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On the impossibility of localised states for molecular rotors with cyclic potentials

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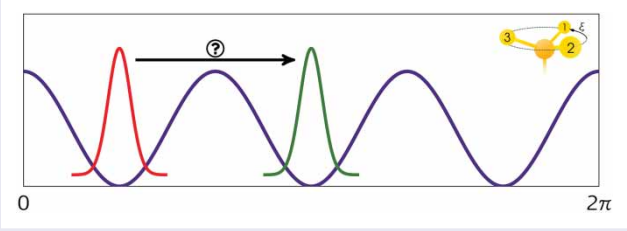
ABSTRACT

We discover a surprising property of an important class of molecular rotors. These rotors have one (e.g. a methyl group) or two (e.g. the planar boron rotor B_{11}^-) moieties that consist of identical nuclei rotating in cyclic model potential energy surfaces with $\mathfrak{h}_{tot}$ equivalent potential wells (e.g. $\mathfrak{h}_{tot} = 3$ for CH_3, $\mathfrak{h}_{tot} = 18$ for B_{11}^-). The familiar semiclassical picture of this contorsion assumes that the potential wells support $\mathfrak{h}_{tot}$ equivalent global minimum structures with corresponding localised wave functions being embedded in the individual potential wells. In contrast, we show that the wave functions of these rotors can never be squeezed into a single potential well, and hence, global minimum structures do not exist. Our quantum mechanical derivation describes the rotors in the frame of the proper cyclic molecular symmetry group $C_{\mathfrak{h}_{tot}}(M)$ and makes use of the spin-statistics theorem and the hypothesis of nuclear spin isomers. We show that if the identical nuclei have zero spins, then a hypothetical localised state would violate the spin-statistic theorem. Otherwise, the hypothetical localised state is ruled out as unphysical superposition of different nuclear spin isomers of the molecular rotors.



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1. Introduction: why molecular rotors call for quantum descriptions

The relationship of chemistry and quantum theory is a difficult one. Even almost a hundred years after the foundation of quantum theory, chemistry is dominated by a semiclassical understanding, and the question if chemistry can be reduced to quantum theory is far from being answered [1–11]. We add a further facet to this debate by showing that in certain cases the motions of molecules must be treated fully quantum mechanically. For molecular rotors with a cyclic potential, semiclassical simulations are physically incorrect.

Molecular rotors are molecules that show internal motions with large amplitude, 'contorsions', in the form of intramolecular rotations, such as torsions or pseudo-rotations. In classic references [12,13], these rotors are treated as semiclassical objects: the motion of the nuclei is described classically, evolving on a specific potential energy surface provided by the electrons. A necessary condition for this description is that the Born–Oppenheimer approximation is correct [1,14,15].

One typical example for such molecular rotors is the combined rotation and pseudo-rotation of planar boron rotors B_{11}^-, B_{13}^+, B_{15}^+, B_{19}^-, which consist of inner molecular 'wheels' that rotate against pseudo-rotating outer 'bearings' [16–23]. For B_{11}^-, for example, the inner 'wheel' and the outer 'bearing' consist of 2 and 9 boron atoms, respectively. In the frame of the Born-Oppenheimer

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*This paper is dedicated to Professor Micha Baer (Tel Aviv) on the occasion of his 80th birthday.

approximation, the electronic ground state potential for the contorsional motion is cyclic with $\mathfrak{h}_{tot} = 2 \cdot 9 = 18$ equivalent potential wells. A semiclassical description associates the corresponding $\mathfrak{h}_{tot}$ potential minima with $\mathfrak{h}_{tot}$ equilibrium structures, also called global minimum structures, of the molecular rotors. We show that these structures do not exist.

It is well known, of course, that quantum effects, such as tunnelling, zero-point energy, interferences or dispersion [24], compromise this simplistic semiclassical approach to chemistry in general, and to molecular rotors in particular. But there are more deeply rooted problems with molecular structures. Theoreticians and philosophers of chemistry have shown that quantum theory, rigorously applied, forbids molecules to have a structure [1,4,7–9,11,14,15,25–31]. A defined molecular structure not only premises the Born–Oppenheimer approximation to be exact. It rejects that molecules and their environment are entangled by Einstein–Podolsky–Rosen correlations; it neglects tunnelling of nuclei between different minima of the electronic potential energy surface; it cannot represent a molecular eigenstate; it violates the indistinguishability of identical nuclei that is reflected by the permutation symmetry of the molecular Hamiltonian and it ignores that molecules must have spherical shapes due to the isotropy of space. Moreover, molecular structures do not emerge automatically from quantum theory; we have to put them into a calculation of molecular eigenstates. It is possible to calculate the eigenenergies of a molecule directly, without employing the Born–Oppenheimer approximation [4,29–31]. But the results from these methods cannot be interpreted in terms of molecular structures [29,30].

Although these arguments are correct, proponents of the semiclassical theory may not find them very convincing: True, the Born–Oppenheimer approximation fails more often than the pioneers of quantum chemistry expected [32–34]. Yet, in many cases, it provides an excellent approximation, at least if the molecule remains in the electronic ground state; semiclassical extensions to propagations on several potential energy surfaces with surface hopping are able to account for non-Born–Oppenheimer effects. Moreover, the isotropy of space can be broken. Properly designed laser fields [35–37], for example, are able to create those directed rotational states that are necessary to speak of a molecular structure. And as the theory of molecular symmetry (MS) groups shows [38–42], not all permutations of identical nuclei are feasible. Permutations and permutation-inversions that do not lead to an observable tunnelling splitting in the molecular spectrum may be neglected. The reduced set of permutations and permutation-inversions of identical nuclei often forms a group that is isomorphic to a molecular point group [41], which, in turn, makes it possible to define a molecular structure. Yes, structures are contingent rather than intrinsic properties of molecules [1,15,27]. But for most scenarios that are relevant in chemistry, the Born–Oppenheimer approximation allows for defining molecular structures in terms of the nuclear configuration.

One might object that some molecules are known for not having a molecular structure even within the Born–Oppenheimer framework. Here, however, we can prepare a quantum analogue of an equilibrium structure in the form of transiently localised states. Consider, for example, ammonia with its double well potential for the umbrella inversion mode [41]. Its eigenstates are delocalised in both potential wells. Nevertheless, ammonia can tunnel periodically between states that are transiently localised in opposite wells. These states are superpositions of the tunnelling doublet states. Hence, this example suggests that we might define analogous states that are localised in one of the potential wells for molecular rotors with cyclic potentials, such as B_{11}^-.

This conclusion, however, is wrong. We show that if the contorting nuclei are identical and the potential of the contorsion is cyclic, molecular rotors can never be prepared in localised states that represent global minimum structures. Even time-dependent states that are squeezed temporarily to (hypothetical) localised wave packets in a single potential well must be ruled out as physical description of such molecular rotors. This surprising property is markedly different from familiar molecular model systems with non-cyclic double or multi-well potentials. An analysis based on the MS groups [38–42] of the molecular rotors, the spin-statistics theorem [41,42] and the nuclear spin hypothesis [43] shows that localised states are unphysical. Depending on the nuclear spin of the contorting nuclei, such states either violate the spin-statistics theorem, or they are superpositions of states belonging to different nuclear spin isomers. The consequences of this result for the molecular dynamics and spectroscopy of molecular rotors are enormous. Molecular dynamics simulations are rendered inadequate, because they necessarily start out from initial conditions that mimic global minimum structures.

Central to our derivation is the assumption that molecules exist in the form of nuclear spin isomers. For homonuclear diatomic molecules, this is an accepted premise. Since the beginnings of quantum mechanics, it is well known that molecular hydrogen, H_2, exists as two nuclear spin isomers, ortho- and para-hydrogen. Although they are interconverted by intramolecular nuclear spin dependent interactions, this process usually takes very long [44], much longer

than the scenarios of laser controlled chemistry. Hence, they can be understood as different molecular species, which is also supported by their different properties. Only recently, experimental studies demonstrated that the sense of rotational motions of diatomic molecules can be steered nuclear spin selectively [45–47]. Other examples supporting the hypothesis that nuclear spin isomers are stable molecular species with potentially very different properties include the alignment of polyatomic molecules [48,49], the conformation dynamics of molecules with observable torsions [50–54] and the quantum dynamics through conical intersections [55–60].

To show that localised states are unphysical representations of molecular rotors with cyclic potentials, it is necessary to derive their MS groups. For this purpose, we determine the set of feasible permutations of identical contorting nuclei employing simple models that facilitate the derivation, while accounting for the essential properties of the molecular rotors. We exemplify our derivations for two molecular rotors: the familiar aligned methyl group and the aligned B_{11}^-. Their MS groups turn out to be the cyclic groups $C_{\mathfrak{h}_{tot}}(M)$. Using their irreducible representations, the spin-statistics theorem and the nuclear spin hypothesis, we identify the nuclear spin isomers of the molecular rotors. Ultimately, this allows us to show that hypothetical localised global minimum structures represented by localised wave functions would either violate the spin-statistics theorem, or they would be coherent superpositions of nuclear spin isomers with different symmetries that cannot be prepared on the time scale of contorsional periods. This leads us to the conclusion that semiclassical simulations are inadequate. Molecular rotors with cyclic potentials call for quantum descriptions.

2. How to characterise the nuclear spin isomers of molecular rotors with cyclic potentials

To follow our argument it is important to understand why molecular rotors, i.e. polyatomic molecules with observable internal motions with large amplitude, exist in the form of nuclear spin isomers. Many textbooks present the two nuclear spin isomers of homonuclear, diatomic molecules with non-zero nuclear spin, usually called para and ortho. Because the overall molecular wave function must be either symmetric or anti-symmetric if both nuclei are exchanged, we can form two distinct combinations of rotational and nuclear spin wave functions. The most prominent example is molecular hydrogen, H_2. Here, the para and ortho versions combine states with even rotational quantum numbers J with an anti-symmetric nuclear spin function, and rotational states with odd J with a symmetric nuclear spin wave function, respectively. These combinations directly follow from the spin-statistics theorem. Hence, for diatomic molecules, different nuclear spin isomers are characterised by different rotational energies, which are also the reason for their distinct properties.

For molecular rotors, finding their nuclear spin isomers is more involved than for diatomic molecules. Although they again follow from the spin-statistics theorem, the complex structure of the molecular eigenstates, even within a zero-order treatment, and the non-trivial symmetry of these molecules make identifying their nuclear spin isomers challenging. Here, at least at low temperatures, different nuclear spin isomers are characterised by different symmetry combinations of rotational–contorsional (rocontorsional) states and nuclear spin states. If we consider scenarios in which electronic transitions take place, identifying the nuclear spin isomers of the molecule becomes even more complex.

To simplify the problem, we employ models in which the contorsion, i.e. the large amplitude internal motion, is approximately decoupled from the other molecular motions. For this purpose, we introduce an effective Hamiltonian, derived from the non-relativistic molecular Hamiltonian (Appendix 1). The nuclear spin isomers of the molecule are then identified by different contorsional states.

Characterising the symmetry of the eigenstates of our model Hamiltonian requires the use of specific symmetry groups, commonly known as MS groups. These are subgroups of the full nuclear permutation–inversion group, which contain all feasible operations. Molecular point groups, the symmetry groups that are predominantly used in molecular theory, are not suitable. First, their operations only act on vibronic coordinates but leave rotational and nuclear spin coordinates unaffected [41,42]. Second, they cannot be used to classify the contorsional eigenstates of molecules [40]. Only permutation–inversion groups allow for classifying the symmetry of all types of molecular states, be it the wave functions describing electronic motions, rotations, vibrations, contorsions or nuclear spins [41,42]. Here, we focus on the general structure of the MS groups for systems with feasible torsions and pseudo-rotations. We show that the relevant subgroup of the MS group for identifying the contorsional eigenfunctions of the nuclear spin isomers is a cyclic group. This allows us to identify the nuclear spin isomers of the model systems in a straightforward manner. The approach is illustrated by two illuminating examples, an aligned methyl group and the aligned boron rotor B_{11}^-.

2.1. Origins of nuclear spin isomers: spin-statistics theorem and nuclear spin hypothesis

Why molecules exist in the form of nuclear spin isomers can be understood with the help of two theoretical concepts, the spin-statistics theorem and the nuclear spin hypothesis.

The spin-statistics theorem requires that molecular states Ψ^{mol} transform under a permutation P of identical nuclei according to

$$P\Psi^{\mathrm{mol}} = \begin{cases} -1 \cdot \Psi^{\mathrm{mol}}, & \text{if } P \text{ permutes an even} \\ & \text{number of fermions,} \\ +1 \cdot \Psi^{\mathrm{mol}}, & \text{else.} \end{cases} \quad (1)$$

Depending on the spin of the nuclei, Ψ^{mol} therefore must transform according to the totally symmetric representation Γ^{ts} or the totally antisymmetric representation Γ^{as} of the complete nuclear permutation group $\mathrm{G}^{\mathrm{CNP}}$ [41]. This molecular representation we denote as Γ^{mol}.

The nuclear spin hypothesis [43] states that we can write every molecular eigenstate Φ^{mol} as

$$\Phi^{\mathrm{mol}} = \Phi^{\mathrm{rcve}} \cdot \Phi^{\mathrm{nu.sp}}, \quad (2)$$

where Φ^{rcve} denote the eigenfunctions for the rotational–contorsional–vibrational–electronic [roconvibronic] motions of the molecule and $\Phi^{\mathrm{nu.sp}}$ the wave function describing its nuclear spins. As the nuclear spins and the spatial motions of a molecule are coupled, Equation (2) is not strictly valid; nuclear spin isomers are interconverted by nuclear spin-dependent intramolecular interactions. Thus, like enantiomers, nuclear spin isomers are only approximate molecular species. Normally, however, nuclear spin conversion takes much longer time than roconvibronic motions. Consequently, Equation (2) is a good approximation for describing the eigenstates of a molecule, and nuclear spin isomers can be considered as stable species on the time scales of roconvibronic motions.

Taking into account the separability of nuclear spin states and roconvibronic states (Equation 2), and the conditions that follow from the spin-statistics theorem (Equation 1), we can identify the nuclear spin isomers of any given molecule by solving the equation:

$$\Gamma^{\mathrm{mol}} \subseteq \Gamma^{\mathrm{rcve}} \otimes \Gamma^{\mathrm{nu.sp}}. \quad (3)$$

It reflects that the direct product of the irreducible representations, also called 'symmetries', Γ^{rcve} and $\Gamma^{\mathrm{nu.sp}}$ generated by the eigenfunctions Φ^{rcve} and $\Phi^{\mathrm{nu.sp}}$, respectively, must contain the irreducible representation Γ^{mol}. Different nuclear spin isomers of a molecule are thus characterised by different combinations of Γ^{rcve} and $\Gamma^{\mathrm{nu.sp}}$; we denote them as $\Gamma^{\mathrm{rcve}}[\Gamma^{\mathrm{nu.sp}}]$. These combinations are unambiguous; once Γ^{rcve} or $\Gamma^{\mathrm{nu.sp}}$ is defined, there exist only one $\Gamma^{\mathrm{nu.sp}}$ and Γ^{rcve}, respectively, such that Equation (3) is fulfilled [61].

Although we do not study this case here, it is worth mentioning that Equation (3) does *not* imply that every molecular state being in accordance with the spin-statistics theorem is a product of one roconvibronic state and one nuclear spin state. For degenerate roconvibronic and nuclear spin states, the correct molecular wave functions are, in general, linear combinations of degenerate products of the type (Equation 2) [69].

2.2. On the MS groups of molecules with cyclic contorsional motions

Using the complete nuclear permutation group $\mathrm{G}^{\mathrm{CNP}}$, we can identify all nuclear spin isomers of a given molecule. Yet, it has been shown that not all permutations contained in the complete nuclear permutation group $\mathrm{G}^{\mathrm{CNP}}$ are 'feasible' [38–42]. To identify the *distinguishable* nuclear spin isomers of a molecule in field-free space, it suffices to consider the elements of the permutation subgroup $\mathrm{G}^{\mathrm{PSMS}}$ of the MS group G^{MS} [41,42].

In our model, however, we do not investigate molecules in field-free space. In particular, we assume that the molecules are perfectly aligned or oriented in space, for example by using non-resonant laser pulses or attaching them to a surface. These manipulations generally lead to a reduction of feasible symmetry operations [41,62,63], so that we cannot simply use the MS group to analyse the symmetry of the eigenfunctions of our model Hamiltonian. Under these circumstances, the correct group is the permutation subgroup $\mathrm{G}^{\mathrm{PSFD}}$ of the field-dressed symmetry group G^{FD} [63]. Deducing the field-dressed symmetry group G^{FD} is difficult and requires an elaborate discussion, because this group contains symmetry operations that are not only permutations or permutations-inversions [62]. However, since we are only interested in the pure permutation subgroup $\mathrm{G}^{\mathrm{PSFD}}$ of the group G^{FD}, we do not need to know the explicit structure of the field-dressed symmetry group. All we have to do is to identify those permutations in the MS groups that remain feasible when the molecule interacts with the aligning field [49,51,52,63].

To find the group $\mathrm{G}^{\mathrm{PSFD}}$ of the molecular rotors, it is necessary to identify the permutation subgroup of the MS group of the molecule in field-free space first. For molecules with observable torsions, the first class of cyclic contorsional motions we consider, we can construct the MS group using a systematic approach [64]. Here, the MS group can be written as

$$\mathrm{G}^{\mathrm{MS}}_{\mathrm{tor}} = \mathrm{G}_{\mathrm{T}} \circledS \mathrm{G}_{\mathrm{F}}, \quad (4)$$

where G_T is the torsional subgroup, G_F is the frame subgroup and Ⓢ denotes the semi-direct product of the two subgroups. Both groups can be obtained in a systematic fashion [64].

We are interested in molecules with only one (con-) torsional degree of freedom. Considering this particular case, the torsional subgroup can be written as [65,66]

$$G_T = G_T^{(1)} \otimes G_T^{(2)}, \tag{5}$$

where $G_T^{(1)}$ and $G_T^{(2)}$ denote the permutation groups of the two moieties that rotate against each other. Both groups are cyclic and therefore generated by a single permutation. For simplicity, let us only consider cases in which one of the moieties does not possess any permutation symmetry, or its motion is hindered and the symmetry operations associated with its torsion are therefore unfeasible. An example for the first instance is the torsion in methanol; the second scenario can be realised by attaching a molecule with feasible torsion to a surface.

Using the MS group (Equation 4), we can identify the feasible permutations of the group in the case where we align the molecule along the torsional axis. We consider the operations of the frame subgroup G_F first. They are either unfeasible permutations or permutation-inversions, which are irrelevant for identifying the nuclear spin isomers of the molecule [65,66]. Hence, the only permutations that remain feasible for an aligned molecule are the operations of the torsional subgroup [51,52,63]. The proper symmetry group for finding the nuclear spin isomers therefore is

$$G_{tor}^{PSFD} = G_T^{(1)} \equiv C_{\mathfrak{h}_{tot}}(M). \tag{6}$$

This group is cyclic and generated by the permutation

$$g = (12 \ldots \mathfrak{h}_{tot}). \tag{7}$$

Thus

$$C_{\mathfrak{h}_{tot}}(M) = \langle g \mid g^{\mathfrak{h}_{tot}} = E \rangle, \tag{8}$$

where $\mathfrak{h}_{tot}$ specifies the permutation symmetry of the moiety that rotates against the frozen rest of the molecule. The example we explicitly consider here, the torsion of a methyl group ($\mathfrak{h}_{tot} = 3$), is illustrated in Figure 1.

Our second example is the concerted rotation and pseudo-rotation of planar boron rotors [23]. The MS groups for these systems in particular, and for pseudo-rotations in general, have not been analysed systematically so far. In Appendix 2, we show that

$$G_X = G^{eq} \otimes C_{in} \otimes C_{out} \qquad X = B_{11}^-, B_{13}^+, B_{15}^+, B_{19}^-, \tag{9}$$

for the example B_{11}^-. In Equation (9), G^{eq} is the MS group of the equilibrium structure of the rigid cluster at

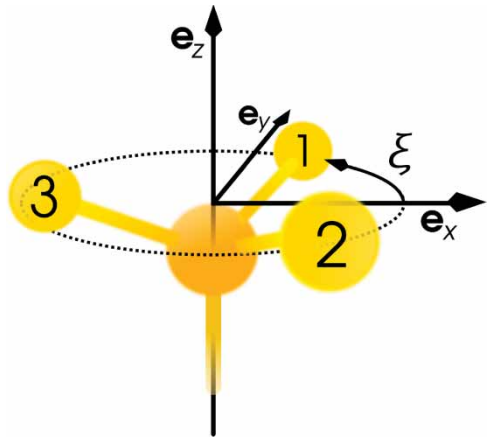

Figure 1. Torsion of an aligned CH_3 group with torsion angle ξ with $(123)\xi = \xi + 2\pi/3$.

one global minimum of the potential energy surface. The presentations of the groups C_{in} and C_{out} are

$$C_{in} = \langle P_{in} \mid P_{in}^{\mathfrak{h}_{in}} = E \rangle, \tag{10a}$$

$$C_{out} = \langle P_{out} \mid P_{out}^{\mathfrak{h}_{out}} = E \rangle, \tag{10b}$$

where $\mathfrak{h}_{in}$ and $\mathfrak{h}_{out}$ correspond to the number of boron nuclei that shape the inner wheel and the outer bearing, respectively. Both groups are cyclic, hence they can be generated by the permutations

$$P_{in} = (12), \tag{11a}$$

$$P_{out} = (\mathtt{aeidhcgbf}), \tag{11b}$$

where we choose the generators such that the product $P_{in} \cdot P_{out}$ interconverts two neighbouring global minima [23]. The direct product group

$$C_{in} \otimes C_{out} \equiv C_{\mathfrak{h}_{tot}}(M), \tag{12}$$

with order $\mathfrak{h}_{tot} = \mathfrak{h}_{in} \cdot \mathfrak{h}_{out}$, is cyclic as well, because the orders of C_{in} and C_{out} are coprime [67] for all boron clusters B_{11}^-, B_{13}^+, B_{15}^+ and B_{19}^- (e.g. $\mathfrak{h}_{in} = 2$ and $\mathfrak{h}_{out} = 9$ for B_{11}^-). It is generated by the operation

$$g = P_{out} \cdot P_{in}, \tag{13}$$

cf. Equation .1.

In case we align the boron rotors to freeze their rotations, the permutation subgroup of the MS group (Equation 9) reduces to

$$G_X^{PSFD} = C_{\mathfrak{h}_{tot}}(M), \tag{14}$$

i.e. the only permutations that remain feasible are the combined elements of the cyclic groups (Equations 10a and 10b). For example, the symmetry group we have to

use to find the nuclear spin isomers of B_{11}^- with frozen rotations, but feasible contorsional motion, is the cyclic group $C_{\mathfrak{h}_{tot}}(M)$ with order $\mathfrak{h}_{tot} = 2 \cdot 9 = 18$.

Hence, for both examples, the relevant symmetry group for identifying the nuclear spin isomers is the cyclic group $C_{\mathfrak{h}_{tot}}(M)$. Finding the irreducible representations Γ_n of $C_{\mathfrak{h}_{tot}}(M)$ is straightforward [41,42,67,68]. For cyclic groups, only one-dimensional irreducible representations exist, and therefore a cyclic group of order $\mathfrak{h}_{tot}$ has in total $\mathfrak{h}_{tot}$ irreducible representations $\Gamma_n, n = 0, 1, 2, \ldots, \mathfrak{h}_{tot} - 1$. The corresponding characters ζ^{Γ_n} are

$$\zeta^{\Gamma_n}[g^z] = \left(\zeta^{\Gamma_n}[g]\right)^z \equiv \eta_{\mathfrak{h}_{tot}}^{n \cdot z}, \qquad z = 1, \ldots, \mathfrak{h}_{tot}, \quad (15)$$

where g for the torsion and the boron clusters is defined in Equations (7) and (13), respectively. Accordingly, the irreducible representations Γ_n of the group $C_{\mathfrak{h}_{tot}}(M)$ are completely determined by the character ζ^{Γ_n} of the generator g. In Appendix 2, we specify $\eta_{\mathfrak{h}_{tot}}$ and the nomenclature for the irreducible representations of the groups $C_3(M)$ and $C_{18}(M)$. Equation (15) also facilitates analysing the symmetry of the contorsional states Φ^{con} and the nuclear spin states $\Phi^{nu.sp}$ to find the proper symmetry combinations $\Gamma^{con}[\Gamma^{nu.sp}]$, as we shall see in the following.

2.3. A model Hamiltonian for cyclic contorsions and its symmetry

In our model, we consider the contorsion along the coordinate ξ to be decoupled from other motions. The effective Hamiltonian for the pure contorsion reads

$$\hat{H}^{con} = -\frac{\hbar^2}{2\mathfrak{I}_{eff}} \frac{\partial^2}{\partial \xi^2} + \frac{V_b}{2}(1 + \cos(\mathfrak{h}_{tot}\xi)). \quad (16)$$

Here, $\mathfrak{I}_{eff}$ is an effective moment of inertia, and V_b is the barrier height of the potential energy surface $V(\xi)$. Both V_b and $\mathfrak{I}_{eff}$ can be obtained from quantum chemical calculations. The symmetry number $\mathfrak{h}_{tot}$ is dependent on the permutation symmetry of the potential, i.e. on the number of symmetry-equivalent minima of the potential energy surface that are converted into each other by the motion along ξ. The Hamiltonian equation (16) has been shown to be a good approximation for describing both molecular torsions [50,51,55,69] and the pseudorotations in boron-clusters such as B_{11}^-, B_{13}^+, B_{15}^+, or B_{19}^- [23].

The contorsional eigenfunctions Φ_{n_ξ} and eigenenergies E_{n_ξ} are the solution of the time-independent Schrodinger equation:

$$\hat{H}^{con}\Phi_{n_\xi}(\xi) = E_{n_\xi}\Phi_{n_\xi}(\xi). \quad (17)$$

Using the variational ansatz

$$\Phi_{n_\xi}(\xi) = \sum_k C_{n_\xi,k}\phi_k(\xi) \quad (18)$$

with the basis functions

$$\phi_k(\xi) = \frac{1}{\sqrt{2\pi}} \exp(ik\xi), \quad (18a)$$

the expansion coefficients $C_{n,k}$ are obtained by diagonalising the matrix representation $\boldsymbol{H}^{con}$ of the Hamiltonian $\hat{H}^{con}$ (Equation 16) in the basis equation (18a). The elements of $\boldsymbol{H}^{con}$ read as

$$H_{k,k'}^{con} = \frac{\hbar^2}{2\mathfrak{I}_{eff}}k^2\delta_{k,k'} + \frac{V_b}{2}\delta_{k,k'} + \frac{V_b}{4}\delta_{k,k'+\mathfrak{h}_{tot}} + \frac{V_b}{4}\delta_{k,k'-\mathfrak{h}_{tot}}. \quad (19)$$

To exactly represent Φ_{n_ξ} in terms of the functions ϕ_k, the basis must be infinite. In practice, however, the matrix $\boldsymbol{H}^{con}$ is diagonalised numerically using a truncated, finite basis set.

The contorsional Hamiltonian $\hat{H}^{con}$ is invariant under the operations of the group $C_{\mathfrak{h}_{tot}}(M)$. Hence, we can classify its eigenfunctions Φ_{n_ξ} according to the irreducible representations Γ_n of $C_{\mathfrak{h}_{tot}}(M)$. To identify the symmetry of the eigenfunctions Φ_{n_ξ} in Equation (18), we use the following theorem. Any eigenfunction with symmetry Γ_n in the MS group can be expanded in terms of basis functions of the same symmetry alone [68]. Conversely, we can deduce the symmetry of the eigenfunctions from the symmetry of the basis functions in Equation (18a). Using

$$g\xi = \xi + \frac{2\pi}{\mathfrak{h}_{tot}} \quad (20a)$$

and [68]

$$g\phi_k(\xi) = \phi_k(g^{-1}\xi), \quad (20b)$$

we obtain

$$g\phi_k = \eta_{\mathfrak{h}_{tot}}^k\phi_k. \quad (21)$$

Here, g is the generator of the group $C_{\mathfrak{h}_{tot}}(M)$, see Equations (7) and (13), and $\eta_{\mathfrak{h}_{tot}}$ is defined by Equation (15) and specified in Appendix 3. It follows that [68,70]

$$\phi_k \sim \Gamma_n \qquad \text{with} \qquad k \bmod \mathfrak{h}_{tot} = n. \quad (22)$$

According to Equation (22), every irreducible representation of the symmetry group $C_{\mathfrak{h}_{tot}}(M)$ occurs in the

Table 1. The irreducible representations $\Gamma_n = \Gamma^{\text{con}}$ of the contorsional basis functions ϕ_k in the symmetry group $C_{\mathfrak{h}_{\text{tot}}}(M)$ for an aligned CH_3 group (top) and for an aligned B_{11}^- cluster (bottom).

Group	Γ_n	Γ^{con}	Conditions for k in Equation (21)
$C_3(M)$	Γ_0	A	$k \bmod 3 = 0$
	Γ_1	E_1	$k \bmod 3 = 1$
	Γ_2	E_2	$k \bmod 3 = 2$
$C_{18}(M)$	Γ_0	$\Gamma_{0,A}$	$k \bmod 9 = 0 \ \wedge \ k \bmod 2 = 0$
	Γ_1	$\Gamma_{1,B}$	$k \bmod 9 = 1 \ \wedge \ k \bmod 2 = 1$
	Γ_2	$\Gamma_{2,A}$	$k \bmod 9 = 2 \ \wedge \ k \bmod 2 = 0$
	⋮	⋮	
	Γ_8	$\Gamma_{8,A}$	$k \bmod 9 = 8 \ \wedge \ k \bmod 2 = 0$
	Γ_9	$\Gamma_{0,B}$	$k \bmod 9 = 0 \ \wedge \ k \bmod 2 = 1$
	Γ_{10}	$\Gamma_{1,A}$	$k \bmod 9 = 1 \ \wedge \ k \bmod 2 = 0$
	⋮	⋮	
	Γ_{16}	$\Gamma_{7,A}$	$k \bmod 9 = 7 \ \wedge \ k \bmod 2 = 0$
	Γ_{17}	$\Gamma_{8,B}$	$k \bmod 9 = 8 \ \wedge \ k \bmod 2 = 1$

The nomenclature of the irreducible representations is explained in Appendix 3.

(reducible) representation spanned by the basis functions ϕ_k. Consequently, the matrix representation $\boldsymbol{H}^{\text{con}}$ of the operator $\hat{H}^{\text{con}}$ in Equation (16), written in the basis equation (18), decomposes according to

$$\boldsymbol{H}^{\text{con}} = \boldsymbol{H}_0 \oplus \boldsymbol{H}_1 \oplus \cdots \oplus \boldsymbol{H}_{\mathfrak{h}_{\text{tot}}-1}. \tag{23}$$

To exemplify these general results, we summarise the symmetries Γ^{con} of an aligned CH_3 group and the aligned B_{11}^- cluster in Table 1. Apparently, all irreducible representations of the group $C_{\mathfrak{h}_{\text{tot}}}$ are realised in the reducible representation Γ^{con}. With the symmetries Γ^{con} at hand, we are now able to identify the nuclear spin isomers for our model systems.

2.4. The nuclear spin isomers of our model systems

Within our model, Equation (3) reduces to

$$\Gamma^{\text{mol}} \subseteq \Gamma^{\text{con}} \otimes \Gamma^{\text{nu.sp}}, \tag{24}$$

because we obtain the effective Hamiltonian $\hat{H}^{\text{con}}$ by integrating the molecular Hamiltonian over the electronic, vibrational and rotational degrees of freedom. Then, different nuclear spin isomers are characterised by different combinations of contorsional states and nuclear spin states, $\Gamma^{\text{con}}[\Gamma^{\text{nu.sp}}]$.

Following the procedure we described in Section 2.1, we use the spin-statistics theorem (Equation 1) to find the correct combinations $\Gamma^{\text{con}}[\Gamma^{\text{nu.sp}}]$. Consider B_{11}^- as an example. For boron, two stable isotopes exist, ^{10}B and ^{11}B, which have nuclear spin quantum numbers

$$\mathcal{I}_{^{10}\text{B}} = 3 \quad \text{with natural abundance of 19.9\%} \tag{25a}$$

$$\mathcal{I}_{^{11}\text{B}} = \frac{3}{2} \quad \text{with natural abundance of 80.1\%.} \tag{25b}$$

From Equation (1), we find

$$\Gamma^{\text{mol}} = \begin{cases} \Gamma_{0,\text{A}}, & \text{if} \quad \text{B} \equiv {}^{10}\text{B}, \\ \Gamma_{0,\text{B}}, & \text{if} \quad \text{B} \equiv {}^{11}\text{B}. \end{cases} \tag{26}$$

Therefore, for B_{11}^- composed of ^{11}B,

$$\Gamma^{\text{nu.sp}} = \Gamma_{n,\text{A}} \quad \Leftrightarrow \quad \Gamma^{\text{con}} = \Gamma_{9-n,\text{B}} \tag{27a}$$

$$\Gamma^{\text{nu.sp}} = \Gamma_{n,\text{B}} \quad \Leftrightarrow \quad \Gamma^{\text{con}} = \Gamma_{9-n,\text{A}}, \tag{27b}$$

where we have used that for the irreducible representations of $C_9(M)$

$$\Gamma_n \otimes \Gamma_n^* = \Gamma_0 \tag{28a}$$

$$\Gamma_n^* = \Gamma_{9-n} \tag{28b}$$

$$\Gamma_9 \equiv \Gamma_0. \tag{28c}$$

Having identified the symmetries of the eigenfunctions Φ^{con} in Section 2.3, cf. Table 1, we still need to find the symmetries $\Gamma^{\text{nu.sp}}$ spanned by the nuclear spin eigenfunctions in the group $C_{\mathfrak{h}_{\text{tot}}}(M)$. Here, we only give the main results; the detailed derivations are given in Appendix 4 [41]. Taking into account the direct product structure of $C_{\mathfrak{h}_{\text{tot}}}(M)$ (see Equation 14), we can determine the symmetry of the nuclear spin states for the groups C_{in} and C_{out} separately. Hence,

$$\Gamma^{\text{nu.sp}}_{C_{\text{in}}} = 10\,\text{A} \oplus 6\,\text{B} \tag{29a}$$

$$\Gamma^{\text{nu.sp}}_{C_{\text{out}}} = 29144\,\Gamma_0 \oplus 29120\,(\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_7 \oplus \Gamma_8) \oplus 29140\,(\Gamma_3 \oplus \Gamma_6). \tag{29b}$$

Equations (29a) and (29b) show that all nuclear spin symmetries are realised in $C_{18}(M)$. Consequently, the aligned cluster B_{11}^- occurs in the form of 18 nuclear spin isomers $\Gamma^{\text{con}}[\Gamma^{\text{nu.sp}}]$, namely

$$\Gamma_{0,\text{A}}[\Gamma_{0,\text{B}}], \Gamma_{0,\text{B}}[\Gamma_{0,\text{A}}], \ldots, \Gamma_{8,\text{A}}[\Gamma_{1,\text{B}}], \Gamma_{8,\text{B}}[\Gamma_{1,\text{B}}]. \tag{30}$$

For our second example, the aligned CH_3 group with $\text{H} \equiv {}^1\text{H}$,

$$\mathcal{I}_{^1\text{H}} = \frac{1}{2}. \tag{31}$$

Hence, the nuclear spin states span the representation [41,69]

$$\Gamma^{\text{nu.sp}} = 4\text{A} \oplus 2\text{E}_1 \oplus 2\text{E}_2, \tag{32}$$

and, as a consequence, the aligned CH_3 group exists as the three nuclear spin isomers

$$\text{A}[\text{A}], \text{E}_1[\text{E}_2], \text{E}_2[\text{E}_1]. \tag{33}$$

Thus, for both examples, $\Gamma^{\text{nu.sp}}$ contains every irreducible representation of $C_{\mathfrak{h}_{\text{tot}}}(M)$, and, as a consequence, every symmetry combination that is allowed

by the spin-statistics theorem is realised. We show in Section 3.2 that this result is not a coincidence, but it holds for all molecular rotors that are composed of nuclei with non-zero spin.

3. Localised states as superposition states of different nuclear spin isomers

To show that a hypothetical localised state is always a superposition of states belonging to different nuclear spin isomers, we have to discuss two aspects in detail: what is the symmetry of a localised state and which nuclear spin isomers of molecular rotors exist in general. Addressing the first question, we show that a localised state in a cyclic potential can only be formed by superimposing contorsional states of different symmetries. In a second step, we then show that for systems with non-zero nuclear spin, each of the contorsional symmetries in $C_{\mathfrak{h}_{tot}}$ indeed represents different nuclear spin isomers. Both arguments are the basis for our conclusion that localised states of contorsional motions are unphysical, which we discuss in detail in Section 4.

3.1. Localised states in cyclic potentials

We begin with showing that every localised contorsional state is a linear combination of contorsional eigenfunctions that belong to different symmetries, considering the torsion of the aligned model CH_3 group as an example. We examine three states Ψ_1^{loc}, Ψ_2^{loc} and Ψ_3^{loc}, which are localised in the vicinity of the minima of the potential at $\xi = \pi/3$, $\xi = \pi$ and $\xi = 5\pi/3$, respectively; see Figure 2 for a graphical representation of Ψ_1^{loc} and Ψ_2^{loc}. We can systematically test if these states are symmetry-adapted by applying the projection operators [67,68]

$$\hat{\mathfrak{P}}^{\Gamma_n} = \frac{1}{\mathfrak{h}_{tot}} \sum_{z=1}^{\mathfrak{h}_{tot}} (\zeta^{\Gamma_n}[g^z])^* g^z \tag{34}$$

to any of the localised states Ψ_m^{loc}, $m = 1, 2, 3$. If for an arbitrary function Ψ

$$\hat{\mathfrak{P}}^{\Gamma_n}\Psi = \text{const}\cdot\Psi \qquad \text{const} \neq 0, \tag{35}$$

then Ψ transforms according to the irreducible Γ_n of the group $C_{\mathfrak{h}_{tot}}(M)$. Yet, for any of the irreducible representations Γ_n of $C_3(M)$, we obtain

$$\hat{\mathfrak{P}}^{\Gamma_n}\Psi_m^{loc} \neq \text{const}\cdot\Psi_m^{loc} \quad \text{for } m = 1, 2, 3 \text{ and } \Gamma_n = A, E_1, E_2. \tag{36}$$

Here, we have taken into account Equation (20b), from which follows

$$g\Psi_1^{loc}(\xi) = \Psi_1^{loc}(\xi + 4\pi/3) \equiv \Psi_2^{loc}(\xi) \tag{37a}$$

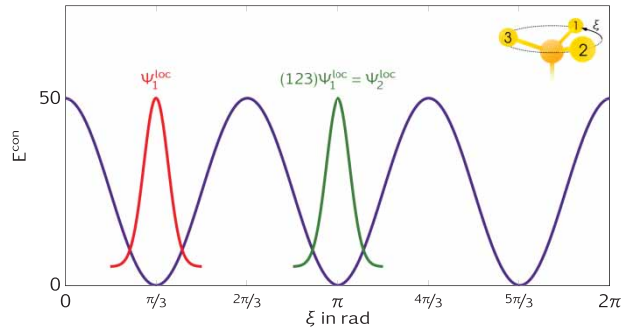

Figure 2. Illustration of two localised states for a potential with $\mathfrak{h}_{tot} = 3$ and $V_b \cdot \mathfrak{I}_{eff}/\hbar^2 = 50$. The first state, Ψ_1^{loc}, is localised in the minimum at $\xi = \pi/3$, the second, Ψ_2^{loc} at $\xi = \pi$. Applying the operation (123) to Ψ_1^{loc} yields the state Ψ_2^{loc}.

$$g^2\Psi_1^{loc}(\xi) = \Psi_1^{loc}(\xi + 2\pi/3) \equiv \Psi_3^{loc}(\xi) \tag{37b}$$

with $g = (1\,2\,3)$ (Figure 2). Hence, localised states do not transform according to any irreducible representation of $C_3(M)$; localised states are not symmetry adapted.

We can, however, use the projection operators $\hat{\mathfrak{P}}^{\Gamma_n}$ to construct three symmetry-adapted functions Ψ^{Γ_n} out of the three localised states Ψ_m^{loc}. For $C_3(M)$, $\mathfrak{h}_{tot} = 3$ and

$$(\zeta^{\Gamma_n}[g^z])^* = (\eta_3^{n\cdot z})^* \quad \text{with} \quad \eta_3 = \exp\left(-\frac{2\pi i}{3}\right) \tag{38}$$

in Equation (34), see also Appendix 3. Applying $\hat{\mathfrak{P}}^{\Gamma_n}$ to Φ_1^{loc} and taking into account Equation (20b) yields

$$\Psi^{A} = \tfrac{1}{\sqrt{3}}(\Psi_1^{loc} + \Psi_2^{loc} + \Psi_3^{loc}) \tag{39a}$$

$$\Psi^{E_1} = \tfrac{1}{\sqrt{3}}(\Psi_1^{loc} + \eta_3^*\Psi_2^{loc} + \eta_3\Psi_3^{loc}) \tag{39b}$$

$$\Psi^{E_2} = \tfrac{1}{\sqrt{3}}(\Psi_1^{loc} + \eta_3\Psi_2^{loc} + \eta_3^*\Psi_3^{loc}). \tag{39c}$$

Hence, the symmetry-adapted wave functions are linear combinations of localised wave functions, which can be formally expressed as

$$\Psi^{\Gamma_{n-1}} = \sum_{m=1}^{3} \mathcal{T}_{nm}\cdot\Psi_m^{loc}, \quad n = 1, 2, 3, \tag{40}$$

with $\Gamma_0 = A$, $\Gamma_1 = E_1$, $\Gamma_2 = E_2$, and

$$|\mathcal{T}_{nm}| = \tfrac{1}{\sqrt{3}}, \tag{40a}$$

see Equation (39).

Introducing the matrix $\boldsymbol{\mathcal{T}}$ allows us to formalise these results. If we write the set of localised functions as the vector $\boldsymbol{\Psi}^{loc}$ with components $(\boldsymbol{\Psi}^{loc})_m = \Psi_m^{loc}$ and the set of symmetry-adapted functions as the vector

$\boldsymbol{\Psi}^{\mathrm{sym}}$ with components $(\boldsymbol{\Psi}^{\mathrm{sym}})_n = \Psi^{\Gamma_n}$, we can use the transformation

$$\boldsymbol{\Psi}^{\mathrm{sym}} = \boldsymbol{\mathcal{T}} \cdot \boldsymbol{\Psi}^{\mathrm{loc}} \tag{41a}$$

to construct a set of symmetry-adapted wave functions Ψ^{Γ_n} out of the localised wave functions Ψ_m^{loc}. For the group $\mathrm{C}_3(M)$, $\boldsymbol{\mathcal{T}}$ reads

$$\boldsymbol{\mathcal{T}} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ 1 & \eta_3^* & \eta_3 \\ 1 & \eta_3 & \eta_3^* \end{pmatrix}. \tag{41b}$$

Since $\boldsymbol{\mathcal{T}}$ is unitary, i.e. $\boldsymbol{\mathcal{T}}^\dagger = \boldsymbol{\mathcal{T}}^{-1}$, we are able to write

$$\boldsymbol{\Psi}^{\mathrm{loc}} = \boldsymbol{\mathcal{T}}^\dagger \cdot \boldsymbol{\Psi}^{\mathrm{sym}}. \tag{42}$$

Thus for the localised state Ψ_1^{mol}

$$\Psi_1^{\mathrm{loc}} = \tfrac{1}{\sqrt{3}}(\Psi^{\mathrm{A}} + \Psi^{\mathrm{E}_1} + \Psi^{\mathrm{E}_2}). \tag{43}$$

Consequently, the localised state Ψ_1^{loc} is a linear combination of the symmetry-adapted states Ψ^{Γ_n}, and so are the localised states Ψ_2^{loc} and Ψ_3^{loc}. Moreover, every irreducible representation of the group $\mathrm{C}_3(M)$ occurs exactly once with equal weight in each of the localised states; see Equation (39) for an example.

Let us generalise our results from $\mathrm{C}_3(M)$ to $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$. In general, there are $\mathfrak{h}_{\mathrm{tot}}$ localised states, $\Psi_1^{\mathrm{loc}}, \ldots, \Psi_{\mathfrak{h}_{\mathrm{tot}}}^{\mathrm{loc}}$, of which Ψ_1^{loc} is localised in the minimum of the potential $V(\xi)$ at $\xi = \pi/\mathfrak{h}_{\mathrm{tot}}$, Ψ_2^{loc} at the minimum at $\xi = 3\pi/\mathfrak{h}_{\mathrm{tot}}$, and so on. As for $\mathfrak{h}_{\mathrm{tot}} = 3$, we can write the set of localised and symmetry-adapted wave functions in form of the vectors $\boldsymbol{\Psi}^{\mathrm{loc}}$ and $\boldsymbol{\Psi}^{\mathrm{loc}}$, respectively. Again, the transformation matrix $\boldsymbol{\mathcal{T}}$ can be constructed systematically using the projection operators for the irreducible representations Γ_n, cf. Equation (34)

$$\boldsymbol{\mathcal{T}} = \frac{1}{\sqrt{\mathfrak{h}_{\mathrm{tot}}}} \begin{pmatrix} 1 & 1 & 1 & \ldots & 1 \\ 1 & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{(\mathfrak{h}_{\mathrm{tot}}-1)} & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{2(\mathfrak{h}_{\mathrm{tot}}-1)} & \ldots & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{(\mathfrak{h}_{\mathrm{tot}}-1)(\mathfrak{h}_{\mathrm{tot}}-1)} \\ 1 & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{(\mathfrak{h}_{\mathrm{tot}}-2)} & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{2(\mathfrak{h}_{\mathrm{tot}}-2)} & \ldots & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{(\mathfrak{h}_{\mathrm{tot}}-1)(\mathfrak{h}_{\mathrm{tot}}-2)} \\ \vdots & & & \ddots & \vdots \\ 1 & \eta_{\mathfrak{h}_{\mathrm{tot}}} & \eta_{\mathfrak{h}_{\mathrm{tot}}}^2 & \ldots & \eta_{\mathfrak{h}_{\mathrm{tot}}}^{\mathfrak{h}_{\mathrm{tot}}-1} \end{pmatrix}, \tag{44}$$

where

$$\eta_{\mathfrak{h}_{\mathrm{tot}}} = \exp\left(-\frac{2\pi \mathrm{i}}{\mathfrak{h}_{\mathrm{tot}}}\right); \tag{45}$$

see also Equation (15). For the group $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$, $\boldsymbol{\mathcal{T}}$ is unitary, too, and

$$|\mathcal{T}_{nm}| = \frac{1}{\sqrt{\mathfrak{h}_{\mathrm{tot}}}}. \tag{46}$$

Thus each localised state Ψ_m^{loc} contains all symmetry-adapted function Ψ^{Γ_i} exactly once and with the same weight $1/\mathfrak{h}_{\mathrm{tot}}$, also in the general case.

Treating localised and symmetry-adapted wave functions within a matrix-vector approach also allows us to use an alternative method to show that localised states are superpositions of symmetry-adapted wave functions. Therefore, we make use of the regular representation Γ^{reg}, a key concept in the representation theory of groups [67,68]. The characters of this representation are

$$\zeta^{\Gamma^{\mathrm{reg}}}[\mathrm{E}] = \mathfrak{h}_{\mathrm{tot}} \tag{47a}$$

$$\zeta^{\Gamma^{\mathrm{reg}}}[g] = 0 \quad \forall\, g \neq \mathrm{E}. \tag{47b}$$

Within this representation, every $\mathfrak{d}_\Gamma$-dimensional irreducible representation of the group occurs just $\mathfrak{d}_\Gamma$ times. Hence, for a cyclic group, the regular representation contains all irreducible representations of the group exactly once. Conversely, if the representation that is spanned by the set of all localised states, Γ^{loc}, contains or is identical to the regular representation Γ^{reg}, each contorsional symmetry that is possible in $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$ does indeed occur. Consequently, if the functions $\boldsymbol{\Psi}_m^{\mathrm{loc}}$ form a basis for a representation that contains Γ^{reg}, the localised states Ψ_m^{loc} are superpositions of symmetry-adapted states Ψ^{Γ_n}.

First, we show that the set of all localised functions forms a basis for a reducible representation of the group $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}$. From

$$g\boldsymbol{\Psi}^{\mathrm{loc}} = g \begin{pmatrix} \Psi_1^{\mathrm{loc}} \\ \Psi_2^{\mathrm{loc}} \\ \vdots \\ \Psi_{\mathfrak{h}_{\mathrm{tot}}}^{\mathrm{loc}} \end{pmatrix} = \begin{pmatrix} \Psi_2^{\mathrm{loc}} \\ \Psi_3^{\mathrm{loc}} \\ \vdots \\ \Psi_1^{\mathrm{loc}} \end{pmatrix}, \tag{48}$$

we first deduce that g is represented by the matrix

$$\boldsymbol{D}^{\Gamma^{\mathrm{loc}}}[g] = \begin{pmatrix} 0 & 1 & 0 & \ldots & 0 \\ 0 & 0 & 1 & \ldots & 0 \\ \vdots & & \ddots & & \vdots \\ 1 & 0 & \ldots & 0 & 0 \end{pmatrix}. \tag{49}$$

Here, we used again Equation (20b). Analogously, we can find the matrices representing $g^2, \ldots, g^{\mathfrak{h}_{\mathrm{tot}}} = \mathrm{E}$ and show that they form indeed a representation Γ^{loc} with dimension $\mathfrak{d}_{\Gamma^{\mathrm{loc}}} = \mathfrak{h}_{\mathrm{tot}}$.

Once we have calculated all matrices of Γ^{loc}, we can determine its character system. We find

$C_{\mathfrak{h}_{\text{tot}}}(M)$	E	g	g^2	...	$g^{\mathfrak{h}_{\text{tot}}-1}$
$\zeta^{\Gamma^{\text{loc}}}$	$\mathfrak{h}_{\text{tot}}$	0	0	...	0

(50)

which is exactly the definition of the regular representation (Equation 47). Consequently, all spatial symmetries that are possible in $C_{\mathfrak{h}_{\text{tot}}}$ are contained in Γ^{loc}; they occur exactly once. Furthermore, since the labelling of the localised states is arbitrary, every localised state is a superposition of symmetry-adapted wave functions in such a manner as every irreducible representation Γ of the symmetry group $C_{\mathfrak{h}_{\text{tot}}}(M)$ occurs exactly once.

3.2. On the symmetries of nuclear spin states for systems with cyclic contorsional motions

Next, we discuss the symmetry of the nuclear spin states of the molecular rotors. In the simplest case, all nuclei carry zero spin, i.e. nuclear spin quantum numbers are $\mathcal{I}_i = 0$. Then, there is just one total nuclear spin state with total spin quantum numbers $\mathcal{I} = 0, m_{\mathcal{I}} = 0$. As the corresponding nuclear spin function $\Phi_{0,0}^{\text{nu.sp}}$ does not change if any of the operations of $C_{\mathfrak{h}_{\text{tot}}}(M)$ are applied, its irreducible representation is the total symmetric representation, $\Gamma^{\text{nu.sp}} = \Gamma_{\mathfrak{0}}$.

In general, the individual nuclei have identical non-zero spins, $\mathcal{I}_i \neq 0$, with magnetic quantum numbers $-\mathcal{I}_i \leq m_{\mathcal{I}_i} \leq \mathcal{I}_i$. Here, the set of all nuclear spin functions span the reducible representation $\Gamma^{\text{nu.sp}}$. We show in the following that $\Gamma^{\text{nu.sp}}$ contains every irreducible representation of $C_{\mathfrak{h}_{\text{tot}}}(M)$, or, in other words,

$$\Gamma^{\text{nu.sp}} \supset \Gamma^{\text{reg}}, \tag{51}$$

i.e. the representation $\Gamma^{\text{nu.sp}}$ contains the regular representation Γ^{reg} (Equation 47). For the moment, we limit our considerations to molecules of which only one of the contorting parts has a permutation symmetry, like for our example of the aligned CH_3 group. If both parts of the molecule have a permutation symmetry, as it is the case for B_{11}^-, our argument has to be slightly modified, see below.

To verify Equation (51), it suffices to find a subset of nuclear spin functions that spans Γ^{reg}. Therefore, consider a subset of nuclear spin states with the same total spin projection quantum number

$$m_{\mathcal{I}} = \sum_{i=1}^{\mathfrak{h}_{\text{tot}}} m_{\mathcal{I}_i}. \tag{52}$$

Assume furthermore that

$$m_{\mathcal{I}} \neq m_{\mathcal{I}^{\max}}^{\max} \quad \text{with} \quad \mathcal{I}^{\max} = \mathfrak{h}_{\text{tot}}\mathcal{I}_i \tag{53a}$$

$$m_{\mathcal{I}} \neq m_{\mathcal{I}^{\max}}^{\min} = -m_{\mathcal{I}^{\max}}^{\max}. \tag{53b}$$

One example that fulfils Equation (53) is when one nucleus has quantum number m_a and all remaining nuclei have quantum number $m_b \neq m_a$. Then, the total nuclear spin projection quantum number is

$$m_{\mathcal{I}} = m_a + (\mathfrak{h}_{\text{tot}} - 1)m_b, \tag{54}$$

in accordance with Equation (53).

There exist $\mathfrak{h}_{\text{tot}}$ nuclear spin functions that fulfil Equation (54); they span a reducible representation $\Gamma_{\text{sub}}^{\text{nu.sp}}$ of the group $C_{\mathfrak{h}_{\text{tot}}}(M)$ [41]. One representative of this subset of basis functions is

$$\Phi_{m_{\mathcal{I}}}^1 \equiv \Phi_{m_a}(\Sigma_1)\cdot\Phi_{m_b}(\Sigma_2)\cdot\ldots\cdot\Phi_{m_b}(\Sigma_{\mathfrak{h}_{\text{tot}}}). \tag{55}$$

To find the subset of matrices that form the representation $\Gamma_{\text{sub}}^{\text{nu.sp}}$, we apply the operation g (Equation 7) to $\Phi_{m_{\mathcal{I}}}^1$ and obtain

$$g\Phi_{m_{\mathcal{I}}}^1 = \Phi_{m_b}(\Sigma_1)\cdot\Phi_{m_a}(\Sigma_2)\cdot\ldots\cdot\Phi_{m_b}(\Sigma_{\mathfrak{h}_{\text{tot}}}) \equiv \Phi_{m_{\mathcal{I}}}^2. \tag{56}$$

Likewise, g is applied to all other basis functions $\Phi_{m_{\mathcal{I}}}^2, \ldots, \Phi_{m_{\mathcal{I}}}^{\mathfrak{h}_{\text{tot}}}$. Subsequently, we can define a vector $\mathbf{\Phi}_{\text{sub}}^{\text{nu.sp}}$ with components $(\mathbf{\Phi}_{\text{sub}}^{\text{nu.sp}})_i = \Phi_{m_{\mathcal{I}}}^i$, analogously to the localised states in Section 3.1. The matrix representation of the generator g is then

$$\mathfrak{D}^{\Gamma_{\text{sub}}^{\text{nu.sp}}}[g] = \begin{pmatrix} 0 & 1 & 0 & \ldots & 0 \\ 0 & 0 & 1 & \ldots & 0 \\ \vdots & & & \ddots & \vdots \\ 1 & 0 & \ldots & 0 & 0 \end{pmatrix}. \tag{57}$$

Following the same line of reasoning as for the representation Γ^{loc} (see Section 3.1), we obtain the matrices for $g^2, \ldots, g^{\mathfrak{h}_{\text{tot}}} = \text{E}$ and show that they form indeed the representation $\Gamma_{\text{sub}}^{\text{nu.sp}}$. These matrices have the character system

$C_{\mathfrak{h}_{\text{tot}}}(M)$	E	g	g^2		$g^{\mathfrak{h}_{\text{tot}}-1}$
$\zeta^{\Gamma_{\text{sub}}^{\text{nu.sp}}}$	$\mathfrak{h}_{\text{tot}}$	0	0	...	0

(58)

Thus the representation $\Gamma_{\text{sub}}^{\text{nu.sp}}$ is identical to the regular representation Γ^{red}, containing each irreducible representation of $C_{\mathfrak{h}_{\text{tot}}}(M)$ exactly once. This completes the proof of Equation (51).

We would like to stress that our result is always valid, because the only constraint we impose in our proof is that the projection quantum number of (at least) one nucleus has to be different from the others, cf. Equations (53) and (54). As this constraint can be always fulfilled if $\mathcal{I}_i \neq 0$, our conclusion is valid for all nuclei with non-zero spin.

Let us illustrate our result that $\Gamma^{\text{nu.sp}}$ necessarily contains the regular representation if $\mathcal{I}_i \neq 0$ for the case of $C_3(M)$ and $\mathcal{I}_i = 1/2$, i.e. for the torsion of an aligned methyl group. Here, the conditions (53) and (54) are fulfilled by the nuclear spin states with $m_{\mathcal{I}} = \pm 1/2$; we only consider states with $m_{\mathcal{I}} = +1/2$. The three product functions corresponding to this projection quantum number are

$$\begin{aligned} &\alpha(\Sigma_1)\cdot\alpha(\Sigma_2)\cdot\beta(\Sigma_3) \qquad \alpha(\Sigma_1)\cdot\beta(\Sigma_2)\cdot\alpha(\Sigma_3) \\ &\beta(\Sigma_1)\cdot\alpha(\Sigma_2)\cdot\alpha(\Sigma_3). \end{aligned} \tag{59}$$

They generate the representation

$$\begin{aligned} \mathfrak{D}^{\Gamma^{\text{nu.sp}}_{\text{sub}}}[\mathrm{E}] &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \mathfrak{D}^{\Gamma^{\text{nu.sp}}_{\text{sub}}}[(123)] &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \\ \mathfrak{D}^{\Gamma^{\text{nu.sp}}_{\text{sub}}}[(132)] &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \end{aligned} \tag{60}$$

with the character system

$C_3(M)$	E	(123)	(132)
$\zeta^{\Gamma^{\text{nu.sp}}_{\text{sub}}}$	3	0	0

(61)

This is again the regular representation of $C_3(M)$, thus confirming our general finding that the representation $\Gamma^{\text{nu.sp}}$ contains all irreducible representations of $C_3(M)$.

If properly modified, the argument is also true for contorting molecules of which both parts exhibit a permutation symmetry. Here, however, we have to consider the nuclear spin states of the two moieties of the molecule separately. In the case of B_{11}^-, for example, we have to analyse the nuclear spin states of the outer bearing with the group $C_9(M)$ and the nuclear spin states of the inner wheel with the group $C_2(M)$. Following the procedure we explained above, we find that the nine nuclear spin states with $m_{\mathcal{I}} = 9\cdot 3/2 - 1 = 25/2$ are a basis for the regular representation of $C_9(M)$, and the two states with $m_{\mathcal{I}} = 2\cdot 3/2 - 1 = 2$ span the regular representation of $C_2(M)$. Taking then into account the direct product structure of $C_{18}(M)$, see Equation (12) and Appendix 3, we can conclude that $\Gamma^{\text{nu.sp}}$ contains every symmetry of $C_{18}(M)$.

3.3. Localised states and the nuclear spin isomers of systems with feasible contorsions

With the results of the last two subsections, we are now able to make some general conclusions about the nuclear spin isomers of systems with one cyclic contorsion and their relationship to localised contorsional states. The simplest case is again the system that is composed only of nuclei with zero spin. Then, from the spin-statistics theorem it follows that

$$\Gamma^{\text{mol}} = \Gamma_0, \tag{62}$$

as all permuted nuclei are bosons. Further, we know from the last section that $\Gamma^{\text{nu.sp}} = \Gamma_0$. Hence, from Equation (24), it follows that $\Gamma^{\text{con}} = \Gamma_0$ is the only contorsional symmetry being consistent with the spin-statistics theorem. Thus for systems with nuclei carrying zero spin only one nuclear spin isomer is allowed, namely $\Gamma_0[\Gamma_0]$; spatial states with $\Gamma^{\text{con}} \neq \Gamma_0$ are symmetry-forbidden. As the discussion in Section 3.1 shows, this restriction has far reaching consequences. Because localised states are linear combinations of contorsional states with different symmetry, for systems with zero nuclear spin, localised states cannot be constructed without violating the spin-statistics theorem.

In the general case with $\mathcal{I}_i \neq 0$, the situation is different. Here, localised states are unphysical linear combinations of wave functions belonging to different nuclear spin isomers. To show this, we make use of the fact that if the symmetries Γ^{mol} and Γ^{con} are given, then the representation $\Gamma^{\text{nu.sp}}$ is fixed as well; for different symmetries Γ^{con} and $\Gamma^{\text{nu.sp}}$, there is only one way to form the irreducible representation Γ^{mol} (Equations 1 and 24) [61].

As we show in Section 3.1, each contorsional symmetry that is possible in $C_{\mathfrak{h}_{\text{tot}}}(M)$ exists. For each of these symmetries, there is a compatible nuclear spin symmetry (see Section 3.2). Hence, each contorsional symmetry represents a different nuclear spin isomer of the molecule. The correct combinations are dictated in Equations (1) and (24). Taking once more into account the results from the discussion of Section 3.1, we conclude that any hypothetical localised state is a linear combination of contorsional functions belonging to different nuclear spin isomers. Consequently, in case the nuclei that are described by the Hamiltonian equation (16) have non-zero spin, any hypothetical localised state in a cyclic potential is a superposition of states of all possible nuclear spin isomers of the molecule.

4. Why coherent superpositions of different nuclear spin isomers are unphysical

What is the problem with hypothetical localised states being linear combinations of wave functions with different contorsional symmetries? They would be superpositions of wave functions that represent different nuclear spin isomers of the molecule. But why is such a linear combination unphysical? Should it not be possible to prepare a localised state out of energy eigenstates, e.g. by using a proper excitation scheme? Moreover, according to Equation (2), nuclear spin isomers are instable, because their existence relies on an approximation. Could we not use mechanisms of nuclear spin conversion to create a coherent superposition of states belonging to different nuclear spin isomers?

The answer to both is no. The first scenario can be ruled out because no type of interaction exists that can excite different contorsional symmetries, if nuclear spin isomers were stable. The second argument fails because mechanisms of nuclear spin conversion take so long that any coherence of molecular eigenstates would be lost. Hence, both strategies cannot succeed, and therefore, localised states must be discarded as physical descriptions of molecular rotors. Let us illustrate why.

4.1. Localised states through external interactions?

In most known cases, nuclear spin isomers are stable species on the time scale of seconds or longer [44]. The only counter-examples that have been discovered until today are specific radicals [71], but they seem to be exceptional.

If nuclear spin isomers were stable, we could create localised states only by an interaction that directly excites superpositions of different symmetries from one state with specified contorsional symmetry. For example, if it was possible to cool down a molecular probe to almost 0K, one would prepare the contorsional ground state, i.e. only the lowest contorsional eigenstate with $\Gamma_{\mathtt{0}}$ symmetry would be populated. Then, creating a localised state is only possible if contorsional states with symmetries $\Gamma_{\mathtt{1}}, \ldots, \Gamma_{\mathfrak{h}_{\mathrm{tot}}-1}$ are excited from the contorsional ground state with symmetry $\Gamma_{\mathtt{0}}$.

To excite a superposition of states with all symmetries in $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$ out of a state with one specific Γ_n, one of the following conditions has to be fulfilled [41,42]: (a) the interaction that is used reduces the symmetry group of the system to $\mathrm{C}_1(M)$ or (b) the corresponding Hamiltonian transforms according to the irreducible representation

$$\Gamma^{\mathrm{int}} = \Gamma_{n'} \otimes \Gamma_n^* \neq \Gamma_{\mathtt{0}}, \tag{63}$$

where Γ_n and $\Gamma_{n'}$ denote the symmetries of the contorsional states that are coupled by the interaction $\hat{H}^{\mathrm{int}}$ with symmetry Γ^{int}. Both conditions follow from the vanishing integral rule, according to which an excitation from a state with symmetry $\Gamma_{n'}$ to a state with symmetry Γ_n using the interaction $\hat{H}^{\mathrm{int}}$ is allowed only if [41,42]

$$\Gamma_{n'}^* \otimes \Gamma^{\mathrm{int}} \otimes \Gamma_n = \Gamma_{\mathtt{0}}. \tag{64}$$

In Equations (63) and (64), we took into account that $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$ has only one-dimensional irreducible representations.

In both scenarios, the symmetry is reduced only if $\hat{H}^{\mathrm{int}}$ breaks the permutation symmetry of the molecular system. For case (a), the field strength is arbitrary, and to understand the effect of the interaction, it is necessary to analyse the symmetry group of field-dressed Hamiltonian [41,42]. Within this group, the Hamiltonian $\hat{H}^{\mathrm{int}}$ transforms according to the totally symmetric representation $\tilde{\Gamma}_{\mathtt{0}}$ of the permutation subgroup of the field-dressed symmetry group [41,62]. Hence, to induce excitations between states that have symmetries Γ_n and $\Gamma_{n'}$ in the field-free case, the symmetries within the field-dressed group have to be complex conjugate to each other, cf. Equation (63). Taking into account that a localised state contains states of all symmetries in $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$, each Γ_n must be reduced to $\tilde{\Gamma}_{\mathtt{0}}$ in the field-dressed group. In other words, the symmetry group must be reduced from $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$ to $\mathrm{C}_1(M)$ by the external field. As $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$ only contains permutations, the external field must therefore break the permutation symmetry. Yet, such an interaction is not known. Neither magnetic or electric fields, nor the combination of both can break the permutation symmetry of a quantum mechanical system [62].

In scenario (b), the field strength is so low that perturbation theory is sufficient to describe the excitation of the molecule. Here, the symmetry of the system can be considered to be conserved and $\hat{H}^{\mathrm{int}}$ can be classified according to the irreducible representations of $\mathrm{C}_{\mathfrak{h}_{\mathrm{tot}}}(M)$. Yet, to induce excitations between different Γ_n, the Hamiltonian $\hat{H}^{\mathrm{int}}$ must contain parts that have symmetry $\Gamma_{\mathtt{1}}, \ldots, \Gamma_{\mathfrak{h}_{\mathrm{tot}}-1}$, otherwise Equation (63) is not fulfilled. Hence, $\hat{H}^{\mathrm{int}}$ is not invariant under the permutation of identical nuclei, which is physically not possible, for the same reasons as in case (a).

There is a second argument why scenario (b) is inappropriate for producing localised states. If the interaction is only a small perturbation, the excited states are prepared with much smaller populations than the ground state. Thus it is impossible to create a localised state, which calls for equal weights of all symmetry-adapted eigenstates (Equations 40a and 46).

Intuitively, the results of this paragraph are clear. Breaking the permutation symmetry would violate the indistinguishability of identical nuclei. Although spectroscopists are searching for such violations, they have not been observed yet [42,72]. Hence, if nuclear spin isomers are considered to be stable species, it is impossible to create a localised state by exciting contorsional eigenstates directly.

4.2. Localised states through nuclear spin conversion?

As an alternative to direct excitation, creating hypothetical localised states indirectly might be possible by using nuclear spin conversion effects. In fact, different nuclear spin isomers are interconverted by nuclear spin dependent interactions, such as the dipolar interaction or the spin–rotation interaction [44]; a probe of one specific nuclear spin isomer will eventually evolve into an incoherent mixture of different nuclear spin isomers. However, the interconversion rates are usually on the time scales of seconds to years. Moreover, most mechanisms of nuclear spin conversion are assumed to be incoherent processes [44]. Hence, they are useless for preparing a coherent superposition of contorsional states belonging to different nuclear spin isomers, like a localised state.

Recent research shows, however, that using time-dependent magnetic fields might accelerate the interconversion of nuclear spin isomers by exciting dipolar-coupled contorsional states [69]. The superpositions of molecular states are coherent; through a change of the nuclear spin state, the magnetic field creates linear combinations of contorsional states with different symmetries, if the dipolar interaction between the nuclei is taken into account.

Unfortunately, there are two problems if this scheme is used. First, the superpositions created by the magnetic field do not contain each contorsional symmetry with equal weight, which, however, is required for preparing a localised state (see Section 3.1). Second, the interconversion still takes place on the time scale of μs, which is much longer than the period of the contorsional motion. Hence, in practice, it is impossible to prepare a localised state, because in a realistic scenario, maintaining coherence on that time scale is very difficult.

Consequently, also by using nuclear spin conversion effects, we are not able to prepare a localised state from an energy eigenstate.

5. Conclusion: molecular rotors are quantum rotors

In summary, we have shown that localised states are unphysical representations of systems with observable contorsional motions in cyclic potentials. For these molecular rotors, localised states are superpositions of symmetry-adapted states, such that each symmetry-adapted function contributes with equal weight. Depending on the spin of the contorting nuclei, localised states are either superpositions of states belonging to different nuclear spin isomers, represented by different contorsional symmetries, or localised states are forbidden by the spin-statistics theorem.

In case the nuclei have zero spin, only contorsional states with symmetry $\Gamma^{\mathrm{con}} = \Gamma_{\mathfrak{0}}$ are physically allowed. Since a localised state contains contorsional states of all symmetries, it is principally impossible to prepare such states. For molecular rotors with non-zero nuclear spin, localised states are superpositions of eigenfunctions of all possible nuclear spin isomers of the molecular rotor. However, it is impossible to create superposition states of different nuclear spin isomers. A direct preparation by means of an electromagnetic field can be ruled out, because the interaction that is used would have to destroy the indistinguishability of identical nuclei; an indirect preparation based on nuclear spin converting effects either takes too long, or the effect is too weak to create a coherent superposition of contorsional states belonging to different nuclear spin isomers. Consequently, whether the nuclear spin is zero or not, localised wave packets do not represent physical states of the molecular rotors we consider here.

Our findings have far reaching consequences for conventional molecular dynamics simulations of molecular rotors. When scientists use classical mechanics to describe the motions of nuclei, they often illustrate their approach with pictures like the one we show in Figure 3 [16–23]. As an example, we depict the concerted rotation and pseudo-rotation of B_{11}^-. The semi-classical simulation starts in *one* specific minimum of the electronic potential energy surface (a), and after passing a transition state (b), it arrives at *one* specific neighbouring minimum (c). Since classical structures can be mimicked quantum mechanically by localised states, so the implicit argument, molecular dynamics simulations generate reliable results, as long as dispersion and tunnelling occur on timescales that are longer than the timescale of the contorsional motion. But this conclusion is wrong, because the localised state is a superposition of symmetry-adapted states belonging to the different nuclear spin isomers of B_{11}^-, they are physically incorrect.

For the boron rotors in particular, the impossibility of localised states also has important consequences for their molecular spectroscopy. Let us assume for a moment that localised states representing global minimum structures would exist. Accordingly, one would observe spectral lines with $\mathfrak{h}_{\mathrm{tot}}$-fold degeneracies for $\mathfrak{h}_{\mathrm{tot}}$

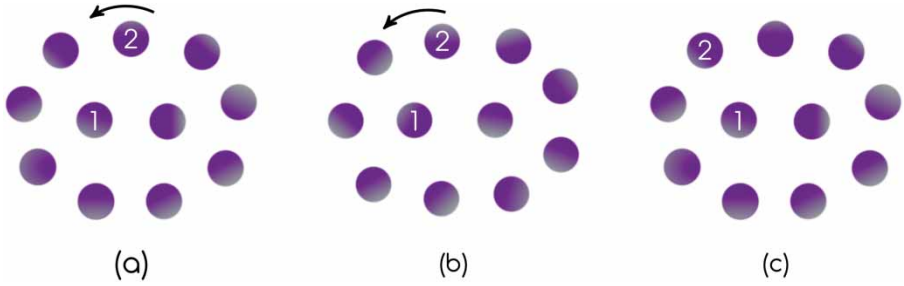

Figure 3. A classical depiction of the concerted rotation and pseudo-rotation in B_{11}^-: from *one* specified minimum of the electronic potential energy surface (a), the nuclei pass a transition state (b) and reach *one* specific neighbouring minimum (c). A quantum analogue for this scenario is the progression of one localised state to the neighbouring one. The figure is adapted from Ref. [20].

equivalent global minimum structures. In contrast, the preparation of molecular eigenstates that are delocalised in $\mathfrak{h}_{tot}$ potential energy wells implies systematic splittings of the hypothetical degenerate lines into non-degenerate ones. If the spectra are taken with lower resolution than the level splittings, the corresponding spectral lines appear broader than the hypothetical lines for individual global minimum structures. Gratifyingly, such broadening has been observed in Ref. [22], but the authors could not explain the reason for the broadening, see also the discussions in Ref. [23].

Concluding, the results of this work show that molecular rotors cannot be described in terms of a semi-classical approach. For molecular rotors like B_{11}^- or molecules with observable torsion, localised states are not physically valid descriptions. Hence, conclusions based on semi-classical molecular dynamics simulations, for example concerning the control of directed contorsional motions, have to be reevaluated. For systems showing contorsion in cyclic potentials, a quantum description of nuclear motions is unavoidable. Such molecular rotors are quantum rotors.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix 1. Molecular symmetry and models of reduced dimensionality

In this work, we use simple models to describe the nuclear spin isomers of aligned molecular rotors. These models are based on the assumption that the contorsional motion can be adiabatically separated from all other internal motions, which includes the following approximations:

- **The Born–Oppenheimer approximation**
  We premise that we can adiabatically separate the electronic motions from the nuclear motions by approximating the nuclear-spin-free roconvibronic wave function as

$$\Phi^{\mathrm{rcve}} = \Phi^{\mathrm{rcv}}_{\mathfrak{e}} \cdot \Phi^{\mathrm{el}}_{\mathfrak{e}}. \tag{A1}$$

  In Equation (A1), $\Phi^{\mathrm{el}}_{\mathfrak{e}}$ is the electronic wave function for the electronic state $\mathfrak{e}$ including electronic spin and $\Phi^{\mathrm{rvc}}_{\mathfrak{e}}$ denotes a roconvibrational wave function for this particular electronic state. Specifically, we assume that the molecule is in the electronic ground state.
- **Adiabatic separation of rotational, contorsional and vibrational motions**
  In addition to the Born–Oppenheimer approximation, we assume that the nuclear wave function $\Phi^{\mathrm{rcv}}_{\mathfrak{e}}$ can be written as

$$\Phi^{\mathrm{rvc}}_{\mathfrak{r}\mathfrak{c};\mathfrak{v};\mathfrak{e}} = \Phi^{\mathrm{rot}}_{\mathfrak{r};\mathfrak{v};\mathfrak{e}} \cdot \Phi^{\mathrm{con}}_{\mathfrak{c};\mathfrak{v};\mathfrak{e}} \cdot \Phi^{\mathrm{vib}}_{\mathfrak{v};\mathfrak{e}}. \tag{A2}$$

  Here, $\Phi^{\mathrm{vib}}_{\mathfrak{v};\mathfrak{e}}$ is the vibrational eigenfunction for the vibrational states $\mathfrak{v}$ within electronic state $\mathfrak{e}$; $\Phi^{\mathrm{rot}}_{\mathfrak{r};\mathfrak{v};\mathfrak{e}}$ denotes the rotational eigenfunctions for electronic state $\mathfrak{e}$ and vibrational state $\mathfrak{v}$ with rotational quantum numbers $\mathfrak{r}$; and $\Phi^{\mathrm{con}}_{\mathfrak{c};\mathfrak{v};\mathfrak{e}}$ represents the eigenfunctions of the contorsional motion within electronic state $\mathfrak{e}$ and vibrational state $\mathfrak{v}$ characterised by the quantum number $\mathfrak{c}$. While separating the vibrations from the rocontorsional motions is quite common, in particular in the theory of molecular spectroscopy [41], the separation of the contorsional motion from the rotations may be questionable, depending on the system. Recent studies on torsional alignment, for example, show that the coupling of rotations with internal motions might be quite distinct [73–78]. Thus our models are highly idealised.
- **Adiabatic separation for field-dressed states**
  In our model, we further assume that controlling the orientation or the alignment of the molecular rotor by manipulating its rotational motions is possible without exiting the contorsional motion. Thus, even within the presence of a laser field, we expect contorsions and rotations to remain decoupled. Systematic studies on the torsional alignment of molecules have shown that a strong coupling of rotations and contorsions may be induced by the aligning field, again depending on the system [73–78]. Our choice therefore underlines the highly idealised character of our model.

The present approximations allow for a rather simple procedure for identifying the nuclear spin isomers of molecular rotors. Using the Born–Oppenheimer approximation, we average the molecular Hamiltonian over the electronic degrees of freedom, so that we obtain an effective Hamiltonian for the nuclear motion in the given electronic state. Likewise, we integrate the remaining nuclear Hamiltonian over the vibrational degrees of freedom, assuming that the molecule remains in the chosen vibronic state. This gives the effective Hamiltonian

$$\hat{H}^{\mathrm{rc}}_{\mathfrak{v};\mathfrak{e}} = \langle \Phi^{\mathrm{vib}}_{\mathfrak{v};\mathfrak{e}} \cdot \Phi^{\mathrm{el}}_{\mathfrak{e}} | \hat{H}^{\mathrm{nuc}} | \Phi^{\mathrm{vib}}_{\mathfrak{v};\mathfrak{e}} \cdot \Phi^{\mathrm{el}}_{\mathfrak{e}} \rangle \tag{A3}$$

for the vibrational state $\mathfrak{v}$ in the electronic state $\mathfrak{e}$.

Accordingly, we suppose that the molecules are aligned by off-resonant laser pulses, which prepare pendular states $\mathfrak{p}$ with wave functions $\Phi^{\mathrm{pen}}_{\mathfrak{p};\mathfrak{v};\mathfrak{e}}$ [35–37], typically the one lowest in energy. In this case, we can define the contorsional Hamiltonian

$$\hat{H}^{\mathrm{con}}_{\mathfrak{p};\mathfrak{v};\mathfrak{e}} = \langle \Phi^{\mathrm{pen}}_{\mathfrak{p};\mathfrak{v};\mathfrak{e}} | \hat{H}^{\mathrm{rc}}_{\mathfrak{p};\mathfrak{v}} | \Phi^{\mathrm{pen}}_{\mathfrak{p};\mathfrak{v};\mathfrak{e}} \rangle \equiv \hat{H}^{\mathrm{con}}. \tag{A4}$$

Appendix 2. The MS group of B_{11}^-

To identify the MS group of non-rigid molecular rotors, we employ a systematic approach starting from the MS group G^{eq} of its rigid energy minimum ('equilibrium') structure [79,80]. Accordingly, we expand the MS group G^{MS} of a molecule with large-amplitude internal motions as

$$G^{\mathrm{MS}} = G^{\mathrm{eq}} \cup \hat{\mathcal{F}}_2 G^{\mathrm{eq}} \cup \cdots \cup \hat{\mathcal{F}}_{n_V} G^{\mathrm{eq}} = \bigcup_{i=1}^{n_V} \hat{\mathcal{F}}_i G^{\mathrm{eq}} \quad \text{with}$$

$$\hat{\mathcal{F}}_1 \equiv E, \tag{B1}$$

whereas the group G^{eq} is isomorphic to the molecular point group of the electronic energy minimum structure [38,39]. As we show in the following, for the boron clusters with observable pseudo-rotation, Equation (B1) has a simple structure

$$G_X = G^{\mathrm{eq}} \otimes G(\{\hat{\mathcal{F}}_i\}) \qquad X = B_{11}^-, B_{13}^+, B_{15}^+, B_{19}^-, \tag{B2}$$

where $G(\{\hat{\mathcal{F}}_i\})$ is a group formed by the set of operators $\hat{\mathcal{F}}_i$. The operator $\hat{\mathcal{F}}_i$ in Equations (B1) and (B2) transforms the reference version 1 into version i. We find all $\hat{\mathcal{F}}_i$ by identifying those permutations and permutation-inversions that interconvert the n_V versions of the molecule that are separated by superable energy barriers. A barrier is superable when it leads to observable tunnelling splittings in the energy spectrum of the nuclear motion on the timescale of the observation time [41,42].

The boron cluster B_{11}^- shows contorsional motions of an inner 'wheel' consisting of $\mathfrak{h}_{\mathrm{in}} = 2$ nuclei that rotates against an outer 'bearing' consisting of $\mathfrak{h}_{\mathrm{out}} = 9$ pseudo-rotating nuclei [23] (see Figure B1 for an illustration). Hence, the potential energy surface for the contorsional motion of B_{11}^- has $\mathfrak{h}_{\mathrm{in}} \cdot \mathfrak{h}_{\mathrm{out}} = 18$ global minima, and the group $G(\{\hat{\mathcal{F}}_i\})$ has the order $\mathfrak{h}_{\mathrm{in}} \cdot \mathfrak{h}_{\mathrm{out}} = 18$. The barriers between the global minima are so low that tunnelling is observable in the picosecond time domain [23].

The group G^{eq} is isomorphic to the point group at the equilibrium structure, which is C_{2v} in case of B_{11}^- [20] (see the picture in the middle of Figure B1). Following the rules derived by Hougen [38,39], we conclude that the $\hat{C}_2$ operation in the molecular point group corresponds to the permutation

$$P_0 = (\mathtt{a\,e})(\mathtt{b\,d})(\mathtt{f\,i})(\mathtt{g\,h})(\mathtt{1\,2}), \tag{B3}$$

generating the group

$$\mathcal{G}_0 = \{E, P_0\}. \tag{B4}$$

As B_{11}^- has a planar energy minimum structure [20,23],

$$G^{\mathrm{eq}} = \mathcal{G}_0 \otimes \mathcal{E}, \tag{B5}$$

where

$$\mathcal{E} = \{E, E^*\} \tag{B5a}$$

is the inversion group. To obtain Equation (B5), we have used that (i) MS groups of rigid molecules contain the inversion E^* if the equilibrium structure is planar [41,42,80] and (ii) E^* commutes with every operation in the MS group [41,42].

To determine the group $G(\{\hat{\mathcal{F}}_i\})$ of the B_{11}^- cluster, we consider exemplarily the two operations

$$P_{\mathrm{in}} = (\mathtt{12}) \tag{B6a}$$

$$P_{\mathrm{out}} = (\mathtt{a\,e\,i\,d\,h\,c\,g\,b\,f})\,; \tag{B6b}$$

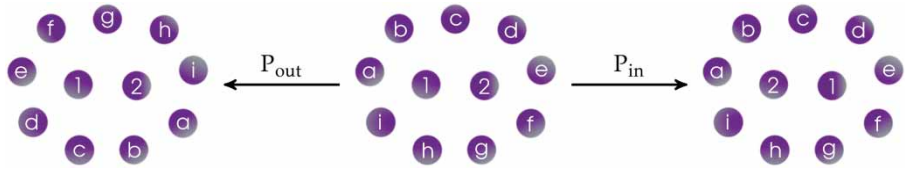

Figure B1. Three versions of the cluster B_{11}^{-}. The reference version (middle) is converted by P_{in} (right) and P_{out} (left) into two other versions, see Equation (B6) for the definition of P_{in} and P_{out}. The motion that interconverts all three versions is the rotation of the inner wheel in the pseudo-rotating outer bearing.

see Figure B1. They generate the groups

$$C_{in} = \langle P_{in} \mid, P_{in}^{\mathfrak{h}_{in}} = E \rangle \tag{B7a}$$

$$C_{out} = \langle P_{out} \mid P_{out}^{\mathfrak{h}_{out}} = E \rangle \tag{B7b}$$

with orders $\mathfrak{h}_{in} = 2$ and $\mathfrak{h}_{out} = 9$, respectively. Applying any combination of these two operations

$$\hat{\mathcal{F}}_i = P_{in}^a P_{out}^b \quad \text{with} \quad a = 1, 2;\ b = 1, \ldots, 9;$$
$$i = 9(a-1) + b = 1, \ldots, 18 \tag{B8}$$

to a reference minimum, we are able to access all of the remaining 17 minima of the potential energy surface. Here, we chose the generators such that $g = P_{in} \cdot P_{out}$ interconverts two neighbouring global minima [23], i.e.

$$g\xi = P_{in} \cdot P_{out}\, \xi = \xi + \frac{2\pi}{18}. \tag{B9}$$

Taking into account that

$$P_{out}\xi = \xi - 4\,\frac{2\pi}{\mathfrak{h}_{out}} \tag{B10a}$$

$$P_{in}\xi = \xi + \frac{2\pi}{\mathfrak{h}_{in}}, \tag{B10b}$$

we see that g has exactly this property if we define P_{out} and P_{in} according to Equation (B6).

Because P_{in}^a and P_{out}^b commute, i.e.

$$P_{in}^a P_{out}^b = P_{out}^b P_{in}^a \quad \forall a, b, \tag{B11}$$

we are able to write

$$G(\{\hat{\mathcal{F}}_i\}) = C_{in} \otimes C_{out} \equiv C_{\mathfrak{h}_{tot}}(M). \tag{B12}$$

Taking further into account that E^* and P_0 both commute with all elements of $C_{\mathfrak{h}_{tot}}(M)$, we finally obtain the complete MS group for B_{11}^{-} with observable pseudo-rotation,

$$G_{B_{11}^-} = G^{eq} \otimes C_{in} \otimes C_{out} = G^{eq} \otimes C_2 \otimes C_9; \tag{B13}$$

see also Equation (9).

Appendix 3. On the irreducible representations of the group $C_{\mathfrak{h}_{tot}}$

To find the irreducible representations of the cyclic group $C_{\mathfrak{h}_{tot}}(M)$, we apply Equation (15). Once we have calculated the character of the generator g for the irreducible representation Γ_n, see Equation (7),

$$\zeta^{\Gamma_n}[g] = \eta_{\mathfrak{h}_{tot}}^n, \tag{C1a}$$

the character of all group elements

$$\zeta^{\Gamma_n}[g^z] = (\zeta^{\Gamma_n}[g])^z \tag{C1b}$$

are fixed (Equation 15). Hence, for cyclic groups, the irreducible representations Γ_n are completely determined by the character Equation (C1a).

For example, for $C_3(M)$, we use

$$\zeta^{\Gamma_n}[(123)] = \eta_3^n = \exp\left(-n\frac{2\pi i}{3}\right) \tag{C2}$$

to determine the three irreducible representations:

$$\begin{aligned} \zeta^{\Gamma_0}[(123)] = 1 \quad &\Leftrightarrow \quad \Gamma = \Gamma_0 \equiv A, \\ \zeta^{\Gamma_1}[(123)] = \eta_3 \quad &\Leftrightarrow \quad \Gamma = \Gamma_1 \equiv E_1, \\ \zeta^{\Gamma_2}[(123)] = \eta_3^* \quad &\Leftrightarrow \quad \Gamma = \Gamma_2 \equiv E_2. \end{aligned} \tag{C3}$$

Here, the irreducible representations E_1 and E_2 are separable degenerate as long as the quantum system of interest is invariant under time-reversal [41].

We could apply the same approach to determine the 18 irreducible representations of $C_{18}(M)$, the symmetry group of B_{11}^{-} with hindered rotations. Defining

$$\eta_{18} \equiv \exp\left(-\frac{2\pi i}{18}\right) \tag{C4}$$

and using Equations (C1a) and (C1b), we then obtain the 18 irreducible representations $\Gamma_0, \ldots, \Gamma_{17}$ that are given in the right column of Table 1. It is instructive, however, to employ an alternative method that makes use of the direct product structure (Equation 12). Consider a group G that can be written as

$$G = U \otimes U'. \tag{C5}$$

Then, according to the representation theory of groups [41,67,68], the character ζ of the element $g_{i,j} = u_i \circ u'_j$ for any irreducible representation $\Gamma^G_{\alpha\bar{\alpha}}$ of the group G can be written as

$$\zeta^{\Gamma^G_{\alpha\alpha'}}[g_{i,j}] = \zeta^{\Gamma^U_{\alpha}}[u_i] \cdot \zeta^{\Gamma^{U'}_{\alpha'}}[u'_j], \tag{C6}$$

where Γ_α and $\Gamma_{\bar{\alpha}}$ denote irreducible representations of the subgroups U and U′. Applying Equation (C6), we are able to write the characters of the irreducible representations of C_{18} as products of the irreducible representations of $C_{in}(M)$ and $C_{out}(M)$.

How we choose the characters of the two cyclic subgroups, $C_9(M)$ and $C_2(M)$, is to some extent arbitrary, as long as Equations (C1a) and (C1b) are fulfilled, and we obtain a different set of characters for each irreducible representation. We choose η

for $C_2(M)$ and $C_9(M)$ such that their irreducible representations properly correlate with the irreducible representations of $C_{18}(M)$. Hence, for the group $C_{in}(M) = C_2(M)$, we define

$$\zeta^{\Gamma_n}[(12)] = \eta_{in}^n = \exp(-n\pi i) \tag{C7}$$

and

$$\begin{aligned} \zeta^{\Gamma_0}[(12)] = 1 \quad &\Leftrightarrow \Gamma = \Gamma_0 \equiv \mathrm{A}, \\ \zeta^{\Gamma_1}[(12)] = -1 \quad &\Leftrightarrow \Gamma = \Gamma_1 \equiv \mathrm{B}. \end{aligned} \tag{C8}$$

Applying Equation (C1b) then gives all characters of A and B.

For the nine irreducible representations of $C_{out}(M) = C_9(M)$, $\Gamma_0, \Gamma_1, \ldots, \Gamma_8$, we choose

$$\zeta^{\Gamma_n}[(\mathtt{a\,e\,i\,d\,h\,c\,g\,b\,f})] = \eta_{out}^n = \exp\left(n \cdot \frac{8\pi i}{9}\right), \tag{C9}$$

cf. Equation (B10a), and calculate the characters of each Γ_n employing Equations (C1a) and (C1b). Here, we find for the irreducible representations

$$\Gamma_n = \Gamma^*_{\mathfrak{h}_{out}-n}. \tag{C10}$$

Again, it follows from representation theory that the pair $(\Gamma_n, \Gamma_{\mathfrak{h}_{out}-n})$ is separable degenerate as long as time-reversal is a symmetry operation of the system [41].

Thus, for B_{11}^-, we can write the 18 irreducible representations of $C_{\mathfrak{h}_{tot}}(M)$ as

$$\Gamma_{0,\mathrm{A}}, \Gamma_{0,\mathrm{B}}, \ldots, \Gamma_{8,\mathrm{A}}, \Gamma_{8,\mathrm{B}}. \tag{C11}$$

Their characters can be directly read off (Equations C1b, C6, C8 and C9, respectively) without calculating the character table of $C_{18}(M)$ explicitly.

The direct product structure of $C_{18}(M)$ (Equation 12) also simplifies assigning the basis functions ϕ_k in Equation (18) according to their symmetries. From Equation (B10) follows

$$\mathrm{P}_{out}\mathrm{P}_{in}\phi_k = \eta_{out}^k \eta_{in}^k \phi_k \tag{C12}$$

with η_{out} and η_{in} being defined in Equations (C9) and (C7). Thus, with the help of Equations (B10) and (C12), we can classify the contorsional basis functions ϕ_k according to irreducible representations of the groups (Equations 10a and 10b) to finally confirm the results in Table 1.

Appendix 4. How to find the number of nuclear spin states with given symmetry

In general, the characters of the reducible representation $\Gamma^{\mathrm{nu.sp}}$ that is spanned by all nuclear spin functions can be found by counting the number of nuclear spin functions that are left invariant if the operation P is applied [41],

$$\zeta^{\Gamma^{\mathrm{nu.sp}}}[\mathrm{P}] = \prod_{k=1}^{N_\mathrm{P}} (2\mathcal{I}_k + 1) \prod_{k'=1}^{\bar{N}_\mathrm{P}} (2\mathcal{I}_{k'} + 1). \tag{D1}$$

In Equation (D1), k labels the N_P nuclear spins belonging to the same $m_{\mathcal{I}_k}$ that are permuted by P, whereas k' denotes the $\bar{N}_\mathrm{P}$ nuclear spins that are not affected by P.

We discuss the nuclear spin states of B_{11}^- as an example. Taking into account the direct product structure of $C_{18}(M)$, cf. Equation (12), we determine the symmetries $\Gamma^{\mathrm{nu.sp}}$ for the groups $C_{in}(M)$ and $C_{out}(M)$ separately. Applying Equation (D1), we obtain for $\Gamma^{\mathrm{nu.sp}}_{C_{in}}$

$$\zeta^{\Gamma^{\mathrm{nu.sp}}_{C_{in}}}[\mathrm{P}_{in}^2] = \left(2 \cdot \frac{3}{2} + 1\right)^2 = 16 \tag{D2a}$$

$$\zeta^{\Gamma^{\mathrm{nu.sp}}_{C_{in}}}[\mathrm{P}_{in}] = \left(2 \cdot \frac{3}{2} + 1\right) = 4. \tag{D2b}$$

Using the formula for reduction [41,67,68]

$$a_{\Gamma_i} = \frac{1}{\mathfrak{h}_{tot}} \sum_{n=1}^{\mathfrak{h}_{tot}} (\zeta^{\Gamma_i}[\mathrm{P}_{in}^n])^* \zeta^{\Gamma^{\mathrm{nu.sp}}_{C_{in}}}[\mathrm{P}_{in}^n], \tag{D3}$$

we find

$$\Gamma^{\mathrm{nu.sp}}_{C_{in}} = 10\,\mathrm{A} \oplus 6\,\mathrm{B} \tag{D4}$$

in accordance with Equation (29a).

Analogously, for the reducible representation $\Gamma^{\mathrm{nu.sp}}_{C_{out}}$

C_{out}	E	P^1_{out}	P^2_{out}	P^3_{out}	P^4_{out}	P^5_{out}	P^6_{out}	P^7_{out}	P^8_{out}
$\zeta^{\Gamma^{\mathrm{nu.sp}}}$	262, 144	4	4	64	4	4	64	4	4

(D5)

Using the characters shown in Equation (D5) and the formula for reduction (Equation .3), for C_9, confirms the results shown in Equation (29b). In particular, we have

$$a_{\Gamma_1} = a_{\Gamma_2} = a_{\Gamma_4} = a_{\Gamma_5} = a_{\Gamma_7} = a_{\Gamma_8} \tag{D6a}$$

$$a_{\Gamma_3} = a_{\Gamma_6}. \tag{D6b}$$

We then obtain the complete representation $\Gamma^{\mathrm{nu.sp}}_{C_{18}}$ by applying Equation (C6).