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Delayed Rejection Variational Monte Carlo

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Abstract

A new acceleration algorithm to address the problem of multiple time scales in variational Monte Carlo simulations is presented. Core electrons usually require smaller time steps than valence electrons. After a first attempted move has been rejected, the delayed rejection algorithm attempts a second move with a smaller time step, so moves of both valence and core electrons can be accepted. Results on Be and Ne atoms as test cases are presented. Correlation time and both average accepted displacement and acceptance ratio as a function of the distance from the nucleus evidence the efficiency of the proposed algorithm in dealing with the multiple time scales problem.

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INTRODUCTION

Variational Monte Carlo (VMC) has become an important technique in quantum chemistry. Since analytical integration is not done it allows the computation of expectation values of an arbitrary trial wave function[1] with no restriction on its functional complexity. The trial wave function can include explicit two-body and higher-order correlation terms, allowing a better description of many body interactions and thus a higher accuracy. The optimization of the variational parameters can be done by minimizing the energy[2-5], the energy variance or the mean absolute deviation of the local energy[6]. Nevertheless, the main problem of any stochastic methods is the need of reducing the statistical uncertainty on the calculated quantities. For this reason large systems are a computational challenge: in fact, Monte Carlo, as all total energy methods, suffers of scaling problems: an increase of the size of the system gives rise to an explosion in the computational cost, proportional to (often) large powers of the system size. This large-power polynomial scaling is surely preferable to the computational exponential dependency on the system size of NP problems; nevertheless, it prevents the treatment of many physically interesting large systems.

Another drawback is that systems containing atoms of large atomic number (Z) would require different time steps in order to efficiently sample both the regions close and far away from the nuclei: this problem is referred to as the multiple time scales problem. Core electrons require a smaller time step than valence electrons. This causes an algorithmic inefficiency since the standard Metropolis algorithm assigns the same time step to all the electrons. Thus sampling in the region close to the nucleus is the bottleneck of VMC simulations. Although Monte Carlo methods scale well with N, they show a poor scaling with the atomic number Z; CPU time is estimated to scale with $Z^{5.5}$ or $Z^{6.5}$.

Analysing the standard Monte Carlo algorithm, Bressanini and Reynolds[7] showed that the optimal move size is a trade-off between the best move size for electrons far from the nucleus (i.e. valence electrons), which needs to be large since the accessible region of configuration space is very large, and the best move size for the electrons close to the nucleus (i.e. core electrons). These latter moves must be small, since the relevant region of configuration space is quite limited, and also because the wave function changes rapidly near the nucleus, meaning that large moves would cause a high rejection rate.

Acceleration algorithms have been suggested to cope with the multiple time scale problem. Belohrec *et al.*[8] proposed the "split-tau" technique, that is they used different time scales for different shells, dividing the electrons into shells on the basis of their distance from the nucleus. Trying to assign a different time step (and so a different time scale) to different electrons does not work. Given a symmetric or antisymmetric wave function, two identical particles (here like-spin electrons) can exchange positions without changing the probability of the configuration. Thus, assigning larger time steps to electrons starting out in the valence region at the beginning of the simulation would not accomplish the goal, since ultimately such electrons exchange their positions with inner electrons, with no energy penalty. Once this happens, the electrons take inappropriate step sizes and detailed balance is no more satisfied. In formulating their “split-tau” technique, Belohrec *et al.*[8] had to assume that the exchange between shells is negligible. However, Sun *et al.*[9] results do not support this hypothesis, showing that it is true only for very small time steps, so for very inefficient simulations.

Umrigar[10] proposed the factorization of the transition matrix in radial and angular parts. Sun *et al.*[9] showed that the inclusion of the second derivatives of the pseudopotential in the transition matrix automatically reduces the step size of the core electrons, while

Mella *et al.*[11] used a transition matrix in which the time step depends on the actual position of the electron. Bressanini and Reynolds[7] showed that, after partitioning the space into equivalent subspaces, it is possible to choose completely independent sampling times for core and valence electrons.

Nevertheless, none of the above mentioned approaches is general. Some of these solutions are impossible to generalize, while others are very difficult to implement.

Here we propose a simple algorithm, easy to implement, that is completely general and that allows to sensibly improve the sampling.

OVERVIEW OF VMC

Since very detailed descriptions of VMC are available elsewhere[12], we only give a short resume. VMC allows to sample a distribution proportional to $\Psi_T^2(\mathbf{R})$, where $\Psi_T(\mathbf{R})$ is a trial wave function. From such a distribution expectation values of non-differential operators can be obtained simply by:

$$\left\langle \hat{O} \right\rangle = \frac{\int \Psi_T^2(\mathbf{R}) \hat{O}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}} \cong \frac{1}{N} \sum_{i=1}^{N} \hat{O}(\mathbf{R}_i) \tag{1}$$

Differential operators can also be simply treated, by writing

$$\left\langle \hat{O} \right\rangle = \frac{\int \Psi_T^2(\mathbf{R}) \frac{\hat{O}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}} \cong \frac{1}{N} \sum_{i=1}^{N} \frac{\hat{O}\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} \tag{2}$$

The problem reduces to sample efficiently a distribution proportional to $\Psi_T^2(\mathbf{R})$. A set of walkers at positions $\mathbf{R}_i'$ is displaced to new positions $\mathbf{R}_i$ by moving each walker. In the

standard Metropolis algorithm a step is generated by "box sampling", that is $\mathbf{R} = \mathbf{R}' + \vec{x}\Delta$, with Δ the step size and $\vec{x}$ a 3-N dimensional vector of uniformly distributed random numbers $\vec{x} \in [-0.5,+0.5]$. This move is followed by the classical Metropolis accept/reject step, in which $\left(\Psi_T(\mathbf{R})/\Psi_T(\mathbf{R}')\right)^2$ is compared to a uniformly distributed random number between zero and one. The move is accepted only if the ratio of trial functions squared exceeds the random number, otherwise the old position is retained. This is one step of the Markov chain. Under very general conditions, this chain results in an asymptotic equilibrium distribution proportional to $\Psi_T^2(\mathbf{R})$.

From the above description of the standard Metropolis algorithm, it is clear that since the move of an electron covers a volume independent from its position, the optimal box size is a trade-off between the best move size for core electrons (which needs to be small) and the one for valence electrons (which needs to be large in order to reach all the accessible regions of the configuration space).

The sampling can be improved using the Langevin sampling algorithm. This scheme is a generalization of the Metropolis sampling in which a Langevin equation $\mathbf{R} = \mathbf{R}' + DtF(\mathbf{R}') + \vec{c}$, containing drift and diffusion (i.e. a "quantum" force F(**R'**) and a white noise $\vec{c}$, a Gaussian random variable with a mean value of zero and a variance 2Dτ), is employed. The quantum force depends on the position, but the overall attempted move is still determined by the time step. Once again, the use of a single time step for all electrons implies a kind of negotiation between valence and core electrons.

DELAYED REJECTION MONTE CARLO

Tuning the time step of the Metropolis algorithm is not an easy task. As outlined in the previous section, there is a trade-off between the time-step and the acceptance ratio of the corresponding proposed move. Furthermore, if we move one electron at a time (local moves), the ”optimal” time step for each move depends on the distance of the electron from the nucleus: the closer a particle is to the nucleus (core region), the smaller the time step should be.

The origin of our proposal is the simple observation that, using the same time step, core-electron moves are rejected more than valence-electron moves. The previously proposed acceleration techniques tried to prevent this rejection, our algorithm, instead, uses this information to improve the sampling by the Metropolis and Langevin algorithms.

The delayed rejection strategy

In a generalized Metropolis algorithm, one samples $p(\mathbf{R}) = \Psi_T(\mathbf{R})^2$ by constructing a Markov chain. Given the current position of the chain at the n-th step, $\mathbf{R}^{(n)} = \mathbf{R}'$, a candidate move $\mathbf{R}_1$ during a time step t_1 is generated by a given transition probability $T_1(\mathbf{R}' \to \mathbf{R}_1; t_1)$. The proposed move is accepted with probability

$$P_1(\mathbf{R}', \mathbf{R}_1) = \min\left[1, \frac{p(\mathbf{R}_1)T_1(\mathbf{R}_1 \to \mathbf{R}'; t_1)}{p(\mathbf{R}')T_1(\mathbf{R}' \to \mathbf{R}_1; t_1)}\right] \tag{3}$$

so that detailed balance with respect to $p(\mathbf{R})$, and thus stationarity, is preserved.

If the move is accepted, the simulation time is advanced and the chain position is updated: $\mathbf{R}^{(n+1)} = \mathbf{R}_1$.

So far the updating mechanism of the Markov chain is just like the one used for a regular Metropolis algorithm. In the delayed rejection algorithm the difference is in what happens upon rejection of the candidate move. In the Metropolis scheme, upon rejection the simulation time is advanced and the current position is retained: $\mathbf{R}^{(n+1)} = \mathbf{R}^{(n)} = \mathbf{R}'$. Although remaining in the current state contributes to preserving the stationary distribution through detailed balance, intuitively it increases autocorrelation in the realized chain and thus reduces the efficiency of the resulting estimators. Substance is given to this intuition by a result stated, and proved for the case of a finite state space, by Peskun[13]; a proof for general state spaces is given by Tierney[14]. Given two Markov chains with stationary distribution π, T_1 and T_2 being the corresponding transition matrices, T_1 is more efficient than T_2 (in the sense of reducing the asymptotic variance of the resulting estimators and thus the autocorrelation time, for any function of interest) if

$$T_1(\mathbf{R}' \to \mathbf{R}) \geq T_2(\mathbf{R}' \to \mathbf{R}) \quad \forall \mathbf{R} \neq \mathbf{R}' \tag{4}$$

In other words, the higher the probability of moving away from the current position, the better the efficiency. Following this intuition, in the delayed rejection strategy[15], upon rejection of a first stage candidate move $\mathbf{R_1}$, a second stage candidate move, $\mathbf{R_2}$, is proposed by generating it from a new transition probability $T_2(\mathbf{R}' \to \mathbf{R}_2; t_2)$. This transition probability is allowed to depend on the rejected value at the first stage, so a time step t_2 is now chosen shorter than the one previously used. In order to maintain the reversibility condition, it is necessary to adjust the acceptance probability as

$$P_2(\mathbf{R}', \mathbf{R}_1, \mathbf{R}_2) = \min\left[1, \frac{p(\mathbf{R}_2)T_1(\mathbf{R}_2 \to \mathbf{R}_1; t_1)(1 - P_1(\mathbf{R}_2, \mathbf{R}_1))T_2(\mathbf{R}_2 \to \mathbf{R}'; t_2)}{p(\mathbf{R}')T_1(\mathbf{R}' \to \mathbf{R}_1; t_1)(1 - P_1(\mathbf{R}', \mathbf{R}_1))T_2(\mathbf{R}' \to \mathbf{R}_2; t_2)}\right] \tag{5}$$

to preserve the detailed balance condition. If $\mathbf{R}_2$ is accepted, we set $\mathbf{R}^{(n+1)} = \mathbf{R}_2$. Otherwise the delayed rejection process can either be interrupted by setting $\mathbf{R}^{(n+1)} = \mathbf{R}^{(n)} = \mathbf{R}'$, or continued with higher stage proposals using an iterative formula for the acceptance probability[16]. Since the acceptance probabilities preserve detailed balance separately at each stage, hybrid strategies can also be considered: upon rejection a coin is tossed and depending on the result the delayed rejection process is either continued or interrupted. It can be proved[15] that an algorithm with delayed rejection dominates, in the Peskun ordering, the corresponding standard algorithm. This is true for Metropolis as well as for Langevin algorithms. The autocorrelation time for any function f is reduced by adding one or more delayed rejection steps. Taking different transition probabilities corresponding, for example, to two different time steps $t_1 \rangle t_2$ allows moving particles far from the nucleus at the first stage and particles in the core at the second stage. Both moves can either be local (one electron at a time) or global (all electrons at once). In a similar way the delayed rejection strategy can be used to combine global (first stage) with local moves (second stage): again global moves are less likely to be accepted, but faster to perform from a computational point of view.

RESULTS AND DISCUSSION

The main purpose of the delayed rejection algorithm is to improve the VMC efficiency, allowing the electrons to move both near the core and far from it. So, as test cases we chose Be and Ne atoms to compare the effect of different Z values. In particular Ne was studied by Sun *et al.*[17], Mella *et al.*[11], and Bressanini and Reynolds [7], so our results can be compared with those of different acceleration algorithms. Efficiency is measured by the asymptotic

variance of the estimator of the quantity of interest, say f(**R**), (typically the local energy) with respect to a distribution known up to a normalizing constant, $p(\mathbf{R})$. Since the estimator is the average of the function f along the Markov chain, its asymptotic variance is the sum of the autocorrelations of f along such path. The autocorrelation time of the local energy can be considered a natural measure of efficiency. It depends both on the sampling inefficiency of the algorithm and on the trial wave function through the fluctuations of the local energy. Thus, in order to make comparisons with different sampling methods, one must use the same trial wave function. In this work a simple SCF wave function multiplied by an electron-electron Jastrow factor was chosen. The Clementi and Roetti basis set[18] was employed for Be atom, while for Ne atom a DZ basis set was optimized. Simulations were performed with different time steps, trying to minimize the energy autocorrelation time. The autocorrelation time is a "macroscopic" measure of the simulation efficiency, it provides information on long term, accumulated effects. To investigate the problem of the multiple time scales, a "microscopic" analysis of the acceptance ratio and the mean accepted displacement in core and valence space is more informative. First of all the electron displacement was evaluated for the standard Metropolis algorithm, in which the move is accepted or rejected only when all electrons have moved to a new position. Since in the delayed rejection algorithm each electron moves independently of the others, also the results obtained with a standard Metropolis algorithm, but moving one electron at a time, were examined.

The delayed rejection algorithm was implemented within the framework of both Metropolis and Langevin algorithms. A comparison between the results obtained with our algorithm and the standard algorithms, both moving all electrons at once and one electron at a time, is presented.

The multiple time scale problem in standard algorithms

First of all, several simulations, obtained with the standard Metropolis algorithm, are analyzed in details. The acceptance ratio is time step dependent and, in particular, it decreases upon increasing the time step. A more detailed analysis of the dependence of the acceptance ratio on the distance from nucleus shows that only small time steps allow electrons to move in the region close to the nucleus. On the contrary, far from the nucleus the acceptance ratio is essentially constant.

The same conclusion could be drawn looking at the behaviour of the mean accepted displacement in different regions of space. In Figure 1 we have plotted the mean accepted displacement versus the distance from the nucleus for Be atom; the algorithm used is the standard Metropolis in which the acceptance / rejection step is done after all the electrons have been moved. Using time steps as large as 0.3 hartree^{-1} the electronic displacement is quite small in the core and the movement in the valence region is affected by the poor acceptance ratio. Decreasing the time step up to 0.03 hartree^{-1}, progressively improves the sampling both for the core and the valence regions. A further decrease of the time step, while improving the sampling of the core region, spoils the sampling of the valence region. When the time step become too small (0.001 hartree^{-1}), the sampling seems to be quite inefficient because of the very small moves at each step. The best sampling is obtained when the acceptance ratio is somewhere around 50%.

The efficiency of the Metropolis algorithm is improved, if one allows the electrons to move independently; that is, the acceptance / rejection step is done after each electron has moved. The results are plotted in Figure 2. As before, the acceptance ratio decreases as the time step increases, while the mean electronic displacement is larger than in the previous

case. When the time step is large, the core electrons do not move at all; on the other hand a decrease of the time step causes a decrease in the displacement of the valence electron. However, compared to the all-electrons-at-once case, this algorithm shows a global increase in the mean accepted displacement.

With the same approach simulations both on Be and Ne were repeated using Langevin Monte Carlo. Also in this case the all-electrons and the one-electron approaches were employed in order to compare the results with those obtained with the delayed rejection algorithm.

The mean accepted displacement with respect to the distance from the nucleus for Ne atom is shown in Figure 3, where the simulation is done using Langevin Monte Carlo, moving all electrons at once. This function shows a maximum corresponding to the maximum of the radial electron density; then it reaches a plateau, remaining fairly constant. Nevertheless the global movement is quite small, resulting in a poor sampling. On the contrary, when the one-electron approach is used, the main electron displacement is larger, as can be seen from Figure 4. When electrons are allowed to move independently, the sampling is much more efficient with respect to the all-electron algorithm; however, if τ is dramatically increased, the core electrons do not move at all, while smaller values of τ cause a better sampling of the region close to the nucleus, but decrease movement in the valence space.

It is clear, from the above analysis, that the efficiency of standard algorithms is affected by the impossibility to find a good time step both for the valence and the core. When trying to improve the movements in the core region, one must choose small time steps, thus decreasing the sampling in the valence. On the other hand, when using large time

steps in order to enlarge the valence electrons displacement, the acceptance ratio in the core definitely drops causing a higher correlation between the moves.

The proposed solution

The main difference between the delayed rejection algorithm and the other standard Metropolis and Langevin algorithms is that in the former an electron can try two different moves with different τ values. The first try has a larger time step (τ_1) and allows valence electrons to move in the space with large displacements. This try will be probably rejected for core electrons; so, the second time step (τ_2) is smaller in order to make efficiently sample the region close to the nucleus.

τ_1 can be tuned to be the best time step for the valence, while τ_2 is used to move core electrons. This allows to sample with high efficiency both the core and the valence region.

The simulations for Be and Ne were repeated applying the delayed rejection approach: the trial wave function was the same used for previous simulations. We chose τ_1 and τ_2, trying to minimize the energy correlation time.

Figure 5 shows the acceptance ratio and the mean accepted displacement as function of the distance from nucleus. The algorithm is delayed rejection Metropolis with $\tau_1 = 0.07$ hartree^{-1} and $\tau_2 = 0.005$ hartree^{-1}. The acceptance ratios for the two moves are respectively 50% and 66%. The acceptance ratio for the first time step is close to zero in the region close to the nucleus, then rises until it reaches a constant value of about 60%. On the other hand the acceptance ratio for the second step is different from zero also in the core region; after a rapid grow, it stabilizes around 80%.

In parallel, the displacement due to the first step is relevant only in the valence region. The second step causes the electron to move in the core region, but does not significantly affect the displacement in the valence region; in fact just in few cases electrons try the second move, because of the high acceptance ratio at the first step. So the global average displacement is affected by the first time step in the valence and by the second in the core region.

Figure 6 is analogous to Figure 5, but now the algorithm is the delayed rejection Langevin. The time steps chosen in order to minimize the energy correlation time are 0.1 and 0.03 hartree^{-1} respectively for the first and the second step, while the global acceptance ratios are 82% and 49% respectively. The electron displacement is dominated in the core by the smaller time step move and in the valence by the larger one; and overall it is larger than the displacement obtained using the delayed Metropolis sampling.

Thanks to the improved efficiency in sampling, in particular in the core region, ergodicity is guaranteed in that space zone. This is an important result, since a better local sampling allows a greater confidence in evaluating properties extremely dependent on electron density in the core region.

As previously said, a useful measure of the efficiency of a sampling algorithm is the autocorrelation time of the local energy. This quantity is related to the time one needs to obtain decorrelated measures of an observable. Obviously, the smaller is the autocorrelation time, the more efficient is the algorithm.

The autocorrelation time of the local energy for Be and Ne were calculated for all the simulations done with the three different algorithms. The best results obtained for each algorithm are reported in Table 1 for Be and in Table 2 for Ne. The correlation time is much smaller for one-electron simulations than for all-electron ones, due to the possibility

of electrons to move independently in the first case. The delayed rejection algorithm further on improves the efficiency both of Metropolis and Langevin Monte Carlo. The positive effect is more apparent for Ne.

Obviously, the delayed rejection algorithm, despite the improvement in the autocorrelation time, requires more CPU time with respect to the standard algorithms: this is due to the fact that for each rejected step, another move is tried, causing a new evaluation of the wave function, its gradient and its Laplacian. The time needed for a delayed rejection simulation is between 20% and 40% longer than the time of a standard one electron at a time simulation. Nevertheless, this drawback is rewarded by the improvement in the autocorrelation time and by the better sampling of the core region.

The delayed rejection algorithm might be also effective in Langevin simulations when the quantum force $\mathbf{F}(\mathbf{R})$ becomes very large, that is when a walker is near a nodal surface or in atomic cluster simulations as atoms coalesce[19]. Then the attempted move and so the transition probability $T_1(\mathbf{R}' \quad \mathbf{R}, \hat{o}_1)$ is very large, while $T_1(\mathbf{R} \quad \mathbf{R}', \hat{o}_1)$ is much smaller. In this case the attempted move is rejected and the walker gets trapped. Imposing an arbitrary cut-off on $\mathbf{F}(\mathbf{R})$ might bias the simulation, even if the probability for a walker to move to a position where the value of $\mathbf{F}(\mathbf{R})$ is extremely large is very low. Instead, a second attempted move with a shorter time step $\hat{o}_2$ has the effect of reducing the contribution of the drift on the attempted move, even if, owing to the very hight value $\mathbf{F}(\mathbf{R})$ might assume, the reduction of the time step should be substantial.

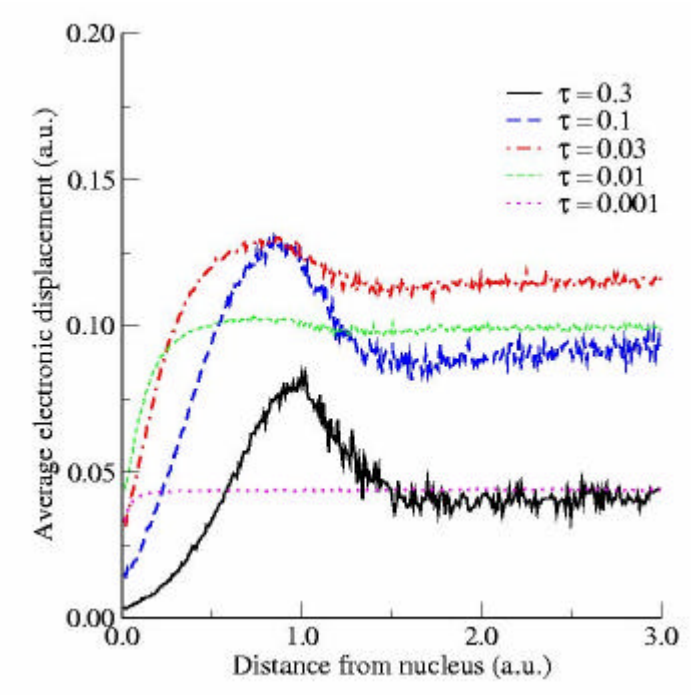
TABLE 1. Time to decorrelate moves for Be with various algorithms. t in hartree^{-1}, while correlation time is dimensionless.

Algorithm	τ_1	τ_2	Correlation time
Metropolis	0.03	-	20
Metropolis: individual electron moves	0.1	-	15
Metropolis with delayed rejection	0.07	0.01	9
Langevin	0.07	-	8
Langevin: individual electron moves	0.1	-	7
Langevin with delayed rejection	0.1	0.03	5

TABLE 2. Time to decorrelate moves for Ne with various algorithms. $\boldsymbol{t}$ in hartree^{-1}, while correlation time is dimensionless.

Algorithm	τ_1	τ_2	Correlation time
Metropolis	0.003	-	50
Metropolis: individual electron moves	0.03	-	10
Metropolis with delayed rejection	0.07	0.005	5.5
Langevin	0.01	-	25
Langevin: individual electron moves	0.03	-	7
Langevin with delayed rejection	0.05	0.005	4.5

FIG. 1. The mean accepted displacement for Be as function of the distance from the nucleus. The algorithm used is standard Metropolis moving all electrons at once.



Nelle figure sull'asse y mettere Mean invece di Average

FIG. 2. The mean accepted displacement for Be as function of the distance from the nucleus. The algorithm used is standard Metropolis moving one electron at a time.

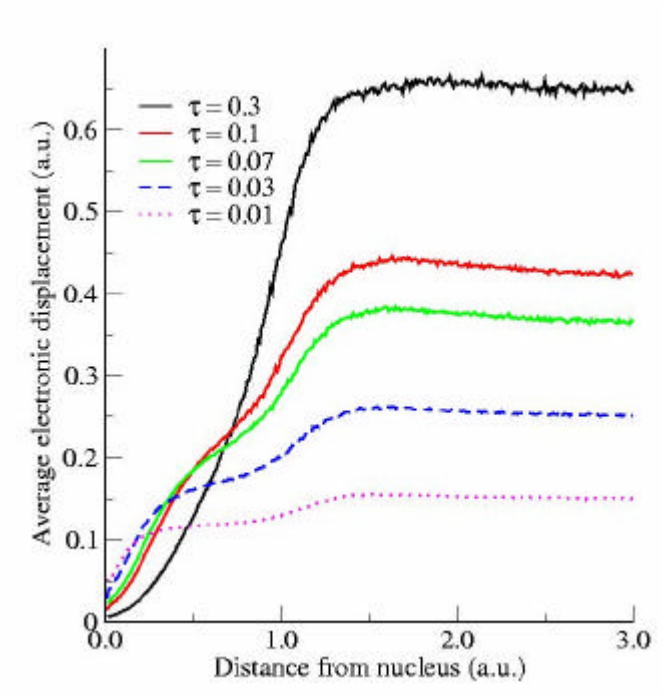


FIG. 3. The mean accepted displacement for Ne as function of the distance from the nucleus. The algorithm used is standard Langevin moving all electrons at once.

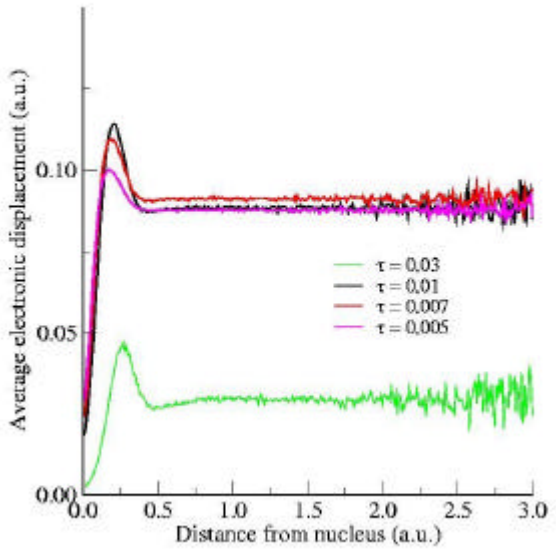


FIG. 4. The mean accepted displacement for Ne as function of the distance from the nucleus. The algorithm used is standard Langevin moving one electron at a time.

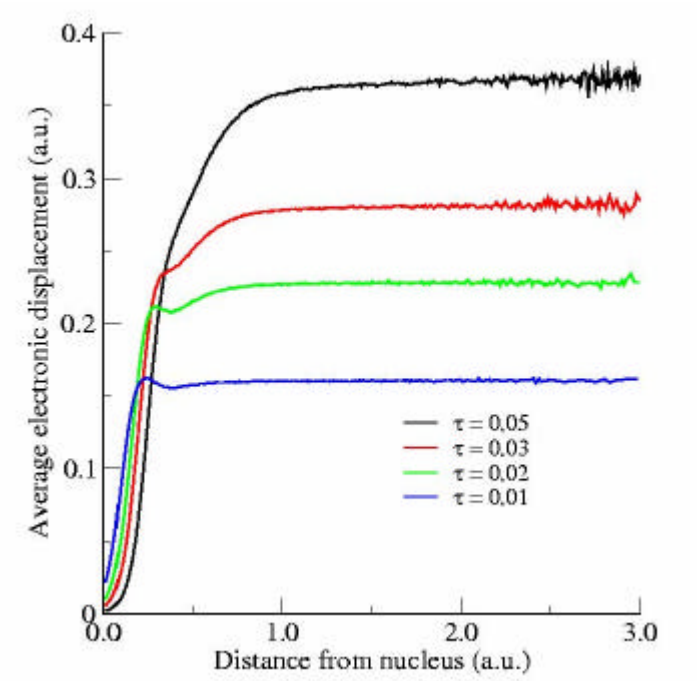


FIG. 5. The mean accepted displacement and the acceptance ratio for Ne as function of the distance from the nucleus. The algorithm used is delayed rejection Metropolis. τ_1 and τ_2 are chosen in order to minimize the autocorrelation time of the local energy (0.07 and 0.005 hartree^{-1} respectively).

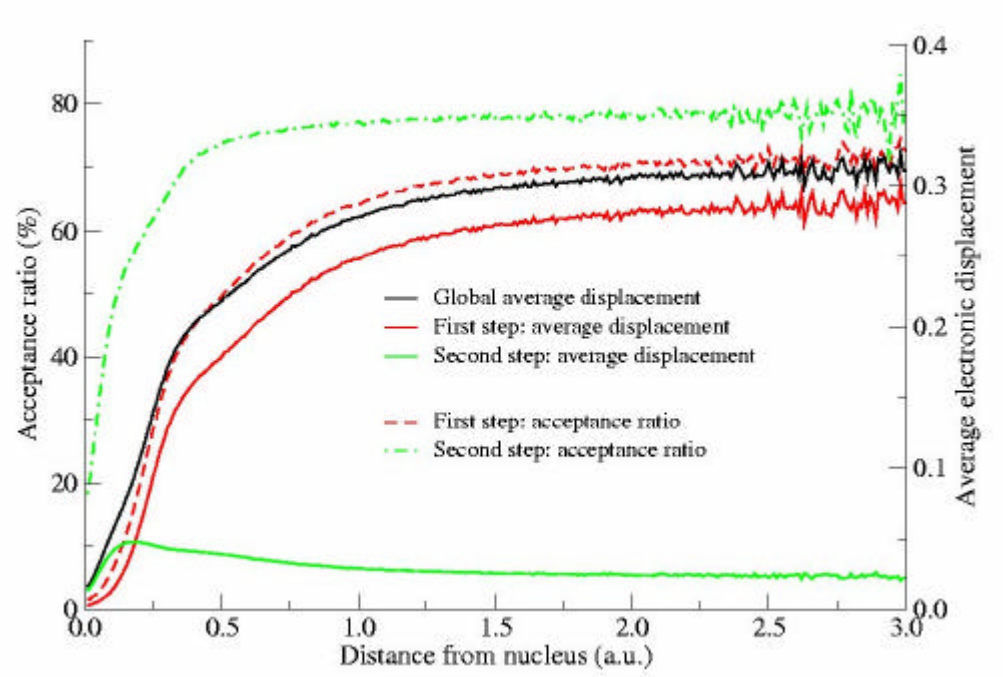
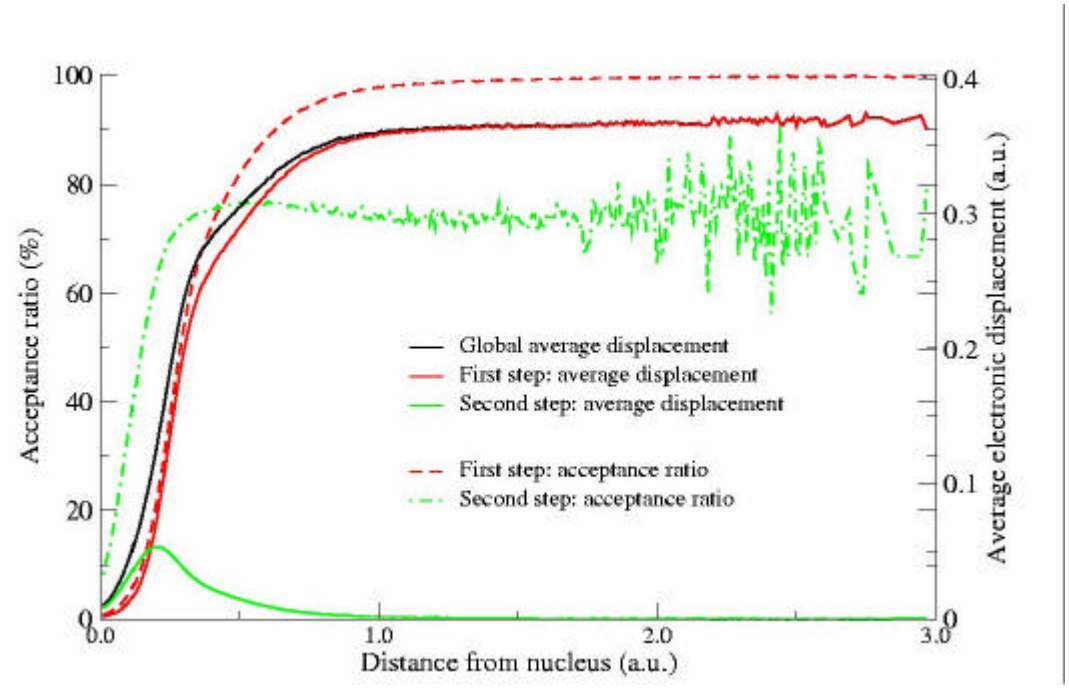


FIG. 6. The mean accepted displacement and the acceptance ratio for Ne as function of the distance from the nucleus. The algorithm used is delayed rejection Langevin. τ_1 and τ_2 are chosen in order to minimize the autocorrelation time of the local energy (0.1 and 0.03 hartree^{-1} respectively).



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References

[1] **D. Bressanini and P. J. Reynolds, in *Monte Carlo Methods in Chemical Physics*, edited by D. M. Ferguson, J. I. Siepmann, and D. G. Truhlar (Wiley, New York, 1999), Vol. 105, p. 37.**

[2] **X. Lin, H. K. Zhang, and A. M. Rappe, J. Chem. Phys. 112, 2650 (2000).**

[3] **M. Casalegno, M. Mella, and A. M. Rappe, J. Chem. Phys. 118, 7193 (2003).**

[4] **F. Schautz and S. Fahy, J. Chem. Phys. 116, 3533 (2002).**

[5] **D. Prendergast, D. Bevan, and S. Fahy, Phys. Rev. B 66 (2002).**

[6] **D. Bressanini, G. Morosi, and M. Mella, J. Chem. Phys. 116, 5345 (2002).**

[7] **D. Bressanini and P. J. Reynolds, J. Chem. Phys. 111, 6180 (1999).**

[8] **P. Belohorec, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. 98, 6401 (1993).**

[9] **Z. Sun, M. M. Soto, R. N. Barnett, and W. A. Lester, Jr., J. Chem. Phys. 101, 394 (1994).**

[10] **C. J. Umrigar, Phys. Rev. Lett. 71, 408 (1993).**

[11] **M. Mella, A. Luchow, and J. B. Anderson, Chem. Phys. Lett. 265, 467 (1997).**

[12] **B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo methods in ab initio quantum chemistry*, 1st ed. (World Scientific, Singapore, 1994).**

[13] **P. H. Peskun, Biometrika 60, 607 (1973).**

[14] **L. Tierney, Annals of Applied Probability 8, 1 (1998).**

[15] **L. Tierney and A. Mira, Statistics in Medicine 18, 2507 (1999).**

[16] **A. Mira, Statistical Science 16, 340 (2001).**

[17] **Z. W. Sun, M. M. Solo, and W. A. Lester, J. Chem. Phys. 100, 1278 (1994).**

[18] **E. Clementi and C. Roetti, At. Data and Nucl. Data Tables 14, 177 (1974).**

[19] **R. N. Barnett and K. B. Whaley, Physical Review A (Atomic, Molecular, and Optical Physics) 47, 4082 (1993).**