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REGULAR ARTICLE

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Monte Carlo simulation of polarizable systems: Early rejection scheme for improving the performance of adiabatic nuclear and electronic sampling Monte Carlo simulations

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Abstract An early rejection scheme for trial moves in adiabatic nuclear and electronic sampling Monte Carlo simulation (ANES-MC) of polarizable intermolecular potential models is presented. The proposed algorithm is based on Swendsen–Wang filter functions for prediction of success or failure of trial moves in Monte Carlo simulations. The goal was to reduce the amount of calculations involved in ANES-MC electronic moves, by foreseeing the success of an attempt before making those moves. The new method was employed in Gibbs ensemble Monte Carlo (GEMC) simulations of the polarizable simple point charge-fluctuating charge (SPC-FQ) model of water. The overall improvement in GEMC depends on the number of swap attempts (transfer molecules between phases) in one Monte Carlo cycle. The proposed method allows this number to increase, enhancing the chemical potential equalization. For a system with 300 SPC-FQ water molecules, for example, the fractions of early rejected transfers were about 0.9998 and 0.9994 at 373 and 423 K, respectively. This means that the transfer moves consume only a very small part of the overall computing effort, making GEMC almost equivalent to a simulation in the canonical ensemble.

Keywords Molecular simulation · Monte Carlo simulation · Polarizable force fields

1 Introduction

In the last few decades, due to the advances in digital computing technology, molecular simulation techniques have become a feasible method for determining macroscopic properties from the microscopic description of matter. The major restriction in employing molecular simulation tools is the lack of accurate molecular models that could mimic the true interaction energies between the molecules. Several intermolecular potential energy functions have been proposed to be used in molecular simulations. Normally, they arise from a classical interaction model with adjusted parameters to reproduce some macroscopic properties or quantum mechanics calculated properties.

One desirable characteristic of intermolecular potential functions (force fields) is transferability, i.e., the ability to model a system under different thermodynamic conditions (temperature, density, concentration, etc.). Therefore, a force field for the simulation of a polarizable system should model electronic charge density changes due to a changing molecular environment. For example, the dipole moment of ideal gas phase water molecules is 1.8 D versus 2.4–3.0 D in liquid phase at 298 K [1]. A good force field to model water should predict this property in the full range of densities, from ideal gas to the condensed phase. An intermolecular potential function with no polarization capabilities is unable to predict such behavior. Many are the ways in which polarizability can be incorporated into an intermolecular potential function. Rick and Stuart [1] present a review on polarizable models, their characteristics and performance in molecular simulations.

In simulations of polarizable systems, both the nuclear and the electronic coordinates should be sampled according to the ensemble constraints. The electronic degrees of freedom have much faster dynamics than the nuclei. In the Born–Oppenheimer approximation (adiabatic limit) [2], each set of nuclear coordinates corresponds to a unique electronic configuration. Given the nuclei positions, in the adiabatic limit, the electronic coordinates can be determined by minimizing the total energy with respect to these coordinates. In a molecular simulation, this is a time-consuming task, because for each nuclear move, the zero force equations should be solved to update the electronic coordinates of the entire system. In Monte Carlo (MC) simulation of water, some researchers [3–5] have used the approximation of updating only the electronic coordinates of the displaced molecule. This does not clearly satisfy the unnecessary but sufficient microscopic reversibility condition, the basis of the MC technique.

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Furthermore, it has also been shown [6] that this procedure can bias the MC sampling.

For molecular dynamics simulations (MD), Carr and Parrinello [7] proposed an extended Lagrangian formalism to solve the equations of motion, treating electronic coordinates as an additional dynamic variable with fictitious mass and kinetic energy. The energy will come close to the adiabatic limit if the electronic mass and temperature (kinetic energy) are low enough. The time step, however, must be kept small for the convergence of the resulting stiff equations of motion.

The MC technique, however, is more suitable than MD in determining some equilibrium properties. Some ensemble constraints, such as constant chemical potential, are easier to implement in MC simulations than in MD. Therefore, similar approaches have been developed for simulations of polarizable models in the context of the MC framework [6,8–10]. Among them, the adiabatic nuclear and electronic adiabatic sampling Monte Carlo (ANES-MC) algorithm has been successfully employed in liquid–vapor Gibbs ensemble Monte Carlo (GEMC) simulations of polarizable models of water [9,11].

The ANES-MC algorithm can be summarized as follows: (i) attempt to move nuclei (translational or rotational displacements and transfer between phases); (ii) for the trial nuclei position, attempt to change the electronic coordinates (electronic move sequence – EMseq) of the entire system R_{elec} times. The new electronic coordinates will be accepted/ rejected using the Metropolis acceptance criterion, with a fictitious electronic temperature T_{elec}; (iii) the combined movement (nuclear and electronic) will be accepted / rejected according to the ensemble probability distribution function. The ANES-MC equivalent to MD time step is the maximum nuclear displacements in a trial move. It has been shown [8, 9] that a suitable combination of maximum displacements, number of electronic moves (R_{elec}) during EMseq and electronic temperature (T_{elec}) allows single phase simulations of fluctuating charge models with a cost increase of less than one order of magnitude, when compared to their parent fixed charge models [8,9]. A detailed description of the ANES-MC method and its statistical mechanics background is provided in Refs. [8] and [9].

The expensive part of the ANES-MC algorithm is the EMseq, especially in swapping molecules between phases. When a molecule is placed in or removed from a phase, the electric environment around the position of the new/old molecule is remarkably affected. Hence, a high number of electronic moves is required to equilibrate the system around the adiabatic limit. In Ref. [9], early rejection schemes were employed to minimize electronic moves in transfers [9], based on the distance between the trial position and the center of the nearest molecules. However, for swaps of molecules from liquid to vapor phase, these schemes are not effective as they are based on the high repulsive contribution to the energy at lower intermolecular distances. Aiming to decrease the processing time due to this kind of movements, the authors in Ref. [4] limited the fraction of swap moves (number of attempts of a swap move between the total number of attempt moves of all kinds in an MC cycle) in 10% at 373 K and in 1% at 473 K [9]. Nevertheless, this restriction reduces the number of successful exchanges between phases in an MC cycle, which means that a larger simulation length is required for chemical potential equalization [12], especially for systems with high liquid densities.

The main goal of this work was to reduce the amount of calculations involved in the ANES-MC method. To do so, an early rejection scheme based on Swendsen–Wang (SW) [13] filters was developed. The idea behind the method is to predict the success of a trial nuclear movement before doing EMseq and correct the bias introduced in the sampling. In the next section, the basis and the equations of the proposed scheme are presented. In Sect. 3, GEMC simulations of the simple point charge-fluctuating charge (SPC-FQ) [14] model of water are described. Conclusions are outlined in the last section.

2 Early rejection scheme for nuclear moves

One not necessary but sufficient condition to assure convergence of a Markov chain in MC simulations is the well-known microscopic reversibility [15]:

$$\rho_o \pi_{on} = \rho_n \pi_{no} \tag{1a}$$

$$\pi_{oo} = 1 - \sum_{n \neq o} \pi_{no}, \tag{1b}$$

where ρ_o is a function proportional to the probability density of state o and π_{on} is the transition probability to go from configuration o to n. The elements of the transition matrix $\boldsymbol{\pi}$ can be decomposed into a product of a probability of attempting one specific movement ($\boldsymbol{\alpha}$) and a probability of accepting it ($\mathbf{f}$):

$$\pi_{on} = \alpha_{on} f_{on}. \tag{2}$$

Metropolis et al. [16] suggested the following acceptance criterion, which satisfies Eqs. (1a) and (1b):

$$f_{on} = \min\left(1, \frac{\rho_n \alpha_{no}}{\rho_o \alpha_{on}}\right). \tag{3}$$

In terms of the energies of the old and new states, Eq. (3) can be rewritten as:

$$f_{on} = \min\left\{1, \frac{\alpha_{no}\alpha^0_{no}}{\alpha_{on}\alpha^0_{on}} \mathrm{e}^{-\beta\left[U(\mathbf{r}_n,\mathbf{q}_n) - U(\mathbf{r}_o,\mathbf{q}_o)\right]}\right\}, \tag{4}$$

where $\mathbf{r}$ and $\mathbf{q}$ represent nuclear and electronic coordinates of the configurations n and o respectively, $\beta = 1/k_{\mathrm{B}}T$, k_{B} is the Boltzman constant, T is the temperature and U is the total potential energy function. The form of the matrix $\boldsymbol{\alpha}^0$ will depend on the ensemble distribution function and on the trial movement type. The elements of $\boldsymbol{\alpha}^0$ in a pure substance NVT GEMC simulation follow the relations:

$$\frac{\alpha^0_{no}}{\alpha^0_{on}} = 1 \quad \text{displacements (translational and rotational)} \tag{5a}$$

$$\frac{\alpha^0_{no}}{\alpha^0_{on}} = \frac{n^{(a)}\left(V - V^{(a)}\right)}{\left(N - n^{(a)} + 1\right)V^{(a)}} \quad \text{transfer molecules between phases} \tag{5b}$$

$$\frac{\alpha^0_{no}}{\alpha^0_{on}} = \left[\frac{V^{(a)}_n}{V^{(a)}_o}\right]^{n^{(a)}} \left[\frac{V - V^{(a)}_n}{V - V^{(a)}_o}\right]^{N-n^{(a)}}, \quad \text{volume changes} \tag{5c}$$

where $n^{(a)}$ and $V^{(a)}$ are the number of particles before swap and the volume of phase a, respectively. N and V are the constant total number of particles and the total volume of the ensemble.

For the sake of improving efficiency in the sampling, the functional form of the underlying matrix $\boldsymbol{\alpha}$ can be chosen in such a way that transitions toward improbable configurations can be rejected before evaluation of the new energy. If the underlying matrix $\boldsymbol{\alpha}$ has the form:

$$\alpha_{on} = \min\left(1, \frac{\alpha^0_{no}}{\alpha^0_{on}} \mathrm{e}^{-\Delta U^f_{on}}\right) \tag{6}$$

a new configuration with very low values of $\alpha^0_{no}\mathrm{e}^{-\beta\Delta U^f_{on}}/\alpha^0_{on}$ will be rejected before performing EMseq. In Eq. (6), ΔU^f_{on} is the change of some characteristic function (filter) that approximates ΔU_{on} (the true difference of energies between new and old states). In the context of the ANES-MC method, this function shall be independent of new electronic coordinates in order to allow the EMseq by passing.

For displacements, one possible choice for the filter function is the difference between the energies of the moved molecule k with new and old nuclear positions ($\mathbf{r}^{(k)}_n$ and $\mathbf{r}^{(k)}_o$), keeping the system with the old electronic configuration ($\mathbf{q}_o$):

$$\Delta U^f_{on} = U\left(\mathbf{r}^{(k)}_n, \mathbf{q}_o\right) - U\left(\mathbf{r}^{(k)}_o, \mathbf{q}_o\right) \tag{7a}$$

$$\Delta U^f_{no} = U\left(\mathbf{r}^{(k)}_o, \mathbf{q}_n\right) - U\left(\mathbf{r}^{(k)}_n, \mathbf{q}_n\right). \tag{7b}$$

As $\alpha^0_{on} = \alpha^0_{no}$ (Eq. 5a) for this type of movement, then:

$$\alpha_{on} = \min\left(1, \mathrm{e}^{-\Delta U^f_{on}}\right) \tag{8a}$$

$$\alpha_{no} = \min\left(1, \mathrm{e}^{-\Delta U^f_{no}}\right). \tag{8b}$$

Thus, the resulting algorithm for displacing molecules inside a single phase will proceed as follows: (i) generate new nuclear coordinates; (ii) calculate the filter function (Eq. 7a); (iii) accept trying the new nuclear configuration with the probability given by Eq. (8a); (iv) if accepted trying the new nuclear configuration, perform ANES-MC EMseq; (v) calculate the filter functions for the reverse move, ΔU^f_{no} (Eq. 7b) and α^f_{no} (Eq. 8b) and (vi) accept/reject the new configuration with probability given by:

$$f_{on} = \min\left\{1, \frac{\alpha_{no}}{\alpha_{on}} \mathrm{e}^{-\beta\left[U\left(\mathbf{r}^{(k)}_n, \mathbf{q}^{(k)}_n\right) - U\left(\mathbf{r}^{(k)}_o, \mathbf{q}^{(k)}_o\right)\right]}\right\}. \tag{9}$$

More improvement will be obtained as the number and complexity of electronic moves increase. For $R_{\text{elec}} = 10$ and 80% acceptance ratio for displacements, the average CPU time was reduced by only 3% in a short MC-NVT SPC-FQ water simulation at 298 K. However, for models and molecules with multiple electronic degrees of freedom, this procedure can avoid a higher number of electronic moves in EMseq. Moreover, the implementation of the scheme is so simple, that it is worth doing it.

On the other hand, as mentioned in the introduction, swap moves require a high number of electronic moves, because the environment around the new and old positions of swapped molecules changes dramatically. Thus, the prospect of reducing computational cost in such moves is high, especially for transfers to vapor phase, where repulsive filters are not effective. In this case, the proposed filter functions to transfer the molecule s from phase a to b are:

$$\Delta U^f_{on} = U^{(b)}\left(\mathbf{r}^{(s)}_n, \mathbf{q}_o; \mathbf{q}_s = \mathbf{q}^{*(b)}\right) - U^{(a)}\left(\mathbf{r}^{(s)}_o, \mathbf{q}_o\right) \tag{10a}$$

$$\Delta U^f_{no} = U^{(a)}\left(\mathbf{r}^{(s)}_o, \mathbf{q}_n; \mathbf{q}_s = \mathbf{q}^{*(a)}\right) - U^{(b)}\left(\mathbf{r}^{(s)}_n, \mathbf{q}_n\right), \tag{10b}$$

where $U^{(a)}$ is the energy calculated with nuclear and electronic coordinates of phase a, and $\mathbf{q}_s$ is the vector of the electronic coordinates of the swapped molecule. $\mathbf{q}^{*(a)}$ and $\mathbf{q}^{*(b)}$ are initial guesses for the vectors of the one-molecule electronic coordinates in phases a and b, respectively. Their values can be set arbitrarily, but if they are close to the average electronic coordinates, the prediction will be better. For the simulations in this work, they were set dynamically, by averaging and updating them in the course of the running.

Hence, the expressions for calculation of the underlying matrix for swapping a molecule from phase a to b will be:

$$\alpha_{on} = \min\left[1, \frac{n^{(a)}\left(V - V^{(a)}\right)}{\left(N - n^{(a)} + 1\right)V^{(a)}} \mathrm{e}^{-\beta\Delta U^f_{on}}\right] \tag{11a}$$

$$\alpha_{no} = \min\left[1, \frac{\left(N - n^{(a)} + 1\right)V^{(a)}}{n^{(a)}\left(V - V^{(a)}\right)} \mathrm{e}^{-\beta\Delta U^f_{no}}\right]. \tag{11b}$$

Finally, the corresponding probability for accepting the transfer will be:

$$f_{on} = \min\left\{1, \frac{n^{(a)}\left(V - V^{(a)}\right)}{\left(N - n^{(a)} + 1\right)V^{(a)}} \frac{\alpha_{no}}{\alpha_{on}} \times \mathrm{e}^{-\beta\left[U^{(b)}\left(\mathbf{r}^{(s)}_n, \mathbf{q}_n\right) - U^{(a)}\left(\mathbf{r}^{(s)}_o, \mathbf{q}_o\right)\right]}\right\} \tag{12}$$

The procedure for swapping will be very similar to the one presented for displacements: (i) generate new nuclear coordinates at destination phase; (ii) calculate the filter function (Eq. 10a) using the initial guess for the swapped molecule electronic coordinates in destination phase; (iii) accept trying the new nuclear configuration with probability given by Eq. (11a); (iv) if accepted trying the new nuclear configuration, perform ANES-MC EMseq; (v) calculate the filter functions for the reverse move, ΔU^f_{no} (Eq. 10b) and α^f_{no} (Eq. 11b) and (vi) accept/reject the new configuration with probability given by Eq. (12).

Table 1 Comparison of results of the Gibbs ensemble Monte Carlo simulations with and without early rejection scheme (ERS)

T	p_{sat}		ρ_{liq}		ρ_{vap}		U_{liq}		U_{vap}	
	ERS	Ref. [9]	ERS	Ref. [9]	ERS	Ref. [9]	ERS	Ref. [9]	ERS	Ref. [9]
373	0.40_1	0.59	0.926_7	0.910	0.0025_2	0.0033	-34.3_2	−34.1	-0.5_2	−0.4
423	1.5_1	2.1	0.84_2	0.827	0.0089_7	0.012	-30.6_7	−29.8	-1.4_4	−1.2
473	49_5	5.7	0.76_2	0.737	0.034_5	0.033	-26.9_6	−25.7	-5_1	−3.5

Temperature (T), vapor pressures (p_{sat}) densities (ρ_{liq} and ρ_{vap}) and internal energies (U_{liq} and U_{vap}) are given in K, MPa, g/ml and kJ/mol, respectively. The last digits (subscripts) are the standard deviations calculated over blocks of 2,000 cycles. The results in Ref. [9] were taken from simulations of 120 SPC–FQ water molecules with the Matrix Minimization technique. See Ref. [9] for results of simulation with other conditions

Table 2 Comparison between simulations with and without the proposed ERS at 373K with 10^5 cycles

	Per cycle						
	Fraction of swap attempts	Number of successful transfers	Time	ρ_{vap}	ρ_{liq}	U_{liq}	U_{vap}
ERS	0.799	0.124	1	0.025_2	0.926_7	-34.3_2	-0.5_2
No ERS	0.100	0.020	4	0.024_1	0.92_1	-34.6_6	-0.33_8

The no ERS simulation begun with an equilibrated configuration obtained with ERS filters. The last digits (subscripts) are the standard deviations calculated over blocks of 2,000 cycles. Densities (ρ_{liq} and ρ_{vap}) and internal energies (U_{liq} and U_{vap}) are given in g/ml and kJ/mol, respectively

3 Simulation details and results

The early rejection scheme (ERS) previously described was employed in the ANES-GEMC simulation of SPC-FQ water. The functional form of this potential, under periodic boundary condition, is [14]:

$$U=\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}4c\left(Lr_{OO}^{ij}\right)\varepsilon\left[\left(\frac{\sigma}{Lr_{OO}^{ij}}\right)^{12}-\left(\frac{\sigma}{Lr_{OO}^{ij}}\right)^{6}\right]$$
$$+U_{\text{tail}}+\sum_{\mathbf{k}}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\sum_{a=1}^{3}\sum_{b=1}^{3}q_a^i q_b^j\left|L\mathbf{r}_{ab}^{ij}+L\mathbf{k}\right|^{-1}$$
$$+\sum_{i=1}^{n}\sum_{a=1}^{3}q_a^i\left[\chi_a^0+\frac{1}{2}\sum_{b=1}^{3}q_b^i J_{ab}\right]+nU_{ig},\qquad(13)$$

where ε and σ are the Lennard–Jones (LJ) characteristic energy and diameter of the oxygen–oxygen interaction, respectively, L is the primitive box length, $L\mathbf{r}_{ab}^{ij}$ is the site–site distance between atom a and b of molecules i and j, $c\left(Lr_{OO}^{ij}\right)$ is one for Lr_{OO}^{ij} less than a cut-off radio and zero otherwise, U_{tail} is the LJ long-range correction, q_a^i is the charge of the atom a of molecule i, $\mathbf{k}$ is the position vector of the primitive box replica, χ_a^0 and J_{ab} are parameters related to the electronegativity and hardness of the sites and U_{ig} is the energy of one molecule under ideal gas conditions. The model parameters are ε, σ, χ_a^0 and J_{ab}, and their values were taken from Ref. [14].

The simulations were performed with 300 water molecules under the usual periodic boundary conditions at 373, 423 and 473 K. For the electrostatic interactions, Ewald sums [12,15] were employed, with the screening parameter set to 5 and the upper bound for the reciprocal space summation [9] also set to 5. The cut-off radio for LJ interactions was 14 Å. The simulations were carried out by changing the configuration in cycles of 300 attempts to displace molecules and one attempt to change the volume of the phases. In order to avoid liquid structure disruption [13], the number of swap attempts was changed during simulation in such a way that the number of successful transfers did not exceed 5% of the total number of molecules in the liquid phase, with a maximum value set to four times the total number of molecules. The average fraction of transfer moves can be seen in Table 2. The type of trial move was selected at random. The maximum displacements for translational and rotational moves and maximum volume changes were tuned to 85% acceptance ratio. For displacements, the number of electronic moves (R_{elec}) was set to ten. EMseq in swaps had 500 moves with preferential molecule selection [9] followed by 500 moves with random molecule selection, in both phases. The electronic temperature used in all simulations was 5 K. The maximum displacement for electronic moves was $0.03e$ (e = electron charge). The averages were taken from the last 10^5 cycles, and approximately other 10^5 cycles were needed to reach the equilibrium. The saturation pressure was calculated using the procedure suggested by Harismiadis et al. [17]. Only the vapor-phase pressure was determined because it has lower fluctuations and uncertainty. To optimize the swap moves, the excluded volume map sampling (EVMS) [18] in the liquid phase and the Shelley and Patey (SP) [13] filter were employed. The EVMS method was implemented by dividing the liquid phase into 60 × 60 × 60 boxes. Every box located within a radius of 2.1 Åof any water molecule was considered occupied. Attempts to put a molecule in the occupied sites on the liquid phase were immediately rejected. The SP filter parameters used were the same as those reported in Ref. [13]. The simulation results are presented in Table 1.

The differences observed between simulation with and without the ERS are not considerable, except for the coexistence vapor density, especially at 373 K. It transpires that the differences in this property do not come from the ERS itself, but from the poor chemical potential equalization in simulations of Ref. [9]. In those simulations, the number

Table 3 Performance of ANES-MC early rejection scheme

		373 K	423 K	473 K
Fraction of swap moves in a cycle		0.799	0.763	0.563
Fraction of early rejected transfers	To liquid	0.9998	0.9991	0.9974
	To vapor	0.9999	0.9993	0.9977

of attempted transfer molecules between phases was very low (10% against 80% in the present work) and longer run lengths would be necessary to reach the chemical potential equalization and equilibrium. In order to confirm this, simulations with the same fraction of swap attempts of Ref. [4] were made with no filter, departing from equilibrated ERS-generated configuration at 373 K. As shown in Table 2, the results agreed with simulations with ERS. It can also be observed that the standard deviations of the liquid and vapor densities show significant differences between the simulations. In the no ERS simulation, these deviations are bigger in the liquid phase and they decreased in the vapor phase. It can be suggested that these fluctuations are caused mainly by volume changes, which strongly affect the liquid density and have minor effects on the vapor phase. In the ERS case, fluctuations on liquid density caused by volume changes are compensated by the improved transfer rate, which accelerates the chemical potential equalization.

In terms of performance, the total number of accepted transfers was approximately eight times higher with ERS, and the run time was reduced in about four times. Hence, the simulations with ERS reduced the time required for equal number of transfers by a factor of 32. Obviously, this figure depends on the fraction of attempt swaps in one MC cycle and on R_{el}.

In Table 3, some performance parameters are presented. The fractions of transfer moves early rejected, for all temperatures, were higher than 99.6%. This means that the productivity difference between simulations with/without ERS with the same swap trial fraction will be, approximately, $2/R_{el}$ of the EMSeq computing time (two molecule energy evaluations against $R_{el} + 2$ in EMSeq).

4 Concluding remarks

The algorithm presented here for early rejection of trial moves in ANES-MC simulations has proven to be effective in reducing computing time for GEMC simulation of fluctuating charge models. It has also made simulations with a high number of transfer attempts per cycle feasible, enhancing chemical potential equalization and GEMC equilibration. One prospective use for this method will be the simulation of more complex force field functions, where the ANES-MC EMSeq would require a big deal of computing effort. Also, the scheme can be easily extended to be used in simulations with other ensembles, such as the gran-canonical or isothermal-isobaric ones, and can be combined with other speeding-up methods, such as configurational/orientational bias. The latter can be done by decomposing the underlying matrix $\boldsymbol{\alpha}$ of the Metropolis acceptance rule (Eq. 3):

$$\alpha_{on} = \alpha_{on}^{(\text{ANES-ERS})} \alpha_{on}^{(1)} \alpha_{on}^{(2)} \cdots \tag{14}$$

where each term $(\alpha_{on}^{(1)}, \alpha_{on}^{(2)}, \ldots)$ corresponds to an acceleration procedure.

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