Rotational eigenstates and spin-permutation symmetry

(PSDS - Ch. 5, 7 )

Review: SF₆ levels and nomograms for Coriolis PQR structure
Review: SF₆ spectral clusters of symmetry species O ⊃ C₄ and O ⊃ C₃ symmetry correlation
Conservation (or not!) of rovibronic spin-symmetry-species
Entanglement and related issues

Diatom or linear molecule symmetry O(3) ⊃ D∞h ⊃ C∞v
Labeling by symmetry O(3) ⊃ D∞h
Coriolis and \( \lambda \) (or \( \Lambda \))-doubling levels
Dipole-allowed transitions

\( S_n \) Young Tableaus and spin-symmetry for \( X_n \) and \( XY_n \) molecules
\( S_4 \) and spin-symmetry for \( XY_4 \) molecules (Introducing hook-length formulae)
\( S_6 \) and spin-symmetry for \( XY_6 \) molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion

\( C_{60} \) Buckminster Fullerene ("Buckyball") structure and spectra
Graphical approach to rotation-vibration-spin Hamiltonian

\[ \langle H \rangle \sim \nu_{\text{vib}} + BJ(J+1) + \langle H^{\text{Scalar Coriolis}} \rangle + \langle H^{\text{Tensor Centrifugal}} \rangle + \langle H^{\text{Nuclear Spin}} \rangle + \langle H^{\text{Tensor Coriolis}} \rangle + \ldots \]

OUTLINE

Introductory review

- Rovibronic nomograms and PQR structure
  - Rotational Energy Surfaces (RES) and \( \Theta' \)-cones
  - Spin symmetry correlation tunneling and entanglement
  - Analogy between PE surface and RES dynamics
  - Rotational Energy Eigenvalue Surfaces (REES)

Example(s)

\( \nu_3 \) and \( \nu_4 \) SF\(_6\)

\( \nu_4 \) P(88) SF\(_6\)

Recent developments

\( \nu_3 \) SF\(_6\)
Review: $SF_6$ levels and nomograms for Coriolis PQR structure

\[
\langle H \rangle \sim \nu_{\text{vib}} + B J(J+1) + \langle H^{\text{Scalar Coriolis}} \rangle + \langle H^{\text{Tensor Centrifugal}} \rangle + \langle H^{\text{Tensor Coriolis}} \rangle + \langle H^{\text{Nuclear Spin}} \rangle + \ldots
\]

\[
\begin{cases}
N+1 & \text{for } J=N+1 \\
0 & \text{for } J=N \\
N & \text{for } J=N-1
\end{cases}
\]

\[
H^{\text{Scalar Coriolis}} = -B\zeta 2J^{\text{Total}} \cdot \ell^{\text{vibe}}
\]

\[
= -B\zeta [ J^2 - (J-\ell)^2 + \ell^2 ]
\]

\[
= -B\zeta [ J^2 - N^2 + \ell^2 ]
\]

\[
= -B\zeta [ J(J+1) - N(N+1) + \ell(\ell+1) ]
\]

Involves:
- angular momentum $\ell$ of vibration “orbits”
- angular momentum $N$ (or $R$) of rotating nuclei
- total momentum $J = \ell + N$ of whole molecule.

Let: $R = N = J - \ell$, and: $N^2 = J^2 - 2J \cdot \ell + \ell^2$

so: $2J \cdot \ell = J^2 - N^2 + \ell^2$

\[
\langle 2J \cdot \ell \rangle = J(J+1) - N(N+1) + \ell(\ell+1)
\]

\[
\zeta = 0 \quad N = 0 \quad N = 1 \quad N = 2
\]

\[
N = 0 \quad J = J \quad N = 1 \quad J = J \quad N = 2 \quad J = J
\]

\[
\nu_4 \text{ SF}_6
\]

mosty goes left handed

\[
\nu_4 \text{ SF}_6
\]

\[
\zeta = -0.22
\]

\[
\langle 2J \cdot \ell \rangle = J(J+1) - N(N+1) + \ell(\ell+1)
\]

\[
\nu_4 \text{ SF}_6
\]

\[
\zeta = -0.22
\]

\[
\langle 2J \cdot \ell \rangle = J(J+1) - N(N+1) + \ell(\ell+1)
\]
Summary of low-J (PQR) ro-vibe structure
(Using rovib. nomogram)
Review: *SF₆* levels and nomograms for Coriolis PQR structure

PQR structure due to Coriolis scalar interaction between vibrational angular momentum \( \ell \) and total momentum \( J = \ell + N \) of rotating nuclei

\( P(N) = P(88) \) structure due to tensor centrifugal/Coriolis due to vibrational \( \ell \) and total momentum \( J = \ell + N \)

Primary AET species mixing increases with distance from "separatrix"
Graphical approach to rotation-vibration-spin Hamiltonian

\[ \langle H \rangle \sim \nu_{\text{vib}} + B(J+1) + \langle H^{\text{Scalar Coriolis}} \rangle + \langle H^{\text{Tensor Centrifugal}} \rangle + \langle H^{\text{Nuclear Spin}} \rangle + \langle H^{\text{Tensor Coriolis}} \rangle + \ldots \]

OUTLINE

- Introductory review
- Rovibronic nomograms and PQR structure
- Rotational Energy Surfaces (RES) and \( \theta^l \)-cones
- Spin symmetry correlation tunneling and entanglement
- Recent developments
- Analogy between PE surface and RES dynamics
- Rotational Energy Eigenvalue Surfaces (REES)

Example(s)

- \( \nu_3 \) and \( \nu_4 \) \( \text{SF}_6 \)
- \( \nu_4 \) \( \text{P}(88) \) \( \text{SF}_6 \)
- \( \nu_3 \) \( \text{SF}_6 \)
Review: SF₆ spectral clusters of symmetry species O ⊆ C₄ and O ⊆ C₃ symmetry correlation

\[ \langle H \rangle \sim v_{\text{vib}} + B J (J+1) + \langle H^{\text{Scalar Coriolis}} \rangle + \langle H^{\text{Tensor Centrifugal}} \rangle + \langle H^{\text{Tensor Coriolis}} \rangle + \langle H^{\text{Nuclear Spin}} \rangle + \ldots \]

**O₂ or T_d Spherical Top:** (Hecht CH₄ Hamiltonian 1960)

\[ H = B \left( J_x^2 + J_y^2 + J_z^2 \right) + t_{440} \left( J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J_0^4 \right) + \ldots \]

\[ = B J^2 \quad + t_{440} \left( T_0^4 + \sqrt{\frac{5}{14}} \left[ T_4^4 + T_{-4}^4 \right] \right) + \ldots \]

\( J = 88 \)

RE Surface
topo-lines track precessing semi-classical \( J \) vector

\( K_4 = 88 \)
\( = 87 \)
\( = 87 \)

etc.

\( \theta_{88} = 6.08^\circ \)
\( \theta_{87} = 10.5^\circ \)
\( \theta_{88} = 13.6^\circ \)

\((J, K)\) cones intersect \( J = 88 \)

RE surface at angle \( \theta_K \)

\[ \theta_K = \cos^{-1} \left[ \frac{K}{\sqrt{J(J+1)}} \right] \]
**Review:** *SF$_6$* spectral clusters of symmetry species $O \supseteq C_4$ and $O \supseteq C_3$ symmetry correlation

**SF$_6$ Spectra of $O_h$ Ro-vibronic Hamiltonian described by RE Tensor Topography**

$$H = B \left( J_x^4 + J_y^4 + J_z^4 \right) + t_{440} \left( J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4 \right) + \cdots$$

$$= BJ^2 + t_{440} \left( T_0^4 + \sqrt{\frac{5}{14}} \left[ T_4^4 + T_{-4}^4 \right] \right) + \cdots$$

**Rovibronic Energy (RE) Tensor Surface**

**J-cone intersection**

$$\Theta_m = \arccos \left( \frac{K}{\sqrt{J(J+1)}} \right)$$

**Precessing J-vector**

**Saddle Point**

**Herzberg rules still apply near separatrices or saddle points**

SF$_6$ nu$_4$ rovib FT spectra~615cm$^{-1}$

Mcdowell et al. LosAlamos
Review: \( \text{SF}_6 \) spectral clusters of symmetry species \( O \supseteq C_4 \) and \( O \supseteq C_3 \) symmetry correlation

PQR structure due to Coriolis scalar interaction between vibrational angular momentum \( \ell \) and total momentum \( J = \ell + N \) of rotating nuclei

\[ P(N) = P(88) \] structure due to tensor centrifugal/Coriolis due to vibrational \( \ell \) and total momentum \( J = \ell + N \)

Superfine structure modeled by \( J \)-tunneling in body frame (Underlying F-spin-permutation symmetry is involved, too.)
Review: $SF_6$ spectral clusters of symmetry species $O \supseteq C_4$ and $O \supseteq C_3$ symmetry correlation

(a) $SF_6 \nu_4$ Rotational Structure

(b) $P(88)$ Fine Structure (Rotational anisotropy effects)

(c) Superfine Structure (Rotational axis tunneling)

4-fold (100)-clusters $C_4$ symmetry

88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 = $K_3$

Primary AET species mixing increases with distance from "separatrix"

Internal/3-fold axial quanta label $C_3$-CLUSTERS

pure $A_1 T_1 E T_2 A_2$ species

(0)$^3$  (1)$^3$ (2)$^3$ = (-1)$^3$

Cubic Octahedral symmetry $O$

<table>
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<th></th>
<th>$A_1$</th>
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</table>

3 modulo 4 equals
-1 modulo 4
and 83 mod 4
83 = 84 - 1

4-fold (100) $C_4$ symmetry clusters

3-fold (111) $C_3$ symmetry clusters

$A_1$  1     •     •
$A_2$  1     •     •
$E$   1     1     1
$T_1$  1     1     1
$T_2$  1     1     1

(2 modulo 3 equals -1 modulo 3 and 86 mod 3)
86 = 88 - 1

Friday, May 1, 2015
Review: \( SF_6 \) spectral clusters of symmetry species \( O \supseteq C_4 \) and \( O \supseteq C_3 \) symmetry correlation

Primary AET species mixing increases with distance from "separatrix"

CASE 1
Unmixed primary \( A_1 \ T_1 \ E \ T_2 \ A_2 \) species
(Whole 6-box tableaus)

CASE 2_3
Broken 3 + 3 Tableaus

CASE 2_4
Broken 4 + 2 tableau state description

Spin-rovib ENTANGLEMENT symmetry
Conservation (or not!) of rovibronic spin-symmetry-species
Entanglement and related issues
CONSERVATION OF ROVIBRONIC SPIN-SPECIES - Two Views:

Old
(1939, 1945, and 1966)

...transitions between...species \((A_1...E...T_2...)\)
...are very strictly forbidden ...

...for diatomic molecules...I p. 150
...for \(D_2\) asymmetric tops...II p.468
...for \(D_n\) symmetric tops...II p.415
...for \(O-T_d\) spherical tops...II p.441-453
...during transitions involving...
...rotational states,...III p.246
...vibrational states,...” ”
... electronic states,...” ”
... collisional states...” ”

versus

New (1978- 2005)

...transitions between...species \((A_1...E...T_2...)\)
...are not strictly forbidden ...

...for diatomic molecules...I p. 150
...for \(D_2\) asymmetric tops...II p.468
...for \(D_n\) symmetric tops...II p.415
...for \(O-T_d\) spherical tops...II p.441-453
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Conservation and preservation?

Strictly versus NOT!

Conversion, perversion or transition?

Sun, Takagi, Matsushima, Science 310, 1938(2005)]

[review of \(C_2H_4\) study:]
CONSERVATION OF ROVIBRONIC SPIN-SPECIES - Two Views:

**Old**
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"...transitions between...species (\(A_1\)...\(E\)...\(T_2\)...)
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... collisional states...” ”

**New (1978- 2005)**

[Nuclear Spin Conversion in Molecules
Jon T. Hougen and Takeshi Oka.

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared, a pure \(\text{H}_2\) sample can be preserved for months as initially shown by Bonhoeffer and Hartack in 1929 (3). Once prepared, a pure \(\text{H}_2\) sample can be preserved for months

[review of \(\text{C}_2\text{H}_4\) study: Sun, Takagi, Matsushima,
Science 310, 1938(2005)]

Strictly versus NOT!

Conservation and preservation?

To conserve vs. To convert
To preserve vs. To pervert

No Way! versus WAY!

Conversion, perversion or transition?

Widespread and extreme mixing of species reported in \(\text{CF}_4\), \(\text{SiF}_4\) and \(\text{SF}_6\):

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

*What preserves it?* versus *What mixes it up?*

| No Way! | WAY! |

and...

*What is it?*

*SPIN SYMMETRY* correlation has a new name...
Conservation (or not!) of rovibronic spin-symmetry-species Entanglement and related issues
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? versus What mixes it up?

No Way! WAY!

and...

What is it?

SPIN SYMMETRY correlation has a new name...

it’s now called ENTANGLEMENT!

Herzberg’s terms: “Overall ...symmetry...”

Better terms: ..Under-all ... or internal symmetry...spin frame..... “Bare” rotor

(From an overall “Coupled” state we **SUBTRACT** vibronic “Activity” to get underlying “Bare” rotor.)
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? versus What messes it up?

$A_{2u}^1$

No Way!
...because nuclear moments...
...are so very slight...”

$E_{2g}^5$

too darn small (~kHz)...
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

**What preserves it?** versus **What mixes it up?**

- **No Way!**
  - "...because nuclear moments...
  - "...are so very slight..."

- **WAY!**
  - "...because levels of different species are forced together by angular wave localization or “level-clustering” or (rarely) by “accidental” degeneracy.

\[
E_{A_1g}^3 - E_{E_{2g}}^5 \quad \text{...too darn small (~kHz)...}
\]

\[
\text{perturbation} \sim |(A_{1g}^3 | \text{spin-rovib.} | E_{2g}^5)|^2
\]

\[
E_{A_1g}^3 - E_{E_{2g}}^5 \quad \text{...too darn big (like 10MHz)...}
\]

- **RE Superhyperfine transitions**
  - **Hyperfine effects may rule!** \( A_1 \ T_1 \ E \ T_2 \ A_2 \) get seriously mixed up.

**References:**
- Lea, Leask & Wolf JPCSol.23,1381(1962)
- Dorney and Watson JMS 42,135(1972)
- Harter and Patterson PRL38,224(1977)
  - JCP 66,4872(1977)
- RE Surface precession vs. tunneling
  - Harter and Patterson JMP 20,1453(1979)
  - JCP 80,4241(1984)
- Harter, Patterson, and daPaixao, Rev.Mod.Phys. 50, 37(1978)
- Harter and Patterson, Phys. Rev. A19,2277(1979) \( \text{(CF}_4\) )
Diatomc or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and $\lambda$-doubling levels

Dipole-allowed transitions
Diatomic or linear molecule symmetry \( O(3) \supset D_{\infty h} \)

\( O(3) \supset D_{\infty h} \) spin-symmetry species

3D Orthogonal group \( O(3) \) correlates with \( D_{\infty h} \) symmetry

Angular momentum label \( \ell \)
- \( \ell = 0 \): \( s \) or \( S \)
- \( \ell = 1 \): \( p \) or \( P \)
- \( \ell = 2 \): \( d \) or \( D \)
- \( \ell = 3 \): \( f \) or \( F \)

\( \sigma \) or \( \Sigma \)
\( \Pi \)
\( \Delta \) or \( \Delta \)

\(| A \rangle, \langle B |, or C Correlations |

\begin{array}{c|cccccc}
\ell \text{ label} & \Sigma^+ & \Sigma^- & \Pi & \Pi & \Delta & \Delta \\
0^+ & 1 & & & & & \\
0^- & & & 1 & & & \\
1^+ & & 1 & & 1 & & \\
1^- & 1 & & 1 & 1 & & \\
2^+ & 1 & & 1 & 1 & 1 & \\
2^- & & 1 & 1 & 1 & & \\
3^+ & & 1 & 1 & 1 & & \\
3^- & 1 & & 1 & 1 & & \\
\end{array}

Types of symmetry labels

- \( A = \) Activity (of vibrations, electrons)
- \( B = \) Bare rotor (rotations, nuclear spin)
- \( C = \) Coupling or Constriction of \( A \otimes B \)

Rev. Mod. Phys. 50,1,1 (1978)
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

$O(3) = D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$
correlates with $D_{\infty h}$ symmetry

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<td>$\phi$ or $\Phi$</td>
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$A$, $B$, or $C$ Correlations

<table>
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<th>$B$</th>
<th>$\Sigma_g^+$</th>
<th>$\Sigma_u^+$</th>
<th>$\Sigma_g^-$</th>
<th>$\Sigma_u^-$</th>
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FIG. 15. Characters of $D_{\infty h} = O_{2i}$ symmetry of $X_2$ rotor.

Types of symmetry labels

$A$ = Activity (of vibrations, electrons)
$B$ = Bare rotor (rotations, nuclear spin)
$C$ = Coupling or Constriction of $A \otimes B$

Rev. Mod. Phys. 50,1,1 (1978)
Diatom or linear molecule symmetry $O(3) \supset D_{\infty h}$

$O(3) \supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular atomic molecular momentum label label

$\ell = 0$ $s$ or $S$ $\sigma$ or $\Sigma$

$\ell = 1$ $p$ or $P$ $\pi$ or $\Pi$

$\ell = 2$ $d$ or $D$ $\delta$ or $\Delta$

$\ell = 3$ $f$ or $F$ $\phi$ or $\Phi$

$A$, $B$, or $C$ Correlations

$B = \Sigma_g^+ \Sigma_u^+ \Sigma_g^- \Sigma_u^- \Pi_g \Pi_u \Delta_g \Delta_u$

$\begin{array}{cccc}
0^+ & 1 & . & . & . \\
0^- & . & . & 1 & . \\
1^+ & . & 1 & . & 1 \\
1^- & 1 & . & . & 1 \\
2^+ & 1 & . & 1 & . \\
2^- & . & 1 & 1 & . \\
3^+ & 1 & . & 1 & 1 \\
3^- & 1 & . & 1 & 1 \\
\end{array}$

TABLE VIII. $O_3^+(O_{2i} = D_{\infty h})$ correlation of representations.

Types of symmetry labels

$A =$ Activity (of vibrations, electrons)

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Rev. Mod. Phys. 50, 1, 1 (1978)
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Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and $\lambda$-doubling levels

Dipole-allowed transitions
Diatomoc or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h}$

$A = \sum$ symmetry $\Lambda = 0$
(no e or v activity)

$A = \Pi$ symmetry $\Lambda = \pm 1$
(unit quantum of e or v activity
"riding" on rotor)

$\Sigma$

$\Lambda = 0$

$J = 3$

$|n| = 0, 1, 2$

$|K| = 0, 1, 2$

"Bare" Rotor

$\Pi$

$\Lambda = \pm 1$

$J = 2$

$|n| = 0, 1 $

$|K| = 0, 1, 2$

"Loaded" Rotor

$J = 1$

$\Sigma$ and $\Pi$ BOA states for symmetric top molecule. The electronic or vibronic "load" is indicated by an ellipsoid surrounding a "bare" dumb-bell rotor. Arrows indicate the direction of rotation of moving wave states and relative amounts of momentum $n$ or $K$. Only for the $(n=0, \Pi)$ states will it be necessary to make up standing waves to form the "A-doublet" states which are shown in Fig. 19.

Rev. Mod. Phys. 50,1,1 (1978)

Types of symmetry labels
$A =$ Activity (of vibrations, electrons)
$B =$ Bare rotor (rotations, nuclear spin)
$C =$ Coupling or Constriction of $A \otimes B$
Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3) \supset D_{\infty h}$ spin-symmetry species

Simple diatomic examples: Hypothetical $C_2$ Levels (Bare rotor)

**3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry**

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**A, B, or C Correlations**

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<tr>
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<tr>
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<tr>
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<td>.</td>
<td>.</td>
</tr>
</tbody>
</table>

$B=\Sigma_g^+$ orbit, spin-0

Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric: Either Even-Odd or Odd-Even

$12C$ has zero nuclear spin $\ 13C$ has nuclear spin-$\frac{1}{2}$
**Diatom or linear molecule: Labeling by symmetry** $O(3) \supseteq D_{\infty h} \supseteq C_{\infty v}$

### 3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

<table>
<thead>
<tr>
<th>Angular momentum</th>
<th>Atomic label</th>
<th>Molecular label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ell=0$</td>
<td>$s$ or $S$</td>
<td>$\sigma$ or $\Sigma$</td>
</tr>
<tr>
<td>$\ell=1$</td>
<td>$p$ or $P$</td>
<td>$\pi$ or $\Pi$</td>
</tr>
<tr>
<td>$\ell=2$</td>
<td>$d$ or $D$</td>
<td>$\delta$ or $\Delta$</td>
</tr>
<tr>
<td>$\ell=3$</td>
<td>$f$ or $F$</td>
<td>$\phi$ or $\Phi$</td>
</tr>
</tbody>
</table>

**A, B, or C Correlations**

$B = \Sigma_g^+ \Sigma_u^+ \Sigma_g^+ \Sigma_u^- \Pi_g \Pi_u \Delta_g \Delta_u$

<table>
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<tr>
<th></th>
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<th>$1^-$</th>
<th>$2^+$</th>
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<td>$0^-$</td>
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<td>1</td>
<td>1</td>
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<tr>
<td>$1^+$</td>
<td>1</td>
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<td>1</td>
<td>1</td>
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<tr>
<td>$1^-$</td>
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<td>1</td>
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<tr>
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<tr>
<td>$2^-$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>$3^+$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>$3^-$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Dipole ($1^-$) Excitation

**“Activity” Label**

**“Coupled” or “Constricted” Rotor**

**Label C**

### Ortho Species (only)

**$12C_2 \Sigma_u^+$ Excited Levels**

- $3^-$
- $2^+$ (excluded)
- $1^-$ (excluded)
- $0^+$ (excluded)

**$12C^{13}C \Sigma$ Excited Levels**

- $3^-$
- $2^+$
- $1^-$
- $0^+$

**$13C_2 \Sigma_u^+$ Excited Levels**

- $3^-$
- $2^+$
- $1^-$
- $0^+$

### “Bare” Rotor Label

$B = \Sigma_g^+$

<table>
<thead>
<tr>
<th>Orbit, spin</th>
<th>$1/2$ orbit, spin-0</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Ortho Species</th>
<th>Para-Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>(only)</td>
<td>(only)</td>
</tr>
</tbody>
</table>

**Friday, May 1, 2015**
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and $\lambda$-doubling levels

Dipole-allowed transitions
Coriolis and λ-doubling levels

A = Π_u

3− □□□□ 3+

2− □□□□ 2+

1− □□□□ 1+

0+ □□□□ 0+

C = Π_u

C = Π_g

Σ_u^+ Π_u(±) Excited Levels

13C_2 Σ_u^+ Π_u(±)

A = Σ_u^+

3− □□□□ 3−

2− □□□□ 2−

1− □□□□ 1−

0+ □□□□ 0+

C = Σ_u^+

C = Σ_g^+

A = Σ_g^+

3− □□□□ 3−

2− □□□□ 2−

1− □□□□ 1−

0+ □□□□ 0+

B = Σ_g^+

B = Σ_u^+

Para-Species

(orbit, spin \frac{1}{2})

Ortho-Species

(orbit, spin \frac{1}{2})
Diatom or linear molecule: Coriolis and $\lambda$-doubling levels

\[
\mathbf{H} = \mathbf{H}_e + \left( J^2 + \mathbf{L}^2 - 2J_x\mathbf{L}_x - 2J_y\mathbf{L}_y - 2J_z\mathbf{L}_z \right)/2I_{xy} \\
|\Sigma^+\rangle \quad |\Pi^+\rangle \quad |\Pi^-\rangle
\begin{pmatrix}
\varepsilon_e + 4 & -2\sqrt{2} & 0 \\
-2\sqrt{2} & \varepsilon_e + 2 & 0 \\
0 & 0 & \varepsilon_e + 2
\end{pmatrix}
\]

\((J = 1)\)-case

(a) WEAKLY COUPLED STATES  (b) BOA CONSTRICTED STATES

\(p\)-electron + \(X_2\) rotor

\[ \Gamma^3^- \quad \Gamma^2^+ \quad \Gamma^3^- \quad \Gamma^3^- \]

\[ A = \Pi_U \]

\[ B = \Sigma_U^+ \quad \Sigma_U^- \]

\[ C = \Sigma_U^+ \quad \Sigma_U^- \]

\[ J^2 \quad J^2 \quad J^2 \quad J^2 \]

\(\lambda\)-(or \(\Lambda\))-doubling

\(J\) (on 2-axis)

\(\Pi^-\) not affected

\(\Pi^+\) into \(\Sigma^+\)

FIG. 19. Correlation diagram for \(l=1\) electronic states in the presence of an \(X_2\) rotor. (a) Weakly-coupled states. (\(NP, B,\) and \(JP\) are good labels.) (b) BOA-constricted states. (\(A, B, C,\) and \(JP\) are good labels.) States with the same \(B = \Sigma_U^+\) and \(JP = 1^+\) are connected by dotted lines. The \(B = \Sigma_U^+\) and \(JP = 1^+\) state (solid line) turns out to be the same for either side as long as \(l=1\) is unspoiled. Note that \(A = \Pi_u\)-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.
Diatomic or linear molecule: Coriolis and $\lambda$-doubling levels

$$|\Sigma^+\rangle \begin{cases} J(J+1)+2 & 2(J(J+1))^{1/2} \text{ (or } \Lambda \text{-doubling)} \\ -2(J(J+1))^{1/2} & \epsilon_\pi+J(J+1) \end{cases} \begin{cases} 0 & 0 \\ -2(J(J+1))^{1/2} & \epsilon_\pi+J(J+1) \end{cases}$$

$$H = H_e + (J^2 + L_z^2 - 2J_x L_x - 2J_y L_y - 2J_z L_z)/2I_{x'y'}$$

$$|\Sigma^+\rangle |\Pi^+\rangle |\Pi^-\rangle$$

$$(\Pi) = \begin{cases} \epsilon_\pi+4 & -2\sqrt{2} \\ -2\sqrt{2} & \epsilon_\pi+2 \\ 0 & 0 \end{cases}/2I_{x'y'}$$

$$(J=1)\text{-case}$$

(a) WEAKLY COUPLED STATES (b) BOA CONSTRICTED STATES

$p$-electron + $X_2$ rotor

$\lambda$-(or $\Lambda$)-doubling

$\Pi^-$ not affected

$\Pi^+$ into $\Sigma^+$

$J$ (on 2-axis)

FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an $X_2$ rotor. (a) Weakly-coupled states. ($N^P$, $B$, and $J^P$ are good labels.) (b) BOA-constricted states. ($A$, $B$, $C$, and $J^P$ are good labels.) States with the same $B=\Sigma^\pi_0$ and $J^P=1^+$ are connected by dotted lines. The $B=\Sigma^\pi_0$ and $J^P=1^+$ state (solid line) turns out to be the same for either side as long as $l=1$ is unspoiled. Note that $A=\Pi^\pi$-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.

FIG. 20. ($n=0$) $J$-level plots ($J=0−8$) for ($l=1$: $\Sigma, \Pi$) as functions of electronic energy difference ($\epsilon_\pi$). The right-hand side of the figure shows the separate $\Pi$ and $\Sigma$ manifolds that will arise in the BOA limit as $\epsilon_\pi \rightarrow \infty$. (In this figure we set $\epsilon_\pi = 0$, and let the rotational constant $B_\text{rot} = 1/I_{x'y'}$ be unity.) Splitting or "$\lambda$ doubling" is seen in the $\Pi$ manifolds increasing with $J$. Corresponding downshifts from the pure rotational spectrum ($\approx B_\text{rot}J(J+1)$) are seen in the $\Sigma$ manifold. For small values of $\epsilon_\pi$ ($\epsilon_\pi < 5$) there is a near degeneracy between $J=N\pm 1$ levels, particularly for larger values of rotor momentum $N$. At $\epsilon_\pi = 0$ and $\epsilon_\pi = 4$ the degeneracy is exact, while between these points the $J=N-1$ level lies slightly below the $J=N+1$ level. Pairs of $J=(N\pm 1)$ weak-coupling levels are analogous to the $\Pi$ pairs seen in the BOA limits, only the former are defined with respect to a laboratory axis. The weakly coupled $J=N$ state can be thought of as a lab analog of a $\Sigma$ state.
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and $\lambda$-doubling levels

$\rightarrow$ Dipole-allowed transitions
Diatomic or linear molecule: Dipole-allowed transitions

When excited states have lower \( B=1/2I \) (Greater inertia \( I \))

FIG. 30. Demonstrating the use of a rovibronic nomogram for the model \( \Sigma \rightarrow \Sigma \) transitions by dipole excitation in a symmetric top molecule.

*Rev. Mod. Phys. 50,1,1 (1978)*
Diatom or linear molecule: Dipole-allowed transitions

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved)

Central Q-branch missing from $\Sigma \leftrightarrow \Sigma$ spectra of $D_{\infty h}$ molecules

FIG. 31. Electric dipole transitions in linear symmetric ($O_h$) molecules $X_2, XYX, \ldots$ (a) $\Sigma_u^+ \rightarrow \Sigma_u^+$, (b) $\Sigma_u^- \rightarrow \Pi_g^-$. Transitions are only allowed between levels lying in the same $B$ corridor. Note that the $(\Sigma_u^- \rightarrow \Pi_g^-) Q$ branch is not $\Lambda$ doubled since the upper $\Pi$ doublet is always involved in a $J \rightarrow J$ transition.
Diatom or linear molecule: Dipole-allowed transitions

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved)

Central Q-branch missing from $\Sigma \leftrightarrow \Sigma$ spectra of $D_{\infty h}$ molecules

FIG. 31. Electric dipole transitions in linear symmetric ($O_h$) molecules $X_2, XYX, \ldots$ (a) $\Sigma_u^+ \rightarrow \Sigma_u^-$, (b) $\Sigma_u^- \rightarrow \Pi_u$. Transitions are only allowed between levels lying in the same $B$ corridor. Note that the ($\Sigma_u^- \rightarrow \Pi_u$) $Q$ branch is not $\Lambda$ doubled since the upper $\Pi$ doublet is always involved in a $J \rightarrow J$ transition.
\[ S_n \text{ Young Tableaus and spin-symmetry for } X_n \text{ and } XY_n \text{ molecules} \]
$S_n$ Young Tableaus and spin-symmetry for $X_n$ and $XY_n$ molecules

Permutation group $S_n$ is equivalent to $G$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear $n$-atomic molecules ($n = 2, 3, 4, \ldots$).

(b) FERMI NUCLEI $1, 3, 5, \ldots$

PERMUTATION POINT GROUP $S_2$

<table>
<thead>
<tr>
<th>Group</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1 2</td>
<td></td>
</tr>
<tr>
<td>$A_2$</td>
<td>1 -1</td>
<td></td>
</tr>
</tbody>
</table>

$S_2 \sim C_2$
Sn Young Tableaus and spin-symmetry for Xn and XYn molecules

\begin{align*}
(a) & |\square\square> = |B = \sum_q^+> \\
(b) & |\bigotimes> = |B = \sum_q^+>
\end{align*}

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules (n = 2, 3, 4, ...).

(a) BOSE NUCLEI 1, 0, 1, 2, ... (b) FERMI NUCLEI \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...
Young Tableaus and spin-symmetry for \( X_n \) and \( XY_n \) molecules

\[ (a) \quad |B\rangle = \sum_{q}^{+}\langle q|B|q\rangle \quad (b) \quad |B\rangle = \sum_{q}^{+}\langle q|B|q\rangle \]

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear \( n \)-atomic molecules \( (n = 2, 3, 4, \ldots) \).

(a) BOSE NUCLEI \( I = 0, 1, 2, \ldots \)

(b) FERMI NUCLEI \( I = 1, 2, 3, 5, \ldots \)

<table>
<thead>
<tr>
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<th>SPIN</th>
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| \( n=2 \) | \[ \begin{array}{l}
1 \\
1 \\
2 \\
3 \\
3 \\
\end{array} \] |
| \( n=3 \) | \[ \begin{array}{l}
1 \\
1 \\
2 \\
3 \\
4 \\
\end{array} \] |

Permutation group \( S_n \) is equivalent to \( G \)

<table>
<thead>
<tr>
<th>( A_1 )</th>
<th>( A_2 )</th>
</tr>
</thead>
</table>
| \( \begin{array}{c}
1 \\
2 \\
3 \\
4 \\
\end{array} \) | \( \begin{array}{c}
1 \\
2 \\
\end{array} \) |

<table>
<thead>
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</table>
| \( \begin{array}{c}
1 \\
\sigma \\
\end{array} \) |

<table>
<thead>
<tr>
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</tr>
</thead>
</table>
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A_1 \\
A_2 \\
E \\
\end{array} \) |

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<thead>
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</table>
| \( \begin{array}{c}
A_1 \\
A_2 \\
E \\
\end{array} \) |

Tetrahedral: \( G = T_d \)

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<thead>
<tr>
<th>( T_d )</th>
<th>( r_{1,4} )</th>
<th>( 180^\circ )</th>
<th>( 1^\cdot 90^\circ )</th>
<th>( 1^\cdot 180^\circ )</th>
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<td>( 1 )</td>
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</tr>
<tr>
<td>( A_2 )</td>
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<td>( 1 )</td>
<td>( 1 )</td>
<td>( -1 )</td>
</tr>
<tr>
<td>( E )</td>
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<td>( -1 )</td>
<td>( 2 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( T_2 )</td>
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<td>( -1 )</td>
</tr>
<tr>
<td>( T_1 )</td>
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<td>( 0 )</td>
<td>( -1 )</td>
<td>( 1 )</td>
</tr>
</tbody>
</table>

Rev. Mod. Phys. 50,1,1 (1978)
Young Tableaus and spin-symmetry for $X_n$ and $XY_n$ molecules

**Permutation group** $S_n$ is equivalent to $G$

**Point group**

$$S_2$$

\[
\begin{array}{ccc}
A_1 & 1 & 2 \\
1 & 1 & 1 \\
1 & -1 & 1 \\
\end{array}
\]

$$C_2$$

\[
\begin{array}{ccc}
A_1 & 1 & \sigma \\
A_1 & 1 & 1 \\
A_2 & 1 & -1 \\
\end{array}
\]

$$S_3$$

\[
\begin{array}{ccc}
A_1 & 1 & 2 & 3 \\
1 & 1 & 1 & (123) \\
A_1 & 1 & 2 & 3 \\
1 & 1 & -1 & (123) \\
A_2 & 2 & -1 & 0 & (23) \\
E & 2 & -1 & 0 & (23) \\
\end{array}
\]

$$C_{3v}$$

\[
\begin{array}{ccc}
A_1 & 1 & \sigma & \sigma_2 \\
A_1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 \\
E & 2 & -1 & 0 \\
\end{array}
\]

$$S_4$$

\[
\begin{array}{ccc}
A_1 & 1 & 2 & 3 & 4 \\
(123) & (4) & (124) & (123) \\
A_1 & 1 & 2 & 3 & 4 \\
(123) & (4) & (124) & (123) \\
A_2 & 1 & 2 & 3 & 4 \\
(123) & (4) & (124) & (123) \\
E & 1 & 2 & 3 & 4 \\
(123) & (4) & (124) & (123) \\
T_2 & 1 & 2 & 3 & 4 \\
(1234) & (123) & (124) & (1234) \\
T_1 & 1 & 2 & 3 & 4 \\
(1234) & (123) & (124) & (1234) \\
\end{array}
\]

**Rev. Mod. Phys. 50,1,1 (1978)**
Sn Young Tableaus and spin-symmetry for Xn and XYn molecules

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules (n = 2, 3, 4, ...).

(a) BOSE NUCLEI

(b) FERMI NUCLEI

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
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<tr>
<td>n=2</td>
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</tr>
<tr>
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<tr>
<td>n=3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n=4</td>
<td></td>
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</table>

Methane-like: XY4

TABLE XIII. Td characters and symmetry.

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<tr>
<th></th>
<th>Td</th>
<th>R(2π/3)</th>
<th>R(π00)</th>
<th>R(π20)</th>
<th>R(π40)</th>
<th>Boson</th>
<th>Fermion</th>
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<tbody>
<tr>
<td>A1</td>
<td>1</td>
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<td>1</td>
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<td>[1][1][1][1]</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>[1][1][1][1]</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>[2][2]</td>
</tr>
<tr>
<td>L1</td>
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<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>[3][1]</td>
</tr>
<tr>
<td>(xyz) F1</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
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TABLE XIV. O4+Td correlation.

<table>
<thead>
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<th>A2</th>
<th>E</th>
<th>F1</th>
<th>F2</th>
<th>A2</th>
<th>A1</th>
<th>E</th>
<th>F2</th>
<th>F1</th>
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<tbody>
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<td>...</td>
</tr>
<tr>
<td>1^+</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>2^+</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>3^+</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td>4^+</td>
<td>1</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>...</td>
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<tr>
<td>5^+</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>6^+</td>
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<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7^+</td>
<td>...</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>7^-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
$S_n$ Young Tableaus and spin-symmetry for $X_n$ and $XY_n$ molecules

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear $n$-atomic molecules ($n = 2, 3, 4, \ldots$).

(a) BOSE NUCLEI $l=0,1,2,\ldots$  (b) FERMI NUCLEI $l=-\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

ORBITAL   SPIN

FIG. 27. Spin tableau--(B) correlation for octahedral $XY_6$ molecule (see Appendix D).

Hexa-fluoride-like: $XY_6$

Rev. Mod. Phys. 50,1,1 (1978)
**Sn Young Tableaus and spin-symmetry for X_n and XY_n molecules**

**Sn Young Tableau irrep dimension formula**

$$\ell^{[\mu_s]}(S_n) = \frac{n!}{\prod_{i=1}^{n-1} (n-i)(n-2) \cdots 3 \cdot 2 \cdot 1}$$

*Dimension of Sn Tableau*

$$\ell^{[\mu_s]}(S_n) = \frac{n!}{n \cdot (n-1) \cdot (n-2) \cdots 3 \cdot 2 \cdot 1}$$

*Hook-length product*

$$\ell^{[\mu_s]}(U_m) = \frac{m!}{m \cdot (m-1) \cdot (m-2) \cdots 3 \cdot 2 \cdot 1}$$

FIG. 28. Robinson formula for statistical weights. The “hook-length” of a box in the tableau is the number of boxes in a “hook” which includes that box and all boxes in the line to the right and in the column below it.

**Examples:**

$$\ell^{A_1} = \ell^{[3,0,0]}(S_3) = \frac{3 \cdot 2 \cdot 1}{3 \ 2 \ 1} = 1$$

$$\ell^{A_2} = \ell^{[1,1,1]}(S_3) = \frac{3 \cdot 2 \cdot 1}{3 \ 2 \ 1} = 1$$

$$\ell^{E} = \ell^{[2,1,0]}(S_3) = \frac{3 \cdot 2 \cdot 1}{3 \ 1 \ 1} = 2$$

$$\ell^{[2,1,0]}(S_3 \ast U(3)) = \frac{3 \cdot 4 \cdot 5}{3 \ 4 \ 5} = 8$$

$$\ell^{[3,0,0]}(S_3 \ast U(3)) = \frac{3 \cdot 2 \cdot 1}{3 \ 2 \ 1} = 10$$
S₄ and spin-symmetry for XY₄ molecules (Introducing hook-length formulae)

FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.

$$\begin{array}{cccc} 5A_1 & 3F_1 & A_1 & 5A_1 \\ 3F_1 & 2E & E_1 & 3F_2 \\ 5A_2 & 3F_2 & F_2 & 5A_2 \\ A_2 & 3F_2 & F_2 & 2E \\ E & 3F_1 & F_1 & 3F_1 \\ 5A_1 & 2E & F_1 & 5A_1 \\ \end{array}$$

N = 7⁺

FIG. 36. Comparison of conventional CH₄ labeling with present labeling. The latter shows clearly the "hidden" structure of inversion doublets which has a structure very much like that of NH₃. For CH₄, however, only the E levels are actually double according to the statistical weight calculations.
Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved here)
(Spin-symmetry species NOT conserved here)

(Spin-symmetry species conserved here)
Example of frequency hierarchy for 16\textmu m spectra of CF$_4$ (Freon-14)

W.G. Harter
Ch. 31
Atomic, Molecular, & Optical Physics Handbook
Am. Int. of Physics
Gordon Drake Editor (1996)
$S_6$ and spin-symmetry for $XY_6$ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion
S₆ and XY₆ molecules

OUTSIDE or LAB
Symmetry reduction results in
Level or Spectral
SPLITTING
External B-field
does Zeeman splitting

Duality: The “Flip Side” of Symmetry Analysis.
LAB versus BODY,
STATE versus PARTICLE,
boils down to:

OUTSIDE versus INSIDE

Example:
Cubic-Octahedral O
reduced to
Tetragonal C₄

<table>
<thead>
<tr>
<th>C₄</th>
<th>0₁</th>
<th>1₄</th>
<th>2₄</th>
<th>3₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>A₂</td>
<td>.</td>
<td>.</td>
<td>1</td>
<td>.</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>.</td>
<td>1</td>
<td>.</td>
</tr>
<tr>
<td>T₁</td>
<td>1</td>
<td>1</td>
<td>.</td>
<td>1</td>
</tr>
<tr>
<td>T₂</td>
<td>.</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Review O ⊃ C₄ correlations:

INSIDE or BODY
Symmetry reduction results in
Level or Spectral
UN-SPLITTING
(“clustering”)

Internal J gets “stuck” on RES axes
Must “tunnel” axis-to-axis at rate s

Friday, May 1, 2015
**S$_6$ and XY$_6$ molecules**

OUTSIDE or LAB

Symmetry reduction results in

Level or Spectral

SPLITTING

External B-field does Zeeman splitting

---

**Duality: The “Flip Side” of Symmetry Analysis.**

LAB versus BODY,

STATE versus PARTICLE,

boils down to:

OUTSIDE versus INSIDE

---

Example:

Cubic-Octahedral O

reduced to

Tetragonal C$_4$

---

**INSIDE or BODY**

Symmetry reduction results in

Level or Spectral

UN-SPLITTING

(“clustering”)

---

Internal $J$ gets “stuck” on RES axes

Must “tunnel” axis-to-axis at rate $s$

---

Review O $\supset$ C$_4$ correlations:

---

| $|U\rangle$ | $|D\rangle$ | $|E\rangle$ | $|W\rangle$ | $|N\rangle$ | $|S\rangle$ |
|--------|--------|--------|--------|--------|--------|
| $H$    | $s$    | $s$    | $s$    | $s$    | $s$    |
| $0$    | $H$    | $s$    | $s$    | $s$    | $s$    |
| $s$    | $s$    | $H$    | $0$    | $s$    | $s$    |
| $s$    | $s$    | $0$    | $H$    | $s$    | $s$    |
| $s$    | $s$    | $s$    | $s$    | $H$    | $0$    |
| $s$    | $s$    | $s$    | $s$    | $0$    | $H$    |
S₆ and XY₆ molecules

OUTSIDE or LAB
Symmetry reduction results in Level or Spectral SPLITTING
External B-field does Zeeman splitting

Duality: The “Flip Side” of Symmetry Analysis.
LAB versus BODY, STATE versus PARTICLE, boils down to:
OUTSIDE versus INSIDE

Example:
Cubic-Octahedral O reduced to Tetragonal C₄

Internal J gets “stuck” on RES axes Must “tunnel” axis-to-axis at rate s

Tunneling (s) between axes splits the 0₄ cluster as shown on following pages

0₄ cluster splitting (derived on following page)
$S_6$ and $XY_6$ molecules

Internal $J$ gets “stuck” on RES axes
Must “tunnel” axis-to-axis at rate $s$

Tunneling $s=-S$ is negative here

<table>
<thead>
<tr>
<th>$s$</th>
<th>$H$</th>
<th>0</th>
<th>0</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$H$</td>
<td>0</td>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>$s$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$s$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

$|U>|D>|E>|W>|N>|S>$

<table>
<thead>
<tr>
<th>$H$</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$s$</td>
<td>$s$</td>
<td>$s$</td>
<td>$s$</td>
<td>+2</td>
</tr>
<tr>
<td>$s$</td>
<td>$s$</td>
<td>$H$</td>
<td>0</td>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>$s$</td>
<td>0</td>
<td>$H$</td>
<td>0</td>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>$s$</td>
<td>0</td>
<td>0</td>
<td>$H$</td>
<td>$s$</td>
<td>+2</td>
</tr>
<tr>
<td>$s$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$H$</td>
<td>+2</td>
</tr>
</tbody>
</table>

Review $O(\theta_4) \supset C_4$ cluster:

$04$ cluster splitting

$\psi= \psi_0$
S₆ and XY₆ molecules

OUTSIDE or LAB
Symmetry reduction results in
Level or Spectral SPLITTING
External B-field does Zeeman splitting

Duality: The “Flip Side” of Symmetry Analysis.
LAB versus BODY,
STATE versus PARTICLE,
boils down to:
OUTSIDE versus INSIDE

Example:
Cubic-Octahedral O
reduced to
Tetragonal C₄

H + 0 - 2s
H + 0
H + 0 + 4s
tunneling matrix eigenvalues

INSIDE or BODY
Symmetry reduction results in
Level or Spectral UN-SPLITTING (“clustering”)

Internal J gets “stuck” on RES axes
Must “tunnel” axis-to-axis at rate s

|U>|D>|E>|W>|N>|S>
H 0 s s s s s
0 H s s s s s
s s H 0 s s s
s s 0 H s s s
s s s H 0 s s
s s s s 0 H

Stronger C₄
higher |B|
“Coerced” Symmetry Breaking

lower |s|
“Spontaneous” Symmetry Breaking

Friday, May 1, 2015
$S_6$ and spin-symmetry for $XY_6$ molecules

Entanglement and Disentanglement

Resulting hyperfine spectra

Superhyperfine spectra

Spin-0 nuclei give Bose Exclusion
Entanglement!

How F-nuclei become entangled
total-spin-I-symmetry $O_h$ species in $SF_6$.

With rotation all six nuclei are equivalent

Greatly simplified sketches of ultra high resolution IR $SF_6$ spectroscopy of
Christian Borde’, C. Saloman, and Oliver Pfister (Pfister did SiF$_4$, too.)
**DISentanglement!**

How F-nuclei become distinguished
**(but not distinguishable)**
in SF$_6$.

Without rotation being stuck on C$_4$ axis
all six nuclei are equivalent

With rotation stuck on C$_4$ axis
polar nuclei are **“left out in the cold”**

**“Brrrrrr it’s cold!”**

**“WE like it HOT!”**

If **polar nuclei** in greater B-field than equatorial-nuclei...

weight 3+1

weight 5

If **equatorial nuclei** in greater B-field than polar-nuclei...

weight 5

weight 3+1

Spin-Permutation to Octahedral Correlations

<table>
<thead>
<tr>
<th>Spin</th>
<th>E$_u$</th>
<th>T$_1g$</th>
<th>T$_{1u}$</th>
<th>T$_{2g}$</th>
<th>A$_{1g}$</th>
<th>A$_{1u}$</th>
<th>A$_{2u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight 1</td>
<td>.</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>.</td>
<td>.</td>
<td>.</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>weight 7</td>
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<td>.</td>
<td>.</td>
<td>.</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Species Spin Weights

8 3 3 6 1 1 10

Greatly simplified sketches of ultra high resolution IR SF$_6$ spectroscopy of
Christian Borde’, C. Saloman, and Oliver Pfister
(Pfister did SiF$_4$, too.)
$S_6$ and spin-symmetry for $XY_6$ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion
$S_6$ and $XY_6$ molecules

Forbidden SF$_6$ species: $E_g$, $T_{2u}$, $A_{2g}$

Example of subtle parity effect in SF$_6$ superfine-hyperfine transitions

$S_6$ and spin-symmetry for $XY_6$ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion
Primary AET species mixing increases with distance from "separatrix".

CASE 1: Unmixed primary $A_1 T_1 E T_2 A_2$ species

CASE 2: Extreme mixing in tight $C_4$-CLUSTERS

CASE 2: Major mixing in lowest two $C_3$-CLUSTERS

weight 8 = 5 + 3
weight 6 = 5 + 1
weight 10 = 7 + 3
Forbidden species: $E_g$, $T_{2u}$, $A_{2g}$

Spin-Permutation to Octahedral Correlations

$S_6 
\cong O_h$

Species Spin Weights

CASE 1.

CASE 2.

$S_6$ and spin-symmetry for $XY_6$ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion
Spin-0 nuclei give Bose Exclusion

For a zero-spin $^X_{16}O_6$ molecule, hundreds of lines would vanish! Just eight $A_1$ singlets remain.

(a) SF$_6$ $I_4$ Rotational Structure

(b) P(88) Fine Structure (Rotational anisotropy effects)

(c) Superfine Structure (Rotational axis tunneling)

(d) Hyperfine Structure (Nuclear spin-rotation effects)

Without nuclear spin: Forget all this stuff!

Goodbye clusters! (Goodbye Columbus)
Spin-0 nuclei give Bose Exclusion

Some examples of Bose Exclusion

Spherical Top Molecules with Spin-0 Nuclei

OsO$_4$

none?...

Only 1 hyperfine state: $I=0$

Spherical Top Molecules with Spin-1/2 Nuclei

CF$_4$, SiF$_4$

SF$_6$

$2^4=16$ hyperfine states: $I=0-2$

$2^6=64$ hyperfine states: $I=0-3$

$2^{60}=1.15 \times 10^{18}$ hyperfine states: $I=0-30$

Example of extreme symmetry exclusion

$Y_h$ Symmetry reduced to $C_V$ by a single neutron (in $^{13}$C)

... (and partial recovery)

Question: Where did those 200 levels go?

Better Question: Where did those 1.15 octillion levels go?

Some examples of Fermi (non) Exclusion
are more like a single bond and those along an edge bordered by two hexagons are more like a double bond. This is illustrated in the stereoscopic drawing in fig. 1. The position of each carbon atom is determined by 60 symmetrically placed orthogonal coordinate triads whose origins are located at the vertices of the Buckyball structure. These are shown in stereo in fig. 2a. This 180-dimensional coordinate system is used to form a harmonic approximation to the classical equations of motion.

$$X_i = -f_{ij}X_j$$

The elements $f_{ij}$ are components of a force matrix.

Fig. 1. Stereoscopic view of Buckyball. "Double bonds" lie along the darker lines and "single bonds" lie along the lighter lines. Carbon atoms are located at the vertices.

Fig. 2. (a) Stereoscopic view of the 60 orthogonal coordinate triads used in the initial formulation of the force matrix. The unit cell is highlighted. (b) Stereoscopic view of the unit cell required for the calculation of the force matrix. Single bond parameters are $p$ and $n$. Double bond parameters are $h$ and $g$.

Table 1: Symmetry-labeled eigenfrequencies of Buckyball for $\epsilon = 1.4 	imes 10^{-3}$ dyn cm$^{-1}$ and $\epsilon = 0.7 	imes 10^{-3}$ dyn cm$^{-1}$

<table>
<thead>
<tr>
<th>Even parity</th>
<th>Odd parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\pi}$</td>
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<tr>
<td>1830</td>
<td>1243</td>
</tr>
<tr>
<td>1662</td>
<td>1878</td>
</tr>
<tr>
<td>1545</td>
<td>1462</td>
</tr>
<tr>
<td>513</td>
<td>618</td>
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<tr>
<td>513</td>
<td>478</td>
</tr>
<tr>
<td>500</td>
<td>1900</td>
</tr>
<tr>
<td>951</td>
<td>1143</td>
</tr>
<tr>
<td>724</td>
<td>1122</td>
</tr>
<tr>
<td>615</td>
<td>526</td>
</tr>
<tr>
<td>358</td>
<td></td>
</tr>
<tr>
<td>2086</td>
<td>G$_{\pi}$</td>
</tr>
<tr>
<td>1813</td>
<td>1845</td>
</tr>
<tr>
<td>1327</td>
<td>1086</td>
</tr>
<tr>
<td>677</td>
<td>876</td>
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<tr>
<td>393</td>
<td>653</td>
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<td>433</td>
<td>360</td>
</tr>
<tr>
<td>2036</td>
<td>H$_{\pi}$</td>
</tr>
<tr>
<td>1910</td>
<td>1797</td>
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<td>1654</td>
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<td>1292</td>
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<td>828</td>
<td>559</td>
</tr>
<tr>
<td>526</td>
<td>470</td>
</tr>
<tr>
<td>413</td>
<td>420</td>
</tr>
</tbody>
</table>

Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p = 7.0 \times 10^{-3}$ dyn cm$^{-1}$ and $n = 0.7 \times 10^{-3}$ dyn cm$^{-1}$. The scale is in units of 1183 cm$^{-1}$. Lines a-d correlate with eigenmodes in fig. 4.

3. Special cases

By a judicious choice of spring constants it is possible to check the validity of the general computational procedure. Here we discuss four different choices of spring constants. Comparison of the results obtained using icosahedral projection is made with those obtained by independently derived analytic formulas.

These four choices are:

1. $p = n = 0$, $h = 1$. Here we have isolated 30 carbon atom pairs each aligned with one of the 30 icosahedral edges. The atoms in each pair are coupled to one another by a hexagonal bond and form a $C_5$ symmetric system. The only non-zero normal mode is the symmetric stretch. The analytic solution of the eigenfrequency for this system is found quite easily to be $\sqrt{2}h/m$. Using our programed projection method with $h = m = 1$ we obtain $\sqrt{5}$ in perfect agreement. For the same set of spring constants in ref. [7] they report a symmetric stretch eigenfrequency of 1, clearly in disagreement with analytic results. In addition to calculating the eigenfrequency

Friday, May 1, 2015
Possible $C_{60}$ Rovibrational Structure

Fine Structure

$J=50$

Fine structure comparing $^{13}C_{60}$ ($2^{60}$ Hyperfine levels) with $^{12}C_{60}$ ($1^{60}$ Hyperfine level)

$W.G.Harter, D.E.Weeks,
Buckyballs “Seen” in Space

A brief history of $C_{60}$ spectroscopy

Bill Harter

UAF - Physics
Buckyballs “Seen” in Space

A brief history of $C_{60}$ spectroscopy
1st Try at “Seeing” in Lab
Mass spectroscopy gives something with atomic weight 720

Richard Smalley, Bob Curl, and Harry Kroto (1985)
Guess structure is $C_{60}$ “soccer ball”
Three *Golden* rectangles
(Ratio: \((\sqrt{5}+1)/2 : 1=1.618...\))

underlie **C\textsubscript{60}**

*Buckminsterfullerene*  
"Buckyball"

60 C atoms: one C at each vertex of a *Soccerball*
2nd Try at “Seeing” in Lab

Rotational spectroscopy predicted
(but still too hard to see)
3·60=180 coordinates of \( C_{60} \)

"Buckyball" vibrational coordinates

3rd Try at "Seeing" in Lab

Vibrational spectroscopy predicted

(Should be easier to see... but not at first)
3rd Try (contd)

Vibration spectra predicted (Easy to see... just 2 pairs of lines)

Table 3
Symmetry-labeled eigenfrequencies of Buckyball for $p = h = 7.6 \times 10^5$ dyn/cm, $\pi = \eta = 0.7 \times 10^5$ dyn/cm

<table>
<thead>
<tr>
<th>Even parity</th>
<th>Odd parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I_s group label</td>
<td>frequency (cm$^{-1}$)</td>
</tr>
<tr>
<td>$A_g$</td>
<td>1830</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>1662</td>
</tr>
<tr>
<td>$T_{3g}$</td>
<td>1900</td>
</tr>
<tr>
<td>$G_g$</td>
<td>2006</td>
</tr>
<tr>
<td>$H_g$</td>
<td>2068</td>
</tr>
</tbody>
</table>

Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p = h = 7.6 \times 10^5$ dyn/cm and $\pi = \eta = 0.7 \times 10^5$ dyn/cm. The scale is in units of 1185 cm$^{-1}$. Lines a–d correlate with eigenmodes in fig. 4.
3rd Try (contd)

Just 2 pairs of lines
Dr. William G. Harter
Dept. of Physics
The University of Arkansas
Fayetteville, Arkansas 72701

Dear Bill,

Here is a copy of the first paper on $C_60$ which has just been accepted for publication in Chem. Phys. Letters.

We have had much fun with your program. It is delightful.

Things are moving very fast in the Buckyball arena. We now think we can concentrate the material and produce it in sufficient quantity for many experiments.

Thanks again for the discussions we have had and for your program.

Sincerely,

Donald R. Huffman
Professor of physics

DrH
Incl.
a tunable laser and discovered that molecular rotation resembles just what its name implies—the rotation of a planet on its axis. As molecules spin around their center of gravity, they wobble in a conical pattern or “precess” as they rotate around a multitude of axes. Also, molecules execute a generally slower “tunneling” or tumbling motion that would be forbidden in a world

**Former Georgia Tech physics professor Dr. William Harter** proposed a molecular rotational dynamics theory he used to make the first predictions on the rotational-vibrational spectra of the soccer ball-shaped molecule Buckminsterfullerene (C60), nicknamed “buckyball.”

This structure had been proposed in 1985 by a group of Rice University researchers, who had seen a mass-spectra peak of atomic mass 720. Subsequently, researchers from the University of Arizona and the Max Planck Institute used Harter and Weeks’ findings and their Macintosh software program to further analyze C60.

In 1989, those researchers realized from Harter and Weeks' vibrational spectral predictions that they had been making C60 since the early 1970s. Other experts were skeptical, but IBM labs at San Jose, Calif. verified the University of Arizona’s results in 1990. Just two years later, *Science* named C60 “Molecule of the Year,” and the Rice University-led research team received a Nobel Prize in chemistry in 1996 for its work with the molecule.

Harter is now a professor of physics at the University of Arkansas, where he studies optimal control theory for quantum systems. In 1995, he was elected a fellow of the American Physical Society. Weeks is a professor at the U.S. Air Force Postgraduate School near Wright Patterson AFB in Dayton, Ohio.

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**Physicist William Harter** has come up with innovative teaching solutions to help reduce the ‘physics anxiety’ of students faced with galloping light waves, quantum mechanics, and the paradoxes of the physical universe. (Photo by Marc Francoeur)
Two (or Three) forms of Carbon on one license plate!