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The symmetry principle of antiaromaticity

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Abstract: Current definitions of aromaticity are purely phenomenological and relate symmetry, reactive stability and the occurrence of molecular diamagnetic response currents. The antithetical concept of antiaromaticity provides a connection between the contrary properties: structural instability or distortion out of higher symmetry, a small HOMO-LUMO gap, and paramagnetic response currents. We reveal the symmetry principle that is underlying antiaromaticity by showing an intimate and strict symmetry induced relation between these properties. The principle is mathematically rigorous and can be formulated like: *First order (and related) Jahn-Teller distorted molecules out of non-cubic and non-icosahedral point groups are prone to induced paramagnetism in magnetic fields parallel to the main axis of symmetry.* We show by the exemplary cases of cyclobutadiene, cyclooctatetraene, pentalene and manganese trifluoride how this principle works and discuss this new perspective on antiaromaticity.

Keywords: closed shell paramagnetism; Jahn-Teller effect; magnetic response; symmetry.

1 Introduction

Aromaticity is one of the most widely used chemical concepts. It aims at an abstraction of different experimentally observed properties in a class of chemical compounds. These properties are typically a high structural or energetic stability, proneness to specific chemical reactions and susceptibility to induced diamagnetic currents when at the same time a theoretical description or also experimental evidence suggests a specific type of electronic structure. One often encounters this in the form of electron count rules, orbital occupation patterns or electronic resonance [1]. A good overview about the state of research

on aromaticity including references to a selection of current reviews is given in the introduction of ref. [2] While the connection of some of these properties seems obvious, no concise connection between all in full generality could ever be established. Here we analyze the antithetical concept of *antiaromaticity* which was originally introduced by Breslow [3] and find an intimate symmetry relation between its defining properties that so far seems to have escaped the general attention. Along the lines of the definition of antiaromaticity from the Gold Book of the International Union of Pure and Applied Chemistry (IUPAC) [4, 5] these are the three properties (a) “... prone to reactions causing changes in their structural type, and display tendency to alternation of bond lengths and fluxional behavior ...”, (b) “... a small energy gap between their highest occupied and lowest unoccupied molecular orbitals ...” and (c) “... an external magnetic field induces a paramagnetic electron current.” A full quote of the definition is given in the Supplementary Information section. To show how these properties are related we use the following arguments

- Paramagnetic molecular response is determined by virtual electronic excitations of angular momentum (or “rotational”) symmetry, where the axis of rotation is parallel to the magnetic field.
- Ground state-excited state (or OMO-UMO) symmetries that give rise to virtual electronic excitations of rotational symmetry are connected with certain Jahn-Teller (JT) distortions out of specific molecular point group symmetries.
- These certain JT distortions are first order JT distortions (or closely related ones, which we later call *primoid* second order JT distortions) and happen out of point group symmetries that are not cubic and not icosahedral (which we call for simplicity “non-isometric”). That is from one of the point groups C_n , C_{nv} , C_{nh} , D_n , D_{nh} for $n > 2$, and D_{nd} and S_{2n} for $n > 1$. (While the isometric point groups are defined to be those point groups where x , y , and z are represented by the the same irreducible representation, and in fact are exactly the family of groups formed by those given in Tables 4 and 5 below).

A consequence of these arguments and our main result is

First order and primoid second order JT distorted molecules out of non-isometric point groups are prone to induced paramagnetism in magnetic fields parallel to the main axis of symmetry.

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We then advocate the view that this is the symmetry principle underlying antiaromaticity. After derivation of these results we discuss some exemplary cases and important implications of this new perspective on antiaromaticity for past and future research and a possible extension to the concept of aromaticity.

This article is organized in a way that the complete results and their heuristic motivation is presented in the abstract plus the introduction and the conclusion section. A rigorous proof, necessary for a deeper understanding of the results is however only presented in the subsections of the discussion and the Supporting Information (SI) available online.

The occurrence of paramagnetic response currents is one of the three central defining properties of antiaromatic molecules. We start the results section with a derivation of a symmetry based “selection rule” for virtual electronic excitations determining paramagnetic response currents.

2 Results

2.1 Paramagnetic response currents

When a molecule is exposed to a magnetic field $\mathbf{B}$, that is in the simplest case static, homogeneous and weak, which we assume throughout this work, it interacts to first order via the total electronic angular momentum and total spin which correspond to permanent molecular magnetic moments. In case the expectation values of both are identically zero, i.e. closed shell singlet molecules, it only interacts to second order via its molecular magnetisability which is for bulk matter also called magnetic susceptibility. In the quasi-classic Bohr model of electrons circling around the nucleus such a field dependent magnetization corresponds to a superimposed precession motion of the orbiting electrons in the field $\mathbf{B}$. While a magnetization in this quasi classical picture must lead to an increase of the energy of the electronic system and hence is classified as diamagnetic response, in the quantum mechanical case the magnetic response in general can be partitioned into either diamagnetic or paramagnetic contributions. Such a paramagnetic magnetization has no quasi-classical counterpart, it however would correspond to a $\mathbf{B}$ field dependent gain in angular momentum, leading to an energetic stabilization of the system. Also the partitioning into dia- and paramagnetic response contribution in general depends on the choice of the gauge, or in the particular case of a vector potential $\mathbf{A}$ of the form $\mathbf{A}_d(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{d})$ on the choice of the

gauge origin $\mathbf{d}$. A natural choice for the gauge origin, however is the origin of reference $\mathbf{r}_0$ for the definition of the angular momentum (operator) $\mathbf{l} = (\mathbf{r} - \mathbf{r}_0) \times \mathbf{p}$, by the momentum (operator) $\mathbf{p}$, which serves also as centre of symmetry in case of non-trivial molecular symmetries and conveniently can be used as origin of the inner coordinate system of the molecule (then $\mathbf{r}_0 = \mathbf{0}$). According to McWeeny's perturbation theoretic formulation [6] and orienting a unit strength magnetic field along the z axis: $\mathbf{B} = (0, 0, 1)^T = \mathbf{B}_z$, the paramagnetic part of the magnetically induced current density field $\mathbf{J}_p^{\mathbf{B}_z}(\mathbf{r})$ is obtained by

$$\mathbf{J}_p^{\mathbf{B}_z}(\mathbf{r}) = -\frac{2ne}{m_e} \Re \int d\mathbf{s}_1 d\mathbf{x}_2 \dots d\mathbf{x}_n \mathbf{B}_z \cdot \Psi^{\mathbf{B}_z}(\mathbf{x}_1, \dots, \mathbf{x}_n) \mathbf{p} \Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_n) \quad (1)$$

with the n the number of electrons, the electronic charge $-e$, the electron mass m_e , and the ground state wave function Ψ_0 that depends on spatial coordinates of the i^{th} electron $\mathbf{r}_i$ and its spin coordinate $\mathbf{s}_i$ which are combined to the space-spin coordinate $\mathbf{x}_i$ and the (purely imaginary) first order magnetic response contribution to the wave function

$$\Psi^{\mathbf{B}_z}(\mathbf{x}_1, \dots, \mathbf{x}_n) = -\frac{e}{2m_e} \sum_{j>0} \Psi_j \frac{\langle \Psi_j | \mathbf{l}_z | \Psi_0 \rangle}{\varepsilon_j - \varepsilon_0}, \quad (2)$$

using $\mathbf{l}_z$ for the z component of the (total) angular momentum operator (alternatively an effective one-particle picture formulation can be easily obtained, resulting in an completely analogous expression for occupied-unoccupied orbital excitations). Thus the possibility of occurrence of a paramagnetic response contribution $\mathbf{J}_p^{\mathbf{B}_z}(\mathbf{r})$ is determined by the size of the terms

$$\frac{\langle \Psi_j | \mathbf{l}_z | \Psi_0 \rangle}{\varepsilon_j - \varepsilon_0}. \quad (3)$$

The condition that the integrals in 3 are non-zero can be interpreted as a selection rule for $\mathbf{J}_p^{\mathbf{B}_z}(\mathbf{r})$ requiring the possibility of virtual excitations between Ψ_0 and Ψ_j of rotational symmetry with respect to an axis parallel to z , which is the direction of the magnetic field $\mathbf{B}_z$. The connection between paramagnetism and rotation to the best of our knowledge was pointed out for the first time by Steiner and Fowler [7]. According to the Wigner-Eckart theorem we can formulate the selection rule, that the decomposition of the direct (tensor) product of the irreducible representations (IRs, Γ) of the ground and excited states must contain the IR of the z component of the angular momentum operator:

$$\Gamma_{\mathbf{l}_z} \subseteq \Gamma_{\Psi_j^*} \otimes \Gamma_{\Psi_0}. \quad (4)$$

The terms and hence total paramagnetic currents in general will be the stronger the larger the integrals $|\langle \Psi_j | \mathbf{l}_z | \Psi_0 \rangle|$ and the smaller the energy gaps $\varepsilon_j - \varepsilon_0$ between the engaged states are.

In this specific choice of gauge, that is a common gauge origin, one can introduce the terms dia- and paratropic [8], which are referring to ring current contributions to the total current density vector field that are flowing either in classical direction or anti-classical direction around the gauge origin and with respect to the external magnetic field, thus giving rise to a dia- or paramagnetic induced magnetisation inside this ring current domain, respectively.

We note, that a connection between non-filled degenerate frontier orbitals and the z component of the angular momentum was previously noted by Tellgren et al. [9].

Representations of angular momentum components play now a central role in our considerations. In the following we will see that there is an intimate connection between tensor squares of two-dimensional IRs and representations of angular momentum components in certain point groups.

2.2 Angular momentum in squares of degenerate IRs in doubly-degenerate point-groups

For here on we adopt the Mulliken conventions of A/a , and B/b for one-dimensional, E/e for two-dimensional, T/t for three-dimensional irreducible representations over $\mathbb{R}$, ρ for a general representation, Γ for an irreducible one and Γ_0 for the trivial (= totally symmetric) representation. Also in this whole work we consider only representations over $\mathbb{R}$.

Classifying the point groups by the dimensions of their IRs yields a partition into three subfamilies that we call $\mathcal{K}_1$, $\mathcal{K}_2$ and $\mathcal{K}_3$. In informal chemical terminology point groups from $\mathcal{K}_1$ are those which only have one-dimensional IRs (over $\mathbb{R}$, as used throughout), point groups from $\mathcal{K}_2$ are those which have two- but no higher dimensional IRs and point groups from $\mathcal{K}_3$ have three- (or higher) dimensional IRs. Alternatively $\mathcal{K}_1$ can be defined as point groups with generators exclusively of order <3 , while point groups $\mathcal{K}_2$ have exactly one generator of order ≥ 3 and $\mathcal{K}_3$ have more than one such generator. Obviously degeneracy in $\mathcal{K}_2$ can be “traced back” uniquely to this higher order generator, which at the same defines also the unique symmetry axis of highest order, while for the “higher symmetric” point groups $\mathcal{K}_3$ no simple relation between IRs and (higher order) symmetry element exists.

We now put our focus on the symmetry properties of the quantum mechanical total angular momentum operator $\mathbf{l}$ and it is z component $\mathbf{l}_z$ in the three point group families. A comparison with Tables 1–5 shows that for all two-dimensional IRs E for all groups $G \in \mathcal{K}_2$ the decomposition of the tensor square of E into irreducible representations always contains Γ_{1_z} , namely in its anti-symmetric part. In particular

$$E \otimes E = \Gamma_{1_z} \oplus \Gamma_0 \oplus \rho_q; \dim(\Gamma_0) = \dim(\Gamma_{1_z}) = 1, \dim(\rho_q) = 2, \quad (5)$$

with

$$[E \otimes E] = \Gamma_{1_z} \quad (6)$$

holds, with $[M]$ denoting the anti-symmetric part of a tensor M (below and in the SI $[M]$ is identified with the so called “alternating square” functor $\text{Alt}^2(M)$).

On the contrary, for groups from $\mathcal{K}_3$, $[E \otimes E]$ does not represent (any components) of $\mathbf{l}$ (see Tables 1–5). Rigorous definitions and a rigorous proof of 6 and details on the relation between $\mathbf{l}$ and the representation space $O(3)$ and further detailed outlines are given in the SI. We note that an inspection of the Tables 1–5 in principle could replace a proof, however as there are infinitely many point

Table 1: Angular momentum and $E \otimes E$ representation tables for $\mathcal{K}_1$ point groups.

Point grp	C_1	C_s	C_2	C_i	C_{2v}	C_{2h}	D_2	D_{2h}
Γ_{1_z}	A	A'	A	A	A_2	A_g	B_1	B_{1g}

Table 2: $\mathcal{K}_2$ cyclic-based point groups.

Point grp, $n \geq 1$	C_{2n+1}	C_{2n+2}	$C_{(2n+1)v}$	$C_{(2n+2)v}$	$C_{(2n+1)h}$	$C_{(2n+2)h}$	S_{4n}^a	S_{4n+2}
$\Gamma_e, i=1 \dots n$	E_i	E_i	E_i	E_i	E'_i, E''_i	E_{ig}, E_{iu}	E_i	E_{ig}, E_{iu}
Γ_{1_z}	A	A	A_2	A_2	A'	A_g	A	A_g
$[\Gamma \otimes \Gamma]$	A	A	A_2	A_2	A'	A_g	A	A_g

^a i ranges from 1 to $2n-1$.

Table 3: $\mathcal{K}_2$ dihedral-based point groups.

Point grp, $n \geq 1$	D_{2n+1}	D_{2n+2}	$D_{(2n)d}^a$	$D_{(2n+1)d}$	$D_{(2n+1)h}$	$D_{(2n+2)h}$
$\Gamma_e, i=1 \dots n$	E_i	E_i	E_i	E_{ig}, E_{iu}	E'_i, E''_i	E_{ig}, E_{iu}
Γ_{1_z}	A_2	A_2	A_2	A_{2g}	A'_2	A_{2g}
$[\Gamma \otimes \Gamma]$	A_2	A_2	A_2	A_{2g}	A'_2	A_{2g}

^a i ranges from 1 to $2n-1$.

Table 4: $\mathcal{K}_t$ type cubic point groups.

Point grp	T		$T_d=O$			T_h				O_h					
Γ_l	T		T_1			T_g				T_{1g}					
Γ	E	T	E	T_1	T_2	E_g	T_g	E_u	T_u	E_g	T_{1g}	T_{2g}	E_u	T_{1u}	T_{2u}
$[\Gamma \otimes \Gamma]$	A	T	A_2	T_1	T_1	A_g	T_g	A_g	T_g	A_{2g}	T_{1g}	T_{1g}	A_{2g}	T_{1g}	T_{1g}

Table 5: $\mathcal{K}_t$ type icosahedral point groups.

Point grp	I
Γ_l	T_1
Γ	T_1
$[\Gamma \otimes \Gamma]$	T_1

Point grp	I_h
Γ_l	T_{1g}
Γ	T_{1g}
$[\Gamma \otimes \Gamma]$	T_{1g}

Γ_l	T_{1g}								
Γ	T_{1g}	T_{2g}	G_g	H_g	T_{1u}	T_{2u}	G_u	H_u	
$[\Gamma \otimes \Gamma]$	T_{1g}	T_{2g}	$T_{1g} \oplus T_{2g}$	$T_{1g} \oplus T_{2g} \oplus G_g$	T_{1g}	T_{2g}	$T_{1g} \oplus T_{2g}$	$T_{1g} \oplus T_{2g} \oplus G_g$	

groups such that an inspection will never be finished (i.e. it is impossible to exclude possible exceptions with this strategy).

So we see that in point groups from $\mathcal{K}_2$ there is an intimate connection between two-dimensional IRs and Γ_{1z} . In the next section we consider branchings of two-dimensional electronic levels at a group theoretical level.

2.3 Distortions

Distorting a molecule from a higher to a lower symmetric structure leads to a restriction of the representations of molecular eigenstates to a subgroup H of G , which can change the shape of its irreducible decomposition. This is usually called 'descent in symmetry' in chemistry, the mathematical discipline concerned with this is 'branching representation theory'.

Consider a point group $\mathcal{H} \subset \mathcal{G}$, and a two dimensional representation E of $\mathcal{G}$. If the restriction of E to $\mathcal{H}$ ($=E|_{\mathcal{H}}$) branches into a direct sum of two one-dimensional representations of $\mathcal{H}$,

$$E|_{\mathcal{H}} = A_\alpha \oplus A_\beta \quad (7)$$

then

$$[E \otimes E]|_{\mathcal{H}} = [E|_{\mathcal{H}} \otimes E|_{\mathcal{H}}] = A_\alpha \otimes A_\beta \quad (8)$$

as is lined out in the SI. If E was a representation of the point group $\mathcal{G}$ on the (x,y) -plane, then

$$\Gamma_{1z}|_{\mathcal{H}} = [E \otimes E]|_{\mathcal{H}} = A_\alpha \otimes A_\beta. \quad (9)$$

The angular momentum representation of $\mathcal{H}$ on the rotations around the z axis is the tensor product of the two representations A_α, A_β .

This implies that if an E -type IR in a non-isometric point group is restricted to a subgroup such that it splits into two non-degenerate hence one-dimensional IRs, then the direct product of these two one-dimensional representations is exactly the representation of the z component of the angular momentum operator (in the subgroup). This is an essential result.

In particular the Jahn-Teller (JT) distortions to be discussed in the next section can trivially be described as a descent in symmetry, such that all considerations from above are valid for JT distortions.

2.4 'Primoid' second order JT systems

We adopt in the following a simplistic view on the Jahn-Teller-Effect based on the original idea from Landau and Teller where distortions were considered in the form of small perturbations and based on a specific situation of electronic degeneracy. As a starting point for a deeper understanding and a contemporary view on the JT effect we refer the reader to I. B. Bersuker's introductory text "Recent Developments in the Jahn-Teller Effect theory" [10]. We are focusing only on the basic integrals occurring in the perturbation expansion [11] of the molecular

energy with respect to a deviation (or distortion) Q from the minimum geometry on the adiabatic potential energy surface. In general Q may be regarded as some symmetry adapted local nuclear distortion coordinate, like a vibrational normal mode. In that sense the occurrence of a first order JT distortion is determined by the size of the first order coefficients in Q :

$$\langle \Psi_0 | \frac{d\hat{H}}{dQ} | \Psi_0 \rangle \quad (10)$$

with the ground state wave function Ψ_0 , while second order JT distortions are controlled by the negative components of the second order coefficients [11]

$$\sum_{i>0} \frac{\left| \left\langle \Psi_0 \left| \frac{\partial \hat{H}}{\partial Q} \right| \Psi_i \right\rangle \right|^2}{\varepsilon_i^0 - \varepsilon_0^0} \quad (11)$$

with the virtual state wave functions Ψ_i , and the corresponding unperturbed state energies ε_i^0 (for $j=0, i$).

Let us consider now a one electron (for simplicity) molecule in a twofold degenerate, E type, one-electron state ψ_0 , then the JT theorem implies that for a non-linear point group symmetry G a non-totally symmetric distortion mode Q exists such that according to expression 10 we have $\Gamma_Q \subseteq \Gamma_{\psi_0}^* \otimes \Gamma_{\psi_0}$.

When we now interpret this one-electron E state as a spatial orbital from which we can build two-electron configuration state functions from symmetry adapted linear combinations of Slater determinants of these (spin)orbitals, we arrive at various possible combinations of ground and virtual state (Ψ_0 and Ψ_i) symmetries:

$\Gamma_{\Psi_0}, \Gamma_{\Psi_i} \subseteq \Gamma_{\psi_0} \otimes \Gamma_{\psi_0} = \Gamma_0 \oplus \text{Alt}^2(E) \oplus \rho_q$ (with eq. 5). From those one can choose $\Gamma_{\Psi_0} = \Gamma_0$ and $\Gamma_{\Psi_i} = \Gamma_Q$, yielding, $\Gamma_Q \subseteq \Gamma_{\psi_0}^* \otimes \Gamma_{\psi_i} = \Gamma_0 \otimes \Gamma_Q = \Gamma_Q$, such that a second order JT distortion by the mode Q is possible. Such a choice we call “**primoid** second order JT system”. In the practice of quantum chemical calculations, primoid second order JT systems reveal their nature in the orbital space from which their state functions can be constructed. This is demonstrated in the degeneracy and branching of orbital energies like in C_4H_4 (see below and Fig. 1).

Also, by this two-electron wave function construction, from an one-electron wave function, both Ψ_0 and the virtual state Ψ_i can only be in the decomposition

Fig. 1: Frontier orbital energies ε for the ground state saddle point (D_{4h}) or minimum structure (D_{2h}) calculated at the generalized valence bond – perfect pairing (GVB(PP)/TZVPP) level of theory for cyclobutadiene (C_4H_4). Orbital energy splitting upon distortion Q from D_{4h} to the D_{2h} minimum is indicated by the dashed lines. The distortion from $D_{4h} \rightarrow D_{2h}$ is a *primoid* second order Jahn-Teller (JT) distortion via a B_{1g} mode. The corresponding electronic levels are shown in Fig. S1 in the SI. Note that the electronic levels are *not degenerate* (second order JT system), but the underlying orbital structure that is depicted here shows degeneracy and branching (*primoid* second order JT system). The direct products $E_g \otimes E_g$ and $B_{2u} \otimes B_{3u}$, the latter corresponding to the paramagnetic virtual excitation, contain or are the IR for the z component of the angular momentum operator. The molecule in the D_{4h} saddle point configuration shows a much stronger paramagnetic response than the D_{2h} minimum structure (compare Fig. 3) but both are classified as antiaromatic.

of $E \otimes E$, which together with the restriction to cases where JT causes only small structural perturbations can warrant that the energy denominator in expression 11 is not too large.

For a counter example of a *non-primoid* second order JT case, consider Si_4F_4 in D_{2h} symmetry [12] which distorts via a B_{1g} mode to C_{2h} , or similarly $Si_2Ge_2F_4$ which distorts from D_{2h} via C_{2h} to C_s . In general, all cases of second order Jahn-Teller distortion which are of a reference (or highest possible) point group symmetry that possesses no degenerate IRs over $\mathbb{R}$, are non-primoid second order Jahn-Teller cases.

“Non-linear open shell singlets” [13], if the open shell character is caused by symmetry and not by accidental degeneracy, are the possibly most important class of primoid second order Jahn-Teller cases in their undistorted idealized high-symmetry reference structures.

2.5 JT and paramagnetism in point groups from $\mathcal{K}_2$

All point groups G in the family $\mathcal{K}_2$ (see Tables 2 and 3) are represented by at least one two-dimensional IR over $\mathbb{R}$, say E and in these point groups $\text{Alt}^2(E)$ represents for all E the z component of the quantum mechanical angular momentum operator $\mathbf{I}_z$. Now molecular systems in electronic states represented by E are due to their degeneracy prone to a first order JT distortion. If such a distortion to a subgroup H of G occurs then E branches into two one-dimensional representations, say A_α and A_β . The corresponding lower lying electronic state say A_α eventually will become the ground state (or a SOMO or HOMO orbital in the effective one-particle picture) while the higher lying state A_β will become some virtual state (or a UMO or possibly the LUMO depending on the size of the distortion). Then and especially if the distortion is not too large, such that the energy difference between occupied and virtual states will not become too large, the system becomes by virtue of the symmetry selection rule for paratropic currents (eqns. 1 and 3) strongly susceptible to induced paratropic currents (since according to eq. 9 $A_\alpha \otimes A_\beta = \Gamma_1$). In this way we see that all first order JT cases arising from point groups G in the family $\mathcal{K}_2$, that is all non-isometric first order JT cases, are inherently prone to paramagnetism.

Since this result is based on group theoretical considerations it can be seen as a completely general symmetry property that combines structure and magnetic response. Similar like e.g. the dipole transition rule which gives a general symmetry property of the molecular response with respect to any dipole fields. Like such spectroscopic selection rules, the predictivity is of course limited by the fact that we deal merely with symmetry rules which are completely independent of the peculiar quantitative electronic properties of a molecule under investigation. But also similar to these selection rules the principle might serve as a basis for the understanding of the phenomenon of antiaromaticity in a very general sense.

It is very important to note that these considerations are not restricted to the first order JT effect since this is bound to open shell systems, and the most important examples for antiaromaticity like 1,3-cyclobutadiene are in their distorted (thus stable) configuration, closed shell cases. From the definition of the *primoid* second order JT case it follows immediately that there is the very same connection between symmetry and paratropic response currents. One example is 1,3-cyclobutadiene, that goes back to states derived from a doubly occupied doubly degenerate orbital.

We now can formulate the main result of this work, as is announced in the introduction:

First order and primoid second order JT distorted molecules out of non-isometric point groups are prone to induced paramagnetism in magnetic fields parallel to the main axis of symmetry.

Assuming small distortions, it is clear that these cases match the complete IUPAC definition of antiaromaticity (see Introduction and SI) such that a strict connection between the defining properties is given. Since to the best of our knowledge there exists no undoubted example for an antiaromatic molecule that does not belong to this class, we suggest that this is the symmetry principle underlying antiaromaticity.

It is important to understand, that JT distortion implies point groups with higher than one-dimensional representations (over $\mathbb{R}$, eg. point group C_3) thus this phrase implies that point groups out of $\mathcal{K}_2$ are addressed. At this stage it might be of interest and importance to note that these point groups are those which have exactly one generator element of order larger than 2, in chemical jargon that might be formulated like: “no more than one rotational axis of order 3 or higher”, while point groups $\mathcal{K}_3$ are point groups “that have more than one non-parallel C_n axis with $n \leq 2$ ”.

In the following we will discuss four representative examples for molecules, each of them reflecting a slightly different situation in hindsight to its antiaromatic character.

2.6 Examples

2.6.1 C_4H_4

1,3-Cyclobutadiene (C_4H_4 , see also Figs. 1, 2 and 3 for an orbital diagram, orbital depictions and an visualization of magnetically induced currents) is such a prominent example for antiaromaticity that it is mentioned in the IUPAC definition (see Ref. [4, 5] and the SI for a full quote). Details on its symmetry, electronic states and the nature of the Jahn-Teller distortion have been worked out by Nakamura and co-workers [14] in the framework of a MCSCF study. It is a case where for the full D_{4h} symmetry we have double occupation of the doubly degenerate e_g orbitals (e_g^2), which results in purely non-degenerate electronic states, the first four of which are in energetically ascending order ${}^1B_{1g}$, ${}^3A_{2g}$, ${}^1A_{1g}$, ${}^1B_{2g}$. Hence, this is a prototypical example for a primoid second order Jahn-Teller case.

Formally removing one electron yields the $[C_4H_4]^+$ cation and a 2E_g ground state. To check the possibility of a non-zero integral term 10, thus the possibility of existence

Fig. 2: Frontier orbitals of the electronic ground state in C_4H_4 at different symmetries, calculated at the GVB(PP)/TZVPP level of theory, displayed as isosurfaces at densities of 0.066. (a) Highest occupied molecular orbital (HOMO) in the D_{4h} saddle point structure. The two-fold degenerate orbital is represented by the e_g IR. (b) HOMO (left) and lowest unoccupied molecular orbital (LUMO, right) in the D_{2h} minimum structure. The HOMO is represented by b_{2u} , the LUMO by the b_{3u} IR.

Fig. 3: D_{2h} electronic ground state, minimum structure (distances given in units of Å) of C_4H_4 , and stream line plot of magnetically induced (field direction indicated by the blue arrow) currents at a plane 0.5 Å below the molecular plane. Integration of currents flowing through the purple surface yields a global molecular ring current of -22.4 nA T^{-1} (paratropic).

of a distortional mode Q leading to an energetic stabilization, which is a condition for a first order JT effect, we need to decompose $E_g \otimes E_g$ into a direct sum of IRs. This yields

$$E_g \otimes E_g = A_{1g} \oplus [A_{2g}] \oplus B_{1g} \oplus B_{2g} \quad (12)$$

Permissible distortional mode symmetries (as must be checked separately) here are either B_{1g} or B_{2g} , these are

related by a 45° rotation around z , and give rise either to a rhombic or a rectangular D_{2h} symmetric structure, respectively. Quantum chemical calculations show that in this case the rhombic structure is preferred [14] and leads to a splitting of the degenerate e_g orbitals into two non-degenerate b_{2u} and b_{3u} orbitals.

Since D_{4h} is a non-isometric point group (case $\mathcal{K}_2$) and E_g is a degenerate level we know according to eq. 5 that $E_g \otimes E_g$ contains the IR for the z component of the angular momentum Γ_{1_z} , which in D_{4h} is A_{2g} . Moreover from eq. 6 follows that this is $\Gamma_{1_z} = \text{Alt}^2(E_g) = [E_g \otimes E_g] = A_{2g}$. Accord-

ing to eq. 9 in the new group D_{2h} the IR for 1_z is contained in the direct product of the two branches of E_u . That this is indeed the case shows a quick check: in D_{2h} we have $B_{2u} \otimes B_{3u} = B_{1g}$, which is identical to Γ_{1_z} in this group.

As we have identified C_4H_4 by its orbital structure as a (potential) primoid second order JT case by recursion to the hypothetical $[C_4H_4]^+$ case, we could easily identify the possible symmetries of the Q mode that could be operational in a second order JT effect. Note that since this a (primoid) second order JT distortion no electronic state degeneracy is involved but only a coupling between the ${}^1B_{1g}$ ground state and an ${}^1A_{1g}$ excited state takes place which is moderated by the B_{1g} type distortion. The degeneracy and branching only is reflected in the underlying orbital structure which leads to the classification as a *primoid* second order JT system. And in addition by the arguments from above on the angular momentum representation we know that in the “real” n -electron state case with a $(e_g)^2$ occupation there will be occupied-to-virtual transitions of Γ_{1_z} a symmetry species available in the accordingly distorted molecule.

We can verify this as well: Eq. 12 shows all permissible two electron states from the $(e_g)^2$ occupation. As a matter of fact the ground state turns out to be of a ${}^1B_{1g}$ symmetry species and out of the virtual states given by the remaining three terms of eq. 12 again only a virtual transition to the ${}^1A_{1g}$ state is of a symmetry species that is in accordance with a permissible distortional coordinate Q (see $[C_4H_4]^+$ case), that is

$$B_{1g} \otimes A_{1g} = B_{1g}. \quad (13)$$

So both models predict of course the same possible symmetries of distortion Q out of D_{4h} to D_{2h} . To find the by virtue of the “primoid” argument predicted virtual transition of Γ_{1_z} symmetry species we have to restrict all terms on the right side of eq. 12 to the subgroup D_{2h} . This gives

$$(A_{1g} \oplus A_{2g} \oplus B_{1g} \oplus B_{2g})_{|D_{2h}} = A_g \oplus B_{1g} \oplus A_g \oplus B_{1g} \quad (14)$$

Since thus the ground state “branches” from B_{1g} to A_g , for example a virtual transition $A_g \rightarrow B_{1g}$ is available which corresponds obviously to a B_{1g} symmetry species and, that as we have used already above, is identical to Γ_{1z} in D_{2h} .

So we have shown how the argument of prediction of virtual transitions of Γ_{1z} symmetry, that is paramagnetic response, for the primoid second order JT case C_4H_4 (out of non-isometric point groups) works. Calculations show (see SI for details) that we can expect a double bond localization, or at least a splitting of C–C distances from 1.426 Å (D_{4h}) to 1.552 and 1.324 Å. The weight of the second configuration is about 4% at the D_{2h} minimum structure, thus it is safe to use a single reference method for calculation of the magnetically induced ring currents (see SI for details). The integral of the total global current susceptibility amounts to -22.4 nA T^{-1} paratropic total current at HF/VTZ level of theory.

For the aromatic benzene we find diamagnetic current contributions of about $+20 \text{ nA T}^{-1}$. One might say C_4H_4 is as paramagnetic as benzene is diamagnetic (but one should note that there are paramagnetic contributions to the benzene currents as well and these are of a size of about -9 nA T^{-1}) [15].

C_4H_4 is the classical example for antiaromaticity, in agreement with that we find that its ground state geometry is derived from a primoid second order Jahn-Teller distortion out of a point group of the family $\mathcal{K}_2$, it has a small HOMO-LUMO gap and thus as a consequence of the latter two arguments shows a strong paramagnetic response with respect to a magnetic field $\mathbf{B}$ parallel to the original C_4 axis.

2.6.2 C_8H_8

Another example from the compound class of the n -annulenes is cyclooctatetraene (C_8H_8) which is similar to C_4H_4 in that it represents also a primoid second order JT case, but as we will see shows some quantitative difference in its paramagnetic response.

The idealized D_{8h} symmetry is not observed as a ground state minimum [16] due to a primoid second order JT distortion (e_u^2 case). Also here we observe a B_{1g} distortion to a D_{4h} structure, which turns out to be no minimum structure either as it undergoes another second order JT distortion along a B_{1u} mode to a D_{2d} symmetric minimum structure. As the first distortion is of primoid type we know that in D_{4h} , the IR Γ_{1z} will be the tensor product of the branches of the e_u orbitals. As these are b_{1u} and b_{2u} and $b_{1u} \otimes b_{2u} = a_{2g}$ and $\Gamma_{1z} = a_{2g}$ in D_{4h} we find our symmetry rule

confirmed. Since C_8H_8 undergoes another second order JT distortion into D_{2d} we still find

$$\begin{aligned}(B_{1u} \otimes B_{2u})|_{D_{2d}} &= A_{2g}|_{D_{2d}} \\ B_{1u}|_{D_{2d}} \otimes B_{2u}|_{D_{2d}} &= A_2 \\ A_1 \otimes A_2 &= A_2\end{aligned}$$

In agreement with this A_2 represents Γ_{1z} in D_{2d} , hence the prediction that the frontier orbital symmetries that were branching out of e_u in this sequence of primoid and non-primoid second order JT distortions relate to each other in Γ_{1z} manner is confirmed (again note that the electronic levels themselves are not degenerate and branch but rather couple by the distortion, see also Fig. 4). In addition paramagnetic response for the D_{2d} minimum of C_8H_8 is predicted, since we started from a non-isometric point group symmetry.

In contrast to the markedly paramagnetic nature of the magnetic response of the ground state minimum of C_4H_4 (-21 nA T^{-1}) for C_8H_8 we find barely -2.5 nA T^{-1} total

Fig. 4: Frontier orbital energies ϵ for the ground state saddle point (D_{8h} of second order, D_{4h} of first order) of minimum structures (D_{2d}) calculated at the generalized valence bond – perfect pairing (GVB(PP)) level of theory for cyclooctatetraene (C_8H_8). See Fig. 5 for depictions of the corresponding orbitals. Orbital energy splitting upon distortion Q from D_{8h} via D_{4h} to the D_{2d} minimum is indicated by the dashed lines. The first distortion $D_{8h} \rightarrow D_{4h}$ is a *primoid* second order Jahn-Teller (JT) distortion via a B_{1g} mode, the second one is a non-primoid JT distortion via a B_{1u} mode. Again, like in C_4H_4 the electronic ground state is non-degenerate (second order JT) but the underlying orbital levels show degeneracy and branching (primoid second order JT system). All three direct products $E_{2u} \otimes E_{2u}$, $B_{1u} \otimes B_{2u}$, and $A_1 \otimes A_2$, the latter two corresponding to the paramagnetic virtual excitation, contain or are identical to the IR for the z component of the angular momentum operator. Virtual excitations represented by the terms given in expression 11 are not only decreasing by virtue of the increasing energy denominator but also due to the decreasing overlap integral in the numerator. Thus the molecule in the D_{4h} saddle point configuration shows a much stronger paramagnetic response than the D_{2d} minimum structure (compare Fig. 6).

Fig. 5: Frontier orbitals of C_8H_8 at different geometries, calculated at the GVB(PP)/TZVPP level of theory, displayed as isosurfaces at densities of 0.05. (a) Highest occupied molecular orbital (HOMO) in the D_{8h} double saddle point structure. The two-fold degenerate orbital is represented by the e_{2u} IR. (b) HOMO (left) and lowest unoccupied molecular orbital (LUMO, right) in the D_{4h} double saddle point structure. The HOMO is represented by b_{1u} , the LUMO by the b_{2u} IR. (c) HOMO (a_1 , left) and LUMO (a_2 , right) in the D_{2d} minimum structure.

induced current. However, the paratropic contribution amounts to -8.2 nA T^{-1} , thus we again see the rule confirmed that first and primoid second order JT distortions lead to systems with paramagnetic response. In this case however the total paramagnetic response is too weak to assign the predicate “antiaromatic” to this molecule. One reason is that the *second* second order JT distortion (which for itself is not of primoid type since the degeneracy of the frontier orbital has already been lifted to b_{1u} and b_{2u}) causes a further increase of the HOMO-LUMO energy gap to 9.7 eV at GVB(PP) level of theory, thus diminishing the magnetic response accordingly. For comparison the value for C_4H_4 at the same level of theory (GVB(PP)) is 7.2 eV.

Fig. 6: D_{2d} electronic ground state, minimum structure (distances given in units of Å) of C_8H_8 , and stream line plot of magnetically induced (field direction indicated by the blue arrow) currents in the average molecular plane (x,y -plane). Integration of currents flowing through the purple surface yields a global molecular ring current of -2.5 nA T^{-1} (purely paratropic contribution), which is comparably weak, thus the D_{2d} electronic ground state minimum structure of C_8H_8 is classified as weakly antiaromatic or non-aromatic.

2.6.3 The General $4n \pi$ annulene and double bond localization (bond length alternation)

In antiaromatic n -annulenes ($C_{4n}H_{4n}$) in the idealized $D_{(4n)h}$ symmetry, double bond localisation can be easily understood as a second order (primoid) JT effect. The saddle point in these cases would have a double occupied e_{nu} or e_{ng} orbital, for even n or for odd n , respectively, thus an $(e_{nu})^2$ or $(e_{ng})^2$ configuration, respectively, that can distort via a b_{1g} mode to $D_{(2n)h}$ symmetry, leading to a branching of e_{nu} to b_{1u} and b_{2u} for even n and similarly with *gerade* symmetry species g for odd n , which would correspond in analogy to the above discussed C_8H_8 to a double bond localization in the first instance.

An introductory discussion of the view of double bond localisation in ring systems as a JT distortion as well as its relation to the Peierls distortion in polyethin is given in Ref. [17].

2.6.4 MnF_3

Manganese trifluoride is a prime example for a first order Jahn-Teller effect which would give in D_{3h} (a non-isometric point group) an E' ground state. In fact the lowest energy species is in the 5B_1 electronic ground state and has a planar C_{2v} symmetric structure which was predicted theoretically

and confirmed by gas-phase electron-diffraction [18]. Magnetic response calculations indeed show magnetically induced paratropic currents around the central manganese atom as well as locally around the fluorine atoms (see Figs. 7 and 8).

Unlike in the previous two examples the induced paramagnetism is hidden to some extent, since experimentally the permanent magnetic moment resulting from the spin dominates the magnetic properties and for the other since in this case the paramagnetic currents are atom-centered which hampers the computational analysis of the current densities due to interference with other atomic current contributions. In addition though, MnF_3 can be observed in the gas-phase [18], in condensed matter the coordinatively unsaturated threefold coordinated Mn^{3+} cation under normal conditions is not observable.

Fig. 7: The 5B_1 electronic ground state structure of MnF_3 with C_{2v} symmetry and the b_1 α -HOMO and a_1 α -LUMO. The LUMO is displayed for a rotated molecule, the angle of rotation is about -120° . The rotational relation between the orbitals is already noticeable with bare eye.

Fig. 8: The 5B_1 electronic ground state structure of MnF_3 with C_{2v} symmetry and a stream-line plot of the magnetically induced currents in the molecular plane ($\mathbf{B}$ field is set perpendicular to the molecular plane). A paratropic current vortex (counterclockwise) around the Mn atom is found.

2.6.5 Pentalene

An interesting case that at first sight seems to be an outlier of our antiaromaticity symmetry rule is pentalene (see above for a molecular formula). Pentalene is a well-known case of antiaromaticity and its magnetisability was recently studied computationally [19]. Its apparent JT idealized symmetry would be D_{2h} (with HOMO a_u and LUMO b_{1u}) while its computationally predicted and experimentally confirmed minimum structure is C_{2h} (HOMO: a_u , LUMO a_u). However, D_{2h} is clearly a class $\mathcal{K}_1$ point group, thus the observed $D_{2h} \rightarrow C_{2h}$ distortion cannot be interpreted as a primoid second order JT type distortion (as outlined in Section 2.4), nevertheless we observe strong paramagnetic response which is dominated by the HOMO-LUMO virtual excitation and a distortion that is in agreement with a double-bond localisation. In essence the crucial argument in this case is that we have to deal with a ring system containing a set of conjugated double bonds on its perimeter. Thus a natural way of interpretation would be to classify pentalene as a perturbed eight membered ring, that derives from an idealized but perturbed D_{8h} point group symmetry, with the perturbation being the additional transannular C–C bond. In this way the fact that the direct products of the HOMO-LUMO IRs are identical to the IR of $\mathbf{I}_z$ is mostly easily seen from the branching of D_{8h} 's E_{2u} into the A_u and B_{1u} IRs. Therefore pentalene cannot directly by using our symmetry rule be classified as an antiaromatic compound.

2.7 Chemical interpretation of dia- and paratropic response currents

Equation 2 means that a magnetic field probes the accessibility of virtual states that ideally differ from the ground state only by a rotational orientation of the wave function in space and thus are spatially very closely related. In case a molecule responds with a strong paratropic current density this can mean that there is a situation of close to degeneracy resembling the spatial symmetry of an atomic open subshell. The optimal symmetry/energy relation in question of eq. 2 in this way can be interpreted as the analog to an atomic open subshell case for a general molecular system, and the magnetic response is a concise probe for that. In addition one also yields information on

the direction of the symmetry relation from the direction of the field **B**.

The type of degeneracy that is probed by the magnetic field is not the only possible type. Other types of (near) degeneracy include ones derived from what is sometimes called “accidental” degeneracy where there is no obvious (close-to-)symmetry relation in $O(3)$ between occupied and empty levels and hence no contribution to paramagnetic response from these.

In contrast the antithetical concept of aromaticity is characterized by induced diamagnetic currents. In the common gauge origin approach, diamagnetic currents to first order are determined by the ground eigenstate Ψ_0 of the **B** field free system and correspond to a precession motion of the electrons in the magnetic field that increases the average expected angular momentum $\langle \Psi | \hat{L}_z | \Psi \rangle$, (for Ψ the wave function in the magnetic field) which will lead in general if the ring current extends over a sufficiently large domain covering sufficiently much of the total electron density in the molecule to an increase in total energy.

An alternative way is to describe diamagnetic response via the “Continuous Transformation of the Origin of the Current Density” (CTOCD-DZ) approach which was introduced to theoretical chemistry by Keith and Bader in 1992 [20]. It allows in particular within Fowler and Steiner’s ipso-centric *ansatz* [7] to express the full magnetic response completely in terms of transitions from occupied to virtual state (or orbital).

In this model the diamagnetic currents are determined by virtual transitions of dipole symmetry, namely dipole transition moments perpendicular to the external field **B**. That means that for example sigma bonds that leave pairs of σ and σ^* type occupied and virtual orbitals, where the bond direction is perpendicular to the external field, contribute to the diamagnetic response. A simple example would be a bonding orbital that has some anti-bonding counterpart with a nodal plane parallel to **B**.

In that way an electronic structure that contains covalent or systems of delocalized covalent bonds (and naturally the corresponding anti-bonding orbitals unoccupied) is diamagnetic. So we can summarize that a strong diamagnetic response current can be a consequence of (full) occupation of bonding orbitals and empty anti-bonding orbitals, which differ from bonding orbitals by additional nodal planes parallel to **B**. Whereas paramagnetic response can indicate incompletely occupied molecular shells which are similar up to a rotation around an axis parallel to **B**. This in effect leads to a distinctly different picture of antiaromaticity as it was originally envisaged by Breslow as he for instance noted “Thus antiaromaticity is a particular aspect of anti-bonding, just as aromaticity

is a particular aspect of bonding” [3], which is according to our analyses not the case since it is not the occupation of anti-bonding orbitals that lead to the characteristic paramagnetic response currents, nor would it lead to a peculiar small HOMO-LUMO energy gap in general, or be connected with structural distortions.

At quick glance it might be surprising that antiaromaticity has often been observed or at least proposed for organic ring systems and related species like polycyclic molecules. In contrast antiaromaticity is rarely mentioned in the context of inorganic coordination compounds and metal clusters. On the basis of our findings this is easily explained, because the vast majority of organic ring systems and related compounds can be deduced from the particular point groups $\mathcal{K}_2$, that is non-isometric point groups with degenerate real irreducible representations. In exactly this symmetry family we have the strict relation between JT distortion and paramagnetic response. While the majority of 3D-cluster systems or coordination compounds are derived from isometric point groups where this strict correspondence does not exist. In addition coordination compounds are of course metal-centered and at least experimentally the induced paramagnetism there is often masked by permanent magnetic moments centered at the metal atoms.

The here introduced analyses might serve as a basis for a deeper understanding of antiaromaticity, but despite its principle significance, antiaromaticity is not a widely spread chemical phenomenon (for obvious reasons, since it is not only connected with structural instability but also instability in the sense of high reactivity by virtue of the small energy gap between occupied and virtual states). At this stage one might speculate if there is some consistent way to define aromaticity by the absence of paramagnetism alone, an idea going back to Bilde and Hansen [21]. In that way the presence or absence of rotationally accessible virtual states and their intimate connection with structural distortions could eventually be the only decisive criteria for presence or absence of aromaticity or antiaromaticity.

An extension of these considerations we are currently working on is the analysis of the symmetry rules of magnetic response and JT distortion in the fully relativistic domain including spin-orbit coupling.

2.8 A response theoretical point of view on antiaromaticity

In general, the possibility of a response theoretic description of the JT effect shows that structural stability of a

symmetric molecule can be described as response property. In particular, possible stabilizing distortion modes can be classified in terms of their symmetry species (IRs). We have shown here, that in certain point groups ($\mathcal{K}_2$) the symmetry species of such stabilizing distortions and the symmetry species of the magnetic field are both contained in the tensor square of any degenerate representation of such a point group. A setting which eventually must lead to induced paramagnetic currents in current loops perpendicular to the main symmetry axis.

2.9 Implications for the synthetic chemistry of antiaromatic compounds

We have shown that antiaromaticity in the sense of the IUPAC definition [4] is inherently connected with structural instability and in general, as for example shown for the case of COT (*vide supra*) one has to deal with a balance of two effects: for the one, a dominant the degeneracy (leading to large values in expr. 3) causes a strong tendency to distortion, while for the other, the stronger the distortion from the idealized symmetry will be, the weaker a paramagnetic response can be expected. In fact, too strong (or too many) distortion modes causes COT to show only a weak antiaromatic or even non-aromatic characteristics. Hence, the design of a sufficiently stable, but still strongly antiaromatic molecule needs to show elements of controlled or accidental “symmetry breaking”. For example antiaromatic norcorroles [22].

Break an idealized D_{4h} symmetry, by the variation from direct to $-CH-$ bridging, to D_{2h} symmetry, while the frontier orbitals still maintain quantitatively enough internal symmetry to give non-zero contributions in (3). Such elements of controlled symmetry breaking may involve for example unsymmetric substitution like $-SiMe_3$ instead of $-Bu$ or sulfur for oxygen, and similar patterns.

3 Conclusions

We have shown by symmetry considerations how Jahn-Teller distortion and paramagnetic response are intimately related in the family of points groups comprised of C_n , C_{nv} , C_{nh} , D_n , D_{nh} , for $n > 2$ and S_{2n} and D_{nd} for $n > 1$.

We suggest that this connection is the underlying symmetry principle of antiaromaticity, since the latter is defined by the central properties of a small HOMO-LUMO gap, proneness to structural distortion or instability and magnetically induced paramagnetic ring currents. We also saw that electronic structure related to covalent or delocalized covalent bonding or filled atomic subshells followed by empty subshells is related to diamagnetic response while electronic situations resembling open atomic subshells are related to paramagnetic response. The sparsity of examples may not only go back to the fact that antiaromaticity is related to low energetic stability but also due the paradoxity between distortion and paramagnetism that is hidden under its definition and that we have revealed in this work. The deepened understanding of antiaromaticity can also guide the design of antiaromatic compounds by use of patterns of controlled symmetry breaking.

4 Supporting information

Supporting Information available online: (S1) Group and representation theoretical details, (S2) Computational details (C_4H_4 , C_8H_8 , MnF_3), (S3) On the physical and chemical interpretation and connection of induced paramagnetism and bonds, (S4) IUPAC definition of Antiaromaticity (DOI: 10.1515/znb-2020-0024).

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