Monte Carlo in quantum systems

VARIATIONAL MONTE CARLO (VMC)

M. Peressi - UniTS - Laurea Magistrale in Physics
Laboratory of Computational Physics - Unit XII

Variational Monte Carlo

A stochastic way of calculating **expectation values of observables** in many-body (in general) systems using a **trial wavefunction** which depends on PARAMETERS.

=> Which are the best parameters?

i.e.:
=> Which is the most reliable expectation value?

=> Which is the best trial wavefunction?

A method based on:
variational principle + Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm

Variational Monte Carlo

1) Start from a trial wavefunction (wfc)

done in Lecture VII for a single-particle problem (harmonic oscillator)

2) Calculate the expectation value of the many-body hamiltonian $\mathcal{H}$ or in general of other observables $\mathcal{O}$ on the wfc transforming the integral in a form suitable for MC integration

3) Change parameters and recalculate the expectation value on the new wfc.

4) Iterate to reach the best estimate of the expectation value

With VMC one can obtain exact properties only if the trial wavefunction is an **exact** wavefunction of the system; it is a **variational** method to find the ground state.

Quantum averages - I

(Ground) state average:

$$< \mathcal{O} >_\psi = \frac{\int \psi^*(R)\mathcal{O}\psi(R)dR}{\int |\psi(R)|^2 dR}$$

R: compact notation for the whole set of variables of the many-body wfc

Quantum averages - I

(Ground) state average:

$\psi(R)\psi^{-1}(R)$

$$< \mathcal{O} >_\psi = \frac{\int \psi^*(R)\mathcal{O}\psi(R)dR}{\int |\psi(R)|^2 dR}$$

Quantum averages - I

(Ground) state average:

$\psi(R)\psi^{-1}(R)$

$$< \mathcal{O} >_\psi = \frac{\int \psi^*(R)\mathcal{O}\psi(R)dR}{\int |\psi(R)|^2 dR}$$

$$= \int \left[\frac{|\psi(R)|^2}{< \psi|\psi >}\right] \left[\frac{\mathcal{O}\psi(R)}{\psi(R)}\right] dR \equiv \int \underline{w(R)}\,\underline{\mathcal{O}_L(R)}dR$$

probability (weighting factor)

"local" operator

Quantum averages - II

integrals in many variables ({R}) =>
suitable for importance sampling - Monte Carlo integration:

$$< \mathcal{O}_L >= \int w(R)\mathcal{O}_L(R)dR \approx \frac{1}{M}\sum_{i=1}^{M}\mathcal{O}_L(R_i)$$

provided that the configurations i are distributed with the probability $w(R_i) = \frac{|\psi(R_i)|^2}{\langle\psi|\psi\rangle}$

error ~ $1/\sqrt{M}$

VMC on one trial wfc - I

Details for the calculation of quantum averages:

2) Calculate the expectation value of the many-body hamiltonian $\mathcal{H}$ on the wfc transforming the integral into a form suitable for MC integration

2a) Equilibration phase:

a walker consisting of an initially random set of particle positions {*R*} is propagated according to the Metropolis algorithm, in order to equilibrate and start sampling $|\psi(\{R\})|^2$. If the problem is many-body, a new configuration can be obtained by moving just one particle and the others are unchanged.

2b) Accumulation phase:

New configurations are generated and energies and other observables are accumulated for statistical analysis.

VMC on one trial wfc - II

I. **Equilibration phase:**

1. Generate initial configuration using random positions for the particles.
2. For every particle* in the configuration:
   1. Propose a move from **r** to **r'**
   2. Compute $w = |\Psi(\mathbf{r}')/\Psi(\mathbf{r})|^2$
   3. Accept or reject move accordingly to Metropolis probability $\min(1, w)$
3. Repeat configuration moves until equilibrated

2. **Accumulation phase:**

1. For every particle in the configuration:
   1. Propose a move from **r** to **r'**
   2. Compute $w = |\Psi(\mathbf{r}')/\Psi(\mathbf{r})|^2$
   3. Accept or reject move accordingly to Metropolis probability $\min(1, w)$
   4. Accumulate the contribution to the local energy and other observables at **r** (if move is rejected) or **r'** (if move is accepted)
2. Repeat configuration moves until sufficient data are accumulated

In this algorithm, a new configuration is considered when one particle is moved, individually.

($*$) If the problem is many-body, **r** and **r'** are single-particle coordinates and therefore differ from **R**.

The variational principle - I

For the ground state:
if $\psi(R)$ is a trial wavefunction and E_0 is the exact ground state eigenvalue, we have:

$$< E >_\psi \quad \geq E_0$$

and the "=" holds if and only if the trial wavefunction is the exact ground state wavefunction ($\psi \equiv \psi_0$).

The variational principle - II

Basic idea for VMC:

calculate $<\mathscr{O}>$ over different trial wavefunctions

and choose the best...

VMC - standard procedure - I

1) Start from a trial wavefunction with a set of parameters α_0

2) Calculate the expectation value of the operator $\mathscr{O}$ with a MC integration:

$$\langle \mathcal{O}_L \rangle_{\alpha_0} = \frac{\int |\psi_{\alpha_0}(R)|^2 \mathcal{O}_L(R) dR}{\int |\psi_{\alpha_0}(R)|^2 dR} = \int w_{\alpha_0}(R) \mathcal{O}_L(R) dR \approx \frac{1}{M} \sum_{i=1}^{M} \mathcal{O}_L(R_i^{\{\alpha_0\}})$$

3) Change the set of parameters α and recalculate from scratch the expectation value on the new wfc:

$$\langle \mathcal{O}_L \rangle_{\alpha} = \frac{\int |\psi_{\alpha}(R)|^2 \mathcal{O}_L(R) dR}{\int |\psi_{\alpha}(R)|^2 dR} = \int w_{\alpha}(R) \mathcal{O}_L(R) dR \approx \frac{1}{M} \sum_{i=1}^{M} \mathcal{O}_L(R_i^{\{\alpha\}})$$

($\mathscr{O}_L$(R) changes (contains the new parameters) but also the w(R) and hence the set of points {R_i} change)

4) Iterate to reach the best estimate of the expectation value

VMC - standard procedure - II

Two problems:

1) time consuming

2) stochastic errors can be comparable to differences between expectation values for different sets of parameters

solution?

“reweighting” technique

A better idea: use the same sampling for similar trial wfc, $\psi_\alpha, \psi_{\alpha_0}$.

Start from α_0. Define: $r_\alpha(R) \equiv \frac{|\psi_\alpha(R)|^2}{|\psi_{\alpha_0}(R)|^2}$

Remembering that : $w_\alpha(R) = \frac{|\psi_\alpha(R)|^2}{\int |\psi_\alpha(R)|^2 dR}$, and similar for w_{α_0}, we have :

$$\langle \mathcal{O}_L \rangle_\alpha = \frac{\int |\psi_\alpha(R)|^2 \mathcal{O}_L(R) dR}{\int |\psi_\alpha(R)|^2 dR} = \frac{\int r_\alpha(R) |\psi_{\alpha_0}(R)|^2 \mathcal{O}_L(R) dR}{\int r_\alpha(R) |\psi_{\alpha_0}(R)|^2 dR} =$$

$$= \frac{\int r_\alpha(R) w_{\alpha_0}(R) \mathcal{O}_L(R) dR}{\int r_\alpha(R) w_{\alpha_0}(R) dR} \approx \frac{\sum_i r_\alpha(R_i) \mathcal{O}_L(R_i)}{\sum_i r_\alpha(R_i)}$$

where the set {R_i} is generated according to $w_{\alpha_0}(R)$

(Check that: $A(\alpha, \alpha_0) \equiv \frac{\left(\sum_i r_\alpha(R_i)\right)^2}{\sum_i r_\alpha^2(R_i)} \approx M$; if not, generate other points)

“zero-variance” property

A very useful note:

if a trial wavefunction is the exact one,

the variance in the numerical estimate of $<\mathcal{O}>$ ($<\mathcal{H}>$)

is zero:

$$\sigma^2 \equiv < \psi|(\mathcal{H} - < \mathcal{H} >)^2|\psi > = 0$$

the criterion to find the best parameter set is precisely defined!

(remark: applicable also to excited states if the exact excited state wfc is contained in the trial wfc set)

possible problems/remarks

- nodes of the trial wfc: not a real problem, provided the trial moves are large enough to overcome nodes
- $\mathcal{H}(R)\psi(R)$ must be defined everywhere
- $\psi(R)$ must have the proper symmetry (bosons or fermions) and proper boundary conditions

Trial wavefunction

The reliability of the VMC estimates
are crucially dependent
on the quality of the trial wfc

Trial wavefunctions for many-body systems

The choice of trial wavefunction is critical in VMC calculations. All observables are evaluated with respect to the probability distribution $|\Psi_T(\mathbf{R})|^2$. The trial wavefunction, $\Psi_T(\mathbf{R})$, must well approximate an exact eigenstate for all $\mathbf{R}$ in order that accurate results are obtained. Improved trial wavefunctions also improve the importance sampling, reducing the cost of obtaining a certain statistical accuracy.

Typical form chosen for the many-body trial wfc:

$$\psi = \exp\left[\sum_{i<j}^{N} -u(r_{ij})\right] \; det[\theta_k(r_i, \sigma_i)]$$

Jastrow or two-body correlation function

Slater determinant on single-particle spin-orbitals

Programs:

on
$/home/peressi/comp-phys/XII-QMC/
[do: $cp /home/peressi/.../XII-QMC/* .]
or on moodle2

metropolis_gaussian.f90
(see also: metropolis_sampling.f90, Unit VII)
metropolis_parabola.f90
metropolis_parabola_vs_a.f90
job_gaussian
job_parabola

Exercises

1) Harmonic oscillator solved with VMC : (a particularly simple example, where everything could be done also analytically, used to test the numerical algorithm)

$$\mathcal{H} = E_{kin} + E_{pot} = \frac{1}{2}p^2 + \frac{1}{2}x^2$$ $(\hbar = 1,\ m = 1)$

1.a) Trial wfc.: $\psi(x) = Ae^{-\beta x^2}$ or $Ae^{-x^2/(4\sigma^2)}$ with : $\beta = \frac{1}{4\sigma^2}$

$$E_{pot,L}(x) \equiv \frac{E_{pot}\psi(x)}{\psi(x)} = \frac{1}{2}x^2$$

$$E_{kin,L}(x) \equiv \frac{E_{kin}\psi(x)}{\psi(x)} = \frac{-\frac{1}{2}\frac{d^2}{dx^2}\psi(x)}{\psi(x)} = -2\beta^2x^2 + \beta$$

$$\langle E_{pot,L}\rangle = \frac{1}{8\beta}, \qquad \langle E_{kin,L}\rangle = \frac{1}{2}\beta$$

$$\frac{d\,\langle E_{tot,L}(\beta)\rangle}{d\beta} = 0 \Longrightarrow \beta = \frac{1}{2}, E_{tot} = \frac{1}{2}$$

variance:

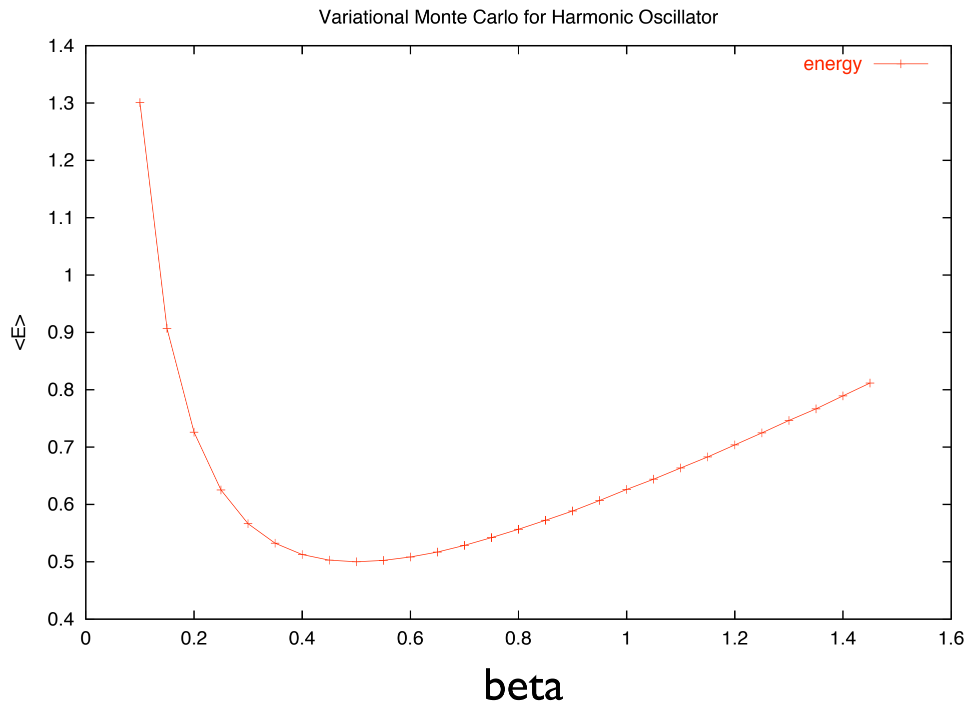
$$\sigma_E^2 = \langle E_{tot,L}^2 \rangle - \langle E_{tot,L} \rangle^2 =$$

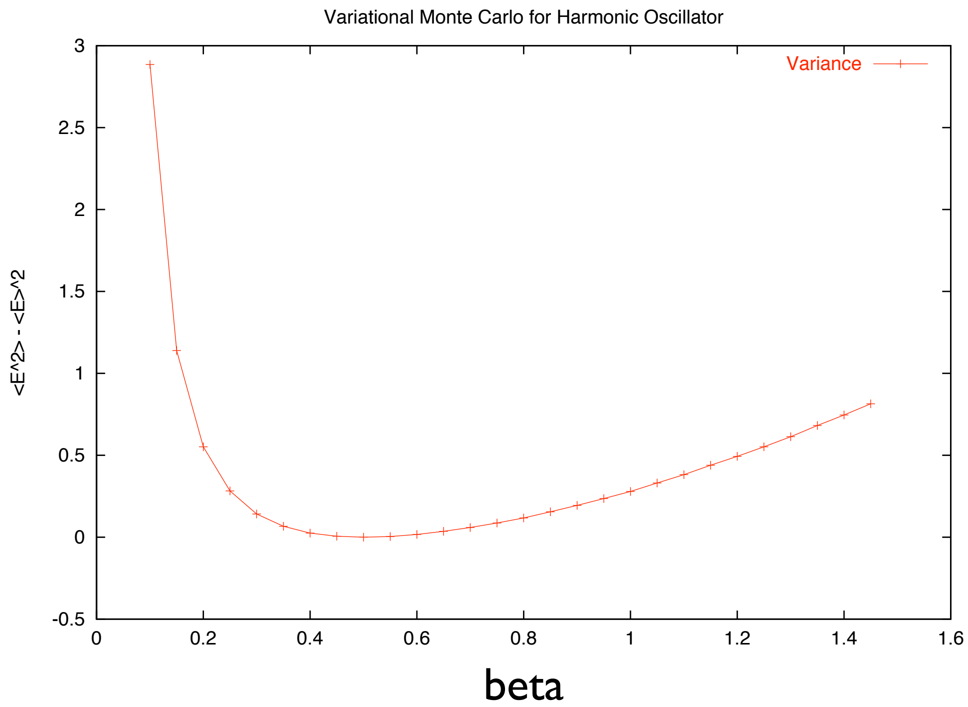
$$= \left\langle \left(\frac{1}{2}x^2 - 2\beta^2 x^2 + \beta \right)^2 \right\rangle - \left(\frac{1}{8\beta} + \frac{1}{2}\beta \right)^2 =$$

$$= \frac{1}{32\beta^2} + \frac{1}{2}\beta^2 - \frac{1}{4}$$

For the exact ground state: $\beta = \frac{1}{2} \quad \Rightarrow \quad \sigma_E = 0$

Notice the zero-variance property for this problem:





$$300 \text{ walkers}^{(*)} \text{ and } \texttt{MCSteps} = 10{,}000$$

(*) In this simple case, even a single walker is enough.

Many independent walkers starting at different random points in the configuration space could be necessary for a better sampling **in more complicate systems** (a single walker might have trouble locating all of the peaks in the distribution; using a large number of randomly located walkers improves the probability that the distribution will be correctly generated)

Exercises

1) Harmonic oscillator solved with VMC:

$$\mathcal{H} = E_{kin} + E_{pot} = \frac{1}{2}p^2 + \frac{1}{2}x^2$$

1.b) Trial wfc.:

(reasonable choice:
satisfies boundary conditions; correct symmetry; only one parameter)

$$\psi(x) = \begin{cases} B(a^2 - x^2), & \text{for } |x| < a; \\ 0, & \text{for } |x| > a. \end{cases}$$

Normalization: $\int_{-a}^{a} B^2(a^2 - x^2)^2 dx = 1 \implies B^2 = \frac{15}{16a^5}$

$$E_L(x) = \frac{\mathcal{H}\psi(x)}{\psi(x)} = \left(\frac{1}{a^2 - x^2} + \frac{1}{2}x^2\right)$$

(in this case the problem can be analytically solved:)

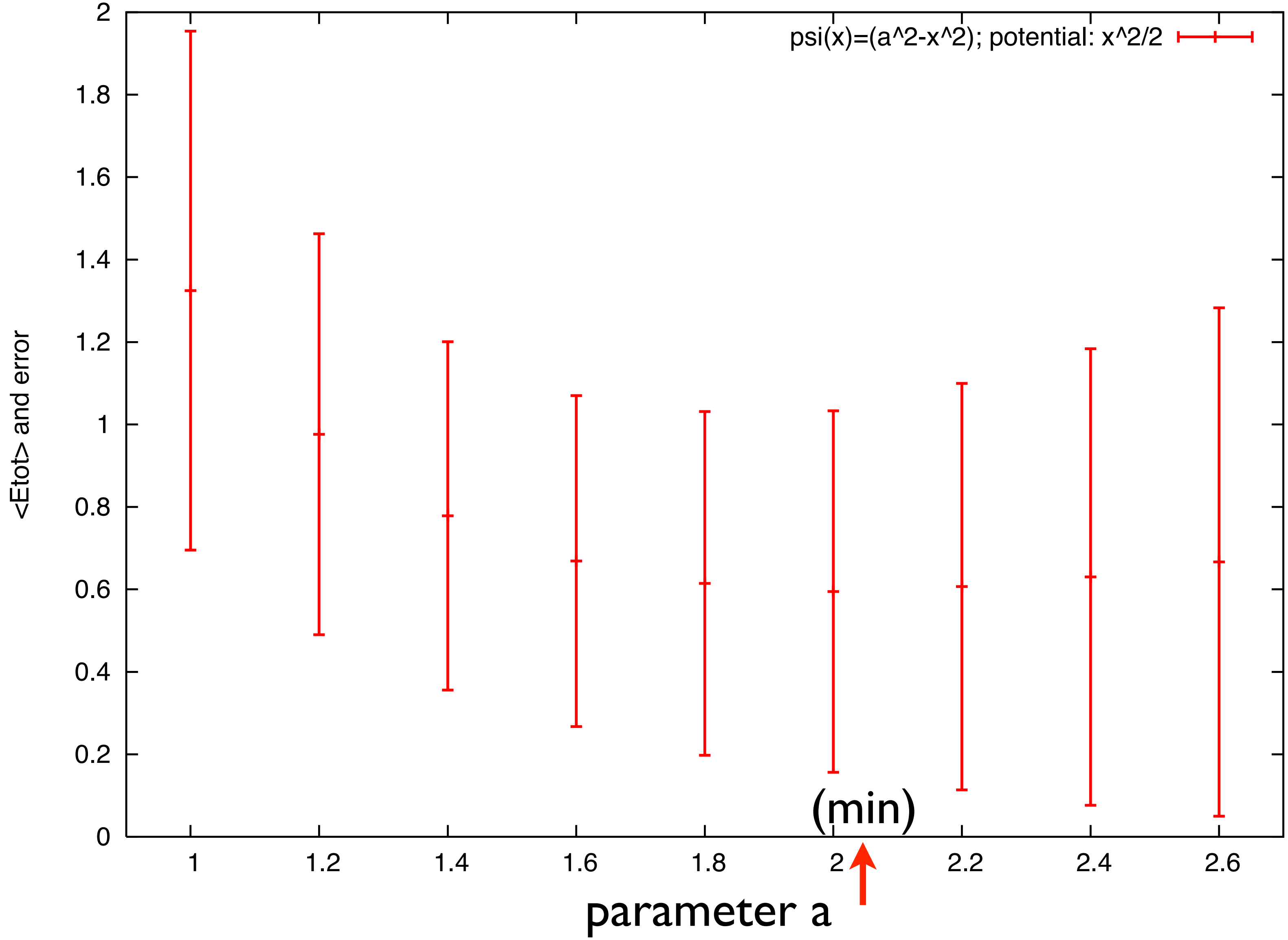
$$\langle E_{tot,L}\rangle = \int_{-a}^{a} \frac{|\psi(x)|^2}{\langle\psi|\psi\rangle} E_L(x)dx = \int_{-a}^{a} B^2(a^2 - x^2)^2 \left(\frac{1}{a^2 - x^2} + \frac{1}{2}x^2\right) dx$$

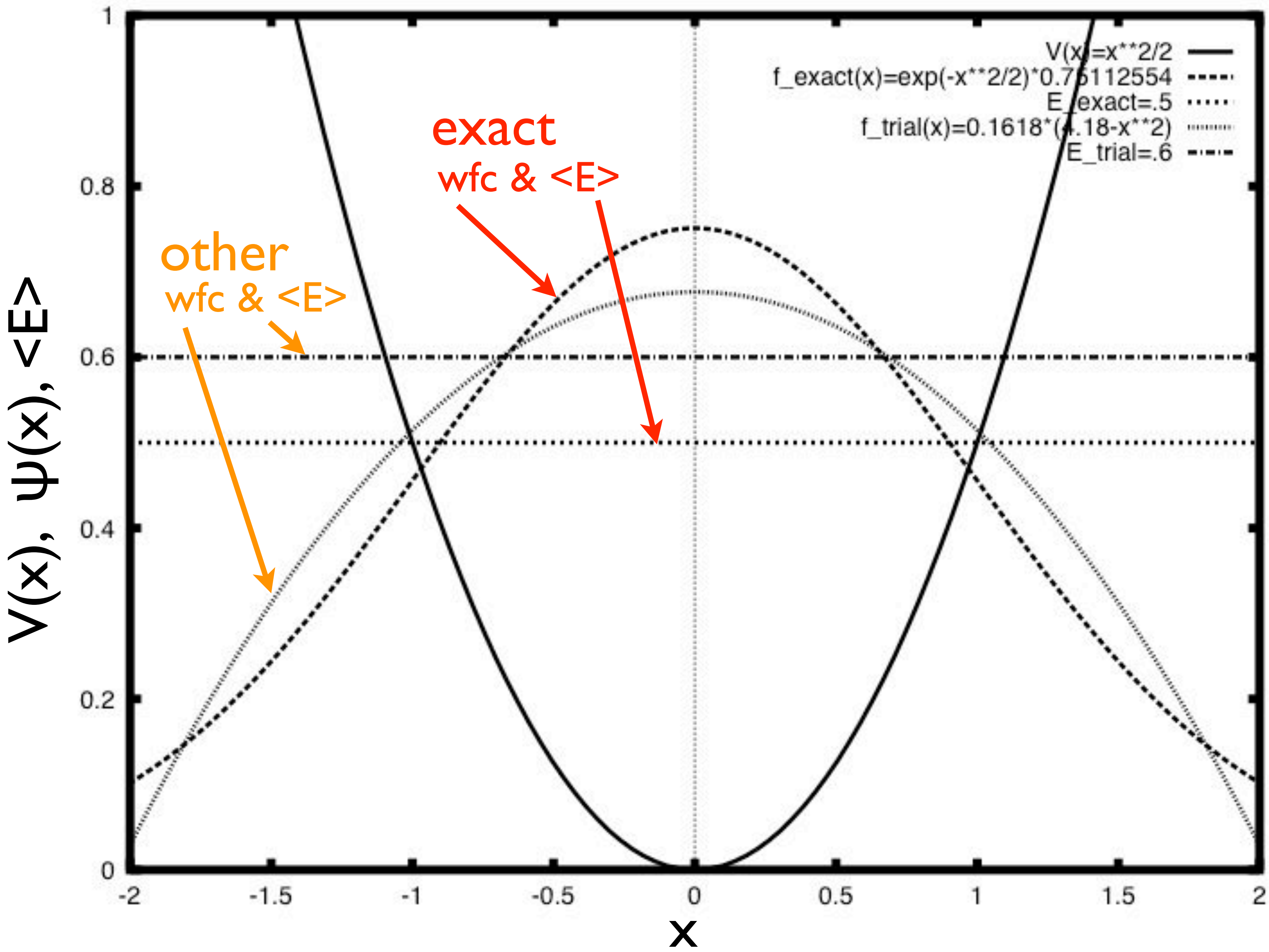
$$= \int_{-a}^{a} B^2(a^2 - x^2)dx + \frac{B^2}{2}\int_{-a}^{a} x^2(a^2 - x^2)^2 dx = \frac{5}{4a^2} + \frac{a^2}{14}$$

$$\frac{d\langle E_{tot,L}(a)\rangle}{da} = 0 \implies a^2 = \sqrt{\frac{35}{2}}, \quad E_{tot} \approx 0.6$$

$a \approx 2.04$

Notice: the zero-variance property does not hold for this class of trial wfc's! and the energy minimum does not correspond to the variance minimum




V(x)=x**2/2
f_exact(x)=exp(-x**2/2)*0.75112554
E_exact=.5
f_trial(x)=0.1618*(4.18-x**2)
E_trial=.6
exact
wfc & <E>
other
wfc & <E>
V(x), ψ(x), <E>
x
1
0.8
0.6
0.4
0.2
0
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2

Exercises

2) Anharmonic oscillator solved with VMC:

$$\mathcal{H} = E_{kin} + E_{pot} = \frac{1}{2}p^2 + \frac{1}{2}x^2 + \frac{1}{8}x^4$$

Trial wfc.:

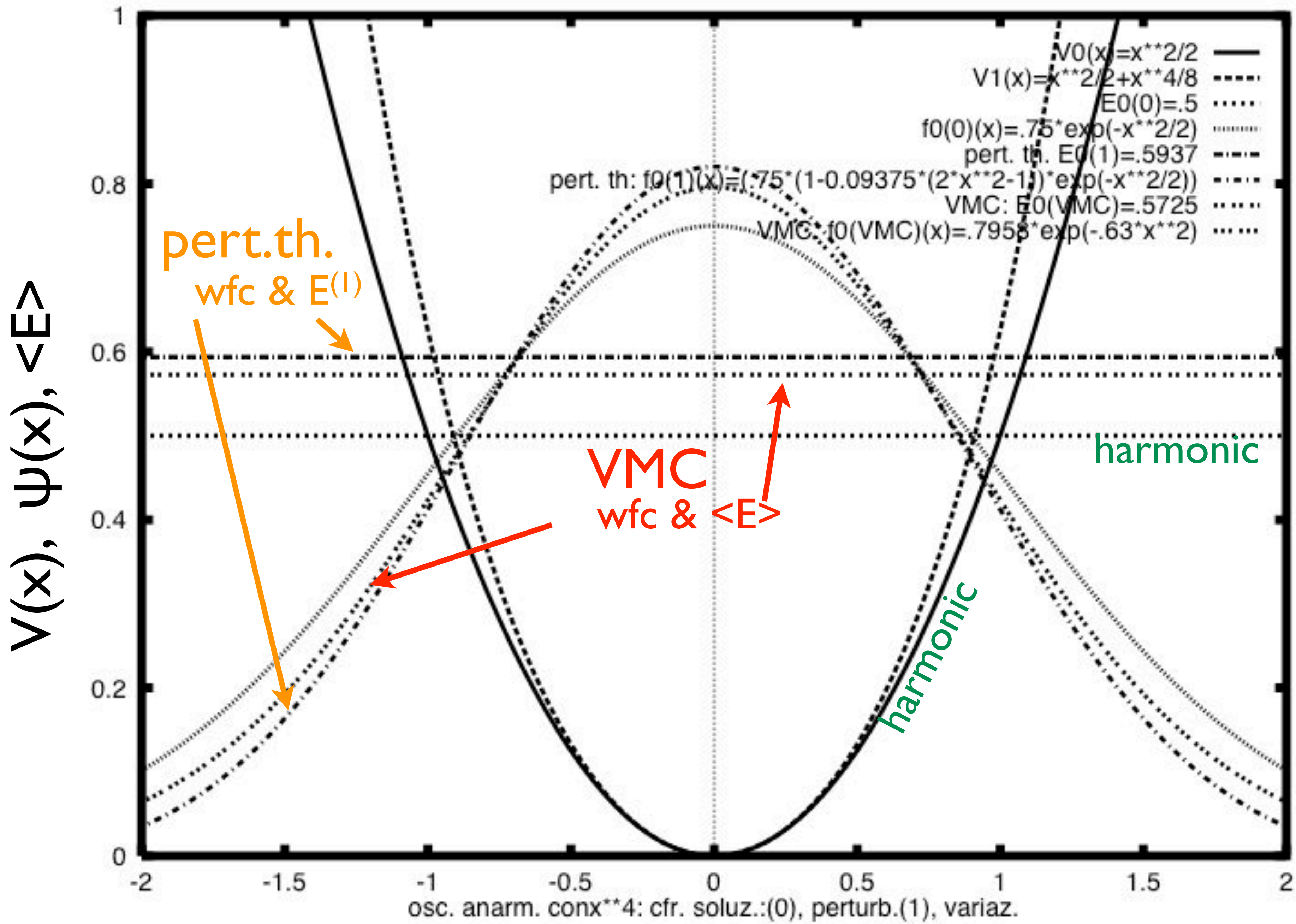
$$\psi(x) = Ae^{-\beta x^2}$$

(also in this case the problem can be analytically solved:)

$$\langle E_{tot,L} \rangle = \left(\frac{1}{2} - 2\beta^2\right)\frac{1}{4\beta} + \beta + \frac{3}{128\beta^2}$$

$$\frac{d\langle E_{tot,L}\rangle}{d\beta} = 0 \implies \beta\left(4\beta^2 - 1\right) = \frac{3}{8} \implies \beta \approx 0.63, \quad E_{tot} \approx 0.5725$$

(better than 1st order perturbation theory)


V(x), ψ(x), <E>
1
0.8
0.6
0.4
0.2
0
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
V0(x)=x**2/2
V1(x)=x**2/2+x**4/8
E0(0)=.5
f0(0)(x)=.75*exp(-x**2/2)
pert. th. E0(1)=.5937
pert. th: f0(1)(x)=(.75*(1-0.09375*(2*x**2-1))*exp(-x**2/2))
VMC: E0(VMC)=.5725
VMC: f0(VMC)(x)=.7958*exp(-.63*x**2)
pert.th.
wfc & E(1)
VMC
wfc & <E>
harmonic
harmonic
osc. anarm. conx**4: cfr. soluz.:(0), perturb.(1), variaz.

managing input/output

job_parabola Note: it must be **executable!**

make it with: ($prompt)> chmod u+x job_parabola
run with: ($prompt)> ./job_parabola

```
for sigma in 0.5  0.6  0.7  0.8  0.9  1.; do
cat > input << EOF
1000
$sigma
0.
5.
EOF

./a.out < input >> dati
```

Other exercises

3) Hydrogen atom solved with VMC:

we need the radial part of the laplacian operator in polar coordinates:

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$$

other Quantum Monte Carlo methods

(not treated here)

* DIFFUSION MONTE CARLO

a technique to project the ground state wavefunction of the system out of a trial wavefunction (provided that the two are not orthogonal).

* PATH INTEGRAL MONTE CARLO

useful for quantum calculations at non-zero temperatures, based on Feynman's imaginary time path integral description