Computational Physics Final Project
Quantum Monte Carlo Schrodinger Solver

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Abstract

We develop a Quantum Monte Carlo (QMC) solver for finding the ground state solution of the Schrodinger's equation for molecules using variational Monte Carlo method. We run test problems for light atoms and molecules such as H, He, H_2^+, and H_2 and compare the QMC results with their exact ground state energy. The solver is implemented in three spatial dimensions and can solve for ground state energy of any molecular structure given a physical trial wavefunction.

I. THEORY

A. Schrödinger's Equation

The Hamiltonian of a system consisting of N electrons with position $\boldsymbol{r}_i$ and K nuclei $(N > K)$ with position $\boldsymbol{R}_j$, different masses M_j, and different charges Z_j is written as follows[1]

$$\mathcal{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{j=1}^{K}\frac{1}{M_j}\nabla_j^2 - \sum_{i=1}^{N}\sum_{j=1}^{K}\frac{Z_j}{|\boldsymbol{r}_i - \boldsymbol{R}_j|} + \sum_{i<i'}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_{i'}|} + \sum_{j<j'}\frac{Z_j Z_{j'}}{|\boldsymbol{R}_j - \boldsymbol{R}_{j'}|}. \quad (1)$$

We assume that the nuclei masses M_j are relative to the mass of electron, m, and distances are relative to Bohr radius $a_0 = 4\pi\varepsilon_0\hbar^2/me^2$ where ε_0 is the permittivity of free space, $\hbar$ is the reduced Planck's constant, and e is the elementary charge. All the terms in the Hamiltonian are relative to $E_0 = e^2/4\pi\varepsilon_0 a_0$. The first two term on the right hand side of Eq. 1 are the kinetic energy of electrons and nuclei, respectively. The third term is the electron-nucleus potential and finally the fourth and fifth terms are electron-electron and nucleus-nucleus potential. The corresponding Schrödinger's equation is $\mathcal{H}\Psi = E\Psi$ where E is the energy of the system and Ψ is the wavefunction of the system. In this project we are interested in the ground state solution of Schrödinger's equation, i.e. finding the minimum E and its corresponding Ψ. To solve this problem efficiently we need to make the following approximations: The temperature is zero, i.e. $T = 0$; the nuclei have fixed position (Born-Oppenheimer approximation); there is no magnetic or spin dependent term in the Hamiltonian of the system.

The Born-Oppenheimer approximation states that the kinetic energy term of the nuclei can be dropped from Hamiltonian in Eq. 1. The reason is that the nuclei are much heavier than the electrons and since they have approximately the same momentum as that of electrons, their kinetic energy is significantly less than that of electrons. Therefore, a good approximation is to assume the position of the nuclei is fixed. Within this approximation the last term of Eq. 1 becomes a constant energy term that can be solved separate from the rest of the terms. Hence, the Born-Oppenheimer Hamiltonian is written as

$$\mathcal{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{j=1}^{K}\frac{Z_j}{|\boldsymbol{r}_i - \boldsymbol{R}_j|} + \sum_{i<i'}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_{i'}|}. \quad (2)$$

The simplest way to solve for the ground state energy of this Hamiltonian is to use Variational

Monte Carlo method which is described in the next section.

B.   Variational Monte Carlo

The variational principle states that for a given Hamiltonian $\mathcal{H}$ and a trial wavefunction Ψ_T, the expectation value of the Hamiltonian $\langle \mathcal{H} \rangle$ is an upper bound to the ground state energy E_0, i.e. $\langle \mathcal{H} \rangle > E_0$. The expectation value of $\mathcal{H}$ is defined as follows

$$\langle \mathcal{H} \rangle = \frac{1}{\mathcal{N}} \int \Psi_T^*(\boldsymbol{R}) \mathcal{H} \Psi_T(\boldsymbol{R}) d\boldsymbol{R} \tag{3}$$

where $\mathcal{N} = \int \Psi_T^*(\boldsymbol{R}) \Psi_T(\boldsymbol{R}) d\boldsymbol{R}$ is the wavefunction normalizer. The variational procedure to minimize $\langle \mathcal{H} \rangle$ and obtain E_0 is as follows[2]:

1. Construct a trial wavefunction $\Psi_T(\boldsymbol{R}, \boldsymbol{\alpha})$ describing a many body system consisting of N electrons at position $\boldsymbol{R} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$. Variational parameters are denoted as $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \cdots, \alpha_m)$.

2. Evaluate $\langle \mathcal{H} \rangle = \frac{1}{\mathcal{N}} \int \Psi_T^*(\boldsymbol{R}, \boldsymbol{\alpha}) \mathcal{H} \Psi_T(\boldsymbol{R}, \boldsymbol{\alpha}) d\boldsymbol{R}$ where $\mathcal{N} = \int \Psi_T^*(\boldsymbol{R}, \boldsymbol{\alpha}) \Psi_T(\boldsymbol{R}, \boldsymbol{\alpha}) d\boldsymbol{R}$

3. Vary $\boldsymbol{\alpha}$ and repeat step 2 to reach the minimum.

The integral in Eq. 3 is $3N$ dimensional (3 spatial coordinates for N electrons). Therefore, direct evaluation of this integral for $N > 1$ becomes intractable. To evaluate $\langle \mathcal{H} \rangle$ efficiently, we use Monte Carlo method along with Metropolis algorithm which is the subject of next section.

C.   Metropolis Algorithm

First we introduce a function called *Local Energy* which is defined as follows

$$\mathcal{E}(\boldsymbol{R}, \boldsymbol{\alpha}) = \frac{1}{\Psi_T(\boldsymbol{R}, \boldsymbol{\alpha})} \mathcal{H} \Psi_T(\boldsymbol{R}, \boldsymbol{\alpha}). \tag{4}$$

This function has a smooth behavior for a trial wavefunction close to the exact wavefunction of the ground state. The sparsity of the function is factored out. We can see that if we replace the trial wavefunction with the exact wavefunction, the local energy becomes constant over the space, i.e. $\mathcal{E}(\boldsymbol{R}, \boldsymbol{\alpha}) = E_0$. Rewriting Eq. 3 in terms of Local Energy, we obtain

$$\langle \mathcal{H} \rangle = \int P(\boldsymbol{R}, \boldsymbol{\alpha}) \mathcal{E}(\boldsymbol{R}, \boldsymbol{\alpha}) d\boldsymbol{R} = \langle \mathcal{E}(\boldsymbol{\alpha}) \rangle, \tag{5}$$

where $P(\boldsymbol{R}, \boldsymbol{\alpha}) = \Psi_T^*(\boldsymbol{R})\Psi_T(\boldsymbol{R})/\mathcal{N}$ is a Probability Density Function (PDF) used to take the expectation value of $\mathcal{E}(\boldsymbol{R}, \boldsymbol{\alpha})$ with. Using Metropolis algorithm, we draw samples from the PDF and calculate $\langle \mathcal{E}(\boldsymbol{\alpha}) \rangle$ as follows

1. Put W walkers at random positions, i.e. $\boldsymbol{R}_1, \boldsymbol{R}_2, ..., \boldsymbol{R}_W$.

2. Select the next walker.

3. Generate the new random position for the walker by shifting the position of a random electron in space, i.e. $\boldsymbol{R}' = \boldsymbol{R} + \Delta\boldsymbol{R}$.

4. Evaluate $r = \Psi_T(\boldsymbol{R}', \boldsymbol{\alpha})/\Psi_T(\boldsymbol{R}, \boldsymbol{\alpha})$; accept the new position with probability $\min(1, r)$.

5. If accepted, replace $\boldsymbol{R}$ with $\boldsymbol{R}'$ and calculate and store energy and variance.

6. Repeat from step 2 until desired variance is achieved.

The step size $\Delta\boldsymbol{R}$ is chosen in such a way that the acceptance rate is roughly 50%.

D.   Trial Wavefunction

The trial wavefunction is an essential part of Variational Monte Carlo for it determines the accuracy of the ground state energy. Any physical function for which the value, gradient, and laplacian can be efficiently computed can be used. Here we use a general well established ground state trial wavefunction suitable for fermionic systems called Slater-Jastrow. The general form of the wavefunciton is as follows

$$\Psi_T(\boldsymbol{R}, \boldsymbol{\alpha}) = \Phi_S(\boldsymbol{R}, \boldsymbol{\alpha}) \prod_{i<j} f(r_{ij}, \boldsymbol{\alpha}) \tag{6}$$

where $\Phi_S(\boldsymbol{R}, \boldsymbol{\alpha})$ is the Slater determinant given as

$$\Phi_S(\boldsymbol{R}, \boldsymbol{\alpha}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\boldsymbol{r}_1, \boldsymbol{\alpha}) & \phi_1(\boldsymbol{r}_2, \boldsymbol{\alpha}) & \cdots & \phi_1(\boldsymbol{r}_N, \boldsymbol{\alpha}) \\ \phi_2(\boldsymbol{r}_1, \boldsymbol{\alpha}) & \phi_2(\boldsymbol{r}_2, \boldsymbol{\alpha}) & \cdots & \phi_2(\boldsymbol{r}_N, \boldsymbol{\alpha}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{r}_1, \boldsymbol{\alpha}) & \phi_1(\boldsymbol{r}_2, \boldsymbol{\alpha}) & \cdots & \phi_1(\boldsymbol{r}_N, \boldsymbol{\alpha}) \end{vmatrix} \tag{7}$$

where $\phi_1(\boldsymbol{r}, \boldsymbol{\alpha}), \cdots, \phi_N(\boldsymbol{r}, \boldsymbol{\alpha})$ are the N single electron atomic orbitals corresponding to the first N quantum numbers. The single electron orbitals in spherical coordinates are given as

$$\phi() \tag{8}$$

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The second part of Eq. 6 accounts for all two-body correlations in the system. A very typical form of $f(r_{ij}, \boldsymbol{\alpha})$ called Pade-Jastrow function is given as follows

$$f(r_{ij}, \boldsymbol{\alpha}) = \exp\left(\frac{\alpha r_{ij}}{2(1 + \beta r_{ij})}\right) \tag{9}$$

where α and β are variational parameters.

II. TEST PROBLEMS

A. Hydrogen Atom (H)

In the case of Hydrogen atom, the trial wavefunciton reduces to the 1s orbital resulting

$$\Psi_T(\boldsymbol{R}, \alpha) = \phi_1(\boldsymbol{r}_1, \alpha) = e^{-\alpha|\boldsymbol{r}_1|} \tag{10}$$

where the nucleus is located at the origin and $\boldsymbol{r}_1$ is the position of the electron. Using this trial wavefunction we calculate the expectation value of the Local Energy, $\langle \mathcal{E}(\alpha) \rangle$, for various values of α. Figure 1 plots $\langle \mathcal{E}(\alpha) \rangle$ as a function of α. As we can see the local energy
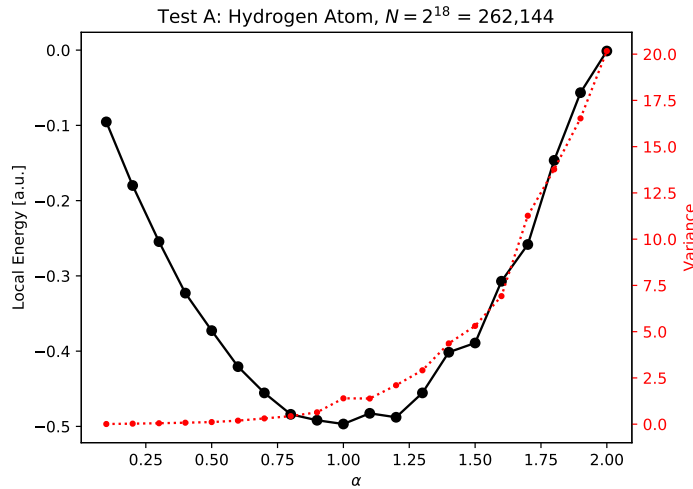

FIG. 1. Expectation value of Local Energy for Hydrogen atom, $\langle \mathcal{E}(\alpha) \rangle$, as a function of α which is the variational parameter. N is the number of Monte Carlo samples at each value of α.

reaches its minimuam, $\langle \mathcal{E}(\alpha) \rangle = -0.4968$ a.u., at $\alpha = 1.0$ which seems reasonable compared to the exact value of $E_0 = -0.5$ a.u.. The variance is also plotted in Fig. 1. The reason that variance is not minimized at $\alpha = 1.0$ is that the trial wavefunction is not equal to the exact wavefunction.

B. Helium Atom (He)

Assuming that the two electrons of Hellium have opposite spins, their first two orbitals would both be equal to the 1s orbitla, i.e. $\phi_1(\boldsymbol{r}, \alpha) = \phi_2(\boldsymbol{r}, \alpha) = e^{-\alpha|\boldsymbol{r}|}$. Therefore the trial wavefunciton for the Helium atom is written as follows

$$\Psi_T(\boldsymbol{R}, \alpha, \beta) = \phi_1(\boldsymbol{r}_1, \alpha)\phi_1(\boldsymbol{r}_2, \alpha)f(r_{12}, \beta) = e^{-\alpha|\boldsymbol{r}_1|}e^{-\alpha|\boldsymbol{r}_2|}e^{r_{12}/2(1+\beta r_{12})}. \tag{11}$$

where α and β are both variational parameters. The nucleus is located at the origin and $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the positions of electrons. Using this trial wavefunction we calculate the expectation value of the Local Energy, $\langle \mathcal{E}(\alpha, \beta) \rangle$, for various values of α and β. Figure 2 plots $\langle \mathcal{E}(\alpha, \beta_0) \rangle$ and $\langle \mathcal{E}(\alpha_0, \beta) \rangle$ as functions of α and β respectively. As we can see the local energy reaches its minimum for $\alpha = 1.8$ and $\beta = 1.7$. The minimum local energy is $\langle \mathcal{E}(\alpha, \beta) \rangle = -2.9039$ whereas the exact ground state energy is $E_0 = -2.85$. Since the wavefunction is more complicated than that of Hydrogen we have used fewer number of Monte Carlo samples for each α and β to reduce computation time. However, this comes at the expense of accuracy as we can see that the error is larger than the case of Hydrogen atom.

C. Hydrogen Molecule Ion (H_2^+)

Extending our test problems, we simlulate an extra nucleus in this section. The equilibruim distance between the two nuclei is $d = 2.0$ a.u. (in terms of Bohr radius). The trial wavefunction in this case is written as follows

$$\Psi_T(\boldsymbol{R}, \alpha, \beta) = \phi_1(\boldsymbol{r}_{1p1}, \alpha) + \phi_1(\boldsymbol{r}_{1p2}, \alpha) = e^{-\alpha|\boldsymbol{r}_1 - \boldsymbol{R}_1|} + e^{-\alpha|\boldsymbol{r}_1 - \boldsymbol{R}_2|}. \tag{12}$$

where $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ are the positions of nuclei. Since there is only one electron in the system, we do not have any electron-electron interaction and hence the Jastrow term drops. Using the trial wavefunction we calculate $\langle \mathcal{E}(\alpha, \beta) \rangle$ for different values of α. Figure 3 illustrates local energy and variance vs. α. As we can see the local energy reaches its minimum $\langle \mathcal{E}(\alpha) \rangle = -0.5985$ at $\alpha = 1.4$. The exact value of ground state energy is $E_0 = -0.6$.
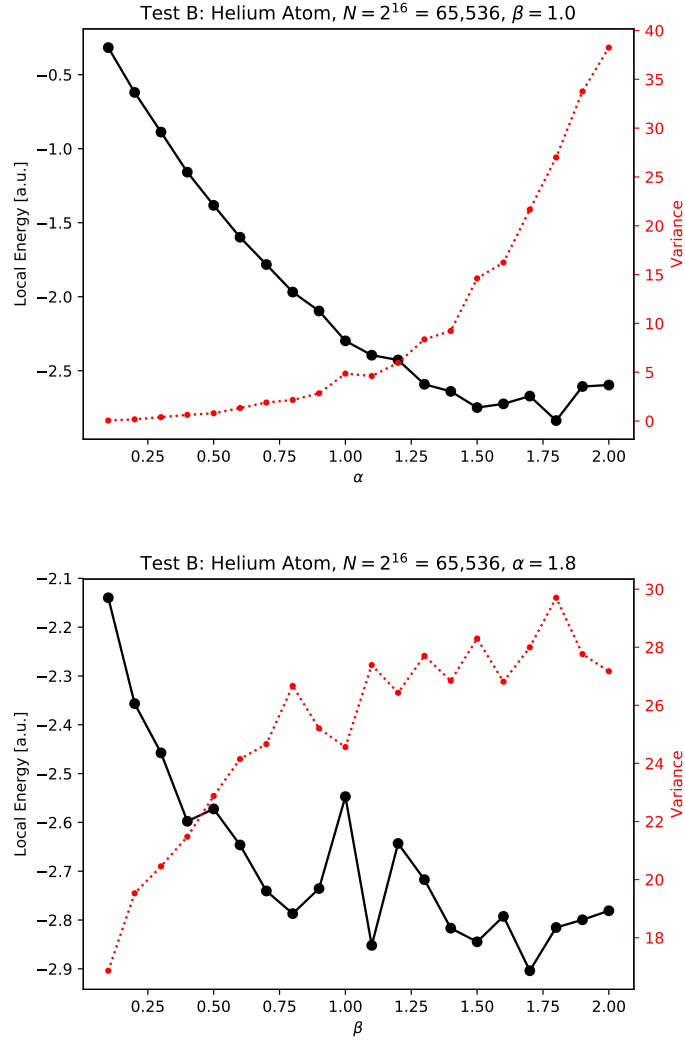
FIG. 2. Expectation value of Local Energy for Helium atom, $\langle \mathcal{E}(\alpha, \beta_0) \rangle$ as a function of α for $\beta_0 = 1.0$ (top) and $\langle \mathcal{E}(\alpha_0, \beta) \rangle$ as a function of β for $\alpha_0 = 1.8$ (bottom)

D. Hydrogen Molecule (H$_2$)

Adding another electron to the prevoius test problems, we simlulate the Hydrogen molecule in this section. The equilibruim distance between the two nuclei is $d = 1.4$ a.u. (in terms of Bohr radius). The trial wavefunction in this case is written as follows

$$
\begin{aligned}
\Psi_T(\boldsymbol{R}, \alpha, \beta) &= (\phi_1(\boldsymbol{r}_{1p1}, \alpha) + \phi_1(\boldsymbol{r}_{1p2}, \alpha))(\phi_1(\boldsymbol{r}_{2p1}, \alpha) + \phi_1(\boldsymbol{r}_{2p2}, \alpha))f(r_{12}, \beta) \\
&= (e^{-\alpha|\boldsymbol{r}_1 - \boldsymbol{R}_1|} + e^{-\alpha|\boldsymbol{r}_1 - \boldsymbol{R}_2|})(e^{-\alpha|\boldsymbol{r}_2 - \boldsymbol{R}_1|} + e^{-\alpha|\boldsymbol{r}_2 - \boldsymbol{R}_2|})e^{r_{12}/2(1+\beta r_{12})}.
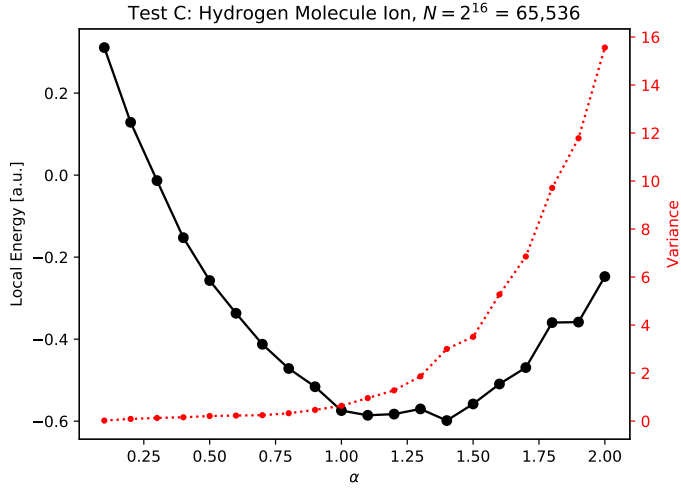\end{aligned}
\tag{13}
$$

FIG. 3. Expectation value of Local Energy, for Hydrogen molecule ion, $\langle \mathcal{E}(\alpha) \rangle$, as a function of α which is the variational parameter.

where $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ are the positions of nuclei and $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the positions of electrons. Figure 4 illustrates local energy and variance vs. α and β. Using the trial wavefunction we calculate $\langle \mathcal{E}(\alpha, \beta_0) \rangle$ in terms of α for the constant $\beta_0 = 1.0$ in the top figure to find the optimum $\alpha = 1.3$. The we calculate $\langle \mathcal{E}(\alpha_0, \beta) \rangle$ in terms of β for the constant $\alpha_0 = 1.3$ to find optimum $\beta = 1.0$. For $\alpha = 1.3$ and $\beta = 1.0$ the local energy reaches its minimum $\langle \mathcal{E}(\alpha, \beta) \rangle = -1.1639$ which is quite remarkable compared to the exact ground state energy of $E_0 = -1.17$ a.u..

[1] Computational Physics, Thijssen, 2012.

[2] Computational Physics, Morten Hjorth Jensen, 2010.

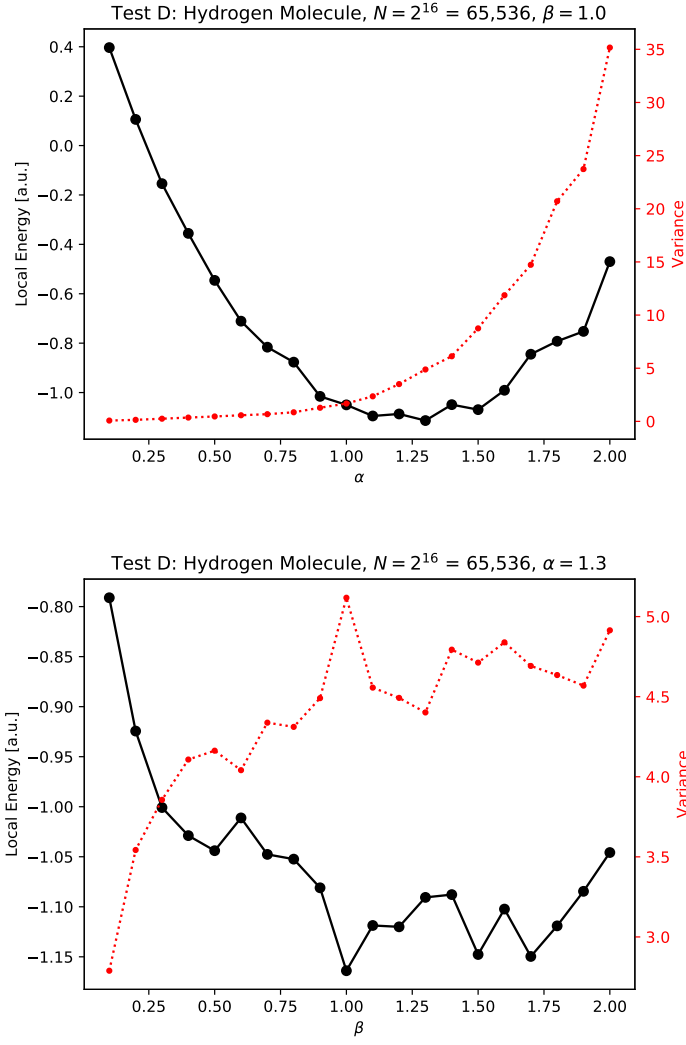FIG. 4. Expectation value of Local Energy for Hydrogen molecule, $\langle \mathcal{E}(\alpha, \beta_0) \rangle$ as a function of α for $\beta_0 = 1.0$ (top) and $\langle \mathcal{E}(\alpha_0, \beta) \rangle$ as a function of β for $\alpha_0 = 1.3$ (bottom)