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Currents in Periodic and Aperiodic Chain Molecules

B L Burrows and J I Millington

Mathematics Division, School of Computing, Staffordshire University, Beaconside Stafford, ST 18 ODG UK

Abstract

The solution of the time-dependent Schrödinger equation for linear chains of atoms is considered and applied to wavepacket propagation of two types of atoms in aperiodic and periodic sequences. The aperiodic sequences considered are the golden mean (Fibonacci) sequence, the silver mean sequence and the Thue-Morse sequence. These are compared with the 2-period sequence and currents are calculated. A measure of average current for such systems is constructed using the probabilities of substrings in the various sequences.

1.Introduction

The application of mathematics to chemistry has broadly taken two, very successful routes. One of these is the highly accurate computational approach which has led to many quantitative descriptions of atomic and molecular systems. An alternative approach is to use simpler models, often relying on graph-theory, to construct models that lead to physical and chemical insight, but which are far more qualitative in their predictions. In this paper we use the latter approach to construct a time-dependent model for a current in a chain. The theory of currents in molecular systems is usually approached using time-independent scattering theory [1-3], and most treatments involve Green's functions [4,5] but here we consider the time-dependent Schrödinger equation in the context of a simple model for the chain. The chain may be considered to be a molecule consisting of atoms which interact with their nearest neighbours so that essentially we are utilising a theory which is equivalent to Huckel theory for large organic molecules or to the tight-binding model for solid state theory [5-8], but it is a very versatile model that can be applied in many situations. The model is developed in section 2 and graph theory utilised to construct an operator approach for the solution of the equation.

The theory developed is a generalization of earlier work [9] ,but here we apply it to chains whose atoms are in both periodic and aperiodic order. In the latter case we consider chains with two types of atoms arranged in aperiodic sequences such as the Fibonacci sequence , often called the golden sequence, its generalization to the silver sequence and the Thue-Morse sequence. The theory of these sequences has been studied in detail in previous work [10,11] and generalized to similar sequences with three types of atom [12]. In section 3 we outline the analysis of the probabilities of strings of atoms in these sequences and in section 4 we illustrate the calculation of the current through these molecules.

2. The solution of the time-dependent Schrödinger equation for the chain molecules.

Consider a chain of atoms with one atomic orbital ω_n associated with each atom and we define

$$<\omega_n | H|\omega_n> = \alpha_n , \quad <\omega_n | H|\omega_{n+1}> = \beta_{n+1} =<\omega_{n+1} | H|\omega_n> \qquad n=1,2,3.....N \tag{1}$$

Here the α_n or the β_n (or both) may take values in aperiodic order and we will also consider chains of length 2N +1 where the atoms have been renumbered from -N....N. Writing the non-stationary wavefunction in the form

$$\psi = \sum_n c_n(t)\, \omega_n \tag{2}$$

and substituting into the Schrödinger equation

$$i\frac{\partial\psi}{\partial t} = H\,\psi \tag{3}$$

we obtain

$$i\frac{dc_n}{dt} = \beta_{n+1}c_{n+1} + \beta_n\, c_{n-1} + \alpha_n\, c_n = L_+c_n + L_-c_n + L_0c_n \tag{4}$$

with

$$L_+\, c_n = \beta_{n+1}c_{n+1} \,,\; L_-\, c_n = \beta_n c_{n-1} \quad ,\; L_0\, c_n = \alpha_n c_n \tag{5}$$

In vector notation, with the $\{c_n\}$ as elements of the column vector c, the solution may be written

$$c = \exp(-it(L_+ + L_- + L_0))c_0 = \{ I - it(L_+ + L_- + L_0) - \frac{t^2}{2} (L_+^2 + L_-^2 + L_0^2 + L_+L_- + L_+L_0 + L_-L_+ + L_-L_0 + L_0L_+ + L_0L_-) + ...) c_0 \tag{6}$$

where c_0 is the initial charge distribution and no commutation of L_+, L_- and L_0 has been applied in the expansion. Since the chain is finite we have the additional boundary conditions

$$L_- c_0 = 0 \tag{7}$$

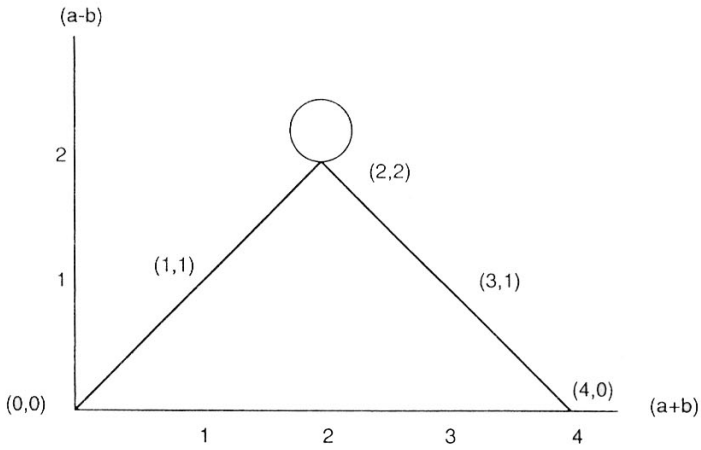
$$L_+ c_N = 0 \tag{8}$$

and these conditions reduce the number of terms in the expansion (6). The vector $\mathbf{c}_0$ can be expanded in terms of the unit vectors $\mathbf{e}_s$, which have elements δ_{sm}, and the linearity of implies that we can obtain the solution as the equivalent combination of solutions with initial charge distributions $\mathbf{e}_s$. Solutions for $\mathbf{c}_0 = \mathbf{e}_s$ correspond to an initial charge distribution only on atom s; when N is large compared to s the condition (8) only affects the higher order terms in the expansion but the condition (7) is more significant. Each term of length n in the expansion (6) consists of a string of p L_+'s, q L_-'s and r L_0's and the condition (7) implies that *for each substring of this string*, as we move from right to left, with a L_+'s and b L_-'s, we have $a-b \geq 1-s$. For example with s =0, so that the initial conditions are $c_n(0) = \delta_{n0}$, the only possible strings of length 4 not including L_0 are $\{ L_- L_+ L_- L_+ , L_- L_- L_+ L_+ , L_- L_+ L_+ L_+ , L_+ L_- L_+ L_+ , L_+ L_+ L_- L_+ , L_+ L_+ L_+ L_+ \}$. Now from (6) we may find an expansion for each of the components of **c** so that

$$c_{s+p-q}(t) = \sum_{p+q+r=n} f(p,q,r) \frac{(-it)^n}{n!} \tag{9}$$

where in principle the sum is from n=0 to ∞, and f(p,q,r) is a function of the α's and β's obtained from applying p L_+'s, q L_-'s and r L_0's to $c_s(0)$ where p+q+r =n and the condition (7) holds for each substring. The terms of this expansion may be illustrated using a graph. Let (x,y) = (a+b, a-b+s) denote integer co-ordinates then any string of the L's can be modelled as a graph from (0,s) to (p +q,p–q+s) where: (i) each L_+ increases a by 1 and can be represented by an edge from (a+b,a–b+s) to (a+b+1,a–b+1+s), (ii) L_- increases b by 1 and can be represented by an edge from (a+b,a–b+s) to (a+b+1,a–b–1+s), (iii) L_0 is represented by a loop at (a+b,a–b+s), This is illustrated in fig 1 where s=0 so that we start at atom1 and the graph represents the string $L_- L_- L_0 L_+ L_+$.

Figure 1



The coefficients f(p,q,r) are conveniently calculated using a recurrence formula of the form

$$f(p,q,r) = \beta_{p-q} f(p-1,q,r) + \beta_{p-q+1} f(p,q-1,r) + \alpha_{p-q} f(p,q,r-1) \qquad (10)$$

with f(0,0,0) =1 and f(p,q,r)=0 if any of the integers p,q or r are negative. This is easily established by noting that any string of L's of length n must have a precursor of length n-1 and the three terms on the left hand side of (10) correspond to the corresponding strings of length n–1 in the precursors.

Given the probability amplitudes in (10) we may calculate the time-dependent current through any subchain of the atoms :

$$j(t) = i \sum_n \beta_n (c_n^* c_{n+1} - c_{n+1}^* c_n) \qquad (11)$$

where the sum is over the n atoms in the subchain and j(t) is necessarily real.

2. The aperiodic sequences

Consider the substitution rule A–> AB , B–> A, then starting at A we may form in turn the following sequences: A, AB, ABA, ABAAB, ABAABABA, ABAABABAABAAB... These form a sequence of atoms making up an aperiodic chain. The particular chain is known as the Fibonacci or golden mean sequence since the ratio of the A's to the B's as the length of the sequence goes to infinity is the golden mean

$$\sigma = \frac{(1+\sqrt{5})}{2} \qquad (12)$$

To see this note that if we use the substitution rule to any sequence of length N to produce a sequence of length $\bar{N}$ and denote the number of A's and the number of B's by N(A) and N(B) then we have

$$\bar{N} = 2N(A) + N(B)\,,\ \bar{N}(A) = N(A) + N(B) \text{ and } \bar{N}(B) = N(A). \qquad (13)$$

(This follows from the basic substitution rule A–> AB , B–> A, since on substitution every A gives rise to one A and one B and every B gives one A in the substituted string; for example ABA-> ABAAB so that N(A) =2,N(B) =1, $\bar{N}(A)$ = 3, $\bar{N}(B)$=2 and $\bar{N}$ =5)

Thus for any string formed by successive substitutions from A or any substring of such a string, when an additional substitution is made, we have

$$\frac{\bar{N}(A)}{\bar{N}(B)} = 1 + \frac{N(B)}{N(A)} \qquad (14)$$

and in the limit as N, $\bar{N}$ –> ∞ we obtain the infinite Fibonacci sequence and from (14) we have

$$\sigma = 1 + \frac{1}{\sigma} \tag{15}$$

and the positive root is the golden mean. Similarly we can deduce that

$$\frac{\tilde{N}(A)}{\tilde{N}} = \frac{N(A)/N(B)+1}{2N(A)/N(B)+1} \rightarrow \frac{\sigma+1}{2\sigma+1} = \frac{\sigma^2}{\sigma^2+\sigma} = \frac{1}{\sigma} \quad \text{as } N \rightarrow \infty \tag{16}$$

Thus we may deduce that $P(A) = \frac{1}{\sigma}$ and $P(A)/P(B) = \sigma$ so that $P(B) = \frac{1}{\sigma^2}$.

(Note that these are the probabilities of A and B in the infinite Fibonacci sequence defined by this substitution process and for any string or substring formed by successive substitutions from A we have $P(A) = N(A)/N$ and $P(B) = N(B)/N$ and the normalization is preserved).

A similar argument shows that as $\tilde{N}, N \rightarrow \infty$

$$\frac{N}{\tilde{N}} = \frac{1}{\sigma} \tag{17}$$

and consequently if we have two substrings S and S' before and after substitution then the number of occurrences of S' in the substituted string is identical with the number of occurrences of S in the original string so that $\tilde{N}(S') = N(S)$ and taking the limit as $\tilde{N}, N \rightarrow \infty$ we may deduce

$$P(S') = \lim \frac{\tilde{N}(S')}{\tilde{N}} = \lim \left(\frac{N}{\tilde{N}} \frac{N(S)}{N} \right) = \frac{1}{\sigma} P(S) \tag{18}$$

(Thus for example if S = ABAA then S' = ABAABAB and the probabilities of S and S' in the infinite string are related by equation (18)).

We note that on substitution $A \rightarrow A_1 = AB \rightarrow A_2 = ABA \rightarrow A_3 = ABAAB \rightarrow \ldots$ The analysis of the substitution can be extended by considering the symbols that must necessarily follow

these : A->AB(A) since A must follow AB. Looking at this more generally we can describe the process by the pattern

$$A \to A_1 A \to A_2 A_1 A \to A_3 A_2 A_1 A \to \ldots \qquad (19)$$

The relationship between this pattern and the original description of the substitution may be elicited as in equation (20) below :

$$A \to AB(A) \to ABA(AB)(A) \to ABAAB(ABA)(AB)(A) \to \ldots \qquad (20)$$

The first substitution from A produces AB and A is appended to this. Applying the substitution rule to AB(A) produces ABA from AB, AB from A and an extra A is again appended to obtain ABA(AB)(A) where the parentheses is used to separate the terms and to illustrate the precursive relationships.

Taking a general string in the sequence in (19), $S=A_{i+1}A_i \ldots A$, we have $S'= A_{i+2} A_{i+1} \ldots A$ and consequently, from (18)

$$P(A_{i+2} A_{i+1} \ldots A) = \frac{1}{\sigma} P(A_{i+1} A_i \ldots A) = \ldots \frac{1}{\sigma^{i+1}} P(A_1 A) = \frac{1}{\sigma^{i+2}} P(A) \quad (21)$$

Suppose now that $A_{i+2} = X_1 X_2 \ldots X_n$ where the X_k are A or B then

$$\bar{N}(A_{i+2} A_{i+1} \ldots A) = \bar{N}(X_1 X_2 \ldots X_n A_{i+1} \ldots A) =$$
$$\bar{N}(X_2 \ldots X_n A_{i+1} \ldots A) = \ldots \bar{N}(X_n A_{i+1} \ldots A) \qquad (22)$$

so that

$$P(A_{i+2}\,A_{i+1}\ldots A) = P(X_1X_2\ldots X_nA_{i+1}\ldots A) = P(X_2\ldots X_nA_{i+1}\ldots A) = P(X_nA_{i+1}\ldots A)$$

(23)

and consequently all the allowed probabilities in the string may be calculated. The probabilities used in this paper are given in the tables.

There is another symmetry in these probabilities. Denoting the reverse sequences of A_i by $\bar{A}_i$, so that $\bar{A}_1 = BA$, $\bar{A}_2 = ABA$, $\bar{A}_3 = BAABA$, ... then (20) may also be denoted by

$$A \to A\bar{A}_1 \to A\bar{A}_1\bar{A}_2 \to A\bar{A}_1\bar{A}_2\,\bar{A}_3 \to \ldots\ldots \qquad (24)$$

This shows for example that at any stage in this process N(AB)=N(BA) so that P(AB) = P(BA) and , more generally, for any sequence S constructed $P(S) = P(\bar{S})$ where $\bar{S}$ is the reverse string to S. This symmetry is apparent in the tables of currents given later.

A similar analysis may be carried out for the other two sequences considered. For the silver mean sequence, A–> AAB, B–> A we have

$$A \to A_1 = AAB \to A_2 = AABAABA \to A_3 = AABAABAAABAABAAAB \to \ldots \qquad (25)$$

and the corresponding result to (20) is

$$A \to A_1AA \to A_2A_1\,A_1AA \to A_3A_2A_2A_1A_1AA \to \ldots. \qquad (26)$$

or in the reverse form

$$A \to AA\bar{A}_1 \to AA\bar{A}_1\bar{A}_1\bar{A}_2 \to AA\bar{A}_1\bar{A}_1\bar{A}_2\bar{A}_2\,\bar{A}_3 \to \ldots\ldots \qquad (27)$$

The probabilities can be calculated analogously to those for the golden mean (but now σ is the positive root of $\sigma^2 - 2\sigma - 1 = 0$) and the reversal symmetry holds.

The final sequence considered is the Thue-Morse sequence A->AB, B->BA so that

$A \rightarrow A_1 = AB \rightarrow A_2 = ABBA \rightarrow A_3 = ABBABAAB \rightarrow \ldots$

and

$$B \rightarrow \bar{A}_1 = BA \rightarrow \bar{A}_2 = BAAB \rightarrow \bar{A}_3 = BAABABBA \rightarrow \ldots \qquad (30)$$

and again the probabilities can be calculated by an analogous procedure to eqns (21)-(23) but with $\sigma = 0.5$. (For a complete description of the calculations of these probabilities see Refs. 10-12). Note that the A_i may be considered as strings of AB's and BA's and the starting from B instead of A leads to the same probabilities of the strings the reversal symmetry follows since that in (30) the strings are either self reverse or the reverse of the equivalent string starting from the other starting point.

3. Currents through aperiodic and periodic chains

In this section we consider 4 types of chain: the golden mean (Fibonacci sequence), the silver sequence, the Thue-Morse sequence and the 2-periodic sequence of atoms in the order ABABABAB..... For each of these we consider the problem of estimating the average current through such chains so that we are essentially estimating the dc molecular current. In principle this is a many electron problem and to use one-electron theory to estimate the current we consider a small subchain of n atoms, S say, and calculate the current due to a wavepacket initially localized at atom 0 which moves onto S so there is a directed current through S. In this model we also connect a lead to atom n so that the wavepacket can move off S and we have a large chain molecule. (We also consider models where there is another lead interacting with atom 0 so that the electron has a probability of moving away from S in the opposite direction .) This model assumes that there is only one wavepacket so that essentially we are assuming that

the times considered are sufficiently small that the probability of two electrons on S is negligible. The components of the wavepacket are $c_{s+p-q}(t)$ in (9) with s =0 since we are starting with a localized charge at atom 0. For large p (or q) the component is small initially and reaches a maximum for some t . This of course applies to the atoms on the leads and shows that the model is suitable to describe the current through S (see [9] for further details of the propagation of such wavepackets). To estimate the average current in S:

$$\bar{j} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} j(t)dt \qquad (31)$$

with j(t) calculated from (11) through the subchain S and into the lead attached to atom n, where $T_1 > 0$ is chosen so that the transient effect of the transfer of the electron onto S has dispersed. The time $T_2 > T_1$ is chosen so that the electron still has a significant probability of being on the chain; T_2 needs to be sufficiently small so that the assumption of only one electron on S is acceptable. In these calculations we have considered subchains of n=7 atoms and the parameters are such that the average currents can be estimated using $T_1 = 2$ and $T_2 = 8$. For the golden mean sequence there are 8 possible subchains S_i of length 7 (see table 1) with probabilities p_i so that the average current through a chain constructed using this sequence can be estimated by the expectation value:

$$\sum_{i=1}^{8} \bar{j}_i \, p_i \qquad (32)$$

In table 1 we list the 8 chains and their probabilities together with the estimates of the currents through these subchains into the leads. In each case we calculate the current through 20 atoms, the first 7 corresponding to the aperiodic sequence and the remaining forming a lead attached to atom 7 (in the final row we give the expected value of the current calculated from (32)). The various currents are calculated using : (i) varying β on the subchain so that $\beta_A = 1.2$, $\beta_B = 0.8$; (ii) varying α on the subchain so that $\alpha_A = 1$, $\alpha_B = 0.8$. The values of α and β for the leads are taken to be 0 and 1 respectively. The calculations are presented for $\beta_0 = 1$ corresponding to a lead attached to atom 0 (so that the chain is from -N...N , N=20) and $\beta_0 = 0$ where there is only one

lead which is attached to atom 7. The results presented in tables 2, 3 and 4 are calculated using the same parameter values but with the silver sequence , the Thue-Morse sequence and the 2-periodic sequence . There are 8 valid sequences of length 7 for the silver mean, 20 for the Thue-Morse sequence and two for the 2-periodic sequence. The pattern of the numerical estimates of the currents is similar in all cases with the magnitude reduced by approximately 1/3 in the cases where there are leads to left of atom 0. In these cases there is of course a current in the opposite direction along the lead at atom 0. The uniformity of the calculated average currents , for a given set of parameters in all subchains any of the sequences suggests that the expected value of the current provides a useful measure of the average or dc component of the current through chain molecules with atoms in these sequences.

TABLE 1 - GOLDEN MEAN SEQUENCE

Sequence	Probability	Average Current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 0$	Average Current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 1$	Average Current $\alpha_A = 1$, $\alpha_B = 0.8$, $\beta_0 = 0$	Average Current $\alpha_A = 1$, $\alpha_B = 0.8$, $\beta_0 = 1$
ABAABAA	0.090169943	1.174612063	0.51810176	1.169983246	0.45512292
ABAABAB	0.145898033	1.183131217	0.46011630	1.234633461	0.48092234
BAABAAB	0.090169943	1.485897057	0.41387039	1.206527135	0.48881733
ABABAAB	0.145898033	1.088958552	0.41005761	1.265907589	0.48419383
BAABABA	0.145898033	1.106593814	0.38200891	1.146297894	0.46544088
AABAABA	0.145898033	1.262268134	0.49784092	1.184807233	0.44920416
AABABAA	0.090169943	1.189373849	0.44643260	1.186791413	0.44838163
BABAABA	0.145898033	1.437004340	0.40016047	1.168308588	0.46243592
		1.229851425	0.43513344	1.19679489	0.46722170

The average currents for all subsequences of length 7 in the Golden Mean chain and the expected value of these currents calculated from (32).

TABLE 2 – SILVER FIBONACCI SEQUENCE

Sequence	Probability	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 0$	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 1$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 0$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 1$
AAABAAB	0.1213203436	1.145209913	0.4939571702	1.206733007	0.4744227503
AABAAAB	0.1213203436	1.167193258	0.4921027052	1.235616685	0.4753738447
AABAABA	0.1715728752	1.262268134	0.4978419193	1.184893399	0.4192738805
ABAAABA	0.1213203436	1.271708512	0.5160659075	1.181031133	0.4625171905
ABAABAA	0.1715728752	1.174612063	05181017568.	1.170077622	0.4550912437
BAAABAA	0.1213203436	1.568799591	0.4574231133	1.118868154	0.4614112255
BAABAAA	0.1213203436	1.609685199	0.4728425987	1.150056423	0.4672868687
BAABAAB	0.0502525317	1.485897057	0.4138703928	1.206510359	0.4888248057
		1.313213158	0.490204985	1.179535865	0.4637415742

The average currents for all subsequences of length 7 in the Silver Mean chain and the expected value of these currents calculated from (32).

TABLE 3 – THUE-MORSE SEQUENCE

Sequence	Probability	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 0$	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 1$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 0$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 1$
AABABBA	0.833333333	1.123128667	0.370972965	1.195242338	0.449908853
AABBAAB	0.416666667	1.133200920	0.369577288	1.245245051	0.473277334
AABBABA	0.416666667	0.930997262	0.326127454	1.206514730	0.450429428
ABAABAB	0.416666667	1.183131217	0.460116297	1.234495504	0.480958151
ABAABBA	0.416666667	0.949378441	0.428003480	1.175732270	0.458046441
ABABBAA	0.416666667	1.073767495	0.373148717	1.200583177	0.457073439
ABABBAB	0.416666667	0.977918027	0.349262000	1.262832185	0.480317363
ABBAABA	0.416666667	1.023239294	0.379712643	1.225923699	0.461894392
ABBAABB	0.416666667	0.974587153	0.369252176	1.286677777	0.488985714
ABBABAA	0.833333333	1.195741004	0.382531915	1.228924830	0.459169204
BAABABB	0.833333333	1.260610898	0.365378964	1.214303085	0.494270339
BAABBAA	0.416666667	1.622886695	0.386225306	1.144394714	0.462329169
BAABBAB	0.416666667	1.255407747	0.328887994	1.207547800	0.486277644
BABAABA	0.416666667	1.437004340	0.400160469	1.168286210	0.462451843
BABAABB	0.416666667	1.429782627	0.350627359	1.234497478	0.492591423
BABBAAB	0.416666667	1.437446846	0.319613827	1.250075296	0.489279538
BABBABA	0.416666667	1.177172316	0.330880895	1.194662032	0.465403219
BBAABAB	0.416666667	1.143051471	0.334598830	1.224111232	0.496767873
BBAABBA	0.416666667	1.406961958	0.353618008	1.157943135	0.472084006
BBABAAB	0.833333333	1.177841052	0.3486 6330	1.256563065	0.500784920
		1.194614990	0.366450546	1.116640048	0.474434707

The average currents for all subsequences of length 7 in the Thue-Morse chain and the expected value of these currents calculated from (32).

TABLE 4 – THE PERIODIC SEQUENCE

Sequence	Probability	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 0$	Average current $\beta_A = 1.2$, $\beta_B = 0.8$, $\beta_0 = 1$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 0$	Average current $\alpha_A = 1$, $\alpha_B = 0.8$ $\beta_0 = 1$
ABABABA	0.5	1.297736369	0.460136197	1.229852885	0.466295343
BABABAB	0.5	0.928759443	0.392182061	1.238351644	0.487050577
		1.113247906	0.426159129	1.234102265	0.476672960

The average currents for all subsequences of length 7 in the 2-Period chain and the expected value of these currents calculated from (32).

Figure 2

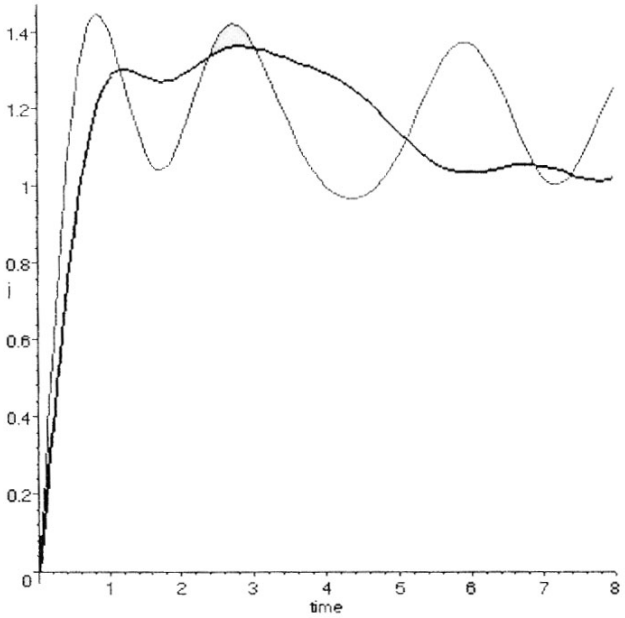
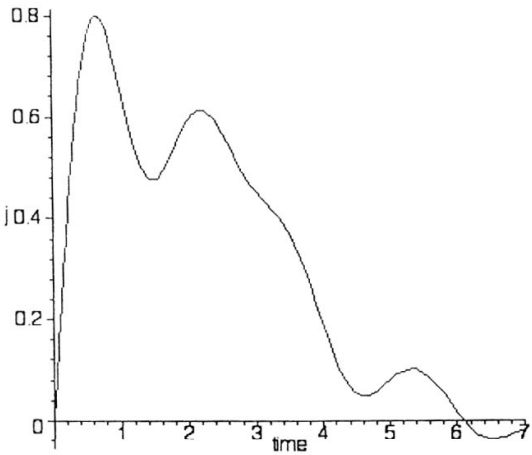


Figure 3



In figure 2 we illustrate the currents through the subsequence ABAABAA from the golden mean, continued into the lead so that it is the current through 20 atoms .These graphs are for case where $\beta_0 = 0$, where β is varying (light shaded curve) and α varying (dark shaded curve). It is clear that, once the transient effects have dispersed, the current with α varying is much uniform. This is repeated for all the calculations so that varying α leads to a more uniform current. For a long chain with equal α's and β's the current is approximately constant when the transient effects have decayed. (See ref [9]). There is no reason to suppose this will be the case with varying α or β since the coefficients $c_n(t)$ depend on α_n and β_n. However they have the same general shape as the corresponding coefficients in the non-varying case, so that it expected that the behaviour will be similar. It is much more significant that in addition the current in (11) has a factor β_n in every term and when the β's are varying will cause further oscillations which persist as the wavepacket moves onto the lead. It is not therefore surprising the effect of varying β's is more pronounced.

Finally, in figure 3 we illustrate the current only through the subchain of 7 atoms using the golden mean sequence ABAABAA with β_0=1 and varying α showing that eventually j(t) is negligible corresponding to the fact that the wavepacket has propagated through the chain .

These calculations suggest that the simple Huckel of tight-binding model, which has provided useful insight in many chemical and solid state systems, can also be useful in time-dependent calculations of currents through chain molecules. The systems that can be treated include atoms in aperiodic order and consequently include quasi-crystals and any newly formed aperiodic chain that may be constructed using STM techniques. The theory considered here can be used to calculate both the transient currents and the average currents whereas conventional calculations do not use the wavepacket approach and usually treat only the average current. The calculation of the average current for chain molecules with the atoms in aperiodic order would conventionally require using a large chain so that all the effects of the various orders of the atoms can be included but here we have shown that a consistent measure may be obtained by calculating the expected value of the average current over a set of small subchains.

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