

Maximally Efficient Symmetry Group Founded Diagonalization of Biophysical and Quantum Chemical Hamiltonians

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Abstract: We show that modified Wigner projector technique and generalized Bloch theorem approach yield maximally efficient diagonalization of the Hamiltonian of the large symmetrical systems. For the sake of illustration, we perform a case study of the simplified DNA molecule model and solve the energy eigenproblem analytically by using the unit symmetry cell (*symcell*) and the corresponding low-dimensional subspaces only. Relevant dynamical parameters are automatically obtained, enabling direct interpretation of the result. Effectiveness of the procedure is based on the two key points: (1) replacing infinite sums over the group elements by modified group projectors which are inherently determined by the group generators only; (2) reducing the dynamics of the system (from the infinite dimensional state space) to the low-dimensional *symcell* subspace, taking the benefit from the induced structure of the state space. Unlike the original Wigner projectors, the modified group projector technique is directly numerically applicable.

Key-Words: Deoxyribonucleic Acid (DNA), Symmetry, Wigner Group Projectors, Modified Group Projector Technique, Generalized Bloch Theorem, Electronic Bands, Eigenproblem, Inductive Spaces, Tight-binding Approximation

1 Introduction

Symmetry, being one of the fundamental concepts in nature, plays a crucial role in science and technology. In the fields of quantum chemistry and biophysics, in particular, the ubiquitous application of symmetry is in diagonalization of the Hamiltonian, via reducing the dimension of its eigenproblem and getting the eigenstates (the so called symmetry adapted basis) and the corresponding eigenenergies labeled by the conserved quantum numbers, which are suitable for the analysis and interpretation of the properties of the system, and for the further calculations of the more complex processes (optical absorption, Raman scattering, thermal transport, electric conductivity etc.)

The usual procedure of the determination of the symmetry adapted basis of a Hamiltonian include Wigner projectors and Wigner transfer operators [1], which are the sums (over the symmetry group elements) of the operators acting in the state space. However, both the dimension of the state space and the number of the symmetry transformations are in many scientifically interesting systems, macromolecules e.g., too large (or even infinite), even in the simplest approximations, making obstacles for

the direct diagonalization or application of the standard Wigner projector technique. However, instead of the standard unit cell, the full symmetry unit cell (*symcell*) can be used, as the latter is the minimal part of the system from which the whole system can be built by the group action.

The Bloch theorem [4] shows that the translational symmetry of the crystals enables to reduce the calculations to the elementary cell only. Its generalization [2] to the arbitrary (nonabelian) group justifies heuristic (but intuitively clearly founded) assumption that the symmetry and *symcell* determine the properties of the entire system. This can be realized by means of the modified Wigner operators, which for Hamiltonian eigenproblem of the whole system provide its isomorphic image in the *symcell* state space (of finite dimension in standard model). Further, the relevant observable, expanded over the irreducible tensor components, obtain its counterpart in the *symcell* space. Apart from the much lower dimensionality the reduction of the problem is substantial as now only the transformations leaving *symcell* invariant are to be considered.

Many important biomolecules are quasi-one-

dimensional, with large symmetry (at least approximately), which rarely reduces to translations only, since symmetry of the quasi-one-dimensional structures is not subjected to the crystallographic restrictions. Hence, the line groups [3] describe the symmetry of these molecules. In a combination with the modified group projector technique, the line groups offer the theoretically maximally efficient framework for investigations of such systems. The method is quite general, approaching the standard models of ionic, electronic and spin dynamics in unified manner; this also includes the relaxation techniques of structural optimization, where minimal independent set of parameters is singled out.

2 Generalized Bloch Theorem

Within the quantum theory, syntagma *system with the symmetry* connotes: the state space \mathcal{S} of the system, symmetry group \mathbf{G} along with the Hamiltonian H of the system and the group representation $D(\mathbf{G})$ (homomorphic image of \mathbf{G}) acting in the state space. Reflecting particular problem under the consideration, state space is an (in)finite-dimensional Hilbert space, Hamiltonian is a Hermitian operator determining evolution of the system, and representation of the group is a set of unitary operators.

Though the (modified) Wigner projector method is applicable to any type of symmetry groups (including Lie groups), here we consider only the groups relevant for quantum chemistry of (bio)molecules and (bio)polymers. Besides point groups, for complex highly symmetric structures (in particular polymers with or without translational periodicity) this includes *line groups* (LGs) [3]. These are the subgroups of the Euclidean group $E(3)$ of geometrical transformation in \mathbb{R}^3 , in Koster-Seitz notation given as $g = (A | \mathbf{v})$, where A is element of the orthogonal group $O(3)$ and \mathbf{v} is a vector in \mathbb{R}^3 , mapping arbitrary point \mathbf{r} into $(A | \mathbf{v})\mathbf{r} = A\mathbf{r} + \mathbf{v}$; notation is extended to sets $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots\}$ as $(A | \mathbf{v})\mathbf{R} = \{(A | \mathbf{v})\mathbf{r}_1, (A | \mathbf{v})\mathbf{r}_2, \dots\}$. Thus, in prototypical Lebesgue state space $\mathcal{L}(\mathbb{R}^3)$ the symmetry transformations act by the coordinate representation: $D(g)f(\mathbf{r}) = f(g^{-1}\mathbf{r})$.

Invariance of the system under the symmetry transformations in the quantum formalism reads as commutation of the (represented) symmetries with the Hamiltonian of the system:

$$[H, D(g)] = 0, \quad \forall g \in \mathbf{G}. \quad (1)$$

As unitary, representation $D(\mathbf{G})$ is decomposed onto the orthogonal sum of its (unitary) irreducible

components each appearing f^μ (frequency numbers) times:

$$D(\mathbf{G}) = \oplus_{\mu=1}^{\mathbf{G}} f^\mu D^{(\mu)}(\mathbf{G}); \quad (2)$$

this accompanies orthogonal decomposition $\mathcal{S} = \oplus_{\mu} \mathcal{S}^\mu$ of the state space onto the isotypic spaces, each being orthogonal sum, $\mathcal{S}^\mu = \oplus_{t=1}^{f^\mu} \mathcal{S}_{t_\mu}^{(\mu)}$ of f^μ replicas of irreducible subspaces $\mathcal{S}^{(\mu)}$ (of the dimension $|\mu|$). Joining the subbases $\{|\mu t_\mu m\rangle \mid m = 1, \dots, |\mu|\}$ (*multiplets*) of all $\mathcal{S}_{t_\mu}^{(\mu)}$, the *standard* [1] or *symmetry adapted basis* (SAB) of \mathcal{S} is built. Obviously,

$$D(g) |\mu t_\mu m\rangle = \sum_{m'} D_{m'm}^{(\mu)}(g) |\mu t_\mu m'\rangle, \quad (3)$$

and in this basis $D(\mathbf{G})$ is block-diagonal, with blocks being the matrices of the irreducible representations $D^{(\mu)}(\mathbf{G})$.

Decomposition $\mathcal{S} = \oplus_E \mathcal{S}_E$ of the state space onto the eigensubspaces of H (energies E are its eigenvalues), due to (1) means that $\mathcal{S}_{t_\mu}^{(\mu)}$ are subspaces of \mathcal{S}_E , i.e. that there is stationary symmetry adapted basis (SSAB) (3) composed of the Hamiltonian eigenvectors:

$$H |\mu t_\mu m\rangle = E_{\mu t_\mu} |\mu t_\mu m\rangle. \quad (4)$$

Note that in this way energies are assigned by the quantum numbers inferred by the irreducible transformation laws of the symmetry group. It remains to represent Hamiltonian in the SAB. In the simple case of the Abelian translational group, this reduces to the Fourier transform of H (Bloch theorem), since irreducible representations are one-dimensional and SSAB consists of the Bloch functions. Generalization, modified group projector technique [2], is we briefly review in the rest of the section.

In order to find a part of SAB corresponding to irreducible representation $D^{(\mu)}(\mathbf{G})$, a conjugated (dual) irreducible representation $D^{(\mu^*)}(\mathbf{G})$ is used: the auxiliary composite space $\mathcal{A}^\mu = \mathcal{S} \otimes \mathcal{H}^{(\mu^*)}$ ($\{|\mu^* m\rangle \mid m = 1, \dots, |\mu|\}$ is the basis of the latter) is equipped with the representation

$$\Gamma^\mu(\mathbf{G}) = D(\mathbf{G}) \otimes D^{(\mu^*)}(\mathbf{G}). \quad (5)$$

Each vector $|x\rangle$ fixed by this representation (i.e. $\Gamma^\mu(g)|x\rangle = |x\rangle, \forall g \in \mathbf{G}$) is correlated: it is composed of the vectors from \mathcal{S} entangled to those from $\mathcal{H}^{(\mu^*)}$ in the way that the group action $D(\mathbf{G})$ in \mathcal{S} cancels with the (irreducible) action in $\mathcal{H}^{(\mu^*)}$. Therefore, the \mathcal{S} -factors are from \mathcal{S}^μ . Clearly, all the fixed points form the subspace \mathcal{F}^μ of \mathcal{A}^μ , being the range of the *modified projector*

$$\mathbf{G}(\Gamma^\mu) = \frac{1}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} D(g) \otimes D^{(\mu^*)}(g). \quad (6)$$

Dimension of this space is trace of $\mathbf{G}(\Gamma^\mu)$, and character theory shows that this equals the frequency number f^μ of (2). Thus, arbitrary orthonormal basis in \mathcal{F}^μ can be denoted as $\{|\mu t_\mu\rangle \mid t_\mu = 1, \dots, f^\mu\}$. However, the partial scalar product with the basis vectors in $\mathcal{H}^{(\mu^*)}$ yields the entangled SAB vectors in \mathcal{S} :

$$|\mu t_\mu m\rangle = \langle \mu^* m \mid \mu t_\mu \rangle, \quad m = 1, \dots, |\mu|. \quad (7)$$

As this shows that choice of basis in \mathcal{F}^μ is biuniquely related to the choice of SAB $|\mu t_\mu m\rangle$ in \mathcal{S}^μ , it remains to find $|\mu t_\mu\rangle$ corresponding to SSAB. To this end we define operator $H^\mu = H \otimes \mathbb{1}_\mu$ in \mathcal{A}^μ . Namely, this is a unique extension of H in \mathcal{A}^μ , not affecting the eigenenergies (reflecting the physics) by the (trivial) action in the artificial space $\mathcal{H}^{(\mu^*)}$. Clearly, (1) implies that H^μ commutes with $\Gamma^\mu(\mathbf{G})$. Finally, it is straightforward to prove that $|\mu t_\mu\rangle$ are eigenvectors of H^μ from the range of $\mathbf{G}(\Gamma^\mu)$,

$$H^\mu |\mu t_\mu\rangle = E_{\mu t_\mu} |\mu t_\mu\rangle, \quad \mathbf{G}(\Gamma^\mu) |\mu t_\mu\rangle = |\mu t_\mu\rangle, \quad (8)$$

if and only if the resulting SAB vectors (7) are eigenvectors (4) of H for the same eigenvalues. Thus, as the auxiliary Hamiltonian H^μ commutes with $\mathbf{G}(\Gamma^\mu)$, the eigenproblem of the restricted operator $\mathbf{G}(\Gamma^\mu)H^\mu$ is to be solved in \mathcal{A}^μ , and the obtained eigenvectors are used as $|\mu t_\mu\rangle$ in (7). Note that all the geometrical groups have finite number of generators g_i ($i = 1, \dots, K$) and that each group element is an ordered monomial over them: $g = g_{\alpha_1 \dots \alpha_K} = g_1^{\alpha_1} \dots g_K^{\alpha_K}$. Obviously, $|x\rangle$ belongs to \mathcal{F}^μ if and only if

$$\Gamma^\mu(g_i) |x\rangle = |x\rangle, \quad i = 1, \dots, K. \quad (9)$$

Therefore, this homogeneous linear system suffices to find \mathcal{F}^μ without summation over the group, which resolves the difficulty in application of the standard Wigner procedure [1] with infinite groups.

3 Tight-binding in Inductive Spaces

Another problem is typically infinite dimension of the state space. In the standard dynamical models of the symmetric infinite systems, it is resolved due to possibility to build \mathcal{S} as a subspace of $\mathcal{L}(\mathbb{R}^3)$ which is direct sum of the subspaces associated to the atoms. Namely, the group action infers the decomposition of the system atoms into the orbits: the set of the positions of the atoms is finite disjoint union $\mathbf{R} = \bigcup_P \mathbf{R}^P$ of the orbits $\mathbf{R}^P = \bigcup_g g r_0^P$. The orbit representatives form symcell, $\mathbf{R}_0 = \{\mathbf{r}_0^1, \mathbf{r}_0^2, \dots\}$, the minimal set of atoms sufficient to generate the whole system by the group action. Each orbit representative defines its stabilizer \mathbf{F}^P (subgroup of \mathbf{G} fixing \mathbf{r}^P). Representatives z_p^P of the cosets of this subgroup suffice

to regain the whole orbit in the form $\mathbf{r}_p^P = z_p^P \mathbf{r}_0^P$; they form transversal \mathbf{Z}^P , and the action of \mathbf{G} on the atomic position is manifested as the ground action on the transversal: $g z_p^P = z_{gp}^P f^P(g, p)$, where z_{gp}^P and $f^P(g, p)$ are elements of the transversal and stabilizer uniquely determined by Lagrange theorem.

The tight-binding state space is modeled by taking for each atom \mathbf{r}_p^P a finite dimensional space \mathcal{S}_p^P , with the basis $|Pp; \psi\rangle$ ($\psi = 1, \dots, |\mathcal{S}_p^P|$); the symmetry requires that it is same space for the atoms within the same orbit. The state space becomes direct sum $\mathcal{S} = \bigoplus_{Pp} \mathcal{S}_p^P$ (though it is not necessary for further results [2], in the following we assume that these atomic spaces are mutually orthogonal). Its subspace is symcell space $\mathcal{S}_0 = \bigoplus_P \mathcal{S}_0^P$.

In the basis $|PP; \psi\rangle$ the Hamiltonian is a matrix $H = \sum_{PQpq} E_{Qq}^{Pp} \otimes h_{Qq}^{Pp}$; here $|\mathbf{R}|$ -dimensional matrices E_{Qq}^{Pp} have all zero elements except 1 in the intersection of the row Pp with the column Qq , while $\langle Pp; \psi \mid H \mid Qq; \phi \rangle$ are matrix elements of $|\mathcal{S}_0^P| \times |\mathcal{S}_0^Q|$ -dimensional blocks h_{Qq}^{Pp} . Usually these essential part of the dynamical model are estimated by various approximations (density-functional, Hartree-Fock, etc.). Note that $h_{Pp}^{Qq} = (h_{Qq}^{Pp})^\dagger$, as Hamiltonian H is a Hermitian operator.

The representation $D(\mathbf{G})$ is naturally derived from the obvious requirement that $D(z_p^P)$ maps \mathcal{S}_0^P into \mathcal{S}_p^P . This shows that each orbit space $\mathcal{S}^P = \bigoplus_p \mathcal{S}_p^P$ is invariant; also, \mathcal{S}_0^P is invariant under the stabilizer \mathbf{F}^P , and the action of \mathbf{F}^P in \mathcal{S}_0^P defines the interior representation $\delta^P(\mathbf{F}^P)$. Altogether, this means that the group action is the direct sum $D(\mathbf{G}) = \bigoplus_P D^P(g)$ of the orbit representations $D^P(\mathbf{G})$, each of them being induced from $\delta^P(\mathbf{F}^P)$ by the ground action $E_{Pp}^{P,gp}$ of the group on the corresponding transversal \mathbf{Z}^P :

$$D^P(g) = \sum E_{Pp}^{P,gp} \otimes \delta(f^P(g, p)). \quad (10)$$

The commutation relation (1) implies

$$\delta^P(f^P(g, p)) h_{Qq}^{Pp} \delta^{Q^+}(f^P(g, q)) = h_{Q,qq}^{P,gp}, \quad (11)$$

imposing a number of constraints to the blocks h_{Qq}^{Pp} . They are technically important to prove [2] the following

Theorem 1 Let $\gamma^{P\mu}(\mathbf{F}^P) = \delta^P(\mathbf{F}^P) \otimes D^{(\mu)*}(\mathbf{F}^P)$. Operator $Z^\mu = \sum_{Pp} \frac{1}{\sqrt{|\mathbf{Z}^P|}} E_{P0}^{Pp} \otimes \mathbb{1}_\delta \otimes D^{(\mu)*}(z_p^P)$ is partial isometry from the symcell auxiliary space $\mathcal{A}_0^\mu = \mathcal{S}_0 \otimes \mathcal{H}^{(\mu^*)}$ into the range of $\mathbf{Z}^\mu \mathbf{Z}^{\mu\dagger}$ in \mathcal{A}^μ . The

modified group and stabilizer projectors are linked as

$$\hat{Z}^{\mu\dagger} \mathbf{G}(\Gamma^\mu) \hat{Z}^\mu = \sum_P E_{P0}^{P0} \otimes \mathbf{F}^P(\gamma^{P\mu}), \quad (12)$$

while the operator $\hat{Z}^{\mu\dagger} \mathbf{G}(\Gamma^\mu) H \hat{Z}^\mu$ is equal to

$$H_{0\mu}^\downarrow = \sum_{PQ} E_{Q0}^{P0} \otimes \sqrt{\frac{|\mathbf{F}^P|}{|\mathbf{F}^Q|}} \mathbf{F}^P(\gamma^{P\mu}) H_{PQ}^\mu, \quad (13)$$

$$H_{PQ}^\mu = \sum_p \chi_{Q0}^{Pp} \otimes d^P(\bar{z}_p^P) h_{Q0}^{Pp} \otimes D^{(\mu^*)}(\bar{z}_p^P).$$

The block H_{PQ}^μ describes interaction of the whole orbit P with the orbit representative r_0^Q ; hence, the sum takes into account only the atoms from r_p^P within radius of interaction of r_0^Q .

This finalizes the prescription: for each irreducible representation the eigenproblem of $H_{0\mu}^\downarrow$ is to be solved in the range of the projectors (12) (commuting with $H_{0\mu}^\downarrow$). As in the range of the partial isometry, the eigenvalues coincide, while the eigenvectors are related by Z^μ . Hence, the whole problem is solved in the finite dimensional symcell space, with help of the stabilizer projectors. Besides the obvious technical advantages, the method can be used to find out the independent interaction parameters, which is essential in building relevant models for complex systems.

4 Symmetry of the DNA Model

Double helix of deoxyribonucleic acid (DNA) molecule, the backbone, is formed of two helical chains composed of alternating 5-carbon sugar (deoxyribose) and phosphate group, and the pairs of bases, adenine (A), guanine (G), cytosine (C) and thymine (T), inside of the double-helix, which are, via glycosidic bonds, connected to the deoxyribose, stabilizing the whole structure. As suggested by Watson and Crick in 1953 [5], the most abundant type of the DNA molecule in nature is of the B-helix form, i.e right-handed with ten pairs of nucleotides per turn and translational period of 3.4 nm. Such a molecule is complex enough for precise numerical calculations, and in order to illustrate the application of the symmetry, here we simplify the B-DNA molecule, considering the model which preserves the symmetry and some of the basic structural properties.

As for the bases (adenine pairs with thymine, and guanine pairs with cytosine), although their positions follow the helical regularity, the sequence of the TA and GC pairs is inherently irregular and represents the most important property of the DNA molecule for its

biological function. Nevertheless, the bases are mutually physically very similar (AT and GC pairs differ in mass and geometry up to 6%), and neither the overall geometrical structure, nor many of the physical and chemical properties of DNA depend on the specific code which the DNA sequence carries. Also, the generic engineering as well as some natural processes show that substitution of the one pair of the bases by another is possible and does not influence the global biochemical characteristics and primary function of the DNA in a living cell. Thus, insight into the properties of DNA can be obtained considering the model consisting of only one pair of bases, which can be taken as the first approximation, improvement of which would be consideration of the model of the DNA molecule with a particular regular arrangements of the both pairs of bases. Further improvement would be taking a random average over a large set of different DNA-models of the latter type. Finally, DNA is in general very long molecule, allowing to be well approximated by the infinite structure generated by the helical line group.

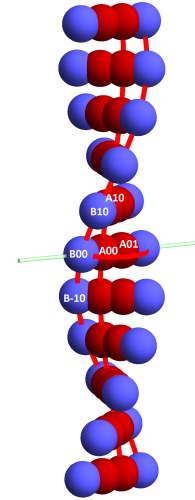


Figure 1: Model: interior and outer helices correspond to basic and backbone units. The units at r_{ts}^P interacting with the symcell units are indicted as Pts (e.g. the orbit representatives are A00 and B00).

Accordingly, the DNA model considered here (Figure 1) has the symmetry of 5th line group family $L^{(5)} = T_Q(f)D_2$ and consists of two orbits: each basis is considered as a single unit A, while the other unit B generates the backbone [6]. The group generators are $\ell_1 = (C_Q|f)$ (rotation for $2\pi/Q$ around z -axis is followed by translation for f along it), $\ell_2 = (C_n|0)$ (rotation for $2\pi/n$ around z -axis), $\ell_3 = (U|0)$ (rotation for π around x -axis) and the group elements are $\ell_{tsu} = \ell_1^t \ell_2^s \ell_3^u$, where $t = 0, \pm 1, \dots$; $s = 0, \dots, -1$; $u = 0, 1$. The double-helix structure (accompanied by

the bases pairing) imposes $n = 2$, while the parameter Q of the helical group can take different (continuously many) values, allowing to accommodate to the variety of the structural forms of DNA. In a case of the B-DNA helix, Q approximately equals ten (namely, there are several close values reported [7]), i.e. in a good approximation ten turns makes a single pure translation (irrational value of Q defines incommensurate structure, lacking the translational periodicity).

The orbit representative units A and B, exhausting the symcell, are taken to be along the x -axis: $\mathbf{r}_0^P = (x_P, 0, 0)$ ($P = A, B$). Their stabilizers are $\mathbf{F}^A = \mathbf{F}^B = \{e, U\}$; the both orbits (bases and backbone) are generated by the same transversal $\mathbf{Z}^A = \mathbf{Z}^B = \mathbf{L}^{(1)} = \mathbf{T}_Q(f)\mathbf{C}_2$, with elements $\ell_{ts} = \ell_{ts0}$ forming a subgroup (from the first line groups family) of $\mathbf{L}^{(5)}$. Hence, the general position of the base and backbone unit is $\mathbf{r}_{ts}^P = \ell_{ts}\mathbf{r}_0^P$.

The choice of orbitals spanning the space \mathcal{S}_p^P is arbitrary in this context, since the model is built out of the units being not the atoms, but the radicals. Therefore, the constraints are imposed by the symmetry solely, through a requirement that the orbit representative interior spaces are invariant under the action of the stabilizer, the only nontrivial element of which is the rotation U . In the irreducible representation of the weight l of the rotational group the matrix of U in the standard basis $|l, m\rangle$ ($m = l, \dots, -l$) is $D^{(l)}(U) = (-1)^l o_{2l+1}$, where o_n is n -dimensional off-diagonal unit matrix. Obviously, one-dimensional invariant subspaces of this matrix are $V_{m+}^l = \text{Span}(|l, m\rangle + |l, -m\rangle)$ ($m = 0, \dots, l$), $V_{m-}^l = \text{Span}(|l, m\rangle - |l, -m\rangle)$ ($m = 1, \dots, l$). In each of the subspaces $V_{m\pm}^l$, representation $D^{(l)}(U)$ is reduced to the one-dimensional representation $\pm(-1)^l$. Hence, the invariance is provided by taking any subset of these subspaces. In the simplest model, with single orbital per unit, it can be taken for example $|A; 10\rangle$ and $|B; 10\rangle$ (p^z orbitals), corresponding to the alternating representations of \mathbf{F}^P ($P = A, B$), i.e. $\delta^P(e) = 1$ and $\delta^P(U) = -1$.

There are two types of irreducible representations of LGs [3] and to allow for the possible incommensurability, the more general, helical irreducible representations are used [3]:

$$kA_m^\Pi(\ell_{tsu}) = \Pi^u e^{i(kft+m\frac{2\pi}{n}s)}, \quad (14)$$

$$\tilde{k}E_{\tilde{m}}(\ell_{tsu}) = \begin{pmatrix} e^{i(\tilde{k}tf+\tilde{m}\frac{2\pi}{n}s)} & 0 \\ 0 & e^{-i(\tilde{k}tf+\tilde{m}\frac{2\pi}{n}s)} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \mathbf{1}_2^{\tilde{k}}$$

here, for one-dimensional irreducible representations $k = 0, \frac{\pi}{f}$ with $m = 0, \frac{n}{2}$, $\Pi = \pm 1$, while for the two-dimensional ones $\tilde{k} \in (0, \frac{\pi}{f})$ is accompanied by $\tilde{m} \in (-\frac{n}{2}, \frac{n}{2}]$ (except that \tilde{m} is positive when $\tilde{k} = 0, \pi/f$).

5 DNA Model Dynamics

Very well justified nearest neighbor approximation is applied. Namely, as long-range interaction between the monomers of the DNA would induce a particular long range order in the DNA chain, preventing the well known almost free interchange between the basic pairs, the approximation used is perfectly natural. The first neighbors (given in terms of the transversal elements) of \mathbf{r}_0^A are $\mathcal{N}_A = \{\mathbf{r}_{10}^A, \mathbf{r}_{-10}^A, \mathbf{r}_{01}^A, \mathbf{r}_0^B\}$, while the neighbors of \mathbf{r}_0^B are $\mathcal{N}_B = \{\mathbf{r}_0^A, \mathbf{r}_{10}^B, \mathbf{r}_{-10}^B\}$. According to the above theory, the relevant Hamiltonian blocks are one-dimensional, $h_{Q0}^{P,ts}$, where for each Q , the neighbors of \mathbf{r}_0^Q from the orbit P (intersection of \mathcal{N}_Q and the P -th orbit) are counted by indices t and s . The constraints (11) (commutativity of the Hamiltonian with the group elements), as well as the fact that Hamiltonian is a Hermitean operator, impose functional relations between interaction parameters $h_{Q0}^{P,ts}$: the action of ℓ_{-100} implies $h_{P,00}^{P,10} = h_{P,-10}^{P,00} = (h_{P,00}^{P,-10})^*$ and $h_{A,00}^{B,00} = (h_{B,00}^{A,00})^*$; also, $(h_{P,00}^{P,01})^* = h_{P,01}^{P,00} = h_{P,00}^{P,01}$ due to the invariance under ℓ_{010} . This leaves one complex ($h_{A00}^{B,00}$) and five real parameters ($h_{A00}^{A,01}, h_{A00}^{A,00}, h_{B00}^{B,00}, h_{A00}^{A,10}, h_{B00}^{B,10}$) which define the dynamics. If it is not assumed that the orbitals associated to the different units are mutually orthogonal, then the overlap matrix S is defined by the four complex parameters: $S_{A00}^{A,10}, S_{A00}^{A,01}, S_{A00}^{B,00}, S_{B00}^{B,10}$.

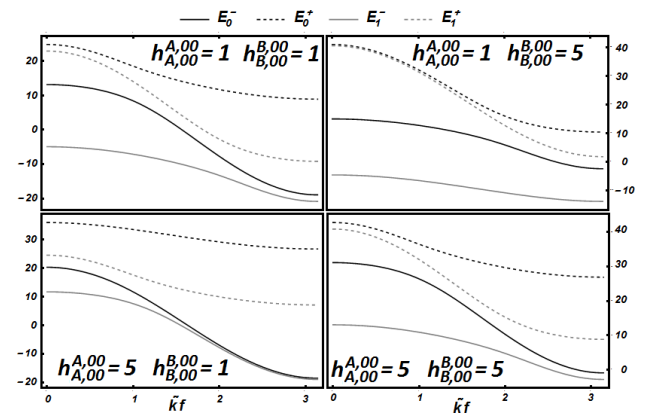


Figure 2: Energy bands of the model. Different panels correspond to the indicated combinations of values of the interaction parameters $h_{A,00}^{A,00}$ and $h_{B,00}^{B,00}$. The other parameters are introduced in the text.

Now we apply Theorem 1 for two-dimensional irreducible representations (14). The modified group projector of the stabilizer is $\mathbf{F}_{\tilde{k},\tilde{m}}^P = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$ and the pulled-down hamiltonian is four-dimensional,

consisting of the two-dimensional blocks H_Q^P :

$$H_{0;\tilde{k}\tilde{m}}^\downarrow = \begin{pmatrix} H_A^A & H_B^A \\ H_A^B & H_B^B \end{pmatrix} = \begin{pmatrix} \chi_A^A & \chi_B^A \\ (\chi_B^A)^* & \chi_B^B \end{pmatrix} \otimes \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (6)$$

$$\chi_A^A = \frac{1}{2}(h_{A,00}^{A,00} + e^{i\pi\tilde{m}}h_{A,00}^{A,01} + e^{i\tilde{k}f}h_{A,00}^{A,10}) \quad (17)$$

$$\chi_A^B = (\chi_B^A)^* = \frac{1}{2}h_{A,00}^{B,00}, \quad (18)$$

$$\chi_B^B = \frac{1}{2}(h_{B,00}^{B,00} + e^{i\tilde{k}f}h_{B,00}^{B,10}). \quad (19)$$

The eigenvalues are given as energy bands $\varepsilon_{\tilde{m}}(\mathbf{k})$, which are parameterized by the mean values and differences of the intra-orbit interaction, $\frac{1}{2}(h_{A,00}^{A,ts} \pm h_{B,00}^{B,ts})$, and inter-bases and base-backbone contributions. Namely, introducing

$$\begin{aligned} \chi_{\tilde{m}}^\pm(\tilde{k}) &= \frac{1}{2}h_{A,00}^{A,01} \cos(\tilde{m}\pi) + \frac{1}{2}(h_{A,00}^{A,00} \pm h_{B,00}^{B,00}) \\ &+ \cos(\tilde{k}f)(h_{A,00}^{A,10} \pm h_{B,00}^{B,10}), \end{aligned} \quad (20)$$

the following expressions for the energy bands are obtained:

$$\varepsilon_{\tilde{m}}^\pm(\tilde{k}) = \chi_{\tilde{m}}^+(\tilde{k}) \pm \sqrt{|h_{A,00}^{B,00}|^2 + \chi_{\tilde{m}}^{-2}(\tilde{k})}. \quad (21)$$

In order to get a physical insight, we estimate roughly the relative magnitudes of the interaction parameters. As the pairs of bases are unique, while backbone structure and nesting of the bases unit within it are DNA type independent, we assume that parameters $h_{A,00}^{A,01}$, $h_{B,00}^{B,10}$ and $h_{A,00}^{B,00}$ are considerably larger than $h_{A,00}^{A,10}$, enabling somewhat arbitrary order of the bases pairs. The results are illustrated in Fig. 2, where to the latter parameter the value of one arbitrary unit is assigned, while to the each element of the former set of parameters the five arbitrary units are ascribed. The remaining parameters are self-energies of the isolated radicals.

6 Conclusion

Modified group projectors method [2], which generalizes the Bloch theorem (from the translational to arbitrary symmetry group) is applied to a simplified model of DNA molecule. Such an application illustrates that the method is theoretically maximally efficient as the full symmetry of the system is employed to reduce the eigenproblem of the Hamiltonian into the subspace of the symcell, in order to diagonalize it in a maximally efficient way (in some cases even analytically). Besides, the relevant set of dynamical parameters is automatically obtained, which enables direct analyses

of the considered physical, chemical and biological properties. The presented procedure is suitable for direct numerical implementation and it has been incorporated into the numerical code *POLSym* [8].

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