

## II Homework

choose one problem (listed here from the simplest to the more demanding):

**harmonic and anharmonic oscillator with Variational Monte Carlo**  
**or**  
**hydrogen atom with Variational Monte Carlo**  
**or**  
**hydrogen atom with Numerov algorithm**

### 1. Quantum oscillator in 1D with VMC

Consider the hamiltonian of the quantum harmonic oscillator  $\mathcal{H} = p^2/2 + x^2/2$  (having chosen  $m = k = \hbar = 1$ ). We want to solve it numerically with VMC. To this purpose consider two different choices for the trial wavefunction:

$$\psi(x) = \begin{cases} B(a^2 - x^2), & \text{for } |x| < a; \\ 0, & \text{for } |x| > a. \end{cases} \quad (1.a)$$

or:

$$\psi(x) = Ae^{-\beta x^2} \quad (1.b)$$

with  $a$  and  $\beta$  variational parameters,  $A$  and  $B$  proper normalization constants.

(a) Calculate

$$\langle E \rangle = \langle E_L \rangle = \frac{1}{M} \sum_{i=1}^M E_L(x_i),$$

with

$$E_L(x) = \frac{\mathcal{H}\psi(x)}{\psi(x)} \quad (\text{local energy})$$

and with the  $x_i$  distributed according  $\psi(x)^2$ . Using the trial wavefunction (1.b), firstly do a Metropolis sampling of a gaussian function with fixed parameters; see the code `metropolis_gaussian.f90`. See `metropolis_parabola.f90` for (1.a).

(b) Verify numerically and analytically that the variational solution gives in the two cases:

(1.a):  $a = (35/2)^{1/4} \approx 2.0453$ ;  $\langle E \rangle = 0.6$

(1.b):  $\beta = \frac{1}{2}$ ;  $\langle E \rangle = 0.5$

*(In this case the exact analytic solution is known,  $E_0 = 0.5$ ; however, in case (1.a) the minimum of  $\langle E \rangle$  as a function of  $a$  is rather flat: use steps of 0.01 for  $a$  and  $n = 100000$  Metropolis accumulation steps to appreciate the minimum)*

(c) Instead of solving the problem by minimizing  $\langle E_L \rangle$ , solve it minimizing the variance:

$$\sigma^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2;$$

you should observe that in the case (1.a) the minimum of the variance is positive, whereas in the case (1.b) is zero.

(Important: note the usefulness of the “zero variance property”; the EXACT minimum of  $\sigma^2$  is 0 is the class of the trial wavefunctions contains the exact result, whereas in general the minimum of  $\langle E \rangle$  is not known!)

- (d) Consider also an anharmonic part in the potential, i.e.  $V(x) = x^2/2 + bx^4$ . Set for instance  $b = 1/8$ , make a plot of  $V(x)$ . Use the first order perturbation theory to calculate the changes at the lowest order in energy of the ground state due to the anharmonic term. Choose a reasonable form for the trial wavefunction, e.g. (1.b), and calculate  $\langle E \rangle$  with VMC. Compare the result obtained with the one obtained using the perturbation theory.

## 2. Hydrogen atom with VMC

- (a) Find numerically the ground state of the H atom using VMC. The hamiltonian is:  $\mathcal{H} = p^2/(2m) - e^2/r$ ; It is convenient to use atomic units ( $\hbar = 1$ ,  $m_e = 1/2$ ,  $e^2=2$ , and therefore to measure all length in terms of Bohr radius,  $a_0 = \hbar^2/(me^2)$ , the energies in Rydberg,  $Ry = me^4/(2\hbar^2)$ ). Consider the trial wavefunction  $\psi(\mathbf{r}) = \psi(r) = e^{-r/a}$ , where  $a$  is a variational parameter. calculate the optimal value of  $a$  and the corresponding energy.

*Hints:*

1) you may reduce the problem (spherical part) to a 1D problem. Pay attention that

$$\langle E_L \rangle = \frac{\int \psi^2(r) E_L(r) d\mathbf{r}}{\int \psi^2(r) d\mathbf{r}} = \frac{\int \psi^2(r) E_L(r) 4\pi r^2 dr}{\int \psi^2(r) 4\pi r^2 dr}$$

and therefore the sampling probability is  $r^2\psi^2(r)$  and not just  $\psi^2(r)$ .

2) Pay attention close to the origin!

- (b) Approach the problem keeping a 3D formulation, considering the isotropy of the trial move (The displacement is a vector!)

## 3. Hydrogen atom - Numerov's algorithm.

Find numerically the first states of the H atom using the Numerov's algorithm (you can see and use `hydrogen_radial.f90` by prof. Paolo Giannozzi -in the Moodle repository of this course, in the material of Unit XII- but you should be able to understand and explain precisely what the code does).