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Quadratic Accuracy Diffusion Monte Carlo

JAN VRBIK AND STUART M. ROTHSTEIN

Departments of Mathematics and Chemistry,
Brock University, St. Catharines, Ontario L2S 3A1, Canada

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We derive a Monte Carlo Green function with a quadratic time-step bias, and point out the importance of properly simulating the *discontinuities* of the drift function at the nuclei. We suggest that for small atoms and molecules, where the nodes in the trial function are well separated, our algorithm enables one to use large time steps, thus gaining in precision of the ground-energy estimate by dramatically reducing the serial correlation of consecutive iterations. © 1986 Academic Press, Inc.

1. THEORY

Consider the time-dependent Schroedinger equation in imaginary time

$$-\frac{\partial\phi(\mathbf{R}, t)}{\partial t} = (\mathscr{H} - E_0)\,\phi(\mathbf{R}, t), \tag{1}$$

where $\mathbf{R}$ is a $3N$-dimensional vector of coordinates of N particles, and E_0 is the ground-state energy of the problem.

Instead of ϕ we will consider the time-dependent function

$$f(\mathbf{R}, t) = \phi(\mathbf{R}, t)\,\psi_T(\mathbf{R}), \tag{2}$$

where ψ_T is a "trial" approximate solution for the ground state of the time-independent version of (1). $f(\mathbf{R}, t)$ can be interpreted as a probability density function of a statistical distribution. In this manner, we obtain a reduced variance of the stochastic estimate of the ground-state energy E_0. This idea was described by Kalos and co-workers [1], and then applied by Ceperley and co-workers [2–4], and Anderson and co-workers [5, 6].

It is important that ψ_T be readily calculable, yet as accurate a solution as such a compromise can allow. If the particles are fermions, care should be taken to have ψ_T approximate the nodal regions as closely as possible [4].

It can be shown [4] that $\phi_0(\mathbf{R})\,\psi_T(\mathbf{R})$, where $\phi_0(\mathbf{R})$ is the exact solution to the time-independent version of (1), is the asymptotic (as $t \to \infty$) solution to

$$-\frac{\partial f(\mathbf{R}, t)}{\partial t} = -D\nabla^2 f + D\nabla\cdot(\mathbf{F}f) + (E_L(\mathbf{R}) - E_0)f, \tag{3}$$

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where E_L is the "local energy" of the trial function, namely

$$E_L(\mathbf{R}) = \psi_T^{-1} \mathscr{H} \psi_T \tag{4}$$

and "the drift" $\mathbf{F}$ is defined as

$$\mathbf{F}(\mathbf{R}) = 2\nabla\psi_T(\mathbf{R})/\psi_T(\mathbf{R}). \tag{5}$$

E_0 is the ground-state energy, common to both (1) and (3).

The objective of our paper is to amend the diffusion Monte Carlo technique for solving Eq. 3 [4] by modifying its algorithm to achieve more favourable time-step bias (without significant increase in computational cost). There exists an alternate technique (Green function Monte Carlo [9]) with no time-step bias; this is accomplished at the expense of substantially increased branching (thus adversely affecting the statistical error of the procedure). We have chosen to work only with the former technique, which we prefer for its relative simplicity and higher statistical accuracy. The error due to finite time step can be easily removed by subsequent regression (see the next section).

Rewriting (3) as

$$-\frac{\partial f}{\partial t} = \sum_{i=0}^{2} \mathscr{H}_i f \tag{6}$$

(the $\mathscr{H}_i$'s corresponding to the three individual terms on the right-hand side of Eq. 3), in a manner similar to that of Grimm and Storer [7], one can express the Green function of Eq. (3), i.e., $\mathscr{G}(\mathbf{R} \to \mathbf{R}', t)$, in terms of the individual Green functions $\mathscr{G}_i(\mathbf{R} \to \mathbf{R}', t)$ of

$$-\frac{\partial f}{\partial t} = \mathscr{H}_i f, \qquad i = 0, 1, 2. \tag{7}$$

The result is

$$\begin{aligned}\mathscr{G}(\mathbf{R} \to \mathbf{R}', t) = \int d\mathbf{R}_1\, d\mathbf{R}_2\, d\mathbf{R}_3\, d\mathbf{R}_4 \mathscr{G}_2(\mathbf{R} \to \mathbf{R}_1, t/2) \cdot \mathscr{G}_1(\mathbf{R}_1 \to \mathbf{R}_2, t/2) \\ \times \mathscr{G}_0(\mathbf{R}_2 \to \mathbf{R}_3, t) \cdot \mathscr{G}_1(\mathbf{R}_3 \to \mathbf{R}_4, t/2) \cdot \mathscr{G}_2(\mathbf{R}_4 \to \mathbf{R}', t/2) + O(t^3),\end{aligned} \tag{8}$$

where $O(t^3)$ is an operator of third order in t.

Green functions $\mathscr{G}_0$ and $\mathscr{G}_2$ are well known:

$$\mathscr{G}_0(\mathbf{R} \to \mathbf{R}', t) = (4\pi D t)^{-3N/2} \exp\{-(\mathbf{R}' - \mathbf{R})^2/4Dt\} \tag{9}$$

$$\mathscr{G}_2(\mathbf{R} \to \mathbf{R}', t) = \exp\{-(E_L(\mathbf{R}) - E_0)\, t\} \cdot \delta(\mathbf{R} - \mathbf{R}'). \tag{10}$$

$\mathscr{G}_1$ (derived in Appendix A) is equal to

$$\mathscr{G}_1(\mathbf{R} \to \mathbf{R}', t) = \delta(\mathbf{R}' - \mathbf{R}(t)), \tag{11}$$

where $\mathbf{R}(t)$ is the position of the particles at time t, if they are subjected to the drift $D\mathbf{F}$, and being initially ($t=0$) at $\mathbf{R}$. More precisely, $\mathbf{R}(t)$ is defined as the solution to the following set of differential equations:

$$d\mathbf{R}(t)/dt = D\mathbf{F}(\mathbf{R}(t)) \tag{12}$$

with $\mathbf{R}(0)=\mathbf{R}$.

After substituting Green functions (9)–(11) into Formula (8), one may perform the trivial integration over $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_4$ to obtain

$$\mathscr{G}(\mathbf{R}\to\mathbf{R}', t) = (4\pi Dt)^{-3N/2}\cdot\exp\{-t[(E_L(\mathbf{R})+E_L(\mathbf{R}'))/2-E_0]\}$$
$$\times\int d\mathbf{R}_3\,\delta(\mathbf{R}'-\mathbf{R}_3(t/2))\cdot\exp\{-(\mathbf{R}(t/2)-\mathbf{R}_3)^2/4Dt\}+O(t^3). \tag{13}$$

The above delta function has as its argument a *function* of $\mathbf{R}_3$, therefore it must be replaced (see [8]) by

$$\delta(\mathbf{R}_3-\mathbf{R}'(-t/2))\cdot J^{-1}(\mathbf{R}_3(t/2),\mathbf{R}_3)|_{\mathbf{R}_3=\mathbf{R}'(-t/2)}, \tag{14}$$

where J is the Jacobian of the transformaton in parentheses. It is evaluated at $\mathbf{R}_3=\mathbf{R}'(-t/2)$ because this is the only value of $\mathbf{R}_3$ which meets

$$\mathbf{R}'-\mathbf{R}_3(t/2)=0. \tag{15}$$

Integration in Formula 13 is now trivial. We get as the result

$$\mathscr{G}(\mathbf{R}\to\mathbf{R}', t) = (4\pi Dt)^{-3N/2}\exp\{-t[(E_L(\mathbf{R})+E_L(\mathbf{R}'))/2-E_0]\}$$
$$\cdot\exp\{-(\mathbf{R}(t/2)-\mathbf{R}'(-t/2))^2/4Dt\}$$
$$\cdot J^{-1}(\mathbf{R}_3(t/2),\mathbf{R}_3)|_{\mathbf{R}_3=\mathbf{R}'(t/2)}+O(t^3). \tag{16}$$

We now expand $\mathbf{R}(t/2)$, defined by (12), as a Taylor series in t:

$$\mathbf{R}(t/2)=\mathbf{R}+Dt\mathbf{F}(\mathbf{R})/2+D^2t^2H(\mathbf{R})\,\mathbf{F}(\mathbf{R})/8+\cdots, \tag{17}$$

where H is the matrix of all spacial derivatives of F. Substituting (17) and its analog for $\mathbf{R}'(-t/2)$ into Eq. (16) leads to the following further simplification:

$$\mathscr{G}(\mathbf{R}\to\mathbf{R}', t) = (4\pi Dt)^{-3N/2}\cdot\exp\{-t[(E_L(\mathbf{R})+E_L(\mathbf{R}'))/2-E_0]\}$$
$$\times\exp\{-[\mathbf{R}'-\mathbf{R}-(Dt/2)(\mathbf{F}(\mathbf{R}')+\mathbf{F}(\mathbf{R}))]^2/4Dt\}$$
$$\times\det\{I-(Dt/2)\,H(\mathbf{R}')\}+O(t^3), \tag{18}$$

where I is the unit matrix. This simplification is due to the fact that the contribution of

$$-(Dt/16)(\mathbf{R}'-\mathbf{R})\cdot[H(\mathbf{R}')\,\mathbf{F}(\mathbf{R}')-H(\mathbf{R})\,\mathbf{F}(\mathbf{R})] \tag{19}$$

(a term in the expansion of the second exponent in Eq. (16)) to the overall $\mathcal{G}$ is the same as that of

$$\frac{D^2t^2}{8}\,\text{Trace}\,\frac{d}{d\mathbf{R}}\,(H\mathbf{F})|_{\mathbf{R}'}, \tag{20}$$

which is the quadratic term in the expansion of the Jacobian. The analytic proof of the legitimacy of this "trade-off" has been published elsewhere [10] by one of us.

One can now simulate (18) by a Monte Carlo procedure combining drift, diffusion, and branching of a random assemble of configurations [4]. Proper care has to be taken to simulate these with the required accuracy. Specifically, as most trial functions result in **F**-discontinuities (at the nuclei), it is erroneous to simulate the drift at $\mathbf{R}_0$ by $tD\mathbf{F}(\mathbf{R}_0)$ when $\mathbf{R}_0$ is very close to a nucleus (the "overshooting" effect), and an appropriate correction is called for (see Sect. 3). (The discontinuities due to two electrons coalescing, being of repulsive nature, can be simulated without any such correction).

Similarly, since $E_L(\mathbf{R})$ has many singularities (due to $V(\mathbf{R})$ and incorrect nodes of ψ_T), one must ensure that the corresponding branching remains t^2-accurate. There is no experimental nor theoretical indication that positive singularities of E_L should create any problem, mainly because of proper convergence of the three-dimensional $\int_V \exp\{-t/r\}\,d\mathbf{r}$ (V is a small volume centered at the origin). On the other hand, for negative singularities, since $\int_V \exp\{+t/r\}\,d\mathbf{r} = \infty$, it is impossible to simulate the *exact* branching correctly. If these singularities are truncated in a t-neighborhood of each singularity, a quadratic perturbation of the original equation will result, and branching poses no difficulty. Furthermore, by keeping the expected number of configurations in each iteration constant (as we propose in Sect. 2), an effective truncation of the singularities is achieved *automatically* (at the expense of introducing a quadratic bias). Keeping in mind the above pitfalls (which will plague *any* simulation algorithm) we proceed with a detailed description of how to simulate (18).

To preserve the *efficiency* of the algorithm, we need to use a procedure requiring only one evaluation of **F** and E_L per time step. At the same time, to preserve the t^2-*accuracy* of (18), it is necessary to use a t^2-accurate $\mathbf{R}'$ (thus, $\mathbf{F}(\mathbf{R}')$ needs to be only t-accurate), followed by branching which requires only a t-accurate value of $E_L(\mathbf{R}')$.

Figure 1 shows how to perform the actual simulation, meeting the above objec-

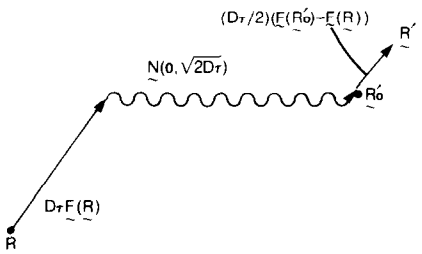

FIG. 1. Description of the move $\mathbf{R} \to \mathbf{R}'$.

tives. The values of $\mathbf{F}(\mathbf{R}_0')$, $E_L(\mathbf{R}_0')$ and $\mathbf{R}'$ are stored to become $\mathbf{F}(\mathbf{R})$, $E_L(\mathbf{R})$ and $\mathbf{R}$, respectively, of the next time step.

In the figure $\mathbf{N}(0, (2Dt)^{1/2})$ represents a random $3N$-dimensional vector with components independently generated from a symmetric distribution centered at zero, with the variance equal to $2Dt$ and the forth moment equal to $12D^2t^2$. The normal distribution is used routinely here, in spite of the fact that it corresponds to the least economical choice, and also results in a large error when not corrected for the discontinuities in $\mathbf{F}$ (see Sect. 3 and Fig. 2). We propose using

$$\pm 2.44886\,(\xi^2 - .0542927), \tag{21}$$

where ξ is uniformly distributed over the interval (0, 1) and $\pm$ represents a random sign, as an attractive alternative.

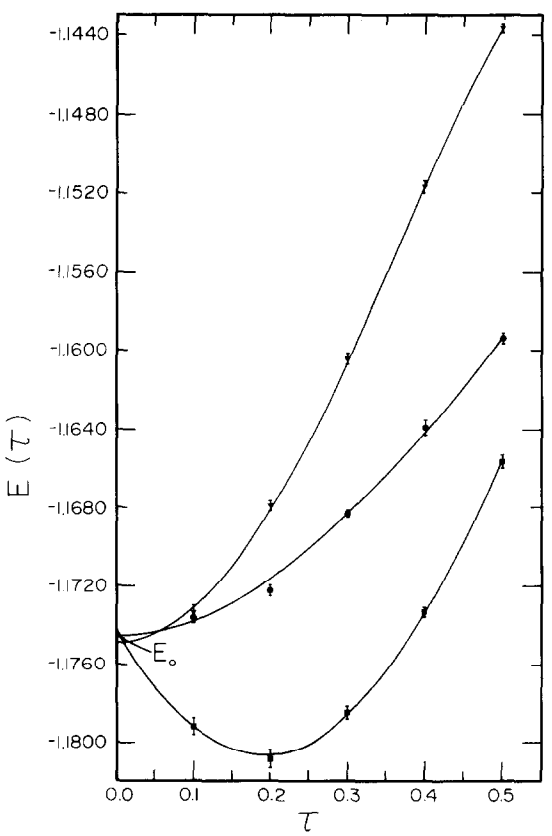

FIG. 2. Total energy of H_2 molecule versus time step. Results with continuity correction (30) and normal distribution (∇), with continuity correction (28), and non-normal distribution of Section 1(O), and without continuity correction and normal distribution ($\square$).

2. ALGORITHM

Choose a specific small value of the time step t, also generate a set of M $3N$-dimensional configurations ${}^{(m)}\mathbf{R}$, $m = 1, 2, \ldots, M$, from an arbitrary initial distribution. Advance each of the M configurations in accord with Fig. 1. Then, for each configuration, compute the following quantity:

$$B_m = \exp\{-t/2(E_L({}^{(m)}\mathbf{R}'_0) + E_L({}^{(m)}\mathbf{R}))\} \tag{22}$$

and find its average value

$$\bar{B} = \sum_{m=1}^{M} B_m/M \tag{23}$$

For each m, take M_m copies of the new configuration ${}^{(m)}\mathbf{R}'$ to create a new list of M' configurations, where

$$M_m = \text{int}\{B_m/\bar{B} + \xi\}, \tag{24}$$

ξ is a uniform random number from the interval (0, 1), M' is the sum of all these M_m-values. At the same time, $-\log_e\{\bar{B}\}/t$ provides an estimate of E_0. One should note (see Appendix B) that this estimate is, within the t^2-accuracy, equivalent to

$$\frac{\sum_{m=1}^{M'} E_L({}^{(m)}\mathbf{R}'_0)}{2M'} + \frac{\sum_{m=1}^{M} E_L({}^{(m)}\mathbf{R})}{2M}, \tag{25}$$

where the first summation is over the new list of configurations (after branching).

The subsequent time steps (iterations) will thus consist of a variable (M' say) number of configurations. The energy estimate is always given by $-\log_e\{\bar{B}\}/t$, where $\bar{B}$ is the average value of B_m over the M' configurations. However, one must use the following modified version of (23) to prevent a random "extinction" or "explosion" of the "population" of configurations, which would otherwise be an inevitable consequence of the well-known laws of stochastic processes:

$$M_m = \text{int}\{(B_m/\bar{B}) \cdot (M/M') + \xi\} \tag{26}$$

Repeat these iterations a large number (usually a few thousand) of times to reduce the statistical error of the overall estimate of E_0 (obtained by simple averaging of the individual estimates, excluding the first few iterations which are required for the process to reach the stationary solution).

To determine the standard error of this overall mean, divide all iterations into several large blocks of the same size, compute the block averages, then combine them using the ordinary statistical formula for *independent* observations (which the block averages practically are) to get the error bar of the E_0-estimate.

Finally, repeat the whole procedure for several (four to six) distinct values of t. Each of the grand-mean estimates of E_0 will have a systematic error (bias) of the t^2-order (i.e., $E_0(t) = E_0 + a \cdot t^2 + \cdots$) which can be removed by the standard

(weighted) least-squares fit. The regression inercept provides an unbiased estimate of the ground-state energy E_0. How to choose an appropriate polynomial model for $E_0(t)$ and how to design a simulation with optimal choice of the t-values and the corresponding *CPU* allocation will be discussed in a future publication [11].

3. Continuity Correction

To ensure continuity of $\mathbf{F}$ at the nuclei (which is required by the quadratic algorithm) we had to modify the simulation of the $tD\mathbf{F}$-drift as follows:

For each of the N electrons, define $\mathbf{r}_{(j)}$ to be the 3-dimensional distance *from* the electron *to* its *nearest* nucleus. Let $\mathbf{F}_{(j)}$ be the corresponding 3-dimensional "component" of $\mathbf{F}$; then

$$t_{(j)} = (\mathbf{r}_{(j)} \cdot \mathbf{F}_{(j)})/[D(\mathbf{F}_{(j)} \cdot \mathbf{F}_{(j)})] \tag{27}$$

is the time at which this electron would reach its closest distance to the nucleus, if it were to move with constant velocity $D\mathbf{F}_{(j)}$. When this point of closest distance is "within sight" of the subsequent $tD\mathbf{F}_{(j)}$ "drift" (see Fig. 1), say when $0 < t_{(j)} < 2t$, redefine $\mathbf{F}_{(j)}$ by replacing it with

$$\mathbf{F}'_{(j)} = (2w_{(j)} - w_{(j)}^2) \cdot [w_{(j)}^{3/2}\mathbf{F}_{(j)} + (1 - w_{(j)}^{3/2})\,\mathbf{r}_{(j)}/Dt_{(j)}], \tag{28}$$

where $w_{(j)} = t_{(j)}/2t$. The first factor causes the magnitude of $\mathbf{F}'$ continuously decrease to zero (at the closest distance to nucleus), the second one results in a continuous change of direction, turning $\mathbf{F}$ towards the nucleus. Thus, the drift actually simulated will prohibit electrons from "overshooting" past a nucleus (algorithms allowing this result in a very detrimental contribution to the error of the $E_0(t)$ estimates).

This modification of $\mathbf{F}_{(j)}$, repeated for each electron, obviously makes it *continuous* at each nucleus. Since the modification is done only in a t-neighborhood of a nucleus, it is *not* necessary to correspondingly modify the local energy $E_L(\mathbf{R})$. This is due to the fact that the difference between the properly modified E_L and the original E_L can be considered a t^2-*order* perturbation of Eq. 3, and as such inconsequential. In choosing (28) we attempted to approximate the *exact* (i.e., continuous in time) drift due to the original $\mathbf{F}(\mathbf{R}(t))$ as accurately as possible. Nevertheless, there is definitely room for additional improvement of this part of the algorithm.

One such alternative (presently without a theoretical justification) is to modify the computation of $\mathbf{F}$ (but not of E_L) at *all* $\mathbf{R}$ by replacing *every* term of the type

$$C(\mathbf{R}) \cdot \mathbf{r}_{(j,k)}/|\mathbf{r}_{(j,k)}| \tag{29}$$

($C(\mathbf{R})$ being a continuous function) by

$$C(\mathbf{R}) \cdot \mathbf{r}_{(j,k)}/(|\mathbf{r}_{(j,k)}| + \alpha \cdot t \cdot |C(\mathbf{R})|), \tag{30}$$

where $\mathbf{r}_{(j,k)}$ is the 3-dimensional distance from the jth electron to the kth nucleus, and α is an adjustable parameter. For the hydrogen molecule, the value of $\alpha = 0.65$ gives very good results in conjunction with the normal distribution (see Fig. 2), the alternate distribution of Formula (21) requires $\alpha = 0.3$.

4. Application and Discussion

For illustration purposes we applied the algorithm to the ground state of Hydrogen molecule. The trial function we used was that of [4], with distances in atomic units:

$$\psi_T = [\exp\{-1.285r_{1a}\} + \exp\{-1.285r_{1b}\}] \cdot [\exp\{-1.285r_{2a}\} + \exp\{-1.285r_{2b}\}] \cdot \exp\{.28r_{12}/(1+.05r_{12})\}. \tag{31}$$

An initial list of $M = 2000$ configurations was randomly generated from an arbitrary distribution. After reaching equilibrium, these were advanced through 200 iterations per block. Sufficient number of blocks were used to make the error bars

TABLE I

Diffusion Monte Carlo Estimates of the Ground State Energy of $H_2^{a,b}$

	With continuity correction				Without continuity correction[d]	
t	$E_0(t)$[c]	σ	$E_0(t)$[e]	σ	$E_0(t)$	σ
0.1	−1.1735	2(−4)	−1.1734	3(−4)	−1.1792	4(−4)
0.2	−1.1722	2(−4)	−1.1679	2(−4)	−1.1809	4(−4)
0.3	−1.1683	1(−4)	−1.1604	2(−4)	−1.1785	2(−4)
0.4	−1.1639	3(−4)	−1.1518	2(−4)	−1.1734	1(−4)
0.5	−1.1594	2(−4)	−1.1435	1(−4)	−1.1656	3(−4)
			Model			
	$E_0(t) = E_0 + at^2 + bt^4$				$E_0(t) = E_0 + at + bt^2 + ct^4$	
$E_0 =$	−1.1745 ± .0002		−1.1749 ± .0003		$E_0 =$ −1.1741 ± .0012	
$a =$	.0735 ± .0037		.1801 ± .0046		$a =$ −.0702 ± .0126	
$b =$	−.0509 ± .0132		−.2180 ± .0154		$b =$ .1905 ± .0321	
					$c =$ −.0640 ± .0497	

[a] All quantities are in atomic units.

[b] Each simulation uses an initial list of 2000 configurations and 200 iterations per block. Averages and standard deviations are obtained from 3 (largest t) to 12 (smallest t) blocks, discarding the results of the first block. $E_0^{\text{exact}} = -1.1745$ a.u. and ψ_T is given by (31), with the nuclei separation of 1.401 a.u. (taken from [4]).

[c] Using continuity correction (28), and non-normal distribution of Section 1.

[d] Without continuity correction, using the normal distribution.

[e] Using continuity correction (30), and the normal distribution.

of individual energy estimates (calculated at five distinct values of t) reasonably small.

The results are reported in Table I (plotted in Fig. 2) for both the normal distribution, and that of Formula (21). Also displayed is a set of results obtained by ignoring the discontinuities in **F**, and using the normal distribution. The weighted least-squares estimates of the $E_0(t=0)$ intercept are calculated, using the inverse of the observed variance for weights. The quadratic behaviour of our results is readily apparent; one can also observe how detrimental is the **F**-discontinuity (especially in combination with the normal distribution) when not properly corrected for.

Appendix A

We require a solution to the following differential equation:

$$\frac{-\partial \mathcal{G}(\mathbf{R} \to \mathbf{R}', t)}{\partial t} = D\nabla_{\mathbf{R}'} \cdot [\mathbf{F}(\mathbf{R}')\, \mathcal{G}] \tag{A1}$$

satisfying the boundary condition $\mathcal{G}(\mathbf{R} \to \mathbf{R}', 0) = \delta(\mathbf{R}' - \mathbf{R})$.

We will demonstrate that the solution is given by

$$\mathcal{G}(\mathbf{R} \to \mathbf{R}', t) = \delta(\mathbf{R}' - \mathbf{R}(t)), \tag{A2}$$

where

$$\frac{d\mathbf{R}(t)}{dt} = D\mathbf{F}(\mathbf{R}(t)) \tag{A3}$$

with $\mathbf{R}(0) = \mathbf{R}$.

By inspection the solution is correct at $t=0$. Now, substituting (A2) and (A3) into (A1) yields

$$D\mathbf{F}(\mathbf{R}(t)) \cdot \delta'(\mathbf{R}' - \mathbf{R}(t)) = D \cdot [\mathbf{F}(\mathbf{R}')\, \delta'(\mathbf{R}' - \mathbf{R}(t)) + \delta(\mathbf{R}' - \mathbf{R}(t))\, \nabla \cdot \mathbf{F}(\mathbf{R}')]. \tag{A4}$$

Multiplying (A4) by an arbitrary function $X(\mathbf{R}')$ and integrating over $\mathbf{R}'$ we obtain

$$-D[\mathbf{F} \cdot \nabla X]_{R(t)} = D \cdot [-(\nabla X)\, \mathbf{F} - X\nabla \cdot \mathbf{F} + X\nabla \cdot \mathbf{F}]_{\mathbf{R}(t)} \tag{A5}$$

which is an identity. Thus (A2) is the desired solution to (A1).

Appendix B

In this Appendix we will establish the equivalence of $-\log \cdot \{\bar{B}\}/t$ and (25), within the t^2-accuracy. In the following $\langle \cdots \rangle$ will denote averaging over all configurations before branching, $\langle\langle \cdots \rangle\rangle$ will imply the same averaging after branching.

From Formula (22) we obtain

$$\langle B_i\rangle = 1 - \frac{t}{2}\langle E_i + E_i'\rangle + t^2\langle (E_i + E_i')^2\rangle/8 + \cdots, \tag{B1}$$

where $E_i = E_L({}^{(i)}\mathbf{R})$, and $E_i' = E_L({}^{(i)}\mathbf{R}_0')$ see Fig. 1.

Thus

$$\begin{aligned} -\log_e\langle B_i\rangle/t &= \frac{1}{2}\langle E_i + E_i'\rangle - t\langle (E_i + E_i')^2\rangle/8 + t\langle E_i + E_i'\rangle^2/8 + \cdots \\ &= \frac{1}{2}\langle E_i + E_i'\rangle - \frac{t}{8}\langle (E_i + E_i')\cdot[E_i + E_i' - \langle E_i + E_i'\rangle]\rangle + \cdots \\ &= \frac{1}{2}\langle E_i\rangle + \frac{1}{2}\langle E_i'\cdot[B_i/\langle B_i\rangle]\rangle + \cdots = \frac{1}{2}\langle E_i\rangle + \frac{1}{2}\langle\langle E_i'\rangle\rangle + \cdots \end{aligned} \tag{B2}$$

since

$$E_i = E_i' + O(t) \tag{B3}$$

and

$$B_i/\langle B_i\rangle = 1 - \frac{t}{2}(E_i + E_i' - \langle E_i + E_i'\rangle) + O(t^2) \tag{B4}$$

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