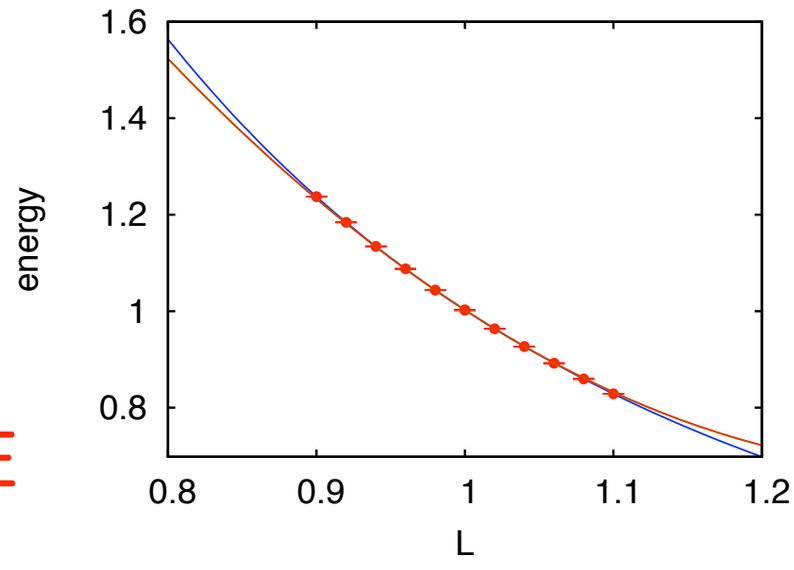
blue line: polynomial fit to points

(green: its quadratic part)

red: $E + E'(L-1) + \frac{1}{2}E''(L-1)^2$

E', E'' consistent with interpolation of E



lithium dimer

Slater-Jastrow trial function:

- 1s,2s,2p STO 3G HF orbitals
- fit LCAO coefficients vs. n-n distance
- e-n cusp correction
- one-parameter e-e Jastrow $\exp(ar/(1+br))$

Probability density: $P(X) = \Psi(R_0) \prod G(R_i, R_{i+1}; \tau) \Psi(R_M)$

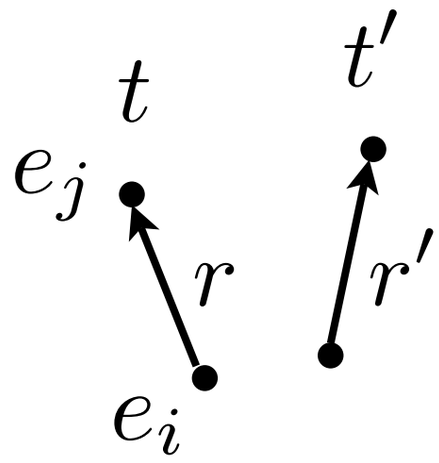
short time approximation:

$$G(R_i, R_{i+1}; \tau) = e^{-(R_i - R_{i+1})^2/2\tau} (1 - e^{-2 d_i d_{i+1}/\tau}) e^{-\sum u(\mathbf{r}_{\alpha\beta}^{(i)}, \mathbf{r}_{\alpha\beta}^{(i+1)})}$$

free-particle nodal pair product

cumulant approximation to pair action (Ceperley, 1983)

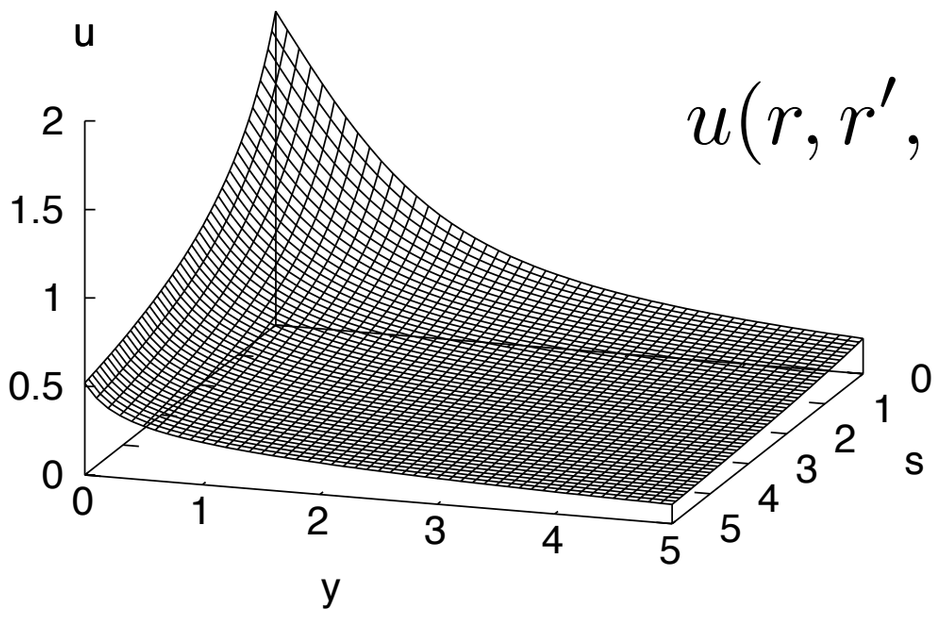
$$G(R', R, \epsilon) \propto \mathrm{e}^{-(R-R')^2/2\epsilon} \left(1 - \mathrm{e}^{-2dd'/\epsilon}\right) \mathrm{e}^{-\sum_{i<j} u(\mathbf{r}_{ij}, \mathbf{r}'_{ij}, \epsilon)}$$



$$s = |r - r'| \, (2\hbar^2\epsilon/\mu)^{-1/2}$$

$$y = (r + r' + |r - r'|) \, (2\hbar^2\epsilon/\mu)^{-1/2}$$

$$\gamma = e_i e_j (2\epsilon\mu/\hbar^2)^{-1/2}$$



$$u(r, r', \epsilon) = \gamma \int_0^1 d\lambda \frac{1}{y + 2s\lambda} \mathrm{erf}\left(\frac{y + 2s\lambda}{2[\lambda(1-\lambda)]^{1/2}}\right)$$

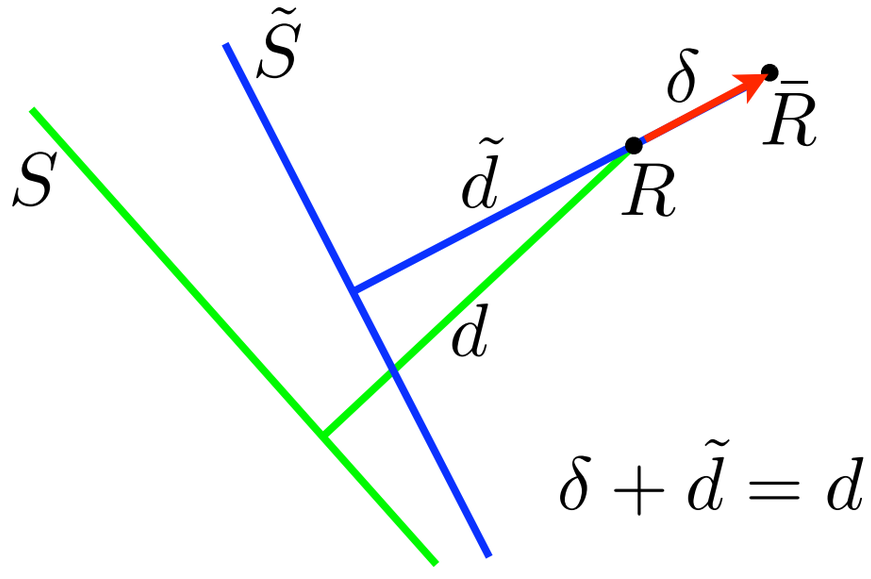
one two-dimensional table

$$dE/d\lambda \simeq (E(\lambda+\Delta) - E(\lambda))/\Delta$$

$\lambda \to \lambda + \Delta$ finite increment

$S \to \tilde{S}$ change of nodal surface

$d \to \tilde{d}$ change of nodal distance

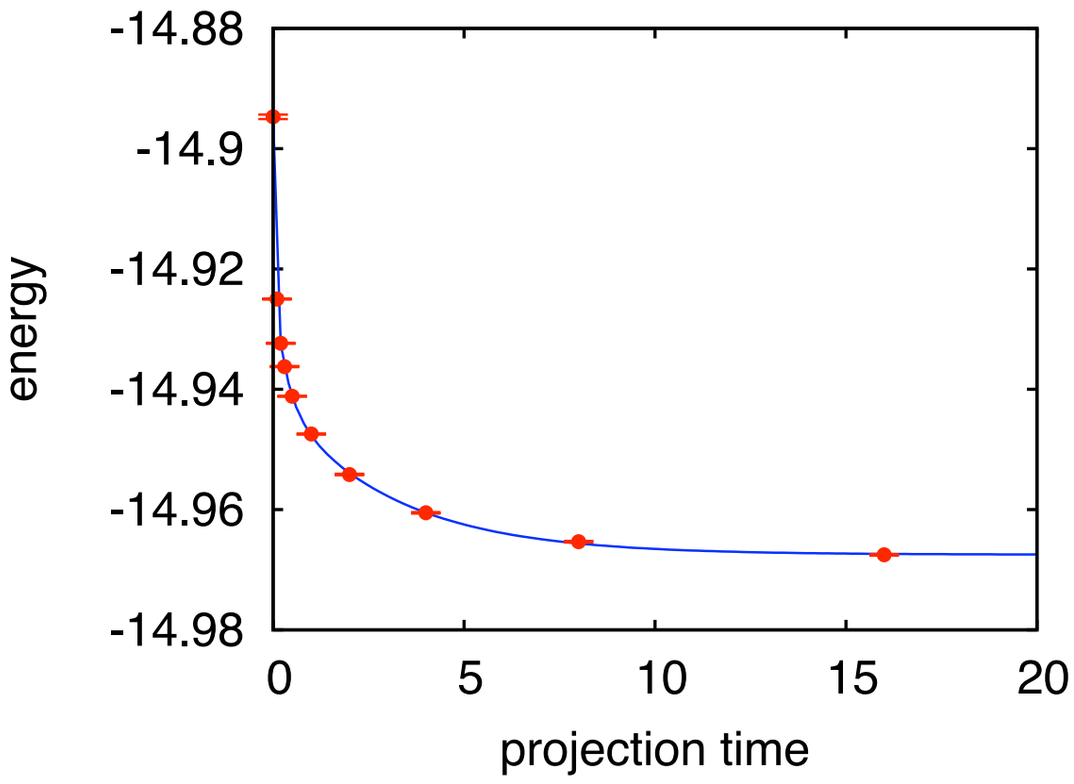


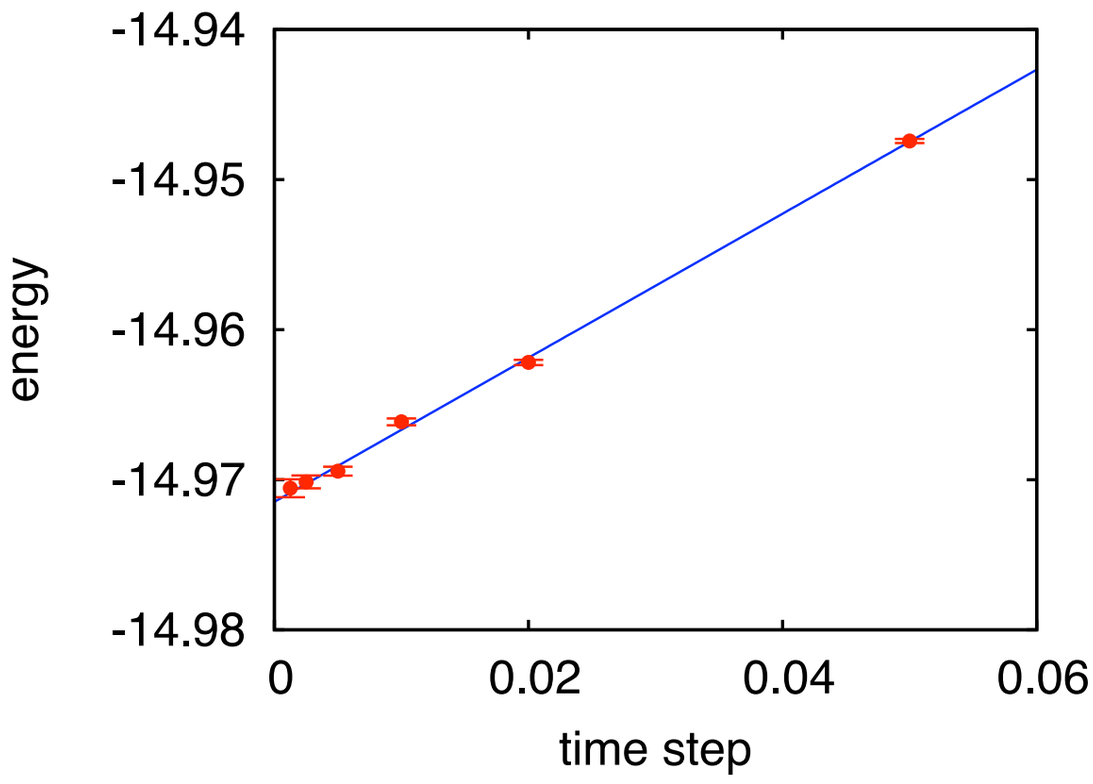
change variables near the nodes so that : $d = d$

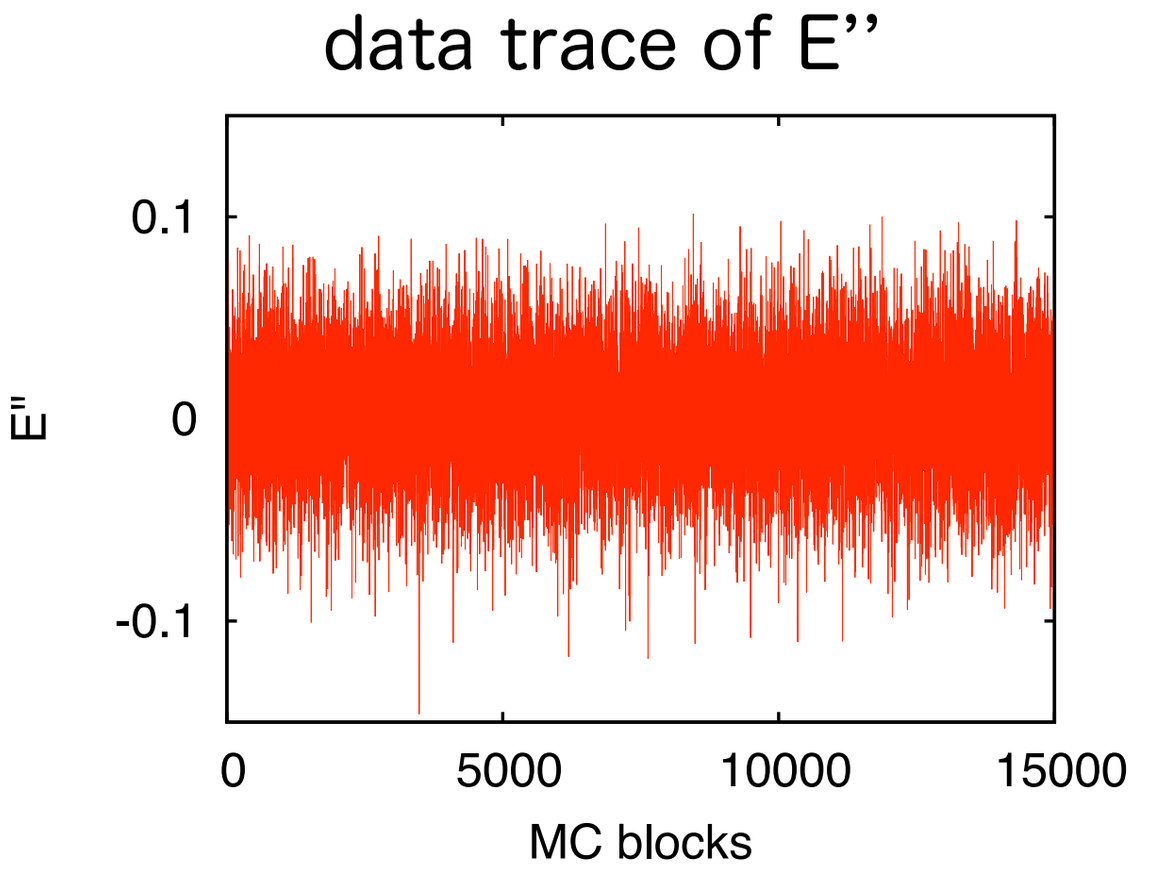
$$\bar{R} = R + \xi(d)(d - \tilde{d})\hat{\tilde{d}}$$

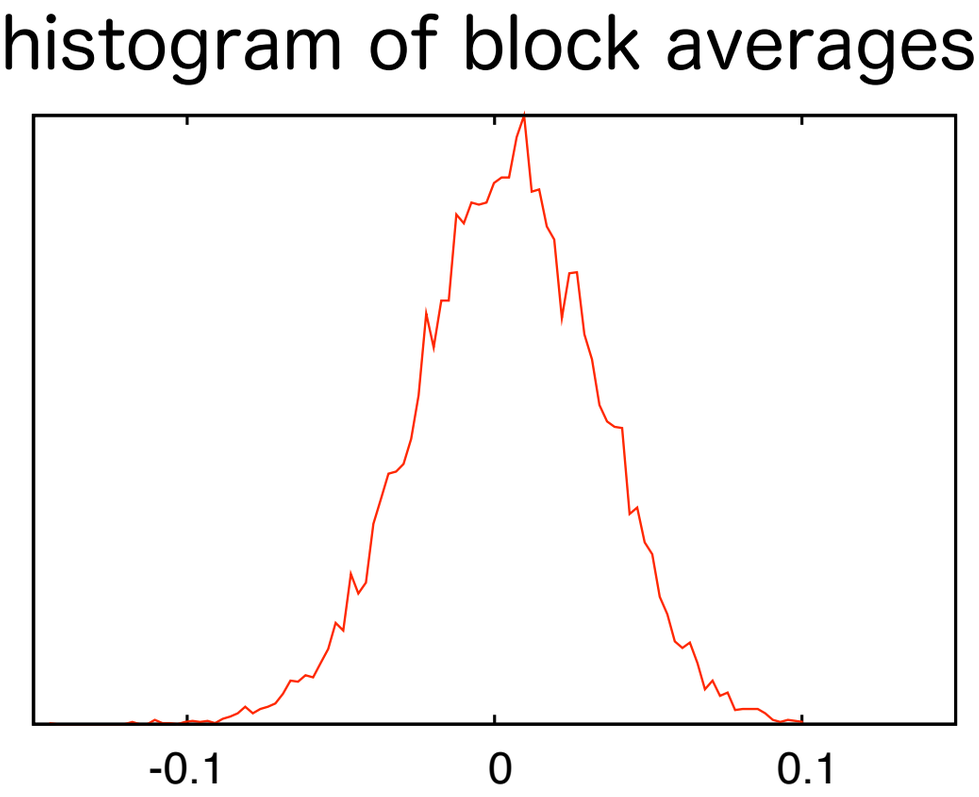
$\xi(d)$ smoothly goes from 0 to 1 as $d \to 0$

$J = 1 - (\tilde{d} - d)\xi'(d)$ (neglecting wave function curvature)


-14.88
-14.9
-14.92
-14.94
-14.96
-14.98
energy
0
5
10
15
20
projection time

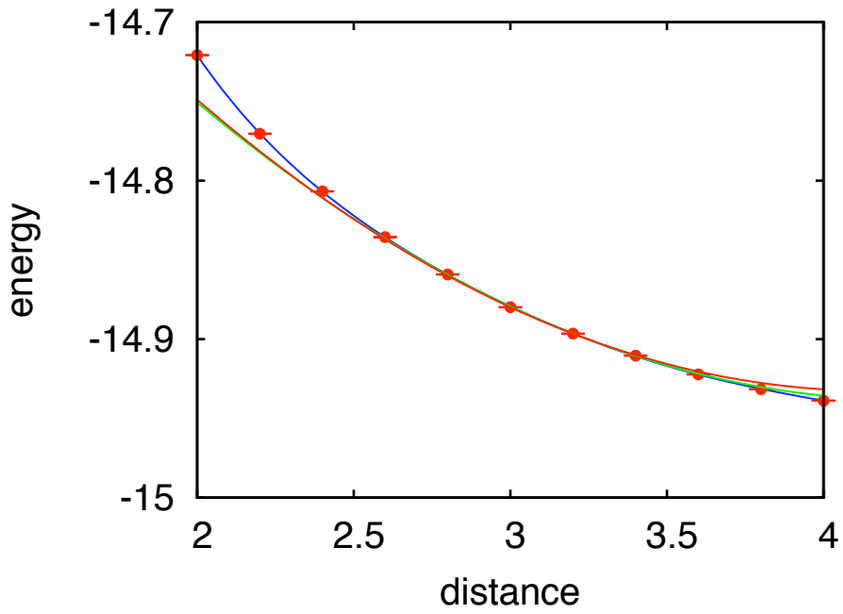

-14.94
-14.95
-14.96
-14.97
-14.98
energy
0
0.02
0.04
0.06
time step

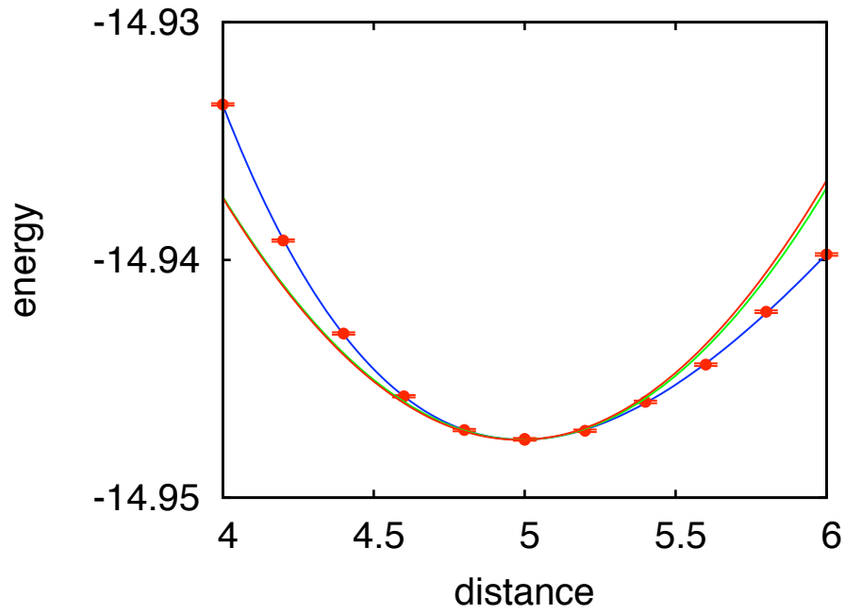

data trace of E''
0.1
0
-0.1
E''
0
5000
10000
15000
MC blocks


histogram of block averages
-0.1
0
0.1

	calc.	fit
E’	-0.9198(36)	-0.9226
E”	0.0791(48)	-0.0773

	calc.	fit
E’	0.00036(12)	0.00018
E”	0.02106(84)	0.02082





blue line: polynomial fit to energies
green line: quadratic part of the fit
red line: quadratic expansion from calculated derivatives