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Comment on “Effective spin Hamiltonians for the quantum-rotor tunneling problem in pulse EPR” [J. Chem. Phys. 163, 064104 (2025)]

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Low-temperature magnetic resonance, neutron scattering, and gas-phase molecular spectroscopy experiments are sensitive to tunneling methyl groups. Based on earlier work by Freed,¹ Apaydin and Clough² established in 1968 that tunneling effects in the rotational ground state can be described using the effective spin Hamiltonian

$$\hat{H}_{\text{eff}} = -\frac{2}{3}\hbar\omega_t(\hat{I}_1\hat{I}_2 + \hat{I}_2\hat{I}_3 + \hat{I}_3\hat{I}_1), \quad (1)$$

where ω_t is the tunneling frequency and $\hat{I}_1$, $\hat{I}_2$, and $\hat{I}_3$ are the spin operators of the three methyl protons or deuterons. This approach indicates an effective exchange coupling between neighboring protons and has been widely and successfully used to describe experimentally observed spectral features.

A recent paper by Kuzin and Jeschke³ posits that Eq. (1) is incomplete and needs to be extended. Here, we show that their treatment fails to correctly take into account the Pauli exclusion principle. A methyl group contains three protons, which are fermions. Since their wavefunctions overlap non-negligibly (as evidenced by the measurable tunnel splitting), it is crucial to take into account the Pauli principle, which states that only states that invert sign upon exchange of two identical fermions are physical. This symmetry for identical fermions is universal.

For the purpose of describing low-temperature magnetic resonance phenomena, the methyl group can be considered rigid and non-rotating, i.e., excited rotational states are not populated. In a rigid methyl group, there are two types of permutations, single and double pair swaps. The barrier between two proton configurations related by a single pair swap is very high, resulting in essentially zero nuclear wavefunction overlap and a non-observably small tunnel splitting. Therefore, the Pauli antisymmetry requirement for single pair swaps can be neglected for the purpose of modeling

experimental observables. However, the barrier between methyl proton configurations related by a cyclic permutation (double pair swap) is lower, resulting in non-zero nuclear wavefunction overlap and observable tunnel splitting. Therefore, the Pauli symmetry requirement for cyclic permutation must be included in modeling.

A cyclic permutation corresponds to two sequential swaps, and therefore, the wavefunction needs to be symmetric with respect to cyclic permutation. Therefore, the relevant permutation group is the alternating group A_3 , a subgroup of the symmetric group S_3 (isomorphic to C_3 , which is a subgroup of C_{3v}) with the three symmetry species labeled A, E_1 , and E_2 (or A, E_a , and E_b ; notation borrowed from C_3).

Note that this isomorphism of A_3 with C_3 is a bit unfortunate, as the point group symmetry of the methyl group is not directly relevant here. The A_3 permutation symmetry applies to any three protons, regardless of spatial positioning. The spatial positioning is only important here in so far as it allows for the proton wavefunctions to overlap. Note that a cyclic permutation of the three protons is different from a rotation of the methyl group. A cyclic permutation permutes both spatial and spin coordinates, whereas a rotation permutes the spatial coordinates only.

Let us consider a wavefunction $|\Psi\rangle$ in the combined rotation–spin space of the methyl group. Any such wavefunction can be written as a symmetry decomposition:

$$|\Psi\rangle = \bigoplus_{\pi} |\Psi^{(\pi)}\rangle, \quad (2)$$

where π runs over all irreducible subspaces under the appropriate symmetry group ($\pi \in \{A, E_1, E_2\}$ for methyls under A_3).

Now the spin-statistics theorem requires that all wavefunctions describing physical states must be antisymmetric upon exchanging spatial and spin coordinates of two identical fermions (such as

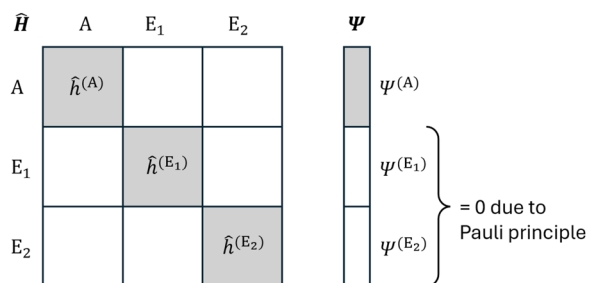


FIG. 1. Block structure of the Hamiltonian (left) and a general wavefunction (right) for a methyl group in a basis symmetry-adapted to the three-proton cyclic permutation group A_3 . The Pauli principle imposes $\Psi^{(E_1)} = \Psi^{(E_2)} = 0$.

$$\hat{H} = \bigoplus_{\pi} \hat{h}^{(\pi)}. \quad (5)$$

Combined with Eq. (3), this means that the system starts in a state of A symmetry and remains entirely in the A subspace during evolution under $\hat{H}$. While there are three sub-Hamiltonians in the symmetry decomposition of Eq. (5), only $\hat{h}^{(A)}$ is relevant.

The above considerations equally apply to tetrahedral rotors such as CH_4 , NH_4^+ and BH_4^- . For those rotors, the relevant permutation group is the alternating group A_4 (isomorphic to point group T) with the symmetry species A, E_1 , E_2 , and T. Again, only the A species is relevant due to the Pauli principle.

In the case of a methyl group with three protons, there are eight states of overall A symmetry, which group into states with different spatial and spin symmetries:

$$8A = 4(A \times A) \oplus 2(E_1 \times E_2) \oplus 2(E_2 \times E_1). \quad (6)$$

Here, the first factors in the products refer to the permutation symmetry regarding spatial coordinates and the second to the permutation symmetry regarding spin coordinates. For tetrahedral rotors, the same analysis reveals 16 A states that group into four sets of states with different spatial and spin symmetries:

$$16A = 5(A \times A) \oplus (E_2 \times E_1) \oplus (E_1 \times E_2) \oplus 9(T \times T). \quad (7)$$

In their paper, Kuzin and Jeschke symmetry-decompose the Hamiltonian [their Eqs. (12) and (21)] and derive explicit expressions for the sub-Hamiltonians [their Eqs. (22) and (23)]. However, they disregard the Pauli principle [our Eq. (3)] and include non-zero amplitude in the unphysical subspaces in their initial states. They proceed in the enlarged space (dimension 24 for methyl, 192 for tetrahedral rotors) instead of the physically relevant A subspace (dimensions 8 and 16, respectively).

Our analysis above assumes (a) that the overall proton wavefunction of the molecule factors into a part depending on the methyl rotation and methyl proton spin degrees of freedom [Eq. (2)] and a part depending on all other degrees of freedom (including vibrations involving the methyl protons) and (b) that the latter factor is symmetric under the cyclic permutation of the three methyl protons. If either of these assumptions is not fulfilled, E_1 and E_2 subspaces could be relevant. However, we are not aware of situations where this is the case.

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protons) and symmetric upon exchange of coordinates of identical bosons (such as deuterons). In either case, the states will be symmetric upon two pair swaps. Therefore, $|\Psi\rangle$ has non-zero amplitude only in the A subspace; it has zero amplitude in all other subspaces (see Fig. 1):

$$|\Psi^{(\pi)}\rangle = 0 \quad \text{for } \pi \neq A. \quad (3)$$

The full Hamiltonian of the molecule is fully symmetric with respect to permutations of any protons or any deuterons, and more specifically to cyclic permutation of the three methyl protons/deuterons. For example, the full Hamiltonian for the dipolar hyperfine interaction is

$$\hat{H}_{\text{hf}} = \sum_i \hat{S}^T \left(\frac{\mu_0}{4\pi} \hbar^2 \gamma_e \gamma_n \frac{1 - 3\mathbf{n}_i \mathbf{n}_i^T}{|\mathbf{R}_i - \mathbf{r}|^3} \right) \hat{I}_i. \quad (4)$$

Here, the sum runs over all protons/deuterons; $\mathbf{r}$ is the position of the unpaired electron; $\mathbf{R}_i$ is the position of proton/deuteron i ; $\hat{S}$ is the electron spin operator; $\hat{I}_i$ is the nuclear spin operator for proton/deuteron i ; $\mathbf{n}_i = (\mathbf{R}_i - \mathbf{r})/|\mathbf{R}_i - \mathbf{r}|$; and γ_e and γ_n are the gyromagnetic ratio of the electron and the proton/deuteron, respectively. A cyclic permutation changes the indices, which just reorders the sum leaving the Hamiltonian invariant. The same holds for every term in the Hamiltonian, not just the dipole hyperfine coupling. Therefore, the Hamiltonian transforms as A under A_3 . Note that Eq. (4) is the full hyperfine Hamiltonian, not the hyperfine term from the effective spin Hamiltonian. In addition, the permutations affect both spatial and spin coordinates. Permuting the spin coordinates in the spin Hamiltonian is generally a different operation.

For any Hamiltonian matrix element $\langle \Psi^{(\pi)} | \hat{H} | \Psi^{(\pi')} \rangle$ to be non-zero, its integrand symmetry must contain the fully symmetric species A. The integrand symmetry is $\pi^* \times A \times \pi' = \pi^* \times \pi'$, where π^* indicates the dual representation of π . For A_3 , this is satisfied only for $(\pi, \pi') = (A, A)$, (E_1, E_1) , and (E_2, E_2) , since $A^* = A$; $(E_1)^* = E_2$; and $(E_2)^* = E_1$. Therefore, the Hamiltonian does not couple the three irreducible subspaces and is block diagonal (see Fig. 1):