993SM - Laboratory of Computational Physics
Unit IX
November 21, 2025

Maria Peressi
Università degli Studi di Trieste - Dipartimento di Fisica
Sede di Miramare (Strada Costiera 11, Trieste)
e-mail: peressi@units.it

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 : $\beta = \frac{1}{4\sigma^2}$

$$\begin{cases} E_{pot,L}(x) \equiv \dfrac{E_{pot}\psi(x)}{\psi(x)} = \dfrac{1}{2}x^2 \\[2ex] E_{kin,L}(x) \equiv \dfrac{E_{kin}\psi(x)}{\psi(x)} = \dfrac{-\frac{1}{2}\frac{d^2}{dx^2}\psi(x)}{\psi(x)} = -2\beta^2 x^2 + \beta \end{cases}$$

$$\begin{cases} \langle E_{pot}\rangle = \dfrac{\langle\psi|\frac{1}{2}x^2|\psi\rangle}{\langle\psi|\psi\rangle} = \dfrac{\int \frac{1}{2}x^2|\psi(x)|^2dx}{\int |\psi(x)|^2dx} = \dfrac{1}{2}\sigma^2 = \dfrac{1}{8\beta} \\[2ex] \langle E_{kin}\rangle = \dfrac{\langle\psi| -\frac{1}{2}\nabla^2|\psi\rangle}{\langle\psi|\psi\rangle} = \dfrac{\int \left(\frac{1}{4\sigma^2} - \frac{x^2}{8\sigma^4}\right)|\psi(x)|^2dx}{\int |\psi(x)|^2dx} = \dfrac{1}{8\sigma^2} = \dfrac{1}{2}\beta \end{cases}$$

Determining the ground state

$$\langle E_{pot,L} \rangle = \frac{1}{8\beta}, \qquad \langle E_{kin,L} \rangle = \frac{1}{2}\beta \qquad\qquad \frac{d\,\langle E_{tot,L}(\beta)\rangle}{d\beta} = 0 \Longrightarrow \beta = \frac{1}{2}, E_{tot} = \frac{1}{2}$$

$(\alpha = \sqrt{2}/2)$

But also, looking at the variance:

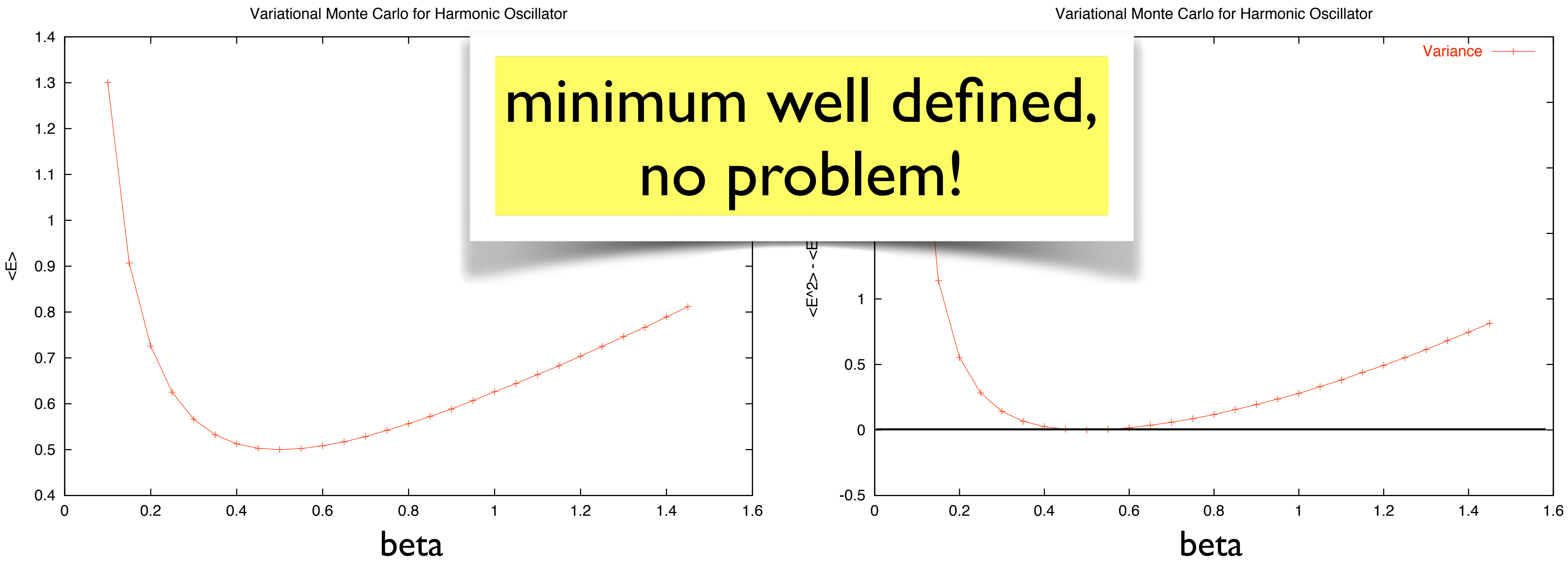
$$\sigma_E^2 = \langle E_{tot,L}^2 \rangle - \langle E_{tot,L} \rangle^2 =$$

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

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

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

Notice the zero-variance property for this problem:



minimum well defined,
no 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: $\int_{-a}^{a} B^2(a^2 - x^2)^2 dx = 1 \implies B^2 = \frac{15}{16a^5}$

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

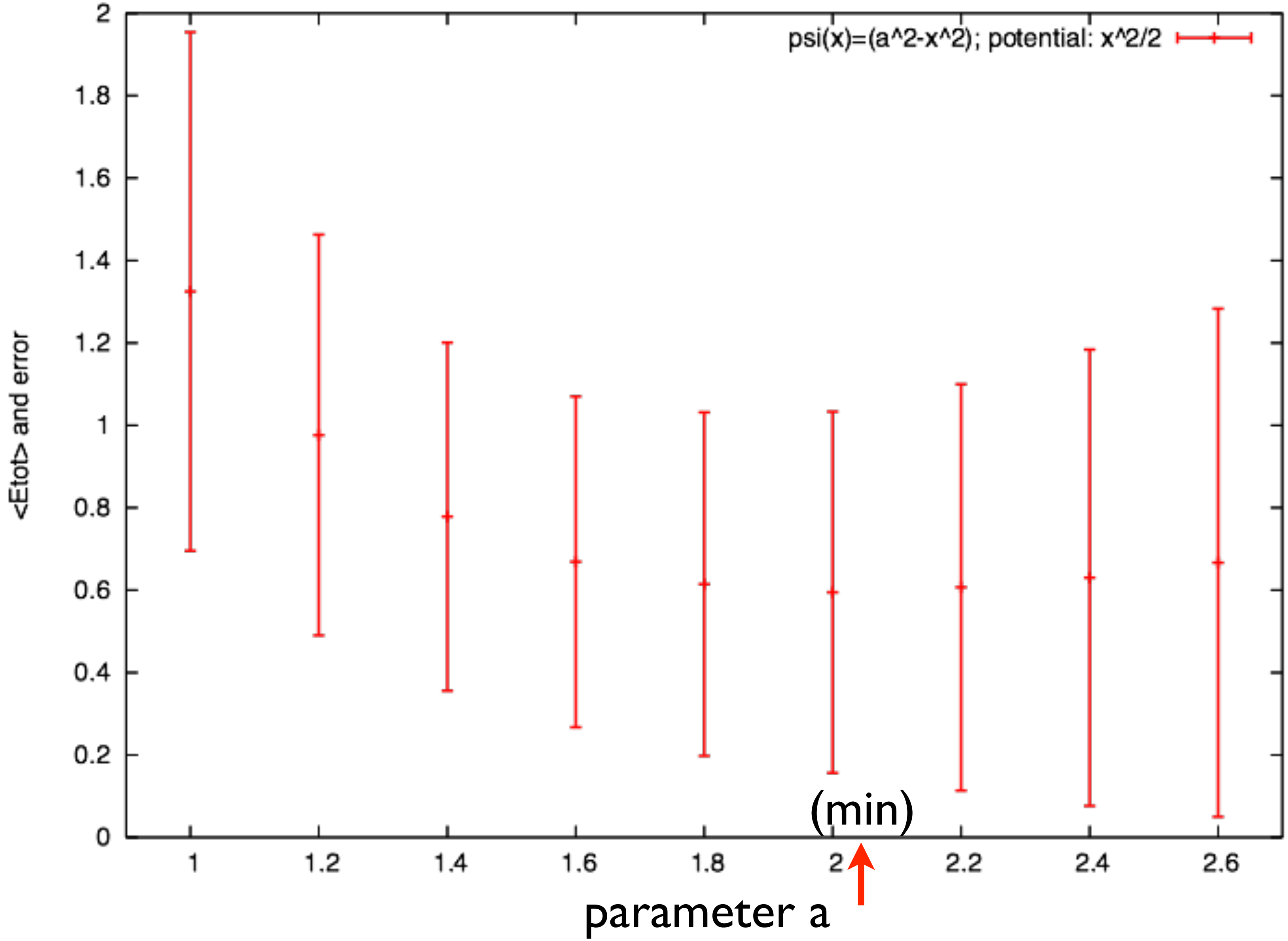
(in this case the problem can be analytically solved:)

$$\begin{aligned} \langle E_{tot,L} \rangle = \int_{-a}^{a} \frac{|\psi(x)|^2}{\langle\psi|\psi\rangle} E_L(x) dx &= \int_{-a}^{a} B^2(a^2 - x^2)^2 \left(\frac{1}{a^2 - x^2} + \frac{1}{2}x^2\right) dx \\ &= \int_{-a}^{a} B^2(a^2 - x^2) dx + \frac{B^2}{2} \int_{-a}^{a} x^2(a^2 - x^2)^2 dx = \frac{5}{4a^2} + \frac{a^2}{14} \end{aligned}$$

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

$a \approx 2.04$

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

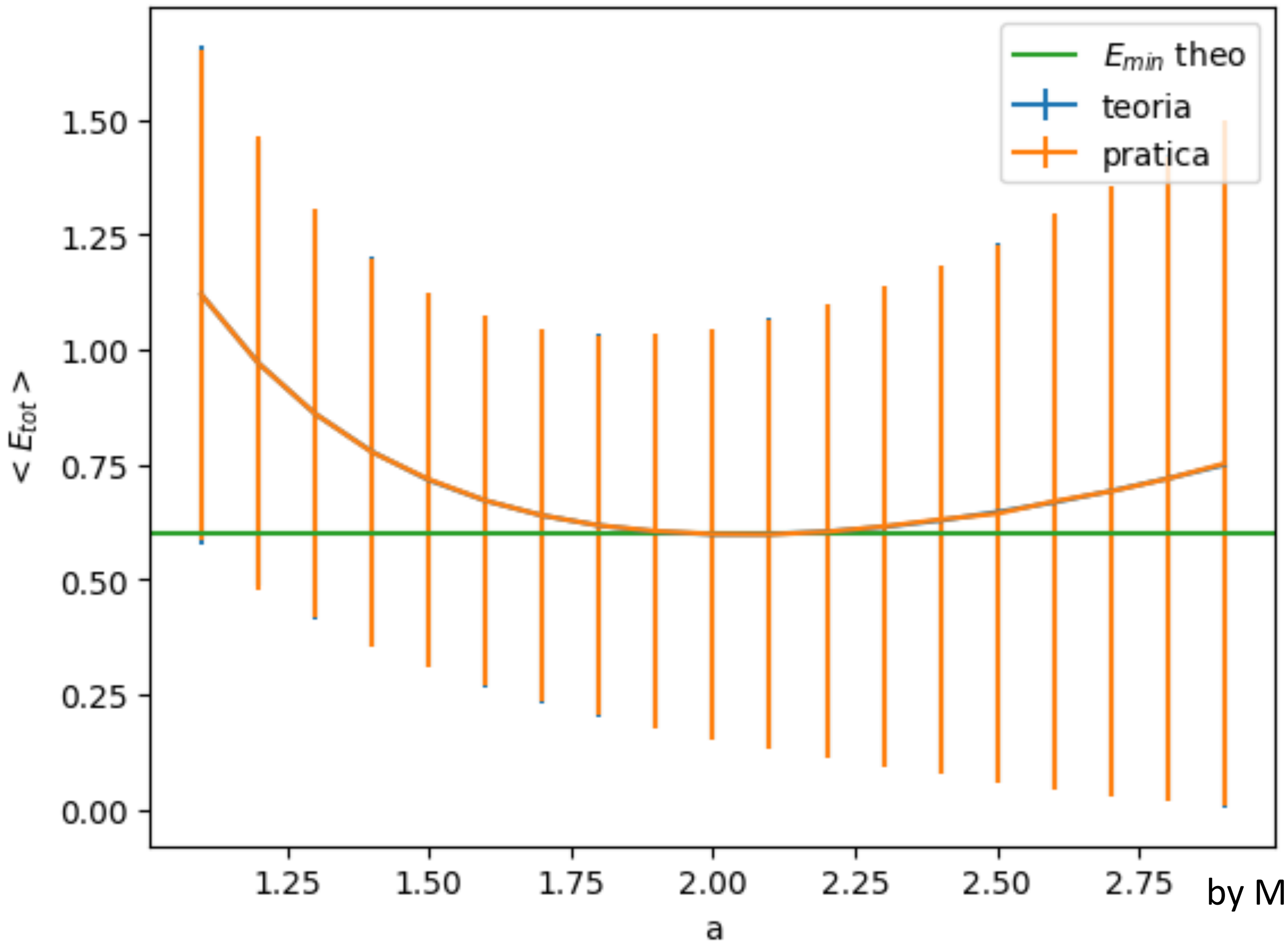


(min)

$$\sigma_{th}^2 = \frac{15}{8a^5}\left(a + \frac{2a^9}{7\cdot 45} + \frac{2a^5}{15}\right) - \left(\frac{5}{4a^2} + \frac{a^2}{14}\right)^2$$

in **metropolis_parabola.f90**:

```
var_th = (15./8/a**5) * ( a + 2*a**9/(7*45) + 2*a**5/15) - &
                         (5./4/a**2+a**2/14)**2
```



by Maria Eleonora Testi

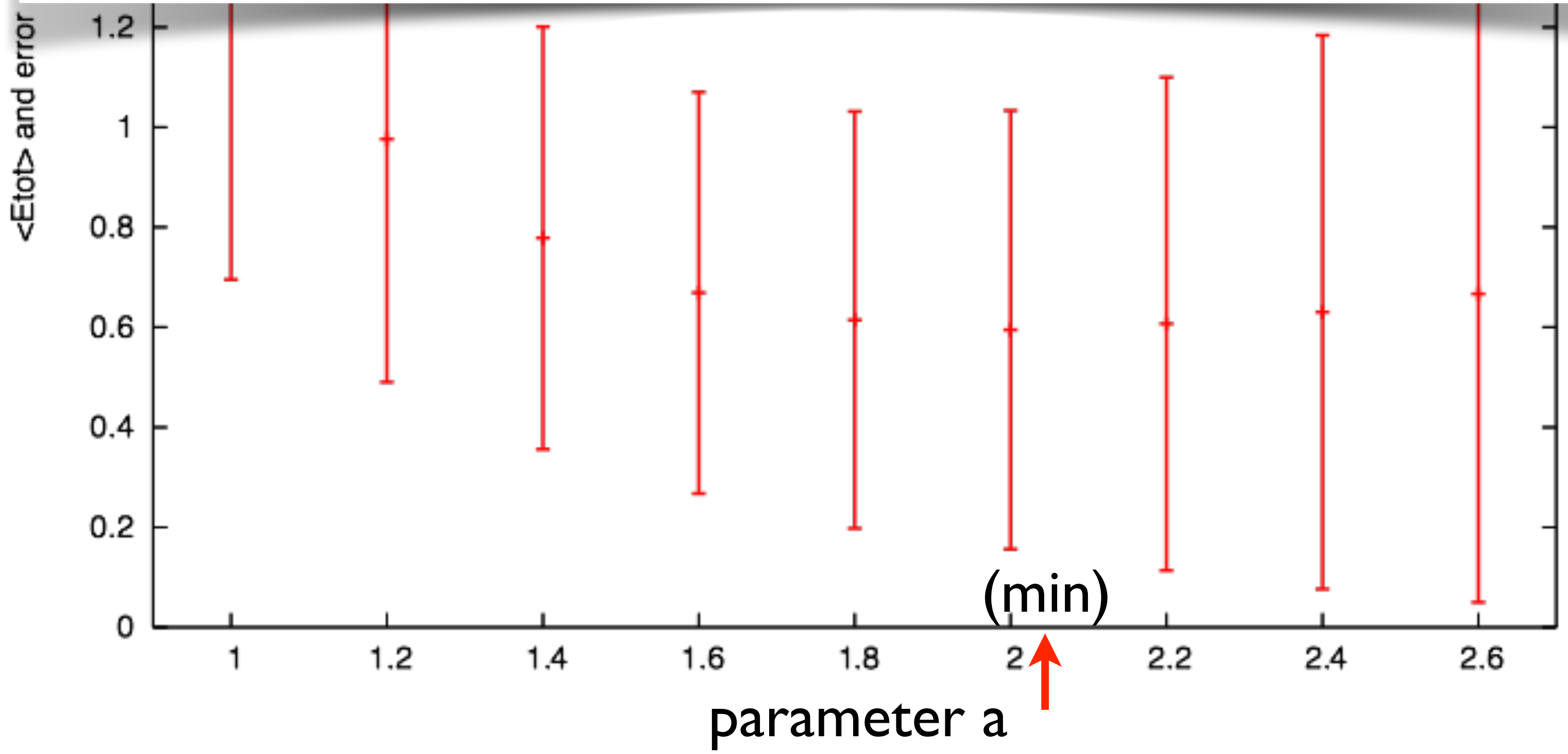
The minimum of the variance is

$$min(\sigma_{th}^2) = \sigma_{th}^2\left(a = (735/16)^{1/8}\right) \approx 0.164.$$

It does not coincide with the energy minimum which is for $a = (35/2)^{1/2}$

another problem...

minimum looks ok on this scale,
but it is not well defined at a finer scale
(zooming in: oscillations compatible with the *rmse*
prevent the identification of the minimum)

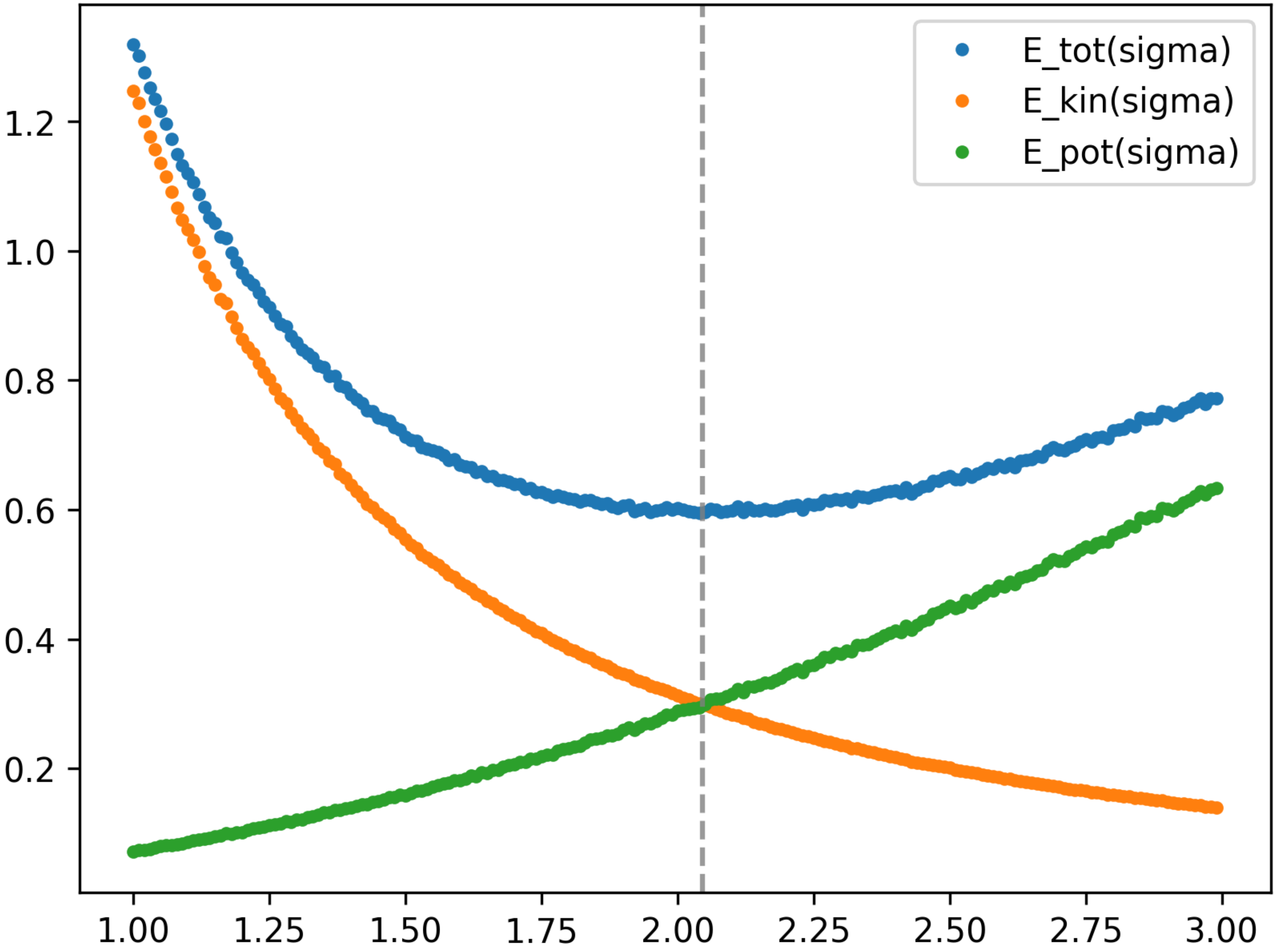


but here we can apply the **VIRIAL THEOREM**

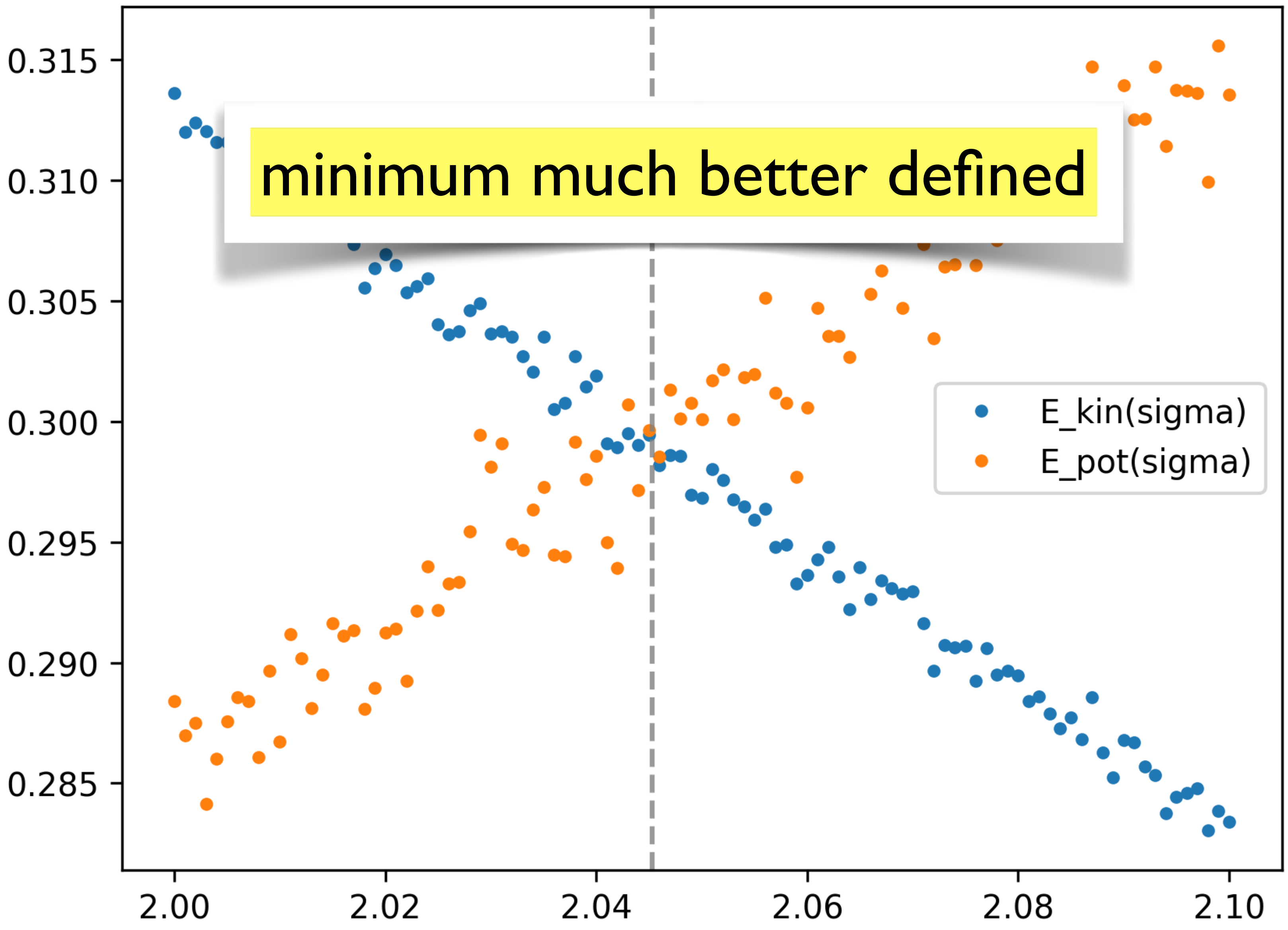
If the force between any two particles of the system results from a potential energy $E_{pot}(r) = \alpha r^n$ that is proportional to some power n of the distance r, the virial theorem takes the simple form $2\langle E_{kin}\rangle = n\langle E_{pot}\rangle$

Here $n = 2$, hence $\langle E_{kin}\rangle = \langle E_{pot}\rangle$

⇒ find the crossing point between E_{kin} and E_{pot}



by Ettore Mancin



minimum much better defined

by Ettore Mancin

2025/26: lecture IX up to here

(next: H and He atoms ~~by FB~~)

3) Hydrogen atom solved with VMC:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}$$

A 3D problem which can be reduced to 1D, using the radial part of the laplacian operator in polar coordinates:

$$H = -\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right] - \frac{e^2}{r}$$

Use atomic units $(\hbar = 1,\ m = 1,\ e^2 = 1 \implies E \textit{ in Hartree })$

Consider a s-type trial wfc with a radial part: $\psi_\alpha(r) = e^{-\alpha r}$

$$E_L(r) = \frac{H\psi_\alpha(r)}{\psi_\alpha(r)} = -\frac{1}{2}\left[\alpha^2 - \frac{2\alpha}{r}\right] - \frac{1}{r}$$

3) Hydrogen atom solved with VMC:

$$E_L(r) = \frac{H\psi_\alpha(r)}{\psi_\alpha(r)} = -\frac{1}{2}\left[\alpha^2 - \frac{2\alpha}{r}\right] - \frac{1}{r}$$

$$\Rightarrow \quad \langle E_L \rangle = \int_0^\infty \frac{\psi_\alpha^2(r)}{\langle \psi_\alpha | \psi_\alpha \rangle} E_L(r) d\mathbf{r} = \int_0^\infty \frac{4\pi r^2 \psi_\alpha^2(r)}{\langle \psi_\alpha | \psi_\alpha \rangle} E_L(r) dr$$

NOTES: using spherical coordinates and 1D integral, pay attention to:

- Generation of new position: must be $r \geq 0$
- Probability of being btw r and r+dr: is $\propto 4\pi r^2$

3) Hydrogen atom solved with VMC:

The harmonic oscillator program **metropolis_gaussian.f90** or what you have done

can be adapted to this problem by changing the form of the trial wave function and local energy:

Accumulate $E_L(r) = \frac{H\psi_\alpha(r)}{\psi_\alpha(r)} = -\frac{1}{2}\left[\alpha^2 - \frac{2\alpha}{r}\right] - \frac{1}{r}$

generating points and accepting or rejecting them according to the ratio

$$w = \left(\frac{r'}{r}\right)^2 \left|\frac{\psi(r')}{\psi(r)}\right|^2$$

3) Hydrogen atom solved with VMC:

Hints:

- use nmcs = 100.000
- Max variation of r = 4 Bohr; adapt it to keep the acceptance ratio of the order of 50%

=> use also the zero variance property!

Alternative approach keeping the full 3D problem:

- consider cartesian (x,y,z) coordinates
- no need of limiting the walk; probability automatically set correctly

He atom solved with VMC:

If we use atomic units with $\hbar = m_e = e = 1$, the Hamiltonian for the motion of the two electrons can be written

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} ,$$

where $r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2|$. The terms $-2/r_i$ represent the negative (attractive) potential energy between each electron with charge -1 and the Helium nucleus with charge $+2$, and the term $+1/r_{12}$ represents the positive (repulsize) potential energy between the two electrons.

A simple choice of variational trial wave function

(1)

H without e-e interaction, ψ without correlation

If the repulsive term $1/r_{12}$ were not present, then the Hamiltonian would be that of two independent Hydrogen-like atoms. It can be shown that the energy and ground state wave function of a Hydrogen-like atom whose nucleus has charge Z are given by

$$E_0 = -\frac{Z^2}{2} , \qquad \psi_0 \sim e^{-Zr} .$$

The wave function of the combined atom with two non-interacting electrons would be the product of two such wave functions:

$$\boxed{\psi(\mathbf{r}_1, \mathbf{r}_2) \sim e^{-2r_1} e^{-2r_2}} .$$

This suggests a trial wave function of the form

$$\Psi_{\mathrm{T},\alpha} = e^{-\alpha r_1} e^{-\alpha r_2} ,$$

similar to what was done for the Hydrogen atom. If the electron-electron interaction is neglected, then the average energy with this wave function can be calculated

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right\rangle = 2 \times \frac{\alpha^2}{2} - 2 \times \alpha ,$$

credits: PHY 411-506 Computational Physics II

He atom solved with VMC:

(2) H with interaction, ψ without correlation

which has a minimum at $\alpha = 1$, which gives $\langle E\rangle = -1$. The experimentally measured ground state energy is $E_0 = -2.904$.

In fact, the average energy can be evaluated exactly for this trial wave function even if the electron-electron interaction is included:

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\rangle = \alpha^2 - \frac{27}{8}\alpha \, ,$$

which has a minimum at $\alpha = 27/16$, which gives $\langle E\rangle = -2.8477$. This shows that the repulsion between the electrons is important and lowers the energy.

(3) H with interaction, ψ with correlation, extremely simple form

Padé-Jastrow wave function

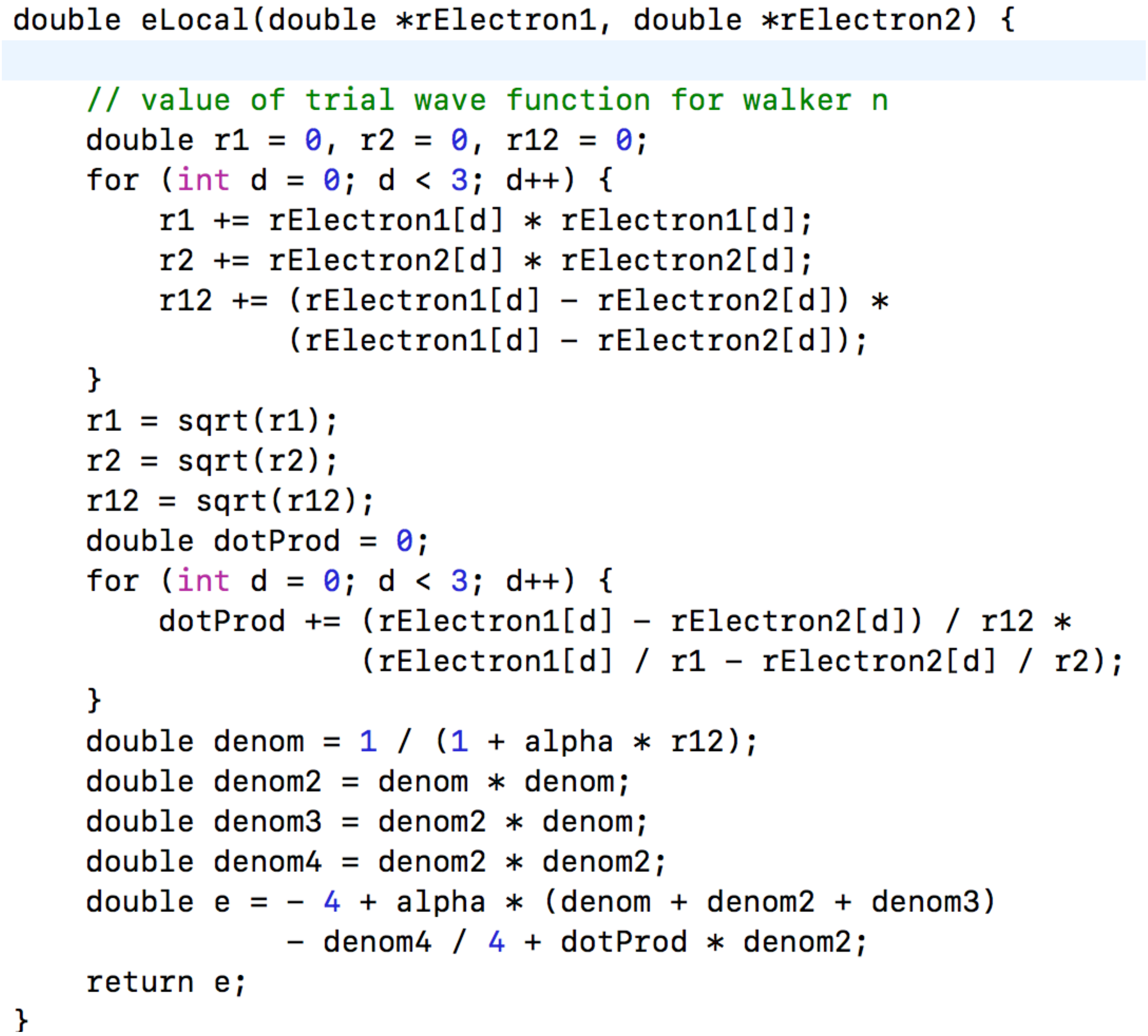
The textbook suggest using a trial wave function

$$\boxed{\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-2r_1} e^{-2r_2} e^{\frac{r_{12}}{2(1+\alpha r_{12})}}} \, ,$$

with α as a variational parameter. The local energy with this wave function can be calculated

$$\begin{aligned} E_{\mathrm{L}}(\mathbf{r}_1, \mathbf{r}_2) = &- 4 + \frac{\alpha}{(1+\alpha r_{12})} + \frac{\alpha}{(1+\alpha r_{12})^2} + \frac{\alpha}{(1+\alpha r_{12})^3} \\ &- \frac{1}{4(1+\alpha r_{12})^4} + \frac{\hat{\mathbf{r}}_{12}\cdot(\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2)}{(1+\alpha r_{12})^2} \, . \end{aligned}$$

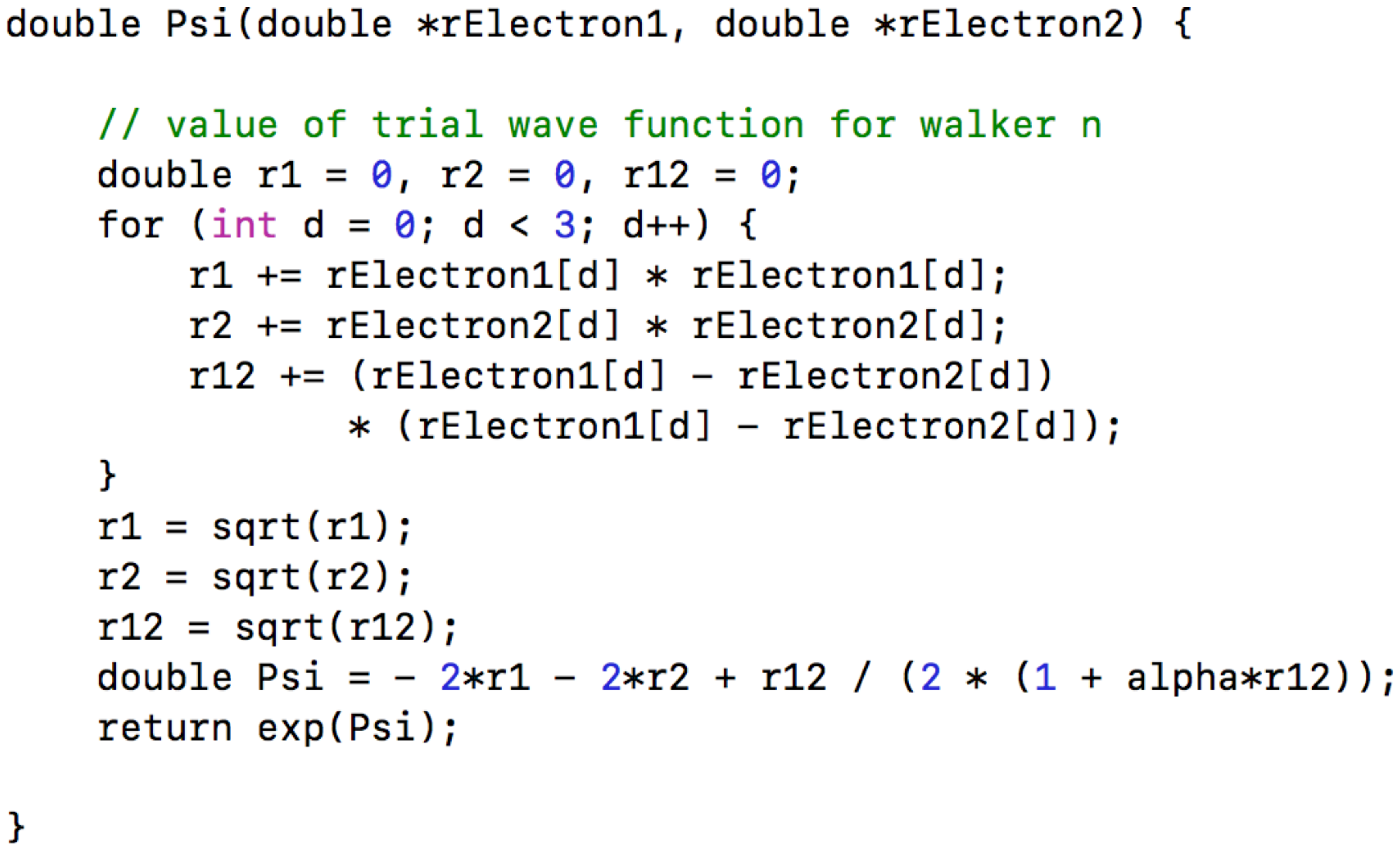
credits: PHY 411-506 Computational Physics II



```
double eLocal(double *rElectron1, double *rElectron2) {

    // value of trial wave function for walker n
    double r1 = 0, r2 = 0, r12 = 0;
    for (int d = 0; d < 3; d++) {
        r1 += rElectron1[d] * rElectron1[d];
        r2 += rElectron2[d] * rElectron2[d];
        r12 += (rElectron1[d] - rElectron2[d]) *
               (rElectron1[d] - rElectron2[d]);
    }
    r1 = sqrt(r1);
    r2 = sqrt(r2);
    r12 = sqrt(r12);
    double dotProd = 0;
    for (int d = 0; d < 3; d++) {
        dotProd += (rElectron1[d] - rElectron2[d]) / r12 *
                   (rElectron1[d] / r1 - rElectron2[d] / r2);
    }
    double denom = 1 / (1 + alpha * r12);
    double denom2 = denom * denom;
    double denom3 = denom2 * denom;
    double denom4 = denom2 * denom2;
    double e = - 4 + alpha * (denom + denom2 + denom3)
               - denom4 / 4 + dotProd * denom2;
    return e;
}
```

credits: PHY 411-506 Computational Physics II



```
double Psi(double *rElectron1, double *rElectron2) {

    // value of trial wave function for walker n
    double r1 = 0, r2 = 0, r12 = 0;
    for (int d = 0; d < 3; d++) {
        r1 += rElectron1[d] * rElectron1[d];
        r2 += rElectron2[d] * rElectron2[d];
        r12 += (rElectron1[d] - rElectron2[d])
               * (rElectron1[d] - rElectron2[d]);
    }
    r1 = sqrt(r1);
    r2 = sqrt(r2);
    r12 = sqrt(r12);
    double Psi = - 2*r1 - 2*r2 + r12 / (2 * (1 + alpha*r12));
    return exp(Psi);

}
```

credits: PHY 411-506 Computational Physics II

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