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The Method of Moments and the Energy Levels of Molecules and Solids

Jeremy K. Burdett[*1], *Stephen Lee, and William C. Sha*

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, U.S.A.

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The method of moments is used to derive the energy levels of a representative series of molecules, crystalline and noncrystalline solids. It provides a direct link between the density of states of the eigenvalue spectrum and the connectivity and topology of the molecular or solid state network.

INTRODUCTION

The traditional method used to obtain orbital energy levels and coefficients via an LCAO approach in both molecules and solids involves the diagonalization of the secular determinant $|\mathbf{H}—\mathbf{SE}| = 0$. The H_{ij} are the Coulomb $(i = j)$ and Resonance $(i \neq j)$ integrals and the S_{ij} the overlap integrals associated with the set of atomic basis functions $\{\varphi_i\}$. (In the simplest possible variant, that devised by Hückel[2] for conjugated organic systems $S_{ij} = \delta_{ij}$. Also H_{ij} $(i \neq j) = 0$ unless the atoms carrying orbitals i and j are linked to each other, in which case $H_{ij} = \beta$.) In principle the energy levels of a molecule are obtained by solution of the secular determinant just once. The energy levels of a crystalline solid are generated by solution of the secular determinant $|\mathbf{H}(k) — \mathbf{S}(k)\mathbf{E}| = 0$ at a representative collection of k points in the Brillouin zone. (k is the wave-vector). Here the atomic basis functions are the Bloch crystal orbitals $\{\varphi_i(k)\}$. This is shown schematically in Figure 1. For those systems where all H_{ii} values

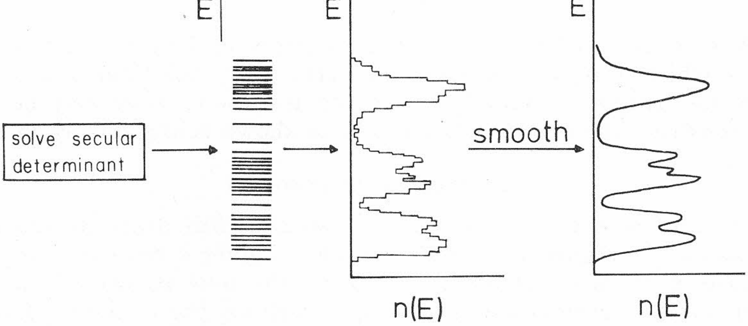


Figure 1. Schematic representation of the traditional method of generation of the energy density of states $n(E)$ or $\varrho(E)$ in this article of a solid material.

are identical (conjugated π systems for example) use of the Hückel approximation leads to a mathematical situation identical with one from graph theory. The Hückel energy levels in this case are simply equivalent to the eigenvalue spectrum of the corresponding graph. In spite of such a correspondence, and the tools from graph theory[3] which can be brought to bear on the problem, it is usually not obvious how the energy level distribution of both molecules and solids is determined by the way the atoms are linked to one another. The problem is especially acute in the solid state where one is particularly interested in the form of the density of states plot and how it controls the stability of one structure over another. In this paper we describe a different approach, based on the method of moments, which gives directly the density of states patterns for molecules and crystalline and amorphous materials. It enables fresh light to be shed upon the energy level distribution and total orbital energy as a function of the number of electrons.

THE MOMENTS METHOD

While traditional calculations involve generating density of states and energy levels by first solving the secular determinant, the moments method provides an alternative technique for determining DOS curves relying primarily on the connectivity or topology of the structure. The definition of the n^{th} moment of E is

$$\mu_n = \sum_i E_i^n \qquad \text{discrete spectrum} \tag{1}$$

$$\mu_n = \int E^n \varrho(E)\, \mathrm{d}E \qquad \text{continuous spectrum} \tag{2}$$

where i denotes a level index and $\varrho(E)$ is the density of states. By solving the secular determinant we diagonalize the corresponding Hamiltonian matrix. Since the trace of a matrix remains invariant under such diagonalization, the n^{th} moment may be simply expressed as $\mu_n = \mathrm{Tr}(H^n)$. The geometrical interpretation of $\mathrm{Tr}(H^n) = \Sigma H_{i1} H_{12} H_{23} \ldots H_{ni}$ links the n^{th} moment to the number of returning walks of length n found in the structure.[4-6] Here the walks refer to steps taken from one orbital i to another atomic orbital j. Each such step is weighted by the corresponding interaction integral H_{ij}. This weighting is particularly simple in the case of π-bonded networks since all $H_{ij} = \beta$ between directly bonded atoms and zero otherwise. So

$$\mu_{\mathrm{n}}^{i} = \nu_n^{i} \beta^n \tag{3}$$

$\beta = H_{kj}\ (k \neq j)$. Here ν_n^i is the number of paths of length n which start at orbital φ_i, which progress through the lattice (or molecule) and eventually return to the orbital φ_i. Once the moments are known they may be used directly to construct the energy DOS, a process shown schematically in Figure 2.

GENERATION OF MOMENTS

Two examples, one molecular, one crystalline will illustrate the application of equation (3). Figure 3a shows the walks of given order explicitly depicted for the case of square cyclobutadiene, using the four $p\pi$ orbitals as a basis. Figure 3b shows a more economical way of deriving the ν_n using what we call propagation diagrams. Notice that $\mu_2 = 4 \times 2\beta^2$, the graph theoretical result. Since each atom in cyclobutadiene is equivalent by symmetry, $\mu_n = 4\mu_n^i$. (The

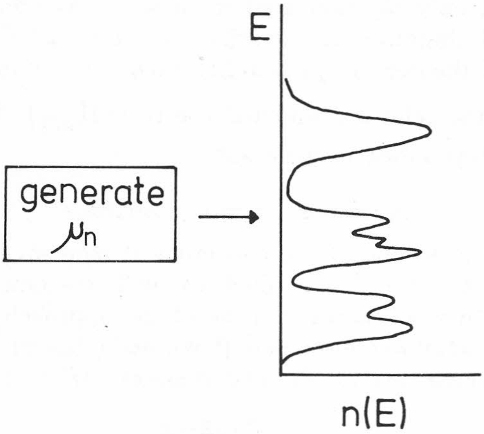


Figure 2. Schematic representation of the direct generation of the energy density of states using the method of moments.

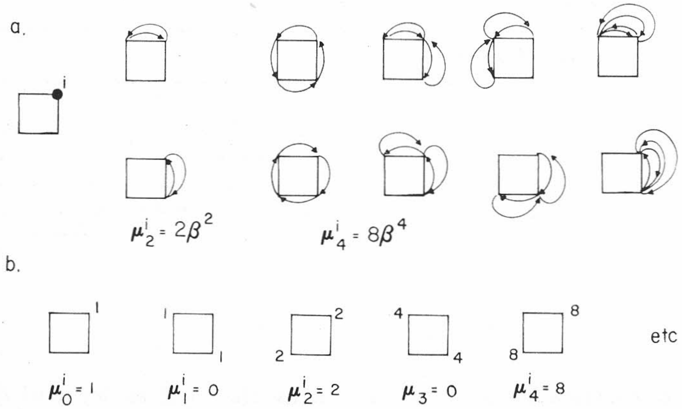
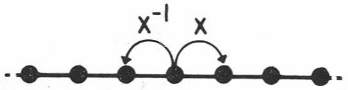


Figure 3. Generation of the number of walks of length n for the levels of cyclobutadiene. a) Explicit consideration of the number of walks of length 2 and of length 4. Notice that it is impossible in this system to return to the home atom after an odd number of steps. As a consequence all odd moments are equal to zero. $\mu_n{}^i$ as calculated needs to be multiplied by 4 to get the μ_n for the molecule since there are four symmetry equivalent orbitals (atoms). b) Use of propagation diagrams in generating the moments by seeing how a point of weight unity is propagated on walking around the lattice in equal steps.

reader may check these numbers by recalling[2] that the energy levels, relative to $\alpha = 0$, for cyclobutadiene are 0 (twice) and $\pm 2\beta$).

1 shows the technique for counting the walks in an infinite system, that of the linear chain.[8] If each walk to the right is weighted by x and each to the



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left by x^{-1} we shall only be interested in those walks which end up back at the home atom and therefore are weighted by $x^{n/2} \cdot x^{-n/2} = x^0$. Recalling the use of the binomial theorem in probability theory the number of such walks is simply given by the relevant binomial coefficient $\binom{n}{n/2}$. These ideas may be extended to crystalline solids in general.[9]

INVERSION OF THE MOMENTS

The problem of inversion of the collection of moments to give the density of states is an old one.[10,11] The method we will use employs the continued fraction method[11]. Only the barest outline of the approach will be given here [Further details are available elsewhere.][9] We make use of the relationships in equations 4 and 5 which link the density of states $\varrho(E)$ to a continued fraction.

$$G(z) = \int_{-\infty}^{\infty} \frac{\varrho(E)\,\mathrm{d}E}{z - E} \tag{4}$$

$$= \cfrac{a_0}{(z + b_0) - \cfrac{a_1}{(z + b_1) - \cfrac{a_2}{(z + b_2) - \cfrac{a_3}{(z + b_3) - \cfrac{a_4}{\ddots}}}}} \tag{5}$$

The a_i and b_i coefficients are determined by the $\{\mu_n\}$ as we will show below. Specifically the problem is to generate $\varrho(E)$ from $G(z)$ given these coefficients. Clearly if the DOS is discrete and y_k is an entry in this eigenvalue spectrum then

$$G(z) = \frac{\varrho(y_1)}{z - y_1} + \frac{\varrho(y_2)}{z - y_z} + \ldots \tag{6}$$

The y_k and $\varrho(y_k)$ are readily extracted from the continued fraction in terms of the a_i and b_i. For a continuous $\varrho(E)$ there is a problem since the continued fraction does not converge on the real axis whenever the value of z is associated with a nonzero contribution to the density of states. In the case of a continuous density of states, ϱ is obtained by taking the imaginary part of the continued fraction $G(z)$

$$\varrho(z) = \mathrm{Im}\{G(z)\} \tag{7}$$

As we noted above the a_i and b_i coefficients of this continued fraction are related to the moments of the DOS. If we define

$$\Delta_n = \begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_n \\ \mu_1 & \mu_2 & \cdots & \mu_{n+1} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \mu_n & \mu_{n+1} & & \mu_{2n} \end{vmatrix} \tag{8}$$

then the a_i are defined *via* the recursion relationship

$$\Delta_n = a_0\, a_1 \, \ldots \, a_n\, \Delta_{n-1} \tag{9}$$

which leads to $a_0 = 1$ (by definition) $a_1 = \Delta_1$, $a_2 = \Delta_2/(\Delta_1)^2$, $a_3 = \Delta_1\, \Delta_3/(\Delta_2)^2$ and in general for $n \geq 3$ $a_n = \Delta_n\, \Delta_{n-2}/(\Delta_{n-1})^2$. The b_i are obtained *via* two relations defining a set of polynomials B_p (E).

$$\int E^{p+1}\, B_p\,(\mathrm{E})\, \varrho\,(\mathrm{E})\, \mathrm{dE} = -\, a_0 \ldots a_p\, (b_0 + b_1 + \ldots b_p) \tag{10}$$

$$B_p\,(\mathrm{E}) = (b_{p-1} + \mathrm{E})\, B_{p-1}\,(\mathrm{E}) - a_{p-1}\, B_{p-2}\,(\mathrm{E}) \tag{11}$$

where $B_{-1}\,(E) = 0$ and $B_0\,(E) = \mu_0$. Manipulation of these two equations, and use of the definition of μ_n in equation (2) allows ready generation of the b_i. The first two are

$$b_0 = -\,\mu_1$$

$$b_1 = \frac{\mu_0\, \mu_1\, \mu_2 - \mu_0\, \mu_3}{a_0\, a_1} + \mu_1 \tag{12}$$

Thus the a_i coefficients are determined by the knowledge of $\mu_0 \ldots \mu_{2i}$ and the b_i coefficients by the knowledge of $\mu_0 \ldots \mu_{2i+1}$. For systems where the energy levels are symmetrically spread about $E = 0$ then the $b_i = 0$. This applies to bipartite systems (with $\alpha = 0$). For many solid state systems the a_i and b_i series converge to a limiting pair of values (a, b) at large enough i. In this case the band limits are very simply given[12] by $-\,b \pm 2\sqrt{a}$.

TWO EXAMPLES

We may use these results to analytically derive the densities of states for the $p\pi$ orbitals of the discrete cyclobutadiene case and the continuous linear chain example. In Table I we show the values of the relevant parameters we need.

The $\mu_A{}^i$ for cyclobutadiene come from Figure 3. We may readily evaluate

$$\Delta_1 = \begin{vmatrix} \mu_0 & \mu_1 \\ \mu_1 & \mu_2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 2 \end{vmatrix} = 2$$

$$\Delta_2 = \begin{vmatrix} \mu_0 & \mu_1 & \mu_2 \\ \mu_1 & \mu_2 & \mu_3 \\ \mu_2 & \mu_3 & \mu_4 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 2 \\ 0 & 2 & 0 \\ 2 & 0 & 8 \end{vmatrix} = 8$$

$$\Delta_3 = \begin{vmatrix} \mu_0 & \mu_1 & \mu_2 & \mu_3 \\ \mu_1 & \mu_2 & \mu_3 & \mu_4 \\ \mu_2 & \mu_3 & \mu_4 & \mu_5 \\ \mu_3 & \mu_4 & \mu_5 & \mu_6 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 2 & 0 \\ 0 & 2 & 0 & 8 \\ 2 & 0 & 8 & 0 \\ 0 & 8 & 0 & 32 \end{vmatrix} = 0 \tag{13}$$

TABLE I

Parameters for Small Rings and the Linear Chain[c]

	Cyclobutadiene	*Benzene*	*Cyclooctatetraene*	*Linear Chain*
μ^i_0	1[a]	1[a]	1[a]	1[b]
μ^i_2	2	2	2	2
μ^i_4	8	6	6	6
μ^i_6	32	22	20	20
μ^i_8	128	88	72	70
μ^i_{10}	512	348	272	252
Δ_0	1	1	1	1
Δ_1	2	2	2	2
Δ_2	8	4	4	4
Δ_3	0	16	8	8
Δ_4	0	0	32	16
a_0	1	1	1	1
a_1	2	2	2	2
a_2	2	1	1	1
a_3	0	2	1	1
a_4	0	0	2	1

[a] Braces indicate those moments identical to those of the linear chain.

[b] $\mu_n = \binom{n}{n/2} \beta^n$.

[c] For notational convenience all the μ_n^i, a_j and Δ_j are shown in dimensionless form without their associated power of β. μ_2^i for example is $2\beta^2$ and the units of Δ_2 are β^6. All the a_j have units of β^2. We shall only include α, β values in our algebra where it is necessary to avoid confusion.

We can quickly see that $\Delta_3 = 0$ since the second and fourth columns are related by a numerical constant (4). So all Δ_i $(i > 3)$ are zero too. These values of the Δ_i may then be used to calculate the a_i. All b_i are of course zero.

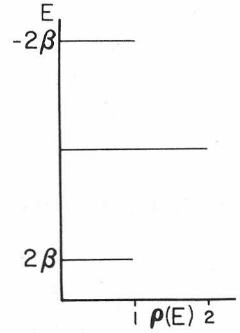
The number of nonzero a_i values tells us immediately how many values will be represented in the eigenvalue spectrum. For the $p\pi$ levels of cyclobutadiene there are three (at 0 and $\pm 2\beta$) but for the linear chain, as we see below there is an infinite number as befits the continuous spectrum. For cyclobutadiene the continued fractions is

$$G(z) = -\cfrac{1}{z - \cfrac{2}{z - \cfrac{2}{z - \cfrac{0}{z}}}} = \frac{z^2 - 2}{z(z+2)(z-2)} \tag{14}$$

Recall that we are using dimensionless expressions for the a_i (Table I) so z has units of β. Equation (14) may be expressed as a set of partial fractions

$$G(z) = \frac{1}{2} \cdot \frac{1}{z} + \frac{1}{4}\left(\frac{1}{z+2}\right) + \frac{1}{4}\left(\frac{1}{z-2}\right) \tag{15}$$

The algebra of the previous section tells us that the spectrum entries occur at $z = 0 \pm 2$. *i. e.*, $E = 0, \pm 2\beta$. There are three terms in $G(z)$ of equation (15). From Table I we note that $a_i = \Delta_i = 0$ for $i > 3$. This is a general result. For a system with j entries in the eigenvalue spectrum then $a_i = \Delta_i = 0$ for $i \geq j$. Since Δ_i is determined by the set of moments $\{\mu_n \mid n \leq 2i\}$ only the moments up to and including $\mu_{2(j-1)}$ are needed. The weight of each partial fraction of equation (15) gives the relevant density of states at this point. The total density of states shown in **2** is simply obtained by multiplying by four (the number of equivalent orbitals) the weights of equation (15). The weights calculated for each spectrum entry is simply the square of the relevant orbital coefficient in the LCAO expansion. **3** shows how the values of equation (15) are related to the cyclobutadiene π-orbital coefficients.



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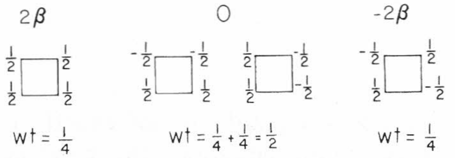

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The linear chain possesses a continuum of levels. The dispersion of the $p\pi$ energy band is given by $E(k) = \alpha + 2\beta \cos ka$ where k, the wavevector, runs from 0 to π/a. (a is the unit cell length). The top and bottom of the energy band then occur at $E = \alpha - 2\beta$ ($k = \pi/a$) and $E = \alpha + 2\beta$ ($k = 0$) respectively. The density of states for systems of this type is described by a function proportional to $(\partial E/\partial k)^{-1}$. Manipulation of the dispersion equation leads to

$$\varrho(E) \propto \frac{1}{2\beta a \sin ka}$$

$$\propto \frac{1}{\sqrt{4\beta^2 - E^2}} \tag{16}$$

Notice that this function is complex for $|2\beta| > |E|$ and is infinite for $E = \pm 2\beta$. We shall now derive this expression via the moments method.

The number of walks of length n are simply given by the binomial coefficient $\binom{n}{n/2}$ as we suggested earlier. These values of the μ_n, and the Δ_i and a_i

which they generate, are shown in Table I. For the linear chain the continued fraction then becomes

$$G(z) = \cfrac{-1}{z - \cfrac{2}{z - \cfrac{1}{z - \cfrac{1}{z - \cfrac{1}{\vdots}}}}} \tag{17}$$

This infinite expression may be simply evaluated by writing

$$G(z) = \cfrac{-1}{z - \cfrac{2}{z + f}} \tag{18}$$

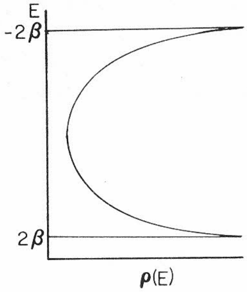
where

$$f = \cfrac{-1}{z - \cfrac{1}{z - \cfrac{1}{z - \cfrac{1}{\vdots}}}} = \frac{-1}{z + f} \tag{19}$$

It should be noted that the above equality is not exactly correct as equation (17) does not always converge while equation (18) is defined for all z.

Rearrangement of equation (18) leads to

$$G(z) = (z^2 - 4)^{-1/2} \tag{20}$$



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In order to convert $G(z)$ into $\varrho(z)$ we need to use the Stieljes transform which for us takes the very simple form

$$\frac{1}{\pi} \operatorname{Im}(G(z)) \Big|_{-\infty}^{t} = \varrho(t) \tag{21}$$

Hence the density of states is

$$\varrho(z) = \frac{1}{\pi}(4 - z^2)^{-1/2} \tag{22}$$

This function is shown in **4**. Note that equation (22) is indeed of the same form as equation (16).

The progression from cyclic polyene to infinite chain is an interesting one to follow. Table I shows some relevant μ_n, a_i and Δ_i values for the $p\pi$ orbitals of such systems. Notice that for the four-ring (cyclobutadiene) μ_0 and μ_2 are the same as the values for the six-ring (benzene) and eight-ring (cyclooctatetraene) and linear chain. In general for a $2m$-ring the μ_n are identical to those of the infinite chain for a $n \leq 2(m-1)$. As a result the a_i for a $2m$-ring are identical to those of the infinite chain for $i \leq 2(m-1)-1$. Equation (23) shows a general expression for the continued fraction when $a_i = 0$ for $i > 4$ and all the $b_i = 0$

$$G(z) = \frac{z^4 - z^2(a_2 + a_3 + a_4) + a_2 a_4}{z^5 - z^3(a_1 + a_2 + a_3 + a_4) + z(a_2 a_4 + a_1 a_4 + a_1 a_3)} \tag{23}$$

Since such a system is bipartite the spectrum entries may be written as $\pm y_1$, $\pm y_2$ or in general as $\{\pm y_i\}$. The continued fraction then becomes

$$\begin{aligned} G(z) &= \frac{z^4 - z^2(a_2 + a_3 + a_4) + a_2 a_4}{z(z^2 - y_1^2)(z^2 - y_2^2)} \\ &= \frac{z^4 - z^2(a_2 + a_3 + a_4) + a_2 a_4}{z^5 - z^3(y_1^2 + y_2^2) + z(y_1^2 y_2^2)} \end{aligned} \tag{24}$$

It is then easy to see that $y_1^2 + y_2^2 = a_1 + a_2 + a_3 + a_4$. As a general result for bipartite systems

$$\sum_{i=1}^{i'} a_i = \frac{1}{2} \sum_i y_i^2 \tag{25}$$

Here $a_{i'}$, is the last nonzero a_i value and y_i is an entry in the eigenvalue spectrum. In the present examples $a_i = 1$ for $1 < i < i'$ and $a_1 = a_{i'} = 2$. So $\sum_{i=1}^{i'} a_i = m + 2$ and a general solution of equation (25) becomes

$$y_j = 2 \cos \frac{\pi j}{m} \quad j = 0, 1, 2, \ldots, m \tag{26}$$

This is a result which may also be derived (in an easier way perhaps) via examination of the form of the secular determinant.[2]

At this stage let us examine approximate ways to solve the problem of the crystalline solid, using the one-dimensional chain as an example. Recall that the a_i values for the cyclic systems form a sequence

$$a_i \quad 1, 2, 1, 1, \ldots, 2 \tag{27}$$

and for the infinite chain

$$a_i \quad 1,\ 2,\ 1,\ 1 \ldots 1 \ldots \tag{28}$$

Two approximations immediately present themselves. First we may just truncate the a_i values of the linear chain with $a_i' = 1$ as

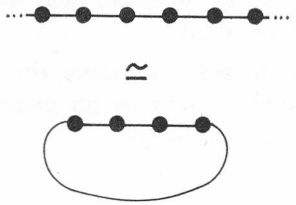
$$a_i \quad 1,\ 2,\ 1,\ 1, \ldots\ 1, \ldots \tag{29}$$

If all $a_i = 0$ for $i > i'$ then there will be a total of $(i' + 1)$ spectrum entries. Moreover these $(i' + 1)$ entries will have the same moments through μ_k where $k = 2\,(i' + 1)$ as those of the linear chain itself. The entries generated in this way are identical to those obtained by use of the special points approach.[13,14] Table II shows how the moments associated with special points sets of various sizes follow the moments of the infinite system. The special points set which generates m levels mimics the moments of the true continuous distribution through μ_{2m}. In more than one dimension analogous results are found. For example the set of points for the primitive cubic zone generated by the one-dimensional pair of points, $\left(\frac{1}{8}, \frac{3}{8}\right)\frac{2\pi}{a}$ are (in units of $2\pi/a$)

$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	weight $\frac{1}{8}$
$\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$	weight $\frac{1}{8}$
$\frac{1}{8}, \frac{3}{8}, \frac{3}{8}$	weight $\frac{3}{8}$
$\frac{1}{8}, \frac{1}{8}, \frac{3}{8}$	weight $\frac{3}{8}$

These lead to the moments correct through μ_4 for the simple cubic lattice with an s orbital located at each node. The three dimensional set of points corresponding to the three one dimensional points $(\frac{1}{12}, \frac{3}{12}, \frac{5}{12})\frac{2\pi}{a}$ give the moments correct through μ_6. Analogous results may be shown analytically for *fcc*, and *bcc* lattices containing a single s orbital at each node, where the dispersion expression may be written in closed form.

Second we may truncate the a_i series for the infinite system with an $a_{i'} = 2$. This leads to a problem identical to the one associated with cyclic systems of Table I. It is then easy to see that this approximation corresponds[15] to the fragment-within-the-solid, or small periodic cluster approach, since all we do is approximate the solid by tying the ends of the chain together (5, 6).



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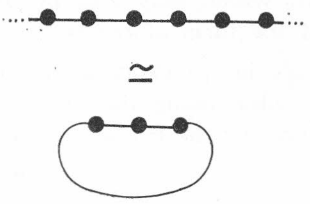

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If there are m levels then they mimic the moments of the truly continuous solid through μ_{m-2} as shown in Table II. Clearly the special points method is more accurate in the sense of reproducing the moments of the continuous density of states. The fragment-within-the-solid approach has its qualitative uses too as we have stressed elsewhere.[15]

TABLE II

Moments for the Infinite Chain and those Obtained via Approximate Methods[a]

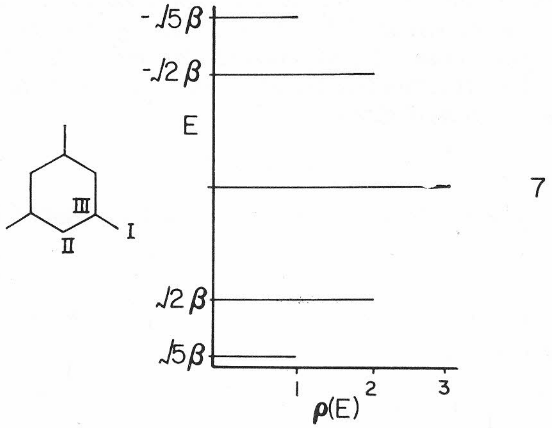
		μ_0	μ_2	μ_4	μ_6	μ_8
	infinite chain	1	2	6	20	70
Special points method	single special point at $(\frac{1}{4})\frac{2\pi}{a}$	$\underline{1}$	0	0	0	0
	two special points at $(\frac{1}{8}, \frac{3}{8})\frac{2\pi}{a}$	$\underline{1}$	$\underline{2}$	4	8	16
	three special points at $(\frac{1}{12}, \frac{3}{12}, \frac{5}{12})\frac{2\pi}{a}$	$\underline{1}$	$\underline{2}$	$\underline{6}$	18	54
	four special points at $(\frac{1}{16}, \frac{3}{16}, \frac{5}{16}, \frac{7}{16})\frac{2\pi}{a}$	$\underline{1}$	$\underline{2}$	$\underline{6}$	$\underline{20}$	68
Fragment-within-the-solid method	two atom fragment	$\underline{1}$	4	16	64	256
	four atom fragment	$\underline{1}$	$\underline{2}$	8	32	64
	six atom fragment	$\underline{1}$	$\underline{2}$	$\underline{6}$	22	86
	eight atom fragment	$\underline{1}$	$\underline{2}$	$\underline{6}$	$\underline{20}$	72

[a] Values underlined are those which are identical with those of the infinite chain.

OTHER MOLECULAR SYSTEMS

Benzene-1,3,5-trimethylene

7 shows the DOS plot for the $p\pi$ levels of this molecule. We will show the origin of the interesting degeneracy that occurs in the energy level spectrum at $E = 0$. This has to be an 'accidental' degeneracy since the point symmetry of the molecule is not high enough to support a triply degenerate representation. (This type of degeneracy has also been called[16] an 'excessive' degeneracy). In this molecule there are three different types of atoms. We may readily count the walks for each type using the technique of Figure 3b. The results are shown in Figure 4. Table III shows the values of the Δ_i and a_i coefficients for the three inequivalent atoms. Evaluation of the respective continued fractions leads to the values of the eigenvalue spectrum entries and of the partial



densities of states associated with each orbital type. These are also shown in Table III.

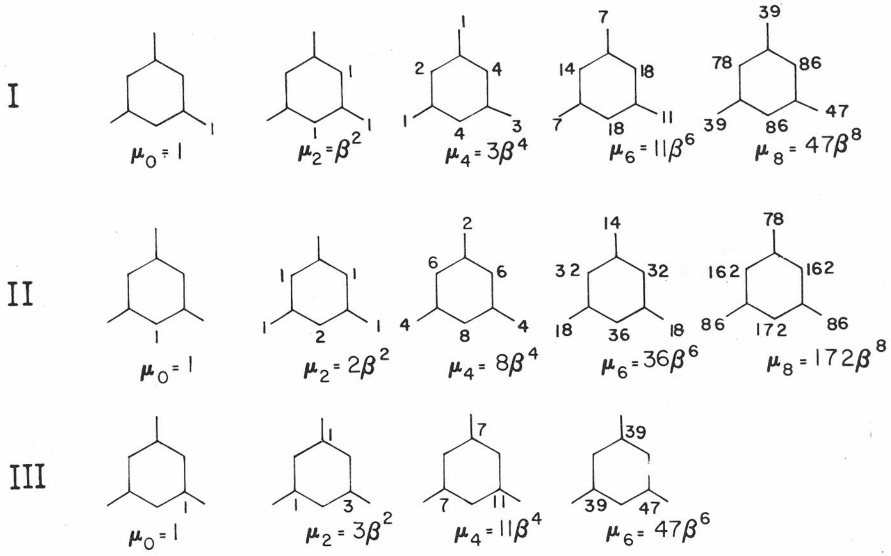


Figure 4. Propagation diagrams for the symmetry inequivalent orbitals in tris-methylene benzene.

For the orbitals of type I

$$G(z) = \frac{z^4 - 6z^2 + 6}{z(z^2 - 2)(z^2 - 5)}$$

$$= \frac{3}{5} \cdot \frac{1}{z} + \frac{1}{6}\left[\frac{1}{(z - \sqrt{2})} + \frac{1}{(z + \sqrt{2})}\right] + \frac{1}{30}\left[\frac{1}{(z - \sqrt{5})} + \frac{1}{(z + \sqrt{5})}\right] \tag{30}$$

TABLE III

Parameters for Trismethylenebenzene

	Atom I	Atom II	Atom III
Δ_0	1	1	1
Δ_1	1	2	3
Δ_2	2	8	6
Δ_3	4	32	40
Δ_4	24	256	0
a_0	1	1	1
a_1	1	2	3
a_2	2	2	2/3
a_3	1	1	10/3
a_4	3	2	0
y_1	$\pm \sqrt{5}$	$\pm \sqrt{5}$	$\pm \sqrt{5}$
y_2	$\pm \sqrt{2}$	$\pm \sqrt{2}$	$\pm \sqrt{2}$
y_3	0	0	—
$\varrho(y_1)$	1/30	2/15	1/6
$\varrho(y_2)$	1/6	1/6	1/3
$\varrho(y_3)$	3/5	2/5	—

For the orbitals of type II

$$G(z) = \frac{z^4 - 5z^2 + 4}{z(z^2 - 2)(z^2 - 5)}$$
$$= \frac{2}{5} \cdot \frac{1}{z} + \frac{1}{6}\left[\frac{1}{(z - \sqrt{2})} + \frac{1}{(z + \sqrt{5})}\right] + \frac{2}{15}\left[\frac{1}{(z - \sqrt{2})} + \frac{1}{(z + \sqrt{5})}\right] \tag{31}$$

For the orbitals of type III

$$G(z) = \frac{z^3 - 4z}{(z^2 - 2)(z^2 - 5)} = \frac{1}{3}\left[\frac{1}{(z - \sqrt{5})} + \frac{1}{(z + \sqrt{2})}\right] + \frac{1}{6}\left[\frac{1}{(z - \sqrt{5})} + \frac{1}{(z + \sqrt{2})}\right] \tag{32}$$

Notice that for atom III with four entries in the eigenvalue spectrum, $a_i = \Delta_i = 0$ for $i \geq 4$. For atoms I and II with five such entries $a_i = \Delta_i = 0$ for $i > 5$. The total density of states picture is shown in Figure 5 and is simply the weighted sum of the partial density of states plots. The factors of 3 compared to the numbers of Table III arise simply because there are three atoms (orbitals) of each type.

An interesting observation concerning Figure 5 is associated with the location of the partial densities of states as a function of coordination number. Notice that the three coordinate atoms (Type III) have the largest density at the top and bottom of the band and that the one-coordinate atom (Type I) has the least. This of course is in keeping with simple bonding ideas; the greater the number of interactions the lower in energy is the most bonding orbital and the higher in energy the highest antibonding orbital. Using the language

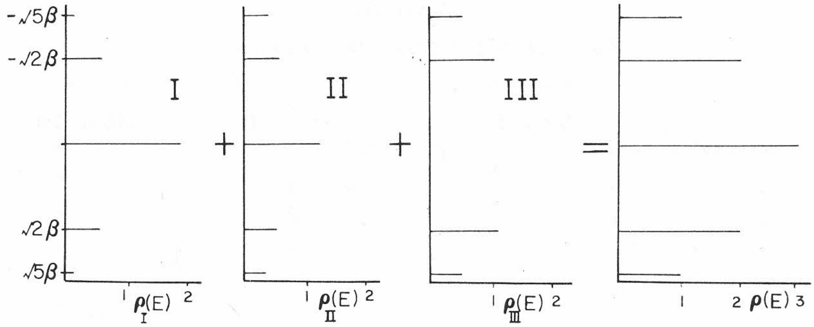


Figure 5. Partial and total densities of states for the $p\pi$ orbitals of trismethylene benzene

of moments Type I, atoms have larger μ_n than Type II or III which is accommodated by a spreading out of the spectrum.

The origin of the triple degeneracy at $E = 0$ may be viewed in other ways of course. Figure 6 shows the assembly of the molecular orbital diagram from a six ring plus three 'ligands'. The levels at $E = 0$ are simply the nonbonding orbitals of *e* and *a* symmetry which result from a typical three orbital problem. In this case there are three pairs of *e* symmetry orbitals and three of *a* symmetry. This degeneracy would be split if second-nearest neighbor interactions were included. Elsewhere[7] we show how use of the propagation diagrams allows a general analysis of orbital degeneracy problems of this type.

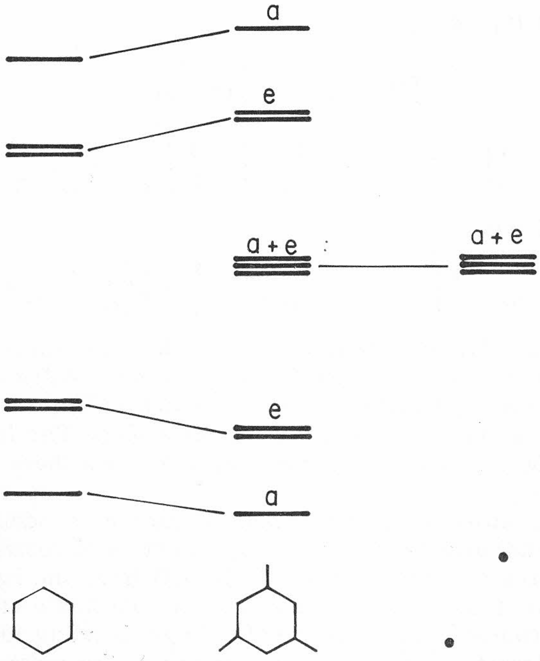


Figure 6. Assembly of the molecular diagram for the $p\pi$ orbitals of trismethylene benzene from those of benzene and three methylene groups.

Cyclopropenyl

Here in this example we show the effect of a nonbipartite, or nonalternant system, where the odd moments and the b_i of the continued fraction will not necessarily be zero. With a total of three atomic $p\pi$ orbitals the maximum number of entries in the eigenvalue spectrum is three (although we know from traditional molecular orbital arguments[2] that there is a double degeneracy) and so the moments through μ_6 are the most that will be needed. Their generation is shown in **8** and the corresponding Δ_i, a_i and b_i shown in Table IV. Notice that since $a_2 = 0$ there can only be two entries in the eigenvalue spectrum. This automatically requires one nondegenerate and one doubly degenerate level. $G(z)$ then becomes

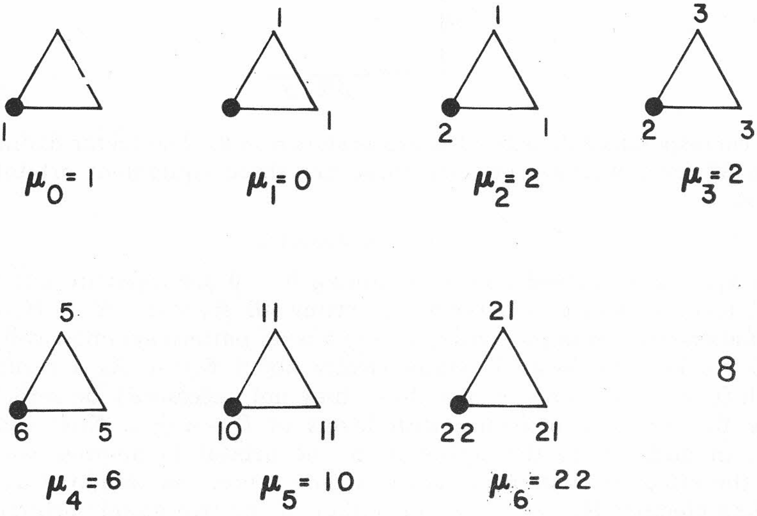


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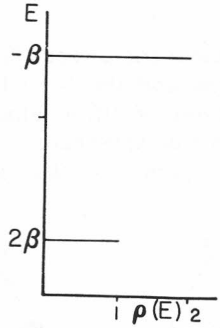
TABLE IV

Cyclopropenyl Parameters

i	μ_i^j	Δ_i	a_i	b_i
0	1	1	1	0
1	0	2	2	—1
2	2	0	0	0
3	2	0	0	0

$$
\begin{aligned}
G(z) &= \cfrac{1}{z - \cfrac{2}{z-1}} \\
&= \frac{z-1}{(z-2)(z+1)} \\
&= \frac{1}{3}\cdot\frac{1}{(z-2)} + \frac{2}{3}\cdot\frac{1}{(z+1)}
\end{aligned}
\tag{33}
$$



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and the corresponding density of states is shown in **9**. (The factor distinguishing equation 33 from **9** arises because three are three equivalent orbitals in the molecule).

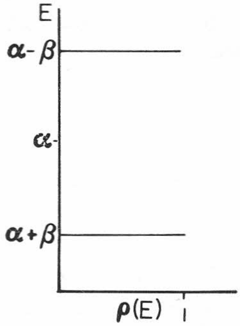
DIATOMIC MOLECULES

The systems described above containing $b_i = 0$ are bipartite but the symmetrical level structure is a result of setting all $H_{ii} = \alpha = 0$. If $H_{ii} \neq 0$ then cyclobutadiene (for example) will not have a level pattern symmetrically located about $E = 0$ but one located symmetrically about $E = \alpha$. As a result of this origin shift the odd moments, and the b_i may not necessarily be zero. Here we examine the ethylene molecule with levels at $E = \alpha \pm \beta$. Now since H_{ii} is nonzero, in addition to the walks from one orbital to another we need to include the effect of 'walking in place' at one center (m) weighted by the corresponding element H_{mm} ($= \alpha$). So for either of the two atomic orbitals $\mu_0 = 1$, $\mu_1 = \alpha$ (*i. e.*, walking in place just once), $\mu_2 = \alpha^2 + \beta^2$ (we have two possibilities here, walking in place twice or walking to the other orbital and back) and $\mu_3 = \alpha^3 + 3\alpha\beta$. So $\Delta_0 = 1$, $\Delta_1 = \beta^2$ which gives $a_0 = 1$, $a_1 = \beta^2$, $b_0 = -\alpha$ and $b_1 = -\alpha$. Thus

$$G(z) = \frac{1}{(z-\alpha) - \dfrac{\beta^2}{(z-\alpha)}} = \frac{z-\alpha}{(z-\alpha+\beta)(z-\alpha-\beta)}$$

$$= \frac{1}{2}\left[\frac{1}{(z-\alpha+\beta)} + \frac{1}{(z-\alpha-\beta)}\right] \tag{34}$$

and the energy levels occur at $E = \alpha \pm \beta$. (**10**).



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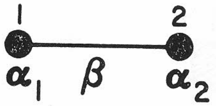
For the heteronuclear diatomic **11**, (representing the π orbitals of formaldehyde for example) for orbital 1 the first few moments are simply $\mu_0 = 1$,



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$\mu_1 = \alpha_1$, $\mu_2 = \alpha_1^2 + \beta^2$, $\mu_3 = \alpha_1^3 + \beta^2\alpha_2 + 2\beta^2\alpha_1$. Since there are only two energy levels we will only need the moments through μ_2 to generate the a_i and through μ_3 to generate the b_i. $\Delta_0 = 1$ and Δ_1 becomes

$$\Delta_1 = \begin{vmatrix} 1 & \alpha_1 \\ \alpha_1 & \alpha_1^2 + \beta^2 \end{vmatrix} = \beta^2 \tag{35}$$

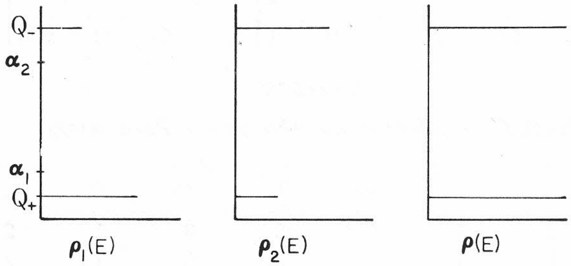
which leads to $a_0 = 1$, $a_1 = \beta^2$, $b_0 = -\alpha_1$ and $b_1 = \alpha_2$. $G(z)$ may then be evaluated as

$$G(z) = \frac{z + \alpha_1 - \alpha_2}{(z - Q_+)(z - Q_-)} \tag{36}$$

where

$$Q_\pm = \frac{\alpha_1 + \alpha_2 \pm \sqrt{(\alpha_1 - \alpha_2)^2 + 4\beta^2}}{2} \tag{37}$$

The eigenvalue spectrum entries then occur at $E = Q_\pm$, a result identical of course to that obtained by solution of the secular determinant. A similar result applies for orbital 2. Evaluation of the weights in the usual way leads to the partial, and total density of states plots of **12**. (These have been drawn assuming arbitrarily that $|\alpha_1| > |\alpha_2|$).



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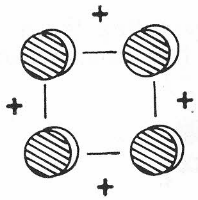
HÜCKEL AND MÖBIUS SYSTEMS

Of some interest is the relationship between Hückel energy levels (*e. g.*, as in the π type orbitals of cyclobutadiene) where there is either an even or zero number of overlap sign changes between adjacent pairs of orbitals (**13**) and those of the Möbius type (*e. g.*, as in the tangential in-plane orbitals of cyclopropenyl) where there is an odd number of sign changes (**14**).[17] In evaluating the weights of the walks in the Möbius system we will need to reverse the sign of the weight of any walk which makes an odd number of complete circuits around the ring. A comparison of the weights and hence moments for



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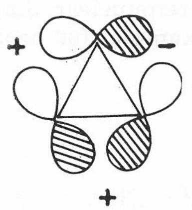

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Hückel and Möbius cyclobutadiene is shown in Figure 7. A comparison between the relevant parameters of the continued fraction is shown in Table V. Note that since $\alpha_2 = 0$ for the Möbius system there can only be two entries in the eigenvalue spectrum. This implies either two doubly degenerate levels or one triply degenerate and one nondegenerate level. Since all the b_i are zero in both systems the latter possibility is excluded since mirror symmetry about $E = 0$ needs to be maintained. $G(z)$ is readily evaluated as

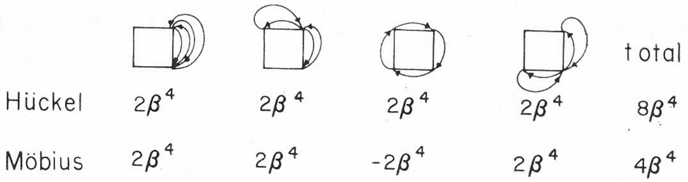


Figure 7. Walks leading to μ_4 for Hückel and Möbius four rings. (Only one walk of each type is shown. Each one has a counterclockwise partner).

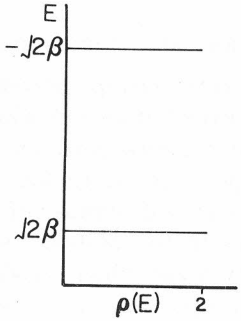
$$G(z) = \frac{z}{(z - \sqrt{2})(z - \sqrt{2})} = \frac{1}{2}\left[\frac{1}{(z - \sqrt{2})} + \frac{1}{(z + \sqrt{2})}\right] \tag{38}$$

TABLE V

Hückel and Möbius Cyclobutadiene Parameters

	μ_2	μ_4	Δ_0	Δ_1	Δ_2	a_0	a_1	a_2
Hückel	2	8	1	2	8	1	2	2
Möbius	2	4	1	2	0	1	2	0

The well-known Möbius pattern is shown in **15.**



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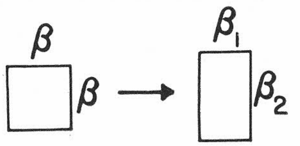
JAHN-TELLER DISTORTION OF CYCLOBUTADIENE

The singlet state of cyclobutadiene, with four $p\pi$ electrons (two pairs) is not square but distorted. Here we will view the distortion of the square to



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the rectangle (**16**). Evaluation of the moments of the $p\pi$ manifold is a simple extension of the result of Figure 3. In general $\mu_n = 0$ for $n =$ odd as before. For $n =$ even

$$\mu_n^i = \frac{1}{2}\left[(\beta_1 + \beta_2)^n + (\beta_1 - \beta_2)^n\right] \tag{39}$$

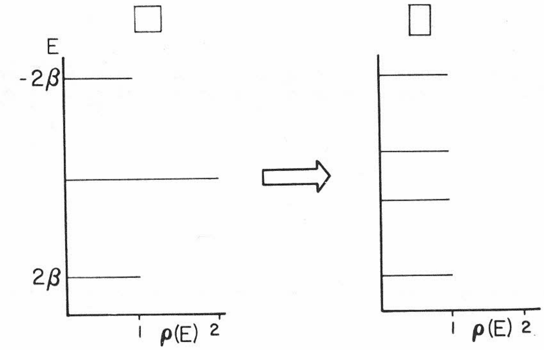
One simplification often used in this problem is to set $\beta_1 + \beta_2 = 2\beta$. If we put $\beta_1 = x\beta + \beta$ and $\beta_2 = -x\beta + \beta$ then

$$\mu_n^i = 2^{n-1}\beta^n\left[1 + x^n\right] \tag{40}$$

and $\alpha_0 = 1$, $\alpha_1 = 2(1 + x^2)$, $\alpha_2 = 2(1 - x^2)(1 + x^2)$ and $\alpha_3 = 8x^2(1 + x^2)$. Evaluation of $G(z)$ leads to

$$G(z) = \frac{1}{4}\left[\frac{1}{(z+1)} + \frac{1}{(z-2)} + \frac{1}{(z+2x)} + \frac{1}{(z-2x)}\right] \tag{41}$$

a result shown pictorially in **17** after multiplication of these weights by 4. A general expression for the energy levels may be obtained by using equation (39), as $E = \beta_1 + \beta_2, \beta_1 - \beta_2, -\beta_1 + \beta_2, -\beta_1 - \beta_2$.



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INFINITE SYSTEMS

In general the density of states for solid materials has to be generated numerically. Few systems lead to simple algebraic expressions such as the one we showed for the linear chain. The details are given elsewhere.[9] An ap-

TABLE VI

a_i Coefficients for Semi-infinite Linear Chain Atom Type

i	A(A)A . . .	A(A)AA . . .	AA(A)AA . . .	AAA(A)AA . . .	AAAA(A)AA . . .	. . . AA(A)AA . . .
0	1	1	1	1	1	1
1	1	2	2	2	2	2
2	1	1/2	1	1	1	1
3	1	3/2	1/2	1	1	1
4	1	2/3	3/2	1/2	1	1
5	1	4/3	1	3/2	1/2	1
6	1	3/4	2/3	1	3/2	1
7	1	5/4	4/3	1	1	1
8	1	4/5	1	2/3	1	1
9	1	6/5	3/4	4/3	1	1
10	1	5/6	5/4	1	2/3	1
11	1	7/6	1	1	4/3	1
12	1	6/7	4/5	3/4	1	1
13	1	8/7	6/5	5/4	1	1
14	1	7/8	1	1	1	1
15	1	9/8	5/6	1	3/4	1
16	1	8/9	7/6	4/5	5/4	1
17	1	10/9	1	6/5	1	1
18	1	9/10	6/7	1	1	1
19	1	11/10	8/7	1	1	1
20	1	10/11	1	5/6	4/5	1
21	1	12/11	7/8	7/6	6/5	1
22	1	11/12	9/8	1	1	1
	.	.	.	.	.	.
	.	.	.	.	.	.
	.	.	.	.	.	.

proximate DOS may be generated using the first few moments but often many moments are needed to get an accurate picture. (Analogously, using the k-space method (Figure 1) we would need to use a large number of k-points to obtain similar accuracy). However, we are often interested in, not the DOS themselves, but the energy difference between two geometrical arrangements as a function of band filling. In another paper[9] we describe an extremely powerful algorithm for evaluating such energy differences in terms of loops of certain length within the basic orbital arrangement.[18]

There are two features of the moments approach which we will use in this section. First is the ability to selectively examine the contribution to the DOS of a particular orbital whether it be in a molecule or in a solid. Second is the applicability of the approach to the study of systems without translational symmetry, such as surfaces, defects, or amorphous materials. We will examine here two simple examples (i) the semi-infinite linear chain AAA . . . AAA . . ., where the first atom in the sequence is the end ('surface') atom and is one-coordinate (all the others are 'bulk' and are two-coordinate) and (ii) the infinite linear chain with an impurity, . . . AAABAAA . . . .

THE SEMI-INFINITE AAA . . . AAA . . . CHAIN

Exact analytic expressions for the function $G(z)$ in equations (4) and (5) can be obtained for atoms throughout the semiinfinite linear chain. For these functions, all b_i coefficients are zero. The a_i coefficients for the first five atoms at the end of this semi-infinite chain are given in Table VI. On moving away from the end of the chain we can see that increasingly large blocks of unit coefficients are interposed between the fractional series of a_i's. Obviously as the atom under consideration moves away from the end of the chain, its DOS will become increasingly like the bulk and $G(z)$ will approach the expression of equation (17). When the DOS of the atoms near the end of the chain are generated numerically from the $G(z)$ functions, they form elegant patterns shown in Figure 8 for the first five atoms. For the DOS of A(A)AA . . ., the single node divides the band area in half. For the DOS of AA(A)AA . . ., the two nodes divide the band area into thirds. For the DOS of AAA(A)AA . . ., the three nodes divide the band area into fourths *etc.*

Such a method is capable of being extended to examine the densities of states associated with surfaces and chemisorbed species.[19]

THE . . . AAA(B)AAA . . . CHAIN

For the infinite linear chain with a defect atom, we will assume that B is more electropositive than A, *i. e.*, $\alpha_B > 0$ and $\alpha_A = 0$. In addition linear chains of pure A and pure B will have the same bandwith 4 where we will set $\beta = 1$. The moments associated with the DOS for the B atom in the chain are shown in Table VII for the case where $\alpha_B = 1.0$. Notice these are different to those for the linear chain itself since walks 'in place' need to be included too.

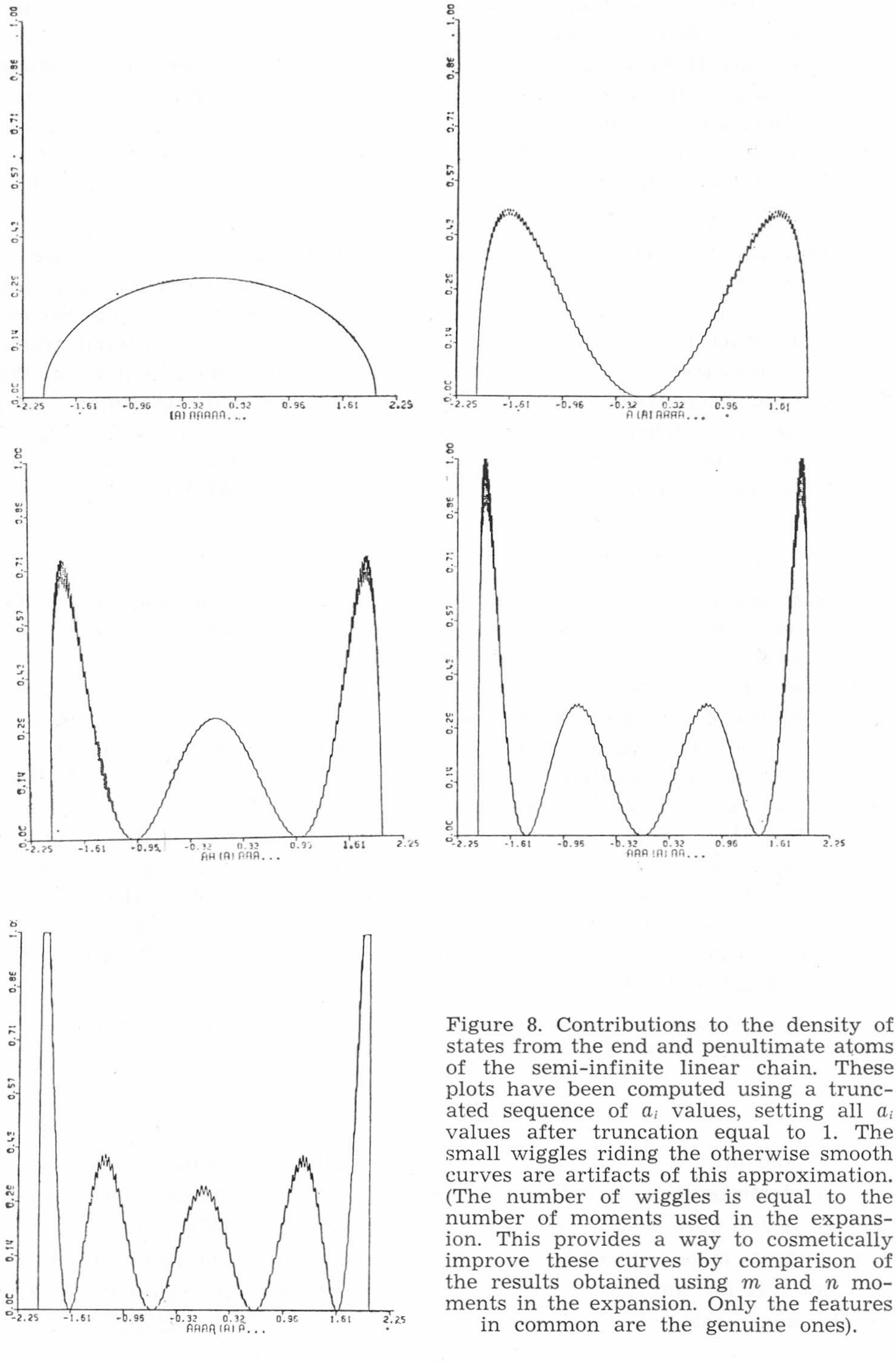


Figure 8. Contributions to the density of states from the end and penultimate atoms of the semi-infinite linear chain. These plots have been computed using a truncated sequence of a_i values, setting all a_i values after truncation equal to 1. The small wiggles riding the otherwise smooth curves are artifacts of this approximation. (The number of wiggles is equal to the number of moments used in the expansion. This provides a way to cosmetically improve these curves by comparison of the results obtained using m and n moments in the expansion. Only the features in common are the genuine ones).

TABLE VII

First Five Moments of the B Atom in an Infinite A Chain

Walks	...A —	A —	A —	A —	A —	(B) —	A —	A —	A —	A —	A...
						μ_i					
0						1					
1					1	1	1				
2				1	1	3	1	1			
3			1	1	4	5	4	1	1		
4		1	1	5	6	13	6	1	1	1	
5	1	5	6	7	18	25	18	7	6	5	1

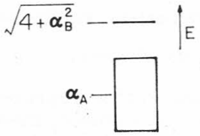
The a_i and b_i coefficients become:

$$\begin{aligned} a_0 &= 1 & b_0 &= -1 \\ a_1 &= 2 & b_i &= 0 \quad i > 0 \\ a_i &= 1 \quad i > 1 \end{aligned} \tag{42}$$

(More generally we can show that $b_0 = -\alpha_B$, a result analogous to the one for the heteronuclear diatomic). Using the substitution technique of equations (18), (19) $G(z)$ may be written in a more tractable form

$$G(z) = \cfrac{1}{z - \alpha_B - \cfrac{2}{z - \cfrac{1}{z - \cfrac{1}{z \cdot \cdot \cdot}}}} = \frac{1}{-\alpha_B + (z^2 - 4)^{-1/2}} \tag{43}$$

$G(z)$ will be complex for $-2 < z < 2$ and hence the partial DOS calculated from $G(z)$ will have a continuum of levels within the band $-2 < E < 2$. In addition $G(z)$ will have a pole at $z = (4 + \alpha_B)^{1/2}$ which corresponds to a discrete antibonding level outside of the band (**18**). To those readers whose experience



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with infinite solids is restricted to crystals this state is something of a novelty. In crystals it is well known that the energy levels in k-space are always continuous. Any discrete jump in the energy density of states can only occur when an entire energy bands is flat, and so such a feature always represents a finite fraction of the DOS for crystalline materials. Here by contrast the discrete level corresponds to a single eigenfunction. In the limit where the chain length is infinite, this discrete level has *no* area associated with it at all.

CONCLUSIONS

The aim of this article is to broadly illustrate the use of the method of moments in determining the Hückel energy levels of molecules and solids. Since the moments themselves are expressed in terms of walks around the molecule or solid, there exists a very direct relationship between the energy level structure and the molecular or solid-state topology. This direct relationship is missing in the usual route via the secular determinant. However, because of the rather indirect relationship between the μ_n and the spectrum entries, via the Δ_i, b_i and a_i the approach may appear more complex. Elsewhere we show aspects of the versatility of the method.[7,9]

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SAŽETAK

Metoda momenata i energijske razine molekula i čvrstih tijela

Jeremy K. Burdett, Stephen Lee i William C. Sha

Izvedeni su izrazi za energijske razine reprezentativne skupine molekula te kristalnih i amorfnih čvrstih tijela primjenom metode momenata. Taj pristup daje direktnu vezu između gustoće stanja spektra vlastitih vrijednosti i topologije molekula i čvrstih tijela.