

A Paramount Problem Solved at Last: Paramagnetic Catalysis of Ortho-Para Hydrogen Conversion

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To the extent that science is about connections, often interdisciplinary, among seemingly disjointed findings, solving the long-standing puzzle posed by the interconversion of molecular hydrogen's allotropic modifications is paramount. Its pieces include the foundations of quantum mechanics, spectroscopy, molecular reaction dynamics, catalysis, nuclear magnetic resonance (NMR), and magnetic resonance imaging (MRI), to name some. The multi- and interdisciplinary effort made to grasp and utilize the ortho-para hydrogen conversion has thus been outstanding in both its intellectual scope and practical impact. However, it is only now, eighty-seven years after its direct experimental demonstration, that the efficient, paramagnetically catalyzed, ortho-para conversion has been fully and quantitatively understood, see the research paper by Xia Zhang, Tijs Karman, Gerrit Groenenboom, and Ad van der Avoird.¹

The saga began in 1927 when Werner Heisenberg² and Friedrich Hund,³ prompted by the then mysterious line intensity alternations observed in the spectra of homonuclear diatomic molecules,^{4,5} inferred from quantum mechanical principles* the existence of two allotropic modifications of molecular hydrogen: ortho (parallel proton spins, odd-J rotational levels) and para (antiparallel proton spins, even-J rotational levels). In the same year, David M. Dennison⁶ invoked the allotropic modifications of H₂ to explain the residual heat capacity of hydrogen gas at low temperatures as due to ortho-H₂. The anomalous behavior of molecular hydrogen's heat capacity was first observed by Arnold

* This inference was deemed important enough to include in Heisenberg's Nobel citation, which reads "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen" <https://www.nobelprize.org/prizes/physics/1932/summary/#:~:text=The%20Nobel%20Prize%20in%20Physics%201932%20was%20awarded,his%20Nobel%20Prize%20one%20year%20later%2C%20in%201933.>

Eucken⁷ in 1912 and tackled, in vain, by Albert Einstein and Otto Stern⁸ in terms of translational zero-point energy in 1913.

Karl Friedrich Bonhoeffer and Michael Polanyi at Fritz Haber's Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry⁹ took Heisenberg's and Hund's inference literally and undertook, together with their coworkers, a search for molecular hydrogen in either of the two presumed allotropic forms.

Bonhoeffer, together with Paul Harteck (later joined by Adalbert and Ladislaus Farkas as well as Erika Cremer), succeeded in 1928-29 to enrich the allotropic mixture of gaseous hydrogen with para-hydrogen (that admits $J=0$) by resorting to cryogenic temperatures and a charcoal catalyst.¹⁰ The enrichment was detected by non-spectroscopic means, namely by observing the vanishing heat capacity of the resultant gas. This was done by measuring the heat conductance of the gas, which is proportional to heat capacity, but experimentally more easily accessible.

But which molecular mechanism was responsible for the ortho-para interconversion of hydrogen? In order to answer this question, Polanyi, jointly with his mutually "trusting but critical" team¹¹ of young theorists, which included Eugene Wigner, Fritz London, and Henry Eyring, launched an all-out theoretical effort. This effort resulted in laying down the foundations of chemical kinetics consistent with quantum theory and foreshadowed chemical reaction dynamics.

In their landmark 1931 paper,¹² Eyring and Polanyi investigated the simplest chemical exchange reaction, $H + H_2 \rightleftharpoons H_2 + H$, which Adalbert Farkas had posited as the mechanism for the interconversion of ortho and para hydrogen. As noted by Francois Lique, one of the referees of the paper highlighted herein, this is also the dominant mechanism that accounts for the ortho-to-para- H_2 ratio observed in interstellar clouds.¹³

Eyring and Polanyi's paper established a visual metaphor for looking at the process of making and breaking of chemical bonds: a marble, representing the configuration of the constituent atoms' nuclei, rolls on the potential energy surface, given by the eigenenergy of the atoms' electrons. En route from the valley of the reactants to the valley of the products, the marble follows a path restricted by the reaction's energy disposal. This view of the reaction entails a separation of the nuclear and electronic motions, known today as the Born-Oppenheimer

approximation, a quantum treatment of the electronic subsystem and a classical treatment of the nuclei. London's, Eyring's, and Polanyi's construction of a potential energy surface as exemplified by that of the H_3 system breathed new life into Svante Arrhenius's 1889 concept of activation energy, by reinterpreting it as the summit-to-be-conquered between the electronic eigenenergy valleys of the reactants and products.¹⁴ The rate at which the marble makes its transit over the summit – and hence the reaction rate – was evaluated in 1932 in Polanyi's group by Hans Pelzer and Wigner.¹⁵ This was the first take on the “transition-state” or “activated complex” theory of chemical reactions, which would be developed, respectively, by Eyring and Polanyi in 1935, and later refined by others.

The investigation of the mechanism of the ortho-para hydrogen conversion took a new turn when in 1933, with the sword of Nazism hanging over them,[†] Ladislaus Farkas and Hans Sachsse examined the role of paramagnetic species (molecules and ions) as efficacious homogeneous catalysts of the conversion process.^{16,17} In a back-to-back paper,¹⁸ Wigner provided a tentative explanation of the catalytic effect by invoking the magnetic dipole-dipole interaction between the electronic spin of the oxygen molecule in its triplet electronic ground-state ($\text{X } ^3\Sigma_g^-$) with the nuclear spins of the two hydrogen atoms. For most geometries of mutual approach, the electronic spin of O_2 would generate an inhomogeneous magnetic field that is different at the two protons of the hydrogen molecule. This inhomogeneity would then in effect make the two protons nonequivalent, whereby the symmetry selection rule that governs the interchange of identical particles would be relaxed and the protons allowed to flip their spins. Wigner's underestimation of the observed catalytic effect prompted a revision of his model fifty-three and sixty-two years later, when Ilisca and Sugano¹⁹ and Minaev and Ågren,²⁰ respectively, invoked an additional interaction that arises in O_2 ($\text{X } ^3\Sigma_g^-$) + H_2 ($\text{X } ^1\Sigma_g^+$) collisions. These authors realized that the approach of the paramagnetic oxygen molecule will induce an electronic spin magnetic moment in the hydrogen molecule by mixing its singlet

[†] Immanuel Estermann used the phrase “the sword of Nazism hanging over our heads” in reference to the race against time as he, like Farkas and Sachsse, was finalizing his work before being banned from the laboratory by the Nazi racial laws. I. Estermann: *History of molecular beam research: Personal reminiscences of the important evolutionary period 1919-1933*, J. Am. Phys. 43, 661-671 (1975).

ground state ($X\ ^1\Sigma_g^+$) with its first electronically excited triplet state ($a\ ^3\Sigma_u^+$). The magnetic moment thereby induced would then interact *within* the hydrogen molecule with its two protons via the Fermi contact interaction and introduce a coupling between them. The coupling between the two protons would then, again, enable spin flips.

We note that the interest in understanding the paramagnetically catalyzed ortho-para hydrogen conversion was rekindled in connection with the application of enhancement methods such as para-hydrogen induced polarization (PHIP) in NMR and MRI: the conversion of the effective para- H_2 to the ineffective ortho- H_2 by the ubiquitous molecular oxygen amounts to a detrimental effect that has to be avoided. This point was addressed by another referee of the paper highlighted herein.

The latest word on the oxygen-catalyzed ortho-para hydrogen conversion,¹ which may well be the last, implements both the dipole-dipole and the Fermi contact interactions in a tour-de-force study that combines ab initio calculations of these interactions with a quantum, coupled-channel (CC), treatment of the rotationally inelastic $H_2 + O_2$ collisions. The latter had been studied previously in conjunction with crossed-beam experiments that corroborated the treatment’s accuracy.^{21,22,23,24} We note that in the quantum treatment, the collision is visualized not by a “marble” but by a wave scattered by the potential energy surface. Given that the ortho-para hydrogen conversion cross-sections corresponding to transitions between rotational states of para- H_2 with even J and of ortho- H_2 with odd J (or vice-versa) are about twelve orders of magnitude smaller than the rotationally inelastic cross sections that preserve the ortho or para modifications of H_2 , no ortho-para conversion was observed in the scattering experiments, cf. Fig. 10 of Ref.²¹. Likewise, the CC scattering calculations were bound to miss out on the ortho-para conversion, as the magnetic couplings that drive it were not included. However, inclusion of the couplings in the channel bases would render the CC calculations of the complete problem unfeasible. In order to make the calculations of the scattering cross-sections for the ortho-para conversion workable yet accurate, Zhang et al. resorted to the Distorted Wave Born Approximation (DWBA) with the nearly exact CC wavefunctions as the undistorted basis functions. This approach was well justified by the disparity (twelve orders of magnitude, as noted above), between the coupling strength driving the rotational transitions on the one hand and the magnetic dipole-dipole and Fermi contact interactions on the other.

The scattering cross-sections for the ortho-para conversion could then be accurately obtained as sums of the squared matrix elements of the magnetic dipole-dipole and Fermi contact operators in the undistorted CC basis. Applied to all initial rotational states populated at a given temperature, this procedure yielded the ortho-para conversion cross-sections needed for evaluating the temperature dependence of the ortho-para conversion rates. This very dependence was measured in the 1933 experiments by Farkas and Sachsse.¹⁶

A sampling of the cross-sections as a function of the collision energy is shown in Fig. 2 of Ref.¹. These exhibit a threshold behavior – at collision energies corresponding to the excitation energies of given state-to-state channels. Fig. 4 of Ref.¹ attests to a good agreement between the ortho-para conversion rate calculated by Zhang et al. with a recent data point by Wagner²⁵ and with the rate's temperature dependence as obtained by Farkas and Sachsse.¹⁶ This agreement resolves the issue of the relative contributions of the magnetic dipole-dipole and the Fermi contact interactions: they come out about the same, in stark contrast to the earlier estimates presented in Refs.^{18,19,20}. While the first did not consider the Fermi contact interaction at all, the latter two overestimated its relative contribution by orders of magnitude. Thus, the highlighted paper by Zhang et al. solved at last a problem that had been awaiting solution for nearly ninety years.

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