

ON THE FIXED-NODE IMPORTANCE-SAMPLING QUANTUM MONTE CARLO METHOD: PERFORMANCE ANALYSIS ON MODEL SYSTEMS

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Performance of Importance-Sampling Quantum Monte Carlo process is considered on simple, model systems, such as: multi-dimensional oscillator, hydrogen-like ions, and "helium oscillator" (quadratic-potential analog of helium atom). A mean and standard deviation of that process is numerically determined and also, in the first two cases, calculated analytically together with the distribution of the process values. Results are presented to show how a mean value precision and necessary computational time depend on an importance function quality and dimensionality of the case. Distributions are shown to be highly asymmetrical which questions the value of variance-based estimators of precision. However, a variance is proposed to be the good estimate of the importance function quality. Finally, effects of fixed-node approximation on the second excited state of oscillator are presented to explain the meaning of the differences between exact and approximate solutions.

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1. Introduction

Accurate calculations of molecular properties such as binding energies, charge distributions, and potential energy surfaces as well as underlying problem of electron correlation effects are an important goal of quantum chemistry [1]. Most of them use some kind of expansion approach: many-body perturbation theory, multiconfiguration self-consistent field, or configuration interaction. However, an order of dependence of computational time on the number of electrons, that decides what size of molecules the method can treat and slow convergence for high precision calculations, is a reason for a seek of alternate methods. A new approach — Quantum

Monte Carlo solution of the many-body Schrödinger equation, based on different ideas, has undergone a number of reformulations and extensions in recent years and is changing toward the form that can be efficient and precise enough to treat electronic molecular systems with less inherent limitations.

A number of studies have already been performed, mostly on atoms and small molecules, using different versions of the QMC idea, that gave promising results, but still many problems have to be eliminated to ensure its wide applicability.

Electronic energy expectation values for systems like He, Be, F (electron affinity), LiH, H₂O, CH₂ radical (splitting between ³B₁ and ¹A₁ states), H₂+H (energy barrier), with different importance functions, have been determined, leading to satisfactory results.

For example, in LiH case, considered by a few authors, 99.1% of the correlation energy was obtained and statistical uncertainty was reduced to a very small level for the internuclear separation 3.015 a.u. ($E = -8.0697 \pm 0.0002$ a.u. [2] compared to the best *ab initio* estimate of the nonrelativistic Born-Oppenheimer energy -8.0704). Also the whole potential energy surface for LiH ground state has been determined [3] being in good agreement with the experiment (differences of the order of ≈ 0.005 a.u. and statistical errors of the order of ≈ 0.001 a.u.).

Other quantities than energy were also calculated, like expectation values $\langle z^2 \rangle$, $\langle r^2 \rangle$ and the quadrupole moment for H₂ molecule [4] and dipole moment of LiH at its equilibrium internuclear separation [2, 5].

One of the main advantages that the QMC method reveals, is its versatility. It is not bounded to any specific wave function representation and its value lies in the fact that it always goes beyond the analytic form used. Because of that, the method can take advantage of any existing results for the considered case by means of an importance function [6, 2] and can even be treated as a "second step" procedure after SCF or other calculations that improves its outcome.

However, besides other limitations, that will be mentioned in the description of the method, Quantum Monte Carlo process has a stochastic character, that cannot be eliminated. As it is always in Monte Carlo methods, the results are mean values over the process and nevertheless the statistical error can in principle be eliminated, it can sometimes take long runs to reach a desired level of precision. The importance-sampling is the technique that we will concentrate on, that helps to reduce the inherent variance of the QMC process. As presented in the results of this work, if no precise information about the system under consideration is available, the statistical uncertainty can become a serious computational problem and will need a special care.

2. The method

The formulation of the method is based on the analogy between the Schrödinger equation, written in imaginary time, and the classical diffusion equation. The first to discuss this analogy were Metropolis and Ulam [7] who attributed the idea to Fermi.

In atomic units, the transformed Schrödinger equation can be written as

follows:

$$-\frac{\partial \phi}{\partial t}(\mathbf{r}, t) = -D\nabla^2 \phi(\mathbf{r}, t) + [V(\mathbf{r}) - E_T] \phi(\mathbf{r}, t), \quad D \equiv 1/2M. \quad (1)$$

Taking into account the diffusion equation analogy, this can be interpreted as the description of the free diffusion process (the first term of the right-hand side) with branching (the second term), where the time-dependent many-body wave function of the system $\phi(\mathbf{r}, t)$ has to be described statistically as the probability density of finding the "particle" that undergoes the process. (It is positive definite, which causes problems of negative wave function values description, but we discuss it later.) The evolution of $\phi(\mathbf{r}, t)$ can be expressed in the following way, using the expansion in eigenfunctions ϕ_i and eigenvalues E_i of the system Hamiltonian:

$$\phi(\mathbf{r}, t) = \sum_n a_n \phi_n(\mathbf{r}) \exp[-(E_n - E_T)t] \quad (2)$$

and at long times, the asymptotic form (for E_T chosen as being equal to E_0) will be:

$$\phi(\mathbf{r}, \infty) = a_0 \phi_0(\mathbf{r}) \exp[-(E_0 - E_T)t] = a_0 \phi_0(\mathbf{r}). \quad (3)$$

Hence, such a Monte Carlo process will evolve to a steady state of the lowest eigenfunction of the Hamiltonian.

The "particles" that undergo the process are meant as sets of $3N$ coordinates, where N is the number of particles in the system, or if we consider Born-Oppenheimer approximation, the number of electrons. These "particles" are usually called "configurations". Expressing the propagation of the configurations by means of the Green function formulation, we can write:

$$\phi(\mathbf{r}', t + \tau) = \int d\mathbf{r} G(\mathbf{r} \rightarrow \mathbf{r}', \tau) \phi(\mathbf{r}, t). \quad (4)$$

The analytic form of G is not generally known, but in so called Short-Time approximation used here, we can express it as:

$$G(\mathbf{r} \rightarrow \mathbf{r}', \tau) \approx (4\pi D\tau)^{-3N/2} \exp\left[-\frac{(\mathbf{r}' - \mathbf{r})^2}{4D\tau}\right] \exp\{-[V(\mathbf{r}) - E_T]\tau\}, \quad (5)$$

a product of two terms: a normalized Gaussian term (representing diffusive motion) and an exponential branching term (representing duplication/elimination of configurations) [8].

However, such a basic process can be significantly improved in terms of obtaining average values, introducing the idea of importance-sampling [9, 10]. It is one of the most efficient ways to reduce variation in process parameters and to eliminate possible instabilities in the branching term, coming from singularities in the potential $V(\mathbf{r})$. If we define an importance function $\psi_T(\mathbf{r})$, we can describe the propagation of distribution $f(\mathbf{r}, t) = \phi(\mathbf{r}, t)\psi_T(\mathbf{r})$ instead of $\phi(\mathbf{r}, t)$ by means of the Green function:

$$G(\mathbf{r} \rightarrow \mathbf{r}', \tau) = (4\pi D\tau)^{-3N/2} \exp \left[\frac{-(\mathbf{r}' - \mathbf{r} - 2D\tau \nabla \ln |\psi_T(\mathbf{r})|)^2}{4D\tau} \right] \times \exp \{-[E_l(\mathbf{r}) - E_T] \tau\} \quad (6)$$

with the "local energy" $E_l(\mathbf{r})$ defined, for the system's Hamiltonian \mathbf{H} , as:

$$E_l(\mathbf{r}) = \mathbf{H}\psi_T/\psi_T = -D \frac{\nabla^2 \psi_T(\mathbf{r})}{\psi_T(\mathbf{r})} + V(\mathbf{r}). \quad (7)$$

There are four main advantages of this approach:

1. The suitably chosen importance function ψ_T can reduce variations in the sample size coming from the branching term, if E_l is smooth and slowly-varying.
2. The new term $-2D\nabla \ln |\psi_T|$ that adds to the diffusive motion description, is related to a drift velocity, superimposed on that motion. This process makes the most important areas of the high ψ_T value better populated by moving configurations.
3. The ground state energy of the system can be simply calculated as the ensemble average of the local energy $E_l(\mathbf{r})$ sampled from the steady-state function $f_\infty(\mathbf{r})$:

$$\langle \mathbf{H}\psi_T/\psi_T \rangle_{f_\infty} = \frac{\int d\mathbf{r} \phi_0 \psi_T (\mathbf{H}\psi_T/\psi_T)}{\int d\mathbf{r} \phi_0 \psi_T} = \frac{\int d\mathbf{r} \phi_0 \mathbf{H}\psi_T}{\int d\mathbf{r} \phi_0 \psi_T} = E_0. \quad (8)$$

4. The Fermi antisymmetry problem can be handled easily. In a basic approach only a positive definite wave function can be permitted, which is obviously not true for molecular systems. However, if ψ_T could have been chosen with the proper location of nodes, separating positive and negative regions, the effective importance function $f_\infty(\mathbf{r})$ would be positive everywhere. The Fixed-Node approximation states that the importance function ψ_T should be specified to have nodes as close to the true ones as it is possible and that the wave function should be forced to have the same nodes, by use of the absorbing barrier for random walks that crosses them.

The computational scheme in the case of the Fixed-Node Short-Time Quantum Monte Carlo version looks as follows:

1. Initialize a set of N_c configurations according to the starting probability density $f(\mathbf{r}, 0)$.
2. For each configuration in the set, realize diffusive random movement based on $3N$ -dimensional Gaussian distribution and drift movement based on ψ_T gradient.
3. If the configuration would cross a node of ψ_T (a sign change), eliminate it from the set.
4. Else, accept the move with the probability:

$$A(\mathbf{r} \rightarrow \mathbf{r}', \tau) = \min \left(1, \frac{\psi_T^2(\mathbf{r}') G(\mathbf{r}' \rightarrow \mathbf{r}, \tau)}{\psi_T^2(\mathbf{r}) G(\mathbf{r} \rightarrow \mathbf{r}', \tau)} \right) \quad (9)$$

which guarantees a detailed balance in the process.

5. Calculate the branching exponential term value M — multiplicity and according to the value: $\text{int}(M + \zeta)$, where ζ is a random (0–1 interval) number, eliminate (0)

or multiply (> 1) the configuration.

6. Continue from (2) for the next configurations, until none of them is left. Then calculate E_l values necessary for estimation of the energy.

7. Repeat steps (2)–(6) until the mean values are computed with the desired precision.

Quantum Monte Carlo method has a possibility of being, in principle, an accurate method, besides its statistical character, but approximations mentioned above, proved to be useful, at least for small atomic and molecular systems. However, it is possible to remove both of them, at least partially.

In Short-Time approximation removal it is noticed that, despite the fact, the Green function (4) is not generally known, it can be iteratively sampled by generating, so called, "intermediate" configurations, leading to a proper propagation for large time steps [11]. This can shorten the computational time necessary to simulate the systems evolution.

When the nodes of the many-body wave function are not known well enough, or not described properly by the importance function, to reach the desired level of precision in calculations, it is necessary to apply the algorithm that lets them adjust properly. Several propositions were described in [11, 12], from which the nodal release method seems to be most useful. In this case, after the Fixed-Node steady state was achieved, absorbing barriers on nodes are eliminated and configurations can cross them. In such a process their contribution changes sign at each crossing. Effectively the distribution changes the nodes position. However, after some period of time, a transition to the Bose ground state occurs, leading to increase of the process variance, which restricts the use of the release node approach.

3. Implementation

The aim of the work presented here was to analyze performance of the FN QMC method and examine possible problems sources, using model systems for which exact solutions for the wave function and energy are known. These were: one-dimensional and multi-dimensional quantum oscillator, hydrogen atom (and hydrogen-like ions), and "helium oscillator" — quadratic-potential analogy of helium atom.

The implementation of the method, used in computations, was based on the one introduced by Reynolds [13]. According to that, the following features have been included. Application of the importance function was as shown in the introduction. In the case of oscillator excited states, the elimination of configurations that crossed nodes of the importance function has been applied to force the wave function to have properly positioned nodes. A procedure of each configuration movement acceptance/rejection has been used to guarantee the detailed balance in the process for any time step size. An estimation of the ground state energy by the mean value of $E_l = (H\psi_T)/\psi_T$ was used and no other averages were computed.

Differently from that implementation, other way to check the quality of the averages was applied, making the comparison of the theoretical and computational

results easier. First, the configurations were propagated during the period of time that was long enough to reach a stationary state. This was examined by tracing $\langle E_t \rangle$ until it was not moving significantly. Then, the process was propagated to compute the average and variance for the stationary "ground state" with the desired precision. The values from all time steps for all configurations were treated equally and used for averaging. Time of the propagation was long enough for the system to lose "memory" of the initial state, so the position of each configuration was treated as in accordance with stationary probability density distribution and the global average was computed basing on all of their values. Forming "blocks" to average over their averages seemed to be unjustified and difficult to represent theoretically. However, this does not change the interpretation of quantities like variance — only their values. The computation was performed until the standard deviation of $\langle E_t \rangle$ value reached 0.0004 level, but not shorter than 200 time steps.

Approximately 300 configurations were propagated simultaneously (the list was normalised only when it exceeded 400 or went down by 200, by random copying or deletions) — the number is of no importance for the process except for the computational time.

The time step size was chosen arbitrarily as 0.005 on the basis of own observations and suggestions of Reynolds et al. All theoretical calculations neglect the time step error and the comparison with the computed results shows that it was not the significant value.

All the results are presented in atomic units.

4. Results for model systems

Influence of the importance function quality on QMC process was studied on two model systems: quantum oscillator and hydrogen atom.

4.1. Multi-dimensional oscillator

The case was defined by a potential considered, for simplicity, with a constant of force being equal to 1 in the form:

$$V = \sum_{i=1}^n \frac{1}{2} x_i^2. \quad (10)$$

The importance function used was in the form:

$$\psi_T = \prod_{i=1}^n \exp \left[-\frac{1}{2} \alpha x_i^2 \right] \quad (11)$$

that makes easy, using constant α , to alter the shape (width) of the function. The constant α can be related to the constant of force disturbance by expression $\alpha = [(1 + \text{f.c.dist})/2D]^{\frac{1}{2}}$.

Considering V and ψ_T as functions defining stochastic process of obtaining E_t

values on the basis of stationary distribution of configurations, i.e. QMC process, the mean values for E_l were computed:

$$\langle E_l \rangle = \frac{1}{2}n, \quad \sigma^2 = \frac{1}{2}n(\alpha - 1)^2, \quad \sigma = \sqrt{\frac{n}{2}}|\alpha - 1|, \quad (12)$$

where $\langle E_l \rangle$ is the value of the energy of the state, σ is the process standard deviation of E_l values and σ^2 is the process variance of E_l values.

If one uses them to determine the quality of $\langle E_l \rangle$, one can relate it easily to computational time necessary to reach the desired level $\sigma_{\langle E_l \rangle}$ of standard deviation of $\langle E_l \rangle$:

$$t = \frac{\text{step size}}{\sigma_{\langle E_l \rangle}^2} \sigma^2. \quad (13)$$

The way in which σ^2 depends on n — the number of dimensions—comes from additivity of independent process variances. One can easily transform this expression if α constant is anisotropic.

The result gives us a view, how computational effort grows up with the number of particles described and with the quality of the importance function for QMC process. However, one also has to take into account that numerical effort of importance function value evaluation grows both with the number of particles involved and with the quality of this function. This dependence can be estimated for applications to chemical systems as proportional to n^2 , because the interparticle distances calculation seems to be the most time-consuming operation. This gives us a n^3 order dependence for the whole procedure.

The results for chosen values of n are plotted in Fig. 1 together with the values of σ obtained from QMC calculations to verify the theoretical approach. The differences are due to statistical errors of σ values.

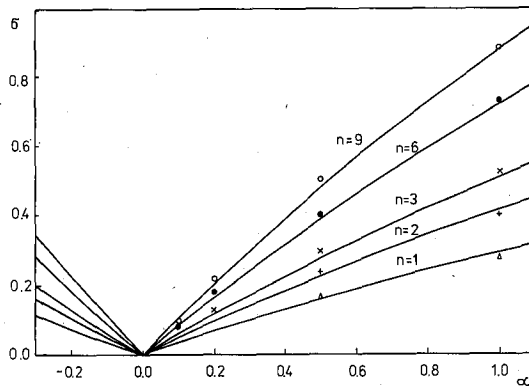


Fig. 1. Multi-dimensional oscillator. Plot of process standard deviation vs. importance function coefficient for different dimensionalities.

In order to examine the way that E_l values deviate from $\langle E_l \rangle$, the probability

density distribution of E_I in QMC process was calculated:

$$\rho(E_I)dE_I = \frac{2 \exp \left[-\frac{2E_I - \alpha}{2(1-\alpha)} \right]}{\sqrt{2\pi(1-\alpha)}\sqrt{2E_I - \alpha}} dE_I \quad (14)$$

and plotted in Fig. 2 for different values of α . One can see that distributions are highly asymmetrical and far from normal distribution, which suggests that σ and $\sigma_{(E_I)}$ should be of very limited employment in the QMC process description.

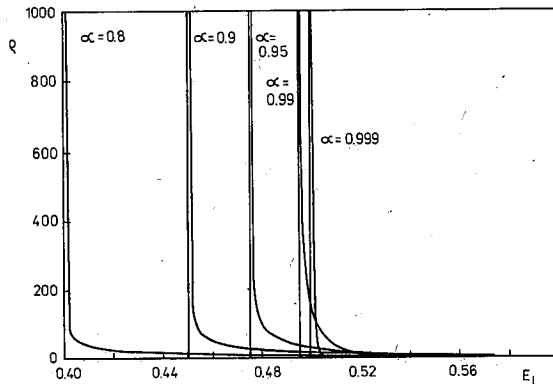


Fig. 2. Oscillator. Distributions of E_I values in QMC process for different values of importance function constant. Mean value = 0.5 for all distributions.

4.2. Hydrogen-like ions

The second model system considered was a hydrogen atom or in general, hydrogen-like ions defined by:

$$V = -\frac{Z}{r}, \quad r = \sqrt{x^2 + y^2 + z^2} \quad (15)$$

with the importance function of the form:

$$\psi_T = \exp(-\alpha r), \quad (16)$$

Z is a nucleus charge.

This case is much more important for molecular applications in Born–Oppenheimer approximation, because of basically the same form of potential and importance function as commonly used (Slater type orbitals). Deviation of the importance function from the exact wave function is achieved by change of α constant, which can be interpreted as a change of nucleus charge screening or simply as using a not optimal Slater function coefficient for calculations.

Analytically calculated parameters of QMC process for E_l values are:

$$\langle E_l \rangle = -\frac{Z^2}{2}, \quad \sigma^2 = \frac{1}{4} (\alpha^2 - Z^2)^2, \quad \sigma = \frac{1}{2} |\alpha^2 - Z^2|. \quad (17)$$

In the independent particles model, the dependence on the number of particles would be the same as it was in the multi-dimensional oscillator model.

The dependence of E_l standard deviation σ on α for $Z = 1$ is plotted in Fig. 3 together with σ obtained from QMC computations.

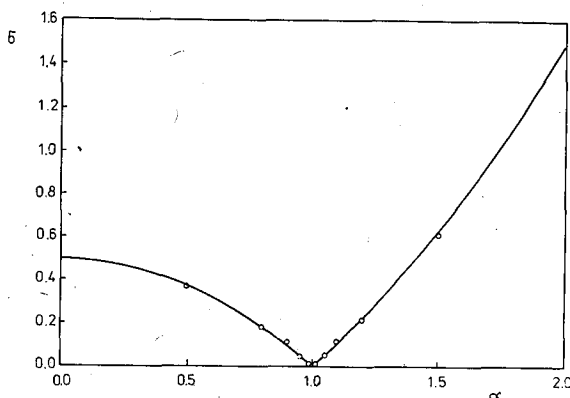


Fig. 3. Hydrogen atom. Plot of process standard deviation vs. importance function coefficient.

The probability density distribution of E_l in QMC process was calculated and is in the form:

$$\rho(E_l)dE_l = \frac{(\alpha^2 - Z^2)^3}{2(E_l + \alpha^2/2)^4} \exp\left(-\frac{\alpha^2 - Z^2}{E_l + \alpha^2/2}\right). \quad (18)$$

This function is plotted in Fig. 4 for different values of α . Asymmetry of the distributions is easily seen, as well as far ranges of their values, which in this case also suggests that σ or σ^2 are improper as distribution parameters.

4.3. Helium oscillator

Another model system that was used to examine QMC procedure was the system of two fermion particles trapped in a quadratic potential well, repelling according to Hook's law, i.e. via also quadratic repulsion term:

$$V = \frac{1}{2}k(r_1^2 + r_2^2) - \frac{1}{2}\beta r_{12}^2, \quad (19)$$

where r_{12} , r_1 , r_2 — are the distance between particles and the distances from the center of the system, respectively. This problem can easily be solved exactly [14].

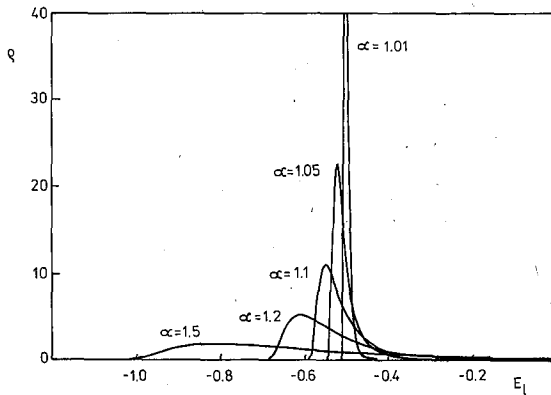


Fig. 4. Hydrogen atom. Distributions of E_l values in QMC process for different values of importance function constant. Mean value = -0.5 for all distributions.

The ground state energy and the wave function are given by:

$$E = \frac{3}{2} \left(\sqrt{k} + \sqrt{k - 2\beta} \right), \quad (20)$$

$$\psi = N \exp \left\{ -\frac{1}{4} \left(\sqrt{k} + \sqrt{k - 2\beta} \right) (r_1^2 + r_2^2) - \frac{1}{2} \left(\sqrt{k} - \sqrt{k - 2\beta} \right) r_1 \cdot r_2 \right\}. \quad (21)$$

Such a system exists only for $\beta < k/2$, in the opposite case repulsion causes its destabilization. The second important feature is that the wave function becomes angularly correlated and contracted with growing β .

Two series of computations were performed, for k stated being equal to 1, with the use of the importance function in the form of the wave function of two independent particles:

$$\psi_T = \exp \left[-\frac{1}{2} \alpha (r_1^2 + r_2^2) \right]. \quad (22)$$

Figure 5 shows a plot of the energy as a function of β calculated from Eq. (11) and computational QMC results obtained for $\alpha = 1$, i.e. for the wave function exact when $\beta = 0$. For small β the numerical results are in good agreement with formula (11), but the computational effort grows quickly with β . However, for $\beta = 0.4, 0.5$, values of $\langle E_l \rangle$ become significantly different from what they should be, in spite of the value of $\sigma_{\langle E_l \rangle}$, being equal for all points. But if ψ_T has a variable parameter α , it is possible to adjust its value to minimise the variance of the process. Figure 6 shows exemplary dependence of σ on α parameter for repulsion $\beta = 0.2$. The values of σ can be obtained with sufficient precision even after very short runs, making possible to optimise the importance function with

little numerical effort. In this case the importance function has only freedom of radial expansion/contraction and the optimal value of α gives the contraction coefficient properly: $\frac{1}{2} (\sqrt{k} + \sqrt{k - 2\beta}) \approx 0.88$ even if the wave function was not computed. However, for further minimization of σ , it would be necessary to include the interparticle correlation factor in ψ_T (like Jastrow pair correlation factor used by Reynolds [13] and others).

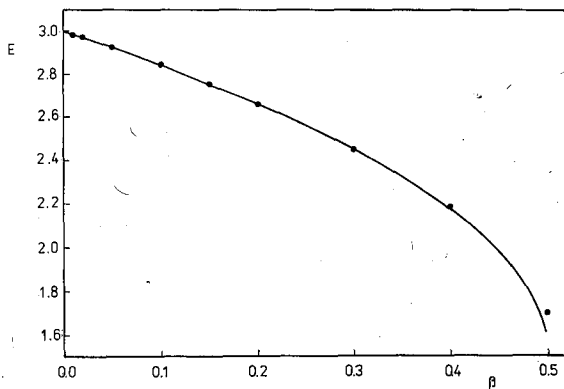


Fig. 5. "Helium oscillator". Plot of ground state energy vs. repulsion constant.

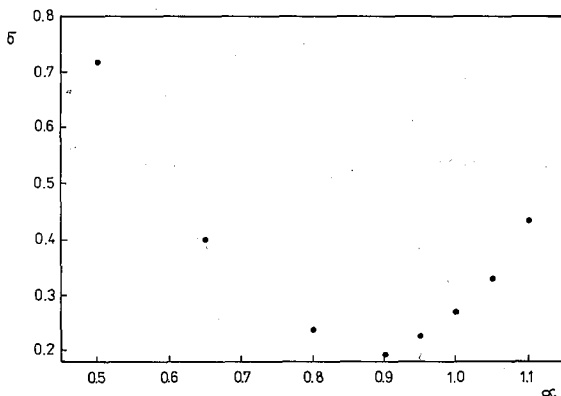


Fig. 6. "Helium oscillator". Plot of process standard deviation vs. importance function coefficient.

4.4. Excited states of oscillator

In all previous examples the problem of wave function nodes did not exist. In real calculations, however, it must occur. To examine importance of nodes position

imposed on the wave function, the energy of the oscillator second excited state was computed from FN QMC process. The importance function used was in the form:

$$\psi_T = \frac{2x^2 - C}{x^4 + A}, \quad C = 2(\sqrt{2} + D)^2, \quad A = \frac{7}{4}C^2, \quad (23)$$

where D is the displacement of nodes from true values, and other constants are chosen in such a way that no singularity in E_1 can occur. As shown in Fig. 7, nodes position influences significantly $\langle E_1 \rangle$. It was shown by Reynolds that for the ground state the Fixed-Node energy is an upper bound to a true energy value, but

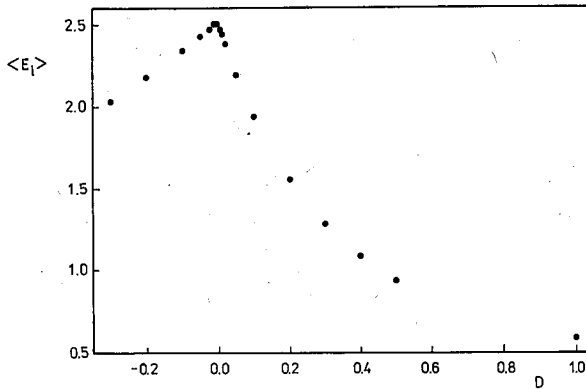


Fig. 7. Oscillator. Second excited state with disturbed nodes position. Plot of computed energy vs. displacement of nodes.

for excited states it is surely not true. As can be seen, $\langle E_1 \rangle$ value for a disturbed nodes wave function includes contribution from lower states and the process tends to reach the lowest possible states for a given nodes position. In the limit of nodes stretched to $+$ and $-$ infinity it reaches the ground state ($E = 0.5$), in the limit of nodes going to the position $x = 0$, it reaches the first excited state ($E = 1.5$).

5. Conclusions

The analysis of properties of Quantum Monte Carlo process performed for a few model systems shows undoubtedly great value of importance-sampling in variance reduction of average values like $\langle E_1 \rangle$. However, it has its effect not only in reducing computational time necessary to reach particular level of average value precision. If disproportion between the importance function and the true wave function is wide, it is shown that distribution of value of interest in QMC process can become asymmetric and far from normal distribution, in which the case values like variance and standard deviation of mean are no longer proper parameters of the distribution and it is unsafe to estimate precision of computations on their basis.

However, it is possible that transformations of the data to "normalise" its distribution, use of different precision estimates or other variance reduction methods can bring much better results if they are adapted to FN QMC characteristics.

It can be seen that the variance of the QMC process is sensitive to differences between the importance function and the true wave function, and often can be determined with little numerical effort. This can be used to optimise the approximate analytical form of the wave function or to prepare the importance function before high precision computations.

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