XIIth-IIC-EMTCCM

European Master in Theoretical Chemistry and Computational Modelling

VQMC

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The variational theorem

The eigenfunctions of a quantum mechanical problem are *complete*. This means that any wave function $\Psi(x)$ can be expressed as a linear superposition

$$\Psi(x) = \sum_n c_n \psi_n(x) \ ,$$

where c_n are complex numbers. According to the rules of quantum mechanics, the average energy of a particle with this wave function is given by

$$\langle E \rangle = \frac{\int \mathrm{d}x \ \Psi^*(x) H \Psi(x)}{\int \mathrm{d}x \ \Psi^*(x) \Psi(x)} \ .$$

The *variational theorem* states that $\langle E \rangle \geq E_0$ for *any* Ψ, and $\langle E \rangle = E_0$ if and only if $\Psi(x) = c_0 \psi_0(x)$.

Variational Monte Carlo (VMC)

In the Variational Monte Carlo method, a trial wave function $\Psi_{\mathrm{T},\alpha}$, which depends on a set of variational parameters $\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_S)$, is carefully chosen.

An efficient way must be found to evaluate the expected value of the energy

$$\langle E \rangle = \frac{\int \mathrm{d}R \ \Psi^*_{\mathrm{T},\alpha} H \Psi_{\mathrm{T},\alpha}}{\int \mathrm{d}R \ |\Psi_{\mathrm{T},\alpha}|^2} \ ,$$

where $R = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ are the positions of the particles in the system. The problem is that this multi-dimensional integral must be evaluated many many times as the program searches the α parameter space for the minimum $\langle E \rangle$.

$$\frac{\int \psi_T^* \hat{H} \psi_T d\mathbf{R}}{\int \psi_T^* \psi_T d\mathbf{R}} = \frac{\int |\psi_T|^2 \frac{\hat{H}\psi_T}{\psi_T} d\mathbf{R}}{\int |\psi_T|^2 d\mathbf{R}}$$

Local Energy

$$E_L(\mathbf{R}) = \frac{\hat{H}\psi_T(\mathbf{R})}{\psi_T(\mathbf{R})}$$

$$\langle E \rangle = \frac{\int |\psi_T|^2 \; E_L \; d\mathbf{R}}{\int |\psi_T|^2 d\mathbf{R}}$$

$$\langle E \rangle \approx \frac{\sum |\psi_T|^2 \; E_L \; d\mathbf{R}}{\sum |\psi_T|^2 d\mathbf{R}}$$

Stochastic Methods

$$\langle E \rangle \approx \frac{\sum |\psi_T|^2 \, E_L \, d\mathbf{R}}{\sum |\psi_T|^2 d\mathbf{R}}$$

- *Draw random numbers in the R domain*
- *Average the integrand on the sample*
- *The variance can be calculated as: $< E^2 > - < E >^2$.*
- *The method is competitive for multi-dimensional functions*

Variatonal Monte Carlo: Importance sampling

$$E = \frac{1}{N} \sum E_L(\mathbf{R}_i)$$

- *By using random numbers uniformly distributed, information is spread all over the domain we are sampling over (areas of very high and low probability are treated on equal foot).*

- *A simple transformation allows Monte Carlo to generate a far better results: drawing numbers from non-uniform density $|\psi|^2$*

- *How to do it? Metropolis algorithm*

Metropolis

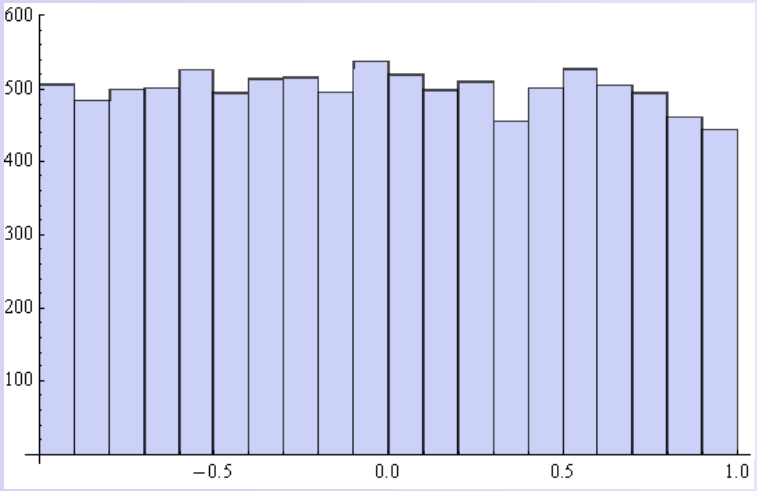
```
% x0 initial position
% r0 length of the coordinate domain or smaller
% rand(idum) random number
% prob(x) = |y|2
% step is the maximum step-length in the random walk

x0=r0*(2*ran(idum)-1)            % x0 initial position
p0= prob(x)                      % p0 probability at the initial position
```

```
% thermalization

cont=0
do i=1,mi
    cont=cont+1
    continue
    stepx=step*(2*ran2(idum)-1) % actual step
    xb=x+stepx                  % new position
    p1=prob(xb)                 % new probability
    w=ran(idum)                 % random probability (0< w <1)

    IF(p1/p0>w) THEN
        x=xb
        ELSE
        cont=cont+1
        goto 1
    ENDIF
enddo

step=step*mi/(0.5d0*cont)          %adjusting  step as to accept 50%
```

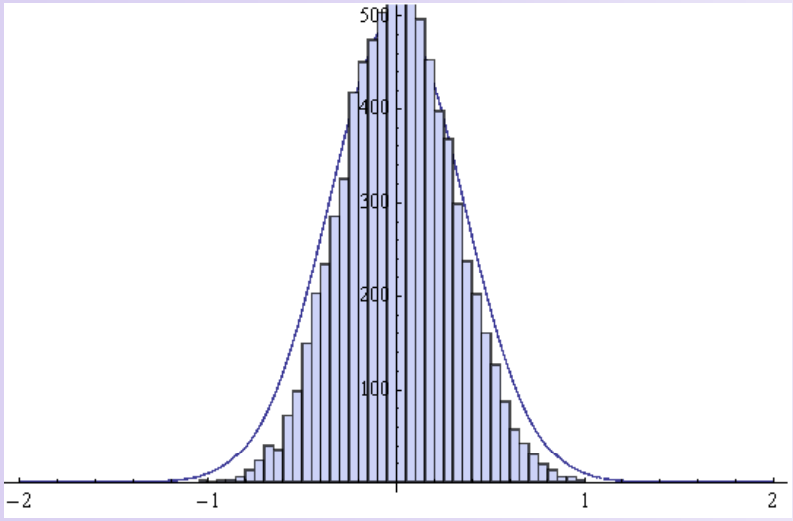
```
% calculation
i2=i
cont=0
do i=i2,m
    cont=cont+1;
    continue
    stepx=step*(2*ran2(idum)-1)      % actual step
    xb=x+stepx                       % new position
    p1=prob(xb)                      % new probability
    w=ran(idum)                      % random probability (0< w <1)
    IF(p1/p0>w) THEN
        aux=ene(xb)                  % ene(x) is function to compute local energy
        llista(i-i2+1)=aux           % collecting local energies
        llista2(i-i2+1)=aux**2       % collecting squared of local energies
        x=xb                         % new position
        p0=p1                        % new probability
    ELSE
        cont=cont+1
        goto 2
    ENDIF
enddo
```

In the main program we calculate the energy and variance:

```
mf = m - mi
ene=sum(llista(1:mf))/mf
ene2=sum(llista2(1:mf))/mf
variance = ene2-ene**2
```



• *Histogram of 10.000 calculated random numbers uniformly distributed in the domain (-1,1)*



• *Histogram of 10.000 random numbers from non-uniform density $|\psi|^2$ in the domain (-1,1) calculated using the Metropolis algorithm*

By using Metropolis we can reach the better accuracy using a shorter sample

Metropolis random walkers

In complex problems, it is conventional to use a large number of independent random walkers that are started at random points in the configuration space.

(In a multi-dimensional space: 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.)

Introducing walkers in the main program

```
do kk=1,walkers
    call metropolis                          % run a walk
    ene=sum(llista(1:mf))/mf                 % energy from this walk
    ene2=sum(llista2(1:mf))/mf               % square of energy from this walk
    llistene(kk)=ene                         % collecting energies of the walks
    llistene2(kk)=ene**2                     % collecting squared energies of the walks
    llistvar(kk)=ene2-ene**2                 % collecting variances of the walks
enddo

energy=sum(llistene(1:walkers))/walkers      % the best energy
energy2=sum(llistene2(1:walkers))/walkers    % the best square energy
varerror=energia2-energia**2                 % variance to calculate error of energy
variance=sum(llistvar(1:walkers))/walkers    % average of variance in the walks
```

Harmonic Oscillator

Trial function

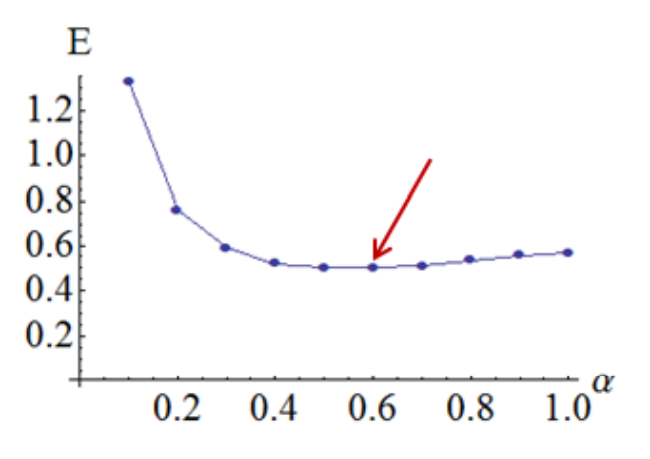
$$\Psi_{\mathrm{T},\alpha}(x) = e^{-\alpha x^2}$$

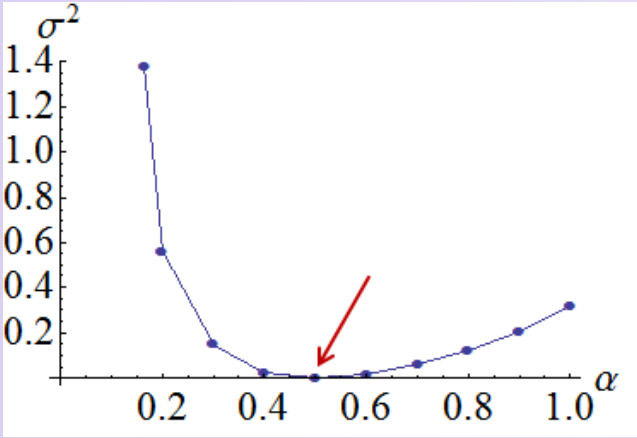
Local Energy

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

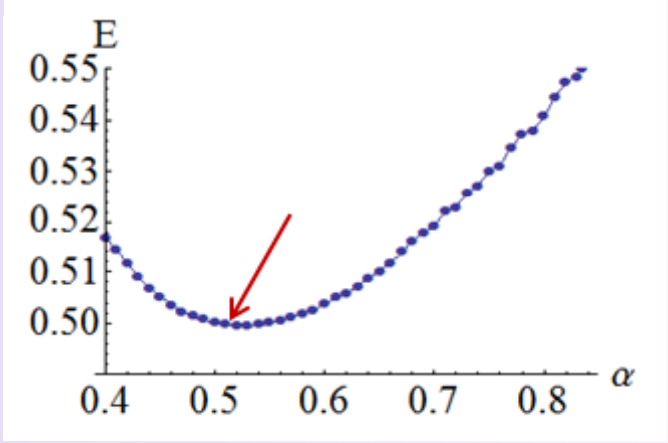
r_0=1, step 0.5

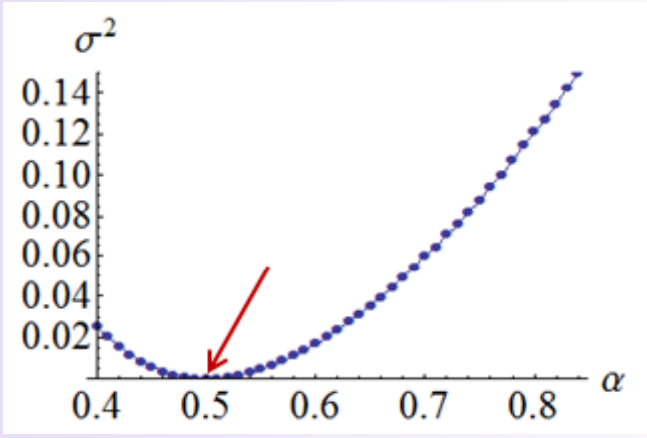
points 10.000 walkers 30





points 10.000 walkers 300





Probability

$$\mathrm{p}(x) = e^{-2\alpha x^2}$$

Variance is better to optimize parameters of the trial function

Using a sample large enough energy and variance points to the same minimum

He atom

Trial function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{(1+\alpha r_{12})}}$$

Local Energy

$$E_{\mathrm{L}}(\mathbf{r}_1, \mathbf{r}_2) = -Z^2 + \frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{r_{12}}\left[1 - \frac{2\beta}{(1+\alpha r_{12})^2}\right] + \frac{2\alpha\beta}{(1+\alpha r_{12})^3} - \frac{\beta^2}{(1+\alpha r_{12})^4} + \frac{Z\beta\,(r_1+r_2)}{r_{12}\,(1+\alpha r_{12})^2}\,\frac{1-\mathbf{r}_1\cdot\mathbf{r}_2}{r_1\,r_2}$$

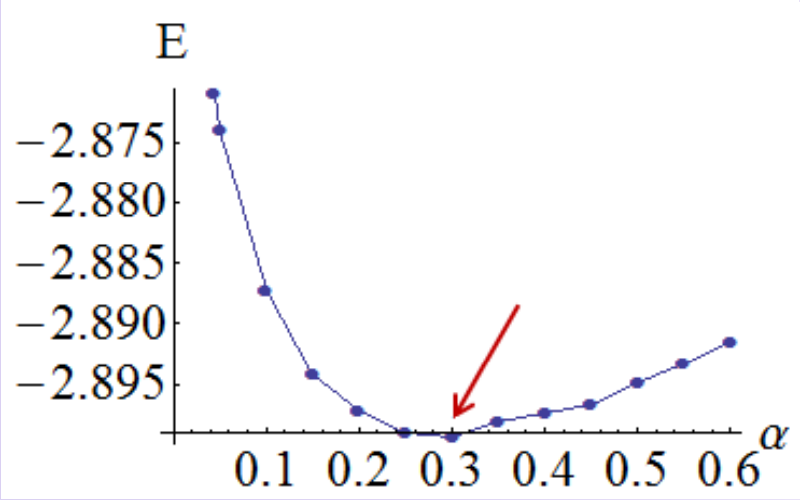
Probability

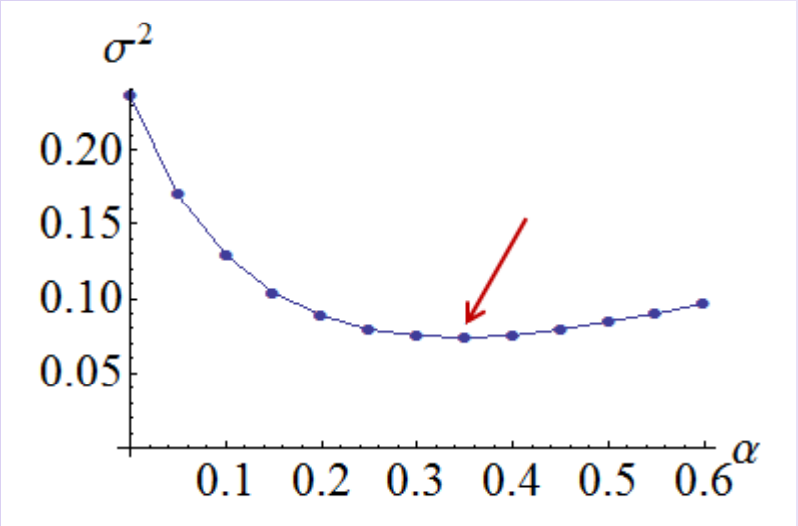
$$\left|\Psi(\mathbf{r}_1, \mathbf{r}_2)\right|^2$$

$r_0 = 1$, step 0.5

Optimizing α for Z=2, β=1/2 (optimum values)

points 100.000 walkers 300





points 300.000 walkers 500