Università degli studi di Trieste
Corso di laurea magistrale in Fisica della materia

Laboratorio di Fisica Computazionale

Unit VIII
Variational Monte Carlo (VMC)

Davide Bernocco
Matricola s285296

Programming language used:
Python

Contents

1 Quantum harmonic oscillator in 1D: variational approach **2**
1.1 Gaussian trial wave function 3
1.2 Parabolic trial wave function 6

2 Anharmonic quantum oscillator in 1D **9**
2.1 Perturbation theory 9
2.2 Variational Monte Carlo 9
2.3 Comparison between the two methods 10

3 Hydrogen atom (optional) **11**

1 Quantum harmonic oscillator in 1D: variational approach

In this unit we are going to apply the Variational Monte Carlo technique to a bunch of examples from quantum theory, where analytical solutions are well known.
The VMC procedure is based upon:

- the application of the *variational principle*
- the use of the *Metropolis algorithm* in evaluating integrals.

Let's focus on quantum systems and the hamiltonian $\mathcal{H}$ with its energy eigenvalue E. We know that if $\psi(R)$[1] is a trial wave function and E_0 the exact ground state eigenvalue for the observable $\mathcal{H}$:

$$\langle \mathcal{H} \rangle_\psi \geq E_0 \tag{1}$$

where the "=" holds if and only if ψ is the exact ground state wave function ψ_0.

Basically the variational MC purpose is to numerically evaluate the expectation value of $\mathcal{H}$ over different trial wave functions - each characterized by one ore more different "variational parameter" α - and identify in which case we get the lowest upper bound for E_0.

The expectation value of the hamiltonian on the trial wave function is calculated transforming the integral in a form suitable for MC integration so that the importance sampling technique can be applied:

$$\langle \mathcal{H} \rangle_\psi = \frac{\int \psi*(R)\mathcal{H}\psi(R)dR}{\int |\psi(R)|^2 dR} = \int \left(\frac{|\psi(R)|^2}{\int |\psi(R)|^2 dR} \right) \left(\frac{\mathcal{H}\psi(R)}{\psi(R)} \right) dR \equiv \int w(R)\mathcal{H}_L(R)dR \approx \frac{1}{n}\sum_{i=1}^{n} \mathcal{H}_L(R_i) \tag{2}$$

where the configurations R_i are distributed according to: $w(R) = \frac{|\psi(R)|^2}{\int |\psi(R)|^2 dR}$.

As discussed in the previous unit in §1.3, the Metropolis algorithm consists of two distinct phases: an initial *equilibration* stage and the *evaluation* stage. During the initial equilibration stage, the walker is moved according to the Metropolis algorithm, but the local energy $\mathcal{H}_L(R_i)$ is not accumulated. This stage is necessary because the initial starting point of the walker is chosen randomly and therefore a set of moves are required before the average along its walk is correctly sampling the distribution $w(R)$. During the energy evaluation stage, instead, the energy of the walker is accumulated after each move when a new configuration is generated[2].

The required number of equilibration steps can be established by exploiting the "variance criterion" we used in the previous unit. In other words, if it exists, we first find the exact analytical variance of the $w_\alpha(R)$ distribution. Then, averaging over different runs, we estimate the *burn-in time* looking at the displacement of the numerical average from the exact one and taking the point for which $\Delta < 0.05$. Repeating this procedure starting from different values of the variational parameter, we can get a rough idea of how the number of equilibration steps changes with α applying an interpolation. The so obtained function $f(\alpha, \{fit\ \ parameters\}; \psi)$ can be used in the main code to establish the number of equilibration steps requested with a certain α, provided the trial function is ψ.

Furthermore, in order to reduce the running times and the amplitude of stochastic errors, we included in the code the possibility of taking advantage of *reweighting*. This technique consist in using more than a single time a generated sampled sequence from the Metropolis algorithm, turning the expectation value integrals into weighted averages. Thanks to this "recycling" approach, starting from a certain α_0 we can generate a sequence of points distributed according to $w_{\alpha_0}(R)$ and use it to evaluate *also* $\langle \mathcal{H}_L \rangle_\alpha$ for $\alpha > \alpha_0$ through a weighted sum, instead of generating another set of values from $w_\alpha(R)$:

$$\langle \mathcal{H}_L \rangle_\alpha = \frac{\int |\psi_\alpha(R)|^2 \mathcal{H}_L(R)dR}{\int |\psi_\alpha(R)|^2 dR} = \frac{\int r_\alpha(R)|\psi_{\alpha_0}(R)|^2 \mathcal{H}_L(R)dR}{\int r_\alpha(R)|\psi_{\alpha_0}(R)|^2 dR} \approx \frac{\sum_i r_\alpha(R_i)\mathcal{H}_L(R_i)}{\sum_i r_\alpha(R_i)} \tag{3}$$

[1] where R stands for the whole set of the quantum system coordinates, being a single particle system or a many-body one

[2] It can be demonstrated that, for many-body systems, it is more convenient moving one particle at a time, individually

The weight factors that take into account how the distribution function changes as the variational parameter changes are $r_\alpha(R) = |\psi_\alpha(R)|^2/|\psi_{\alpha_0}(R)|^2$. However, if the parameters α and α_0 move too far away, the weights span too large of a range and the error bars of the calculated energy become large. We should thus check that the number of effective points of the weighted sum is close enough to the number of points

$$N_{eff} = \frac{\left(\sum_i r_\alpha(R_i)\right)^2}{\sum_i r_\alpha^2(R_i)} \approx n \tag{4}$$

If it is not the case, the algorithm must resample and generate new points.

In what follows we will study both the problem of minimizing the expected value of local energy and the variance, with the possibility of using an important property in the latter case. In fact, if within the set of all the parametric wave functions we test it happens to be the exact solution corresponding to the hamiltonian ground state, the numerical simulation will yield to the exact value of zero for the variance. This feature, usually referred to as *zero variance property*, holds in general for any hamiltonian, even for those harder cases where the minimum of $\langle E \rangle$ is not known. Since it can allow us to save quite a lot of time, we are going to apply it whenever there will be the opportunity.

The hamiltonian we will refer to in this section is the iconic[3]:

$$\mathcal{H} = E_{kin} + E_{pot} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \tag{5}$$

1.1 Gaussian trial wave function

The first trial function we employ is $\psi_\beta(x) = Ae^{-\beta x^2}$, with A the normalization constant and β the variational parameter.

Before proceeding any further with the actual integration, we perform an early *calibration* on two distinct features we need to track when dealing with Metropolis-like algorithms. They consist in:

- studying how the equilibration length changes with the variational parameter
- checking the acceptance ratio approximately oscillates between 0.3 and 0.5 when the variational parameter is updated

Since we are focusing on a gaussian trial function, we know from the previous unit that fixing $\delta = 5\sigma = 5 * 1/2\sqrt{\beta}$ should provide us an optimal acceptance ratio throughout the whole simulation. As for the equilibration length, according to what explained few paragraphs above, we can fit the trend obtained from the variance criterion with a power law. It gives some coefficients we will use in the VMC routine in order to establish the burn in period for each iteration over β. Image 1.1 shows the situation.

Now, let's come to the heart of the code. As explained earlier, in order to evaluate $\langle \mathcal{H} \rangle$ with the VMC technique we will pass through the "local" quantities:

$$\begin{cases} E_{\mathrm{kin},L}(x) \equiv \frac{E_{\mathrm{kin}}\psi(x)}{\psi(x)} = \frac{-\frac{1}{2}\frac{d^2}{dx^2}\psi(x)}{\psi(x)} = -2\beta^2x^2 + \beta \\ E_{\mathrm{pot},L}(x) \equiv \frac{E_{\mathrm{pot}}\psi(x)}{\psi(x)} = \frac{1}{2}x^2 \end{cases} \tag{6}$$

The integrals we aim to calculate are the following expectation values:

$$\begin{cases} \langle E_{\mathrm{kin},L} \rangle = \frac{\langle \psi | E_{\mathrm{kin},L} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \left(\frac{1}{4\sigma^2} - \frac{x^2}{8\sigma^4} \right) |\psi(x)|^2 dx}{\int |\psi(x)|^2 dx} = \frac{\beta}{2} \\ \langle E_{\mathrm{pot},L} \rangle = \frac{\langle \psi | E_{\mathrm{pot},L} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \frac{x^2}{2} |\psi(x)|^2 dx}{\int |\psi(x)|^2 dx} = \frac{1}{8\beta} \end{cases} \tag{7}$$

which lead to $\langle E_L \rangle = \langle E_{kin,L} \rangle + \langle E_{pot,L} \rangle = \frac{1}{8\beta} + \frac{\beta}{2}$.

[3]Throughout this entire report, we will use the *atomic units* where $\hbar, m, e = 1$. In this way, the lengths are implicitly measured in terms of *Bohr radius* $1a_0 = \frac{\hbar^2}{me^2}$ and the energies in terms of *Rydberg* $1Ry = \frac{me^4}{2\hbar^2}$

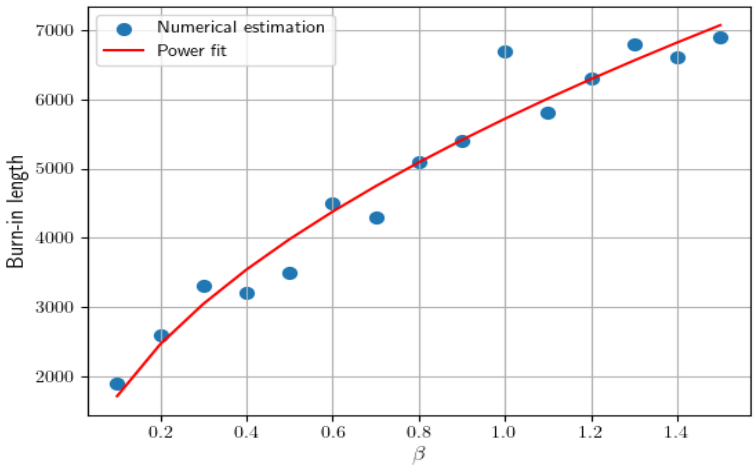

Fig 1.1 Gaussian trial function: equilibration sequence length over β.

Then the variational principle tells us how to find the parameter β which minimizes the energy expectation energy:

$$\frac{d\langle E_L\rangle}{d\beta} = 0 \Longrightarrow \beta_{min} = \frac{1}{2} \qquad \text{and so} \qquad \langle E_L(\beta_{min})\rangle = \frac{1}{2}$$

In this particular case the variational upper limit coincides with the value of the exact analytical solution for the ground state energy, $E_0 = 1/2$. We know this is due to the peculiar choice of the trial wave function: the gaussian function with $\beta = 1/2$ happens indeed to be the exact solution ψ_0 for the ground state of the quantum harmonic oscillator.
Later, it will be interesting looking at least at one other example where the exact result in not contained in the class of the trial wave functions, and see what will occur at the minimum of the $\langle E_L\rangle$ curve. According to what the variational principle tells us, we can easily anticipate it will not longer provide the exact estimation of E_0.

Anyway, when we run the VMC code and numerically evaluate the integrals in eq. (7) through the importance sampling method implemented with the reweighting trick, we get a series of point like the ones in fig 1.2. In order to find the β that corresponds to the trend minimum and confront it to the theoretical expectations, we are going to extract the necessary information from a fit on the data. In particilar, we can set:

$$\langle E_L\rangle = \frac{a}{\beta} + b\beta \Longrightarrow \frac{d\langle E_L\rangle}{d\beta} = -\frac{a}{\beta^2} + b \qquad \text{hence} \qquad \beta_{min} = (a/b)^{1/2}$$

Using $n_{MCsteps} = 10^5$ and taking as error bars the *block average* error estimation on each parameter iteration, the regression gives:

$$a = 0.1248 \pm 0.0003 \qquad b = 0.501 \pm 0.001 \qquad \sigma_{ab} = -3.26 * 10^{-7}$$

The values of β_{min} and $\langle E_L(\beta_{min})\rangle$ can thus be compared to the analytical expected values $\beta_{min} = 1/2$ and $\langle E_L(\beta_{min})\rangle = 1/2$ (the relative uncertainty on the numerical results comes from the *error propagation formula*):[4]

$$\beta_{min} = 0.499 \pm 0.002$$
$$\langle E_L(\beta_{min})\rangle = 0.500 \pm 0.002$$

The numerical simulation thus confirm what expected for this first easy example.

[4] $\sigma_{\beta_{min}} = \sqrt{\left(\frac{d\beta_{min}}{da}\right)^2 \sigma_a^2 + \left(\frac{d\beta_{min}}{db}\right)^2 \sigma_b^2 + 2\left(\frac{d\beta_{min}}{da}\right)\left(\frac{d\beta_{min}}{db}\right)\sigma_{ab}^2}$ and similarly for $\langle E_L(\beta)\rangle$

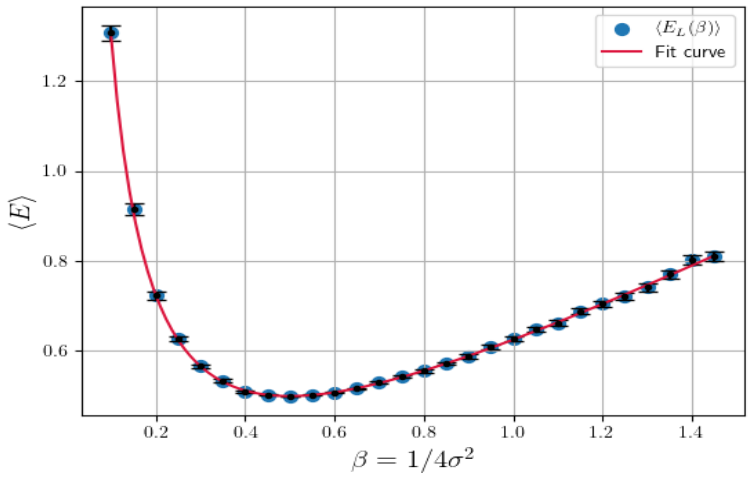

Fig 1.2 Gaussian trial function: local energy expectation value over β.

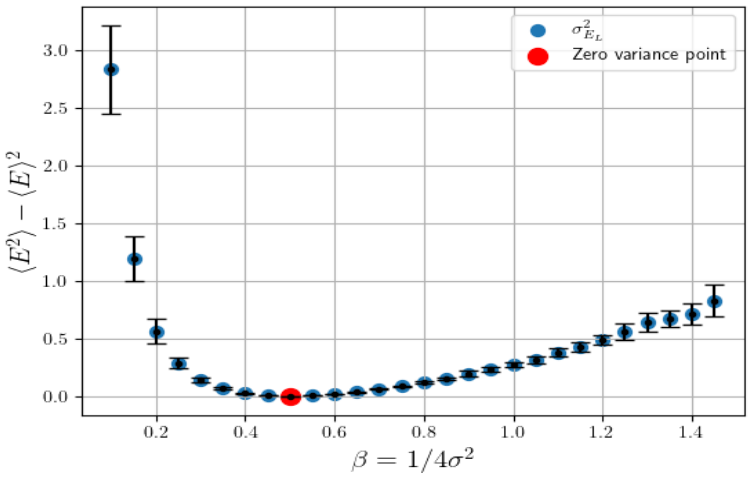

Fig 1.3 Gaussian trial function: energy variance over β.

What has been done so far with the energy can be repeated minimizing the variance:

$$\sigma^2_{E_L} = \langle E_L^2\rangle - \langle E_L\rangle^2$$

We just have to apply the variational algorithm so that we can collect data on the variance and study how it behaves when changing β.
The convenience of this alternative approach is manifestly evident in those cases for which the "zero variance" criterion holds. In fact, whenever such circumstances arise, not only the minimum of the variance curve matches the one of the energy curve, but it is exactly null, making it way easier to identify the β_{min}. Clearly this is not true in general: we will learn more about it with the next example.
In the actual example, instead, we expect the algorithm supply a value (the only one, we hope!) compatible with zero for $\beta = 1/2$, let's say within $1/10^5$. This is indeed what we find looking at fig 1.3, where :

$$\text{for} \quad \beta = 1/2, \qquad \sigma^2_E(\beta_{min}) = 2.5 * 10^{-6}$$

1.2 Parabolic trial wave function

We will follow step by step the procedure of the previous subsection, this time using a different trial wave function:

$$\psi(x) = \begin{cases} B(a^2 - x^2) & \text{if } |x| < a \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

with B the normalization constant and a the variational parameter.

The study of the burn-in length with respect to the variational parameter is analogue to what we did before: the situation is reported in fig 1.4.
As for the acceptance ratio, instead, it is slightly more complicated. In fact, since δ and a are no longer related as δ and β in the gaussian case (where $\delta/\sigma = cost$), the acceptance ratio becomes a function of both these two variables. Through a 3D plot like the one in fig 1.5 we are able to understand when it approximately lies between the ideal values of 0.3 and 0.5. Considering an interval of length 2 around the exact value of a_{min} we will soon calculate, $\delta = 2.7$ appears to be a satisfactory choice.

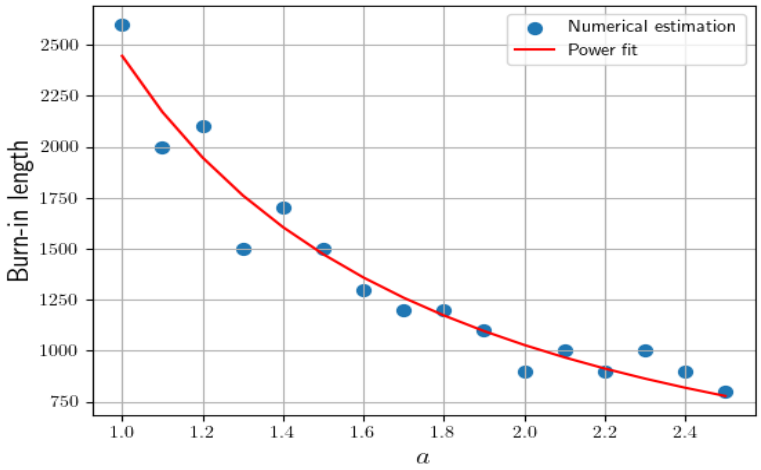

Fig 1.4 Parabolic trial function: equilibration sequence length over a.

Although the shape of the parabola is similar to a gaussian in the interval $[-a, a]$, the variational principle tells us the slight deviation from the exact eigenfunction will necessary lead to an overestimation of the ground state energy.
Even with a very simple example like this one, we can already grasp how critical is the choice of the trial wave function in VMC calculations. In fact, since all the observables are evaluated with respect to the probability distribution $|\psi_T(x)|^2$, the more the trial wave function well approximate the exact eigenstate, the more accurate the results will be. Not to mention that a reasonable trial wave function also improve the importance sampling, reducing the cost of obtaining a certain statistical accuracy.

Here the local quantity we will work on is:

$$E_L(x) \equiv \frac{\mathcal{H}\psi(x)}{\psi(x)} = \frac{1}{a^2 - x^2} + \frac{x^2}{2} \tag{9}$$

Which brings to following expectation value:

$$\langle E_L \rangle = \frac{\int E_L(x)|\psi(x)|^2 dx}{\langle \psi | \psi \rangle} = \frac{5}{4a^2} + \frac{a^2}{14} \tag{10}$$

Again, the variational principle tells us how to find the parameter a which minimizes the energy expectation energy:

$$\frac{d\langle E_L \rangle}{da} = 0 \Longrightarrow a_{min} = \left(\tfrac{35}{2}\right)^{1/4} \quad \text{and so} \quad \langle E_L(a_{min}) \rangle = \sqrt{\tfrac{5}{14}} \approx 0.5976 > 0.5$$

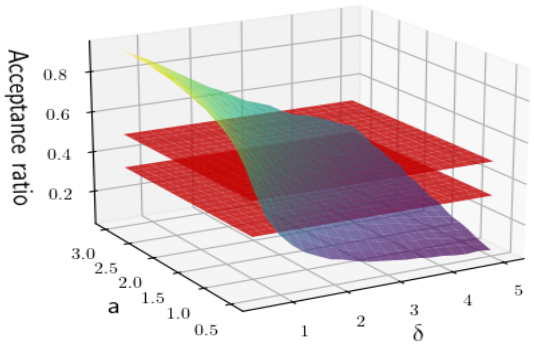

Fig 1.5 Parabolic trial function: acceptance ratio dependence on δ and a.

As suggested before, using a parabolic trial function, the analytical minimum value of $\langle E_L \rangle_\psi$ lies above the exact ground state energy $E_0 = 1/2$.

Running the VMC code and numerically evaluating the integrals in eq. (10) through the importance sampling method implemented with the reweighting trick, we get a series of point like the ones in fig 1.6. Furthermore, we set as before:

$$\langle E_L \rangle = \frac{c_1}{a^2} + c_2 a \implies \frac{d\langle E_L \rangle}{da} = -2\frac{c_1}{a^3} + 2c_2 a \qquad \text{hence} \qquad a_{min} = (c_1/c_2)^{1/4}$$

Using $n_{MCsteps} = 2{*}10^5$ and taking as error bars the *block average* error estimation on each parameter iteration, the regression gives:

$$c_1 = 1.251 \pm 0.002 \qquad c_2 = 0.0714 \pm 0.0001 \qquad \sigma_{c_1 c_2} = -1.04 * 10^{-7}$$

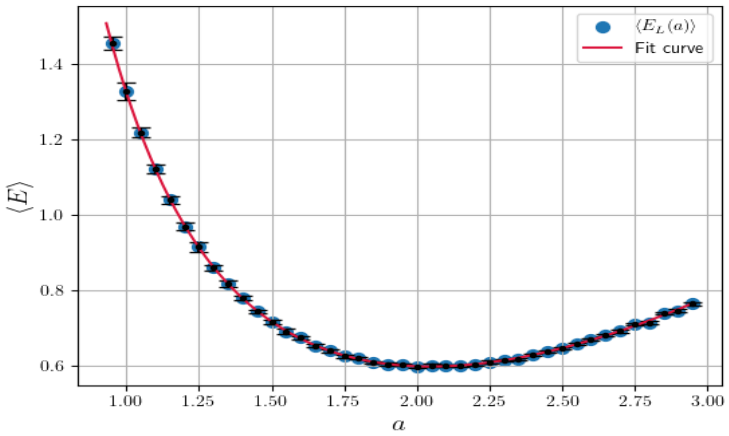

Fig 1.6 Parabolic trial function: local energy expectation value over a.

The values of a_{min} and $\langle E_L(a_{min}) \rangle$ can thus be compared to the analytical expected values $a_{min} = \left(\frac{35}{2}\right)^{1/4}$ and $\langle E_L(a_{min}) \rangle = \sqrt{\frac{5}{14}}$:

$$a_{min} = 2.046 \pm 0.001$$
$$\langle E_L(a_{min}) \rangle = 0.5977 \pm 0.0003$$

The numerical simulation confirm our expectation for this second example.

What about the variance? Plotting it as a function of the variational parameter, we obtain the curve of fig 1.7, whose minimum occur at a certain $\sigma^2 > 0$ for a value of a different from the one we found for the energy. As we mentioned at the end of §1.1, this is a direct consequence of the fact that the parabolic function does not correspond to the exact eigenfunction of the quantum HO.
Fitting the data with the function:

$$\sigma^2_{E_L(a)} \equiv \langle E_L(a)^2 \rangle - \langle E_L(a) \rangle^2 = \frac{5}{16a^4} + \frac{a^4}{147} + \frac{1}{14} = \frac{c'_1}{a^4} + c'_2 a^4 + c'_3 \tag{11}$$

we find indeed the following results:

$$\begin{cases} c'_1 = 0.30 \pm 0.01 \\ c'_2 = 0.0068 \pm 0.0001 \\ c'_3 = 0.071 \pm 0.002 \end{cases} \implies \begin{cases} a_{min} = 1.664 \pm 0.004 \\ \sigma^2_{E(a_{min})} = 0.162 \pm 0.001 \end{cases} \tag{12}$$

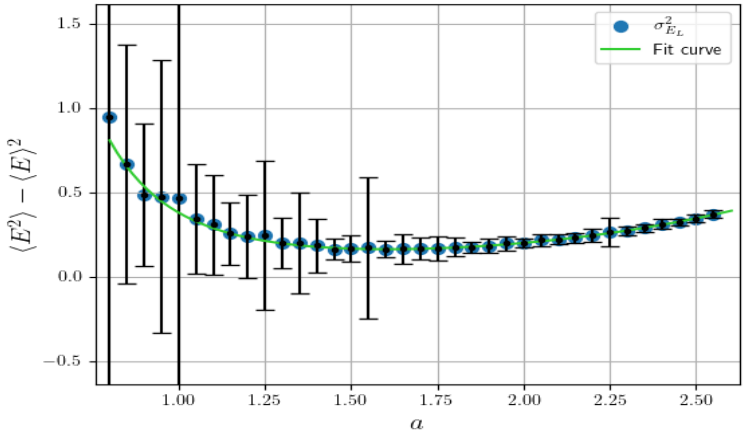

Fig 1.7 Parabolic trial function: energy variance over a.

2 Anharmonic quantum oscillator in 1D

In this section we will study the problem of a quantum harmonic oscillator but with an extra *anharmonic* potential, so that the hamiltonian becomes:

$$\mathcal{H} = E_{kin} + E_{pot}^{harm} + E_{pot}^{anharm} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 + \frac{1}{8}x^4 \tag{13}$$

At this stage, we will compare two possible ways of proceeding: the *quantum perturbation theory* (at the first order) and the VMC.

2.1 Perturbation theory

The process[5] starts with an unperturbed hamiltonian $\mathcal{H}_0$ to which we add a perturbation V representing a weak physical disturbance: $\mathcal{H} = \mathcal{H}_0 + \lambda V$. Here λ is a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (full perturbation). The objective of the perturbation theory is to express the generic E_n and $|n\rangle$ in terms of the energy levels $E_n^{(0)}$ and eigenstates $|n^{(0)}\rangle$ of the unperturbed Hamiltonian. If the perturbation is sufficiently weak, they can be written as a (Maclaurin) power series in λ. Assuming for simplicity that the energies are on a discrete scale, at the first order the energy shift corresponds to:

$$E_n^{(1)} = \frac{\langle n^{(0)} | V | n^{(0)} \rangle}{\langle n^{(0)} | n^{(0)} \rangle} \tag{14}$$

In our example we can take as $\mathcal{H}_0$ the harmonic piece of the overall hamiltonian, and set the anharmonic potential as the perturbation V ($\lambda = 1$): in so doing, the ground state eigenfunction will naturally coincides with the aforementioned gaussian (with $\beta = 1/2$). If we consider the anharmonic term as a small correction to the armonic potential, we can do the algebra and see what result the perturbation theory gives us under this assumption:

$$E_0^{(1)} = \frac{\int \frac{x^4}{8} e^{-x^2} dx}{\int e^{-x^2} dx} = \frac{3}{32} \qquad \Longrightarrow \qquad E_0 \approx E_0^{(0)} + E_0^{(1)} \approx 0.594 \tag{15}$$

This estimation of the anharmonic hamiltonian ground state will be compared to the one obtained with VMC.

2.2 Variational Monte Carlo

Taking as reference eq (13), let us follow the same procedure developed in the first section. Since we know the exact solution to the harmonic case, a reasonable starting point in the choice of the trial wave function for the anharmonic problem is the gaussian: $\psi_\beta(x) = Ae^{-\beta x^2}$.[6]

In so doing, the local energy we take as a reference is the same as the one we took in the very first case, except for the $\mathcal{O}(x^4)$ piece:

$$E_L(x) \equiv \frac{\mathcal{H}\psi(x)}{\psi(x)} = -2\beta^2 x^2 + \beta + \frac{x^2}{2} + \frac{x^4}{8} \tag{16}$$

This brings to following expectation value:

$$\langle E_L \rangle = \frac{\int E_L(x) |\psi(x)|^2 dx}{\langle \psi | \psi \rangle} = \frac{3}{128\beta^2} + \frac{1}{8\beta} + \frac{\beta}{2} \tag{17}$$

The parameter β which minimizes the local energy expectation value can be found as usual through the variational principle. However, since the calculi are rather long and complicated in this less trivial example, we helped ourselves with Mathematica, and report here just the final results:

[5] See "Perturbation theory (quantum mechanics)" from Wikipedia

[6] For such a function the study of the equilibration phase and the acceptance rate has already been carried out in §1.1

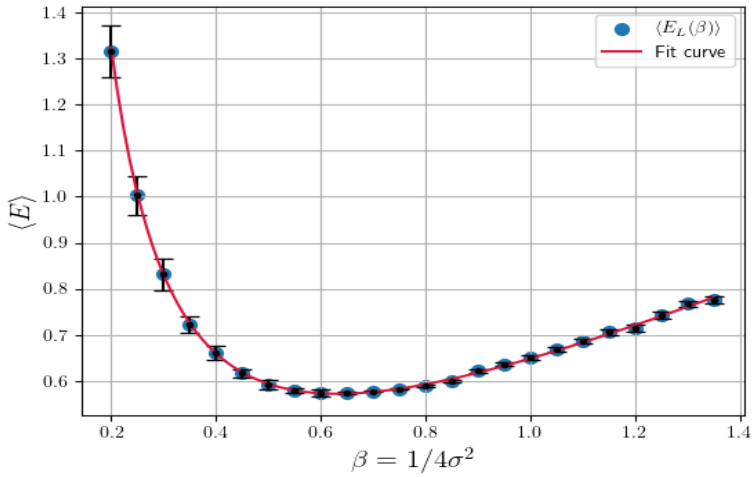

Fig 2.1 Gaussian trial function for anharmonic hamiltonian: local energy expectation value over β.

$$\frac{d\langle E_L\rangle}{d\beta} = 0 \Longrightarrow \beta_{min} \approx 0.631 \qquad \text{and so} \qquad \langle E_L(\beta_{min})\rangle \approx 0.572$$

Running the VMC code and numerically evaluating the integrals in eq. (17), we get a series of point like the ones in fig 2.1. Furthermore, we write the fitting function as:

$$\langle E_L\rangle = \frac{c_1}{\beta^2} + \frac{c_2}{\beta} + c_3\beta a \Longrightarrow \frac{d\langle E_L\rangle}{d\beta} = \frac{-2c_1-\beta c_2+\beta^3 c_3}{\beta^3} \qquad \text{hence} \qquad \beta_{min} = f(c_1,c_2,c_3)^7$$

Using $n_{MCsteps} = 10^5$ and taking as error bars the *block average* error estimation on each parameter iteration, the regression on $\langle E\rangle$ gives:

$$\begin{array}{lll} c_1 = 0.024 \pm 0.002 & c_2 = 0.122 \pm 0.004 & c_3 = 0.502 \pm 0.003 \\ \sigma_{c_1c_2} = -6.48 * 10^{-6} & \sigma_{c_1c_3} = 3.76 * 10^{-6} & \sigma_{c_2c_3} = -9.91 * 10^{-6} \end{array}$$

The values of β_{min} and $\langle E_L(\beta_{min})\rangle$ can thus be compared to the analytical expected values $\beta_{min} = 0.631$ and $\langle E_L(\beta_{min})\rangle = 0.572$:

$$\begin{array}{c} a_{min} = 0.631 \pm 0.003 \\ \langle E_L(a_{min})\rangle = 0.572 \pm 0.001 \end{array}$$

The outcomes of the numerical simulation are in accordance with the theoretical expectations.

2.3 Comparison between the two methods

As mentioned in §2.1, we close with a brief comparison between the two results, one from perturbation theory and the second from the variational technique.
Our main purpose is to provide a good estimation to the ground state energy. Accordingly - as happens most of the time - if its exact value cannot be analytically determined, the best we can do is to find an upper limit that is as closest as possible to it. In other words, the *lower* the estimation, the better it is. For this reason, we conclude that with the considered hamiltonian (13) the VMC method works better than first order perturbation theory, since:

$$\langle E\rangle_{VCM} = 0.572 \quad < \quad \langle E\rangle_{1OrdPert} = 0.594 \tag{18}$$

[7] $f(c_1,c_2,c_3) = \dfrac{c_2}{\left(3(9c_1c_3^2+\sqrt{3(-c_2^3c_3^3+27c_1^2c_3^4)})\right)^{1/3}} + \dfrac{\left((9c_1c_3^2+\sqrt{3(-c_2^3c_3^3+27c_1^2c_3^4)})\right)^{1/3}}{3^{2/3}c_3}$

3 Hydrogen atom (optional)

The third and last example we analyze is the hydrogen atom, for which we are going to provide the best numerical estimation of the energy ground state through the VCM technique. The starting hamiltonian reads:

$$\mathcal{H}_{TOT} = -\frac{1}{2}\nabla^2 - \frac{1}{\mathbf{r}} \tag{19}$$

This general 3D problem can be naturally separated into a 1D radial part and an angular part passing through polar coordinates. Then, since we are interested in the lowest energy state which has spherical spacial symmetry, the considered problem can be reduced to 1D:

$$\mathcal{H} = -\frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) - \frac{1}{r} \tag{20}$$

Thus, it comes rather spontaneous choosing as trial function the *s-type* function $\psi_\alpha(r) = Ae^{-\alpha r}$ with α variational parameter and A normalization constant (not to be specified at this stage!).

Before proceeding any further, exactly as we did for the other two cases, we need to study the distribution *calibration* as well. The same logical considerations followed for the parabola still holds here, so we will just report the outcomes.
In fig 3.1 is shown the burn-in length trend with respect to the variational parameter, alongside the fitting function. Whereas, considering an interval of approximate length of 2 around the expected theoretical value of α_{min}, if we fix $\delta = 2.7$ we can have acceptance ratio values in $[0.3, 0.5[$

The local energy we will work on is:

$$E_L(r) = \frac{\mathcal{H}\psi_\alpha(r)}{\psi_\alpha(r)} = -\frac{1}{2}\left(\alpha^2 - \frac{2\alpha}{r}\right) - \frac{1}{r} \tag{21}$$

To calculate the energy expectation value there are a couple of details we need to be aware of: first the overall integration is made over $d\mathbf{r} = r^2 \sin\theta d\theta d\phi dr$. Secondly, the radial integration interval must go from 0 to ∞.

$$\langle E_L \rangle = \frac{\int E_L(r)|\psi_\alpha(r)|^2 d\mathbf{r}}{\langle\psi_\alpha|\psi_\alpha\rangle} = \frac{\int_0^\infty 4\pi r^2 E_L(r)|\psi_\alpha(r)|^2 dr}{\langle\psi_\alpha|\psi_\alpha\rangle} = \frac{\alpha^2}{2} - \alpha \tag{22}$$

The parameter α that minimizes $\langle E_L \rangle$ is given by the variational principle:

$$\tfrac{d\langle E_L\rangle}{d\alpha} = 0 \Longrightarrow \alpha_{min} = 1 \qquad \text{and so} \qquad \langle E_L(\alpha_{min})\rangle = -\tfrac{1}{2}$$

In this case the variational upper limit we find coincides with the value of the exact analytical solution we know from the early courses of Quantum Mechanics. This is a clear consequence of the choice of the trial wave function, since it corresponds to the hydrogen atom ground state eigenfunction.

When running the VMC code to numerically evaluating the integral in eq. (22), the generated points from the Montecarlo algorithm have to be accepted or rejected according to the ratio:

$$\frac{(r')^2|\psi_\alpha(r')|^2}{(r)^2|\psi_\alpha(r)|^2} \tag{23}$$

The data we obtain are showed in fig 3.2.
The fitting function is set as:

$$\langle E_L \rangle = c_1\alpha^2 + c_2\alpha \Longrightarrow \tfrac{d\langle E_L\rangle}{d\alpha} = 2c_1\alpha + c_2 \qquad \text{hence} \qquad \alpha_{min} = \tfrac{-c_2}{c_1}$$

Using $n_{MCsteps} = 2{*}10^5$ and taking as error bars the *block average* error estimation on each parameter iteration, the regression gives:

$$c_1 = 0.500 \pm 0.001 \qquad c_2 = 1.000 \pm 0.001 \qquad \sigma_{c_1 c_2} = -6.24 * 10^{-6}$$

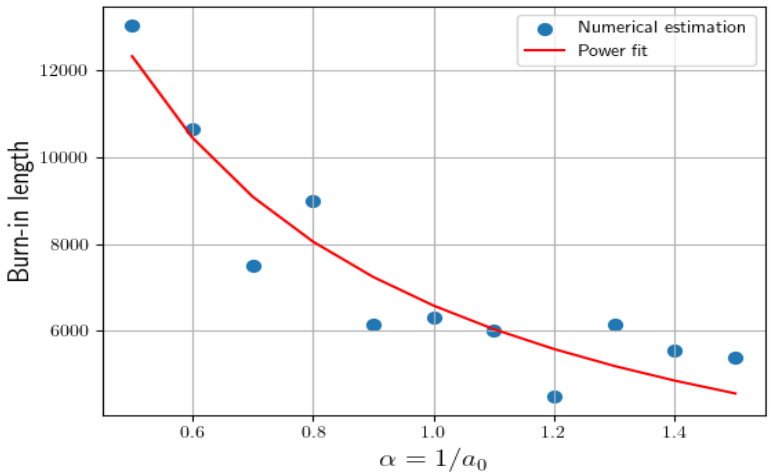

Fig 3.1 Exponential trial function: equilibration sequence over α.

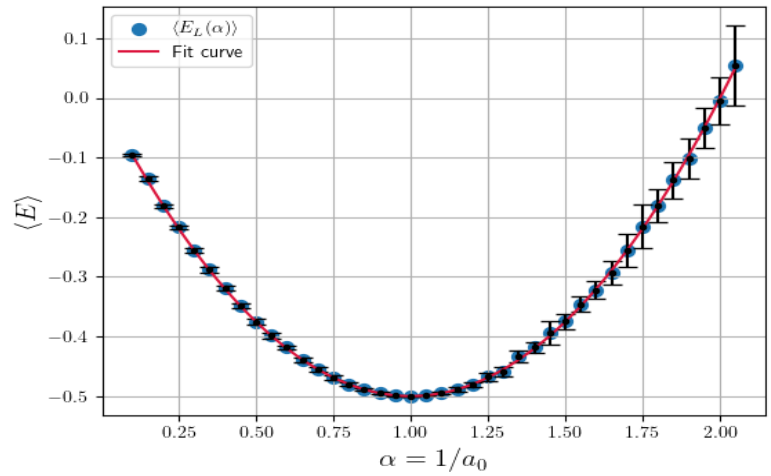

Fig 3.2 Exponential trial function for H-atom hamiltonian: local energy expectation value over α.

The values of α_{min} and $\langle E_L(\alpha_{min}) \rangle$ can thus be compared to the analytical expected values $\alpha_{min} = 1$ and $\langle E_L(\alpha_{min}) \rangle = -0.5$:

$$\alpha_{min} = 1.000 \pm 0.001$$
$$\langle E_L(\alpha_{min}) \rangle = -0.50000 \pm 0.00002$$

The agreement of the numerical simulation with the theoretical expectations is evident.

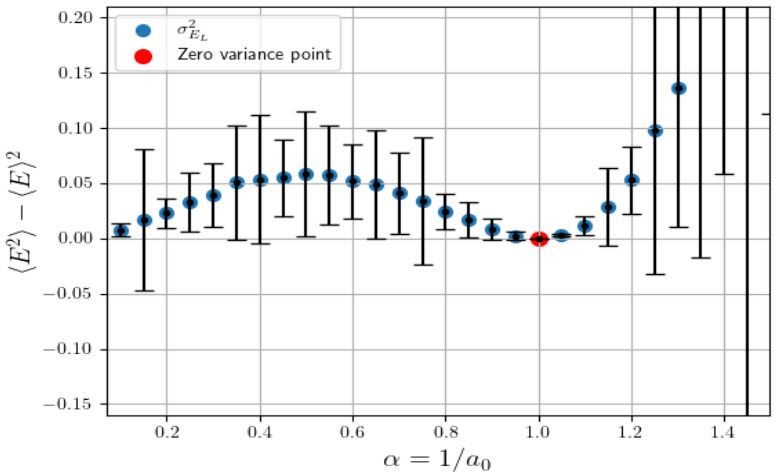

Fig 3.3 Exponential trial function for H-atom hamiltonian: energy variance over α.

If we repeat the procedure, studying instead of the energy its variance, we should get the same results according to the "zero variance" criterion. Taking as a reference the points showed in fig 3.3, we see that exactly for $\alpha = 1$ the energy variance is compatible with zero within the threshold of 10^{-5}:

$$\text{for} \quad \alpha = 1, \qquad \sigma_E^2(\alpha_{min}) = 1.3 * 10^{-6}$$