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Exact algorithm for d-dimensional walks on finite and infinite lattices with traps. II. General formulation and application to diffusion-controlled reactions

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A method for calculating exactly the expected walk length $\langle n \rangle$ for random walks on d-dimensional lattices with traps, reported recently by the authors [Phys. Rev. Lett. 47, 1500 (1981)], is elaborated in some detail in order to exhibit the underlying structure of the theory and to demonstrate the generality of the approach. Formulated as a problem in matrix transformation theory, the properties of a certain linear operator A and its inverse A^{-1} are explored in $d=1,2,3$. In $d=1$, the analytic result $\langle n \rangle = N(N+1)/6$ derived by Montroll for trapping on a (periodic) chain with a single, deep trap is recovered. In the higher dimensions $d=2,3$, extensive new data are reported on the results of *exact* calculations of $\langle n \rangle$ for two types of reaction-diffusion processes. The first is that of a reactant migrating toward a target molecule in a volume of d dimensions, and reacting there irreversibly upon first encounter. Then, it is assumed that the $N-1$ sites surrounding the target molecule are not passive (nonabsorbing, neutral) but may react with the diffusing molecule to form an excited-state complex which may, with nonzero probability s, result in the irreversible removal of reactant from the system. In both models, the efficiency of reaction is studied as a function of the spatial extent of the reaction volume and of the boundary conditions imposed on the underlying lattice.

I. INTRODUCTION

Theories of condensed matter based on lattice models have played a central role in elucidating the qualitative and quantitative features of many equilibrium and nonequilibrium phenomena. Both analytic and numerical (Monte Carlo, molecular dynamics) methods have been implemented to study successfully such phenomena as phase transitions,[1] the equilibrium and transport properties of liquids[2] and polymers,[3] and many problems in solid-state dynamics.[4] Recently, we have formulated an exact algorithm[5] for calculating the expected walk length $\langle n \rangle$ (or diffusion time) for a walker (atom, molecule, excitation) undergoing random (or biased) displacements on a finite or infinite (periodic) d-dimensional lattice with multiple and/or variable-depth traps (reactive sites). The method, which expands considerably the class of lattice models accessible to exact analysis, is based on a classification of the symmetry of the sites surrounding the reactive site and a coding of the fate of a mobile, reactant species as it encounters a site of a given symmetry. As will be illustrated in this paper, the theory is capable of generalization to many problems in lattice statistics for which, previously, concrete results could be obtained only via large-scale numerical simulation.[6-8] Not only does the present theory lead to *exact* results in any dimension, but the time scale required for its numerical implementation is orders of magnitude less costly in central processing unit (cpu) time than the direct application of Monte Carlo methods.

The purposes of the present contribution are twofold. First, we elaborate in some detail a general formulation of the theory in order to lay stress on the underlying structural features of the method as well as to indicate the class of physical problems to which it may be applied. We exploit the fact that the theory has a natural expression as a problem in matrix transformation theory and we point out that the information contained in the matrix operator A of the problem, and especially in its inverse A^{-1}, casts light on the statistical factors involved in calculations of $\langle n \rangle$. For example, we show how manipulations on A^{-1} lead directly to the analytic result $\langle n \rangle = N(N+1)/6$, the classic result obtained[9-11] by Montroll and Weiss for trapping on a $d=1$ lattice with a single deep trap. Within the context of the one-dimensional (1D) problem, we show that the matrix elements of A^{-1} have a simple geometrical interpretation, one that reflects the

fraction of probability phase space encountered by the random walker as it seeks the trap. Then, by analyzing the (exact) results generated in calculations of the matrix elements of the inverse operator A^{-1} in $d=2,3$, we are able to derive general invariance relations which, when coupled with scaling relations derived from a sequence of decimationlike transformations, allow the calculation of $\langle n \rangle$ for an $n \times n = N$ site lattice to be replaced by simpler calculations on an $n' \times n' \equiv N'$ site lattice (where $N' < N$). It is suggested that this procedure may open up a new avenue for obtaining analytic results in the dimensions $d=2,3$ to complement those already derived for the dimension $d=1$.

The second main objective of this paper is to demonstrate the utility of the theory as a calculational tool. We do this by presenting the results of exact calculations of $\langle n \rangle$ for lattices up to $21 \times 21 = 441$ sites in $d=2$ and up to $15 \times 15 \times 15 = 3375$ site lattices in $d=3$. Two sorts of problems in reaction-diffusion theory are considered. First, we treat the case of a single deep trap (trapping probability, $T=1$) surrounded by $N-1$ nontrapping sites in d dimensions, with the underlying lattices subject to a variety of boundary conditions. Then, we relax the assumption that the $N-1$ background sites are passive (or neutral) and consider the case that there exists a finite probability s $(0<s<1)$ of reaction at each of the $N-1$ sites surrounding a centrosymmetric deep trap. Again (exact) results are tabulated for a range of lattice sites and attendant boundary conditions, and a simple analytic result is derived for the dependence of $\langle n \rangle$ on the background trapping probability s.

Given these two distinct aims, the paper is organized in the following way. In Sec. II we develop the theory and show explicitly how the formulation may be changed to allow situations of increasing generality to be treated. The ideas are developed using the example first elaborated in Ref. 5, the 5×5 periodic lattice with a single centrosymmetric, deep trap. Then in Sec. III we consider the one-dimensional chain for this same problem and show how the classic result of Montroll[9–11] can be recovered. It is particularly easy to introduce the geometrical interpretation of the elements of the inverse matrix A^{-1} within the context of the one-dimensional problem, and this is included in Sec. III as well. In Sec. IV we identify relations in $d=2,3$ and illustrate how decimationlike transformations may be performed on the 5×5 periodic lattice problem treated earlier. Also included in this section are extensive new data on random walks on large lattice systems in $d=2,3$ with traps. Then in Sec. V, via calculation and simple analysis, we show how the results obtained assuming the $N-1$ background sites to be passive are changed (and dramatically so) when the $N-1$ sites compete with the central deep trap for capture of the diffusing reactant. Some physical and chemical implications of our results are discussed in Sec. VI, where we indicate as well problems presently under study using the methods laid down in this paper.

II. THE THEORY AND ITS GENERALIZATIONS

Let us proceed by assuming initially that the 5×5 lattice displayed in Fig. 1 is subject to periodic boundary conditions. If each of the $N-1$ sites surrounding the centrosymmetric deep trap $(T=1)$ is characterized by the same nonvanishing probability s of trapping $(0 \leq s < 1)$, the point group symmetry of the lattice unit, by inspection, will be D_{4h}. In particular, one finds only five distinct types of sites (labeled 1–5 in Fig. 1) apart from the central trap. Let us imagine the walker to be situated at one of the sites labeled 1 and try to work out the expected walk length $\langle n \rangle_1$ for a walk originating from this site. The simplest possible case would be the one for which: (1) the $N-1$ background sites do not compete with the centrosymmetric site for trapping of the walker (i.e., $T=1$ and all $s=0$); (2) the walker on moving away from site 1 has an equal *a priori* probability of translating to the trap T, the site 3, or either of the sites labeled 2. The latter constraint means that there is one chance in four that the walker will move one step to the site labeled 3. In a strictly Markovian situation, the walker, after having landed on this new site 3 will have no "memory" of ever having been on the original site 1. The walker will continue his walk just as if he had started originally from site 3, except that his walk length must be incremented by the one previously taken step. Taking into account all four sites

5	4	3	4	5
4	2	1	2	4
3	1	T	1	3
4	2	1	2	4
5	4	3	4	5

FIG. 1. 5×5 lattice with a centrosymmetric trap T. The numbers classify the symmetry of the sites of the lattice.

surrounding the site labeled 1, together with the probability $p=\frac{1}{4}$ of a neighboring site having been reached in a (random) displacement from site 1, the following relation may be written:

$$\langle n\rangle_1=\tfrac{1}{4}(\langle n\rangle_T+1)+\tfrac{1}{4}(\langle n\rangle_2+1)+\tfrac{1}{4}(\langle n\rangle_{\bar{2}}+1)+\tfrac{1}{4}(\langle n\rangle_3+1)\,. \quad (1)$$

The above relation for $\langle n\rangle_1$ has several immediate generalizations and before proceeding with the further elaboration of the approach, we may indicate some of these. For example, suppose the site labeled 1 is characterized by a nonvanishing probability of trapping the walker (i.e., we set $0<s<1$). In this case, the factor on the right-hand side of the expression (1) must be weighted by the probability $(1-s)$ and, to account for the possibility that the walker is actually trapped at the site 1 at the very outset, we must include the factor $s\{1\}$. The expression for $\langle n\rangle_1$ in this more general situation (one considered in greater detail in a later section of this paper) then becomes

$$\langle n\rangle_1=s\{1\}+(1-s)\times[\tfrac{1}{4}(\langle n\rangle_T+1)+\tfrac{1}{4}(\langle n\rangle_2+1)+\tfrac{1}{4}(\langle n\rangle_{\bar{2}}+1)+\tfrac{1}{4}(\langle n\rangle_3+1)]\,. \quad (2)$$

The simpler case, Eq. (1), is recovered upon setting $s=0$. Going further, notice that the formulation of $\langle n\rangle_1$ is not restricted in any essential way by the particular choice of constraints, all $s_i=s$ or all $p_i=p=\frac{1}{4}$. For example, if it were the case that all sites on the lattice were characterized by a different setting of s, the above result would generalize to

$$\langle n\rangle_1=s_1\{1\}+(1-s_1)\times[\tfrac{1}{4}(\langle n\rangle_T+1)+\tfrac{1}{4}(\langle n\rangle_2+1)+\tfrac{1}{4}(\langle n\rangle_{\bar{2}}+1)+\tfrac{1}{4}(\langle n\rangle_3+1)]\,, \quad (3)$$

where we have used the tilde to distinguish the two sites previously labeled 2. Or suppose, due to the presence of some external field, that the probability p of moving from site 1 to neighboring sites is *not* characterized by equal *a priori* probabilities, e.g., suppose that the walker is a charged particle and is influenced by the presence of an electrical field. Then the bias in motion can be accounted for by assigning different probabilities of moving away from the site labeled 1, depending on the direction taken. In this case, the above expression (3) generalizes to read

$$\langle n\rangle_1=s_1\{1\}+(1-s_1)\times[p_T(\langle n\rangle_T+1)+p_2(\langle n\rangle_2+1)+p_{\bar{2}}(\langle n\rangle_{\bar{2}}+1)+p_3(\langle n\rangle_3+1)]\,. \quad (4)$$

In fact, in the specification of the p_i the only restriction is that $\sum_i p_i=1$; there is no requirement that the p_i be constant at all.

Returning now to the elaboration of the method, if we restrict attention to the case where all $p_i=\frac{1}{4}$ and all $s_i=s$, expressions analogous to Eq. (2) can be written down for $\langle n\rangle_2,\ldots,\langle n\rangle_5$. These are as follows:

$$\langle n\rangle_2=s\{1\}+\tfrac{1}{4}(1-s)[2(\langle n\rangle_1+1)+2(\langle n\rangle_4+1)]\,, \quad (5)$$

$$\langle n\rangle_3=s\{1\}+\tfrac{1}{4}(1-s)[(\langle n\rangle_1+1)+(\langle n\rangle_3+1)+2(\langle n\rangle_4+1)]\,, \quad (6)$$

$$\langle n\rangle_4=s\{1\}+\tfrac{1}{4}(1-s)[(\langle n\rangle_2+1)+(\langle n\rangle_3+1)+(\langle n\rangle_4+1)+(\langle n\rangle_5+1)]\,, \quad (7)$$

$$\langle n\rangle_5=s\{1\}+\tfrac{1}{4}(1-s)[2(\langle n\rangle_4+1)+2(\langle n\rangle_5+1)]\,, \quad (8)$$

where we have set $\langle n\rangle_T=0$, since the expected walk length from a deep trap ($T=1$) is zero. The system of equations, Eq. (2) and Eqs.(5)–(8), comprise five equations in five unknowns which can be solved exactly for the $\langle n\rangle_i$ and from which information the overall expected walk length $\langle n\rangle$ can be computed:

$$\langle n\rangle=\frac{4\langle n\rangle_1+4\langle n\rangle_2+4\langle n\rangle_3+8\langle n\rangle_4+4\langle n\rangle_5}{24}\,. \quad (9)$$

The coefficients prefacing the $\langle n\rangle_i$ count the number of sites of the lattice corresponding to the specification i; in effect, they reflect the symmetry of the lattice and may be associated with symmetry numbers σ_i. For the problem at hand, we may write

$$\langle n\rangle=\frac{\sigma_1\langle n\rangle_1+\sigma_2\langle n\rangle_2+\sigma_3\langle n\rangle_3+\sigma_4\langle n\rangle_4+\sigma_5\langle n\rangle_5}{N-1}\ , \tag{10}$$

where $\sigma_1=\sigma_2=\sigma_3=\sigma_5=4$, and $\sigma_4=8$ (with $N=\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5$).

The information displayed in Eqs. (2) and (5)–(8) can be recast into the following matrix representation:

$$\begin{bmatrix} 1 & -2q & -q & 0 & 0 \\ -2q & 1 & 0 & -2q & 0 \\ -q & 0 & 1-q & -2q & 0 \\ 0 & -q & -q & 1-q & -q \\ 0 & 0 & 0 & -2q & 1-2q \end{bmatrix} \begin{bmatrix} \langle n\rangle_1 \\ \langle n\rangle_2 \\ \langle n\rangle_3 \\ \langle n\rangle_4 \\ \langle n\rangle_5 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \quad \text{and } q\equiv\frac{(1-s)}{4}\ . \tag{11}$$

Once s has been specified, the square matrix on the left can be dealt with by standard numerical procedures and the data for the $\langle n\rangle_i$ extracted using Cramer's rule. In turn, the expected walk length $\langle n\rangle$ can be calculated immediately, with the overall time scale for the calculation essentially negligible compared with the time required to determine $\langle n\rangle$ via a standard Monte Carlo calculation.[6–8] As noted in Ref. 5, to obtain $\langle n\rangle$ for the higher-dimensional, $5\times5\times5$ periodic lattice with a central deep trap ($T=1$) and absorption probability at the $N-1=124$ remaining sites set at $s=0.01$, the Monte Carlo simulation required 270 *minutes* of cpu time on an IBM 370 (9000 walks initiated from each site were required to produce good histograms), whereas implementation of Cramer's rule for the same problem required 1.74 *seconds* on the same machine. It is this practical consideration, coupled with the great flexibility of the approach (illustrated earlier in this section), that provides the promise of obtaining *exact* results on lattice problems previously inaccessible to analysis. In fact, in Secs. IV and V we shall report extensive data on lattice problems for which it is fair to say that the Monte Carlo simulation would never have been attempted, owing to the staggering amounts of cpu time that would have been required. However, the ability to calculate $\langle n\rangle$ economically is only part of the appeal of the approach described here. One can, in fact, extract information from the representation (11) that casts light on the underlying statistical features of the class of reaction-diffusion problems considered here, and it is to this objective that we shall now turn our attention.

We wish to consider the matrix $\underline{A}$, where [see Eq. (11)]

$$\underline{A}=\begin{bmatrix} 1 & -2q & -q & 0 & 0 \\ -2q & 1 & 0 & -2q & 0 \\ -q & 0 & 1-q & -2q & 0 \\ 0 & -q & -q & 1-q & -q \\ 0 & 0 & 0 & -2q & 1-2q \end{bmatrix}\ , \tag{12}$$

together with its inverse $\underline{A}^{-1}$. First of all, as can easily be checked by assigning a positive sign to the matrix element a_{ij} if $i>j$ or a negative sign if $i<j$ and accounting for the symmetry number σ_i of the lattice sites, both of Kirchhoff's laws (for junctions and closed loops) are satisfied, which is an immediate consequence of the conservation of probability implicit in our approach. Of greater interest is the structure of the inverse matrix $\underline{A}^{-1}$ itself. The elements of the inverse matrix corresponding to (12) (for arbitrary s) are listed in Appendix A. For the particular case $s=0$, we have

$$\underline{A}^{-1}=\frac{2}{5}\begin{bmatrix} 10 & 10 & 10 & 20 & 10 \\ 10 & 14 & 12 & 26 & 13 \\ 10 & 12 & 16 & 28 & 14 \\ 10 & 13 & 14 & 32 & 16 \\ 10 & 13 & 14 & 32 & 21 \end{bmatrix} \tag{13}$$

from which representation the validity of the junction and loop theorems can also be verified (again, accounting for the various σ_i). Having computed the inverse, we find that the solution of the problem follows directly from the matrix equation

$$\begin{bmatrix} \langle n \rangle_1 \\ \langle n \rangle_2 \\ \langle n \rangle_3 \\ \langle n \rangle_4 \\ \langle n \rangle_5 \end{bmatrix} = \begin{bmatrix} 4 & 4 & 4 & 8 & 4 \\ 4 & 5.6 & 4.8 & 10.4 & 5.2 \\ 4 & 4.8 & 6.4 & 11.2 & 5.6 \\ 4 & 5.2 & 5.6 & 12.8 & 6.4 \\ 4 & 5.2 & 5.6 & 12.8 & 8.4 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} . \quad (14)$$

$$\begin{bmatrix} 1 & -2q & -q & 0 & 0 \\ -2q & 1 & 0 & -2q & 0 \\ -2q & 0 & 1 & -2q & 0 \\ 0 & -2q & -q & 1 & -q \\ 0 & 0 & 0 & -4q & 1 \end{bmatrix} \begin{bmatrix} \langle n \rangle_1 \\ \langle n \rangle_2 \\ \langle n \rangle_3 \\ \langle n \rangle_4 \\ \langle n \rangle_5 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} . \quad (15)$$

In effect, summing the elements of the first row gives directly the walk $\langle n \rangle_1$, summing across the second row gives $\langle n \rangle_2$, etc. The numbers obtained are $\langle n \rangle_1 = 24$, $\langle n \rangle_2 = 30$, $\langle n \rangle_3 = 32$, $\langle n \rangle_4 = 34$, and $\langle n \rangle_5 = 36$, which, together with Eq. (9), gives the exact result $\langle n \rangle = 31.67$ (see Ref. 5). Hence, the sum of the elements of row i gives directly information on the expected walk length $\langle n \rangle_i$ from a particular site i to a central trap. From such information, one can assess directly the influence of spatial extent (and dimension) on reaction-diffusion processes involving strictly irreversible reactions (the case here with $T=1$, $s=0$) or quasireversible reactions (the case $T<1$, $s=0$) or competing chemical reactions [$0<T\leq 1$, $0<s<1$ (the case presented in Sec. V)].

The individual elements α_{ij} of the inverse matrix $\underline{A}^{-1}$ are of considerable interest. If one regards the matrix equation, Eq. (11), as a kind of principal axis transformation in phase space, then the elements α_{ij} can be given a geometrical interpretation; this will be illustrated explicitly in the following section. More importantly, knowledge of the individual elements α_{ij} plays a central role in deriving general invariance relations and in identifying lattice scaling transformations; these points will be illustrated in Sec. V for the planar lattice of Fig. 1. For now we simply comment on the structural changes in the original matrix $\underline{A}$ of our problem when boundary conditions other than periodic are employed. (The cases cited below are specified and illustrated in Ref. 6.) For the case of a *centrosymmetric* trap T, periodic and nontransmitting (confining) boundary conditions lead to exactly the same matrix equation (11) and hence to the same numerical results; of course, if the deep trap moves off center, imposition of these two boundary conditions necessarily leads to different matrix equations and hence to different results (a point which was documented numerically in our earlier study, Ref. 6). Dramatically different results can be obtained using reflecting boundary conditions. Here the rows 3–5 of the matrix equation (11) are changed slightly, but rows 1 and 2 are unaffected. Specifically, we have

The remarkable "focusing effect" of this class of boundary conditions will be illustrated in the data reported later in this paper. Whatever the boundary conditions imposed, there will be a certain block of interior sites of the lattice whose specification in the associated matrix $\underline{A}$ will remain unchanged. In particular, for a two-dimensional lattice of N sites, there will be a core of $\frac{1}{8}(N+1)(N-5)$ distinct sites whose specification will be invariant to changes in the boundary conditions, $\frac{1}{2}(N+1)$ distinct sites on the boundary of the lattice which reflect changes in the boundary conditions, and a group of $\frac{1}{2}(N-1)$ distinct sites just inside the boundary layer of the lattice that comprise the interior sites influenced by the boundary conditions imposed. (Similar results can be written down in $d=1,3$.) This classification of sites is also useful in the design of scaling transformations, as will be shown in Sec. IV.

III. ANALYTIC RESULTS IN DIMENSION $d=1$

In the approach taken in this paper, the dependence of the overall walk length $\langle n \rangle$ on the parameters specifying the lattice (e.g., N, s_i, σ_i) is not exposed directly. That is, the $\langle n \rangle$ is an implicit function of these variables. It is therefore of some interest to see if the theory can be inverted analytically in order to display explicitly the dependence of $\langle n \rangle$ on the variables of the problem. This turns out to be particularly easy in the dimension $d=1$ where we have already at our disposal the classic result of Montroll[9,11] and Montroll and Weiss.[10] In particular, it is shown by these authors that an exact analytic result for $\langle n \rangle$ in terms of N can be written down for $d=1$ in the case where periodic boundary conditions are assumed, and where the lattice contains a single deep trap ($T=1$) with all other sites specified by $s_i=0$. We now show how the result for this case,

$$\langle n\rangle=\frac{N(N+1)}{6}\ , \tag{16}$$

can be recovered from the matrix $\underline{A}^{-1}$ defining the problem.

Two separate cases can be considered and these are illustrated in Fig. 2. In case (a), we imagine an odd lattice with a centrosymmetric trap; in case (b), we consider an even lattice with an off-center trap.

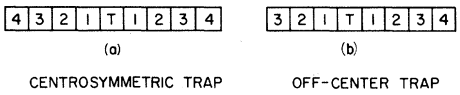

FIG. 2. One-dimensional lattices with a centrosymmetric trap [case (a)] and an off-center trap [case (b)].

Considering case (a) first, and with the use of the notation of the preceding section, the matrix equation to be solved is

$$\begin{bmatrix} 1 & -q & 0 & \cdots & 0 & 0 & 0 \\ -q & 1 & -q & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots\vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -q & 1 & -q \\ 0 & 0 & 0 & \cdots & 0 & -q & 1-q \end{bmatrix} \begin{bmatrix} \langle n\rangle_1 \\ \langle n\rangle_2 \\ \vdots \\ \langle n\rangle_{(N-3)/2} \\ \langle n\rangle_{(N-1)/2} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \\ 1 \end{bmatrix}, \tag{17}$$

where $q=(1-s)/2$. Specifically, $\underline{A}$ is an $[(N-1)/2]\times[(N-1)/2]$ matrix, where N is the total number of sites on the chain. If $q=(1-s)/2\rightarrow\frac{1}{2}$ (that is, if we set the absorption probability s of all background sites to zero), then Eq. (17) has the very simple inverse $\underline{A}^{-1}$:

$$\begin{bmatrix} 2 & 2 & 2 & \cdots & 2 & 2 & 2 \\ 2 & 4 & 4 & \cdots & 4 & 4 & 4 \\ 2 & 4 & 6 & \cdots & 6 & 6 & 6 \\ \vdots & \vdots & \vdots & \vdots\vdots & \vdots & \vdots & \vdots \\ 2 & 4 & 6 & \cdots & . & . & 2[(N-1)/2] \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} = \begin{bmatrix} \langle n\rangle_1 \\ \langle n\rangle_2 \\ \langle n\rangle_3 \\ \vdots \\ \langle n\rangle_{[(N-1)/2]} \end{bmatrix}. \tag{18}$$

Thus,

$$\langle n\rangle_1=\left\lfloor\frac{N-1}{2}\right\rfloor 2=N-1\ ,$$

$$\langle n\rangle_2=\left\lfloor\frac{N-3}{2}\right\rfloor 4+2=2N-4\ ,$$

$$\langle n\rangle_3=\left\lfloor\frac{N-5}{2}\right\rfloor 6+4+2=3N-9\ ,$$

$$\cdots$$

and in general,

$$\langle n\rangle_i=iN-i^2\ . \tag{19}$$

The expression for overall $\langle n\rangle$ may be determined at once from the weighted average:

$$\langle n\rangle=\frac{2\sum_{i=1}^{(N-1)/2}\langle n\rangle_i}{N-1}=\frac{2\sum_{i=1}^{(N-1)/2}(iN-i^2)}{N-1}$$

$$=\frac{2}{N-1}\left[\frac{N(N-1)(N+1)}{8}-\frac{N(N-1)(N+1)}{24}\right],$$

$$\langle n\rangle=\frac{N(N+1)}{6}\ .$$

To consider the case of an off-center trap [Fig. 2(b)], the matrix $\underline{A}^{-1}$ is of rank $N/2$, and has the structure

$$\underline{A}^{-1}=\begin{bmatrix} 2 & 2 & 2 & \cdots & 2 & 2 & 1 \\ 2 & 4 & 4 & & 4 & 4 & 2 \\ 2 & 4 & 6 & & 6 & 6 & 3 \\ \vdots & \vdots & \vdots & & & & \\ 2 & 4 & 6 & & N-2 & & \frac{N}{2} \end{bmatrix} . \tag{20}$$

The relation $\langle n\rangle_i = iN - i^2$ can be derived just as easily in this case, and the construction of

$$\langle n\rangle = \frac{2\sum_{i=1}^{(N/2)-1}\langle n\rangle_i + \langle n\rangle_{N/2}}{N-1}$$

gives the same (Montroll) result. Although, to the best of our knowledge, an explicit analytic result for the case $s_i \neq 0$ in dimension $d=1$ has not been reported, it turns out that the use of the matrix inversion technique in conjunction with the methods of function theory leads to an analytic expression for one-dimensional periodic lattices with $s_i \neq 0$. This calculation is sufficiently detailed that it will be presented elsewhere.[12]

We remarked in the preceding section that it was possible to give a geometrical interpretation to the individual elements in the inverse matrix $\underline{A}^{-1}$. This interpretation can be made particularly transparent in the case $d=1$ and we illustrate the idea for an odd lattice with $N=7$, a centrosymmetric trap, and $s_i \neq 0$. Here, the matrix $\underline{A}$ is

$$\begin{bmatrix} 1 & -q & 0 \\ -q & 1 & -q \\ 0 & -q & 1-q \end{bmatrix}\begin{bmatrix} \langle n\rangle_1 \\ \langle n\rangle_2 \\ \langle n\rangle_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} . \tag{21}$$

Let us define unit vectors $\vec{e} \equiv \{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$ and the phase space vectors defined by the row elements of Eq. (21):

$$\vec{v}_1 = \vec{e}_1 - q\vec{e}_2 , \tag{22a}$$

$$\vec{v}_2 = -q\vec{e}_1 + \vec{e}_2 - q\vec{e}_3 , \tag{22b}$$

$$\vec{v}_3 = -q\vec{e}_2 + (1-q)\vec{e}_3 . \tag{22c}$$

In this notation, the expression for $\underline{A}^{-1}$ reads:

$$\underline{A}^{-1} = \frac{1}{(\vec{v}_2\times\vec{v}_3)\cdot\vec{v}_1}\begin{bmatrix} (\vec{v}_2\times\vec{v}_3)\cdot\vec{e}_1 & (\vec{v}_3\times\vec{v}_1)\cdot\vec{e}_1 & (\vec{v}_1\times\vec{v}_2)\cdot\vec{e}_1 \\ (\vec{v}_2\times\vec{v}_3)\cdot\vec{e}_2 & (\vec{v}_3\times\vec{v}_1)\cdot\vec{e}_2 & (\vec{v}_1\times\vec{v}_2)\cdot\vec{e}_2 \\ (\vec{v}_2\times\vec{v}_3)\cdot\vec{e}_3 & (\vec{v}_3\times\vec{v}_1)\cdot\vec{e}_3 & (\vec{v}_1\times\vec{v}_2)\cdot\vec{e}_3 \end{bmatrix} . \tag{23}$$

As noted in Sec. II, the sum of the elements of row i gives, in effect, the expression for $\langle n\rangle_i$. Thus here,

$$\langle n\rangle_1 = \frac{[(\vec{v}_2\times\vec{v}_3)+(\vec{v}_3\times\vec{v}_1)+(\vec{v}_1\times\vec{v}_2)]\cdot\vec{e}_1}{(\vec{v}_2\times\vec{v}_3)\cdot\vec{v}_1} = \frac{1-q^2}{1-q-2q^2+q^3} , \tag{24}$$

$$\langle n\rangle_2 = \frac{[(\vec{v}_2\times\vec{v}_3)+(\vec{v}_3\times\vec{v}_1)+(\vec{v}_1\times\vec{v}_2)]\cdot\vec{e}_2}{(\vec{v}_2\times\vec{v}_3)\cdot\vec{v}_1} = \frac{1+q-q^2}{1-q-2q^2+q^3} , \tag{25}$$

$$\langle n\rangle_3 = \frac{[(\vec{v}_2\times\vec{v}_3)+(\vec{v}_3\times\vec{v}_1)+(\vec{v}_1\times\vec{v}_2)]\cdot\vec{e}_3}{(\vec{v}_2\times\vec{v}_3)\cdot\vec{v}_1} = \frac{1+q}{1-q-2q^2+q^3} . \tag{26}$$

The geometrical interpretation of $\langle n\rangle_1$ follows once we have identified the significance of the term in brackets in the numerators of Eqs. (24)–(26), viz.,

$$[(\vec{v}_2\times\vec{v}_3)+(\vec{v}_3\times\vec{v}_1)+(\vec{v}_1\times\vec{v}_2)] . \tag{27}$$

Recall that the vectors $\vec{v}_1$, $\vec{v}_2$, and $\vec{v}_3$ are defined in terms of a coordinate system with unit vectors $\vec{e}_1, \vec{e}_2, \vec{e}_3$. Then $\vec{v}_2 \equiv \vec{L}$, $\vec{v}_3 \equiv \vec{M}$, and $\vec{v}_1 \equiv \vec{N}$ are simply vectors to noncolinear points L,M,N lying in a plane p. Since, by construction, the origin of the coordinate system is chosen *not* to lie in the plane p, it can be shown that the vector (27) appearing in Eqs. (24)–(26) must be perpendicular to p. The quantity $\langle n\rangle_1$ is then just the projection of this resultant vector along the axis $\vec{e}_1$, divided by the volume of the parallelepiped $(\vec{v}_2\times\vec{v}_3)\cdot\vec{v}_1$. The individual elements of the first row, $(\vec{v}_2\times\vec{v}_3)\cdot\vec{e}_1$, $(\vec{v}_3\times\vec{v}_1)\cdot\vec{e}_1$, and $(\vec{v}_1\times\vec{v}_2)\cdot\vec{e}_1$, are the three possible parallelepiped volumes one can construct choosing one length to be the unit vector $\vec{e}_1$. Thus, it would appear that the principal axis transformation defined by the inverse matrix $\underline{A}^{-1}$ amounts to projecting out and normalizing the volume of probability phase space traversed by a random walker as it

moves away from some initial site of the lattice (here site 1) and confronts $N-1$ sites where the trapping probability is $s \neq 0$ and one site where the trapping probability is unity. The farther the initial site is from the centrosymmetric deep trap, the longer the expected walk length, which is to say the larger the volume of probability phase space sampled by the diffusing particle before it is irreversibly trapped. Notice that as s increases from zero, this probability volume decreases and in Sec. V we will give evidence as to just how dramatic the decrease in volume is when background absorption (the case of competing reactions) is possible. Finally, we note that the sum of the elements of any given *column* can also be given a geometrical interpretation; in the example studied above, the sum of the elements of column 1 of Eq. (23) is just $(\vec{v}_2 \times \vec{v}_3) \cdot \vec{e}$, the volume of a parallelepiped constructed by considering the vectors $\vec{v}_2, \vec{v}_3$, and the resultant unit vector $\vec{e} \equiv \vec{e}_1 + \vec{e}_2 + \vec{e}_3$ of magnitude $\sqrt{3}$.

IV. THE CASE OF A SINGLE, IRREVERSIBLE REACTION IN $d=2,3$

In this section we consider a single, irreversible reaction:

$$A + B \rightarrow C \ ,$$

where A is the migrating species [a single atom, molecule, or excitation undergoing random displacements on a square (cubic) lattice], and B is the fixed trap (a target molecule or reactive site, positioned at a centrosymmetric position on the host lattice). This was the case considered in our earlier study, Ref. 6, where Monte Carlo results were reported for $\langle n \rangle$, the average number of steps required for trapping. In that work, a variety of constraints on the migrating molecule as it encountered the boundaries of the system were imposed (periodic, reflecting, confining boundary conditions) and the consequences explored. In the bank of Monte Carlo data reported in Refs. 6–8, the largest lattice considered was a $5 \times 5 \times 5 = N = 125$ site lattice. Inasmuch as the investment of computer time was already excessive in this case (see the remark in Sec. II), it was our belief that this particular avenue for obtaining results on the role of boundaries and system size in influencing the dynamics of chemically reacting systems was essentially closed down. It is in this sense that one can appreciate the power of the method introduced in Ref. 5 since, by use of the algorithm, *exact* results can be obtained for significantly larger lattices on time scales which are on the order of seconds. Indeed, from a numerical point of view, the limitation of the method is not the time factor at all, but rather the (small) round-off error that one accumulates in inverting the matrix $\underline{A}$ for the problem under study. Moreover, as already stressed in this paper, solving the algorithm for a given problem allows the tabulation of a more detailed set of data than just $\langle n \rangle$ alone; we can also determine the $\langle n \rangle_i$ and the individual elements of the inverse matrix $\underline{A}^{-1}$ and, in interpreting their significance, try to obtain perhaps deeper insights into the physical and chemical nature of the problem. Reported in this section, then, is an extensive bank of data for odd lattices with a centrosymmetric deep trap in dimensions $d=2,3$. In particular, we tabulate $\langle n \rangle_i$ and $\langle n \rangle$ for two-dimensional square lattices (up to a lattice of $21 \times 21 = 441$ sites) and for three-dimensional cubic lattices (up to a lattice of $15 \times 15 \times 15 = 3375$ sites). Estimates for $\langle n \rangle$ for higher-dimensional periodic lattices can, of course, be obtained using the asymptotic theory developed[9–11] by Montroll and Weiss; however, to compute the higher-order terms in the Montroll theory (as is necessary for larger lattices), a summation of the structure function must be carried out for every site on the lattice (~ 3400 sites for the $15 \times 15 \times 15$ case cited above) and such calculations are very tedious. (When one considers boundary conditions other than periodic ones, the Montroll theory is extremely difficult to generalize and one must rely almost entirely on Monte Carlo results for reliable estimates.)

We now move to a presentation of the data and its interpretation. The coding for the two-dimensional lattices studied here is given in Fig. 3 and the data for $\{\langle n \rangle_i\}$ for periodic and reflecting lattices with a centrosymmetric deep trap ($T=1$) and all $s_i=0$ are given in Tables I and II. (Note

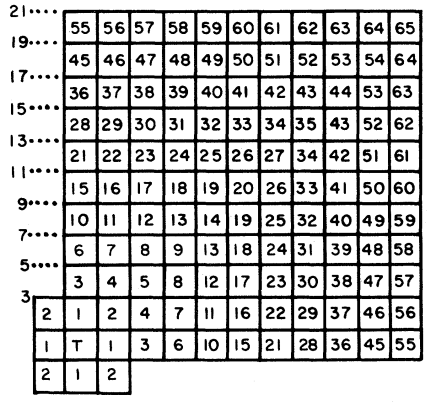

FIG. 3. Symmetry specification of sites for a $d=2$ odd lattice with a centrosymmetric trap.

TABLE I. 2D odd periodic-confining lattices with a single deep centrosymmetric trap. Footnotes indicate Montroll estimates for two dimensions (Refs. 9–11).

	3×3	5×5	7×7	9×9	11×11	13×13	15×15	17×17	19×19	21×21
$\langle n \rangle$	9.0[a]	31.7[b]	71.6[c]	130.6[d]	209.9[e]	310.6[f]	433.5[g]	579.4[h]	748.9[i]	942.4
$\langle n \rangle_1$	8.0	24.0	48.0	80.0	120.0	168.0	224.0	288.0	359.9	439.8
$\langle n \rangle_2$	10.0	30.0	60.5	101.2	152.1	213.2	284.5	365.9	457.5	559.3
$\langle n \rangle_3$		32.0	67.1	113.7	171.8	241.6	323.0	416.0	520.6	636.8
$\langle n \rangle_4$		34.0	70.9	120.3	182.2	256.4	342.9	441.9	553.2	676.8
$\langle n \rangle_5$		36.0	76.0	130.0	197.7	279.1	374.1	482.7	604.8	740.5
$\langle n \rangle_6$			74.5	129.9	198.9	281.6	378.0	488.2	612.1	749.7
$\langle n \rangle_7$			76.2	132.6	203.1	287.6	386.3	499.0	625.7	766.5
$\langle n \rangle_8$			79.1	137.6	211.3	299.8	403.2	521.5	654.4	802.2
$\langle n \rangle_9$			81.1	142.3	219.7	313.0	422.0	546.7	687.1	843.0
$\langle n \rangle_{10}$				136.9	213.8	305.7	412.7	534.9	672.3	824.8
$\langle n \rangle_{11}$				138.4	215.9	308.6	416.8	540.3	679.2	833.5
$\langle n \rangle_{12}$				141.7	220.6	315.7	426.6	553.5	696.2	854.7
$\langle n \rangle_{13}$				145.0	226.1	324.1	438.8	570.0	717.7	881.9
$\langle n \rangle_{14}$				147.0	230.6	331.8	450.5	586.5	739.7	910.1
$\langle n \rangle_{15}$					220.5	319.8	435.2	566.7	714.6	878.7
$\langle n \rangle_{16}$					221.9	321.6	437.5	569.9	718.6	883.8
$\langle n \rangle_{17}$					225.4	326.1	443.7	578.1	729.3	897.3
$\langle n \rangle_{18}$					229.5	331.9	451.9	589.3	743.9	915.8
$\langle n \rangle_{19}$					233.0	337.5	460.3	601.1	759.7	936.2
$\langle n \rangle_{20}$					235.0	341.9	467.6	612.0	774.9	956.1
$\langle n \rangle_{21}$						326.5	448.9	588.3	744.8	918.5
$\langle n \rangle_{22}$						327.8	450.5	590.4	747.4	921.8
$\langle n \rangle_{23}$						331.3	454.8	595.9	754.6	930.8
$\langle n \rangle_{24}$						335.9	460.8	603.8	764.8	943.8
$\langle n \rangle_{25}$						340.6	467.2	612.5	776.5	958.8
$\langle n \rangle_{26}$						344.2	472.9	620.9	788.0	974.0
$\langle n \rangle_{27}$						346.2	477.1	627.9	798.3	988.2
$\langle n \rangle_{28}$							455.5	601.8	765.8	947.7
$\langle n \rangle_{29}$							456.7	603.3	767.7	950.0
$\langle n \rangle_{30}$							460.3	607.5	772.8	956.4
$\langle n \rangle_{31}$							465.2	613.5	780.4	965.9
$\langle n \rangle_{32}$							470.7	620.4	789.3	977.2
$\langle n \rangle_{33}$							475.7	627.1	798.3	989.0
$\langle n \rangle_{34}$							479.4	632.9	806.6	1000.3

that the results obtained for periodic and confining boundary conditions will be the same in this case.) In these tables, comparison is also made with existing Monte Carlo results and Montroll-Weiss estimates, where available. A coding of the sites for three-dimensional lattices is presented in Fig. 4 and the corresponding data are reported in Tables III and IV.

It can be seen at once from the data that $\langle n \rangle_1$ in all dimensions is $\langle n \rangle_1 = N - 1$. That this should be true follows at once from the studies[9–11] of Montroll and Weiss wherein they find that the expected walk length required to return to the origin (for a walk starting from the origin) is N. If the trap is considered to be the origin, then $\langle n \rangle_1$ gives the first passage time from site 1 to the origin (since here the walker can only be trapped at the origin). But, of course, the expected walk length from site 1 to the origin should be exactly the same as the expected walk length from the origin to site 1. That is, for a walker to return to the origin in N steps, it is necessary that its $(N-1)$th step be on a site 1, since that is the only site of access to the trap; hence, $\langle n \rangle_1 = N - 1$. This result holds for chains, square lattices, or cubic lattices on which periodic boundary conditions have been imposed. In his deri-

TABLE I. (*Continued.*)

$\langle n \rangle$	3×3 9.0[a]	5×5 31.7[b]	7×7 71.6[c]	9×9 130.6[d]	11×11 209.9[e]	13×13 310.6[f]	15×15 433.5[g]	17×17 579.4[h]	19×19 748.9[i]	21×21 942.4
$\langle n \rangle_{35}$							481.4	637.1	813.4	1010.2
$\langle n \rangle_{36}$								608.3	779.2	968.3
$\langle n \rangle_{37}$								609.6	780.6	970.0
$\langle n \rangle_{38}$								613.1	784.6	974.9
$\langle n \rangle_{39}$								618.3	790.7	982.2
$\langle n \rangle_{40}$								624.3	797.9	991.1
$\langle n \rangle_{41}$								630.3	805.4	1000.6
$\langle n \rangle_{42}$								635.5	812.4	1009.9
$\langle n \rangle_{43}$								639.3	818.2	1018.1
$\langle n \rangle_{44}$								641.3	822.4	1024.8
$\langle n \rangle_{45}$									785.6	981.5
$\langle n \rangle_{46}$									786.9	982.9
$\langle n \rangle_{47}$									790.4	986.8
$\langle n \rangle_{48}$									795.8	992.9
$\langle n \rangle_{49}$									802.2	1000.3
$\langle n \rangle_{50}$									809.0	1008.4
$\langle n \rangle_{51}$									815.4	1016.4
$\langle n \rangle_{52}$									820.7	1023.6
$\langle n \rangle_{53}$									824.6	1029.4
$\langle n \rangle_{54}$									826.6	1033.6
$\langle n \rangle_{55}$										988.0
$\langle n \rangle_{56}$										989.2
$\langle n \rangle_{57}$										992.8
$\langle n \rangle_{58}$										998.2
$\langle n \rangle_{59}$										1005.0
$\langle n \rangle_{60}$										1012.4
$\langle n \rangle_{61}$										1019.7
$\langle n \rangle_{62}$										1026.4
$\langle n \rangle_{63}$										1031.8
$\langle n \rangle_{64}$										1035.7
$\langle n \rangle_{65}$										1037.7

[a] 8.92. [b] 31.6. [c] 71.6. [d] 130.6. [e] 209.9. [f] 310.6. [g] 433.6. [h] 579.5. [i] 749.1.

vation of the result $\langle n \rangle_1 = N-1$, Montroll notes that the result is independent of the structure of the lattice but that all other first passage times *do* depend on the structure of the lattice. These insights of Montroll are absolutely confirmed in our calculations. The result $\langle n \rangle_1 = N-1$ also appears in calculations presently being carried out on hexagonal lattices.[13] Even for square (cubic) lattices, when finite boundary conditions (other than nontransmitting ones) are imposed, the relation $\langle n \rangle_1 = N-1$ no longer holds.

There is another simple relation involving $\langle n \rangle_i$ that becomes evident upon inspection of the data in Tables I and II. Consider the corner site of a periodic lattice together with its immediately adjacent sites. Specifically, let i be a corner site and $i-1$ a next-to-the-corner site (see Fig. 5). As is seen, it is always the case that

$$\langle n \rangle_i - \langle n \rangle_{i-1} = 2 .$$

The reason for this two-step difference (for the case of periodic boundary conditions) is that in a random walk the next step from site i will either be to another site i (located symmetrically on the "other side" of the lattice) or to a site $i-1$. Thus, we must have

$$\langle n \rangle_i - \langle n \rangle_{i-1} = \sum_{j=1}^{\infty} j\left(\tfrac{1}{2}\right)^j = \frac{1/2}{(1-\frac{1}{2})^2} = 2 .$$

If, on the other hand, reflecting boundary conditions are assumed, since the walker on site i *must* land on a site $i-1$ on taking the next step, the relation

$$\langle n\rangle_i-\langle n\rangle_{i-1}=1$$

must hold, and it does (see Tables II and IV). These relations constitute completely general *invariance relations* for the lattice and boundary conditions considered.

As mentioned in Sec. II, the information laid down in the inverse matrix $\underline{A}^{-1}$ for the class of trapping problems considered here may also be useful in identifying new procedures for obtaining analytic results in dimensions $d=2,3$. We wish to illustrate how this might be done by designing a kind of decimation transformation for a certain two-dimensional problem. Qualitatively, in a decimation transformation, one proceeds by thinning out a number of degrees of freedom of the system while, at the same time, rescaling the effective interactions between the sites remaining on the lattice. For definiteness, let us focus on the 5×5 periodic lattice displayed in Fig. 1, for which the inverse matrix $\underline{A}^{-1}$ is given by Eq. (13). Suppose we replace the sites labeled 1 in Fig. 1 by traps and then construct new matrices $\underline{A}'$ and $(\underline{A}')^{-1}$ corresponding to the new lattice generated. The new inverse matrix for the problem is

$$(\underline{A}')^{-1}=\begin{bmatrix}1.6 & 0.8 & 2.4 & 1.2\\ 0.8 & 2.4 & 3.2 & 1.6\\ 1.2 & 1.6 & 4.8 & 2.4\\ 1.2 & 1.6 & 4.8 & 4.4\end{bmatrix}. \tag{28}$$

Estimates for the $\langle n\rangle_i$ can be obtained by summing across the rows. Whereas for the original matrix $\underline{A}^{-1}$,

$$\langle n\rangle_1=24\,,$$
$$\langle n\rangle_2=30\,,$$
$$\langle n\rangle_3=32\,,$$
$$\langle n\rangle_4=34\,,$$
$$\langle n\rangle_5=36\,,$$

the new $\langle n\rangle_i$ values are

$$\langle n\rangle_2'=6\,,$$
$$\langle n\rangle_3'=8\,,$$
$$\langle n\rangle_4'=10\,,$$
$$\langle n\rangle_5'=12\,.$$

A second stage in this procedure might involve the replacing of sites 2 and 3 by traps; the resulting inverse matrix $(\underline{A}'')^{-1}$ for the problem then becomes

$$(\underline{A}'')^{-1}=\begin{bmatrix}2 & 1\\ 2 & 3\end{bmatrix}, \tag{29}$$

where now,

$$\langle n\rangle_4''=3\,,$$
$$\langle n\rangle_5''=5\,.$$

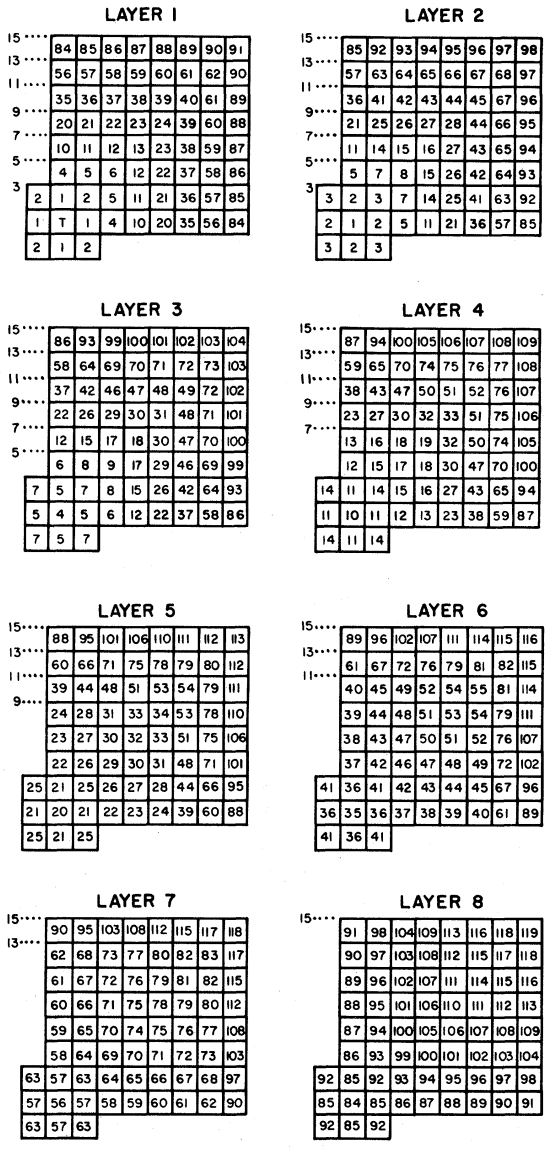

FIG. 4. Symmetry specification of sites for a $d=3$ odd lattice with a centrosymmetric trap.

TABLE II. 2D odd reflecting lattices with a single deep centrosymmetric trap. Footnotes indicate Monte Carlo results (Refs. 9–11).

	3×3	5×5	7×7	9×9	11×11	13×13	15×15	17×17	19×19	21×21
$\langle n \rangle$	3.5[a]	19.1[b]	50.7[c]	100.7[d]	170.4[e]	260.9[f]	373.3[g]	508.3[h]	666.6[i]	848.7
$\langle n \rangle_1$	3.0	15.0	35.0	63.0	99.0	143.0	195.0	255.0	323.0	398.9
$\langle n \rangle_2$	4.0	18.7	43.9	79.5	125.4	181.4	247.5	323.9	410.4	507.1
$\langle n \rangle_3$		18.7	48.1	88.9	141.3	205.3	280.8	368.0	466.8	577.2
$\langle n \rangle_4$		20.3	50.9	94.1	149.7	217.7	298.1	390.9	496.0	613.4
$\langle n \rangle_5$		21.3	54.2	101.3	162.1	236.7	324.9	426.7	542.0	670.9
$\langle n \rangle_6$			51.7	100.5	162.7	238.6	328.1	431.4	548.4	679.1
$\langle n \rangle_7$			53.3	102.6	166.1	243.6	335.2	440.8	560.6	694.3
$\langle n \rangle_8$			55.6	106.5	172.6	253.7	349.7	460.5	586.1	726.5
$\langle n \rangle_9$			56.6	109.7	179.0	264.3	365.5	482.4	614.9	763.1
$\langle n \rangle_{10}$				103.9	173.5	257.9	357.3	471.9	601.7	746.6
$\langle n \rangle_{11}$				105.4	175.2	260.3	360.8	476.6	607.8	754.4
$\langle n \rangle_{12}$				108.3	179.1	266.2	369.2	488.1	622.8	773.4
$\langle n \rangle_{13}$				110.9	183.4	273.0	379.3	502.3	641.8	797.7
$\langle n \rangle_{14}$				111.9	186.6	279.0	389.0	516.4	661.0	822.7
$\langle n \rangle_{15}$					176.8	268.2	375.5	498.9	638.6	794.6
$\langle n \rangle_{16}$					178.1	269.7	377.5	501.7	642.2	799.2
$\langle n \rangle_{17}$					181.3	273.6	382.8	508.8	651.6	811.2
$\langle n \rangle_{18}$					185.0	278.5	389.7	518.4	664.4	827.7
$\langle n \rangle_{19}$					187.7	283.0	396.6	528.4	678.2	845.7
$\langle n \rangle_{20}$					188.7	286.1	402.4	537.5	691.1	863.2
$\langle n \rangle_{21}$						271.5	385.6	516.5	664.4	829.5
$\langle n \rangle_{22}$						272.7	387.0	518.3	666.7	832.4
$\langle n \rangle_{23}$						276.1	390.8	523.2	673.1	840.5
$\langle n \rangle_{24}$						280.4	396.1	530.0	682.1	852.1
$\langle n \rangle_{25}$						284.4	401.5	537.5	692.2	865.3
$\langle n \rangle_{26}$						287.2	406.1	544.5	702.0	878.6
$\langle n \rangle_{27}$						288.2	409.2	550.0	710.6	890.8
$\langle n \rangle_{28}$							388.8	526.4	681.6	854.5
$\langle n \rangle_{29}$							390.1	527.8	683.2	856.5
$\langle n \rangle_{30}$							393.5	531.6	687.9	862.3
$\langle n \rangle_{31}$							398.2	537.0	694.6	870.8
$\langle n \rangle_{32}$							403.1	543.1	702.4	880.8
$\langle n \rangle_{33}$							407.4	548.9	710.3	891.2
$\langle n \rangle_{34}$							410.3	553.6	717.2	901.0
$\langle n \rangle_{35}$							411.3	556.7	722.7	909.3
$\langle n \rangle_{36}$								529.7	691.5	871.4
$\langle n \rangle_{37}$								530.9	692.8	873.0
$\langle n \rangle_{38}$								534.4	696.5	877.4
$\langle n \rangle_{39}$								539.3	702.1	884.0
$\langle n \rangle_{40}$								545.0	708.6	892.0
$\langle n \rangle_{41}$								550.4	715.3	900.5
$\langle n \rangle_{42}$								554.8	721.4	908.6
$\langle n \rangle_{43}$								557.7	726.1	915.5
$\langle n \rangle_{44}$								558.7	729.2	920.9
$\langle n \rangle_{45}$									694.7	881.2
$\langle n \rangle_{46}$									695.9	882.5
$\langle n \rangle_{47}$									699.4	886.2

The question now is whether this procedure of replacing neutral sites by traps can be given any systematic basis and whether one can recover $\langle n \rangle$ for the original 5×5 lattice using the (scaling) information implicit in the transformation and information derived from invariance relations proved for the de-

TABLE II. (*Continued.*)

$\langle n \rangle$	3×3 3.5[a]	5×5 19.1[b]	7×7 50.7[c]	9×9 100.7[d]	11×11 170.4[e]	13×13 260.9[f]	15×15 373.3[g]	17×17 508.3[h]	19×19 666.6[i]	21×21 848.7
$\langle n \rangle_{48}$									704.6	891.9
$\langle n \rangle_{49}$									710.7	898.8
$\langle n \rangle_{50}$									717.0	906.1
$\langle n \rangle_{51}$									722.8	913.2
$\langle n \rangle_{52}$									727.3	919.5
$\langle n \rangle_{53}$									730.2	924.3
$\langle n \rangle_{54}$									731.2	927.3
$\langle n \rangle_{55}$										884.4
$\langle n \rangle_{56}$										885.7
$\langle n \rangle_{57}$										889.1
$\langle n \rangle_{58}$										894.5
$\langle n \rangle_{59}$										901.0
$\langle n \rangle_{60}$										908.0
$\langle n \rangle_{61}$										914.8
$\langle n \rangle_{62}$										920.8
$\langle n \rangle_{63}$										925.4
$\langle n \rangle_{64}$										928.4
$\langle n \rangle_{65}$										929.4

[a]3.5. [b]19.1. [c]50.8. [d]100.7. [e]170.3. [f]260.9. [g]373.1. [h]507.8. [i]665.7.

cimated lattice.

A systematic procedure for constructing the inverse $(\underline{A}'')^{-1}$ starting from the original inverse matrix $\underline{A}^{-1}$ can, in fact, be identified:

(1) Average the information contained in the rows of the inverse matrix corresponding to the sites being replaced by traps.

(2) Subtract the resultant average from the remaining rows corresponding to sites not affected by the decimation to generate an inverse matrix of rank $n-\alpha$, where α corresponds to the number of lattice sites deleted and replaced at that stage of the transformation by traps.

Thus, in the example being considered, $(\underline{A}')^{-1}$ is generated from $\underline{A}^{-1}$ by averaging row 1 (with itself in this case) and subtracting the result, elementwise, from the other rows of the matrix $\underline{A}^{-1}$. Then, $(\underline{A}'')^{-1}$ may be generated from $(\underline{A}')^{-1}$ by averaging (elementwise) the rows of $(\underline{A}')^{-1}$ corresponding to sites 2 and 3 [viz., the first two rows of $(\underline{A}')^{-1}$] and subtracting the result (elementwise) from the remaining rows of $(\underline{A}')^{-1}$ to generate $(\underline{A}'')^{-1}$. This procedure, used to generate $(\underline{A}')^{-1}$ and $(\underline{A}'')^{-1}$, also gives directly the $\langle n \rangle_i'$ and the $\langle n \rangle_i''$ starting from the original $\langle n \rangle_i$. The formal set of equations describing the transformation are

$$\langle n \rangle_2' = \langle n \rangle_2 - \tfrac{1}{2}[\langle n \rangle_1 + \langle n \rangle_1] = \langle n \rangle_2 - \langle n \rangle_1 , \tag{30}$$

$$\langle n \rangle_3' = \langle n \rangle_3 - \langle n \rangle_1 , \tag{31}$$

$$\langle n \rangle_4' = \langle n \rangle_4 - \langle n \rangle_1 , \tag{32}$$

$$\langle n \rangle_5' = \langle n \rangle_5 - \langle n \rangle_1 , \tag{33}$$

and secondly,

$$\langle n \rangle_4'' = \langle n \rangle_4' - \tfrac{1}{2}[\langle n \rangle_2' + \langle n \rangle_3'] , \tag{34}$$

$$\langle n \rangle_5'' = \langle n \rangle_5' - \tfrac{1}{2}[\langle n \rangle_2' + \langle n \rangle_3'] . \tag{35}$$

This set of equations inter-relates variables which must satisfy, as well, the invariance relationships derived earlier. The first of these is the Montroll result: $\langle n \rangle_1 = N-1$. This result taken in conjunction with the self-consistency condition, Eq. (1), for periodic lattices (with $T=1$) provides the con-

TABLE III. 3D odd periodic-confining lattices with a single deep centrosymmetric trap.

	$3\times3\times3$	$5\times5\times5$	$7\times7\times7$	$9\times9\times9$	$11\times11\times11$	$13\times13\times13$	$15\times15\times15$
$\langle n \rangle$	30.5	157.3[a]	455.3	997.4	1856.1	3104.2	4814.7
$\langle n \rangle_1$	26.0	124.0	341.9	728.0	1330.0	2196.0	3374.0
$\langle n \rangle_2$	31.0	146.5	404.6	862.1	1575.6	2602.0	3998.2
$\langle n \rangle_3$	33.0	154.6	427.7	912.0	1667.4	2762.0	4232.4
$\langle n \rangle_4$		152.2	427.3	913.6	1671.6	2852.9	4245.2
$\langle n \rangle_5$		157.7	441.1	943.3	1726.4	2953.9	4385.2
$\langle n \rangle_6$		162.4	455.2	975.3	1786.6	2754.1	4541.9
$\langle n \rangle_7$		160.8	448.8	959.9	1757.2	2904.3	4464.6
$\langle n \rangle_8$		164.0	458.8	983.0	1801.0	2978.1	4579.4
$\langle n \rangle_9$		166.0	464.6	996.4	1826.8	3021.9	4647.8
$\langle n \rangle_{10}$			451.4	974.4	1788.4	2958.7	4550.5
$\langle n \rangle_{11}$			455.9	982.9	1803.9	2984.6	4590.7
$\langle n \rangle_{12}$			462.7	996.5	1829.4	3027.8	4658.0
$\langle n \rangle_{13}$			467.1	1007.8	1852.3	3067.8	4721.6
$\langle n \rangle_{14}$			459.2	989.1	1815.2	3003.6	4620.0
$\langle n \rangle_{15}$			464.7	1000.2	1836.2	3039.2	4675.8
$\langle n \rangle_{16}$			468.4	1010.0	1856.2	3074.4	4731.9
$\langle n \rangle_{17}$			468.5	1007.8	1850.5	3063.6	4714.3
$\langle n \rangle_{18}$			471.1	1015.0	1865.4	3090.0	4756.5
$\langle n \rangle_{19}$			473.1	1020.0	1875.6	3108.2	4785.9
$\langle n \rangle_{20}$				995.3	1837.0	3045.8	4689.3
$\langle n \rangle_{21}$				999.0	1842.8	3055.4	4704.2
$\langle n \rangle_{22}$				1006.6	1855.2	3075.8	4736.1
$\langle n \rangle_{23}$				1013.9	1868.3	3098.2	4771.8
$\langle n \rangle_{24}$				1018.1	1878.4	3117.3	4803.6
$\langle n \rangle_{25}$				1002.2	1847.8	3063.5	4716.7
$\langle n \rangle_{26}$				1008.9	1858.8	3081.6	4745.2
$\langle n \rangle_{27}$				1015.5	1870.7	3102.2	4777.9
$\langle n \rangle_{28}$				1019.3	1880.1	3120.0	4807.7
$\langle n \rangle_{29}$				1014.0	1867.2	3095.6	4767.0
$\langle n \rangle_{30}$				1019.1	1876.7	3112.1	4793.5
$\langle n \rangle_{31}$				1022.3	1884.5	3127.0	4818.5
$\langle n \rangle_{32}$				1023.0	1883.8	3124.4	4813.3
$\langle n \rangle_{33}$				1025.4	1889.8	3136.0	4832.8
$\langle n \rangle_{34}$				1027.4	1894.5	3144.7	4847.5
$\langle n \rangle_{35}$					1856.1	3088.4	4762.5
$\langle n \rangle_{36}$					1859.4	3093.0	4769.4
$\langle n \rangle_{37}$					1867.2	3104.3	4786.4
$\langle n \rangle_{38}$					1876.3	3118.0	4807.6
$\langle n \rangle_{39}$					1883.8	3130.8	4828.3
$\langle n \rangle_{40}$					1887.9	3140.3	4845.4
$\langle n \rangle_{41}$					1862.3	3097.2	4775.7
$\langle n \rangle_{42}$					1869.6	3107.7	4791.5
$\langle n \rangle_{43}$					1878.1	3120.6	4811.5
$\langle n \rangle_{44}$					1885.1	3132.7	4831.1
$\langle n \rangle_{45}$					1889.1	3141.8	4847.5
$\langle n \rangle_{46}$					1875.5	3116.3	4804.6
$\langle n \rangle_{47}$					1882.7	3127.3	4821.6
$\langle n \rangle_{48}$					1888.7	3137.8	4838.7

TABLE III. (*Continued.*)

$\langle n \rangle$	3×3×3 30.5	5×5×5 157.3[a]	7×7×7 455.3	9×9×9 997.4	11×11×11 1856.1	13×13×13 3104.2	15×15×15 4814.7
$\langle n \rangle_{49}$					1892.1	3145.8	4853.3
$\langle n \rangle_{50}$					1888.3	3136.1	4835.1
$\langle n \rangle_{51}$					1893.2	3144.6	4849.1
$\langle n \rangle_{52}$					1896.0	3151.3	4861.3
$\langle n \rangle_{53}$					1897.2	3151.5	4860.2
$\langle n \rangle_{54}$					1899.4	3156.9	4870.1
$\langle n \rangle_{55}$					1901.4	3161.3	4878.1
$\langle n \rangle_{56}$						3106.6	4802.0
$\langle n \rangle_{57}$						3109.6	4806.0
$\langle n \rangle_{58}$						3117.5	4816.4
$\langle n \rangle_{59}$						3127.7	4830.4
$\langle n \rangle_{60}$						3137.7	4844.8
$\langle n \rangle_{61}$						3145.3	4857.4
$\langle n \rangle_{62}$						3149.5	4866.6
$\langle n \rangle_{63}$						3112.5	4809.7
$\langle n \rangle_{64}$						3120.0	4819.7
$\langle n \rangle_{65}$						3129.7	4833.0
$\langle n \rangle_{66}$						3139.2	4846.9
$\langle n \rangle_{67}$						3146.6	4859.1
$\langle n \rangle_{68}$						3150.6	4867.9
$\langle n \rangle_{69}$						3126.5	4828.3
$\langle n \rangle_{70}$						3135.0	4840.2
$\langle n \rangle_{71}$						3143.5	4852.6
$\langle n \rangle_{72}$						3150.1	4863.7
$\langle n \rangle_{73}$						3153.7	4871.8
$\langle n \rangle_{74}$						3142.1	4850.1
$\langle n \rangle_{75}$						3149.2	4860.7
$\langle n \rangle_{76}$						3154.9	4870.2
$\langle n \rangle_{77}$						3158.0	4877.2
$\langle n \rangle_{78}$						3155.1	4869.4
$\langle n \rangle_{79}$						3159.8	4877.4
$\langle n \rangle_{80}$						3162.4	4883.3
$\langle n \rangle_{81}$						3163.8	4884.0
$\langle n \rangle_{82}$						3166.0	4889.0
$\langle n \rangle_{83}$						3168.0	4893.4
$\langle n \rangle_{84}$							4819.6
$\langle n \rangle_{85}$							4822.6
$\langle n \rangle_{86}$							4830.5
$\langle n \rangle_{87}$							4841.4
$\langle n \rangle_{88}$							4853.1
$\langle n \rangle_{89}$							4863.6
$\langle n \rangle_{90}$							4871.4
$\langle n \rangle_{91}$							4875.5
$\langle n \rangle_{92}$							4825.4
$\langle n \rangle_{93}$							4833.0
$\langle n \rangle_{94}$							4843.5
$\langle n \rangle_{95}$							4854.9
$\langle n \rangle_{96}$							4865.0
$\langle n \rangle_{97}$							4872.6
$\langle n \rangle_{98}$							4876.6
$\langle n \rangle_{99}$							4839.8

TABLE III. (*Continued.*)

	3×3×3	5×5×5	7×7×7	9×9×9	11×11×11	13×13×13	15×15×15
$\langle n \rangle$	30.5	157.3[a]	455.3	997.4	1856.1	3104.2	4814.7
$\langle n \rangle_{100}$							4849.4
$\langle n \rangle_{101}$							4859.7
$\langle n \rangle_{102}$							4869.0
$\langle n \rangle_{103}$							4876.0
$\langle n \rangle_{104}$							4879.7
$\langle n \rangle_{105}$							4857.6
$\langle n \rangle_{106}$							4866.6
$\langle n \rangle_{107}$							4874.8
$\langle n \rangle_{108}$							4881.0
$\langle n \rangle_{109}$							4884.3
$\langle n \rangle_{110}$							4874.2
$\langle n \rangle_{111}$							4881.2
$\langle n \rangle_{112}$							4886.5
$\langle n \rangle_{113}$							4889.4
$\langle n \rangle_{114}$							4887.2
$\langle n \rangle_{115}$							4891.7
$\langle n \rangle_{116}$							4894.2
$\langle n \rangle_{117}$							4895.7
$\langle n \rangle_{118}$							4897.9
$\langle n \rangle_{119}$							4899.9

[a]Monte Carlo result is 157.5. Montroll refined estimate is 157.3 [computed by M. D. Hatlee (private communication)].

straint:

$$\langle n \rangle_1 = N - 1 = 1 + \tfrac{1}{2}\langle n \rangle_2 + \tfrac{1}{4}\langle n \rangle_3 , \tag{36}$$

where $N = 25$ for the 5×5 lattice. For periodic lattices, we have proved that all corner (i) and next-to-the-corner ($i-1$) sites must satisfy the relation $\langle n \rangle_i - \langle n \rangle_{i-1} = 2$, which requires here that

$$\langle n \rangle_5 = \langle n \rangle_4 + 2 , \tag{37}$$

$$\langle n \rangle'_5 = \langle n \rangle'_4 + 2 , \tag{38}$$

$$\langle n \rangle''_5 = \langle n \rangle''_4 + 2 . \tag{39}$$

It can also be shown that

$$(\langle n \rangle_4 - \langle n \rangle_2) + 2 = \langle n \rangle_2 - \langle n \rangle_1 , \tag{40}$$

a relation which is satisfied for *any* group of five sites (three distinct) on an $n \times n$ lattice which bears the same spatial relation to each other as do sites 1, 2, and 4 in Fig. 1; Eqs. (37)–(39) represent special cases of this constraint. Equations (30)–(35), subject to the constraints (36)–(40), comprise a nearly complete system for calculating the $\langle n \rangle_i$ (from which one may calculate $\langle n \rangle$) for the 5×5 periodic lattice considered here. To complete the specification of the system one must be able to say something about the variables of the final decimated lattice, i.e., the one which results upon replacing sites 1,2,3 by traps. Here, however, the great advantage is that the analysis of and calculations on the simpler lattice are easier to carry out. For example, a self-consistency condition on possible *two-step* paths from site 5″ to site 4″ on this truncated lattice gives immediately the constraint

$$\langle n \rangle''_5 = \tfrac{3}{5}\langle n \rangle''_4 + \tfrac{16}{5} . \tag{41}$$

Or, going further, by counting the *total* number of ways one can pass from site 4 to the trap and considering all possible walk lengths, the following exact expression can be written down:

$$\langle n \rangle''_4 = \tfrac{1}{2}(1) + (\tfrac{1}{2})(\tfrac{1}{4})(2) + (\tfrac{1}{2})(\tfrac{1}{4}) \left[\sum_{n=3}^{\infty} (\tfrac{1}{2} + \tfrac{1}{4})^{n-2} n \right] . \tag{42}$$

Summing the series, one finds $\langle n \rangle''_4 = 3$, a result obtained earlier by direct calculation. By combining the information contained in the transformation equations (30)–(35), by utilizing general invariance

TABLE IV. 3D odd reflecting lattices with a single deep centrosymmetric trap.

	3×3×3	5×5×5	7×7×7	9×9×9	11×11×11	13×13×13	15×15×15
$\langle n \rangle$	8.8	78.9[a]	283.6	696.1	1386.9	2434.6	3906.3
$\langle n \rangle_1$	7.0	63.0	215.0	511.0	998.0	1727.0	2743.0
$\langle n \rangle_2$	9.0	74.4	254.2	604.9	1181.7	2046.1	3250.3
$\langle n \rangle_3$	10.0	78.6	268.5	639.8	1250.3	2165.6	3440.6
$\langle n \rangle_4$		74.4	267.2	640.3	1253.1	2171.5	3450.7
$\langle n \rangle_5$		78.6	276.0	661.0	1294.0	2242.8	3564.4
$\langle n \rangle_6$		80.8	284.4	682.9	1338.6	2321.7	3691.3
$\langle n \rangle_7$		80.8	280.9	672.6	1317.6	2283.1	3628.8
$\langle n \rangle_8$		82.2	286.8	688.3	1349.3	2340.6	3721.7
$\langle n \rangle_9$		83.2	290.3	697.3	1368.2	2374.6	3776.9
$\langle n \rangle_{10}$			278.3	680.7	1339.1	2324.9	3697.9
$\langle n \rangle_{11}$			282.3	686.8	1350.7	2345.2	3730.4
$\langle n \rangle_{12}$			287.5	696.4	1369.5	2378.7	3784.7
$\langle n \rangle_{13}$			289.7	703.7	1386.0	2409.5	3835.7
$\langle n \rangle_{14}$			285.1	691.2	1359.1	2360.0	3754.2
$\langle n \rangle_{15}$			289.2	699.1	1374.6	2387.7	3799.1
$\langle n \rangle_{16}$			290.9	705.4	1388.9	2414.6	3844.0
$\langle n \rangle_{17}$			291.9	704.4	1385.1	2406.6	3830.1
$\langle n \rangle_{18}$			293.1	709.0	1395.7	2426.7	3863.8
$\langle n \rangle_{19}$			294.1	712.3	1403.0	2440.5	3887.1
$\langle n \rangle_{20}$				690.7	1372.6	2391.2	3809.0
$\langle n \rangle_{21}$				694.2	1377.2	2398.8	3821.0
$\langle n \rangle_{22}$				700.8	1386.7	2414.8	3846.8
$\langle n \rangle_{23}$				706.3	1396.4	2432.0	3875.3
$\langle n \rangle_{24}$				708.4	1403.3	2446.2	3900.3
$\langle n \rangle_{25}$				697.1	1381.0	2405.1	3831.2
$\langle n \rangle_{26}$				702.8	1389.5	2419.4	3854.1
$\langle n \rangle_{27}$				707.7	1398.4	2435.1	3880.2
$\langle n \rangle_{28}$				709.6	1404.7	2448.4	3903.6
$\langle n \rangle_{29}$				707.0	1396.0	2430.2	3871.7
$\langle n \rangle_{30}$				710.7	1403.0	2442.9	3892.7
$\langle n \rangle_{31}$				712.2	1408.2	2453.9	3912.3
$\langle n \rangle_{32}$				713.6	1408.3	2452.4	3908.5
$\langle n \rangle_{33}$				714.7	1412.3	2460.9	3923.7
$\langle n \rangle_{34}$				715.7	1415.5	2467.4	3935.2
$\langle n \rangle_{35}$					1381.9	2421.3	3865.9
$\langle n \rangle_{36}$					1385.0	2425.2	3871.6
$\langle n \rangle_{37}$					1392.2	2434.4	3885.4
$\langle n \rangle_{38}$					1400.0	2445.5	3902.6
$\langle n \rangle_{39}$					1405.7	2455.3	3918.9
$\langle n \rangle_{40}$					1407.7	2461.9	3931.9
$\langle n \rangle_{41}$					1387.8	2428.6	3876.7
$\langle n \rangle_{42}$					1394.4	2437.2	3889.6
$\langle n \rangle_{43}$					1401.6	2447.6	3905.7
$\langle n \rangle_{44}$					1406.9	2456.9	3921.2
$\langle n \rangle_{45}$					1408.9	2463.2	3933.7
$\langle n \rangle_{46}$					1399.6	2444.3	3900.3
$\langle n \rangle_{47}$					1405.6	2453.1	3914.0
$\langle n \rangle_{48}$					1410.1	2461.1	3927.5

relations [exemplified here by the constraints (36)–(40)], and by deriving an exact result (42) for the eventual, simplified lattice (two distinct, neutral sites 4 and 5, with the rest traps), $\langle n \rangle$ for the original 5×5 periodic lattice can be recovered *exactly*. We now point out that if the *analytic* relationship

TABLE IV. (*Continued.*)

	3×3×3	5×5×5	7×7×7	9×9×9	11×11×11	13×13×13	15×15×15
$\langle n \rangle$	8.8	78.9[a]	283.6	696.1	1386.9	2434.6	3906.3
$\langle n \rangle_{49}$					1411.7	2466.6	3938.5
$\langle n \rangle_{50}$					1410.2	2460.1	3924.9
$\langle n \rangle_{51}$					1413.8	2466.6	3935.9
$\langle n \rangle_{52}$					1415.1	2471.2	3945.1
$\langle n \rangle_{53}$					1416.7	2471.9	3944.7
$\langle n \rangle_{54}$					1417.8	2475.5	3952.1
$\langle n \rangle_{55}$					1418.8	2478.7	3958.2
$\langle n \rangle_{56}$						2430.2	3894.2
$\langle n \rangle_{57}$						2433.2	3897.6
$\langle n \rangle_{58}$						2440.6	3906.6
$\langle n \rangle_{59}$						2449.9	3918.4
$\langle n \rangle_{60}$						2458.4	3930.3
$\langle n \rangle_{61}$						2464.2	3940.2
$\langle n \rangle_{62}$						2466.2	3946.6
$\langle n \rangle_{63}$						2435.9	3900.8
$\langle n \rangle_{64}$						2442.9	3909.3
$\langle n \rangle_{65}$						2451.7	3920.6
$\langle n \rangle_{66}$						2459.8	3932.1
$\langle n \rangle_{67}$						2465.4	3941.6
$\langle n \rangle_{68}$						2467.3	3947.8
$\langle n \rangle_{69}$						2448.9	3916.7
$\langle n \rangle_{70}$						2456.5	3926.7
$\langle n \rangle_{71}$						2463.6	3936.9
$\langle n \rangle_{72}$						2468.5	3945.6
$\langle n \rangle_{73}$						2470.3	3951.2
$\langle n \rangle_{74}$						2462.8	3935.0
$\langle n \rangle_{75}$						2468.6	3943.7
$\langle n \rangle_{76}$						2472.8	3951.1
$\langle n \rangle_{77}$						2474.2	3956.0
$\langle n \rangle_{78}$						2473.5	3950.9
$\langle n \rangle_{79}$						2476.9	3957.0
$\langle n \rangle_{80}$						2478.1	3961.2
$\langle n \rangle_{81}$						2479.8	3962.2
$\langle n \rangle_{82}$						2480.9	3965.7
$\langle n \rangle_{83}$						2481.9	3968.8
$\langle n \rangle_{84}$							3902.9
$\langle n \rangle_{85}$							3905.7
$\langle n \rangle_{86}$							3913.3
$\langle n \rangle_{87}$							3923.5
$\langle n \rangle_{88}$							3934.1
$\langle n \rangle_{89}$							3943.0
$\langle n \rangle_{90}$							3948.9
$\langle n \rangle_{91}$							3950.9
$\langle n \rangle_{92}$							3908.4
$\langle n \rangle_{93}$							3915.7
$\langle n \rangle_{94}$							3925.5
$\langle n \rangle_{95}$							3935.7
$\langle n \rangle_{96}$							3944.3
$\langle n \rangle_{97}$							3950.0
$\langle n \rangle_{98}$							3952.0
$\langle n \rangle_{99}$							3922.1

TABLE IV. (*Continued.*)

	3×3×3	5×5×5	7×7×7	9×9×9	11×11×11	13×13×13	15×15×15
$\langle n \rangle$	8.8	78.9[a]	283.6	696.1	1386.9	2434.6	3906.3
$\langle n \rangle_{100}$							3930.9
$\langle n \rangle_{101}$							3940.1
$\langle n \rangle_{102}$							3948.0
$\langle n \rangle_{103}$							3953.2
$\langle n \rangle_{104}$							3955.0
$\langle n \rangle_{105}$							3938.4
$\langle n \rangle_{106}$							3946.4
$\langle n \rangle_{107}$							3953.2
$\langle n \rangle_{108}$							3957.7
$\langle n \rangle_{109}$							3959.3
$\langle n \rangle_{110}$							3953.0
$\langle n \rangle_{111}$							3958.8
$\langle n \rangle_{112}$							3962.6
$\langle n \rangle_{113}$							3964.0
$\langle n \rangle_{114}$							3963.7
$\langle n \rangle_{115}$							3967.0
$\langle n \rangle_{116}$							3968.1
$\langle n \rangle_{117}$							3969.9
$\langle n \rangle_{118}$							3971.0
$\langle n \rangle_{119}$							3972.0

[a]Monte Carlo result is 78.8.

[Eqs. (39) and (42)] between sites 4 and 5 of the simplified lattice could be reconstructed in terms of the variables (N,d) of the problem, this could be used to derive an *analytic* expression for $\langle n \rangle$ for the original problem. It is in this sense that we believe that the procedure sketched out above may provide a new avenue for deriving analytic results for random walks on periodic (or finite) lattices with traps.

V. THE CASE OF COMPETING CHEMICAL REACTIONS

Consider a lattice in which there is a central deep trap ($T=1$) surrounded by $N-1$ sites at which there exists a finite probability ($0<s<1$) of the walker being trapped in its d-dimensional, random motion on the lattice. This lattice problem is of considerable chemical interest in that it allows one to treat reaction-diffusion problems in which the diffusing reactant molecule can undergo reaction at the $N-1$ auxiliary sites prior to reacting (irreversibly) at the centrosymmetric reaction center. The energy transfer process in photosystem I can be studied using this model, since energy may be lost (via such competing processes as fluorescence and internal conversion) during the migration of an excitation through a chlorophyll network before the excitation actually reaches the reaction center.

In Tables V and VI we present the (exact) results for the average walk length $\langle n \rangle$ for a diffusing species moving on a periodic lattice in dimensions $d=2,3$, when the probability s_i of background absorption is assumed to be the same for all sites of the lattice. Comparison of the results presented in Tables V and VI with the corresponding results of Tables I–IV (where all the s_i were set to zero) reveals that the effect of incorporating background absorption (i.e., including competing reaction centers) is quite dramatic. For example, in the case of a 15×15×15 periodic lattice, $\langle n \rangle$ drops from ~ 5000 when $s=0$ to ~ 20 when the trapping probability of the $N-1$ sites surrounding the trap is set at $s=0.05$. In fact, examination of the data on systems of different dimensionality, spatial extent and boundary conditions shows that the influence of these variables on the outcome of the calculations is of far less significance than the effect derived from switching on competing reaction centers. This may be seen in a more graphic way by displaying the results of representative calculations of $\langle n \rangle$ versus the parameter s (see Figs. 6 and 7). The structure of the curves laid down in these figures strongly suggests that $\langle n \rangle$ is asymptotically dependent on s (more precisely, $1/s$). That this is the case can be seen in a simple calculation. In our setup of the al-

TABLE V. 2D periodic-confining lattices with a centrosymmetric trap and background trapping ($s \neq 0$). Footnotes indicate Monte Carlo results.

s	3×3 $\langle n \rangle$	5×5 $\langle n \rangle$	7×7 $\langle n \rangle$	9×9 $\langle n \rangle$	11×11 $\langle n \rangle$	13×13 $\langle n \rangle$	15×15 $\langle n \rangle$	17×17 $\langle n \rangle$	19×19 $\langle n \rangle$	21×21 $\langle n \rangle$
0.0	9.00	31.67	71.61	130.60	209.93	310.63	433.54	579.42	748.87	942.43
0.05	6.40	12.39	15.64	17.27	18.16	18.68	19.01	19.23	19.38	19.49
0.10	4.97	7.71[a]	8.79	9.27	9.51	9.65	9.74	9.80	9.84	9.87
0.15	4.06	5.60	6.12	6.34	6.45	6.51	6.55	6.57	6.59	6.61
0.20	3.44	4.40	4.69	4.82	4.88	4.91	4.93	4.95	4.96	4.97
0.25	2.98	3.62	3.81	3.89	3.92	3.95	3.96	3.97	3.97	3.98
0.30	2.63	3.08[b]	3.21	3.26	3.28	3.30	3.31	3.31	3.32	3.32
0.35	2.35	2.68	2.77	2.80	2.82	2.83	2.84	2.84	2.85	2.85
0.40	2.13	2.37	2.44	2.46	2.47	2.48	2.49	2.49	2.49	2.49
0.45	1.94	2.13	2.17	2.19	2.20	2.21	2.21	2.21	2.22	2.22
0.50	1.79	1.93[c]	1.96	1.98	1.99	1.99	1.99	1.99	2.00	2.00
0.60	1.54	1.63	1.65	1.65	1.66	1.66	1.66	1.66	1.66	1.66
0.70	1.36	1.41	1.42	1.42	1.42	1.43	1.43	1.43	1.43	1.43
0.80	1.21	1.24	1.24	1.25	1.25	1.25	1.25	1.25	1.25	1.25
0.90	1.10	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11

[a] 7.71.
[b] 3.08.
[c] 1.93.

gorithm (Sec. II), we defined a walk in which the walker is trapped at the site of the walk's origin as having a length of one step. In this convention, the probability $p(n)$ that the walker is trapped on the nth site is given by

$$p(n)=(1-s)^{n-1}s \ ,$$

with

$$\langle n \rangle \equiv \sum_{n=1}^{\infty} np(n) \ .$$

We find:

$$\langle n \rangle = \sum_{n=1}^{\infty} ns(1-s)^{n-1}$$

$$= s \sum_{n=1}^{\infty} n(1-s)^{n-1} \ .$$

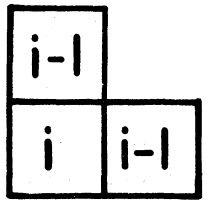

FIG. 5. Coding of corner and next-to-corner sites on an $n \times n$ square lattice.

Since $(1-s)<1$ for $s \neq 0$ (the series is obviously not convergent for $s=0$), then

$$\sum_{n=1}^{\infty} n(1-s)^{n-1} = \frac{1}{[1-(1-s)]^2} = \frac{1}{s^2}$$

or,

$$\langle n \rangle = \frac{1}{s} \ .$$

Thus, in a system in which the background sites have been switched on, the expected duration of the walk throughout the system is bounded by $1/s$. For

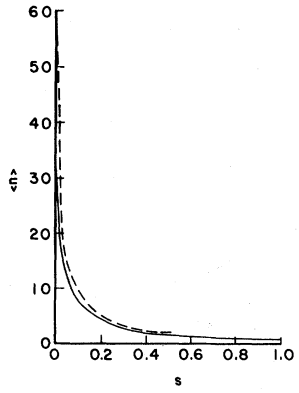

FIG. 6. Expected walk length $\langle n \rangle$ on a 5×5 square planar lattice vs the background absorption probability s for $T=1$ and s ranging from 0 to 1 (solid line) and for $T=0.5$ and s ranging from 0 to 0.5 (dotted line).

TABLE VI. 3D periodic-confining lattices with a centrosymmetric trap and background trapping ($s \neq 0$).

s	$3\times3\times3$ $\langle n \rangle$	$5\times5\times5$ $\langle n \rangle$	$7\times7\times7$ $\langle n \rangle$	$9\times9\times9$ $\langle n \rangle$	$11\times11\times11$ $\langle n \rangle$	$13\times13\times13$ $\langle n \rangle$	$15\times15\times15$ $\langle n \rangle$
0.0	30.46	157.32	455.27	997.37	1856.06	3104.24	4814.69
0.05	12.27	17.80	19.17	19.61	19.78	19.87	19.91
0.10	7.68	9.44[a]	9.79	9.90	9.95	9.97	9.98
0.15	5.59	6.42	6.58	6.62	6.64	6.65	6.66
0.20	4.40	4.87	4.95	4.98	4.99	4.99	5.00
0.25	3.63	3.92	3.97	3.99	3.99	4.00	4.00
0.30	3.08	3.28	3.31	3.32	3.33	3.33	3.33
0.35	2.68	2.82	2.84	2.85	2.85	2.86	2.86
0.40	2.37	2.47	2.49	2.50	2.50	2.50	2.50
0.45	2.13	2.20	2.22	2.22	2.22	2.22	2.22
0.50	1.93	1.99	1.99	2.00	2.00	2.00	2.00
0.60	1.63	1.66	1.66	1.67	1.67	1.67	1.67
0.70	1.41	1.42	1.43	1.43	1.43	1.43	1.43
0.80	1.24	1.25	1.25	1.25	1.25	1.25	1.25
0.90	1.11	1.11	1.11	1.11	1.11	1.11	1.11

[a]Monte Carlo result is 9.44.

large systems with $s=0$ (i.e., background sites neutral or passive), the data in Tables I–IV show that $\langle n \rangle$ tends rapidly to larger and larger values. However, introducing even a small absorption probability (reactivity) on the background of $N-1$ sites causes a precipitous change in the efficiency of reaction with respect to the centrosymmetric reactant (T). The presence of competing reaction centers effectively negates differences in the geometry of the cluster considered and causes an asymptotic enhancement in the destruction of the diffusing reactant.

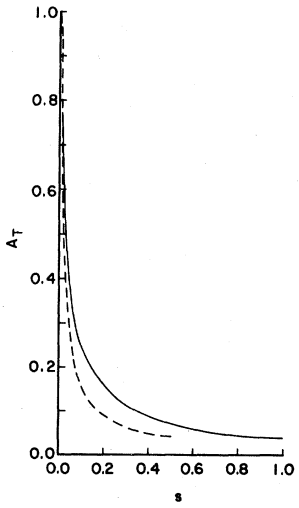

FIG. 7. Normalized absorption probability A_T (fraction of walks terminated at the trap on a 5×5 square planar lattice) vs the background absorption probability s for $T=1$ and s ranging from 0 to 1 (the solid line) and for $T=0.5$ and s ranging from 0 to 0.5 (the dotted line).

VI. DISCUSSION

In this paper we have elaborated a theory for calculating exactly certain characteristic numbers which calibrate the efficiency of reaction-diffusion processes in d-dimensional spaces of finite or of infinite extent. These numbers are as follows: $\langle n \rangle$, the overall expected walk length of the diffusing molecule to a specific reaction site, $\langle n \rangle_i$, the expected walk length of that molecule from a particular location in the system to the target molecule, and, finally, the matrix elements a_{ij} of the transformation matrix $\underline{A}$, and α_{ij}, the matrix elements of the inverse matrix $\underline{A}^{-1}$. The information contained in these numbers and their inter-relationship provide a means of assessing the role of spatial extent and of the dimensionality of the reaction space in influencing the outcome of diffusion-controlled chemical reactions. The reactions studied in this paper are of two types: strictly irreversible reactions or quasireversible reactions. In particular, supposing that A is the diffusing molecule and B is the target molecule, then the class of reactions studied in Sec. IV was of the type $A+B\rightarrow C$, where it was assumed that the $N-1$ background sites visited by the diffusing molecule were inert (or neutral or unreactive) *vis-à-vis* the molecule A. A broader class of reactions was considered in Sec. V where the background sites were assumed to have a certain probability, $0<s<1$, of reacting with the diffusing molecule. That is, one envisioned the $N-1$ sites surrounding the reaction center to be populated

with reactive species. For simplicity, suppose the $N-1$ reactive species are also B molecules, so that assigning a nonvanishing probability of reaction at these $N-1$ sites means that we are, in effect, considering the reaction

$$A+B\rightleftarrows(AB)^*\rightarrow C\ .$$

A remarkable feature found in this series of calculations was the astonishing change in the qualitative behavior of the system once one assumed that the activated complex could, even with probabilities $s<0.05$, lead to irreversible removal of the diffusing molecule from the reaction space of the system. The number $\langle n\rangle$, a measure of the efficiency of reaction, dropped precipitously once s was allowed to assume nonzero values [in fact, $\langle n\rangle\sim 1/s$ for sufficiently large lattices (or reaction volumes)]. Given the important role the idea of an activated complex plays in theories of chemical dynamics, it would be interesting to incorporate an Arrhenius-type temperature dependence into the parameters of the model and explore systematically the consequences of assuming the existence of a transition state in problems for which experimental data are available.

The results displayed in Tables I–VI have immediate relevance to two physical problems. As noted in the preceding section, the possibility of processes such as fluorescence or internal conversion at sites of the chlorophyll network other than at the target molecule may compromise seriously the efficiency of energy migration and trapping in this system. The data suggest that even trivial chemical modifications of the basic chlorophyll unit or antenna system may lead to a dramatic reduction in light-energy conversion; the extent to which a chemically modified unit (or a different model system) enhances the possibility of fluorescence or internal conversion at sites other than the target molecule is in direct relationship to the breakdown in efficiency of the process. The $\langle n\rangle=1/s$ functionality here is dramatic and decisive. There is, however, a case where the functionality is a saving grace. Consider the problem of catalytic conversion. Suppose one were to start with a catalyst support which is prepared initially so that all N sites of the support are catalytically active. The poisoning of the catalyst would then correspond to a systematic deterioration in the efficiency of reaction at the N sites of the support. What the calculations show is that the poisoning of the surface can proceed quite far before the catalytic activity of the surface becomes seriously impaired. Following the curves displayed in Figs. 6 and 7 from right to left allows a calibration of the efficiency of a catalyst support with respect to covering the surface sites with inert matter. It is quite likely that the calculations in Sec. V can be parametrized using experimental and/or quantum chemical data to provide a more detailed picture in particular systems of interest, and calculations along these lines are underway at the present time.

Given the flexibility of the approach described in Sec. II, a wide variety of other chemical dynamic models can be invented, with again the point to be emphasized that calculations of $\langle n\rangle$, $\langle n\rangle_i$, etc. can be carried through exactly and with a minimal expenditure of computer time. Among the problems currently under study are a lattice theory of bimolecular reactions,[14] one in which the full geometry of the reactant molecule is considered explicitly, the problem of electron transport in low-dimensional materials (e.g., linear chain conductors), and triplet energy migration and scission in polymers. These studies will be reported elsewhere. The theoretical points raised in Secs. III and IV are also of interest and worth exploring, particularly those which deal with the geometrical interpretation of the elements of the inverse transformation matrix and with the use of exact transformations and invariance relations to construct analytic expressions for the timing and efficiency of chemical reactions in systems of finite and infinite extent. Already, however, the approach presented in this paper has led to many new and exact results, ones that extend considerably (we believe) our understanding of the underlying reaction-diffusion processes. Hence, in conclusion, it may be worth offering some general remarks on why these lattice problems have yielded to exact solution here whereas they seem to be so much more intractable when approached using standard methods available in the literature. Generally speaking, theories were formulated previously and expressions for $\langle n\rangle$ were sought which incorporated almost from the very outset the functional dependence on the *global* geometrical parameters of the system (the connectivity, size, and dimensionality of the lattice). We suppress this desideratum in our initial formulation of the problem and seek instead a correct *local* description. We assume, in effect, that the systems being studied are strictly ergodic and then rely on (a weak form of) the implicit function theorem to recover numerical and analytic results. The exact correspondence found between our numerical results and those obtained in full scale Monte Carlo calculations argues strongly that the replacing of a strictly probabilistic mode of cal-

culation by a much simpler, deterministic one "works." The recovery of Montroll's exact analytic result in the one-dimensional problem shows that the explicit *global* dependence on the variables of the problem can be reconstructed from the *local* theory via standard methods of analysis. Indeed, it is the latter aspect of the problem which seems (to us) to be a most intriguing avenue to pursue, inasmuch as it opens up the possibility of obtaining analytic results on a variety of problems previously resistant to exact solution.

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APPENDIX

Listed below are the matrix elements α_{ij} of the inverse transformation matrix $\underline{A}^{-1}$ for the 5×5 periodic lattice with a centrosymmetric deep trap ($T=1$) and a uniform background absorption probability s [$q=(1-s)/4$]. For simplicity we do not include explicitly the common divisor of the 25 elements. This divisor is as follows:

$$\det\underline{A}=(1-2q)[(1-q)^2-3q^2(1-q) -2q^3-4q^2(1-q)^2+2q^4] -2q\{q(1-q)-q^3-4q^3(1-q)\} .$$

Then,

$$\alpha_{11}=(1-q)^2(1-2q)-2q^2(1-q) -2q^2(1-2q)-2q^2(1-q)(1-2q) ,$$

$$\alpha_{12}=2q(1-q)^2(1-2q)-4q^3(1-q) -2q^3(1-2q)=\alpha_{21} ,$$

$$\alpha_{13}=2q^3(1-2q)+q(1-q)(1-2q)-2q^3 =\alpha_{31} ,$$

$$\alpha_{14}=4q^2(1-q)(1-2q)+2q^2(1-2q) =2\alpha_{41} ,$$

$$\alpha_{15}=4q^3(1-q)+2q^3=\alpha_{51} ,$$

$$\alpha_{22}=(1-q)^2(1-2q)-2q^2(1-q) -2q^2(1-2q)-q^2(1-q)(1-2q)+2q^4 ,$$

$$\alpha_{23}=2q^2(1-2q)+2q^2(1-q)(1-2q)-4q^4 =\alpha_{32} ,$$

$$\alpha_{24}=2q(1-2q)(1-q)+2q^3(1-2q) =2\alpha_{42} ,$$

$$\alpha_{25}=2q^2(1-q)+2q^4=\alpha_{52} ,$$

$$\alpha_{33}=(1-q)(1-2q)-2q^2-2q^2(1-2q) -4q^2(1-q)(1-2q)+8q^4 ,$$

$$\alpha_{34}=2q(1-2q)-4q^3(1-2q)=2\alpha_{43} ,$$

$$\alpha_{35}=2q^2-4q^4=\alpha_{53} ,$$

$$\alpha_{44}=(1-q)(1-2q)-q^2(1-2q) -4q^2(1-q)(1-2q) ,$$

$$\alpha_{54}=2q(1-q)-2q^3-8q^3(1-q)=2\alpha_{45} ,$$

$$\alpha_{55}=(1-q)^2-3q^2(1-q)-2q^2 -4q^2(1-q)^2+2q^4 .$$

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