The Jahn-Teller and pseudo Jahn-Teller effect in materials science

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Abstract. Defining materials science as a translation from microscopic foundations of matter to macroscopic performance in applications, this mostly review paper is devoted to the special features of matter with Jahn-Teller (JT) and pseudo JT (PJT) centers that makes it outstanding in the search of novel properties and applications as novel materials. There are three kinds of problems in this respect. The first is related to the difficulties in the use of computer simulation of observable properties (a methodology widely employed in materials science) in application to systems with dynamic JT and PJT effects. The second is due to the specifics of such systems in interaction with external perturbations, which contribute with a strong orientational effect that enhances the observable properties by orders of magnitude. The third kind of problems relevant to materials science is in the use of the JT and PJT effects in revealing the origin of structural properties of a relevant polyatomic system and working out methods to influence them in designing novel materials.

The paper formulates these problems and provides for examples that demonstrate their importance. For the second group of problems, illustrative examples include flexoelectricity, permittivity, and electrostriction in systems with dynamical JT and PJT centers, and it is shown that the latter enhance the observable properties by several orders of magnitude. Also related to this group of problems are the magnetic-dielectric bistabilities in molecular systems and solids induced by JT and PJT effect, illustrated on molecules like CuF$_3$ and crystals of the type LiCuO$_2$. The third group of problems is shown by the already multiply used application of the PJTE to reveal the origin of distortions of planar configuration in 2D (graphene-like) and quasi-2D materials and to work out methods of restoration of their planar configurations by means of external perturbations.

1. An open problem for materials simulation: density functional theory (DFT) does not take into account local JT and PJT dynamics

One of the most important features of polyatomic systems with a JT effect (JTE) or pseudo JTE (PJTE) is the very strong vibronic coupling between the electronic cloud and nuclear motions that does not allow to fully separate their coordinates in the adiabatic approximation (see [1-3] and references therein). For a visible example, consider a polyatomic formation in a degenerate or pseudodegenerate state for which the adiabatic potential energy surface (APES) has several or an infinite number of equivalent minima induced by the JTE or PJTE. The stationary states of such a
system can be presented as a linear combination of the states in the minima, each of which is a product of local electronic and nuclear-vibrational functions, and there is no way to separate their electronic and nuclear coordinates in the total wavefunction. For systems without such dynamic JT or PJT centers the modern computer simulation methods rely heavily on electronic structure calculations based on density-functional theory (DFT) (see, e.g., [4-7]). However, the existing DFT methods do not include the nuclear motions of the disordered distortions produced by the centers with independent dynamic JTE or PJTE (before the phase transition to the cooperative JT phase). In a paper of 1997 [8] we have outlined the difficulties of the DFT in application to degenerate and pseudodegenerate states. The main assumption of DFT is that the electron-nuclear V(q, Q) and nuclear-nuclear V''(Q) interactions, V(q, Q) = V'(q, Q) + V''(Q), where q and Q stand for all the electron and nuclear coordinates, respectively, may be regarded as an "external potential" to the electronic subsystem of the polyatomic system. Under this assumption, the Hohenberg-Kohn (HK) theorem [4] establishes a one-to-one correspondence between the electronic density σ of the ground state and the potential V, and hence between σ and the energies and wavefunctions of the Hamiltonian H, since the latter is determined by V and the number of electrons which enter σ by normalization. In the original HK theorem the ground state of the system is assumed to be non-degenerate. This limitation has been formally removed by the Levy-Lieb constraint search formulation [6] in which the density σ is that of one of the degenerate states, provided the main assumption remains valid.

However, it seems unlikely that the Schrodinger wavefunction contains waste information. This means that the description by multidimensional functions can hardly be reduced to the 3-D case without loss of information about the system. As stated by N. March (private communication) this loss of information is intentional: if properly managed, it simplifies the calculations without loss of accuracy for some particular results. Then one must know explicitly what kind of information is lost and how it influences the DFT and the limits of its applicability. In both degenerate and pseudodegenerate cases with sufficiently strong vibronic coupling, any DFT formulation of the problem, at least in the form of the DFT known so far, is impossible because, as mentioned above, in these cases the wavefunction is non-multiplicative with regard to the electronic and nuclear subsystems. In such situations the Born-Oppenheimer adiabatic approximation is violated, the assumption of electrons moving in the field of a fixed configuration of the nuclei does not hold, and the basic assumption of DFT that the electron-nuclear and nuclear-nuclear interactions V(q,Q) can be regarded as an external perturbation to the electronic density is inapplicable [8].

Essential improvements in the DFT and applications to systems without JT and PJT centers were achieved in the last two decades (see [9-12] and references therein), but the degeneracy and pseudodegeneracy problem resulting in nonadiabaticity and inseparability of the electronic and nuclear motions was not properly countered and not solved. For example, in one of the latest contributions to the extension of the DFT that is aimed at improving materials simulation [10] the electronic density and related properties of solids are considered as a function of the (fixed) nuclear framework, in a way that any changes in the latter as a whole (phase transitions, ferroelectricity, etc.) can be taken into account in the electronic density. However, again, the electronic and nuclear motions are separated in this approach, and the nonadiabaticity in the local JTE and PJTE independent (non-cooperative!) dynamic distortions is fully ignored (the same problem remains in Ref. [11] in which the nuclear coordinates are incorporated in a DFT scheme). In the Levy-Lieb constraint search formulation [6] all the f electronic densities of the f-fold degenerate state can be defined, in principle, for fixed nuclear configurations. Distinct from the nondegenerate state for f=1, these electronic densities in the ensemble density matrix have no independent physical meaning, they are not observable, and separately they do not determine the charge distribution and energy spectrum of the system. Note that the same is true for the wavefunctions and eigenvalues of a degenerate state obtained for fixed nuclei. Again, the point is here in the inseparability of the electronic and nuclear coordinates. In another recent improvement of DFT calculation [12], which combines the basic DFT with elements of Coupled Cluster methods, more accurate numerical results of electronic structure calculations with
fixed nuclei were achieved, but the nuclear motion problem and nonadiabacity are even not mentioned. They are not mentioned also in the otherwise inclusive review article [9].

In the next Section we show where and why is the inseparable nuclear dynamics important in description of the properties of matter relevant to materials science.

2. In interaction with external perturbations dynamic JT and PJT effects enhance observable properties by several orders of magnitude

Interactions of polyatomic systems with external perturbations are well studied and documented in many original publications and textbooks. For dielectric systems, very important are their properties in external electric fields and under strain, in particular, permittivity, flexoelectricity, electrostriction, and structural phase transitions under pressure. Many theoretical investigations are devoted to these properties (see, e.g., [13] and references therein). These works are based on the theoretical fundament of the adiabatic approximation, which separates electronic and nuclear motions, assuming that nonadiabatic effects in such systems are negligible. As stated above, this assumption does not hold in some specific, but very important situations of the JTE and PJTE that lead to spontaneous symmetry breaking (SSB) [1-3]. In the presence of these effects the electronic and nuclear motions are not fully separated, the electronic states are mixed by nuclear displacements, and hence the adiabatic approximation is violated. Another misperception is that in the absence of electronic degeneracy the PJTE may occur only when the energy gap \( \Delta \) to the exited state is small. In fact, the criterion of occurrence of this effect includes three parameters (see below), among which the energy gap \( \Delta \) between the interacting electronic states may be very large (there are cases of PJTE instability at \( \Delta \sim 14 \) eV [14]). Since the JTE and PJTE are essentially of local origin, they strongly depend on the local electronic (atomic) structure and vibronic coupling constants. The majority of papers on dielectric properties do not take into account these nonadiabatic vibronic coupling effects. Note that the PJT mixing of electronic states with differing symmetries makes them dependent on nuclear displacements with appropriate symmetry, and hence it is essentially different from orbital hybridization, which takes place without nuclear displacements.

In polyatomic systems with JT and PJT centers, in the absence of external perturbations and/or strong interaction between the centers the distortions at each center are independent from the others, and they locally resonate between the equivalent minima by means of tunnelling or over-the-barrier transitions. In such dynamic systems the quantum-mechanically averaged expectation values of observables are that of unbroken high symmetry. In the presence of lower symmetry perturbations the possibility to reveal the SSB in such systems is time and frequency dependent, and hence directly related to the methods of observation [3]. Denote the (temperature dependent) “lifetime” of the system in the minimum of the APES by \( \tau = 2\pi/\omega_0 \), where \( \hbar \omega_0=\delta_0 \) is the splitting of the vibrational levels in the minima due to the tunneling between them, and the “time of measurement” of the specific method of observation by \( \tau' = 2\pi/\omega_p \), where \( \omega_p \) is the characteristic frequency of the perturbation influence. Distorted configurations can be revealed only if \( \tau' < \tau \), while for \( \tau' > \tau \) the system is seen averaged over the equivalent minima with unbroken high symmetry.

Consider the properties of dielectric polyatomic systems with dynamic JT or PJT centers (finite \( \tau \) values) under external perturbations with either \( \tau' \to \infty \) (constant electric field or strain), or \( \tau' > \tau \) (low-frequency field or strain), for which the SSB is not revealed explicitly: the system is seen as averaged, totally symmetric with regard to such perturbations. Dielectric polyatomic formations with a JTE or PJTE in any high-symmetry environment without strong cooperative interactions (in solids, at temperatures above structural phase transitions) are systems with finite \( \tau \) values. In these cases the JTE and PJTE effects induce observable properties by several orders of magnitude [15, 16]. This statement is illustrated below by estimates of polarization, permittivity, and striction in electric fields, and flexoelectricity under strain gradients.

The statement of several orders of magnitude larger properties induced by the dynamic JTE or PJTE is very strong and requires background explanation. For clarity, consider an illustrative example,
dielectric polarization of a liquid with dipolar molecules, e.g., water. According to the classical Debye theory the permittivity \( \varepsilon \) in this case follows the well-known equation:

\[
\varepsilon = \varepsilon_0 \left[ 1 + \frac{X_d}{1 + (\alpha_p \tau_d)^2} + \frac{X_o}{1 + (\alpha_p \tau_o)^2} \right] 
\]

(1)

where \( X_d \) and \( X_o \) are the displacive and orientational dielectric susceptibilities, respectively, \( \tau_d \) and \( \tau_o \) are the relaxation times in the corresponding processes, \( \alpha_p \) is the perturbation frequency, and \( \varepsilon_0 \) is the permittivity of vacuum. The orientational contribution to the polarization is always much larger than the displacive one (in water \( X_o = 72, X_d = 5 \)). This is quite understandable: it is much easier to rotate a ready-made dipole than to polarize a stable polyatomic formation. The **enhanced properties in systems with dynamic JTE or PJTE are due to the orientational contribution, which is not there without these effects.** In systems with multiminimum APES streaming from the SSB in the high-symmetry configuration, any external perturbation of lower symmetry makes the minima non-equivalent and stops the tunnelings between some of them, locking the system in a broken symmetry configuration. This process is similar to (but easier than) rotating (orienting) a rigid dipole along the equivalent and stops the tunnelings between some of them, locking the system in a broken symmetry configuration.

Consider the PJTE in the paraelectric phase of BaTiO\(_3\) [17, 18]. Very briefly, in cluster language for TiO\(_6\)\(^{8-}\), the PJTE emerges from the (nonadiabatic) mixing of the ground state A\(_{1g}\) formed by the fully occupied t\(_{1u}\) combinations of oxygen atomic 2\(p\) states, with the excited state T\(_{1u}\) (produced by one-electron (t\(_{1u}\) \(\rightarrow\) t\(_{2g}\)) excitations to the three empty 3\(d\) (t\(_{2g}\)) states of the Ti\(^{4+}\) ion) by the polar t\(_{1u}\) type normal coordinates \( Q_o, Q_x, \) and \( Q_z \). The numerical results below were obtained recently [18] by the Green’s functions method taking into account the interaction of the Ti ion with the whole crystal via its electronic and vibrational bands. With the linear vibronic coupling terms included, the solution of the secular equation of this \((A_{1g} + T_{1u}) \otimes t_{1u}\) problem yields the following APES [17, 18] \((Q^2 = Q_x^2 + Q_y^2 + Q_z^2)\):

\[
U(Q) = \frac{1}{2} K_0 Q^2 - 2 \sqrt{\Delta^2 + 2F^2 (Q^2 - Q_x^2)} + \sqrt{\Delta^2 + 2F^2 (Q^2 - Q_y^2)} + \sqrt{\Delta^2 + 2F^2 (Q^2 - Q_z^2)}
\]

(2)

where \( \Delta \) is the energy gap between the mixing electronic states (appropriately band-averaged in the Green’s functions approach [18]), \( K_0 \) is the primary force constant for the \( Q \) displacements (stiffness of the crystal without the vibronic coupling), and \( F \) is the vibronic coupling constant \((H \text{ is the Hamiltonian})\),

\[
F = \langle 2p z(0) \left| \frac{\partial H}{\partial Q_x} \right| 3d_{xz}(\text{Ti}) \rangle
\]

(3)

The three-dimensional APES (2) has a specific form. Under the condition

\[
\Delta < 8F^2/K_0
\]

(4)

the surface (2) has a maximum (meaning instability) when the Ti ion is in the center of the octahedron, eight equivalent minima placed along the four trigonal axes in which the Ti ion is displaced toward three oxygen ions (away from the other three); higher-in-energy 12 equivalent saddle points along the six \( C_{2v} \) axes at which the Ti ion is displaced toward two oxygen ions (at the top of the lowest barrier between two near-neighbor minima); and next six higher-in-energy equivalent saddle points at which the Ti ion is displaced to one of the oxygen ions along the fourfold axes [17]. For BaTiO\(_3\) the vibronic coupling parameters were estimated using the Green’s functions description [18] and two experimentally determined structural constants: the energy gap \( 2\Delta = 2.8 \text{ eV} \) and the vibrational frequency at the bottom of the trigonal minimum \( h\omega_e = 193\text{cm}^{-1} \). With these data all the essential
parameters were estimated (table 1), including $K_0$, $F$, the positions of the minima $Q_x=Q_y=Q_z=0$, and first saddle points $Q_x=Q_y=Q_z=0$, their PJTE stabilization energies, and the tunnelling splitting $\delta_0$.

**Table 1.** Numerical values of the PJTE vibronic coupling and APES parameters of the Ti active centers in the BaTiO$_3$ crystal [18].

| $K_0$  | $2\Delta$  | $F$   | $h\omega_0$ | $Q_0$  | $q_0$  | $E_{JT}[111]$ | $E_{JT}[110]$ | $\delta_0$ |
|--------|-------------|-------|-------------|--------|--------|----------------|----------------|-----------|
| 55eV/Å$^2$ | 2.8 eV   | 3.42eV/Å | 193 cm$^{-1}$ | 0.14 Å | 0.16 Å | -1250 cm$^{-1}$ | -1130 cm$^{-1}$ | 34 cm$^{-1}$ |

The four phases of BaTiO$_3$ emerge directly from this APES by gradually populating the states in the minima with temperature and stepwise overcoming its barriers [17, 19]. Of particular interest here is the prediction of disorder in the orthorhombic and tetragonal ferroelectric phases and in the cubic paraelectric phase. It was confirmed later together with a variety of other predictions of the theory that have no explanation in displacive theories (see in [17, 18]). The basic experimental conclusions is that in all the phases the Ti ion is instantly displaced in the trigonal direction in disagreement with displacive theories in which the metal off-center displacement occurs as a result of the phase transition to the ferroelectric phases. This was confirmed directly by a variety of experimental methods, noticeable diffuse X-ray scattering [20], EXAFS [21], ESR [22], NMR [23], neutron scattering [24], light refraction [25], etc. Not only is the Ti ion displaced along the [111] type direction in the paraelectric phase where the averaged symmetry is cubic, but it is as well displaced in this trigonal direction in the tetragonal phase where the crystal symmetry and the macroscopic polarization are tetragonal [24].

The order of magnitude of the tunnelling frequency was estimated in ESR experiments with probing ions by substituting Ti$^{4+}$ with the Mn$^{2+}$ ion which produces a very similar APES [22] (Mn$^{2+}$ is a “ferroelectric” ion [26]) yielding $10^{-9} > \tau > 10^{-10}$. It is also seen indirectly by EXAFS [21] and NMR [23] experiments: in the former $\tau' \sim 10^{-15}$, and the Ti ion is seen in the trigonal minima in all the phases of BaTiO$_3$, while in NMR experiments $\tau' \sim 10^{-8}$, and only an averaged picture is revealed. The vibronic coupling theory was extended recently to formulate the necessary condition of coexisting magnetic and ferroelectric (multiferroicity) properties in ABO$_3$ perovskite crystals with B as a transition metal ion in a $d^0$ configuration, $n=1, 2, \ldots 10$ [26], that found already confirmation in experiments [27, 28] and ab initio calculations.

In the paraelectric phase of BaTiO$_3$ the Ti ions are displaced in the trigonal minima, but in the macroscopic picture the crystal is cubic and centrosymmetric because of their noted tunnelings and over-the-barrier transitions. Perturbations of lower symmetry make the PJTE minima non-equivalent, thus terminating a part or all the tunnelings. If the perturbation is a homogeneous electric field $E$ directed along the trigonal axis, it has the same direction for all the unit cells leading to the polarization of the crystal in this direction. We assume that the polar distortions become fully oriented when the energy difference between two opposite minima of the APES $\Delta E$ reaches the order of magnitude of the tunnelling splitting, $\Delta E=k\delta_0$, where $k$ is a numerical coefficient, $k \leq 1$. Since $\Delta E=2d_0E$, where $d_0$ is the dipole moment of the unit cell when the Ti ion is locked in one of the minima, in the electric field $E_m=kd_0/2d_0$ all the Ti ions are displaced along the same trigonal direction, and the polarization of the crystal in this direction is $P=kd_0\lambda^3$, where $\lambda$ is the unit cell constant. Hence for the orientational dielectric susceptibility $\chi_o$ in the relation $P_o=\chi_oE$ up to $E=E_m$ we get:

$$\chi_o=2d_0^2/k\lambda^3\delta_0$$  \hspace{1cm} (5)

The data for the BaTiO$_3$ crystal in table 1 allow us to estimate the numerical value of the susceptibility and permittivity. Under the conditions $\tau' \rightarrow \infty$ or $\tau' > \tau$, outlined above, $\epsilon/\epsilon_0 \approx 1 + \chi_o + \chi_T$, and in all the cases below $\chi_o > \chi_T$ we have: $d_0=|e|Z^*\sqrt{3}Q_0$, where $Z^* \approx 7.8$ is the effective (Born) charge of the Ti ion [18], and in the limits of the coefficient $k=0.1 \leftrightarrow 1.0$ we get for the orientational dielectric
susceptibility of the BaTiO$_3$ crystal $\chi_d=0.45 \times 10^3 \leftrightarrow 0.45 \times 10^3$. This agrees well by orders of magnitude with experimental measurements of permittivity in this system (see, e.g., [29, 30]). On the other hand, ignoring the PJTE, the polarization of the unit cell $P_0$ is limited by its stiffness $K_0$ with respect to the polar distortions along the above normal coordinate $Q$. Hence the electric force $2|e|Z*E$ producing the dipole moment $|e|Z*Q$ is compensated by the elastic force $K_0Q$. Thus $2|e|Z*E=K_0Q$ and $P_0=|e|Z*Q/a^3=\chi_dE$, which leads us to the expression: $\chi_d=2(eZ*)^2/a^4K_0$. Using the same numerical values as above and the $K_0$ value from table 1 we get the following estimate: $\chi_d=1.22$. This yields a typical value expected for permittivity in systems without orientational contribution. Compared with the value $\chi_d=0.45 \times 10^3$ $0.45 \times 10^3$, obtained above, we see that by taking into account the PJTE the permittivity of BaTiO$_3$ increases by more than three orders of magnitude.

In fact the whole permittivity in the field $E$ up to the orientational saturation at $E=E_{sw}$ is of PJTE origin, acquiring a less-significant displacive-only addition in higher fields. The value of $E_{sw}$ can be estimated from the above expression $E_{sw}=k\delta_d/2a^3$. For BaTiO$_3$ $E_{sw}=k\times 1.15 \times 10^3$ V/m. It follows that up to this voltage the permittivity is strongly enhanced by the orientational contribution of the dynamic PJTE, reaching the value of polarization $P= d_0/a^3 \approx 0.47$ Cm$^{-2}$ which coincides approximately with that of the ferroelectric phase. Very similar to BaTiO$_3$ are the expected properties of KNbO$_3$ perovskites; the NbO$_6$ centers have a qualitatively similar to the TiO$_6$ PJTE polar instability producing local dipole moments (BaTiO$_3$ and KNbO$_3$ were the first two crystals in which the order-disorder nature of the phase transitions predicted in [17] was observed by X-ray diffuse scattering [20]; see also [31]).

Since the tunnelling splitting is temperature dependent, the permittivity will be temperature dependent too, especially near the phase transition to the tetragonal phase. In a more elaborate investigation of the induced by the PJTE orientational contribution to the permittivity of perovskite ABO$_3$ crystals [32], its temperature dependence was revealed, and it was also shown that the permittivity in this case has a cubic anisotropy with maximum values along the trigonal axes. This anisotropy is unexpected in cubic crystals without the PJTE.

As mentioned above, polyatomic formations with trigonal symmetry may have multiminimum APES with dipolar distortions in the minima, and such dielectric systems in gas, liquid and solid state are vast. For instance, there is a whole class of molecular systems with a typical hidden PJTE [33] producing equivalent distorted configurations with nonzero dipole moments, and hence an expected giant permittivity in the regime of the dynamic effect. As an example, in CuF$_3$ the resonating dipole moment $d_0=1.67$ D [33], and this molecule is notable also by its possessing bistability properties, namely, coexistence of the dipole equilibrium configuration with $d_0=1.67$ D, but no magnetic moment, $\mu=0$ (electronic $1A$ state), with a slightly higher in energy undistorted $D_{3h}$ one in the electronic state $3A$ that has no dipole moment, $d_0=0$, but a nonzero magnetic moment $\mu=1.82 \mu_B$ [33] (see Section 3 below). Another class of molecular systems and solids with expected enhanced permittivity is presented by tetrahedral molecular formations and solid states with tetrahedral AX$_4$ or X$_4$ unit in an electronic $T$ state, in which the JTE creates four equivalent polar configurations with one long and three shorter $A-X$ bonds [1] (examples see, e.g., in [1], Chs. 7, 8). Note, however, that the JTE distortions and hence all expected observable properties based on their dynamic nature are, in general, smaller in tetrahedral systems as compared with octahedral systems or with some PJTE systems.

In line with permittivity is flexoelectricity where the polarization of a centrosymmetric dielectric crystal is induced by a strain gradient instead of the electric field. All theoretical estimates (without involving JTE or PJTE) show that the flexoelectric coefficient $f$ (the component of the tensor of proportionality between the polarization $P$ and strain gradient $G$ in one-dimensional models, $P=\gamma(G)$, is rather small, of the order of nCm$^{-1}$[34-36], whereas the experimental measurements for some systems yield several orders of magnitude larger values [37-40]. The biggest flexoelectric coefficient $f$ occurs in the paraelectric phase of BaTiO$_3$, and it is, in general, approximately proportional to the permittivity of the system. This is quite understandable: both dielectric and flexoelectric polarization
in the presence of dynamic JTE or PJTE are produced by the same orientational contribution of the local dipolar distortions trapped in the direction of the external perturbation.

For the paraelectric BaTiO$_3$ with the strain gradient $G$ along the trigonal direction, similar to the considered above dielectric polarization, we assume that the tunnelling between the dipolar minima of the APES is suppressed when the energy difference between the opposite minima induced by the strain gradient $\Delta_e=2gG$ (where $g=dA/dG$ with $A$ as the strain energy) is of the order of magnitude of the tunnelling splitting, $\Delta_e=k\delta_0$ with $k\leq1$. For the strain gradient we have: $G=(dS/dx)\sim\Delta S/a$, where $S$ is the unit cell strain, $\Delta S=Q/a$, where $Q$ is the introduced above normal coordinate of the dipolar distortion of the unit cell along the (opposite to strain) trigonal direction, and $G=Q/a^2$. Then for the strain energy we have: $A=(1/2)K_0Q^2=(1/2)K_0a^4G^2$, where $K_0$ is the stiffness in the $Q$ direction, and $g=dA/dG=K_0a^4G$. Putting together these formulas we find that the strain gradient $|G_m|= (k\delta_0/2K_0a^4)^{1/2}$ restores the dipole moment of the unit cell $d_0$, and hence the polarization of the crystal $P=-d_0/ja^4$ along the trigonal direction. It follows that the flexoelectric coefficient $f=P/G_m$ is:

$$f\approx -(d_0/a)(2K_0/k\delta_0)^{1/2}$$ (6)

With the same numerical values of the parameters, employed above, we get the following estimate: $f \approx -(0.43 \cdot 10^{-6} \div 0.43 \cdot 10^{-5})$ Cm$^{-1}$. Thus instead of (and in addition to) producing a polar charge redistribution in a rigid cubic crystal of the order of nCm$^{-1}$ the strain gradient in the paraelectric phase of a PJTE ferroelectric just recovers the virtual local dipole moments (suppresses their dynamical averaging) inducing the ferroelectric polarization of the order of $\mu$Cm$^{-1}$. This removes the main controversy in the theory of flexoelectricity explaining the origin of the 3-4 orders of magnitude larger flexoelectric coefficient $f$ in paraelectric BaTiO$_3$ as compared with systems without the PJTE. The enhanced flexoelectricity takes place for $G$ values below $G_m$, at which point the dynamic PJTE is quenched and the orientational contribution to the polarization is maximal; for larger values of $G$ the additions to $f$ are much smaller. The numerical data above yield $|G_m|= (k\delta_0/2K_0a^4)^{1/2} \sim 10^{-4}$ m$^{-1}$.

As the PJTE and JTE are of local origin, the enhanced flexoelectric effect takes place everywhere these effects produce local dipolar distortions. The mentioned above similarity between KNbO$_3$ and BaTiO$_3$ explains the origin of the enhanced flexoelectricity in perovskite systems that contain a significant amount of NbO$_3$ centers, e.g., Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ [40] and (Bi$_{1/2}$Zn$_{1/2}$Zn$_{0.5}$Zn$_{0.5}$O$_{12}$)/Ag [41]. The different flexoelectric properties of the two at-face similar crystals, paraelectric BaTiO$_3$ and SrTiO$_3$, find also explanation: the criterion of PJTE polar instability (4) holds well for the Ti center in BaTiO$_3$ (table 1) [18], but it does not hold for the same ion in SrTiO$_3$. The reason of this is straightforward: the size of the Sr$^{2+}$ ion that controls the unit cell dimensions is smaller, and hence, the interatomic Ti–O distance is smaller in the latter case, and this, in turn, leads to larger stiffness and smaller vibronic coupling constant value, both deteriorating the condition of instability [17, 18]. For the same reason, SrTiO$_3$ becomes ferroelectric under negative pressure that increases the Ti–O distance, Ba$_x$Sr$_{1-x}$TiO$_3$ becomes ferroelectric when $x>0.45$ [42], and the nonferroelectric CaMnO$_3$ becomes ferroelectric when Ca is substituted by Ba [43] (as mentioned above, according to the PJTE theory Mn$^{4+}$ is a “ferroelectric” ion [26]). Although not ferroelectric, the SrTiO$_3$ crystal is a virtual ferroelectric: the PJTE in its Ti centers is not strong enough to obey the condition of dipolar instability [17, 18], but it is very near to it, so the criterion of the PJTE instability may be induced by the strain gradient. Indeed, the latter is softening the crystal in at least one direction thus lowering its stiffness, hence allowing dipolar distortion (polarization) in this direction. This explains (qualitatively) the order of magnitude larger flexoelectric coefficient in this crystal [44] as compared with expected in the theory without the PJTE. The assumptions in some publications (e.g., [39, 40]) of possible polar formations in the bulk crystal that are responsible for the enhanced flexoelectricity, in a way resonate (are compatible) with these results. Obviously, many other crystals with dipolar centers of PJTE or JTE origin including organic and biological systems may have similar enhanced flexoelectric properties.
One of the consequences of the orientational origin of the polarization in the enhanced flexoelectricity is in its frequency dependence in case of dynamical strain gradient, e.g., in sonic or ultrasonic perturbations. The mechanism of relaxation of distortions does not depend directly on the perturbation that produces the distortion. This means that the Debye formula (1) for relaxation in dielectrics is applicable also to flexoelectric polarization. As the orientational contribution to the latter is much larger than the displacive one, we can assume that the frequency dependence of the coefficient of flexoelectric polarization follows Eq. (6), which is thus a characteristic equation of frequency dependent flexoelectric piezo-effect. For the paraelectric BaTiO$_3$ system, in the regions where the tunneling frequency is high compared with ultrasound frequencies, the system may serve as a flexoelectric ultrasound transducer.

If the electric field along the trigonal axis of BaTiO$_3$ suppresses the tunnelling between the dipolar minima of the APES trapping all the units of the system in the same kind of trigonal minimum along the whole crystal, the latter will be not only polarized, but also strained in this direction. Similar to permittivity and flexoelectricity, the change in the dimensions of the unit cell in the electric field $E$ (the electrostriction) can be estimated for the BaTiO$_3$ crystal. In fact the electrostriction problem is closely related to the inverse of flexoelectricity: instead of polarization $P$ induced by strain gradient $G$ in flexoelectricity, electrostriction is the strain $S$ (not strain gradient) induced by the polarization. In the one-dimensional model with the electric field and strain along the same trigonal axis of the crystal we have: $S = \gamma P^2$, where $\gamma$ is the coefficient of electrostriction. More convenient is to measure the strain as a function of the $E$. $S = \eta E^2$. At $E_m = (10^6 - 10^7) \text{ Vm}^{-1}$ in the trigonal direction the full orientational ordering of the local unit cell dipoles is reached resulting in the strain $S = Q/a \approx \sqrt{3} Q_a/4 \approx 0.05$. Without the orientational contribution of the dynamic PJTE, from the data above we have: $2|e|Z^*E = K_0 Q$ which at $E = E_m$ yields the strain $S \approx 10^{-5}$, a typical value for a regular ionic crystal. Again, as for permittivity and flexoelectricity, we obtain a giant electrostriction of about three orders of magnitude bigger than that in similar systems without the dynamic PJTE, and this effect is in accord with experimental measurements [45, 46].

3. The JT and PJT effects produce a novel class of molecular and solid state materials with correlated magnetic and dielectric bistability

Molecular systems and solids with two coexisting stable and close-in-energy configurations that exhibit markedly different magnetic and structural properties with controllable conversion between them (bistability) are very attractive for application in electronics as high-density information storage materials and sensor devices [47-52]. So far, the most studied systems with magnetic bistability involve transition metal spin crossover complexes (TMSCC) that are virtually possible in $d^4$-$d^7$ transition metal compounds with octahedral symmetry and $d^3$-$d^7$ in tetrahedral or cubic environment. In these systems the low-spin (LS) to high-spin (HS) transition can be induced by temperature or pressure changes or by light irradiation [51, 52]. The latter case is best suited for information storage devices. However, in spite of almost three decades of study, the lifetime of the metastable state populated after irradiation before its decay to the ground state in these materials is typically [51, 52] a few nanoseconds which is too short for practical application. The decay of the metastable state is strongly dependent on the spin-orbital coupling and the energy barrier between the HS and LS states involving the structural changes in the conformational transformation [51], which in TMSCC is characterized by a metal-ligand distance change of $\sim 0.2 \text{ Å}$. The TMSCC are thus restricted in chemical variety and parameters that influence their properties.

On the other hand, it was shown recently [33] that in molecular systems and solids with at least one threefold (or higher) symmetry axis and a half filled degenerate valence shell (valence orbital configurations $e^2$ or $t'$, where $e$ and $t$ are symmetrized molecular orbitals or analogous states in solids), a similar to the spin-crossover (but richer) bistability effect takes place. According to Hund’s rule the two (in $e^2$) or three (in $t'$) electrons should have parallel spins in the ground state (figure 1a), but in these electronic configurations low-lying low-spin excited states are strongly involved in the formation of the stable configurations via the pseudo Jahn-Teller effect (PJTE) [33]. In many cases the latter
produces an additional low-spin state accompanied by structural distortions, as illustrated in Figure 1b. In fact the PJTE mechanism explains why and how orbital disproportionation and additional covalency lead to the formation of the second stable state [33]. The two equilibrium configurations in this class of polyatomic systems are close in energy, have different spin values (magnetic bistability) and geometries (structural bistability). Both bistabilities are strongly correlated and are switchable by external perturbations.

The general results obtained in [33] were applied to specific systems, and it was shown that the above properties may be indeed observable [53]. The PJTE induced bistabilities have not only much better parameters and lifetimes (by orders of magnitude) than the TMSCC magnetic bistability, but are accompanied by symmetry breaking with changes from non-polar to dipolar or quadrupolar structures (dielectric bistability) (Figure 1). In other words, switching from one magnetic state to the other one in these systems simultaneously changes their dielectric properties. In addition, some of these systems in the solid-state display also strong magnetoelastic and ferroelastic properties, and all these effects can be tuned by means of external perturbations. The vast variety of systems with such properties which have in common a special feature of electronic structure, half-filled degenerate valence shells, form a class of materials which can be termed half-filled–shell (HFS) materials (HFSM). As the number of molecular and solid state systems with $e^2$ and $t^3$ electronic configurations is practically infinite, we thereby suggests an inexhaustible source of materials with bistability properties. Such systems may occur in all aggregate states of matter formed by organic and inorganic, main group and transition metal compounds in all varieties of crystal structures and impurity centers in crystals, as well as in clusters, quantum dots, and thin films.

**Figure 1.** [Illustration to the formation of two coexisting configurations with different magnetic and structural properties: (a) In a typical energy level scheme of the electronic $e^2$ configuration (A) the ground state $^3{A}_2$ is formed by the two electrons with parallel spins, each of them occupying one $e$ orbital, resulting in the $e_0 \uparrow e_0 \downarrow$ configuration which is totally symmetric and does not distort the system; the pictures show examples of planar triangular (e.g., CuF$_3$) and octahedral systems (e.g., the CuO$_6$ units in the LiCuO$_2$ and NaCuO$_2$ crystals considered below) with the $e^2$ configuration which have the high-symmetry geometry in this state; the energy terms of this configuration are shown in (B); (b) In the first excited singlet state $^1{A}_1$ the electron configuration $(1/\sqrt{2})(e_0 \uparrow e_0 \downarrow + e_e \uparrow e_e \downarrow)$ is totally...](figure1.png)
symmetric too, but due to the PJT interaction with the higher \(^1E\) state it undergoes orbital disproportionation resulting in either \(e_g \uparrow e_g \downarrow\) or \(e_g \uparrow e_g \downarrow\), both having a lower symmetry of charge distribution that distorts the systems in the \(e\) mode direction, as shown in the pictures and energy levels \((B)\); (c) Ab initio calculated energy levels of CuF\(_3\) as a function of the angle \(\alpha\) (\(e\) mode distortion) fully confirm the theoretical predictions in \((a)\) and \((b)\). At \(\alpha=120^\circ\) the ground state is a spin-triplet \(^3A_2\) with a magnetic moment of 1.62 \(\mu_B\) and planar, regular-triangular geometry, but due to the strong pseudo Jahn-Teller effect between the lowest two excited spin-singlet states \(^1A_1\) and \(^1E\), the molecule acquires a global minimum at \(\alpha=93^\circ\) in which it is distorted with a dipole moment of 1.67 D, but no magnetic moment (the values of \(B\) and \(\Delta E\) are given in table 2).

The common properties of this class of materials and their origin can be illustrated using the mentioned above CuF\(_3\) molecule as an example. In the high-symmetry configuration this molecule is planar regular triangular with the D\(_{3h}\) symmetry and the electron configuration \(e^2\) (so it is a representative of HFSM). Figure 1c shows the results of ab initio calculations of its ground and excited electronic states as a function of the angle \(\alpha\) (FCuF). We see that when the molecule is an equilateral triangle (\(\alpha=120^\circ\)) the ground state is \(^3A_2\) with the lowest excited states \(^1A_1\) and \(^1E\), which is typical for all electronic \(e^2\) configurations (note, however, that the order of occurrence of the two singlet states may be inverted, in octahedral systems the \(^1E\) level is lower than \(^1A_1\), but this does not alter the general conclusions). The spin-triplet ground state \(^3A_2\) in the D\(_{3h}\) geometry is stable, but there is a strong PJT coupling between the two excited states \(^1A_1\) and \(^1E\) by \(e\) type distortions: the lower state \(^1A_1\) goes down, crosses the \(^3A_2\) state, and produces a global minimum in which the initial geometry D\(_{3h}\) is reduced to C\(_3\)\(_v\) and the electronic state is a spin-singlet \(^1A_1\). The origin of this PJTE is quite understandable [33, 53]: when the system is distorted the non-magnetic structure with the two electrons paired in one orbital is energetically more convenient than the totally symmetric magnetic distribution with two electrons in two orbitals with parallel spins because of additional covalency gained by distortion (figure 1b). As a result the molecule CuF\(_3\) has two stable states: the triplet (high-spin, HS) state has a magnetic moment of \(\mu_H=1.82\ \mu_B\) and a zero dipole moment \(p_z=0\), whereas the low-spin (LS) state has a zero magnetic moment \(\mu_L=0\) and a strong dipole moment of \(p_z=1.67\ \text{D}\). The HS state is higher in energy by \(\Delta E \approx 0.2\ \text{eV}\) and it has an energy barrier of \(B=0.33\ \text{eV}\) to the point of spin crossover with the LS state (energy values are read off the zero vibrations).

We have thus two coexisting bistabilities, magnetic and dielectric (dipolar), which are strongly correlated: you may have either a HS state with a zero dipole moment, or a zero spin state with nonzero dipole moment. This means that by magnetic switching from LS \(\mu_L=0\) to HS \(\mu_H=1.82\ \text{MB}\) the system simultaneously undergoes a dipolar switching from \(p_z=1.67\ \text{D}\) to \(p_z=0\), and vice versa. Such correlations between magnetic and polar properties are typical for multiferroics. Hence the CuF\(_3\) molecule may be termed as a single-molecule multiferroic. An ensemble of such molecules, e.g., organized on a thin film is a representative of HFSM. This picture of bistabilities demonstrated for the example of the CuF\(_3\) molecule is qualitatively the same for all the systems with \(e^2\) configurations, but with varying parameter values. Table 2 shows the parameters of instability calculated ab initio for several molecular systems with \(e^2\) and \(r^2\) electronic configurations.

Solid state HFSM may be even more important in applications because of their larger variety and better parameters. They may include virtually all the cubic symmetry coordination compounds, ionic crystals, and impurity centers in crystals containing transition metal ions with the electronic configuration \(e^2\) \(d^4\) ions in octahedral coordination and \(d^2\) ions in tetrahedral or cubic environment), and \(t^2\) \(d^3\) in octahedral and \(d^5\) in tetrahedral coordination). Remarkably, these transition metal systems are not TMSCC. Experimentally [54, 55], there is evidence of magnetic bistability in Ni\(_{12}\)\(^6\)\((d^4)\) complexes where a reversible equilibrium between octahedral magnetic and square-planar diamagnetic complexes has been observed. Electronic structure calculations for two solids from the HFSM class, the crystals LiCuO\(_2\) and NaCuO\(_2\) were performed in Ref. [53]. The structure of these crystals is formed by alternating layers of vertex-sharing Cu\(^{II}\)(O\(^2\))\(_6\) octahedrons and Li\(^+\) or Na\(^+\) ions, respectively.
(see figure 2). The Cu$^{3+}$ ion has a ($d^8$)e$^2$ electronic configuration (in general e denotes molecular orbital or symmetrized band states).

Table 2. HS-LS distortions, totally symmetric $Q_1$ and $e$ type $Q_2$ and $Q_3$, energy difference $\Delta E$, barrier $\beta$ (read off the zero-point energy), and lifetimes $\tau$ at low temperatures ($T=5K$) calculated by two methods for several HFSM (the CuO$_6$ system is taken as a cluster in the LiCuO$_2$ crystal).

| System | $Q_1$ (Å) | $Q_2$ (Å) | $Q_3$ (Å) | $\Delta E$ (eV) | $\beta$ (eV) | $\tau$ (s) method 1 | $\tau$ (s) method 2 |
|--------|----------|----------|----------|----------------|------------|---------------------|---------------------|
| Si$_3$ | 0.34     | 0.06     | 0.00     | 0.17           | 0.12       | 340                 | 12·10$^{-8}$        |
| CuF$_3$| 0.61     | 0.20     | 0.00     | 0.21           | 0.33       | 1040                | 29·10$^{-6}$        |
| Si$_4$ | 0.82     | 0.22     | 0.79     | 1.08           | 0.72       | 166                 | 30·10$^{-1}$        |
| Ge$_4$ | 0.79     | 0.05     | 0.81     | 0.82           | 0.81       | 1940                | 26·10$^{-3}$        |
| C$_2$H$_4$| 0.56   | 0.06     | 0.00     | 0.78           | 0.13       | 1.2                 | 37·10$^{-7}$        |
| CuO$_6$| 1.24     | 0.46     | 0.00     | 0.23           | 0.17       | 890                 | 67·10$^{-13}$       |

As predicted by the general theory and shown above for molecular cases, the HS configuration of these crystals is undistorted, while the LS state is diamagnetic with a very strong elongation of the CuO$_6$ octahedrons (figure 2). In Ref [53], Density Functional Theory (DFT) calculations with the hybrid B1WC functional [56] was used to optimize the LiCuO$_2$ and NaCuO$_2$ crystal structures in both the HS (ferromagnetic and antiferromagnetic) and LS (diamagnetic) states. A summary of the numerical results is presented in table 3. As expected, the ferromagnetic and antiferromagnetic phases have very similar geometries with regular octahedral coordination of the oxygen atoms around Cu, whereas the diamagnetic phase is strongly distorted to almost square-planar coordination (in LiCuO$_2$ the metal-ligand distance in the magnetic phase is 2.01Å, while in the diamagnetic phase the equatorial and axial ligands are at 1.86Å and 2.76Å, respectively). In NaCuO$_2$ the same pattern is found, although the lattice parameter and distortions are by about 10% larger than in LiCuO$_2$. The results obtained for the geometry of the diamagnetic phase of these crystals agree well (within 2%) with the experimental data [57,58]; the interatomic distance changes are here 3-4 times larger than in TMSCC.

Table 3. Experimental (in parenthesis) and calculated by DFT B1WC lattice parameters A, B, C (in Å), lattice angle $\gamma$ (degrees), interatomic equatorial dCu-O$_{eq}$ and axial dCu-O$_{ax}$ distances in the diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AF) phases of LiCuO$_2$ and NaCuO$_2$ and their relative energies $\Delta E$ (in cm$^{-1}$).

| System | Phase | A (Å) | B (Å) | C (Å) | $\gamma$ | dCu-O$_{eq}$ (Å) | dCu-O$_{ax}$ (Å) | $\Delta E$ (cm$^{-1}$) |
|--------|-------|-------|-------|-------|----------|-----------------|------------------|---------------------|
| LiCuO$_2$ | DM    | 5.61  | 2.742 | 5.539 | 119.9    | 1.858           | 2.768            | 20                  |
|         |       |       | (5.733) | (2.718) |          | (5.622)         | (120.7)          | (1.836)            |
| LiCuO$_2$ | FM    | 5.032 | 2.910 | 5.032 | 109.4    | 2.009           | 2.012            | 230                 |
| LiCuO$_2$ | AF    | 5.021 | 2.905 | 5.021 | 108.6    | 2.008           | 2.012            | 0                   |
| NaCuO$_2$ | DM    | 6.265 | 2.785 | 6.032 | 120.3    | 1.862           | 3.013            | 0                   |
|         |       |       | (6.358) | (2.750) |          | (6.059)         | (120.5)          | (1.846)            |
| NaCuO$_2$ | FM    | 5.203 | 3.004 | 5.493 | 108.3    | 2.034           | 2.030            | 700                 |
| NaCuO$_2$ | AF    | 5.207 | 3.006 | 5.493 | 108.3    | 2.021           | 2.032            | 1420                |
Figure 2. Giant magnetoelastic effect in LiCuO$_2$ and NaCuO$_2$ crystals. The vertex-sharing CuO$_6$ octahedrons forming the CuO$_2$ layers in the two coexisting magnetic-undistorted (left) and non-magnetic-distorted (right) phases are shown in the upper pictures with Cu in red and O in light-green (front) and dark-green (rear); in the lower part the tilting of the CuO$_2$ units to accommodate the octahedral elongations induced by the PJTE is illustrated (Li and Na ions are shown in blue). In the graphic insertions (a) the total energy of the magnetic (red) and non-magnetic (blue) phases of the two crystals is plotted as a function of lattice strain (coordinate of distortion) termed as 0 in the undistorted magnetic phase and 100% in the distorted non-magnetic phase, and (b) the c-axis lattice elongation in % to that of the magnetic phase as a function of the same strain is shown. We see that at ~35% of strain in NaCuO$_2$ and ~50% in LiCuO$_2$ the two phases become approximately degenerate with a lattice relaxation of ~0.8% in the former and 0.2% in the latter systems in a magnetic phase transition.

The magnetic to diamagnetic phase transition has a strong repercussion on the crystal structure along the c-axis enlarging the unit cell by ~10% (=0.5Å) but the geometrical difference between the two bistability states does not translate in a large energy difference between them. Indeed, as shown in table 3 and figure 2 the energy difference between the phases is only of a few hundred cm$^{-1}$. In the case of LiCuO$_2$ the calculations yield that the magnetic phase (at the minimum of the APES) is lower by 150 cm$^{-1}$ than the diamagnetic one, but with the vibrational zero-point-energy correction the two phases are almost degenerate. In NaCuO$_2$ the non-magnetic phase is more stable. Due to these small energy differences between the phases it should be relatively easy to trigger a phase transition between them by external perturbation. Indeed, for LiCuO$_2$ a phase transition [59] is observed at T=180K. For NaCuO$_2$ the ab initio calculations [53] show that a diamagnetic to magnetic phase transition is achievable at a pressure of ~6 GPa.

In view of the close energy values of the two phases, the possibility was explored [53] to further tune the system by means of epitaxial strain, so that they become almost degenerate and hence more vulnerable to external perturbations. The in-plane geometry of the unit cell of these crystals is almost...
hexagonal (figure 2), so their growth on a particular hexagonal substrate could constrain the in-plane lattice constant to a particular value. Geometry optimizations with the in-plane lattice parameters fixed to a value between that of the magnetic phase and the diamagnetic phase while the rest of the parameters were let free to vary for LiCuO$_2$ and NaCuO$_2$ (figure 2b) show that at some intermediate strains (~50% for LiCuO$_2$, ~35% for NaCuO$_2$) the magnetic and non-magnetic phases become degenerate. At this point a diamagnetic to magnetic phase transition can easily be triggered by a magnetic field, resulting in a strong distortion of the crystal along the c-axis; as seen from figure 2b, the lattice parameter of LiCuO$_2$ (~5Å) changes by ~0.2% which amounts to ~ 1pm. Such changes in lattice parameters are typical in ferroelectrics, but very seldom found in magnetic transitions. In fact such distortions are termed in literature as giant magnetoelastic effects (see, e.g., [60]). Moreover, a similar change in the lattice parameter of NaCuO$_2$ is ~0.8% (figure 2b), almost 4 times larger than those of LiCuO$_2$. In the strained systems this change in lattice parameter is realized by a tilting of the CuO$_2$ (almost) square planar units in the diamagnetic phase toward the formation of CuO$_6$ octahedrons by the near neighbour rows in the magnetic phase (figure 2).

Note that, as mentioned above, in the whole class of HFSM the distortion of the high-symmetry (magnetic) configuration toward the diamagnetic one by the PJTE in two excited states is accompanied by orbital disproportionation [33] due to which the two electrons in two e orbitals with parallel spins (and symmetric charge distribution) prefer to occupy one orbital with anti-parallel spins lowering the symmetry of the system, but gaining additional covalent metal-ligand bonding. This explains also the insulating properties of the diamagnetic NaCuO$_2$ or LiCuO$_2$ crystals that are subject to discussion in the literature [61]: the orbital disproportionation splits the two-fold degenerate ($3z^2-r^2$ and $x^2-y^2$ of Cu) E level (band) and fully occupies the lower one (figure 1).

One of the most important characteristics of the bistability with regard to possible applications is the lifetime $\tau$ (relaxation time) of the induced higher energy state (in cases in table 1 the spin-triplet state) with respect to its thermal relaxation to the lower (spin singlet) state. This is less a problem for solids where the cooperative interactions stabilize well the two states in the bistability. For molecular systems or small aggregates the relaxation lifetime depends on several factors, mainly on the spin-orbital interaction, the barrier height and width between the two minima of the APES, and the dissipation of energy in interaction with the environment. Direct calculation of the lifetimes $\tau$ is not trivial; in Ref 53 [62, 63] we employed two approximations to estimate the $\tau$ values for a series molecular systems and for (isolated) octahedral units in LiCuO$_2$ (taken as examples of the HFSM class). The results are shown in table 2, while figure 3 illustrates the temperature dependence of some of them. As expected, the distortions in all HFSM are dominated by the symmetry-breaking coordinate ($Q_1$ in table 2), while in normal TMSCC they are dominated by the totally symmetric coordinate $Q_2$, and in general they are larger or much larger in the former case than in the latter. This feature increases essentially the lifetime of HFSM as compared with TMSCC because of the strong dependence of the overlap of the vibrational functions of the two states, which decreases exponentially with the distortion. A decrease in $\tau$ is also achieved in organic and other compounds of non-heavy elements due to their smaller spin-orbital coupling constant.

In table 2 Si$_3$ has the shortest lifetime (comparable to that of most TMSCC) which increases in systems with larger distortions, and reaches macroscopic values in Si$_4$, Ge$_4$ and LiCuO$_2$ at low temperatures (but in Ge$_4$ there are low-lying triplet excited states that may reduce the lifetime). In the crystals LiCuO$_2$ and NaCuO$_2$ the estimates of the lifetime of the HS configuration are carried out for a separate cluster unit CuO$_6$; it is extremely large at low temperatures (due to the large distortions in the diamagnetic phase) and remains macroscopic at room temperature. Since the cooperative interactions between the complexes in the condensed phases obviously increase the lifetimes, the values in table 2 and in figure 3 show the lower limit of the expected lifetimes. This means that the crystals LiCuO$_2$ and NaCuO$_2$ are quite feasible for practical use as bistability materials, and their large lifetime of both states in this bistability indicates that they can be used in the form of clusters, quantum dots, or thin films.
Figure 3. Temperature dependence of lifetimes estimated for the higher in energy high-spin states of Si$_3$, CuF$_3$ and an isolated octahedral center in NaCuO$_2$ by means of model calculations.

With practically inexhaustible numbers and with the shown above examples of their feasibility for practical use polyatomic systems with electronic configurations $e^2$ and $t^3$ may be regarded as a "database" of novel materials with bistabilities for information storage and sensor devices.

4. The PJT effect is instrumental in design of compounds with required properties: "planarization" of puckered 2D (graphene-like) or quasi-2D compounds

Two-dimensional (2D) or quasi-2D materials have unique physical properties due to a variety of their planar-surface-specific physical and chemical properties. The best-known example of this kind is graphene [64, 65]. Similar properties are sought for in silicene [66], boron nitride [67], zinc oxide [68], phosphorene [69], gallium nitride [70], as well as in other attractive subjects like 2D transition metal dichalcogenids and oxides [71], and there is an unlimited number of other organic and inorganic 2D and quasi-2D compounds with expected similar properties.

One of the main structural features that makes these compounds special in applications is their planarity or quasi-planarity. On the other hand, it was shown that all deviations from the planar configurations of polyatomic systems in nondegenerate states in the form of puckering (or buckling) are due to, and only to the pseudo Jahn-Teller effect (PJTE) [1-3]. In degenerate states, both the JTE and PJTE may be active, which for extended systems results in Peierls distortions (see in [1, 2]). In application to a series of cyclic and heterocyclic compounds the PJTE explains the origin of their out-of-plan distortions, puckering (see [3] and references therein; puckering as a PJTE was first formulated in [72]). Explaining the origin and mechanism of such distortions leads us directly to another important problem related to the possible use of these compounds in applications: if the system under consideration is out-of-plan distorted, how can we restore the planar configuration with minor other changes?

Starting with the high-symmetry (planar) configuration of 2D systems, the PJTE reveals the active excited states that produces the instability of the ground state, its symmetry and energy, and the numerical condition of instability [1-3]. Therefore we can try to influence the system by means of external perturbations that violate the PJTE condition of instability of the ground state mainly by changing the active excited states. In principle, there are two possibilities to do this: (1) increasing just the energy gap between the electronic states mixed by the PJT vibronic coupling, e.g. by weak coordination with outside systems, and (2) changing the symmetry of the active excited states in a
redox process by removing or adding electrons (which may change all the parameters of the PJTE including the energy gaps). The possibility (1) was first demonstrated in the mechanism of hemoglobin oxygenation [73] in which the PJTE out-of-plane displacement of the iron atom from the porphyrin ring returns into the plane by oxygenation due to the increase of the energy gap to the active excited state, thus suppressing the PJTE. Examples of realization of the mechanism (2) were demonstrated recently [74, 75]. For instance, by coordination of two chloride anions to nonplanar excited state, thus suppressing the PJTE. Examples of realization of the mechanism (2) were porphyrin ring returns into the plane by oxygenation due to the increase of the energy gap to the active hemoglobin oxygenation [73] in which the PJTE out-of-plane displacement of the iron atom from the including the energy gaps). The possibility (1) was first demonstrated in the mechanism of redox process by removing or adding electrons (which may change all the parameters of the PJTE

The PJTE has been involved in exploration of the origin of out-of-plane (puckering) distortions and possible ways of restoration of the planar configuration of quite a number of small and large virtual 2D systems [73-82]. For illustration and as an example consider the mechanism of distortion and restoration of the planar configuration of a series of tetra-heterocyclic 1,2-diazetes, C\textsubscript{2v}N\textsubscript{2}E\textsubscript{4}, E= H, F, Cl, Br [80]. These compounds are well known and studied before in their ground state [83]. According to the general PJTE theory, the study of possible equilibrium geometries of any molecular system in nondegenerate electronic states starts with a reference configuration of the highest possible symmetry for which all the first derivatives of the APES with respect to the nuclear displacements are zero (see, e.g. [1, 3]). In case of the C\textsubscript{2v}N\textsubscript{2}E\textsubscript{4} molecules the planar nuclear configuration of the C\textsubscript{2v} symmetry is the starting one. The eight-atom systems C\textsubscript{2v}N\textsubscript{2}E\textsubscript{4} have eighteen vibrational degrees of freedom. In the planar configuration of C\textsubscript{2v} symmetry they transform according to the irreducible representations 7A\textsubscript{1} + 3A\textsubscript{2} + 2B\textsubscript{1} + 6B\textsubscript{2}. Five symmetrized displacements, three of \textit{a\textsubscript{2}} type and two of \textit{b\textsubscript{1}} type, correspond to the out-of-plane distortions that transforms the planar C\textsubscript{2v} nuclear configuration to the puckered structures of C\textsubscript{2} or C\textsubscript{s} symmetry, respectively (figure 4).

**Figure 4.** Illustration to the C\textsubscript{2v} → C\textsubscript{s} and C\textsubscript{2v} → C\textsubscript{2} puckering transformations of the C\textsubscript{2v}N\textsubscript{2}E\textsubscript{4} systems resulting from the (1\textit{A}\textsubscript{1} + 1\textit{A}\textsubscript{2})\textcircled{a\textsubscript{2}} and (1\textit{A}\textsubscript{1} + 1\textit{B}\textsubscript{1})\textcircled{b\textsubscript{1}} PJTE problems, respectively.

To reveal the vibronic origin of the out-of-plane distortions of these molecules the three-mode (1\textit{A}\textsubscript{1} + 1\textit{A}\textsubscript{2})\textcircled{(a\textsubscript{2} + a\textsubscript{2} + a\textsubscript{2})} and the two-mode (1\textit{A}\textsubscript{1} + 1\textit{B}\textsubscript{1})\textcircled{(b\textsubscript{1} + b\textsubscript{1})} PJTE problems should be solved. Direct solution of these problems requires the construction of the 3×3 and the 2×2 secular matrices and calculation of a large number of vibronic coupling constants. Fortunately, the problem can be simplified by employing the results of electronic structure calculations and vibrational frequency analysis of the systems in the high-symmetry C\textsubscript{2v} configuration. Indeed, in all these cases calculations show the presence of two imaginary frequencies: the one with a larger absolute value corresponds to the \textit{a\textsubscript{2}} type nuclear displacements, and the second one describes displacements of the \textit{b\textsubscript{1}} type.

In other words, the high-symmetry C\textsubscript{2v} nuclear configurations of all the considered molecules are unstable with respect to both types of the out-of-plane distortions. The calculated normal coordinates of the \textit{a\textsubscript{2}} and \textit{b\textsubscript{1}} types, which are linear combinations of corresponding symmetrized displacements, comply with the lines of the steepest descent in energy toward the two minima on the APES of the molecules. The first one, being the absolute minimum, corresponds to the C\textsubscript{2} structure (figure 4),
whereas the second, local minimum of \( C_{s} \) symmetry is above the first one by an amount of 5-8 kcal/mol. For this reason, we further analyse only the cross section of the APES of the systems along the \( Q_{a2} \) coordinate leading to the equilibrium minimum energy of the \( C_{2} \) configuration. The \( a_{2} \) mode of distortions is illustrated in figure 5.

**Figure. 5.** Puckering \( a_{2} \) normal modes in the \( C_{2}N_{2}H_{4} \) (left) and \( C_{2}N_{2}E_{4} \) (E=F, Cl, Br) systems; the arrow lengths show expected relative (not absolute) displacements.

The calculations [80] show that the geometry of the molecules under consideration varies significantly when bloating. First, it refers to the N-N-C=C dihedral angles that characterize the puckering of the planar heterocyclic rings. The dihedral angles E-N-N-E decrease in the series of halogen-substituted molecules from 45.1º in \( C_{2}N_{2}F_{4} \) to 40.2º and 38.6º in \( C_{2}N_{2}Cl_{4} \) and \( C_{2}N_{2}Br_{4} \), respectively. The dihedral angles E-C=C-E, on the contrary, increase from F to Cl-, and Br-substituted compounds. It is also seen that there is a significant decrease in the values of the imaginary vibrational frequencies, which is due to an increase in the reduced mass of vibrations and the subsequent change of the vibrational \( a_{2} \) mode.

Several lowest electronic terms with the same multiplicity of the \( C_{2}N_{2}E_{4} \) molecules, and their electronic configurations in the planar \( (C_{2v}) \) geometry are presented in table 4. The numbers “1” and “-1” are used to denote electrons in two opposite spin orientations. It is seen that the ground state in all the considered molecules is the closed-shell spin-singlet, and the lowest excited \(^1B_1\) and \(^1A_2\) terms are produced by the one-electron excitations \( b_{1}\rightarrow a_{1} \) and \( a_{2}\rightarrow a_{1} \) from HOMO-1 \( b_{1} \) and HOMO \( a_{2} \) to the LUMO \( a_{1} \), respectively. Calculations with a larger number of configurations show that the next excited \(^1A_2\) states are much higher in energy (more than 10 eV), and their PJT mixing with the ground state is included in the \( p \) parameters introduced below.

**Table 4.** Main electronic configurations, wavefunctions weight coefficients, and relative energies \( \Delta E \) (eV) of several electronic terms of the \( C_{2}N_{2}E_{4} \) molecules in the optimized planar \( C_{2v} \) nuclear configuration calculated at the CAS(4,3) level of theory; 1 and -1 in the power of single-populated orbitals indicate two spin orientations.

| State symmetry | Main Electronic Configuration | Weight coefficients | \( C_{2}N_{2}H_{4} \) | \( C_{2}N_{2}F_{4} \) | \( C_{2}N_{2}Cl_{4} \) | \( C_{2}N_{2}Br_{4} \) |
|----------------|-------------------------------|---------------------|----------------|----------------|----------------|----------------|
| \(^1A_1\)     | \( b_{1}^2a_{2}^1 \)          | 0.9999              | 0.9995         | 0.9997         | 0.9997         | 0.9997         |
| \( \Delta E \) |                               | 0.00                | 0.00           | 0.00           | 0.00           | 0.00           |
| \(^1B_1\)     | \( b_{1}^1a_{2}^1a_{1}^{-1} \)| -0.7071              | -0.7071         | -0.7071        | -0.7071        | -0.7071        |
|                | \( b_{1}^{-1}a_{2}^1a_{1}^1 \)| 0.7071              | 0.7071          | 0.7071         | 0.7071         | 0.7071         |
| \( \Delta E \) |                               | 6.55                | 4.72           | 4.48           | 3.51           |
| \(^1A_2\)     | \( b_{1}^2a_{2}^{-1}a_{1}^{-1} \)| -0.7071              | 0.7071          | -0.7071        | 0.7071         | -0.7071        |
|                | \( b_{1}^1a_{2}^2a_{1}^{-1} \)| 0.7071              | -0.7071         | 0.7071         | -0.7071        | 0.7071         |
| \( \Delta E \) |                               | 7.03                | 5.67           | 5.09           | 4.08           |
As mentioned above, the PJTE theory states that the only reason of spontaneous symmetry breaking followed by the low-symmetry distortion of any molecular system in the nondegenerate electronic state is the sufficiently strong PJT mixing between this state and one or more higher in energy electronic states [1, 3]. If \(| \Gamma \rangle \) and \(| \Gamma' \rangle \) are the wavefunctions of the nondegenerate ground and excited states and the energy gap between them is \( \Delta \), then the condition of instability of the ground state with respect to the nuclear displacements \( Q \) is [1] (cf. Eq. (4)):

\[
\Delta < \frac{\left( F_{\Gamma \Gamma'} \right)^2}{2K_0} \tag{7}
\]

where \( F_{\Gamma \Gamma'} \) is the linear vibronic coupling constant between the ground and excited states, and \( K_0 \) is the primary force constant.

\[
F_{\Gamma \Gamma'} = \left\langle \Gamma \left| \frac{\partial H}{\partial Q} \right| \Gamma' \right\rangle \tag{8}
\]

\[
K_0 = \left\langle \Gamma \left| \left( \frac{\partial^2 H}{\partial Q^2} \right) \right| \Gamma \right\rangle \tag{9}
\]

and \( H \) is the adiabatic electronic Hamiltonian of the system which includes all Coulomb interactions between electrons and nuclei. The value of \( F_{\Gamma \Gamma'} \) is nonzero only if two states \( | \Gamma \rangle \) and \( | \Gamma' \rangle \) obey the symmetry restriction: \( \Gamma \otimes \Gamma' \) contains the symmetry of \( Q \). At small \( Q \) the total force constant \( K \) which determines the curvature of the adiabatic potential energy surface (APES) in the direction of nuclear displacement \( Q \), is equal to

\[
K = K_0 - \frac{(F)^2}{2\Delta} \tag{10}
\]

If the condition of instability (1) holds, then the value of \( K \) becomes negative.

In any polyatomic system, the number of excited states is practically infinite, and there are always excited states of relevant symmetry, albeit at large energy gaps \( \Delta \). Their contribution to the PJTE problem may be rather small, just lowering the curvature of the ground state from \( K_0 \) to \( K_0 - p \), \( p > 0 \), and not producing instability [3, 84]. Denote by \( K_1 \) and \( K_2 \) the primary force constants in the ground and the active excited states, respectively, and by \( p_1 \) and \( p_2 \) the corrections to them produced by the PJT coupling to all the higher excited states of appropriate symmetry [3, 84]:

\[
W_{\Gamma \Gamma'} = -2 \sum_n \frac{|F_{\Gamma n}|^2}{E_n - E_{\Gamma}} Q^2 = -p_1 Q^2 \tag{11}
\]

\[
W_{\Gamma' \Gamma} = -2 \sum_n \frac{|F_{\Gamma' n}|^2}{E_n - E_{\Gamma'}} Q^2 = -p_2 Q^2 \tag{12}
\]

Then, the APES \( \varepsilon(\mathbf{Q}) \) can be obtained from the secular equation of the perturbation theory:

\[
\begin{vmatrix}
\frac{1}{2} (K_1 - p_1) Q^2 - \varepsilon & FQ \\
FQ & \frac{1}{2} (K_2 - p_2) Q^2 + \Delta - \varepsilon
\end{vmatrix} = 0 \tag{13}
\]

The roots of this secular equation are:

\[
\varepsilon_{gr,ex} = \frac{\Delta}{2} \sqrt{1 + \frac{1}{4\Delta^2} \left( K_1 - p_1 - (K_2 - p_2) \right)^2 Q^2 - \frac{K_1 - p_1 - (K_2 - p_2)}{K_1} - \frac{4F^2}{\Delta}} \tag{14}
\]

At small values of \( Q \) we get:

\[
\varepsilon_{gr} = \frac{\Delta}{2} \left( K_1 - p_1 - \frac{2F^2}{\Delta} \right) Q^2 \tag{15}
\]
Then the condition of instability at $Q=0$ of the ground state due to the PJT vibronic coupling is:

$$ K_1 - p_1 < \frac{2F^2}{\Delta} \quad (16) $$

The direct *ab initio* calculation of the constants $F, K_1-p_1$ and $K_2-p_2$ encounters difficulties. In the present paper these constants were estimated by fitting the general formula, obtained from the vibronic coupling theory (Eq. (14)), to the *ab initio* data for the adiabatic potential curves (energy profiles) - cross-sections of the APES along the $Q_{a_2}$ coordinates. These calculated energy profiles of the $C_2N_2E_4$ compounds in the ground and lowest excited states are shown in figure 6. In the configuration of $C_{2v}$ symmetry all the four systems are unstable becoming stabilized along the puckered geometry of $C_2$ symmetry, while the PJT active excited states $A_2$ become destabilized. By fitting Eq. (14) to these energy profiles we can extract the PJT constants. Estimated in such a way, the values of the PJT parameters are given in table 5.

Table 5. PJTE coupling constants $F$ (in eV/Å), energy gaps $\Delta$ (in eV), primary force constants $K_1-p_1$ and $K_2-p_2$ and full force constants $K_{gr}=K_1-p_1-\left(\frac{2F^2}{\Delta}\right)$ (in eV/Å$^2$) in the reference $C_{2v}$ configuration of 1,2-diazetes $C_2N_2H_4$ obtained by fitting Eq. (14) to the ab initio calculated energy profiles.

| Molecules     | $K1-p1$ | $K2-p2$ | $F$  | $\Delta$ | $K_{gr}$  | $K_{gr}$  |
|---------------|---------|---------|------|----------|-----------|-----------|
| $C_2N_2H_4$   | 6.18    | 11.65   | 5.61 | 7.03     | -2.77     | -1.87     |
| $C_2N_2F_4$   | 5.11    | 5.25    | 6.77 | 5.67     | -11.06    | -10.27    |
| $C_2N_2Cl_4$  | 2.41    | 3.29    | 4.05 | 5.09     | -4.03     | -4.10     |
| $C_2N_2Br_4$  | 2.82    | 3.46    | 3.58 | 4.08     | -3.46     | -3.21     |

Figure 6. Ab initio calculated energy profiles (APES cross sections) along the $a_2$ puckering coordinates for the three lowest electronic terms of the $C_2N_2E_4$ (E=H, F, Cl, Br) compounds. For the ground state term $A_1$ the results of both ab initio and analytical (Eq. (14)) calculations are shown, respectively, by points and curves (the ground state minima for the stable puckered configurations are at larger distances not shown in the graphics).
The numerical data of tables 4 and 5 allow one to verify the condition of PJTE instability (10). For each of these systems we calculated the resulting value of the curvature \( K_2 \) according to Eq. (9). As we can see from table 5 (penultimate column), all these values are negative, hence the condition of puckering instability \( K_1 - p_1 < 2 \varepsilon^2 / \Delta \) is fully satisfied. Furthermore, from figure 6 it is seen that in all the cases the ab initio calculated points of the energy profiles coincide with those estimated by the formulas of the general theory using the PJT parameters from table 6. Based on these results, and given the fact that \( K_1 - p_1 > 0 \), we may conclude that the instability of the high-symmetry \( C_{2v} \) nuclear configuration of the molecules under consideration with respect to the \( a_2 \) puckering modes and their distortions are due to the PJT mixing of the ground \( ^1A_1 \) and the first excited \( ^1A_2 \) states. It is important to note that these numerical estimates are not intended to prove that the puckering is of PJTE origin, this is done in the general theory [1, 2] where it is proved that any distortion of high-symmetry configurations is due to, and only to the PJTE; the proof here is to show that in the specific systems under consideration the revealed vibronic coupling between the specific electronic states describes the observed distortions with sufficient accuracy.

| Molecule          | Cations \( C_2N_2E_4^+ \) | Anions \( C_2N_2E_4^- \) | Triplet state | Dications \( C_2N_2E_4^{2+} \) | Dianions \( C_2N_2E_4^{2-} \) |
|-------------------|--------------------------|--------------------------|--------------|--------------------------|--------------------------|
| Imag. Freq.       | \( a_2/b_1 \) | \( a_2/b_1 \) | \( a_2/b_1 \) | \( a_2/b_1 \) | \( a_2/b_1 \) |
| \( C_2N_2H_4 \)  | 454.2/ --     | 999.8/939.3   | 1069.3/978.7 | -- / --                | 942.1/971.6    |
| \( C_2N_2F_4 \)  | 600.1/489.4  | 1079.0/839.1  | 685.8/119.5  | 117.8/ --              | Problem in calculation |
| \( C_2N_2C_1 \)  | 327.9/213.8  | 419.3/351.2   | 873.4/689.7  | -- / --                | 435.2/409.0    |
| \( C_2N_2Br_4 \) | 293.8/189.7  | 665.6/53.75   | -- / --      | -- / --                | 45.0/121.3     |

In order to restore the high-symmetry planar configuration of the 1,2-diazetes under consideration we have to quench the PJTE that triggers their puckering. As mentioned in the Introduction, this can be done by either increasing the just energy gap \( \Delta \) to the same active excited state (in our case \( \Delta = \varepsilon (A_2) - \varepsilon (A_1) \) in the planar configuration) by weak coordination to external groups, or to change all the parameters of PJTE instability by adding or removing electrons. The point is to achieve planarization without destroying the basic cyclic structure and accompanying properties of the system (changing the ligands leads to \textit{a priori} another chemical structure). In case of ionization, stable bulk materials with the tetra-heterocycles under consideration (or in similar problems with other PJT systems) can be obtained by compensating their charges with appropriate opposite-charged ions.

To try this possibility we performed ab initio calculations of the four tetra-heterocyclic 1,2-diazetes, \( C_2N_2E_4 \), \( E=H, F, Cl, Br \), in their cation, anion, dication, dianion, and triplet (HOMO-LUMO) states of the planar configuration and revealed their \( a_2 \)- and \( b_1 \)-type instabilities, as well as the energy gaps \( \Delta \) to their new lowest \( A_2 \) electronic states that could induce the PJTE puckering instability. The obtained imaginary frequencies are shown in table 6. We see that in the anion states the instability, in general, increases, more in the dianion than in the anion states, while in the cation states it decreases, and three of the four systems become stable in the dication state; one of them is stable also in the excited triplet state. The first (more obvious) reason for the weakening of the PJTE in these cases is the much higher position of the (changed) lowest excited \( ^1A_2 \) state. The calculated new energy gaps \( \Delta = \varepsilon (A_2) - \varepsilon (A_1) \) in the dications \( C_2N_2E_4^{2+} \) are (in eV): 10.81, 9.65, 7.89, and 5.72 for \( E=H, F, Cl, \) and Br, respectively, compared to 7.03, 5.67, 5.09, 4.08 for the neutral molecules (table 5). The other parameters in the condition of instability (10) include the primary force constant \( K \) which increases by removing electrons (excess inter-electron repulsions \textit{ceteris paribus} soften the system), thus...
weakening the PJTE too, while the vibronic coupling constant $F$ formed by similar electronic states is expected to remain of the same order of magnitude.

On the basis of these calculations we can conclude that the planar configurations of the $C_2N_2E_4$ heterocycle compounds under consideration, distorted by the PJTE, can be restored in the dication state produced, for instance, by a “triple-decker sandwich” structure with two additional electron acceptors on both sides of the neutral cycle, or two negative ions in both sides of the dication, similar to some previous suggestions for other systems [75].

5. Conclusions

We accentuated several problem that demonstrate the specific features of polyatomic system with the JTE and PJTE that make them exceptional in view of possible applications in search for novel materials with sought for properties. One of them is related to computer simulation of expected properties of possible useful materials that in its most efficient approaches employs DFT methods. The latter, unfortunately, are not applicable to systems with dynamic JTE or PJTE. Computer simulation for such systems remains and open, unsolved problem.

Important effects emerge in the interaction of dynamic JTE and PJTE systems with external perturbations. It has been found recently that external perturbation quench the local JT tunnelling or over-the-barrier transitions between the minima of the APES, producing an additional (orientational) contribution to the observable properties which enhances them by several orders of magnitude. This property is demonstrated on permittivity, flexoelectricity, and electrostriction of paraelectric BaTiO$_3$ and similar systems with dynamic (disordered) JTE and PJTE.

In systems with electronic $e^2$ or $t^3$ orbital configurations a special arrangement of ground and lowest excited states produces two coexisting equilibrium configurations with different symmetry, dipole moment, and spin. This brings us to a whole class of materials with magnetic-dielectric bistabilities. Examples of the CuF$_3$ molecule and two crystals, LiCuO$_2$ and NaCuO$_2$, demonstrate this materials’ property.

As examples of application of the JTE and PJTE theory to rationalize the origin of special structural features of matter and to design novel system with required properties, we mention a series of publications on two-dimensional (2D) and quasi 2D systems that use the PJTE in order to reveal the origin of their puckering out-of-plan distortions, and methods of restoration of the planar configuration by external perturbations. The latter were shown to include coordination to other species, oxidation, reduction, and substitution, as well as optical excitations. The detailed procedure on how this works is shown on the example of tetra-heterocycles of 1,2-diazetes, $C_2N_2E_4$, $E$=H, F, Cl, Br.

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