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Density of states and random walks in tetrahedrally bonded solids

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Abstract. The hamiltonian of Thorpe and Weaire is used to obtain a general expression for the density of states in a tetrahedrally bonded solid in terms of the number of returns to the origin. This expression is therefore valid for topological disorder and enables the density of states to be calculated if the number of returns to the origin is known. Application to a periodic solid and use of results on the number of returns to the origin in this case checks with the known expression for the density of states.

1. Introduction

The relationship between the density of states in a tight-binding model and the number of returns to the origin in a random walk on a lattice has been investigated by a number of authors (eg Cyrot-Lackmann 1968, Thorpe 1972). If the hamiltonian is given by

$$\boldsymbol{H} = V \sum_{(i,j)} |\phi_i\rangle\langle\phi_j|, \tag{1.1}$$

where V is the overlap integral between states on adjacent lattice sites, it is possible to prove the following relation: if $n(E)$ denotes the density of states at energy E

$$\int_{-\infty}^{+\infty} E^l n(E)\,\mathrm{d}E = V^l r_l \tag{1.2}$$

where r_l is the number of returns to the starting point in a walk of l steps, an average being taken over all starting points in the structure. This relation proved useful, for example, in investigating the relationship between the values of r_l on different types of lattices (Thorpe 1972).

In this paper we consider the more general two-band hamiltonian considered by Weaire and Thorpe (1971):

$$\boldsymbol{H} = V_1 \sum_{\substack{i \\ j \neq j'}} |ij\rangle\langle ij'| + V_2 \sum_{\substack{i \neq i' \\ j}} |ij\rangle\langle i'j|\,\delta_{i,s_{i'},j} = \boldsymbol{H}_1 + \boldsymbol{H}_2 \tag{1.3}$$

where $|ij\rangle$ refers to the valence orbital associated with site i whose bond index is j, and limit ourselves to structures with fourfold coordination. Here the symbol $\delta_{i,s_{i'},j}$ is defined as follows:

$$\delta_{i,s_{i'},j} \begin{cases} = 1 \text{ if } i' \text{ is the nearest neighbour of atom } i \text{ associated with bond } j \\ = 0 \text{ otherwise} \end{cases}$$

and has been introduced to make explicit the restriction on the summation over i' implicit in the Weaire–Thorpe model.

We show that a number of interesting relations exist between terms which occur in the expansion of the Green function and r_l, and finally that the density of states can be written in terms of the number of returns to the origin. By explicitly evaluating this expression for a periodic lattice we obtain a density of states which is found to be identical with that of Thorpe and Weaire for this model. A number of other mathematical properties of the model are obtained. An important feature of our expression for the density of states is that for the case of topological disorder it also applies to disordered lattices. The existence of disorder manifests itself only through the expression for the number of returns to the origin, and by evaluating this function for a topologically disordered lattice another method of calculating the density of states for such systems is obtained.

In § 2, we derive an expression for the matrix elements of each term in the Dyson expansion of the total Green function. In § 3, we relate such terms to the number of returns to the origin. By rearranging the terms of the series we obtain a compact expression for the density of states as a sum of contributions over all values of t of the number of returns to the origin after t steps. Using the explicit expression for the number of returns to the origin given by Thorpe this is then evaluated to give the density of states for a periodic lattice.

2. Calculation of the full Green function

The matrix

$$\langle i,j|E\boldsymbol{I}-\boldsymbol{H}^{(1)}|k,l\rangle = \delta_{ik}\{(E+V_1)\,\delta_{jl}-V_1\} \tag{2.1}$$

is a block matrix which is easily inverted to give

$$\langle i,j|\boldsymbol{G}_0|k,l\rangle = \delta_{ik}(A+B\,\delta_{jl}) \tag{2.2}$$

where

$$A = \frac{V_1}{(E-3V_1)(E+V_1)}, \qquad B = \frac{1}{E+V_1}. \tag{2.3}$$

This result is easily checked by direct substitution. The density of states per particle is given in the usual way in terms of $\boldsymbol{G}^+ = (E-\boldsymbol{H}+\mathrm{i}\epsilon)^{-1}$ as

$$n(E) = -\pi^{-1}N^{-1}\,\mathrm{Im}\mathrm{Tr}\,(\boldsymbol{G}^+) = -\pi^{-1}N^{-1}\,\mathrm{Im}\sum_{i,j}\langle ij|\boldsymbol{G}^+|ij\rangle \tag{2.4}$$

so that we now turn to the calculation of the diagonal matrix elements of the full Green function. This can be expanded by Dyson's equation:

$$\boldsymbol{G} = \boldsymbol{G}_0+\boldsymbol{G}_0\boldsymbol{H}_2\boldsymbol{G}_0+\cdots. \tag{2.5}$$

Using the notation $N(t, i, k)$ to denote the number of walks of length t starting on atom i and ending on atom k we have in the notation of equation (1.3)

$$\sum_{\substack{\alpha_1\ldots\alpha_{t+1}\\ \beta_1\ldots\beta_t}} \delta_{i,S_{\beta_1}}\alpha_1\,\delta_{\beta_1,S_{\beta_2}}\alpha_2\ldots\delta_{\beta_t,S_k}\,\alpha_{t+1} = N(t,i,k). \tag{2.6}$$

We also note

$$\sum_{\beta_1}\delta_{i,S_{\beta_1}}\alpha_1\,\delta_{\beta_1,S_{\beta_2}}\alpha_1 = \delta_{i,\beta_2}. \tag{2.7}$$

We refer to the term with n factors $\boldsymbol{H}_2$ in equation (2.5) as the nth order term $\boldsymbol{T}_n$. In appendix 1 we prove its matrix elements to have the following form:

$$\begin{aligned}\langle ij|\boldsymbol{T}_n|kl\rangle &= \langle ij|\boldsymbol{G}_0\boldsymbol{H}_2\boldsymbol{G}_0\ldots\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle\\ &= V_2^n \sum_{\substack{\alpha_1\ldots\alpha_{n+1}\\ \beta_1\ldots\beta_n}} (A+B\,\delta_{j,\alpha_1})\ldots(A+B\,\delta_{\alpha_{n+1},l})\,\delta_{i,s_{\beta_1}}\alpha_1\ldots\delta_{\beta_n,s_k}\alpha_{n+1}.\end{aligned} \tag{2.8}$$

The last factor suggests by comparison with (2.6) that the matrix elements of the nth order term may be related to the number of random walks starting and ending at the origin. This is not possible in the expression as it stands owing to the fact that the summations in the factors are not independent.

3. Relation of the matrix elements to the number of walks

To enable the summations to be separated it is necessary first to prove a relation between the matrix elements $\langle ij|\boldsymbol{T}_n|ij\rangle$ and $\langle ij|\boldsymbol{T}_n|il\rangle$. This is done in appendix 2 and we find that

$$\sum_{i,j}\langle ij|\boldsymbol{T}_n|ij\rangle = \frac{2A(2A+B)}{(4A+B)^2}\sum_i\sum_{j,l}\langle ij|\boldsymbol{T}_n|il\rangle + V_2^2B^2\sum_{i,j}\langle ij|\boldsymbol{T}_{n-2}|ij\rangle. \tag{3.1}$$

It is then possible to express the matrix element $\langle ij|\boldsymbol{T}_n|il\rangle$ in terms of the total number of walks. This is done in appendix 3 and we find

$$\begin{aligned}\sum_{i,j,l}\langle ij|\boldsymbol{T}_n|il\rangle = V_2^n(4A+B)^2\Bigg(&\frac{A}{V_2^{n-1}(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_{n-1}(N(t+1,i,i)|il\rangle\\ &+\frac{B(4A+B)}{V_2^{n-2}(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_{n-2}(N(t,i,i)|il\rangle\Bigg).\end{aligned} \tag{3.2}$$

The matrix element $\Sigma_{i,j,l}\langle ij|\boldsymbol{G}|il\rangle$ may then be expressed as a series as follows:

$$\begin{aligned}\sum_{i,j,l}\langle ij|\boldsymbol{G}|il\rangle = \sum_i [\![&4(4A+B)N(0,i,i)+\{V_2(4A+B)^2N(1,i,i)\}+\{V_2^24B(4A+B)^2N(0,i,i)\\ &+V_2^2A(4A+B)^2N(2,i,i)\}+[V_2^3(4A+B)^2B\{4A+(4A+B)\}N(1,i,i)\\ &+V_2^3A^2(4A+B)^2N(3,i,i)]+\ldots]\!].\end{aligned} \tag{3.3}$$

By collecting the coefficients of $N(t,i,i)$ we obtain the following expression proved in appendix 4:

$$\sum_{i,j,l}\langle ij|\boldsymbol{G}|il\rangle = \sum_i\left\{\frac{(4A+B)^2}{A}\frac{(1-V_2^2B^2)}{1-z}\sum_{t=0}^{\infty}\left(\frac{V_2A}{1-z}\right)^tN(t,i,i)+\left(4(4A+B)-\frac{(4A+B)^2}{A}\right)\right\} \tag{3.4}$$

where $z = V_2^2B(4A+B)$. This may now be substituted into equation (3.1) to obtain

$$\sum_{i,j}\langle ij|\boldsymbol{G}|ij\rangle = \sum_i\left(\frac{2BN(0,i,i)}{1-V_2^2B^2}+\frac{V_2B^2N(1,i,i)}{1-V_2^2B^2}\right)+\sum_i\frac{2(2A+B)}{1-z}\sum_{t=0}^{\infty}\left(\frac{V_2A}{1-z}\right)^tN(t,i,i). \tag{3.5}$$

Finally we can write down the density of states from (2.4):

$$n(E) = -\pi^{-1}N^{-1}\,\mathrm{Im}\sum_i\left\{\frac{2BN(0,i,i)}{1-V_2^2B^2}+\frac{V_2B^2N(1,i,i)}{1-V_2^2B^2}+\frac{2(2A+B)}{1-z}\sum_{t=0}^{\infty}\left(\frac{V_2A}{1-z}\right)^t N(t,i,i)\right\}. \tag{3.6}$$

This expression is valid both for a periodic lattice and also in the presence of topological disorder provided that the matrix elements are taken to be unchanged and that the fourfold coordination is maintained.

4. Application to the periodic lattice

Thorpe (1972) has given an explicit expression for the number of walks $N(t, i, i)$ on a (periodic) diamond lattice and Weaire and Thorpe (1971) have given an expression for the density of states. By substituting for $N(t, i, i)$ in (3.6) it is therefore possible to check the correctness of this expression for the density of states. This we now proceed to do.

The expression given by Thorpe (1972) is

$$N(2t,i,i) = \frac{4^t}{(2\pi)^3}\iiint_{-\pi}^{\pi}(1+\cos x\cos y+\cos y\cos z+\cos z\cos x)^t\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

$$N(t,i,i) = 0 \qquad \text{for } t \text{ odd.}$$

Let us write

$$N(2t,i,i) = \frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\{4(1+\alpha_{xyz})\}^t\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z. \tag{4.1}$$

Substituting this into (3.6)

$$n(E) = -\frac{1}{\pi}\mathrm{Im}\left\{\frac{2B}{1-V_2^2B^2}+\frac{2(2A+B)}{(2\pi)^3(1-z)}\iiint_{-\pi}^{\pi}\sum_{t=0}^{\infty}\left(\frac{V_2A}{1-z}\right)^{2t}\{4(1+\alpha_{xyz})\}^t\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\right\}$$

$$= -\frac{1}{\pi}\mathrm{Im}\left\{\frac{2B}{1-V_2^2B^2}+\frac{2(2A+B)(1-z)}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}{(1-z)^2-4V_2^2A^2(1+\alpha_{xyz})}\right\}. \tag{4.2}$$

Using the result that

$$(1-z)^2-4V_2^2A^2(1+\alpha_{xyz})$$
$$= \left(1-\frac{V_2^2}{(E-3V_1)(E+V_1)}\right)^2-\frac{4V_2^2V_1^2(1+\alpha_{xyz})}{(E-3V_1)^2(E+V_1)^2}$$
$$= \frac{1}{(E-3V_1)^2(E+V_1)^2}[\{(E-3V_1)(E+V_1)-V_2^2\}^2-4V_2^2V_1^2(1+\alpha_{xyz})]$$

we finally obtain

$$n(E) = -\frac{1}{\pi}\operatorname{Im}\left\{\frac{2(E+V_1)}{(E+V_1)^2-V_2^2}+\frac{2(E-V_1)\{(E-3V_1)(E+V_1)-V_2^2\}}{(E-3V_1)^2(E+V_1)^2(2\pi)^3}\right.$$
$$\left.\times\iiint\frac{(E-3V_1)^2(E+V_1)^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}{\{(E-V_1)^2-4V_1^2-V_2^2\}^2-4V_2^2V_1^2(1+\alpha_{xyz})}\right\}$$
$$= -\frac{1}{\pi}\operatorname{Im}\left\{\frac{2(E+V_1)}{(E+V_1)^2-V_2^2}+\frac{2(E-V_1)\{(E-V_1)^2-4V_1^2-V_2^2\}}{(2\pi)^3}\right.$$
$$\left.\times\iiint_{-\pi}^{\pi}\frac{\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}{\{(E-V_1)^2-4V_1^2-V_2^2\}^2-4V_2^2V_1^2(1+\alpha_{xyz})}\right\}. \tag{4.3}$$

This expression agrees exactly with that obtained by Weaire and Thorpe (1971).

5. Conclusion

An expression has been obtained for the density of states of a system described by the hamiltonian (1.3) in terms of the number of returns to the origin, provided the matrix elements remain constant. This is also valid for a topologically disordered lattice if the fourfold coordination is maintained. The expression has been checked by evaluating it for the diamond lattice and gives the known density of states for this case.

Appendix 1. Proof of equation (2.8)

The proof follows by induction. By inserting complete sets of states we have

$$\langle ij|\boldsymbol{T}_{n+1}|kl\rangle = \sum_{\theta,T}\langle ij|\boldsymbol{T}_n|\theta T\rangle\langle\theta T|\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle.$$

Now

$$\langle\theta T|\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle = \sum_{\alpha_1\beta_1}\langle\theta T|\boldsymbol{H}_2|\alpha_1\beta_1\rangle\langle\alpha_1\beta_1|\boldsymbol{G}_0|kl\rangle$$
$$= \sum_{\alpha_1\beta_1}V_2\delta_{T,\beta_1}\delta_{\theta,S^T_{\alpha_1}}\delta_{\alpha_1,k}(A+B\delta_{\beta_1,l})$$
$$= V_2(A+B\delta_{T,l})\delta_{\theta,S^T_k} \tag{A1.1}$$

and by assumption

$$\langle ij|\boldsymbol{T}_n|\theta T\rangle = \sum_{\substack{\alpha_1\ldots\alpha_{n+1}\\ \beta_1\ldots\beta_n}}V_2^n(A+B\delta_{j,\alpha_1})\ldots(A+B\delta_{\alpha_{n+1},T})\delta_{i,S^{\alpha_1}_{\beta_1}}\ldots\delta_{\beta_n,S^{\alpha_{n+1}}_\theta}.$$

Thus

$$\langle ij|\boldsymbol{T}_{n+1}|kl\rangle = \sum_{\substack{\alpha_1\ldots\alpha_{n+1}\\ \beta_1\ldots\beta_n}}\sum_{\substack{\theta\\ T}}V_2^{n+1}(A+B\delta_{j,\alpha_1})\ldots(A+B\delta_{\alpha_{n+1},T})(A+B\delta_{T,l})$$
$$\times\delta_{i,S^{\alpha_1}_{\beta_1}}\ldots\delta_{\beta_n,S^{\alpha_{n+1}}_\theta}\delta_{\theta,S^T_k}.$$

Letting $\theta = \beta_{n+1}$, $T = \alpha_{n+2}$ the right-hand side becomes

$$V_2^{n+1} \sum_{\substack{\alpha_1 \ldots \alpha_{n+2} \\ \beta_1 \ldots \beta_{n+1}}} (A+B\delta_{j,\alpha_1}) \ldots (A+B\delta_{\alpha_{n+2},l})\delta_{i,S_{\beta_1}^{\alpha_1}} \ldots \delta_{\beta_{n+1},S_k^{\alpha_{n+2}}}$$

which is the same expression as that assumed except that n is replaced by $n+1$. To complete the proof we show it is true for $n = 1$. Now

$$\langle ij|\boldsymbol{G}_0\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle = \sum_{\alpha_1\beta_1} \langle ij|\boldsymbol{G}_0|\alpha_1\beta_1\rangle\langle\alpha_1\beta_1|\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle.$$

Using equation (A1.1)

$$\langle\alpha_1\beta_1|\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle = V_2(A+B\delta_{\beta_1,l})\delta_{\alpha_1,S_k^{\beta_1}}.$$

Therefore

$$\langle ij|\boldsymbol{G}_0\boldsymbol{H}_2\boldsymbol{G}_0|kl\rangle = \sum_{\alpha_1\beta_1} \delta_{i,\alpha_1}(A+B\delta_{j,\beta_1})V_2(A+B\delta_{\beta_1,l})\delta_{\alpha_1,S_k^{\beta_1}}$$
$$= V_2 \sum_{\beta_1} (A+B\delta_{j,\beta_1})(A+B\delta_{\beta_1,l})\delta_{i,S_k^{\beta_1}}$$

on letting $\beta_1 \mapsto \alpha_1$ we have the required expression and by the inductive hypothesis it is true for all n.

Appendix 2. Proof of equation (3.1)

We have from equation (2.8) that

$$\langle ij|\boldsymbol{T}_n|il\rangle = V_2^n \sum_{\substack{\alpha_1 \ldots \alpha_{n+1} \\ \beta_1 \ldots \beta_n}} (A+B\delta_{j,\alpha_1}) \ldots (A+B\delta_{\alpha_{n+1},l})\delta_{i,S_{\beta_1}^{\alpha_1}} \ldots \delta_{\beta_n,S_i^{\alpha_{n+1}}}$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle = V_2^n \sum_i \sum_{\substack{\alpha_1 \ldots \alpha_{n+1} \\ \beta_1 \ldots \beta_n}} \left(\sum_{j,l} (A+B\delta_{j,\alpha_1})(A+B\delta_{\alpha_{n+1},l})\right)(A+B\delta_{\alpha_1,\alpha_2})$$
$$\ldots (A+B\delta_{\alpha_n,\alpha_{n+1}})\delta_{l,S_{\beta_1}^{\alpha_1}} \ldots \delta_{\beta_n,S_i^{\alpha_{n+1}}}$$
$$= V_2^n(4A+B)^2 \sum_{\substack{\alpha_1 \ldots \alpha_{n+1} \\ \beta_1 \ldots \beta_n \\ i}} (A+B\delta_{\alpha_1,\alpha_2}) \ldots (A+B\delta_{\alpha_n,\alpha_{n+1}})\delta_{i,S_{\beta_1}^{\alpha_1}} \ldots \delta_{\beta_n,S_i^{\alpha_{n+1}}}. \quad \text{(A2.1)}$$

Now

$$\sum_{ij} \langle ij|\boldsymbol{T}_n|ij\rangle = V_2^n \sum_i \sum_{\substack{\alpha_1 \ldots \alpha_{n+1} \\ \beta_1 \ldots \beta_n}} \left(\sum_j (A+B\delta_{j,\alpha_1})(A+B\delta_{\alpha_{n+1},j})\right)(A+B\delta_{\alpha_1,\alpha_2})$$
$$\ldots (A+B\delta_{\alpha_n,\alpha_{n+1}})\delta_{i,S_{\beta_1}^{\alpha_1}} \ldots \delta_{\beta_n,S_i^{\alpha_{n+1}}}$$

but

$$\sum_j (A+B\delta_{j,\alpha_1})(A+B\delta_{j,\alpha_{n+1}}) = 2A(2A+B)+B^2\delta_{\alpha_1,\alpha_{n+1}}.$$

Hence

$$\sum_{ij}\langle ij|\boldsymbol{T}_n|ij\rangle = V_2^n 2A(2A+B)\sum_{\substack{\alpha_1\ldots\alpha_{n+1}\\ \beta_1\ldots\beta_n\\ i}}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_{n+1}})\delta_{i,S^{\alpha_1}_{\beta_1}}\ldots\delta_{\beta_n,S^{\alpha_{n+1}}_{i}}$$

$$+B^2V_2^n\sum_{\substack{\alpha_1\ldots\alpha_{n+1}\\ \beta_1\ldots\beta_n\\ i}}\delta_{\alpha_1,\alpha_n}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_{n+1}})\delta_{i,S^{\alpha_1}_{\beta_1}}\ldots\delta_{\beta_n,S^{\alpha_{n+1}}_{i}}$$

$$= C+D.$$

The first term in the above can be written using (A2.1) as

$$C = \frac{2A(2A+B)}{(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_n|il\rangle.$$

The second term, however, is more difficult to interpret and we proceed as follows. Summing over α_{n+1} we obtain

$$D = V_2^nB^2\sum_{\substack{\alpha_1\ldots\alpha_n\\ \beta_1\ldots\beta_n\\ i}}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_1})\delta_{i,S^{\alpha_1}_{\beta_1}}\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\ldots\delta_{\beta_{n-1},S^{\alpha_n}_{\beta_n}}\delta_{\beta_n,S^{\alpha_1}_{i}}$$

but

$$\delta_{i,S^{\alpha_1}_{\beta_1}}\delta_{\beta_n,S^{\alpha_1}_{i}} = \delta_{\beta_1,\beta_n}\delta_{\beta_1,S^{\alpha_1}_{i}}.$$

Hence

$$D = V_2^nB^2\sum_{\substack{\alpha_1\ldots\alpha_n\\ \beta_1\ldots\beta_{n-1}\\ i}}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_1})\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\ldots\delta_{\beta_{n-1},S^{\alpha_n}_{\beta_1}}\delta_{\beta_1,S^{\alpha_1}_{i}}.$$

Taking the sum over i through we have

$$\sum_i\delta_{\beta_1,S^{\alpha_1}_{i}} = 1$$

so

$$D = V_2^nB^2\sum_{\substack{\alpha_1\ldots\alpha_n\\ \beta_1\ldots\beta_{n-1}}}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_1})\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\ldots\delta_{\beta_{n-1},S^{\alpha_n}_{\beta_1}}$$

$$= V_2^2B^2\sum_{\alpha_1\beta_1}\left(V_2^{n-2}\sum_{\substack{\alpha_2\ldots\alpha_n\\ \beta_2\ldots\beta_{n-1}}}(A+B\delta_{\alpha_1,\alpha_2})\ldots(A+B\delta_{\alpha_n,\alpha_1})\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\ldots\delta_{\beta_{n-1},S^{\alpha_n}_{\beta_1}}\right).$$

Making the following substitution

$$\alpha_1\mapsto j \qquad \alpha_2\mapsto\alpha_1 \qquad \alpha_3\mapsto\alpha_2 \quad\ldots\quad \alpha_n\mapsto\alpha_{n-1}$$

$$\beta_1\mapsto i \qquad \beta_2\mapsto\beta_1 \qquad \beta_3\mapsto\beta_2 \quad\ldots\quad \beta_{n-1}\mapsto\beta_{n-2}$$

we have

$$D = V_2^2B^2\sum_{i,j}\left(\sum_{\substack{\alpha_1\ldots\alpha_{n-1}\\ \beta_1\ldots\beta_{n-2}}}V_2^{n-2}(A+B\delta_{j,\alpha_1})\ldots(A+B\delta_{\alpha_{n-1},j})\delta_{i,S^{\alpha_1}_{\beta_1}}\ldots\delta_{\beta_{n-2},S^{\alpha_{n-1}}_{i}}\right)$$

$$= V_2^2B^2\sum_{i,j}\langle ij|\boldsymbol{T}_{n-2}|ij\rangle.$$

Thus collecting the various terms together gives

$$\sum_{i,j}\langle ij|\boldsymbol{T}_n|ij\rangle = \frac{2A(2A+B)}{(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_n|il\rangle + V_2^2B^2\sum_{i,j}\langle ij|\boldsymbol{T}_{n-2}|ij\rangle$$

which is equation (3.1).

Appendix 3. Proof of equation (3.2)

This equation follows by simply writing down the expressions for the first few terms. Thus

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_0|il\rangle = \sum_i 4(4A+B)N(0,i,i)$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_1|il\rangle = \sum_i V_2(4A+B)^2 N(1,i,i)$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_2|il\rangle = \sum_i V_2^2(4A+B)^2\left\{A\sum_{\substack{\alpha_1\\ \beta_1}} \delta_{i,S^{\alpha_1}_{\beta_1}}\left(\sum_{\alpha_2}\delta_{\beta_1,S^{\alpha_2}_i}\right)+4B\right\}$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_3|il\rangle = \sum_i V_2^3(4A+B)^2\left\{A\sum_{\substack{\alpha_1\\ \beta_1}} \delta_{i,S^{\alpha_1}_{\beta_1}}\left(\sum_{\substack{\alpha_2\alpha_3\\ \beta_2}}(A+B\delta_{\alpha_2,\alpha_3})\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\delta_{\beta_2,S^{\alpha_3}_i}\right)\right.$$
$$\left.+B(4A+B)\sum_{\alpha_3}\delta_{i,S^{\alpha_3}_i}\right\}$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_4|il\rangle = \sum_i V_2^4(4A+B)^2\left\{A\sum_{\substack{\alpha_1\\ \beta_1}} \delta_{i,S^{\alpha_1}_{\beta_1}}\left(\sum_{\substack{\alpha_2\alpha_3\alpha_4\\ \beta_2\beta_3}}(A+B\delta_{\alpha_2,\alpha_3})(A+B\delta_{\alpha_3,\alpha_4})\delta_{\beta_1,S^{\alpha_2}_{\beta_2}}\cdots\delta_{\beta_3,S^{\alpha_4}_i}\right)\right.$$
$$\left.+B(4A+B)\sum_{\substack{\alpha_1\alpha_2\\ \beta_1}}(A+B\delta_{\alpha_1,\alpha_2})\delta_{i,S^{\alpha_1}_{\beta_1}}\delta_{\beta_1,S^{\alpha_2}_i}\right\}.$$

It follows that if the functional dependence of $\boldsymbol{T}_n$ on the number of walks is explicitly denoted by $\boldsymbol{T}_n[N(n,i,i)]$ we have

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle = V_2^n(4A+B)^2\left(\frac{A}{V_2^{n-1}(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_{n-1}[N(t+1,i,i)]|il\rangle\right.$$
$$\left.+\frac{B(4A+B)}{V_2^{n-2}(4A+B)^2}\sum_{i,j,l}\langle ij|\boldsymbol{T}_{n-2}|il\rangle\right)$$

which is equation (3.2).

Appendix 4. Evaluation of equation (3.4)

By applying equation (3.2) successively to each term in the series we obtain

$$\begin{aligned}\sum_n \langle ij|\boldsymbol{T}_n|il\rangle = {} & 4(4A+B)N(0,i,i)+V_2(4A+B)^2N(1,i,i)+V_2^2 4B(4A+B)^2N(0,i,i)\\ & +V_2^2A(4A+B)^2N(2,i,i)+V_2^3(4A+B)^2B\{4A+(4A+B)\}N(1,i,i)\\ & +V_2^3A^2(4A+B)^2N(3,i,i)+V_2^4 4B^2(4A+B)^3N(0,i,i)\\ & +V_2^4(4A+B)^2\{4A+2(4A+B)\}N(2,i,i)+V_2^4A^3(4A+B)^2N(4,i,i)+\dots\end{aligned} \tag{A4.1}$$

By collecting terms the coefficient of $N(0, i, i)$ is found to be

$$4(4A+B)+V_2^2 4B(4A+B)^2+V_2^4 4B^2(4A+B)^3+V_2^6 4B^3(4A+B)^4+\dots$$

$$=\frac{4(4+B)}{1-z} \qquad \text{where } z = V_2^2 B(4A+B).$$

The coefficient of $N(t, i, i), t > 1$, can be calculated similarly if we remember the following identities:

$$\sum_{j=0}^{t} \frac{j(j+1)\dots(j+r)}{(r+1)!} = \frac{t(t+1)\dots(t+r+1)}{(r+2)!}$$

$$\frac{\mathrm{d}^r}{\mathrm{d}z^r}\frac{z^{r-1}}{(1-z)} = \frac{r!}{(1-z)^{r+1}}.$$

It is

$$V_2^t A^{t-1}(4A+B)\left(\frac{4Az}{(1-z)^{t+1}}+\frac{4A+B}{(1-z)^t}\right) = \left(\frac{V_2 A}{1-z}\right)^t \frac{4A+B}{A}\left(\frac{4Az}{1-z}+4A+B\right).$$

Hence

$$\sum_{i,j,l}\langle ij|\boldsymbol{G}|il\rangle = \sum_i \frac{4A+B}{A}\left(\frac{4Az}{1-z}+4A+B\right)\sum_{t=1}^{\infty}\left(\frac{V_2 A}{1-z}\right)^t N(t,i,i)+\sum_i \frac{4(4A+B)}{1-z}N(0,i,i)$$

$$=\sum_i \left\{\frac{4A+B}{A}\left(\frac{4Az}{1-z}+4A+B\right)\sum_{t=0}^{\infty}\left(\frac{V_2 A}{1-z}\right)^t N(t,i,i) + \left(4(4A+B)-\frac{(4A+B)^2}{A}\right)N(0,i,i)\right\}.$$

Using the result that

$$\frac{4A+B}{A}\left(\frac{4Az}{1-z}+4A+B\right) = \frac{(4A+B)^2}{A}\frac{(1-V_2^2 B^2)}{1-z}$$

we obtain

$$\sum_{i,j,l}\langle ij|\boldsymbol{G}|il\rangle = \sum_i\left\{\frac{(4A+B)^2}{A}\frac{(1-V_2^2B^2)}{1-z}\sum_{t=0}^{\infty}\left(\frac{V_2A}{1-z}\right)^t N(t,i,i) + \left(4(4A+B)-\frac{(4A+B)^2}{A}\right)N(0,i,i)\right\}$$

which is equation (3.4).

References

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