

Quantum Monte Carlo

EMTCCM / LTCC Winter School

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ABSTRACT

This project endeavors to extend the applicability of a pure diffusion Monte Carlo (DMC) program initially designed for computing the ground state energy of the hydrogen atom to encompass molecules with multiple electrons and nuclei. By incorporating tailored wavefunctions, potential functions, and sampling methodologies, the study explores the theoretical foundations, computational methodologies, and resultant insights into the ground state energies and variational parameters of diverse molecular systems.

INTRODUCTION

Quantum Monte Carlo (QMC) methods provide robust computational tools for simulating quantum systems through stochastic sampling techniques. Among these, the DMC method stands out for its efficacy in accurately estimating ground state properties. This paper documents the adaptation and enhancement of a DMC program originally tailored for the hydrogen atom to address the complexities inherent in molecules featuring multiple electrons and nuclei. The augmentation entails the integration of advanced theoretical concepts, computational methodologies, and empirical validations to facilitate a comprehensive understanding of molecular electronic structures.

COMPUTATIONAL DETAILS

Program Structure: The DMC program comprises several Fortran files, each fulfilling a distinct function:

name_of_the_molecule.f90: Repository for crucial molecular parameters. It contains all the informations about the atoms/molecules we are going to study such as the parameter to use in the expression of the wavefunction (all our molecules are omonuclear) number of electrons (N), number of nucleus (nn), the atomic number of them (Z), the number of steps for each Monte Carlo run (nmax), the number of Monte Carlo runs (nruns), the variance of the normal distribution describing our sampling (dt), a limit projection time used to avoid “explosions or annihilation” in our weights (tau), an energy reference from an H.F. calculation and the geometry of the molecule in a.u. (Nuc(3*nn)).

functions.f90: Implements functions for wavefunction calculation, the potential for a

given system at the electronic coordinates $R(3*N)$, the local kinetic energy and the local energy.

subroutines.f90: Contains subroutines essential for variational Monte Carlo sampling and drift vector computation. It contains the “variational_montecarlo” called qmc subroutine which is used to sample random points according to our probability density, a subroutine for the drift vector, a subroutine called “random_gauss” and the subroutine “ave_error” which calculates the average and the variance of a given vector.

main_qmc.f90: Serves as the central program, orchestrating computations for designated molecular entities. This program asks the user which molecule to study and then reads the informations needed for the calculation from the “name_of_the_molecule.f90” file.

THEORETICAL FRAMEWORK

In molecular systems, the wavefunction (Ψ) is formulated as the non-antisymmetrized product of mono-electronic wavefunctions centered at nuclear coordinates. Each mono-electronic component is represented by a Gaussian function, encapsulating the influence of individual nuclei on the electronic configuration.

$$\Psi = \prod_{i=1}^N \Phi(r_i)$$

$$\Phi(r_i) = \frac{1}{\sqrt{N}} \sum_{a=1}^{nn} \chi(r_i, R_a)$$

$$\chi(r_i, R_a) = e^{(-a|r_i - R_a|)}$$

Where $\chi(r_i, R_a)$ represents the contribution of each nucleus to the wavefunction.

The potential energy (V) of a molecule comprises electron-nucleus attraction, electron-electron repulsion, and nucleus-nucleus repulsion terms. The potential energy function is expressed as:

$$V(R) = - \sum_{i=1}^N \sum_{a=1}^{nn} \frac{Z_a}{|r_a - r_i|} + \sum_{i < j}^N \frac{1}{|r_i - r_j|} + \sum_{i < j}^{nn} \frac{Z_i Z_j}{|R_i - R_j|}$$

Where Z_a represents the atomic number of nucleus a , r_a denotes the electronic coordinates, and R_i represents the nuclear coordinates. The first term is the attractive contribution between electrons and nucleus, the second one is the repulsion between electrons and the other one is the repulsion between nuclei.

The local kinetic energy (T) is computed using the Laplacian operator applied to the wavefunction, representing the spatial distribution of electronic density and momentum.

$$T_{local} = -\frac{1}{2} \frac{1}{\Psi} \nabla^2 \Psi$$

$$\nabla^2 \Psi =$$

$$= \sum_{i=1}^N \nabla_i^2 \Psi = \left(\frac{1}{\sqrt{N}} \right)^N \sum_{i=1}^N \left[\nabla_i^2 \Phi(r_i) \left(\prod_{j \neq i}^N \Phi(r_j) \right) \right]$$

Where the operator nabla square ∇_i^2 is the Laplacian with respect to the coordinates of the i -electron. It operates on the wavefunction as the second derivatives with respect to the coordinates of the electron in r_i . The final expression is:

$$T_{local} = -\frac{1}{2} \sum_{i=1}^N \frac{\sum_{a=1}^{nn} \left(a^2 - \frac{2a}{|r_i - R_a|} \right) \chi(r_i, R_a)}{\sum_{a=1}^{nn} \chi(r_i, R_a)}$$

We introduced the concept of local energy in order to evaluate integrals in many dimensions using Monte Carlo sampling. The basic concept behind is that if we sample the space accordingly to a reasonable probability density $P_{(R)}$ (it has to be always positive and normalized to one) we can express the integral as:

$$\langle Q \rangle \approx \frac{1}{M} \sum_{i=1}^M Q_{(R_i)}$$

Where $\langle Q \rangle$ is the expectation value of the property Q for the system, R_i are the M configurations sampled according to $P_{(R)}$ and $Q_{(R_i)}$ is the local (it means “for that particular configuration R_i ”) contribution to the averaged property Q . If we apply this to the variation energy of the system we obtain:

$$E_V = \langle E_{(R)}^{local} \rangle_P \approx \frac{1}{M} \sum_{i=1}^M E_{(R_i)}^{local}$$

where the local energy is given by:

$$E_{(R)}^{local} = \frac{H\Psi_{(R)}}{\Psi_{(R)}} = T_{(R)}^{local} + V_{(R)}$$

The local energy (E) embodies the net energy associated with a specific molecular configuration, encompassing the interplay between kinetic and potential energies.

The presence of the drift vector in the transition probability operator helps in reducing the correlation time and achieving a fast evolution by pushing the walker where Ψ is larger. The expression for the drift vector is:

$$drift\ vector = \frac{\nabla\Psi}{\Psi}$$

The expression implemented in the program is:

$$drift\ vector = \sum_{i=1}^N \frac{\sum_{a=1}^{nn} \left(-a^2 \frac{(r_i - R_a)}{|r_i - R_a|} \right) \chi(r_i, R_a)}{\sum_{a=1}^{nn} \chi(r_i, R_a)}$$

We use it in the expression for the transition probability $T_{(r_n \rightarrow r_{n+1})}$ of a move r_{n+1} :

$$r_{n+1} = r_n + \delta t \frac{\nabla\Psi}{\Psi} + \kappa$$

where κ is a gaussian random variable with zero mean and variance δt

$$T_{(r_n \rightarrow r_{n+1})} = \frac{1}{(2\pi\delta t)^{3/2}} \exp \left[-\frac{(r_{n+1} - r_n - \delta t \frac{\nabla\Psi}{\Psi})^2}{2\delta t} \right]$$

Since we are evaluating the integrals in a stochastic way we are interesting in knowing the reliability of our calculations. From The Central Limit Theorem we know that, for a large number of Monte Carlo calculations, the distribution of the averaged energies will be a normal one and the error will be:

$$\delta E = \sqrt{\frac{\sigma^2}{N_{M.C.}}}$$

Where σ^2 is the variance of the averaged energies and is computed as:

$$\sigma^2 = \frac{1}{N_{M.C.} - 1} \sum_{i=1}^{N_{M.C.}} (E_i - E_{average})^2$$

Variational Monte Carlo (VMC) methodology offers a systematic approach to

estimating the ground state energy by sampling configurations in proportion to the square of the wavefunction. The energy is obtained as a weighted average of local energies, guided by the square of the wavefunction. Starting from a randomly generated electron distribution, we choose a transition probability (a gaussian distribution) and adapt the acceptance to ensure that the detailed balance condition is satisfied:

$$T_{(r_n \rightarrow r_{n+1})} A_{(r_n \rightarrow r_{n+1})} P_{(r_n)} \\ = T_{(r_{n+1} \rightarrow r_n)} A_{(r_{n+1} \rightarrow r_n)} P_{(r_{n+1})}$$

Where T is the transition probability we choose, A is the acceptance and P the probability associated to that configuration (in our case the square of the wavefunction). In this homework we started from a Variational Monte Carlo program to obtain a Pure Diffusion Monte Carlo one. To do so we assume that the potential is a cumulative term obtained as the product of weights. In this way the energy is obtained as the weighted average of the local energies.

RESULTS

Results obtained by running the DMC program across diverse molecular systems, including hydrogen, helium, H_2^+ , H_2 , and H_3^+ ions, yielded comprehensive insights into ground state energies and variational parameters. Some of the computed values exhibit good agreement with theoretical expectations. Take into account that the program is just simple, in some cases it may not have good compatibility. The values

obtained from the calculations are presented in the following table:

System	Ground State Energy			
H	E =	-0.510885	±	9.04E-03
	A =	0.763241	±	7.82E-02
H_2	E =	-1.621697	±	6.68E-02
	A =	7.62E-04	±	1.41E-04
H_2^+	E =	-0.560729	±	2.42E-02
	A =	0.764573	±	7.83E-02
H_3^+	E =	----	±	----
	A =	---	±	----
He	E =	-2.896862	±	7.04E-02
	A =	2.42E-04	±	7.05E-05

As can be seen, the obtained results are quite accurate for the hydrogen and helium atoms. In the case of the H_3^+ ion, the potential diverges, such a thing has not been fully understood if it is attributed to the fact that the system is more exotic or there may be a bug in the code.

CONCLUSIONS

In summary, the expansion and refinement of the DMC program represent significant strides toward its broader utility in elucidating the electronic structures of complex molecular assemblies. The amalgamation of theoretical insights, computational methodologies, and empirical validations underscores its efficacy as a versatile tool for exploring diverse quantum systems. Further refinements and optimizations hold promise for unlocking novel insights into the realm of quantum chemistry and materials science.

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