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Matrix Defectivity and Strange Electronic States of Polymers*

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The significance of matrix defectivity in creating unusual electronic states in polymers and crystals is discussed in (i) non-self-consistent, (ii) self-consistent, (iii) better than self-consistent and (iv) real physical level of approximations. The simplest intermediate and almost intermediate one-electron states are derived in a very elementary way for end-perturbed finite monoatomic linear chains by the direct recursion (transfer matrix) method. A linear model chain is given with two-atomic elementary cells, which has the inner-band intermediate state. Instead of the usual energy-wave vector plot of the band theory, a simpler lambda-x dispersion (LXD) diagram is introduced to represent the band structure. Better terminations are proposed to the creation of intermediate states in earlier studied polymers at the second (*ab initio* Hartree-Fock) level on the ground of trivial first (Hückel) level calculations. More complicated defectivities are sketched. Design of polymeric intermediate states is treated.

1. INTRODUCTION

Non-self-consistent LCAO procedures, such as the Hückel or extended Hückel methods, describes sometimes surprisingly well certain dominating properties of a broad class of molecules, polymers and solids. Applying self-consistent or even more refined methods to these classes, some common dominating mathematical characteristics must appear at all level of the methods. Properties connected with a translational symmetry of the systems belong to the above category. Therefore, it is not superfluous to search for newer phenomena with the aid of the simplest LCAO approaches which usually lead to linear matrix eigenvalue problems.

If the studied systems have translational symmetry, then the above matrices have (at least partly) periodic block-structure(s) and one can apply the direct recursion (transfer matrix) method (DRM)¹⁻⁶ to reduce the order of the eigenvalue problem. The recursion matrix T describes how the one-electronic states propagate from monomer to monomer in polymers or from layer to layer in crystals. If T is diagonalizable, then only two kinds of states can be produced. One is the delocalized bulk state which

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propagates with constant amplitude through the periodic part(s) of the system. The another is the localized state which falls off exponentially. Such are the defect, surface, impurity and interface states, for example. To create states of different character, the defectivity of T is required.

A usual objection against the significance of the defective matrices is that they are very rare. This is confirmed also by computer experiences. Really, at the present accuracy of computers, a very small change in the matrix elements is completely satisfactory to avoid certain singular properties connected with defectivity, without any essential change in the calculated quantities. However, the example

$$\lim_{n \rightarrow \infty} [\lim_{\varepsilon \rightarrow +0} (I - \varepsilon I + P)^n] = I + \infty P \neq \lim_{\varepsilon \rightarrow +0} [\lim_{n \rightarrow \infty} (I - \varepsilon I + P)^n] = 0$$

(here $I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, $P = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ and $I + P$ is a Jordan block) shows that counter-

examples also exist. In the language of physics, one can state that, for example, the periodicity of the system can enhance the otherwise negligible differences between the diagonalizable and the defective matrices.

Thus, one can find new phenomena at the first, non-SCF (or simple) LCAO level of approximations. Let the SCF studies belong to a second level. We shall speak also on a third, better than SCF level. The fourth level will represent the physical reality itself as the most important one. The possible validity of the above discussed enhancement phenomena at the higher levels is our next question.

To the best of our knowledge⁵, not too much attention is given to the role of defective matrices in the electronic structure of polymers and crystals. The third kind of their one-electronic states, the hypothetical intermediate state (IS) has been treated in a few papers^{4,7-16}. The IS is connected with the appearance of the simplest Jordan blocks^{4,7-9}. Its history has been recently outlined in the introduction of⁵. The present stage of the IS -hypothesis, in relation to molecular biology (see also¹⁰), is discussed in a forthcoming paper¹⁴. A possible interpretation of the pyroelectric luminescence¹⁷ by an IS -mechanism¹³ may lead from a first to a fourth level study. Quantum size effect¹⁸ (QSE) experiments of the fourth level were proposed to the observation of the IS s¹¹. A second level (*ab initio* Hartree-Fock) study¹⁵ confirmed the earlier conjectures⁷ that the IS which was discovered at the first (Hückel) level, does really appear at the second level, too. Speculations on the applicability of the IS s in the future molecular computers will be soon published in more detail¹⁴ than earlier¹⁶. Finally, we quote here a mixed first and third level study which was given for Kronig-Penney models both in relativistic (unpublished) and non-relativistic approximations¹². The IS s proved to be exact solutions of both the Dirac and the Schrödinger equations, demonstrating that their appearance is not a by-product of the finite basis (LCAO) approximation.

An elementary derivation for the simplest IS , an analytically solvable model to produce an IS inside a band, first (Hückel) level proposals to a second level (HF) study of more conveniently terminated polymers than

edges lie at $\lambda = 2\varepsilon\beta$. Outside the band $|\mu| < 1$, $\mu = e^\alpha$ ($\alpha < 0$) and then $S_j = \frac{\sinh(j\alpha)}{\sinh \alpha}$ yields a localized solution when it is substituted into (2):

$$c_j = (S_j - aS_{j-1}) c_1. \quad (5)$$

Inside the band $|\mu| = 1$, $\mu = e^{i\alpha}$ ($0 < \alpha < \pi$) and $S_j = \frac{\sin(j\alpha)}{\sin \alpha}$. Approaching the band edge from either side, $S_j \rightarrow \varepsilon^{j-1} j$. Therefore, the fundamental equation (3) will be valid for all of the possible electronic states (bulk, localized and intermediate) if one substitutes just the above spectral resolution:

$$S_{N+1} - (a + g) S_N + agS_{N-1} = 0. \quad (6)$$

The direct derivation for the defective T yields just the above limit⁷ $S_j = \varepsilon^{j-1} j$ at the band edges. Thus, one can obtain from both procedure the same fundamental equation for the IS from (6) (note that $\varepsilon^2 = 1$):

$$N + 1 - \varepsilon(a + g)N + ag(N - 1) = 0. \quad (7)$$

This equation will have an extremely simple and N -independent form for the new terminal parameters A and G defined as

$$a = \varepsilon \left(1 + \frac{A}{N-1}\right) \quad \text{and} \quad g = \varepsilon \left(1 + \frac{G}{N-1}\right). \quad (8)$$

Namely,

$$A + G = AG \quad (7')$$

as it was shown and discussed earlier⁷.

For $0 < \alpha < \pi/(8N)$, $\sin(N\alpha) \approx N\alpha$ in a (graphically) acceptable approximation. If (6) has a solution with such a α value, then the one-electron state of energy $\lambda = \beta(\mu + \nu) = 2\beta \cos \alpha \approx \beta(2 - \alpha^2)$ will be very similar to the exact IS as it is striking from (5), in the same or even better approximation (depending on the actual atomic site):

$$c_j \approx \varepsilon^j (e^j - a[j - 1]) c_1.$$

Therefore, it is an AIS. Roughly speaking, a critical energy interval⁸⁻⁹ $|\lambda - 2\varepsilon\beta| < \beta \pi^2/(64N^2)$ exists, where all states become similar to the central exact IS; they are AISs

3. IS INSIDE A BAND: AN ANALYTICALLY SOLVABLE MODEL

At least two atoms (or orbitals) must occupy the elementary cells of linear polymers or atomic chains to create Van Hove singularities inside a band where ISs can also appear (it is a »matrix effect«). One cannot get general closed expressions for the electronic structure of these systems. Therefore, it seems to be useful to search for easily solvable models to study inner-band ISs. We describe here such a model characterized by second order intra- (A) and intercell (B) Hückel matrices.

Let

$$A = \begin{pmatrix} 4 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} 2 & 1 \\ -1 & 0 \end{pmatrix}.$$

Then

$$T = \begin{pmatrix} 0 & I \\ -B^{-1}B' & -B^{-1}H \end{pmatrix} \quad \text{with} \quad H = A - \lambda I$$

is the recursion matrix which has the reduced characteristic equation⁴⁻⁵

$$|B' t^{-1} + H + Bt| = 0. \quad (9)$$

Let $t + t^{-1} = 2x$ and $t - t^{-1} = y$. Then (9) reduces to

$$\Delta(\lambda, x) = (2x - \lambda)^2 - 4(\lambda + 1) = 0, \quad (10)$$

where the relation $y^2 = 4(x^2 - 1)$ was utilized. It is convenient to plot a lambda-x dispersion diagram (LXD-diagram) to characterize the band structure of our model (see Figure 1.). The LXD-diagram is simpler than the usual energy-wave vector plot of the band theory because the opposing wave vectors are treated together and the complication caused by the exponential dependence is eliminated. What is that diagram and how to use it?

Evidently, $|t| = 1$ if and only if $t = e^{ix}$ with a real x . Then $x = 1/2(e^{ix} + e^{-ix}) = \cos x$ is also real and

$$-1 \leq x \leq 1 \quad (11)$$

defines the allowed bands. If curve $\Delta(\lambda, x) = 0$ crosses the region defined by (11) in the (λ, x) plane then it belongs to the allowed band(s). Outside that region $|t| \neq 1$ on one hand and t may have even complex values on the other band. So we need generally a complex variable x to describe the localized states, i. e., a third imaginary axis as it is done in Figure 1.

For $\lambda > -1$, (10) represents a parabola. This shows the most important characteristics of the more general models: Band edge-type IS (*BE-IS* in Figure 1), Van Hove-type innerband IS (*VH-IS*), doubly degenerated band edge -type ISs with really complex t (complex *Be-IS*) and $t = -1$ without the appearance of the *IS* (no *IS*).

The *VH-IS* produces also the turning over process⁷, i. e., under the effect of appropriately varied boundary conditions, the slope of the wave function's linear envelope can change its sign. Correspondingly, the center of charge of this one-electronic state moves from one side of the chain the other. By further variation of the boundary condition, the *IS* can be transformed either into a bulk or into a localized state. One can then easily imagine that a well localized state of one side of the chain can be transferred into another localized state of its other side through an *IS* (*BE-IS* or *VH-IS*, as well). This is the state-pump mechanism⁷⁻⁹ which can work even in the case of perfectly insulating chains or crystals, promising beautiful applications in a very broad field, starting with molecular electronics up to certain processes in molecular biology, and back⁷⁻¹⁶. The above described simple band-model can largely help the further studies of these problems. Especially the appearance of the doubly degenerated complex *BE-IS* seems to be very promising.

4. HÜCKEL PROPOSALS FOR POLYMER TERMINATIONS IN HARTREE-FOCK CALCULATIONS

Ab initio self-consistent field Hartree-Fock calculations for finite chains of hydrogen atoms, $C_{10}H_2$ («pentacetylene», PA henceforth) and an eight-membered Water-stack have shown that, in concordance with earlier conje-

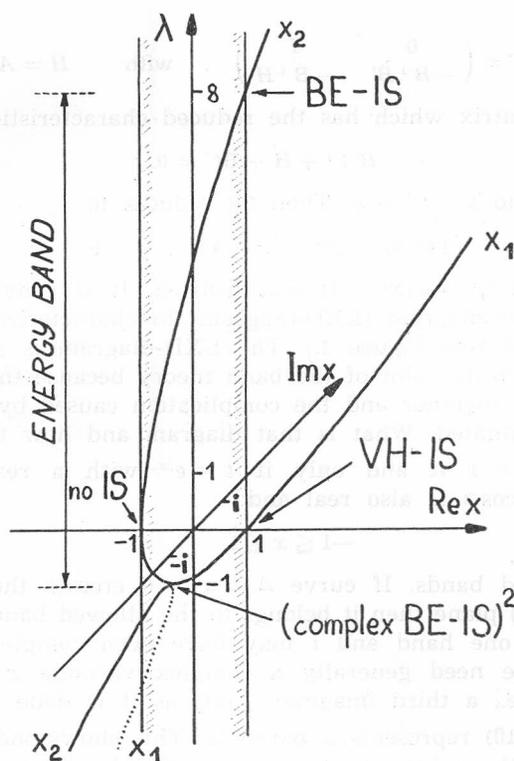


Figure 1. The λ - x dispersion (LXD) diagram of a special (see text) model polymer with two atoms in the elementary cells. λ is the one-electron energy, $x = (t + t^{-1})/2 = \cos(Ck)$, where t and t^{-1} are eigenvalues of the recursion matrix T , k is the wave vector (one-dimensional) and C is a constant. The figure shows the $\Delta(\lambda, x) = |B^* t^{-1} + A - \lambda I + Bt| = 0$ curve in the 3-dimensional space with one imaginary axis $\text{Im}x$. The section of the curve running between the straight lines (see shading) $x = +1$ and $x = -1$ defines the allowed band on the real $(\lambda, \text{Re}x)$ plane. In the case of our special example, this curve is a parabola defined by the two roots $x_1 = (\lambda/2) + (\lambda + 1)^{1/2}$ and $x_2 = (\lambda/2) - (\lambda + 1)^{1/2}$. Thus, the band has two branches for energy values taken between -1 and 0 and one branch from 0 to 8 . Intermediate states (IS) may appear where shown by the arrows (BE = band edge-type, VH = Van Hove-type, »complex« means that the IS belongs to a complex eigenvalue of T [here $\exp(\pm 2\pi i/3)$] and $()^2$ denotes double degeneracy. Below the lower edge of the band ($\lambda = -1$) x_1 and x_2 become complex and run along another parabola, the plane of which is perpendicular to plane $(\lambda, \text{Re}x)$. The dotted branch x_1 is behind plane $(\lambda, \text{Re}x)$.

tures⁷, the ISs do really appear at the second level, at the self-consistent field level of approximations¹⁵. However, the end perturbations (namely, variations of the terminal bond lengths) necessary to generate ISs in the above listed model chains were artificially large. Therefore, we are now searching for better models. In the first step, simple Hückel calculations were performed for substituted PAs, using Streitwieser's parameters¹⁹ to study their π -electron systems. These are simple desk calculations, if the direct recursion (transfer matrix) method¹⁻⁶ is applied. We found that the upper edge of the valence (π) band of $(\text{OH})\text{C}_{10}(\text{OH})$, $(\text{NH}_2)\text{C}_{10}(\text{NH}_2)$, and

(OH)C₁₀(NH₂), the lower edge of the same band for ClC₁₀Cl and (CH₃)C₁₀(CH₃), as well as the lower edge of the conduction (π) band of (BH₂)C₁₀(BH₂), (BH₂)C₁₀F, and (OH)C₁₀(NH₂) can probably produce *IS* more easily, already after a small variation of the terminal bond lengths around their equilibrium value. Naturally, the parameterization of the Hückel method includes some parts of the correlation energy, which is absent in the *HF* method, so one must compare them carefully. One can hope, however, that the dominating characters are appropriately included into both methods, so the above predictions may be useful orienting points in a *HF* study.

5. MORE COMPLICATED DEFECTIVITIES AND THEIR DESIGN

In the general second order case, the intra- and intercell matrices *A* and *B* lead to general second order algebraic polynomials $\Delta(\lambda, x)$. These represent conics in the real (λ, x) plane. The sections of the conics lying between lines $x = +1$ and $x = -1$ represent the allowed band structure (see equation (11)). The intersections of the conics with the above straight lines can generally yield *ISs* (both *BE-* and *VH-ISs*) only if appropriate boundary conditions are fulfilled, but they generally cause singularities in the density of states (DOS) of the infinite systems, in both cases: (i) when the systems are periodic and (ii) when they are bounded but taken in the infinite size limit. Both the *ISs* and the above singularities are, however, absent for the conic's tangent points to the straight lines $x = +1$ or $x = -1$.

Thus, keeping in mind the graphs of the different conics (ellipses, circles, parabolas, hyperbolas, as well as their trivial limit cases, the points, straight lines and their crossing pairs), one can easily imagine how to form the usual one- and two-band systems, say, with partly, completely overlapping or separated bands. The parabolic *LXD*-diagram (Figure 1.) shows roughly what is given doubly in the elliptic and hyperbolic cases in general.

In the more general case when *A* and *B* are of order *n*, $\Delta(\lambda, x) = 0$ as an algebraic polynomial equation of the same order can produce a more complicated *LXD*-diagram, but the notable characters remain similar to those which were found in the second order case. Naturally, the higher order recursion matrices can have Jordan blocks of higher size as well as pairs of truncated Jordan blocks being *k* by *k* + 1 and *k* + 1 by *k* rectangular matrices in their normal forms. So, the way is open to discover newer and more complicated strange electronic states than the *ISs*. How to manipulate with these singular or defective *T* matrices? An inversion-free *DRM* (*IF DRM*) was developed to treat simple (diagonalizable) but singular *T* matrices⁶. Its generalization for the defective matrices is in progress²⁰. The classification for the characteristic defectivities of the *T* matrices as well as the procedure to obtain the normal forms will be given there. The effect of these defectivities on the electronic wave function will be also studied.

Finally, in the knowledge of the above mathematical results, it will be possible to tell which parameter sets included in matrices *A* and *B* can produce the desired strange electronic structure, so we shall be able to search for a realistic physical system which is characterized by just such a parameter set. In this way the design of systems with strange electronic states will become a realistic task with the advantages described elsewhere⁷⁻¹⁴.

6. CONCLUSION

It was shown that matrix defectivity can produce interesting phenomena in the approximated electronic structure of linear polymers. These results are acceptable for three-dimensional crystals, as well, because their description in the direction of a crystal axis is mathematically analogous to the problems of linear polymers. It is not yet clear, whether the above phenomena are really observable, i.e., whether they appear in the real world or not. This question was discussed elsewhere^{7-11,13-14} as well as quantum size effect (QSE) experiments were proposed to observe the ISs¹¹.

We believe that matrix defectivity has a significance in many diverse fields of the nature. We should like to mention here only two such fields, where it is quite clear from the similarity of the formalism, namely, the vibrations of polymers and crystals and the electrical circuits. It would be interesting to review the role of defective matrices in natural sciences. If any of the readers of the present paper do it, then it will have achieved its aim.

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SAŽETAK

Defektnost matrica i neobična elektronska stanja polimera

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Razmatrana je signifikantnost defektnosti matrica u kreiranju neobičnih elektronskih stanja polimera i kristala u nekoliko aproksimacija.