Development of the Physics of Spin Isomers and its Application to Astrochemistry:

(1) The story of spin and spin isomers
(2) Orders of magnitude and symmetry, the two pillars of spectroscopy
(3) Conservation and variation of spin isomers by collision and radiation

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Zentrum für astrochemische Studien, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany, September 23 - 27, 2016
(1) The Story of Spin and Spin Isomers

September 23, Friday 10:30 -
The Story of Spin

Sin-itiro (Sin'ichirō) Tomonaga  1906 – 1979
Founder of quantum electrodynamics together with
  Julian Schwinger, Richard Feynman  Physics Nobel 1965
  Freeman Dyson

Translator’s preface
Lecture 1: Before the Dawn
Lecture 2: Electron Spin and the Thomas Factor
Lecture 3: Pauli's Spin Theory and the Dirac Theory
Lecture 4: Proton Spin
Lecture 5: Interaction between Spins
Lecture 6: Pauli-Weisskopf and the Yukawa Particle
Lecture 7: The Quantity Which Is neither Vector nor Tensor
Lecture 8: Spin and Statistics of Elementary Particles
Lecture 9: The Year of Discovery: 1932
Lecture 10: Nuclear Force and Isospin
Lecture 11: The Thomas Factor Revisited
Lecture 12: The Last Lecture
Epilogue
Ortho/Para He

1922 Gerlach and Stern. Experimental proof of space quantization (ZPhy 9, 349).
1922 A. Fowler. Use of ortho-helium and parhelium as recommendation by Bohr.
1924 Pauli. Introduction of nuclear spin for hyperfine structure (NW 12, 742).
1925 Mecke. Discovery of intensity alternation in N₂⁺ spectrum (ZPhy 28, 261).
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1926 Uhlenbeck and Goudsmit. Introduction of electron spin (NW 13, 953).


**1927 Heisenberg.** Ortho-H₂ (J odd) and para-H₂ (J even) (ZPhy 41, 239).

Hori. Observation of 3:1 intensity alternation in H₂ spectrum (ZPhy 44, 834).
Dennison. Stable o-, p-H₂ to explain the specific heat (Proc. R. Soc. A115, 483).
1933 Wigner. Theory for the stability of ortho and para H₂ (ZPC B23, 28).
Mecke. Observation of intensity alternation in H₂O (ZPhy 81, 313).
1940 Pauli. Theoretical proof of Pauli’s exclusion principle (PhRv 58, 716).
1970 Ozier et al. Observation of o-p transition of CH₄ in magnetic field (PhRvL 24, 642).
1985 Chapovsky et al. First study of conversion rate in polyatomics, CH₃F (CP 97, 449).
1997 Uy et al. Experimental nuclear spin selection rules in reaction (PhRvL 78, 3844).
2000 Chapovsky et al. Separation of spin isomers of CH₃Cl (CPL 322, 424).

Tanaka et al. Observation of interactions between o- and p-C₂H₄ (JChPh 120, 3604).
2014 Takagi et al. High spin conversion rate in CH₃OH (private communication).
the name *Helium* should be given only to the second element, the spectrum of which includes $D_3$. The first element Professor Stoney has proposed to call *Parhelium*. In all the spectra of
Pauli’s Exclusion Principle

W. Pauli Z. Physik 31, 765 (1925) “We cannot give a more precise reason”

W. Heisenberg Z. Physik 38, 411 39, 499 (1926) 41, 239 (1927)

\[(1,2)\Psi(r_1, p_1, I_1; r_2, p_2, I_2) = \Psi(r_2, p_2, I_2; r_1, p_1, I_1) = -\Psi(r_1, p_1, I_1; r_2, p_2, I_2)\] for fermion
\[= +\Psi(r_1, p_1, I_1; r_2, p_2, I_2)\] for bosons

Self-effacing Dirac

Heisenberg’s equation of motion (1925)
Pauli’s exclusion principle (1926)
Einstein’s coefficient (1927)
Fermi’s golden rule (1927)

W. Pauli, Phys. Rev. 58, 716 (1940)
The most subtle and ingenious design of nature

Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arguments of quantum field theory and relativity. He has shown that the two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved. For the moment, you will just have to take it as one of the rules of the world.

The Feynman Lectures on Physics Vol. 3, p 4-3


I. Duck & E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*
World Scientific, Singapore (1997)
The all mighty formula

\[ \mathcal{D}_{I_1} \otimes \mathcal{D}_{I_2} = \mathcal{D}_{I_1+I_2} \oplus \mathcal{D}_{I_1+I_2-1} \oplus \cdots \oplus \mathcal{D}_{|I_1-I_2|} \]


\[ \left[ D_{1/2} \right]^2 = D_1 \oplus D_0 \]

The principle of superposition of states
The Nobel Prize in Physics 1932
Werner Karl Heisenberg
"for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"
Orh o/Para He

1922 Gerlach and Stern. Experimental proof of space quantization (ZPhy 9, 349).
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1940 Pauli. Theoretical proof of Pauli’s exclusion principle (PhRv 58, 716).
1967 Cull et al. Theory for spin conversion in polyatomic molecules (JChPh 46, 3220).
1970 Ozier et al. Observation of o-p transition of CH₄ in magnetic field (PhRvL 24, 642).
1985 Chapovsky et al. First study of conversion rate in polyatomics, CH₃F (CP 97, 449).
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2014 Takagi et al. High spin conversion rate in CH₃OH (private communication).
Stability of ortho and para \( \text{H}_2 \); Wigner’s near symmetry

Z. Physik. Chem. B23, 28 (1933)

“the special stability of para-\( \text{H}_2 \) is based on a symmetry property of the quantum mechanical energy operator of the hydrogen molecule; it is not only invariant when the entire set of coordinates of both protons are exchanged but also nearly invariant when only the Cartesian coordinates are exchanged leaving the spin coordinates unchanged.”

\[ \Psi = \psi_e \cdot \psi_v \cdot \psi_r \cdot \psi_I \]

Nuclear spin interactions \( I \cdot I \) \( I \cdot J \)

<table>
<thead>
<tr>
<th>Type</th>
<th>Energy</th>
<th>Mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>10^{-2}</td>
</tr>
</tbody>
</table>

\( \kappa^2 \) \( \kappa^4 \) \( \alpha^2 \kappa^8 \)
The all mighty formula

\[ \mathcal{D}_{I_1} \otimes \mathcal{D}_{I_2} = \mathcal{D}_{I_1+I_2} \oplus \mathcal{D}_{I_1+I_2-1} \oplus \cdots \oplus \mathcal{D}_{|I_1-I_2|} \]


\[ \left[ D_{1/2} \right]^2 = D_1 \oplus D_0 \]

The principle of superposition of states

\[ \begin{align*}
    \text{H}_2 & \quad \left[ D_{1/2} \right]^2 = D_1 \oplus D_0 \\
    \text{H}_3^+ & \quad \left[ D_{1/2} \right]^3 = D_{3/2} \oplus 2D_{1/2} \\
    \text{CH}_4 & \quad \left[ D_{1/2} \right]^4 = D_2 \oplus 3D_1 \oplus 2D_0 \\
    \text{CH}_5^+ & \quad \left[ D_{1/2} \right]^5 = D_{5/2} \oplus 4D_{3/2} \oplus 5D_{1/2}
\end{align*} \]
Ortho/Para He

H₂

Tomonaga

H₂O, H₂CO, C₃H₂, NH₃, CH₃OH, CH₄, C₂H₄

H₂O⁺, H₂S⁺, H₂Cl⁺, H₃O⁺, H₃S⁺, CH₅⁺

Handbook

Nuclear spin

Electron spin

1922 A. Fowler. Use of ortho-helium and parhelium as recommendation by Bohr.
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    Mecke. Discovery of intensity alternation in N₂⁺ spectrum (ZPhy 28, 261).
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Polyatomic molecules

Nuclear Spin State Equilibration through Nonmagnetic Collisions

\[ H = H_{\text{rot}} + T_{\alpha} \left[ (I_{1a} - I_{2a}) J_{b} + (I_{1b} - I_{2b}) J_{a} \right] \]

\[ H_{1b} = \left( \frac{3}{8} \right) \left[ J_{a} \left[ (I_{1a} + I_{2a} - I_{3a} - I_{4a}) + (I_{1a} - I_{2a} + I_{3a} - I_{4a}) \right] + J_{b} \left[ (I_{1a} - I_{2a} - I_{3a} + I_{4a}) + (I_{1a} - I_{2a} + I_{3a} - I_{4a}) \right] \]

\[ H_{2a} = \frac{1}{2} B \left[ (I_{1a} J_{3a} + \epsilon I_{1a} J_{3a} + \epsilon I_{1a} J_{3a}) + (I_{1a} J_{3a} + \epsilon I_{1a} J_{3a} + \epsilon I_{1a} J_{3a}) \right] \]

\[ H_{2b} = -\frac{3}{8} B \left[ (I_{1a} J_{3a} + I_{1a} J_{3a} - I_{3a} J_{3a} - I_{3a} J_{3a}) + (I_{1a} J_{3a} + I_{1a} J_{3a} - I_{3a} J_{3a} - I_{3a} J_{3a}) \right] \]

\[ \hat{H}_{i,J} = M_{XZ}(I_{1X} - I_{2X}) J_{Z} + M_{ZX}(I_{1Z} - I_{2Z}) J_{X} + T_{r} \]

\[ \hat{H}_{i,J} = N_{XZ}(I_{1X} I_{2Z} - I_{1Z} I_{2X}) + T_{r} \]

\[ \hat{H}_{i,J}^{'\dagger} = N_{ZX}^{+} [2(I_{1Z} I_{2X} + I_{2Z} I_{1X}) - (I_{1Z} + I_{2Z}) I_{3X} \]

\[ - I_{3Z}(I_{1X} + I_{2X}) - \sqrt{3}(I_{1Z} - I_{2Z}) I_{3Y} \]

\[ - \sqrt{3} I_{3Z}(I_{1Y} - I_{2Y}) + N_{ZX}^{+} [2(I_{1Z} I_{2Y} - I_{2Z} I_{1Y}) + (I_{1Z} - I_{2Z}) I_{3Z} - I_{3Z}(I_{1Y} - I_{2Y}) \]

\[ - \sqrt{3}(I_{1Z} + I_{2Z}) I_{3X} + \sqrt{3} I_{3Z}(I_{1X} + I_{2X}) \]

\[ + N_{XY} [2(I_{1X} I_{2X} - I_{1Y} I_{2Y}) - (I_{2X} I_{3X} + I_{3X} I_{1X} \]

\[ - I_{2Y} I_{3Y} - I_{3Y} I_{1Y}) - \sqrt{3}(I_{2X} I_{3Y} - I_{3Y} I_{1X} \]

\[ + I_{2Y} I_{3X} - I_{3X} I_{1Y})] \]

J. Chem. Phys. 46, 3220 (1967)
Applications to interstellar molecules

Ortho↔Para conversion in interstellar space

Neutral molecules

\[ H^+ + o-H_2 \rightleftharpoons H^+ + p-H_2 \]
\[ H^+ + o-H_2CO \rightleftharpoons H^+ + p-H_2CO \]
\[ H^+ + H_2(J=0) \rightarrow H^+ + H_2(J=1) - 170 \text{ K} \]
\[ H_3^+ + H_2(J=0) \rightarrow H_3^+ + H_2(J=1) - 170 \text{ K} \]

Ions

\[ H_2 + o-H_3^+ \leftrightarrow H_2 + p-H_3^+ \]
\[ H_2 + p-H_2O^+ \rightarrow H + H_3O^+ \]
Nuclear spin selection rules

Detailed symmetry selection rules for reactive collisions

by MARTIN QUACK† Mol. Phys. 34, 477 (1977)

\[ \text{H}_2^+ + \text{H}_2 \leftrightarrow (\text{H}_4^+)^* \leftrightarrow \text{H} + \text{H}_3^+ \quad \text{H}_3^+ + \text{H}_2 \leftrightarrow (\text{H}_5^+)^* \leftrightarrow \text{H}_2 + \text{H}_3^+ \]

Observation of Ortho-Para H_3^+ Selection Rules in Plasma Chemistry


<table>
<thead>
<tr>
<th>spin species</th>
<th>Weight</th>
<th>( oo )</th>
<th>( op )</th>
<th>( po )</th>
<th>( pp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( oo )</td>
<td>12</td>
<td>37/5</td>
<td>1</td>
<td>14/5</td>
<td>4/5</td>
</tr>
<tr>
<td>( op )</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>( po )</td>
<td>12</td>
<td>14/5</td>
<td>2</td>
<td>28/5</td>
<td>8/5</td>
</tr>
<tr>
<td>( pp )</td>
<td>4</td>
<td>4/5</td>
<td>0</td>
<td>8/5</td>
<td>8/5</td>
</tr>
</tbody>
</table>

Proton hop \[ \text{H}_3^+ + \tilde{\text{H}}_2 \rightarrow \text{H}_2 + \tilde{\text{H}}_2 \text{H}^+ \]

Proton exchange \[ \text{H}_3^+ + \tilde{\text{H}}_2 \rightarrow \text{H}_2 \tilde{\text{H}} + \text{HH} \]

\( 2.4 : 1 \)

Crabtree, McCall et al. (2011)
Nuclear spin selection rules in chemical reactions 
by angular momentum algebra

Quack Permutation inversion group (Molecular symmetry group)

\[ \Psi = \psi_{\text{coordinate}} \psi_{\text{spin}} \]

Rotation group \( D_I \)

\[
D_{I_1} \otimes D_{I_2} = D_{I_1+I_2} \oplus D_{I_1+I_2-1} \oplus \cdots \oplus D_{|I_1-I_2|}
\]

Advantages
- Simplicity
- Any value of \( n \)
- Any value of spin

Discriminating reactions

Frobenius’ reciprocity

G. Frobenius Sitzber. Preuss. Akad. 501 (1898)

J. Mol. Spectrosc. 228, 635 (2004)

C\(_{2v}\), C\(_{3v}\), D\(_{2d}\), D\(_{3h}\), T\(_d\), …
E, C\(_2\), C\(_3\), \( \sigma_v \), \( \sigma_h \), I, …
A\(_1\), A\(_2\), B\(_1\), B\(_2\), A’, A”, E, F, …

Microcanonical statistical study of ortho-para conversion in the reaction
\( \text{H}_3^+ + \text{H}_2 \rightarrow (\text{H}_5^*) \rightarrow \text{H}_3^+ + \text{H}_2 \) at very low energies

Kisam Park and John C. Light
Ortho ↔ para spontaneous emission in open shell molecules

Closed shell (non-magnetic) molecules  $I\cdot I I\cdot J \quad \kappa^8\alpha^2 \sim 10^{-12} \quad 10^{10}$ years
Open shell (paramagnetic) molecules  $S\cdot I \quad \kappa^4\alpha^2 \sim 10^{-8} \quad 10^2$ years

Fig. 3. Column density distribution of ortho-H$_2$O$^+$ and para-H$_2$O$^+$ (upper panel), o/p ratio (central panel) and $T_{\text{nuclear spin}}$ distribution (lower panel).


Ortho–Para Mixing Hyperfine Interaction in the H$_2$O$^+$ Ion and Nuclear Spin Equilibration

Keiichi Tanaka,*†‡§ Kensuke Harada,*‡ and Takeshi Oka§

520 years

$\text{H}_2\text{O}^+$

$\text{NH}_3$

**Calculated Time for Spontaneous Emission $t$ and Absorption Coefficient $\gamma$ at Room Temperature**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$t$ ($10^9$ sec)</th>
<th>$\gamma$ ($10^{-7}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(2,2) \rightarrow (1,1)$</td>
<td>28.53</td>
<td>7.32</td>
<td>0.06</td>
</tr>
<tr>
<td>$(3,3) \rightarrow (2,0)$</td>
<td>25.93</td>
<td>1.37</td>
<td>0.9</td>
</tr>
<tr>
<td>$(4,4) \rightarrow (3,1)$</td>
<td>23.36</td>
<td>0.69</td>
<td>0.9</td>
</tr>
<tr>
<td>$(5,5) \rightarrow (4,2)$</td>
<td>20.80</td>
<td>0.50</td>
<td>1.2</td>
</tr>
<tr>
<td>$(6,6) \rightarrow (5,3)$</td>
<td>18.25</td>
<td>0.44</td>
<td>2.4</td>
</tr>
</tbody>
</table>

PHOTOGRAPH OF THE SPECTRUM OF CLÉVEITE GAS TAKEN IN THE FIRST ORDER OF A LARGE ROWLAND CONCAVE GRATING.

There are some impurities visible, principally hydrogen and traces of the cyanogen band $\lambda 3885$ and of nitrogen bands. The strong lines are accompanied by "ghosts" on either side. Two photographs are given of the region from $\lambda 3500$ to $\lambda 3700$. 