
THEORY OF MOMENTS, HÜCKEL RULE AND STABILITY

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday

The connection between moments of the electronic Hamiltonian and topology of a quantum mechanical system is studied. Based on simplifications similar to those usually employed in simple chemical and physical theories, criteria resembling the Hückel rule for cyclic conjugated systems are suggested. Several examples of interest in chemistry and solid state physics are discussed. No information on the wave function is necessary in the present approach.

The prediction of stable structures is one of the central problems both in chemistry and physics. At present, several criteria exist for which a symmetry analysis (group theory) is crucial. Contrary to rigorous results (the Jahn–Teller theorem¹), most of these theories rely on an intuitive generalization of a fundamental idea (cf. the theory of the pseudo-Jahn–Teller effect², the Landau theory of phase transitions³, etc.). Attempts to find a simple correlation between topology and stability were also undertaken^{1,4–7}. Among them, the Hückel rule for cyclic conjugated systems¹ is classical.

It is interesting to mention that a connection between topology and moments of the electronic Hamiltonian was stressed in the literature⁶. The use of moment methods is of an old date in solid state physics. Recently^{8,9}, these methods became a powerful numerical tool for studying the electronic structure of solids. The moment analysis of simple models yields also interesting results^{10–12}. Below, an attempt is made to link topology and moments together. The present study was inspired by comment¹³ on the paper¹⁴ and by numerical results obtained in ref.¹⁵.

THEORETICAL

In this section, selected definitions and results from the theory of moments and the one-electron theory of bonding are summarized.

For a one-electron Hamiltonian \mathbf{h} with eigenvalues E_r , we define the k -th order

moment of \mathbf{h} as

$$m_k = \sum_j \langle j | \mathbf{h}^k | j \rangle = \text{Tr } \mathbf{h}^k = \sum_r E_r^k, \quad k = 0, 1, \dots \quad (1)$$

For extended structures (crystals) with a continuous spectrum, it is convenient to introduce the density of states $\varrho(E)$, which is non-zero on the spectrum of \mathbf{h} . In this case,

$$m_k = \int E^k \varrho(E) dE. \quad (2)$$

When expressing $\varrho(E)$ as a sum of Dirac delta-functions $\delta(E - E_r)$, the identity (1) acquires the form (2). On the other hand, any continuous distribution $\varrho(E)$ can be approximated by a set of discrete energy levels leading to Eq. (1). As a rule, a limited number of such levels (corresponding to several points from the Brillouin zone or to a finite cluster) are sufficient to describe the most important features of the system correctly. In this case, any discrete level represents a set of states with similar properties.

Following refs^{10,11,16}, let us consider a continuous function $f(E)$ defined on the interval $J = (a, b)$. Supposing the moments $m_k(f) = \int E^k f(E) dE$ vanish up to the order $(n - 1)$, an interesting theorem holds true: *f changes its sign at least n-times on J*. Below, it will be useful to know that for the function $F(E)$ defined on J as $F(E) = \int_a^E \varepsilon f(\varepsilon) d\varepsilon$, moments up to the $(n - 3)$ -th order are zero. Indeed, integrating by parts, one finds for $k = 0, \dots, n - 3$

$$m_k(F) = \int E^k F(E) dE = (k + 1)^{-1} (b^{k+1} m_1(f) - m_{k+2}(f)) = 0. \quad (3)$$

Consequently, F crosses zero at least $(n - 2)$ -times on J . Below, we refer to this result as to the (F, f) -theorem.

In one-electron theory of bonding, the electronic energy is expressed as the following sum of one-electron energies taken over occupied states (the factor 2 arises from the two spin orientations and ε is a constant)

$$E_{e1} = 2 \sum_{\text{occ}} (E_r - \varepsilon) \quad (E_{e1} < 0), \quad (4)$$

or in analogy to Eq. (2),

$$E_{e1} = 2 \int^{E_F} (E - \varepsilon) \varrho(E) dE, \quad (5)$$

E_F being the Fermi energy. Of course, energy of an infinite crystal is infinite. Hence, the energy (5) should be related to an appropriate unit, e.g. to one atom. The validity of the one-electron approximation (4), (5) was discussed by many authors^{1,17,18}; despite of severe simplifications, it is still quite successful especially when the energy difference ΔE_{e1} between two similar structures is treated. To obtain the total energy, a pair potential describing repulsion between constituent atoms should be added¹².

That is why a higher absolute value of E_{e1} is necessary but not sufficient for the stabilization of the corresponding structure. Nevertheless, an essential gain in E_{e1} points to an instability or at least to a softening (reduction of some force constants) of the original configuration.

Let us consider ΔE_{e1} as a function of E_F (or as a function of the electron occupation number N_e), and denote the corresponding difference of the electronic state densities as $\Delta\varrho$. Clearly, the (F, f) -theorem applies to the $(\Delta E_{e1}, \Delta\varrho)$ pair and the number of sign changes of ΔE_{e1} can be estimated from below. The experience shows^{10,11} that in simple situations this estimate gives the exact number of the sign changes.

RESULTS AND DISCUSSION

It is obvious that a simplified theory remains valid only under appropriate assumptions. Here, three constraints (A, B, C) are imposed:

A. Changing, if necessary, the energy zero, we suppose $m_1 = 0$. We assume that the energy spectrum of \mathbf{h} is invariant with respect to the transformation $E \rightarrow -E$. This property is typical for alternant hydrocarbons^{1,6}. An equivalent condition reads $m_{2n+1} = 0$, $n = 0, 1, \dots$. The latter relation is fulfilled approximately in the d -band models of the transition metal crystals where the odd moments are much smaller than the even ones (cf. also ref.¹⁰).

It is convenient to change slightly the notation, denoting the "bonding" energy levels as E_r ,

$$0 > E_1 > E_2 \dots > E_N. \quad (6)$$

For the "antibonding" levels $E_r^* > 0$, one has $E_r^* = -E_r$. For Hamiltonians with an odd number of eigenvalues, there is always a level $E_0 = 0$. It remains unperturbed due to the restriction A and can be ignored⁶. We disregard a possible energy degeneracy as well, supposing that the complications it causes can be handled by group-theoretical methods.

B. We suppose that the electronic energy band (the set of energy levels) is approximately half-filled ($E_F \approx 0$). By using the (F, f) -theorem, this condition will be partly released in the course of the following discussion.

C. We postulate that the energy level E_1 is the most important one. Explicitly, we assume that from the change ΔE_1 of E_1 , one can conclude on the influence of a small perturbation on the stability. An analogous assumption supported by the 2nd-order perturbation theory is, in fact, used in the theory of the pseudo-Jahn-Teller effect², frontier orbital theory¹⁹, in the theory of Peierls instability¹⁹, Fermi surface nesting and Kohn anomalies¹⁷, in the Stoner criterion of ferromagnetism¹¹, etc. Modifications of the condition C are admissible in our approach, e.g., one can assume that the perturbations $|\Delta E_r|$ decrease with increasing r . Nevertheless, it is possible to

construct simple ad hoc examples for which a low-order moment analysis is misleading. Hence, a kind of restriction similar to the assumption *C* is indispensable.

Together with the original structure, let us consider its perturbed form with energies $E'_r = E_r + \Delta E_r$, $E_r^{*'} = -E'_r$. According to the assumption *C*, the sign and magnitude of ΔE_1 are decisive. First, let us express the moment changes Δm_{2k} as functions of ΔE_r . From Eq. (1) and the assumption *A* one finds in the approximation linear in ΔE_r (the notation (6) is used)

$$-(4k)^{-1} \Delta m_{2k} = \sum_r -E_r^{2k-1} \Delta E_r, \quad k = 1, \dots, N. \quad (7)$$

In the matrix form,

$$\mathbf{X} \Delta \mathbf{E} = \mathbf{M}, \quad (8)$$

where \mathbf{X} is the $(N \times N)$ matrix with elements $X_{rs} = -E_s^{2r-1} > 0$ and $\Delta \mathbf{E}$, \mathbf{M} are column vectors with components ΔE_s and $-(4k)^{-1} \Delta m_{2k}$, respectively. The matrix \mathbf{X} belongs to the class of so-called generalized Vandermonde matrices²⁰. According to results of ref.²⁰, the determinant and all the minors x_{rs} of \mathbf{X} are positive. By solving the set of linear equations (8) using the Kramer rule, the contribution to ΔE_1 due to Δm_{2k} is

$$-\Delta m_{2k} (-1)^{k+1} x_{k1} (4k \det \mathbf{X})^{-1}. \quad (9)$$

For $2k = 4n + 2$, the contribution is negative (stabilizing) if $\Delta m_{4n+2} > 0$. The situation is reversed for $2k = 4n$. In other words, an increase of m_{4n+2} (a decrease of m_{4n}) is energetically favourable. Usually, the contribution from low order moments is most important. Only when there is no or small change of m_{2k} , the analysis of m_{2k+2} is justified.

Accepting once that the signs of ΔE_1 and ΔE_{e1} are the same, the (F, f) -theorem may be used. Let us apply it in two special cases ($F = \Delta E_{e1}$, $f = \Delta Q$). First, let us suppose $\Delta m_0 = \Delta m_1 = 0$, $\Delta m_2 > 0$. We find an energy gain for a system with a half-filled spectrum and no change is expected when the electron occupation varies. This conclusion agrees with results of previous investigations. If $\Delta m_k = 0$, $k = 0 - 3$, $\Delta m_4 > 0$, a destabilization is predicted for $E_f \approx 0$. However, E_{e1} changes its sign (at least) twice and the m_4 -criterion should be reversed for systems with almost empty or almost filled electronic levels.

To illustrate the above theory, several simple examples are considered:

Example 1. The Hückel rule. According to this rule^{1,4}, $(4n + 2)$ -membered rings R_{4n+2} are more stable than R_{4n} . Let us find the moments for the corresponding Hückel Hamiltonians. When comparing molecules with different number of atoms, values of extensive quantities per one atom are to be introduced. Defining $\mu_k(R_m) = m_k(R_m)/m$, we obtain $\mu_k(R_{4n+2}) = \mu_k(R_{4n})$, $k = 0, \dots, 4n - 1$. However, μ_{4n} is

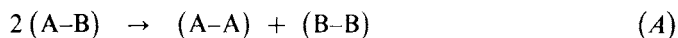
higher for R_{4n} due to contributions of the $h_{12}h_{23} \dots h_{4n1}$ -type, suggesting its lower stability.

Example 2. Branching and bond energy in acyclic carbon chains. As it is shown in refs^{4,6}, the bond energy decreases with branching. Let us consider the simple example shown in Fig. 1. The direct evaluation gives for the Hückel matrices $m_0 = 4$, $m_1 = m_3 = 0$, $m_2 = 6\beta^2$ in either case. m_4 is higher for the branched form ($18\beta^4$) than for the linear one ($12\beta^4$). The higher value of m_4 is caused by the atom at the branching site. The situation is very same for more complicated branched structures.

Example 3. Continuous fraction termination. In surface physics problems, the moments are lower due to a reduced coordination at the surface. Usually, the continuous fraction expansion for energy is terminated^{8,9,15} by using bulk values of moments after several steps. This approximation results in an overestimation or underestimation of energy¹⁵ consistent with the rules formulated above.

Example 4. The W(001) face reconstruction. Stability of possible surface structures utilizing the value of m_4 is discussed in ref.¹⁴. The results of the present paper give another justification of this approach.

Example 5. Ordering in transition metal alloys. Consider a paramagnetic transition metal alloy $A_{1-x}B_x$. According to literature²¹, the electronegativity difference together with d -band filling are crucial for the ordering. Let us consider the following simple Hamiltonian respecting this opinion: Interactions between d -orbitals on the nearest-neighbour lattice sites i, j are described by (5×5) matrices \mathbf{h}_{ij} , $\mathbf{h}_{ji} = \mathbf{h}_{ij}^+$, regardless of the type (A or B) of atoms at sites i and j . The on-site Coulomb integrals for atom A or B are (5×5) matrices $\alpha_A \mathbf{E}$ and $\alpha_B \mathbf{E}$, respectively (\mathbf{E} is the unit matrix). From the condition $m_1 = 0$, $\alpha_A \alpha_B < 0$ follows. The disordering process can be viewed as the reaction



taking place for some ordered nearest-neighbour pairs A-B. For the rearrangement (A), $\Delta m_k = 0$, $k = 0-3$, whereas $m_4(2(A-B)) - m_4(A-A) - m_4(B-B) = 2(2\alpha_A \alpha_B - \alpha_A^2 - \alpha_B^2) \text{Tr}(\mathbf{h}_{ij} \mathbf{h}_{ij}^+ + \mathbf{h}_{ij}^+ \mathbf{h}_{ij}) < 0$ (the products of the matrices in parentheses are

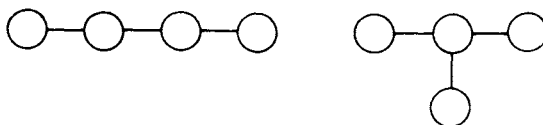


FIG. 1

Two structures considered in Example 2

positively semidefinite). Hence, we predict the ordered phase formation for alloys with roughly half-filled d -band^{11,21}.

Example 6. m_4 and phase stability. For transition metal crystals, this question was considered in ref.¹⁰.

Note added in proof: The recent review article²² presents useful ideas and examples complementary to those considered above.

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