RECENT PROGRESS IN QMC SIMULATIONS OF SYSTEMS WITH MULTIPLE TIME SCALES: HYBRID NONADIABATIC QMC

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1. Abstract

A hybrid QMC-VMC approach similar to a previously used "damped core" method for separating valence and core time scales is used here to perform nonadiabatic calculations. A number of simple trial wave functions are constructed. Variational and hybrid energies are calculated for the system HD^+. An energy of –0.59784 (4) hartree is obtained with relatively little computational effort, to be compared to the exact result of –0.5978979... hartree. The Monte Carlo result is essentially exact, despite the hybrid approximation. Additional precision is obtainable by running longer simulations. Also of note is how much better the hybrid result is than the variational energy obtained from the same wave function. This variational energy is –0.59652 (2) hartree.

2. Introduction

Systems with a large number of correlated degrees of freedom present formidable difficulties in simulations of physical problems. This is manifested by a power-law increase in relevant time scales such as decorrelation times, and a correspondingly large increase in computational cost. A particular manifestation of this has been the large-Z problem in various forms of Green's function Monte Carlo simulations of atomic, molecular, and condensed-matter systems. The problem is caused by a Z-dependent ratio of both time and energy scales between the innermost core and the outermost valence electrons.[1] Earlier work with a hybrid "damped-core QMC" method [2] attempted to address this while maintaining the advantages of an all-electron approach. Unfortunately, the approximations involved in damped-core QMC are not fully understood. The fundamental approximation is that of performing separate QMC and VMC simulations on different parts of the system. In damped-core QMC, the chemically less important core region is treated by VMC with a simple but nevertheless correlated trial wave function; the

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chemically significant valence electrons are treated by a full, branching QMC simulation. Other approximations were made in this approach, in order to simplify the problem. Possibly the most significant approximation was a factorization of the wave function, resulting in a loss of antisymmetry between core and valence electrons and a loss of proper accounting for exchange among them.

In order to isolate the fundamental approximation of performing separate QMC and VMC simulations on different parts of a system, we consider here a model problem of this type. Specifically, we explore a hybrid QMC treatment of the non-adiabatic energy calculation of HD^+. Nuclear motion is treated by VMC while electronic "motion" is treated by diffusion QMC. Since the corresponding parts of the wave function are not to be antisymmetrized here, the approximation due to factorization is not present. Moreover, with only one electron, we also avoid for the time being consideration of the sign problem or use of the fixed-node approximation. We find that our results are amazingly accurate. This is an indication that the fundamental approximation in hybrid QMC is a sound one. Moreover, the hybrid approach for the nonadiabatic problem results in a much faster algorithm than exact QMC carried out on all the particles. This is so because the diffusion constant for the nuclei can be chosen independently of that for the electrons.

3. Form of the Nonadiabatic Wave Function

Quantum Monte Carlo treatments which include both the electrons and the nuclei on an equal footing have been previously performed for H_2 [3]. The guiding wave function [4] used in importance sampling should be such that the Langevin term (often referred to as the "quantum force" or "drift" term [5]) has components for the nuclei as well as for the electrons. This requires that the guiding wave function have a functional dependence on the R_α, i.e. on the nuclear coordinates, as well as on the electronic coordinates, r_i. The simplest such form is a product of an electronic wave function and a function of the nuclear coordinates,

$$\Psi(\{r_i\},\{R_\alpha\}) = \psi_{el}(\{r_i\},\{R_\alpha\})\psi_{nuc}(\{R_\alpha\}) \ . \tag{1}$$

Such a form is approximate; a fully general form is that of Born and Huang [6]

$$\Psi(\{r_i\},\{R_\alpha\}) = \sum_m \psi_{m,el}(\{r_i\},\{R_\alpha\})\psi_{m,nuc}(\{R_\alpha\}) \ . \tag{2}$$

In our tests of hybrid QMC we have taken the oft-used approach of choosing our trial wave functions (used in the evaluation of the local energy) as identical to the guiding functions. These we chose of the form of Eq. 2 with N, the number of terms on the right hand side, equal to one, two, and four. Since our test system is HD^+, we take each term to be of the form

$$\Psi_m(\{r_i\},\{R_\alpha\}) = d_m \exp[-a_m r_1 - b_m r_2 - c_m (R_{\alpha\beta} - R_{0,m})^2] \,, \qquad (3)$$

with r_1 and r_2 the distances of the single electron from the H nucleus and the D nucleus respectively. With just two nuclei, the use of an internuclear coordinate $R_{\alpha\beta}$ in Eq. 3 is more compact, but equivalent to Eq. 2 if we consider the origin to be located at one of the nuclei.

The linear coefficients d_m, as well as the parameters a_m, b_m, c_m, and $R_{0,m}$ were obtained using the now almost-standard QMC optimization of Ref. [7]. Effectively the approach minimizes a linear combination of the energy and the variance associated with the trial wave function. The optimization proved quite difficult to perform, especially in determining the nuclear parameters. This can be largely attributed to the fact that the nuclear motion contributes quite little to the energy, or to its variance, in comparison with the electronic part of the wave function. It was necessary to use from 1,000 to 10,000 walkers for the optimization process.

Tables 1 – 3 give our one, two, and four term trial functions respectively.

Table 1. $N = 1$ term trial wave function.

Parameter	*Value*
d	1.0
a	–0.6765
b	–0.6740
c	7.9867
R_0	2.0401

Table 2. $N = 2$ term trial wave function.

Parameter	*m=1*	*m=2*
d_m	1.0	0.9980
a_m	–1.2107	–0.2271
b_m	–0.2014	–1.0733
c_m	6.0147	6.0252
$R_{0,m}$	2.0667	2.0793

As can be seen particularly well for $N = 1$ and $N = 2$ (in the latter case from the relative magnitude of the linear terms), the wave function is almost symmetric. It is perhaps more symmetric than one might expect based on the mass asymmetry between H and D. Although there is approximately a factor of two difference in their masses, H and D are almost identical from the point of view of the mass scale of the electrons. The $N = 2$ case is a superposition of two states, each with the electron closer to one of the two nuclei. The $N = 1$ case forces the electron to be in an average region of space, hence between the two nuclei. Thus additional symmetry is forced on the system, which can be seen from the closeness of the values of a and b. This results in a variational energy which is quite poor. It is amazing how well the hybrid QMC fixes this poor trial wave function (as we shall see below). Another interesting observation is that for the four-term expansion the wave function has a spurious node. This makes it unsuitable for a QMC simulation, as it will necessarily raise the energy artificially. This is possibly a result of an incomplete convergence of the optimization procedure. It may also be an artifact of the fact that the optimization procedure acts on a linear combination of the energy and the variance, and perhaps a pure energy optimization would avoid it. However, since the nodal regions

have little effect on the variational energy of a trial function, this may not fix the problem either. In any event, as a result of this spurious node, we report only a VMC energy for this case.

Table 3. $N = 4$ term trial wave function.

Parameter	*m=1*	*m=2*	*m=3*	*m=4*
d_m	–0.55996	0.97662	–0.54764	0.96236
a_m	–0.11068	–0.14412	–0.98739	–1.04300
b_m	–0.98147	–1.03413	–0.12965	–0.15579
c_m	6.69193	6.62704	7.58907	7.14093
$R_{0,m}$	1.96534	1.99736	1.96390	1.99714

4. Approach

Here we briefly describe our algorithm. As mentioned earlier, the approach we use here is identical to the damped-core method [2], with the exception that it is the nuclei rather than the core electrons that are treated by VMC, and it is all the electrons rather than the valence electrons that are treated with the full-blown QMC.

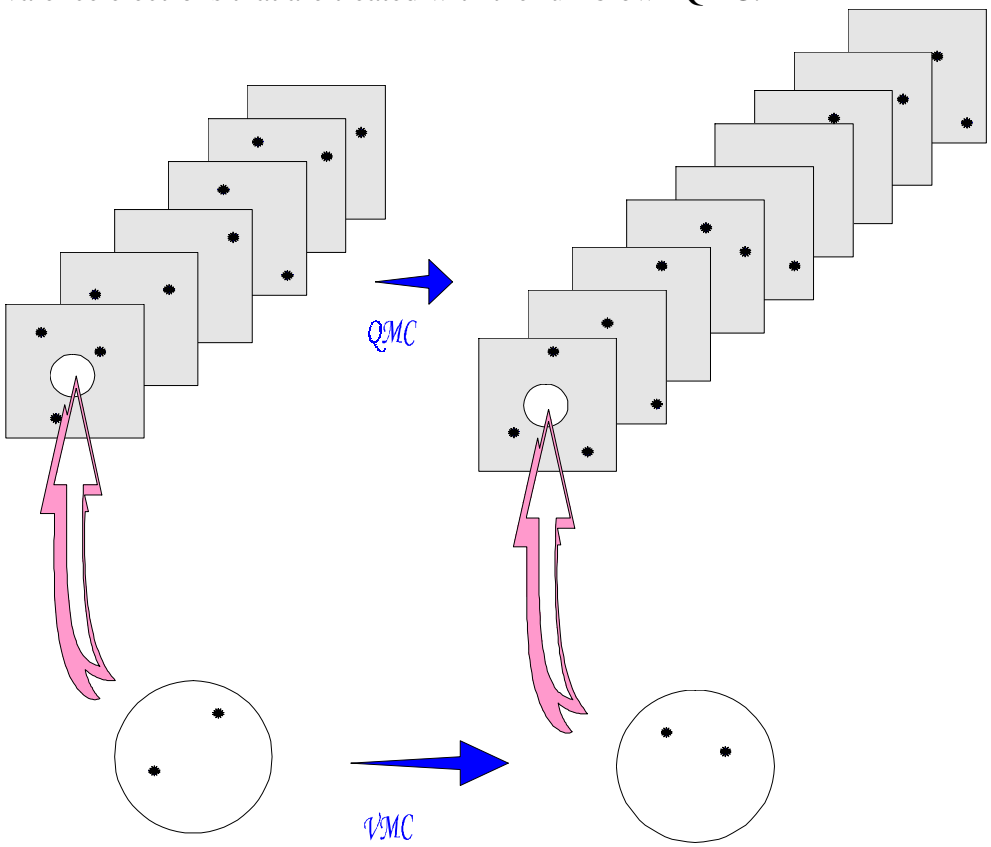

Figure 1. Illustration of the damped-core method. A single nuclear configuration, updated by VMC serves as an evolving core potential for the valence electron QMC.

For our model nuclear problem, the method is essentially as follows. Begin by moving the nuclei with VMC. As we describe below, the way we make our move results in a configuration of coordinates **R**, sampled from $|\Psi(\mathbf{R},\mathbf{r})|^2$. With this set of nuclear coordinates fixed, allow the electrons, **r**, to relax for a while, following a QMC walk. In our case the QMC walk is diffusion QMC. Discard the initial energies so obtained, allowing equilibration of the coordinates **r** to be achieved. After this, accumulate data for some fixed time. Now iterate this procedure, allowing the nuclei to be moved again as above, and continue to repeat the entire process until statistically significant data has been accumulated. Appendix A provides a pseudocode description of this process.

Sampling the nuclear distribution

In order to carry out the above approach, we need first of all to sample a distribution for the nuclei. One solution would be to take a nuclear wave function from the literature for the system we seek to study. This relies on there being such a wave function already computed. Moreover, this places one at the mercy of the accuracy of that calculation. A more self-contained and self-consistent solution, and the one we adopted here, is to use the information contained within the many-particle wave function generated by the variational Monte Carlo optimization process. This approach is very simple. What we need to sample is

$$\rho(\{R\}) = \frac{\left|\varphi(\{R\})\right|^2}{\int \left|\varphi(\{R\})\right|^2 dR} \quad ; \qquad \left|\varphi(\{R\})\right|^2 = \int \left|\Psi(\{r\},\{R\})\right|^2 dr \,. \quad (4)$$

Combining these equations we see that

$$\rho(\{R\}) = \frac{\int \left|\Psi(\{r\},\{R\})\right|^2 dr}{\int \left|\Psi(\{r\},\{R\})\right|^2 dr\, dR} \quad . \quad (5)$$

This form is ideal for sampling by VMC. For example, one can generate a random walk (either with a Metropolis or a Langevin algorithm) that samples $|\Psi(\{r\},\{R\})|^2$, and then simply discard the electronic coordinates. Note that, unlike in the method of taking a wave function from the literature, here we do not need to know the analytical form of the nuclear distribution.

This approach decouples the time scales of electronic diffusion and nuclear diffusion. In fact, since the nuclei are moved by a VMC algorithm, there is no need to even use a diffusion-type algorithm for the otherwise much slower nuclei. Various forms of acceleration algorithms [8] may be fruitfully employed, if desired, on this VMC part of the algorithm.

5. Results

Table 4 reports our hybrid QMC results for the $N = 1$ and $N = 2$ trial wave functions. These were obtained using various time step sizes for the electrons, ranging from 0.005 h^{-1} to 0.001 h^{-1}, and have been extrapolated to zero time-step size. VMC, whether used for updating the nuclei in the hybrid algorithm or for the full calculation of the variational energies, was done with a simple box-sampling Metropolis algorithm. A box move is a uniform sampling along each Cartesian coordinate from $-L$ to $+L$. For the nuclei we had $L_{nuc} = 0.01$ a.u. while for the electrons $L_{el} = 0.1$ a.u. In the hybrid QMC we took 200 VMC moves to update a nuclear configuration.

The hybrid QMC results are compared with the variational energy of the trial wave functions on the one hand (computed here by VMC), and the exact nonadiabatic energy[9] and a 200-term Gaussian expansion[10] on the other hand. For $N = 4$ we only computed the VMC energy since the corresponding trial function has spurious nodes.

Table 4. Hybrid QMC energies (extrapolated), VMC energies, and exact nonadiabatic energies.

Wave function	*VMC energy*	*Hybrid QMC energy*
$N = 1$	–0.5742 (4)	–0.5978 (1)
$N = 2$	–0.59652 (2)	–0.59784 (4)
$N = 4$	–0.597633 (9)	Ψ *has nodes*
200 Gaussians [10]	–0.597361	
Exact [9]	–0.5978979...	

One can clearly see the improving quality of the wave function with the increase in N, both from the better VMC energies and from the increasing precision of those energies. (The total computational time used for the different wave functions was not identical, but it was comparable when one takes into account the additional time required to compute the larger functions.) The hybrid QMC is remarkable in recovering essentially *all* the nonadiabatic energy, even with the simplest trial function. In contrast, a linear combination of 200 Gaussians [10] is poor, even compared to the last VMC energy.

One might attempt to quantify how well the hybrid approximation works by calculating the percentage of the way hybrid QMC takes us from the variational ("starting") energy of the trial wave function used, toward the exact nonadiabatic energy. For $N = 1$ this is 99.6 (4)%. For $N = 2$ it is 95.8 (3.0)%. Despite $N = 2$ giving a better hybrid energy than $N = 1$, it appears worse by the above measure. This appearance is largely illusional; it is due to the much improved (VMC) starting point of the $N = 2$ trial wave function. In fact, considering the error bars, both results are consistent with the hybrid approach bringing us approximately 99% of the way towards the exact result (with the better trial function yielding the expected lower variance). However, the hybrid approach *is* an approximation, and more precision would be desirable to discern the level of accuracy it really achieves. Moreover, this discussion is based on just two trial wave functions and one physical system. Clearly there is more to be done.

6. Discussion

In treating HD^+ in the above-described hybrid approach we have isolated the hybrid approximation from all others made in the damped-core method. We find that to a reasonably good precision the hybrid approach makes negligible error. Longer simulations will be necessary to discern the magnitude of the approximation.

A next step in understanding the damped-core method is to re-introduce the complexities of the core-valence problem one at a time. First we need to progress to two electrons, where the effects of electron correlation can be judged. Since QMC in general is exact in its handling of correlation, we do not expect any problem here. In fact, we have performed preliminary work on H_2, and are beginning work on HD.[11] Our results to date are consistent with our conclusions drawn here from HD^+.

Proceeding to many electrons, one encounters the fermion sign problem. Various exact algorithms have been proposed and tested for simple systems.[12] There is no reason to believe that these would not work as well for the nonadiabatic problem, and by inference in the hybrid QMC approach. Likewise, the much-used and generally very accurate fixed-node approximation is not expected to interact in any way with the hybrid approximation *as used here*. That is, the fixed-node approximation should have no effect on the quality of the hybrid approximation when treating *different* species of quantum particles. However, the essence of the damped-core method is that core and valence electrons are being separated, and these are *in*distinguishable particles. We believe that a better treatment of exchange is the first step toward an improved damped-core algorithm.

7. Appendix A: Algorithm Pseudocode

0) Choose:

$\Psi(\{r\},\{R\})$ – a trial many body wave function including electrons and nuclei

τ_e – time step for the electron moves

τ_n – time step for the nuclear moves

N_e – the number of walkers (the ensemble size) for the electrons

s_1 – number of relaxation steps (steps before equilibrium is assumed)

s_2 – number of accumulation steps (steps that go into the averages)

$\{r_n\},\{R\}$ – initial coordinates of the "nuclear walkers," later updated by VMC

$\{r\}$ – an ensemble of electron coordinates initially derived from the above walkers (sampled from $|\Psi(\{r\},\{R\})|^2$) and updated by QMC.

1) Do a VMC move for the "nuclear walker": $\{r_n\},\{R\} \rightarrow \{r'_n\},\{R'\}$. That is, move all coordinates – electronic and nuclear – followed by a Metropolis acceptance/rejection step. Iterate until a new, uncorrelated, nuclear configuration is generated.

2) For each electronic walker (keeping the nuclear coordinates fixed):
do s_1 steps of a QMC walk to relax the electrons for the new nuclear coordinates;
do not accumulate the energies and other properties.

3) For each electronic walker (keeping the nuclear coordinates fixed):
do s_2 steps of a QMC walk;
accumulate the energies and other properties.

4) Go to 1.

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