Unified rotational and permutational symmetry and selection rules in reactive collisions

Nuclear spin effects in astrochemistry
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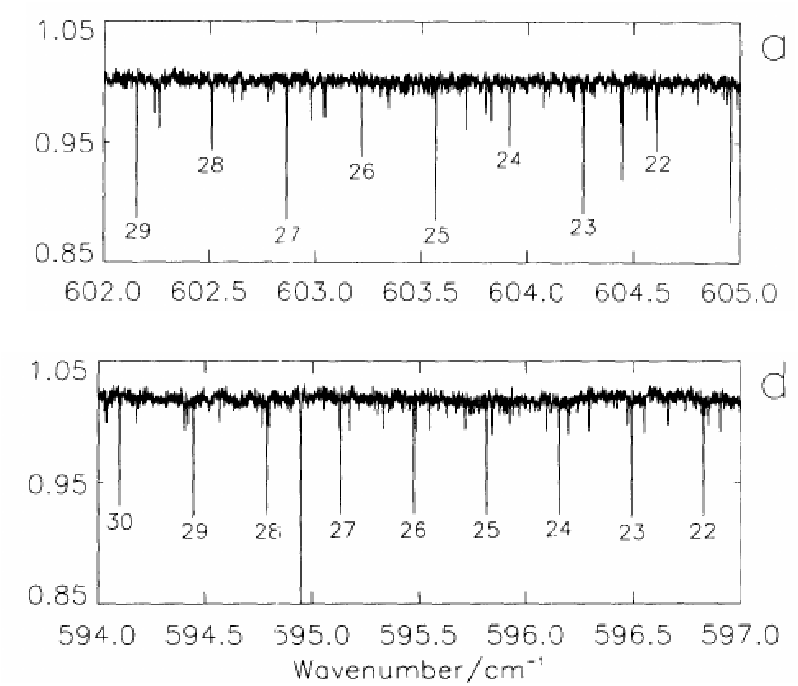
Part I: Nuclear spin statistics in molecular spectra



from Bunker/Jensen Molecular symmetry and Spectroscopy, NRC Research press 2006

Nuclear spin statistical weights g_{ns}

- Origin: Couple rovibrational to nuclear spin states to fulfill Paulis principle
- Result: Change intensities of molecular transitions

Example:

a) $^{14}N^{12}C^{12}C^{14}N$, ratio 1/2 for e/o J

d) $^{15}N^{12}C^{12}C^{14}N$, ratio 1/1 for e/o J

Where do these weights come from? Symmetry!

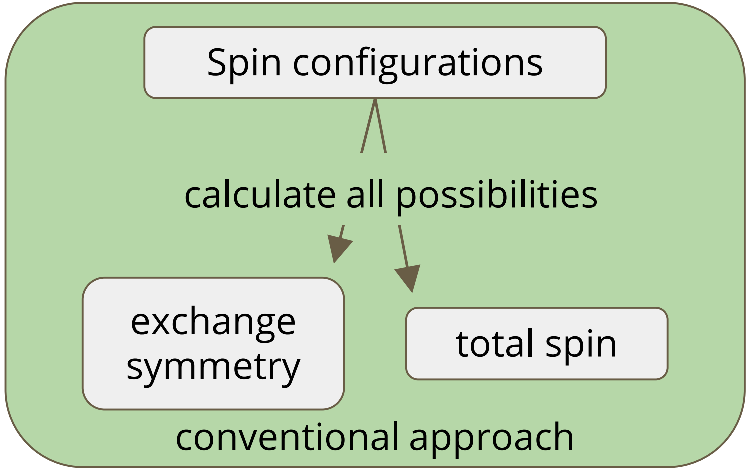
$$\psi_{mol} = \psi_{el}\,\psi_{rovib}\,\boxed{\psi_{nspin}}$$

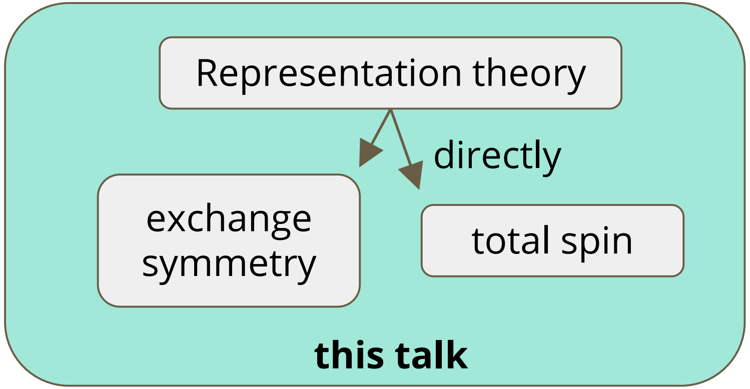
- Two types of symmetry: Permutation and rotational symmetry
  - Permutation of identical nuclei (CNP group) -- Spin-statistical weights
  - Rotation of nuclear spin (SO(3), rotation group) -- total spin quantum number

Example: molecular hydrogen H_2

Configuration	S_2-symmetry	I_{tot}	M_I	
↑↑	A	1	1	
↓↓	A	1	−1	$g_{ns}(B)=3$
↑↓ + ↓↑	A	1	0	
↑↓ − ↓↑	B	0	0	$g_{ns}(A)=1$

H_2 is simple, what about more nuclei?

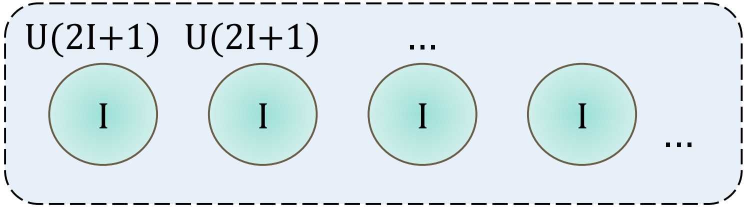




What can representation theory tell us?

1) $U \in U(2I+1)$ leaves $|\langle\psi|\psi\rangle|^2$ invariant ($U^{\dagger}U = Id.$)

2) $P \in S_N$ describes permutation of particles

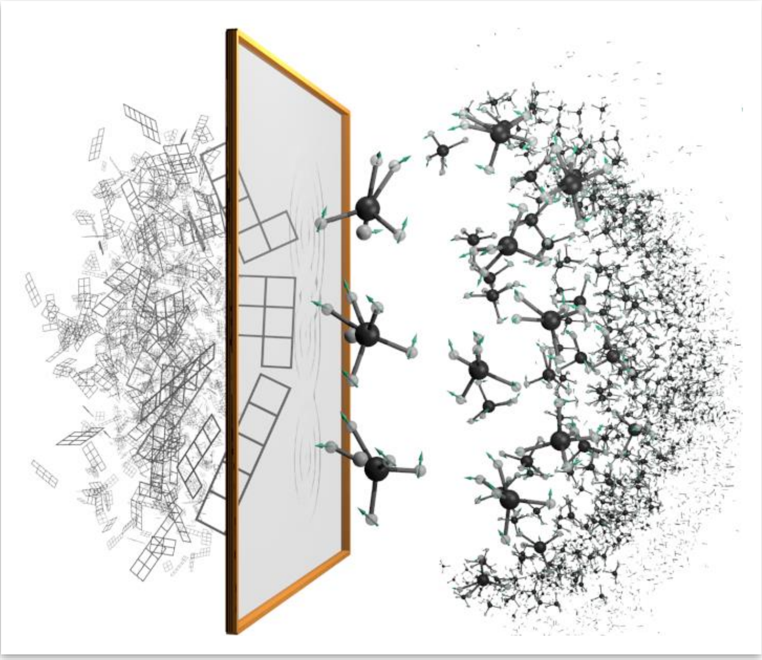


$S_N \times U(2I+1)$

The nuclear spin wave function of N *identical* particles of spin I spans a representation of the product group $S_N \times U(2I+1)$

Representation theory gives a simple prescription to find this!

Young diagrams for depicting representations



- For permutation groups:

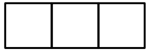
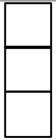
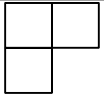
  Each particle represented by a box
  N boxes must be adjusted to
  $p \leq N$ rows,
  rows have $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_p$ boxes

- For unitary groups:

  Each spin represented by a box
  N boxes must be adjusted to
  $p \leq d$ rows,
  rows have $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_p$ boxes

Young diagrams for depicting representations

Example $N=3$:

S_3	Young diagram	partition	$U(2)$	partition	spin I
A_1		(3,0,0)		{3,0}	3/2
A_2		(1,1,1)		--	--
E		(2,1,0)		{2,1}	1/2

- For permutation groups:

  Each particle represented by a box
  N boxes must be adjusted to
  $p \leq N$ rows,
  rows have $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_p$ boxes

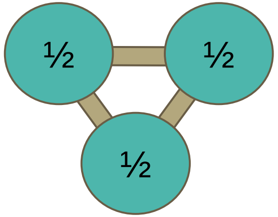
- For unitary groups:

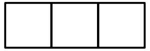
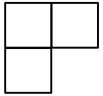
  Each spin represented by a box
  N boxes must be adjusted to
  $p \leq d$ rows,
  rows have $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_p$ boxes

Schur-Weyl duality: The combination of both

The wave function of N identical spins I spans a representation, which is a combination of the *same* Young diagrams for S_N and $U(d=2I+1)$

Example H_3^+:



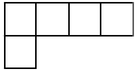
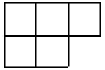
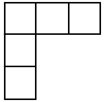
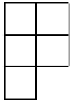
S_3	Young diagram	partition	$U(2)$	partition	spin I
A_1		(3,0,0)		{3,0}	3/2
E		(2,1,0)		{2,1}	1/2

Joint representation: $(3A_1,\{3\})+(E,\{2,1\})$
better known as: $(3A_1,I=3/2)+(E,I=1/2)$

Schur-Weyl duality makes life easier!

Setting up the Young diagrams for N particles is straightforward, as it is for large I!

Example D_5

Young diagram	U(3)	SO(3)	S_5	Label
	{5, 0, 0}	5,3,1	(5,0)	A_1
	{4, 1, 0}	4,3,2,1	(4,1)	G_1
	{3, 2, 0}	3,2,1	(3,2)	H_1
	{3, 1, 1}	2,0	$(3,1^2)$	I
	{2, 2, 1}	1	$(2^2,1)$	H_2

Part II: Reactive collisions and selection rules

Spin selection rules play important role, e.g., in population of molecular states

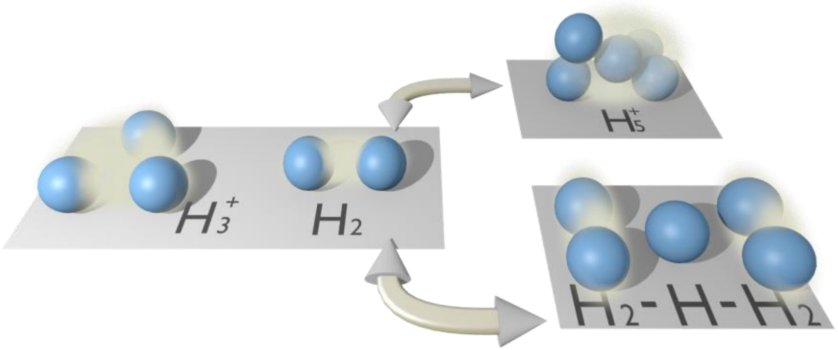
Selection rules may change possible final states in reactions

Popular example: The ortho-to-para conversion in reactive collisions of H_2

Our aim:

Determine symmetry-based selection rules for reactive collisions

Our example: Two pathways for same product



Intermediate

Initial:	$S_3 \times S_2$	symmetry group
S_5 group		$S_2 \times S_1 \times S_2$ group
Final:	$S_3 \times S_2$	symmetry group

First guess: Symmetry of intermediate complex is decisive for symmetry of final states!

State-to-state “reactions”

$$\psi_{H_2} \times \psi_{H_3^+} \longrightarrow \psi_{H_5^+} \longrightarrow \psi_{H_2} \times \psi_{H_3^+}$$

$\psi = \psi_{\text{rovib}}\, \psi_{\text{nspin}}$

must at all times fulfill Pauli principle!

Changing CNP irrep

Conserved spin

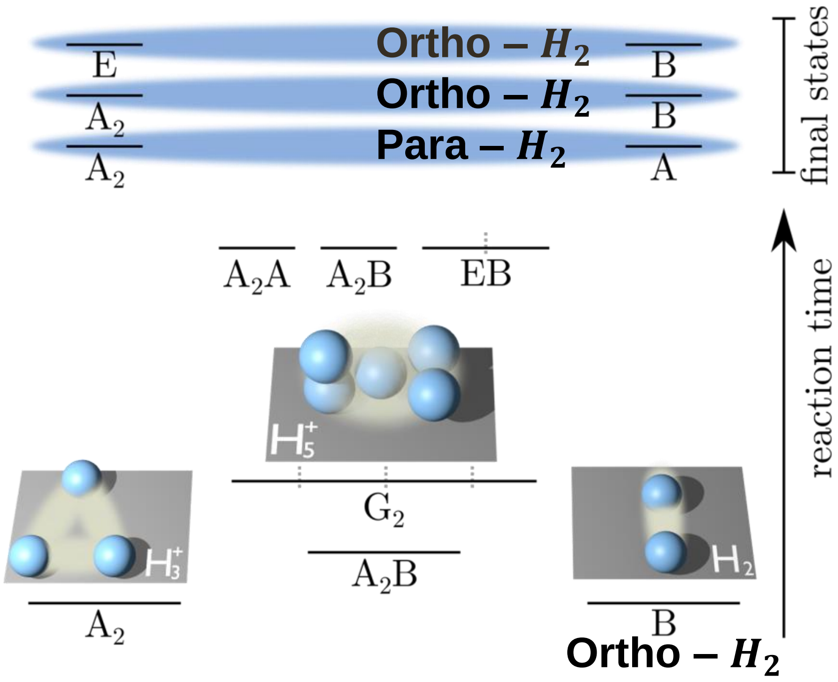
S_2	dim	S_3	dim	S_5	dim
A	1	A_1	1	A_1	1
B	1	A_2	1	A_2	1
		E	2	G_1	4
				G_2	4
				H_1	5
				H_2	5
				I	6

Spins and rovibrational functions

H_2	Γ_{nspin}	$(3A, I=1)$	$(B,0)$	
	Γ_{rovib}	B	A	
H_3^+	Γ_{nspin}	$(4A_1, 3/2)$	$(2E, 2\times 1/2)$	
	Γ_{rovib}	A_2	E	
H_5^+	Γ_{nspin}	$(4G_1, 4\times 3/2)$	$(2H_1, 5\times 1/2)$	$(6A_1, 5/2)$
	Γ_{rovib}	G_2	H_2	A_2

S_2	dim	S_3	dim	S_5	dim
A	1	A_1	1	A_1	1
B	1	A_2	1	A_2	1
		E	2	G_1	4
				G_2	4
				H_1	5
				H_2	5
				I	6

One example of reaction "pathway" for $I_{tot}=3/2$



rovibrational states

S_2	S_3	S_5
A	A_1	A_1
B	A_2	A_2
	E	G_1
		G_2
		H_1
		H_2
		I

Ortho-to-para conversion for different intermediates

Intermediate S_5 symmetry	Intermediate $S_2 \times S_1 \times S_2$ group
$P[\Gamma_{rovib}(H_2) = B \rightarrow A] = 9/50$	$P[\Gamma_{rovib}(H_2) = B \rightarrow A] = 4/135$

Different ortho-to-para transition rate depending on internal symmetry!

Conclusion: Unified symmetries and symmetry dependent pathways

Part I:

- Calculation of symmetry of nuclear spin wave function simplified
- Intimate correlation of unitary (spin) and permutation symmetry
- No one-to-one correspondence for $I>1/2$

Part II:

- Reaction "pathways" depend on symmetry of intermediate complex
- Symmetry selection rules and state-to-state reaction rates differ
- Used results of Part I to simplify calculations

And now? The open questions

- Use correlation of spin and permutation for large molecules?
- Use correlation for molecules with different nuclei
- What about I>1/2 in reactions involving deuterated species?
- Does the unitary symmetry group influences selection rules?
- *Hint:* No one-to-one correspondence of unitary symmetry and I, which one is conserved?

Thank you for your attention

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