Mini-Symposium Wuppertal

Schur-Weyl duality in molecular physics: A new glance at nuclear spin states in molecules

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The background

Conventional approximations in molecular theory

1st step Born-Oppenheimer approximation
$\Rightarrow$ Separate nuclear and electronic degrees of freedom

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Molecular Hamiltonian and wave function

$$\mathcal{H} = \mathcal{H}_{\mathrm{el}} + \mathcal{H}_{\mathrm{rovib}} + \mathcal{H}_{\mathit{nspin}}$$

$$\Psi = \psi_{\mathrm{el}}\ \psi_{\mathrm{rovib}}\ \psi_{\mathrm{nspin}}$$

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The exchange principle and permutation groups

Exchange of identical **fermions** $\Rightarrow$ Sign change in wave function
Exchange of identical **bosons** $\Rightarrow$ No sign change

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Permutation group and character table

$\mathbf{S}_4$	E 1	(12) 6	(12)(34) 3	(123) 8	(1234) 6
A_1	1	1	1	1	-1
A_2	1	-1	1	1	1
E	2	0	2	-1	0
F_1	3	1	-1	0	-1
F_2	3	-1	-1	0	1

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The nuclear wave function

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The total nuclear wave function $\psi_{\mathrm{rovib}}\ \psi_{\mathrm{nspin}}$ must be (anti-)symmetric for (fermionic) bosonic nuclei.

Ro-vibrational part: Quantum numbers (J, ν_i)
Nuclear spin part: # of identical particles and their spin

$$\psi_{\mathrm{rovib}}\ \psi_{\mathrm{nspin}} = \psi_{J,\nu_i} \times \left.\begin{array}{c} \psi^{1}_{\mathrm{nspin}} \\ \vdots \\ \psi^{g}_{\mathrm{nspin}} \end{array}\right\} \Rightarrow \Gamma_{\mathrm{(anti)sym}}$$

g is the nuclear spin statistical weight

The question

How to find the permutation symmetry of nuclear spin states

The pedestrian way

- Construct all possible combinations of individual spin states
- Determine their total spin and permutation symmetry

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Example: The H_2 molecule

Configuration	$\mathbf{S}_2$	$\mathrm{I}_{\mathrm{tot}}$	M_{I}
$\uparrow\uparrow$	A	1	1
$\downarrow\downarrow$	A	1	-1
$\uparrow\downarrow + \downarrow\uparrow$	A	1	0
$\uparrow\downarrow - \downarrow\uparrow$	B	0	0

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Cumbersome and lengthy for large N or I

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Correspondence of permutation and angular momentum symmetry

Is there any one-to-one correspondence of total spin quantum number and the respective permutation symmetry of a molecular system?

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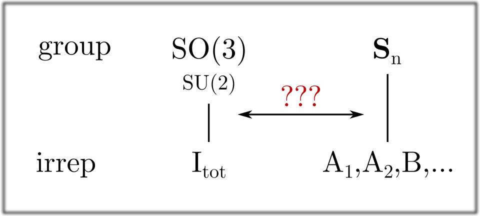

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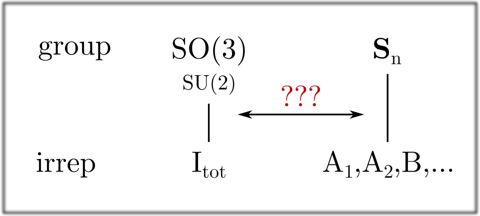

If yes, can I use it to simplify the calculation of the symmetry properties?

Preparation of the answer

Unitary symmetry of spins

Assumption No influence of nuclear spin on molecular energy levels

Implication Symmetry group of ψ_{nspin}:
Unitary group U(d), $d = 2\mathrm{I} + 1$

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Unitary group $\mathrm{U}(d)$, $d = 2\mathrm{I} + 1$

Unitary group: The most basic transformations in quantum mechanics

- Restriction for symmetry of nuclear spin states: $|\langle\psi_{\mathrm{nspin}}|\psi_{\mathrm{nspin}}\rangle|^2$ conserved!
- All unitary transformations $U^\dagger U = \mathbb{1}$ fulfill this constraint.
- Dimension: $2\mathrm{I} + 1$ functions for single I

Preparation of the answer

Unitary symmetry group: The irreducible representations

U(d) Partition $\lambda = \{\lambda_1, \lambda_2, \ldots \lambda_d\}$ of positive descending integers is unambigous characterization of U(d) irrep.

- For characterization in terms of spin I: SO(3) $\subset$ U(d)

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Simple examples

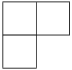
$$\mathsf{U}(2): \quad \{2,1\} \rightarrow \mathsf{SO}(3): \mathrm{I} = 1/2$$
$$\mathsf{U}(3): \quad \{3,1,1\} \rightarrow \mathsf{SO}(3): \mathrm{I} = 2, 0$$

There exist general rules for U(d)→SO(3)!

Preparation of the answer

The tool: Young diagrams for irreducible representations of U(d)

Young diagrams

- A partition λ sets up a diagram of boxes: $\{2,1\} =$ 

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- Many particle states span the irreps $\lambda = \{\lambda_1, \lambda_2, \ldots \lambda_d\}$

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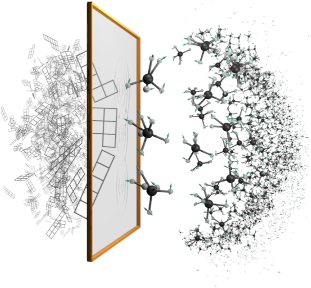
- Single particle of spin I is characterized by $\square$ of U(2I+1)
- Many particle states span the irreps $\lambda = \{\lambda_1, \lambda_2, \ldots \lambda_d\}$
- Total spin quantum number calculated by branching rule U(d)$\rightarrow$ SO(3)

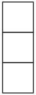
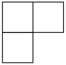
Preparation of the answer

The tool: Young diagrams for irreducible representations of $\mathbf{S}_n$

Partition $\lambda = \{\lambda_1, \lambda_2, \ldots, \lambda_p\}$ with $\sum \lambda_i = n$ and all λ_i descending integers describes irrep of $\mathbf{S}_n$

Example $\mathbf{S}_3$



$\mathbf{S}_3$	λ	Young	E	(12)	(123)
A_1	$\{3\}$		1	1	1
A_2	$\{1,1,1\}$		1	-1	1
E	$\{2,1\}$		2	0	-1

The answer

Schur-Weyl duality: Irreducible representations of same shapes correlate

Assumption Hilbertspace: $\mathcal{H}_d^N := \mathcal{H}_d \otimes \mathcal{H}_d \otimes \ldots \otimes \mathcal{H}_d$ (N copies)
with: $d = 2\mathrm{I} + 1$ and N number of particles

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The Schur-Weyl theorem

Irreducible reperesentation of the product symmetry group $\mathrm{U}(d) \times \mathbf{S}_n$:

$$\Gamma_d^{(N)} = \bigoplus_{\lambda \vdash N}^{l(\lambda) \leq d} ((\lambda), \{\lambda\})$$

(λ): Irrep of $\mathbf{S}_n$

$\{\lambda\}$: Irrep of $\mathrm{U}(d)$

$l(\lambda) \leq d$: Fixed number of rows

$\lambda \vdash N$: $\sum \lambda_i = N$

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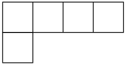
“Sum” of identical Young diagrams form irrep for product group

What is it good for?

Simplification of calculations: Example H_5^+

$$\Gamma_2^{(5)} = ((5), \{5\}) \oplus ((41), \{41\}) \oplus ((32), \{32\})$$

The correspondence to usual names

Young diagram	U(2)	SO(3)	$\mathbf{S}_5$	label
	$\{5,0\}$	$5/2$	(5,0)	A_1
	$\{4,1\}$	$3/2$	(4,1)	G_1
	$\{3,2\}$	$1/2$	(3,2)	H_1

$$\boxed{\Gamma_{\rm nspin}(H_5^+) = (6A_1, \mathcal{D}_{5/2}) \oplus (4G_1, 4\mathcal{D}_{3/2}) \oplus (2H_1, 5\mathcal{D}_{1/2})}$$

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	$\{4, 1\}$	$3/2$	(4,1)	G_1
	$\{3, 2\}$	$1/2$	(3,2)	H_1

Result: Simple numerical code to get Γ_{nspin} for arbitrary N, I!

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Second part

Statistical state-to-state reaction rates

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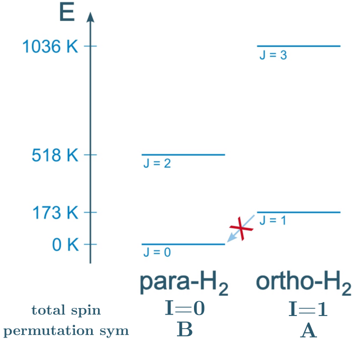
Application of Schur-Weyls duality

The question

Spin-dependent reaction rates for molecules

The well-known ortho/para species of molecular hydrogen



- No electromagnetic transition between ortho- and para states
- Collisional cooling cannot flip spins

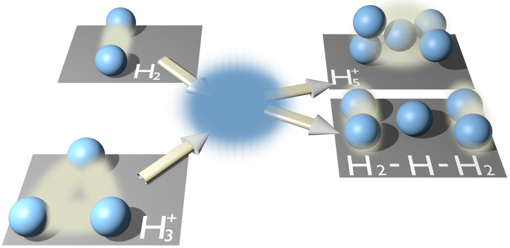
$\Rightarrow$ Reactive collisions?

Spin-flip probability in reactive collisions

Reactive collision Two reactants form intermediate complex before dissociating into initial parts

- Symmetry of the intermediate complex highly influential for reaction rates

Example: $H_2 + H_3^+ \rightarrow (H_5^+)^* \rightarrow H_3^+ + H_2$



State-to-state reactions and probabilities

Ideal experiment Prepare and measure reactants/products in single quantum states
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Statistics	No energy assumptions, only spin-statistical weights and spin conservation

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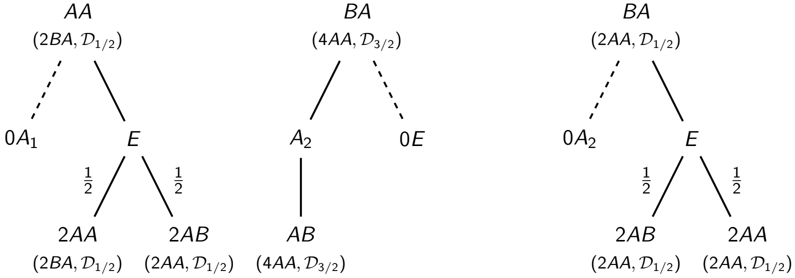
A first example: $H_2 + H^+ \rightarrow H_3^+ \rightarrow H_2 + H^+$



Intermediate symmetry decisive for state-to-state rates

The H_5^+ cation

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  Ab-initio surfaces flat!

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$\Rightarrow$ Expectation: Different ortho-to-para ratios for H_2 and H_3^+

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First results:

Full $\mathbf{S}_5$ MS group:	$P(\text{ortho-to-para } H_2) = 9/50$
Smaller group, only H^+ released:	$P(\text{ortho-to-para } H_2) = 4/135$

Wrap-up: Schur-Weyl, Young, and reactive collisions

First part: Representations of the nuclear spin wave functions

Schur-Weyl duality Prescription for correlation of spin and permutation symmetry

- No restriction on I or N, easy to implement

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Second part: Reactive collisions

State-to-state rates Specific state transitions

E.g. ortho-to-para in $H_2 + H^+$ reaction

Intermediate complex Symmetry decisive for reaction paths

Thank you for your attention!

And greetings from Cologne

Schmiedt, Jensen, Schlemmer; JCP **145**, 074301, *(2016)*;
Doi: 10.1063/1.4960956