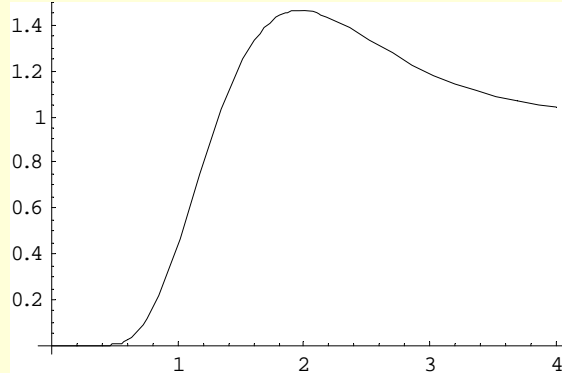
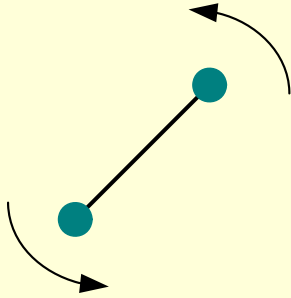


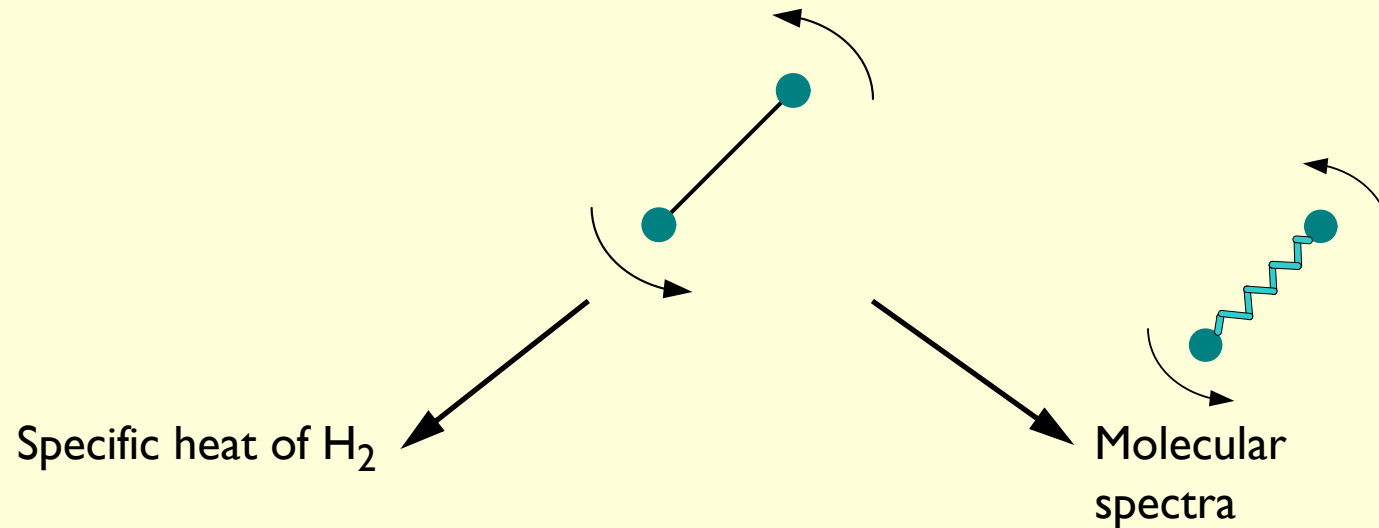
DAVID DENNISON, THE SPECIFIC HEAT OF HYDROGEN, AND THE DISCOVERY OF NUCLEAR SPIN:



Clayton Gearhart
St. John's University
(Minnesota)

HQ-2: Conference on the History of Quantum Physics
Utrecht
July 2008

RIGID ROTATOR (ROTATING DUMBBELL)



- The rigid rotator was among the earliest problems taken up in the old (pre-1925) quantum theory.
- No accurate theoretical description of the specific heat of hydrogen emerged in the old quantum theory

SPECIFIC HEAT OF HYDROGEN: AN UNSOLVED PROBLEM IN THE OLD (PRE-1925) QUANTUM THEORY



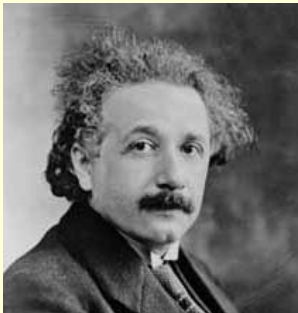
Planck



Lorentz



Eucken



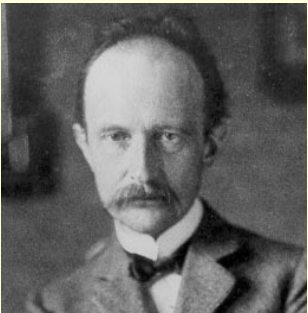
Einstein



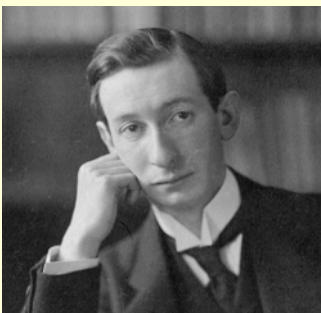
Ehrenfest



Bohr



Planck



Reiche



Kemble



Tolman



Schrödinger



Van Vleck

Some of the more prominent physicists and physical chemists who worked on the specific heat of hydrogen, 1911–1926.

HEISENBERG: 1932 NOBEL PRIZE



for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen

NERNST'S HEAT THEOREM AND THE SPECIFIC HEAT OF MOLECULAR HYDROGEN



Walther Nernst

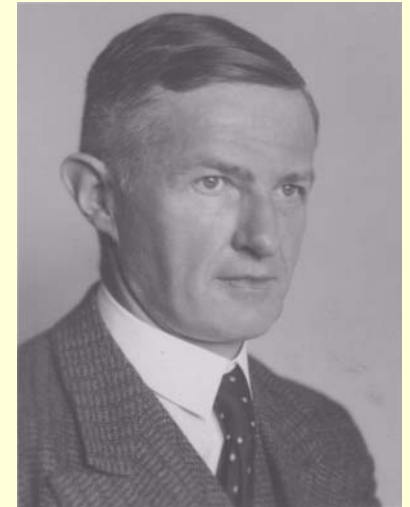
- By 1910, Walther Nernst had seen the relation of his heat theorem to quantum theory
- Early in 1911, he speculated that the rotational and vibrational degrees of freedom **for gases** might show quantum behavior.
- Because of its low mass and low liquification temperature,
... The determination of the specific heat of hydrogen at low temperatures would therefore be especially interesting.

(Nernst 1911)

Arnold Eucken was one of Nernst's assistants, and had been closely involved in the measurements of the specific heats of solids.

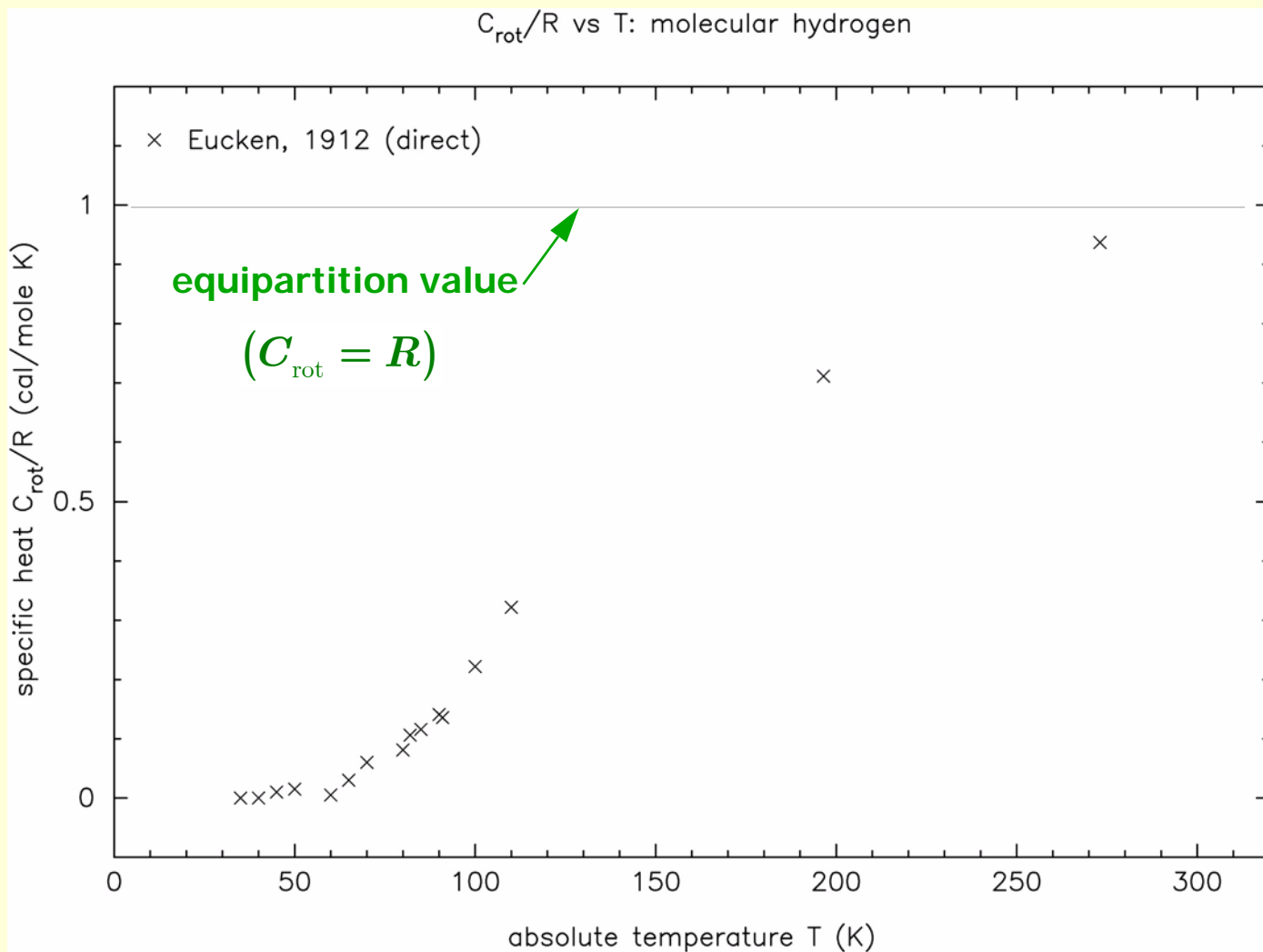
In 1912, he packed about 0.2 moles of H_2 into a 39 cm^3 thin-walled steel chamber (pressure about 100 atm!), measured the specific heat down to about 30K.

Both the experiment and the data reduction were difficult. Eucken found ...



Arnold Eucken

EUCKEN'S DATA



The two rotational degrees of freedom are “frozen out”!

AND NOW THE THEORY

QUANTUM THEORY OF THE RIGID ROTATOR APPLIED TO THE SPECIFIC HEAT OF HYDROGEN

STAGES

1. The unquantized rotator: Nernst, Einstein, Otto Stern, and Adriaan Fokker, 1911–1913
2. Quantized rotators with one degree of freedom: Lorentz, Paul Ehrenfest, Erik Holm, others; 1913–1916 or so
3. Old quantum theory: Fritz Reiche and quantized rotators with two degrees of freedom: Max Planck, Fritz Reiche, Edwin C. Kemble, Niels Bohr, others; 1915–1925
4. Modern quantum mechanics: John Van Vleck, Werner Heisenberg, Friedrich Hund, David Dennison, others; 1926 on

Molecular spectra became increasingly important part of the story

- Vibration-rotation spectra (e.g., HCl):
- independent measurement of the moment of inertia of H_2
- lines of alternating intensity in homonuclear diatomic molecules

No single actor; no single theoretical theme; instead, one intractable problem

FRITZ REICHE



- Ph.D. with Planck, 1907
- 1908–11: in Breslau
- 1913: Privatdocent in Berlin
- 1915–18: assistant to Planck
- 1919–1920: advisor to Fritz Haber in the Physical Chemistry Institute in Berlin
- 1921–1933: Professor in Breslau
- 1921: widely read quantum theory textbook

1919: “On the Quantum Theory of the Rotational Heat of Hydrogen”

REICHE AND THE SPECIFIC HEAT OF H₂

Calculations: Recipe

1. Calculate energy for rotator with two degrees of freedom:

$$W_{n_1, n_2} = (n_1 + n_2)^2 \frac{h^2}{8\pi^2 J}$$

n_1 and n_2 are the quantum numbers associated with two rotational degrees of freedom

2. Calculate “partition function” Q (usually to 6 terms)

$$Q = \sum_{n_1} \sum_{n_2} e^{-W_{n_1, n_2} / kT} = \sum_{n_1} \sum_{n_2} e^{-\sigma(n_1 + n_2)^2} \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

If one writes out the first few terms, it becomes evident that

$$Q = \sum_{n=0}^{\infty} (2n + 1) e^{-\sigma n^2}$$

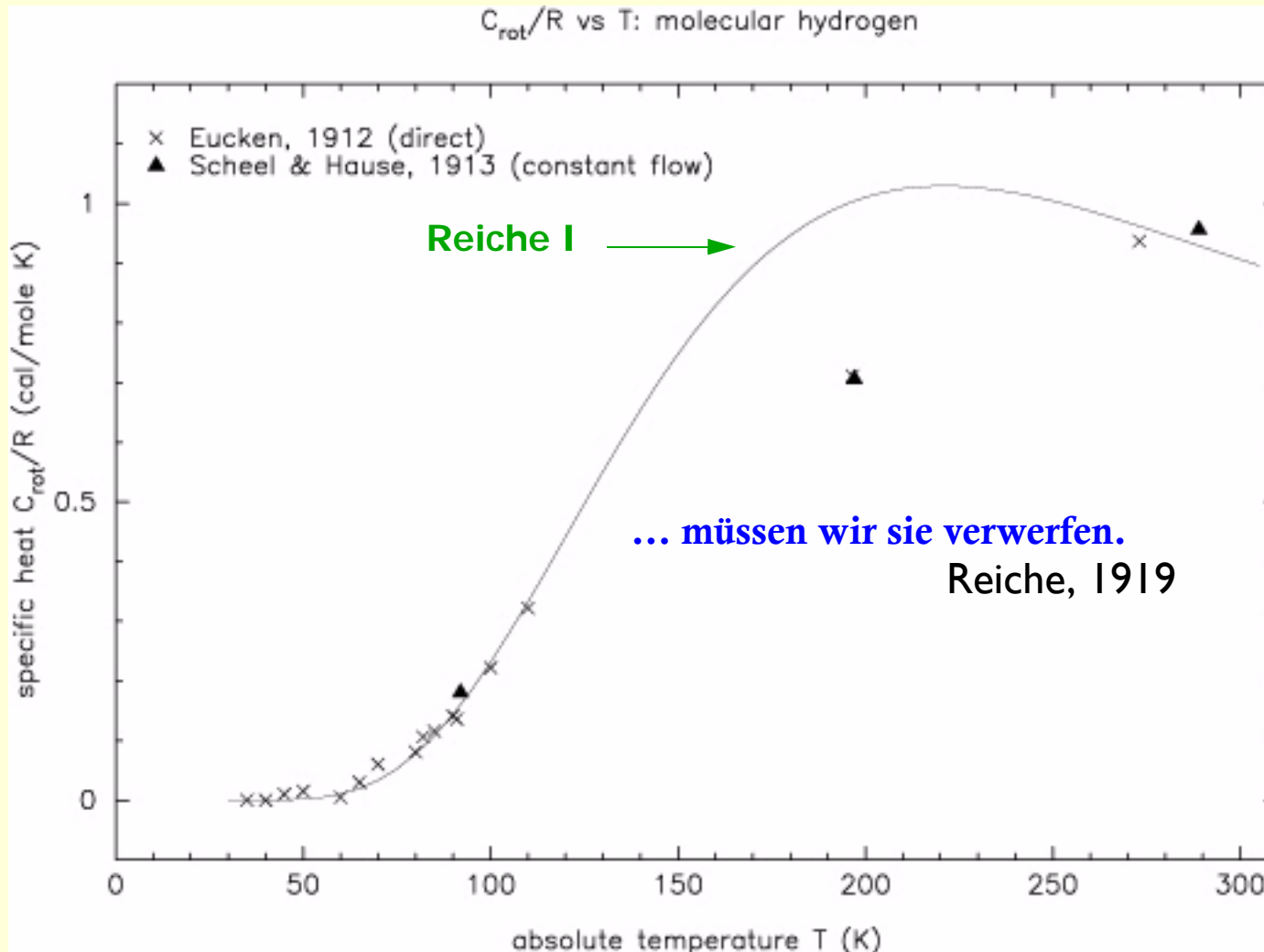
“weight,” or number of degenerate quantum states for a given energy

3. Calculate the specific heat

$$c_R = Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}$$

The calculation is difficult.

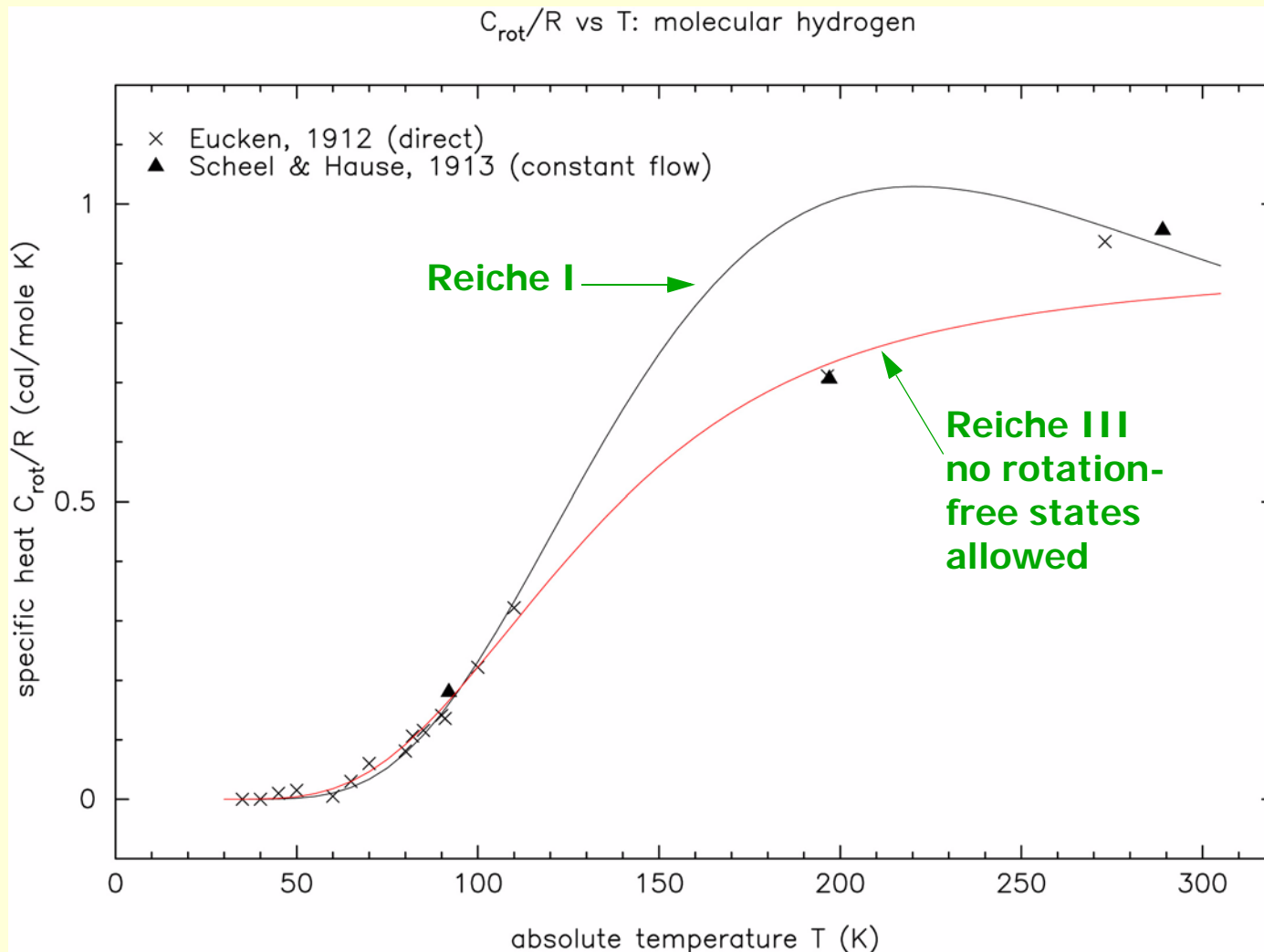
REICHE CURVE I



A similar peak had first been seen by Paul Ehrenfest in 1913.

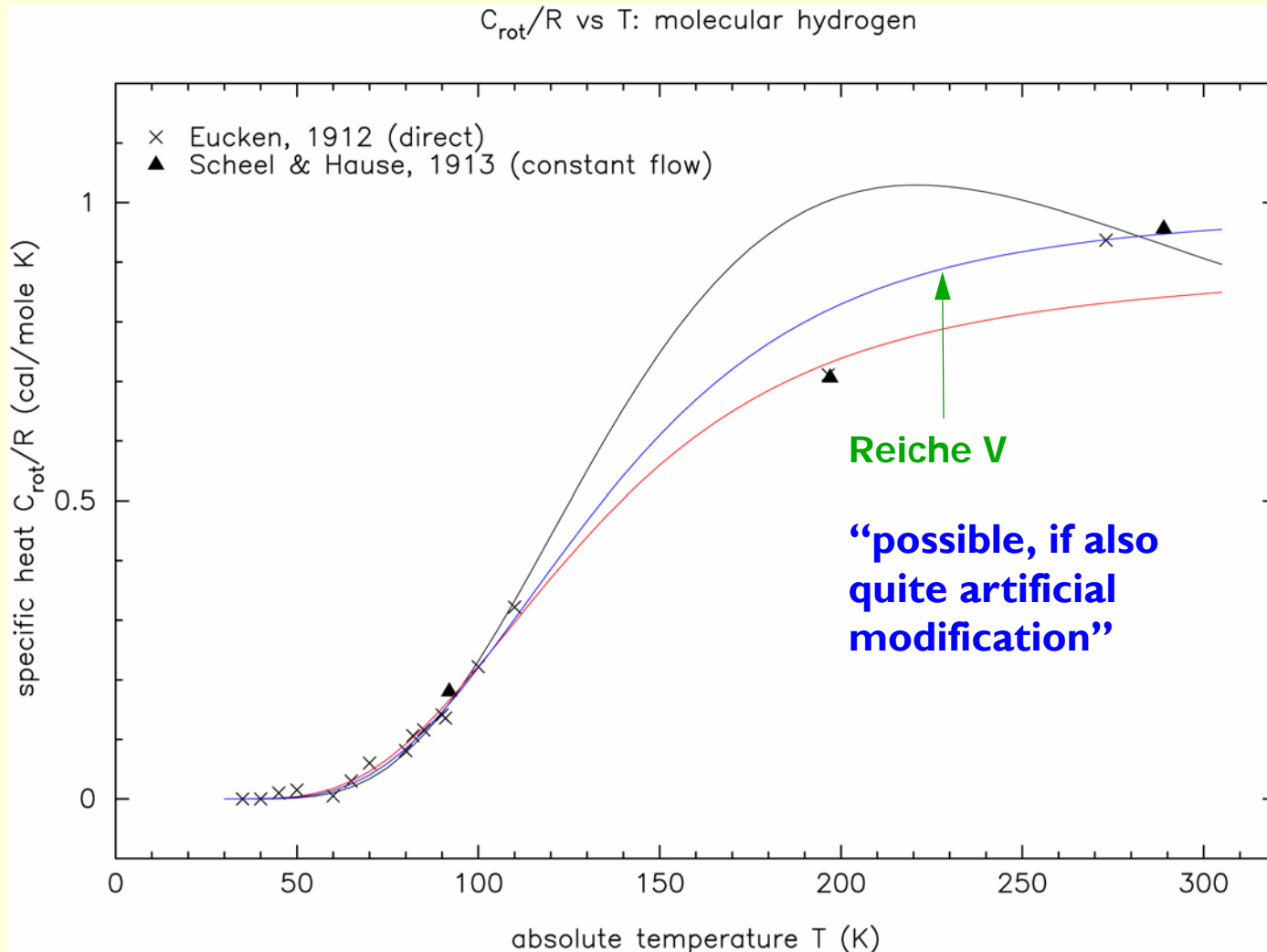
REICHE CURVE III

One might therefore make the hypothesis, that the rotationless state ... does not exist, that is, one forbids the quantum state $n = n_1 + n_2 = 0$



REICHE CURVE V

Consider a possible, if also quite artificial, modification. It consists therein, that one forbids not only the quantum state $n = n_1 + n_2 = 0$, but also all states for which $n_2 = 0$



This condition places a seemingly arbitrary restriction on the plane of rotation.

JOHN VAN VLECK AND ELMER HUTCHISSON

ON THE QUANTUM THEORY OF THE SPECIFIC HEAT OF HYDROGEN

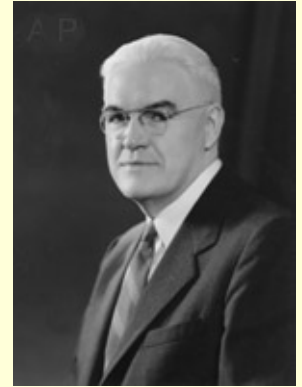
Physical Review, August 1926



John Van Vleck

Late in 1926, Van Vleck and Hutchisson (his first Ph.D. student at the University of Minnesota) published back-to-back articles in the *Physical Review*, summarizing the theoretical and experimental status of the specific heat of hydrogen:

... the quantum theory has been revolutionized by the new mechanics developed by Born, Heisenberg, Jordan, and Schrödinger.



Elmer Hutchisson

Unfortunately, an impossible specific heat curve is obtained ... from the simple theory of the rotator in the new mechanics....

We shall list below several specific ways of crawling out of the specific heat dilemma Most of the suggestions appear rather artificial and are frankly only conjectures ...

--Van Vleck 1926

HOW THE QUANTUM MECHANICAL EXPLANATION EMERGED IN 1926–1927

STAGES IN THE DISCOVERY OF THE QUANTUM MECHANICAL EXPLANATION

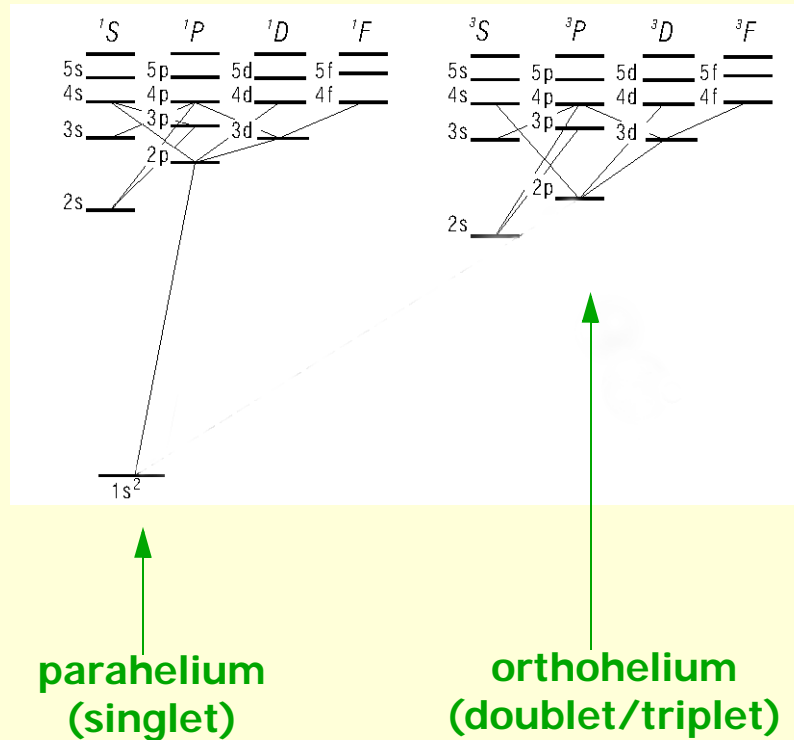
1. Werner Heisenberg discovered the implications of identical particles in the new quantum mechanics and applied these ideas successfully to the spectrum of helium. (June 1926)
2. Heisenberg (December 1926) and Friedrich Hund (February 1927) applied these ideas to molecular spectra, and Hund applied them (unsuccessfully) to the specific heat of hydrogen
3. In an experimental breakthrough in 1926–27, molecular spectroscopists saw for the first time transitions involving the ground state of molecular hydrogen, and as a result, accurately measured the **moment of inertia** in the ground state.

EXPERIMENTAL PHYSICS ALSO HAS A HISTORY

4. David Dennison, an American theorist from Michigan, combined all of these themes, and a few of his own, to come up with the modern theory. (May 1927)

All of these theorists, and a good many of the experimentalists, were at Bohr's institute in Copenhagen in 1926–1927, often citing each others preprints!

TERM DIAGRAM FOR HELIUM



Note that:

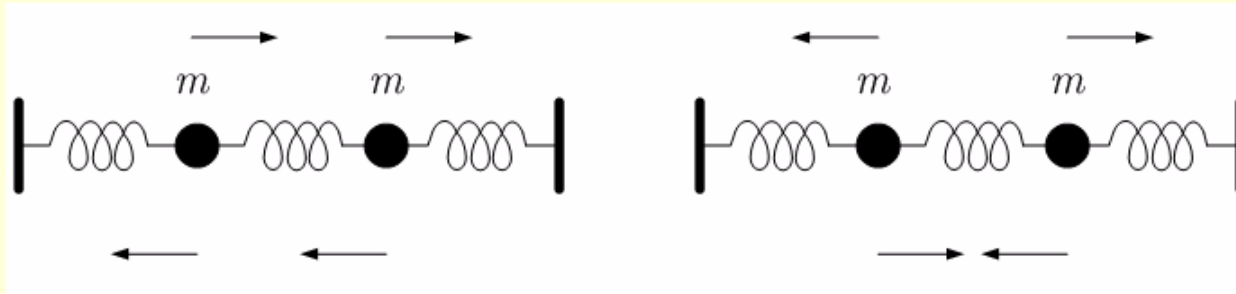
- para and ortho terms do **not** combine
- ortho terms are lower lying
- ground state missing for ortho

WERNER HEISENBERG, COUPLED OSCILLATORS, AND THE NON-COMBINING TERMS OF THE HELIUM SPECTRUM

MULTIPLE BODY PROBLEMS AND RESONANCE IN QUANTUM MECHANICS, JUNE 1926

Yes, I remember quite well this paper was also full of excitement for me because so many new things came up.

Heisenberg, AHQP interview, 1962

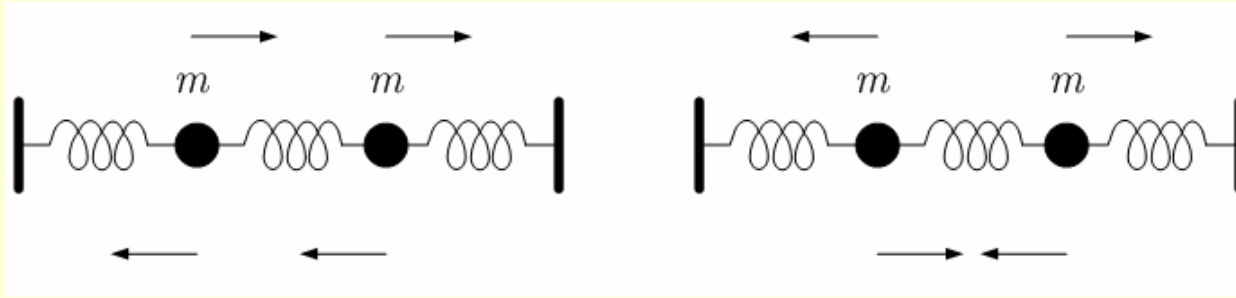


$$H = \frac{1}{2m} p_1^2 + \frac{m}{2} \omega^2 q_1^2 + \frac{1}{2m} p_2^2 + \frac{m}{2} \omega^2 q_2^2 + \lambda q_1 q_2$$

$$q_1' = \frac{1}{\sqrt{2}} (q_1 + q_2); \quad q_2' = \frac{1}{\sqrt{2}} (q_1 - q_2) \quad \text{normal modes}$$

$$H = \frac{1}{2m} p_1'^2 + \frac{m}{2} \omega_1'^2 q_1'^2 + \frac{1}{2m} p_2'^2 + \frac{m}{2} \omega_2'^2 q_2'^2$$

WERNER HEISENBERG, COUPLED OSCILLATORS, AND THE NON-COMBINING TERMS OF THE HELIUM SPECTRUM

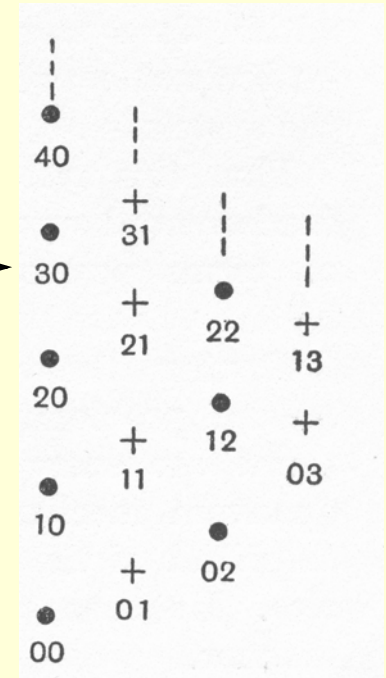


term diagram for quantized normal modes

$$H_{n'_1, n'_2} = \frac{\omega'_1 h}{2\pi} \left(n'_1 + \frac{1}{2} \right) + \frac{\omega'_2 h}{2\pi} \left(n'_2 + \frac{1}{2} \right)$$

quantized normal modes:

n'_1, n'_2 →



Heisenberg used a correspondence principle [!] argument to show that the • and + terms do not combine.

The non-existence of intercombinations is however tied to the original sameness [Gleichheit] of the coupled oscillators. ...

Are both term systems + and •, or only the one system • or + realized in nature?

HEISENBERG, MATRIX MECHANICS, AND THE NON-COMBINING TERMS OF THE HELIUM SPECTRUM

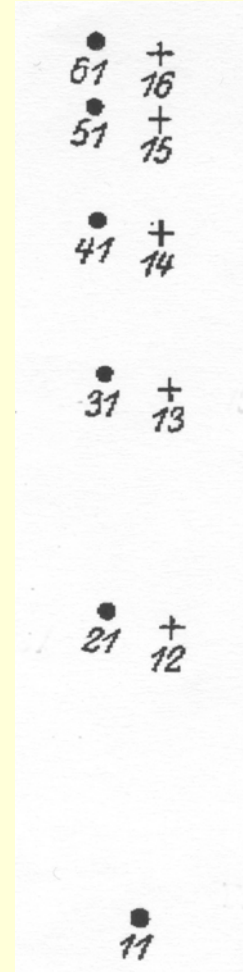
I would like to show that coupled systems in quantum mechanics always behave similarly to the above-explained example.

Heisenberg extended these ideas to quantum mechanics (both matrix and wave), and applied them to the two identical electrons in helium.

Result:

- two non-combining term series (para and ortho helium)
- either symmetric or antisymmetric wave functions (in Schrödinger's language)

The two term systems ... are para and ortho helium. Intercombinations between them are for the time being forbidden.



HEISENBERG, SPIN, AND THE NON-COMBINING TERMS OF THE HELIUM SPECTRUM

Heisenberg next introduced spin, and showed that there are four spin states, three symmetric and one antisymmetric. The combined space-spin states result in **two** complete (para and ortho) systems, + and •.

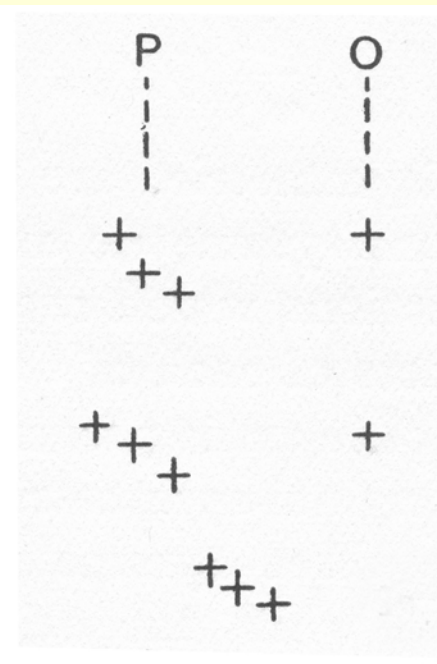
Weak intercombinations between para and ortho states are permitted **within** each system.

Which system (+ or •) exists in nature?

If only the one (•) of the two systems exists in nature, then ... Pauli's ban of equivalent orbits is ... automatically satisfied.



antisymmetric



symmetric

HEISENBERG AND MOLECULAR SPECTRA

MULTIPLE BODY PROBLEMS AND RESONANCE IN QUANTUM MECHANICS II, DECEMBER 1926

PROBLEM: Consider diatomic molecules with identical nuclei:

Molecular spectra show lines of *alternating* intensity (N_2^+ , 1924)

OLD QUANTUM THEORY had no satisfactory explanation; Heisenberg refers to “**notorious quarter quanta**” (Gerhard Dieke)

SOLUTION: **Connect the intensity alterations with a resonance in the nuclei.**

Heisenberg takes spin 1/2 nucleus **as an example**

$$\Psi_{\text{total}}^{\text{antisym}} = \begin{cases} \psi_{\text{rotational}}^{\text{even}} \psi_{\text{nuclear}}^{\text{odd}} & \text{para} \\ \psi_{\text{rotational}}^{\text{odd}} \psi_{\text{nuclear}}^{\text{even}} & \text{ortho} \end{cases} \quad (\text{ground state})$$

tentatively assumed the overall state is **antisymmetric**, in analogy to helium

ortho and para systems combine very weakly (similar to Helium singlet/triplet systems)

ortho states have greater statistical weight (nuclear triplet); hence spectroscopic transitions between ortho states are brighter

HEISENBERG, FRIEDRICH HUND, AND MOLECULAR SPECTRA

Heisenberg and his friend and colleague Friedrich Hund were both in Copenhagen in late 1926 and early 1927, and were talking to each other about these problems:

citation in Heisenberg, December 1926:

F. Hund, ZS f. Phys. (in press). I am indebted to Herr Hund for the opportunity to study this work before publication, and for many discussions of these problems.

Which term system exists in nature?

Heisenberg, December 1926

One will first of all think of the antisymmetric system, in order to make the analogy of the statistics of protons to electrons complete. But one cannot be certain which system is selected.

Heisenberg, December 1926

Friedrich Hund, February 1927

... one must assume a new property of the nucleus and further assume that only term systems symmetric in the nuclei appear. It thus shows a different behavior from two electrons.

Hund, February 1927

The choice determines which rotational states are more heavily weighted.

FRIEDRICH HUND AND THE SPECIFIC HEAT OF HYDROGEN

ON THE INTERPRETATION OF MOLECULAR SPECTRA II, FEBRUARY 1927



In this third of a groundbreaking series of papers on molecular spectra, Hund took over Heisenberg's formalism and extended it in great detail to molecules with identical nuclei.

Discussion of specific heat of hydrogen came at end.

An intensity alteration in the bands of the H_2 molecule is perhaps present, but it is not wholly certain. But we have yet another criterion, the behavior of the specific heat of hydrogen at low temperatures. ...

We will ... show that the empirical behavior of the specific heat of hydrogen is explained if one assumes that the [even] rotation states of the ground terms have an approximately doubled statistical weight. ...

$$Q = \beta \left(\sum_{m \text{ even}} (2m + 1) e^{-E_m/kT} \right) + \sum_{m \text{ odd}} (2m + 1) e^{-E_m/kT}$$

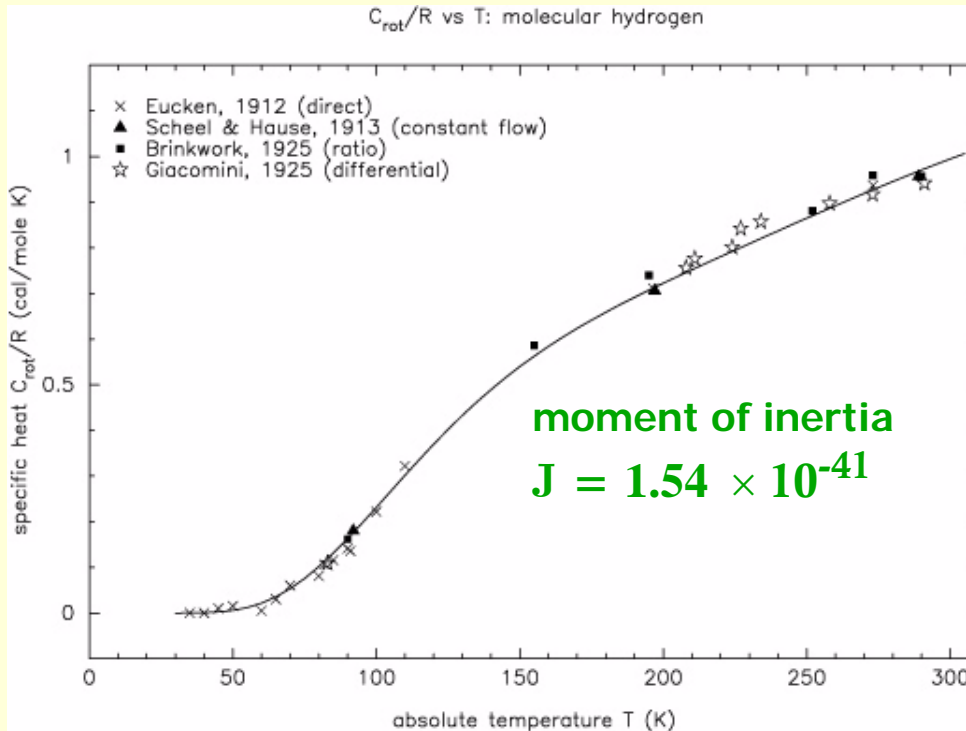
↑
nuclear spin weight

$\beta = 2$, the appropriate choice for a **symmetric** total wave function and **nuclear spin 1** (as Hund does NOT say!)

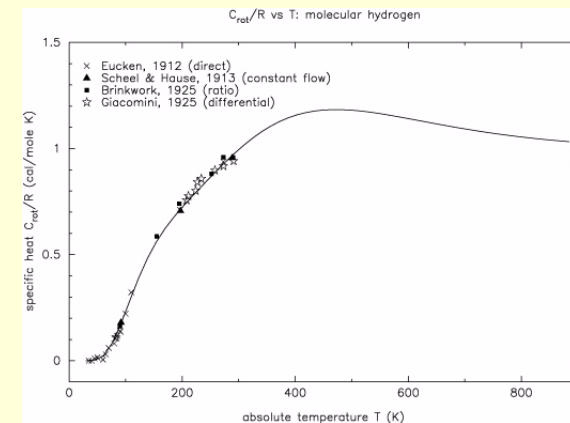
This choice of a symmetric term system was entirely empirical—no theoretical justification!

HUND AND THE SPECIFIC HEAT OF HYDROGEN

... the theoretical curve with $\beta = 2$ satisfactorily describes the empirical results.



Note the numerical value for the moment of inertia.



THE MOMENT OF INERTIA OF HYDROGEN BEFORE 1927:

The moment of inertia J is the only free parameter in the rigid rotator; chosen so that the theoretical curve lines up with the data at the lowest temperatures.

By early 1920s, spectroscopic measurements began to give independent values for the moment of inertia J .

J from specific heat of hydrogen	
	J (in gm-cm ²)
Reiche (1919)	2.2 to 2.3 $\times 10^{-41}$
Schrödinger (1924)	1.43 to 1.48 $\times 10^{-41}$
Van Vleck (1926)	2.0 to 3.0 $\times 10^{-41}$
Hund (1927)	1.54 $\times 10^{-41}$

J from molecular spectra	
	J (in gm-cm ²)
Lenz (1919)	1.85 $\times 10^{-41}$
Allen (1924)	1.5 to 1.8 $\times 10^{-41}$
Curtis (1925)	1.25 to 1.8 $\times 10^{-41}$

THIS ROUGH AGREEMENT WOULD BE SEEN AS SPURIOUS BY MID-1927.

MOLECULAR BAND SPECTRA AND MOMENTS OF INERTIA

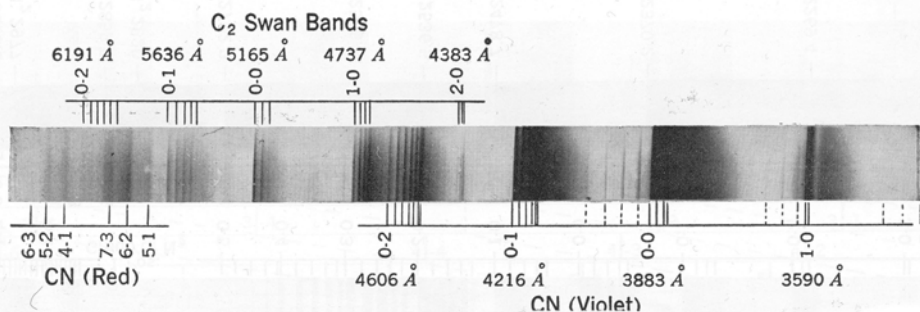
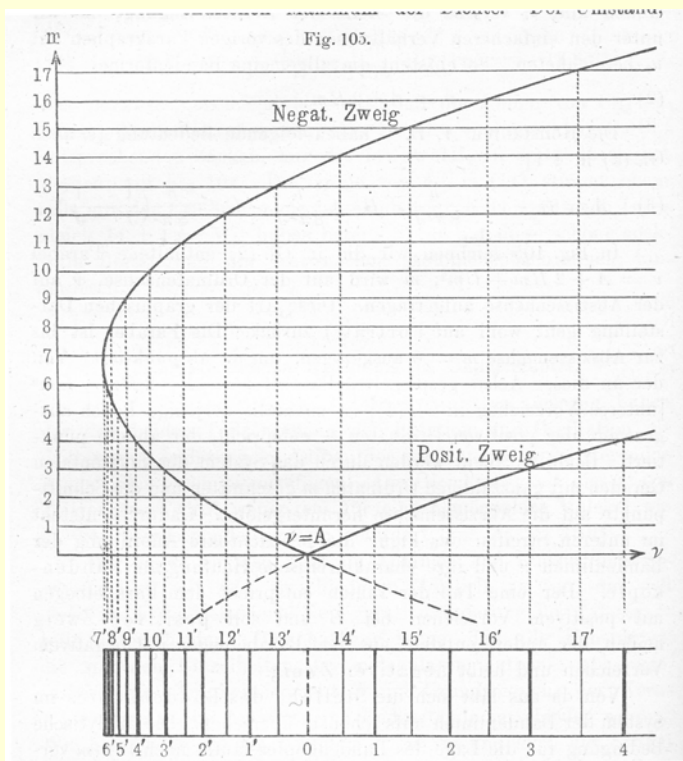
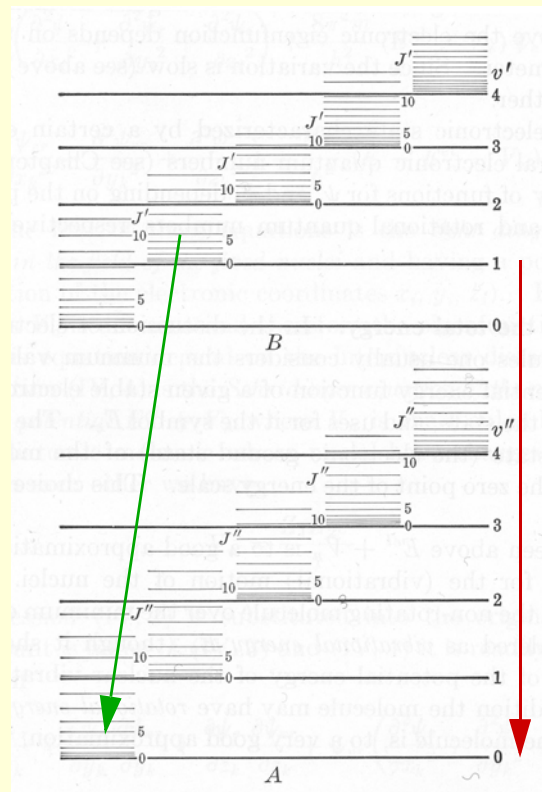


FIG. 7. Band Spectrum of the Carbon Arc in Air (Bands of the Molecules CN and C₂).



frequency

Each **band** represents a transition between specific *vibrational* levels in different electronic states.

Each band, under high resolution, consists of **lines** representing transitions among rotational states; line spacings allows the calculation of moments of inertia.

THE MANY-LINED SPECTRUM OF MOLECULAR HYDROGEN

- very complex—many hundreds of lines in visible and ultraviolet **emission** spectra
- no band heads (particularly in visible region); band structure not obvious
⇒ estimates of moments of inertia of hydrogen were difficult and uncertain; and
- say nothing about the moment of inertia in the ground state ... **since as is well known, none of these series appears in absorption.** (Schrödinger, 1924)

Worse yet: Transitions to the ground state should appear in the far ultraviolet:

- where as Theodore Lyman tells us: ... **the transparency of hydrogen [is] uncommonly great.** (Theodore Lyman, 1914)
- **vacuum** spectroscopy: air absorbs strongly in ultraviolet and so spectroscopes must be evacuated—adding another layer of experimental complexity!

A number of investigators are now working on the hydrogen spectrum ... but ... the conclusions of various investigators are very conflicting, even in regard to the most fundamental points...

Raymond Birge (NRC report, 1926)

JOHN JOSEPH HOPFIELD, GERHARD DIEKE, AND THE ABSORPTION BANDS OF MOLECULAR HYDROGEN SEPTEMBER 1926

John Joseph Hopfield and Gerhard Dieke, working at the University of California, were the first to see *absorption* bands (and hence the ground state) in molecular hydrogen.

Hopfield is doing the best vacuum spectroscopy of anyone in the world.

Raymond Birge to John Van Vleck, 1929

HOPFIELD, DIEKE, AND THE ULTRAVIOLET ABSORPTION BANDS OF MOLECULAR HYDROGEN

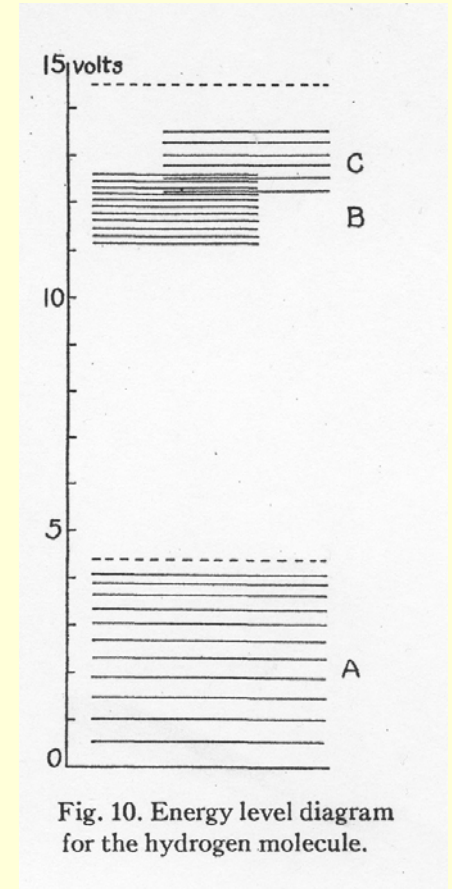
Dieke and Hopfield in September 1926:

- measured and identified bands in the extreme ultraviolet in both absorption and emission;
- organized bands into “systems” that corresponded to transitions between the ground state (A) and two excited electronic states (B and C); and
- inferred an energy level diagram.

Published at about the same time (1926):

- Lyman bands (subset of $B \rightarrow A$, **emission**)
- Werner Bands ($C \rightarrow A$), **emission**; (Sven Werner, working at Niels Bohr’s Institute of Theoretical Physics in **Copenhagen**)

Upshot: By late 1926, the vibrational structure of the ground state A and the excited states B and C was well understood. The rotational structure was still largely unanalyzed.



Dieke-Hopfield term diagram: Lines represent vibrational levels in each electronic state

EXPERIMENTAL SPECTROSCOPY IN COPENHAGEN



... the *Carlsberg Foundation* has made available to me a considerable sum of money for the construction and installation of a large *grating spectrograph*.

Niels Bohr, 1921

Dear Professor N. Bohr,

Allow me to give a brief account of my education up to the present and express my ardent wishes that I entertain now.

... I am sent by the Japanese government to Europe for the furtherance of my study.

Since I am specially interested in spectroscopy, ... I am naturally attracted to your laboratory ...

Takeo Hori (in Berlin) to Bohr, 9 May 1926

I am almost beside myself with joy to have received your letter, in which you have kindly permitted me to work in your laboratory ...

Hori to Bohr, 21 May 1926

TAKEO HORI AND THE MOMENT OF INERTIA OF HYDROGEN

Last year Werner has found a new band system for hydrogen in the extreme ultraviolet ... At the suggestion of Professor Bohr I have carried on the investigation of these bands ...

While the work was in progress, an important work by Dieke and Hopfield appeared
Hori, July 1927

Hori remeasured and reanalyzed Werner bands (Dieke & Hopfield's C → A)

Hori reanalyzed Lyman bands (subset of Dieke & Hopfield's B → A)

Dieke & Hopfield: ground state, vibrational energy levels, term diagram

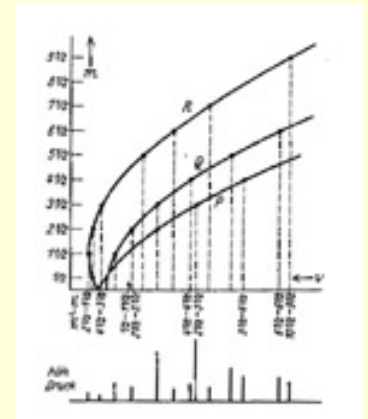
Result: Hori gave the first detailed analysis of the rotational structure of the H₂ ultraviolet bands, and found

$$J = 4.67 \times 10^{-41} \text{ gm-cm}^2$$

more than **triple** Hund's value; and exactly the value that David Dennison would need for his specific heat model.

I would like to thank Prof. N. Bohr ... To Dr. S. Werner I owe special thanks for unhesitating assistance and valuable advice. Likewise I also thank Dr. Dennison, Dr. Fues, Dr. Hund, and Dr. Nishina for much useful advice.

Hori 1927



HORI, HUND, AND ALTERNATING INTENSITIES

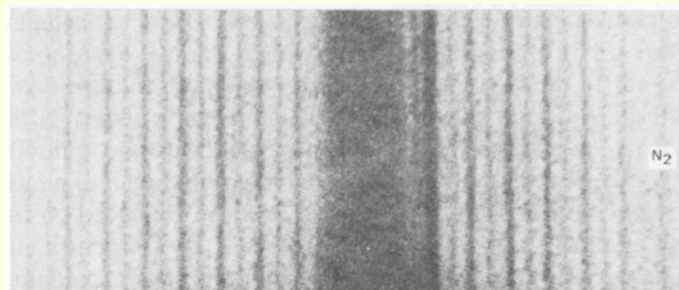
The term systems of the H_2 molecule given by Dieke and Hopfield, in combination with an analysis of the band structure, which Hori has carried out with the bands of Werner and Witmer, have not yet been brought into agreement with the theoretical statements made here.

Hund 1927

[Hund] obtains $\beta = 2$, that is, the [even] rotational states of the ground term have approximately doubled statistical weight, as the [odd] rotational states. This does not agree with the result obtained from the analysis of the bands, which makes it necessary to adopt a value $\beta < 1$.

Hori 1927

Recall that Hund's choice ($\beta = 2$) implied that transitions between **symmetric** rotational states should be brighter; Hori's observations showed transitions between **antisymmetric** rotational states ($\beta < 1$) are brighter.



alternating intensities
in spectrum of N_2

DAVID DENNISON AND THE SPECIFIC HEAT OF HYDROGEN



- 1924: Ph.D. at University of Michigan (on structure and infra-red spectrum of methane; first theoretical thesis there!)
 - supervised by Walter Colby and Oscar Klein
- Bohr visited Michigan late in 1923; visit resulted in invitation for Dennison to come to Copenhagen:

At this time it was decided I would go to Copenhagen. Just how I was to go, this was another question. But I was absolutely positive I was going. There was just no question.

And on learning that one fellowship required him to remain in the U.S.,

So I wrote and told them to go roll a hoop.

Dennison, AHQP interview, 1964

Travels in Europe

Copenhagen: late summer 1924 to spring 1926

Summer 1926: back in Michigan

Zürich: fall 1926 (Schrödinger)

Münich: January, early February 1927

Copenhagen again: late February, March 1927

Cambridge: spring 1927 (Fowler)

Leiden: early summer 1927 (Ehrenfest)

DENNISON AND THE NEW QUANTUM MECHANICS

1926: The Rotation of Molecules (submitted to the *Physical Review* from Copenhagen, April 1926) — treated both rigid and symmetric rotators.

Dennison was fond of pointing out that it was **“the first article on matrix mechanics to appear in the *Physical Review*.”**

Also continued work in molecular spectra. And he had been thinking about the specific heat of hydrogen—Heisenberg later recalled talking to him about it.

Oh yes, I certainly had thought about the specific heat much earlier, and how it would be related to the spectra and to the moment of inertia.

... it was a problem I was thinking about ... some came out and some didn't, and this was one that hadn't come through.

Dennison, AHQP interview, 1964

Fall 1926 found Dennison in Zürich (with Schrödinger), and continuing to think about the specific heat of hydrogen in a letter to *Nature* (at about same time as Heisenberg's December 1926 paper). By now he was using the language of wave functions.

DENNISON IN ZÜRICH

WAVE MECHANICS AND THE ROTATION OF HOMOPOLAR MOLECULES

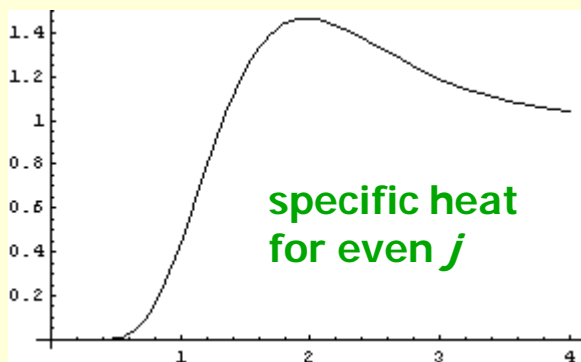
NATURE, DECEMBER 1926

... a new postulate, ... that ... $\Phi \psi$ rather than ψ alone shall be a regular single-valued function. ... the function $\Phi \psi$ seems to represent the electrical density, whereas the function ψ alone has no such physical meaning. ... we are led to two independent solutions

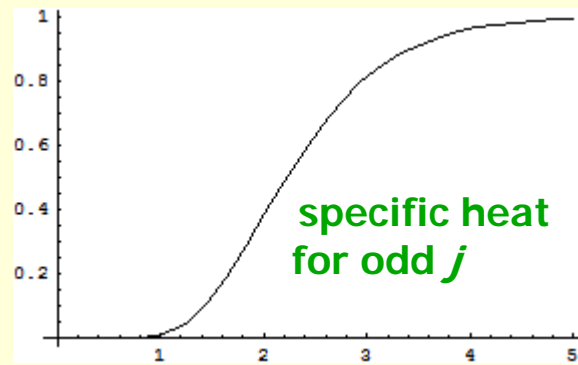
$$\left. \begin{array}{l} (3) \quad j = 0, 2, 4, \dots \\ (3') \quad j = 1, 3, 5, \dots \end{array} \right\} E = \frac{h^2}{8\pi^2 I} (j^2 + j) \quad \begin{array}{l} \text{odd and even} \\ \text{rotational states} \end{array}$$

These solutions, which are complete in themselves and admit no intercombinations, seem to correspond respectively to the symmetrical and antisymmetrical solutions found by Dirac and Heisenberg ...

Dennison noted that even j led to an impossible graph; odd j seemed more plausible.



SEPARATE
plots for
odd and
even j



I hope to publish in the near future a more detailed paper covering the calculations.

DENNISON IN ZÜRICH

I was delighted by your letter to Nature. ... I should love to have in advance an account of your discussion of the sp ht of H₂. ...

Won't you come for a visit to Cambridge on your way back to the states, or when you leave Zurich?

Ralph Fowler to Dennison, 27 February 1927

DENNISON IN CAMBRIDGE

ON BEING PREPARED FOR CLASS : MAY 1927

While I was in Cambridge, Fowler asked me to give three lectures to his graduate class. ... I could see that I was running out of material for the third lecture ... and it occurred to me to take another crack at the problem of the specific heat of hydrogen.

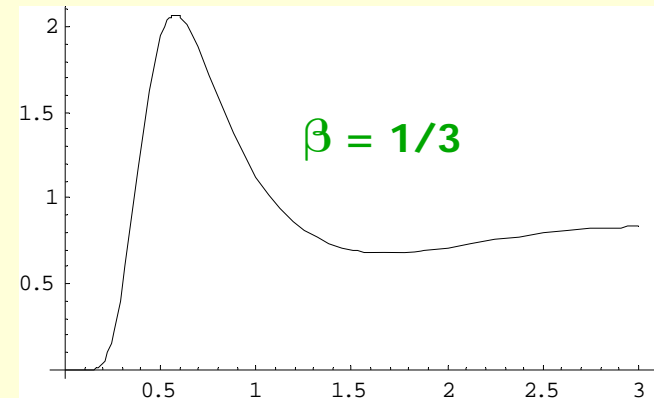
Dennison 1974

By this time, Dennison had read Heisenberg's December 1926 and Hund's February 1927 papers, and was familiar with Hori's as yet unpublished results:

- nuclear spin allows odd and even rotational states to combine weakly
- Hori: H₂ spectra clearly show alternating intensities

Dennison pointed out that

- Hori's value for J rules out Hund's $\beta = 2$ specific heat curve;
- Hori's alternating intensities imply $\beta \approx 1/3$ and lead to an impossible specific heat curve



**AS LONG AS PARA AND ORTHO TERMS COULD COMBINE,
NO VALUE OF HUND'S β WOULD WORK!**

DENNISON IN CAMBRIDGE

THE SOLUTION TO THE SPECIFIC HEAT OF HYDROGEN

Let us make the assumption that the time of transition between a state symmetrical in the rotation, and an antisymmetrical state is very long compared with the time in which the experiments are made. ...

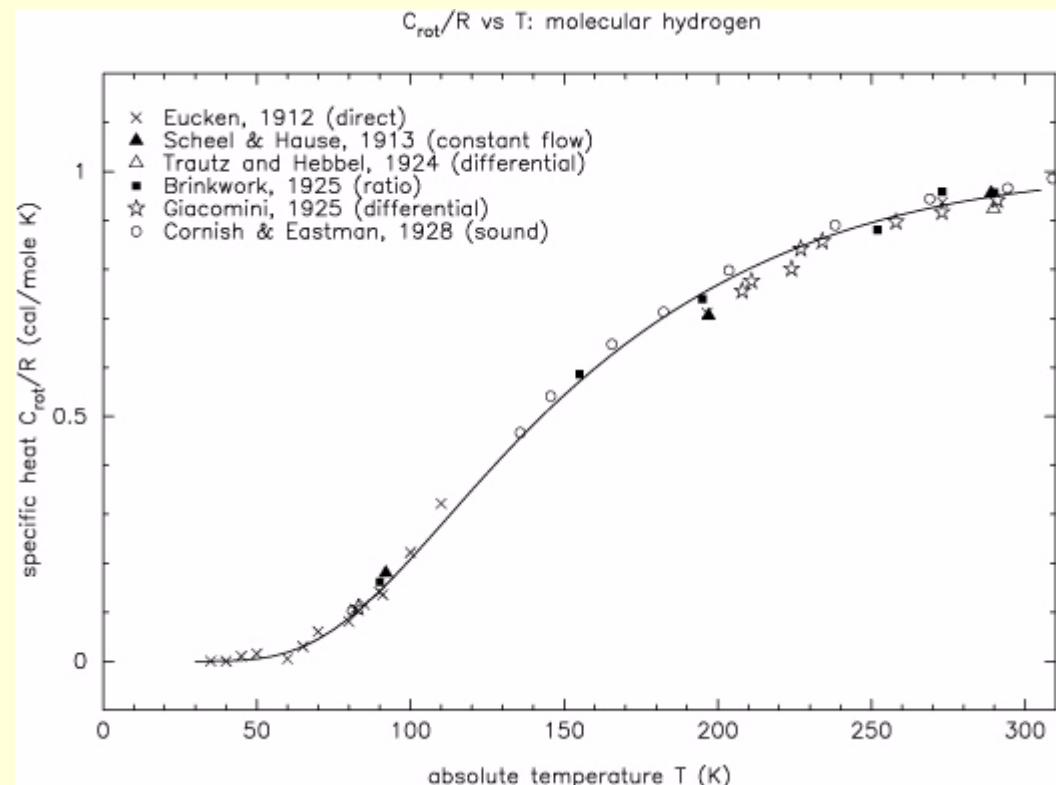
... we obtain a specific heat curve which follows the observed curve to within the errors of observation, and that moreover the constants ... are in good agreement with the values ... found in the band spectrum of H_2 .

Added in proof (at Bohr's suggestion)

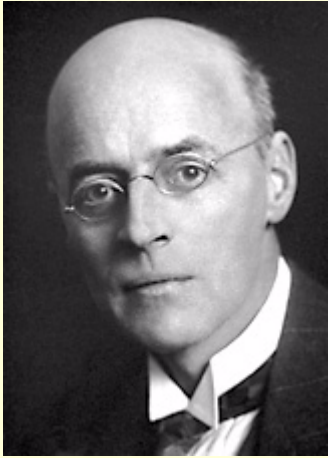
... the ratio of 3 to 1 of the antisymmetrical and symmetrical modifications of hydrogen ... is just what is to be expected if the nuclear spin is taken equal to that of the electron, and only the complete antisymmetrical solution of the Schrödinger wave equation allowed.

Somehow this point had seemed so obvious to me that it had not seemed worth belaboring.

Dennison 1974



THE IMPORTANCE OF BEING IN COPENHAGEN



In 1924, Owen Richardson (Nobel Prize 1928, for thermionic emission) published the first in a long series of papers on the many-lined spectrum of hydrogen, primarily in the visible.

Richardson's work eventually led to a fuller understanding and integration of the visible and ultraviolet spectrum of molecular hydrogen, eventually collected in his 1932 book *Molecular Hydrogen and its Spectrum*.

In late 1926 and early 1927, drawing on his own work in the visible, and on Werner, Witmer, and Dieke and Hopfield, he used an indirect method to estimate the moment of inertia of a hydrogen molecule in the ground state, and found a result about the same as Hori found later in 1927.

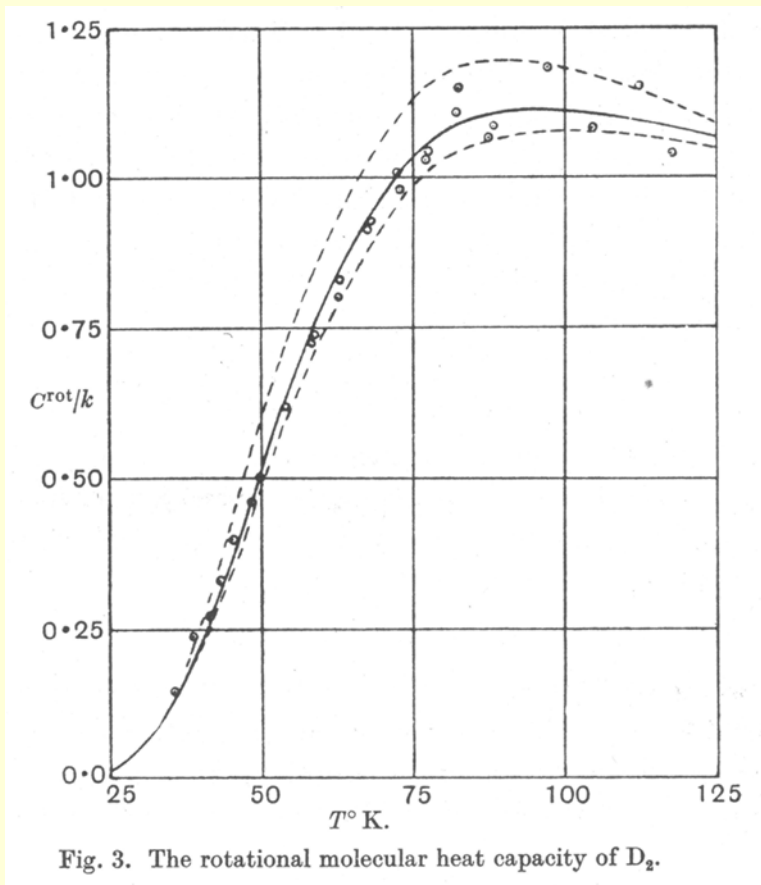
Nevertheless, Hori's result for the moment of inertia is almost exclusively cited. Richardson seemed a little put out. In his book he spent several pages describing his own results, and concluded dryly that

Hori's value ..., got from his analysis of the Werner and Lyman bands, was also published about the same time.

Richardson, 1932

LATER EXPERIMENTAL DEVELOPMENTS

experimental work continued through 1930s (Eucken, Paul Harteck, Karl Clusius, Ernst Bartholomé, and others) and included measurements of the specific heat of HD and D_2



from Fowler & Guggenheim,
Statistical Thermodynamics, 1939

A FEW REFERENCES

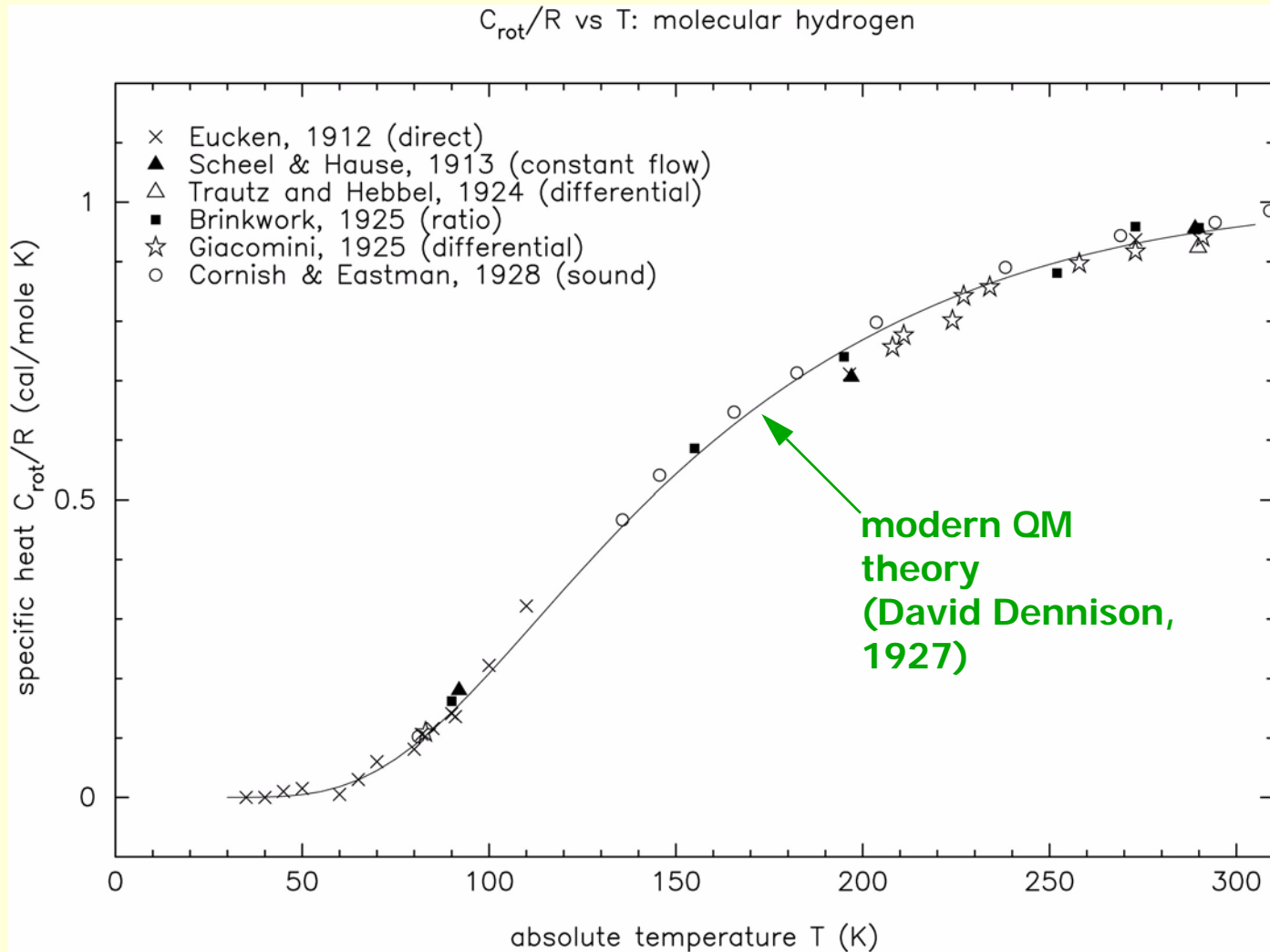
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THEORY AND EXPERIMENT BY THE LATE 1920S



MODERN QUANTUM MECHANICS (DAVID DENNISON, 1927)

Consider a hydrogen molecule (rigid rotator —two degrees of freedom)

$$E_n = n(n+1) \frac{h^2}{8\pi^2 J}, \quad n = 0, 1, 2 \dots$$

- The two nuclei (protons) are **identical fermions** (spin 1/2)
- total nuclear spin/rotational wave function must be **anti-symmetric**

? There are therefore **two varieties** of molecular hydrogen:

PARAHYDROGEN

- singlet nuclear state (anti-symmetric) / symmetric rotational state (n even)

ORTHOHYDROGEN

- triplet nuclear state (symmetric) / antisymmetric rotational state (n odd)

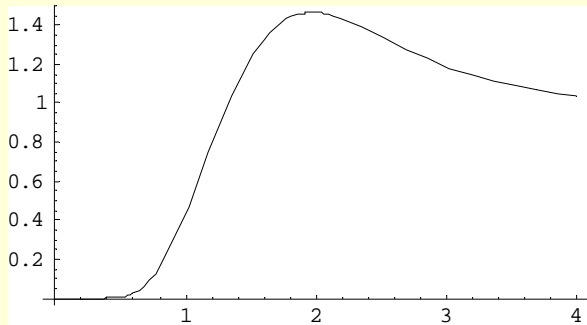
ORTHOHYDROGEN / PARAHYDROGEN TRANSITION IS SLOW

MODERN QUANTUM MECHANICS (DAVID DENNISON, 1927)

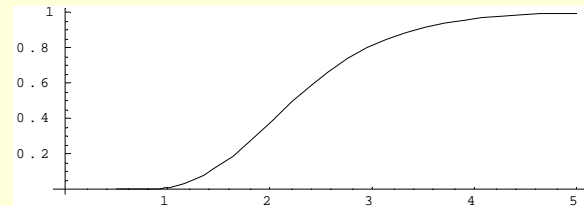
To calculate the specific heat of molecular hydrogen:

Treat hydrogen as a mixture of para- and orthohydrogen, in the ratio 1:3 (room temperature ratio for spin 1/2 fermions).

specific heats of para- and orthohydrogen are quite different at low temperatures



parahydrogen



orthohydrogen

If one combines these two curves in the ratio 1 part para to 3 parts ortho, one obtains a smoothly decreasing curve that agrees well with experiment.