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Abstract

Title: David Dennison, the specific heat of hydrogen, and the discovery of nuclear spin

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The specific heat of hydrogen gas at low temperatures, first measured by Arnold Eucken in 1912, decreases sharply as the two rotational degrees of freedom freeze out. The “old quantum theory” could never account for this behavior quantitatively, despite persistent efforts—I have talked about aspects of this history at HQ-0 and HQ-1. Even in the early days of the new quantum mechanics, John Van Vleck, in a long and insightful 1926 review article, concluded that arbitrary assumptions were needed to get even reasonable agreement with the specific heat data. But by June 1927, a surprising combination of theoretical and experimental developments enabled the American physicist David Dennison to formulate a quantitatively accurate theory.

In a series of three papers in 1926–27, Werner Heisenberg showed that in the new quantum mechanics, identical particles displayed a “resonance phenomenon” that implied either symmetric or antisymmetric wave functions under exchange. Heisenberg employed this concept together with electron spin to explain the division of the helium spectrum into two non-combining term series (para- and orthohelium). For helium, he chose an anti-symmetric wavefunction to ensure agreement with Pauli's new “prohibition of equivalent orbits.” Heisenberg speculated that a similar analysis might explain the recent discovery of rotational lines of alternating intensity in the rotational spectra of diatomic molecules with identical nuclei.

Friedrich Hund applied these ideas both to molecular spectra and to the rotational specific heat of hydrogen. However, he concluded that the wave function of the hydrogen nuclei should be symmetric under exchange, probably because this assumption led to seemingly satisfactory agreement with the specific heat data, and to a value for the moment of inertia that was consistent with earlier estimates.

The analysis of molecular band spectra can yield moments of inertia. However, the “many-lined spectrum” of molecular hydrogen had long been a puzzle. In the visible range, the lines are not easily identified as bands, and at least by the mid 1920s, it had become clear that none of the visible lines involved the ground state. An experimental breakthrough came in 1926, when for the first time, John Joseph Hopfield and Gerhard Dieke found absorption bands in molecular hydrogen in the far ultraviolet, and hence could identify transitions involving the ground state. Sven Werner, an experimental spectroscopist at Bohr's institute in Copenhagen, identified one set of these transitions in emission at about the same time. Further measurements in Copenhagen by the Japanese spectroscopist Takeo Hori, at the suggestion of Niels Bohr, led to a moment of inertia for molecular hydrogen more than double earlier estimates. Using this result and a remarkable theoretical argument that postulated non-combining odd and even rotational states, David Dennison devised the modern theory for the specific heat of hydrogen in 1927, and in the process, found persuasive evidence for proton spin. Heisenberg, Hund, Dennison, Werner, and Hori were all at Bohr's institute in Copenhagen in 1926–27; their interactions play a central role in this story.