

THE HFS OF H_2^+ : ELECTRON-NUCLEAR COUPLING OF SPINS AND MOMENTA

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Progress in calculations on the hyperfine structure (hfs) of the hydrogen molecular ion is summarized taking a long view with emphases on Alex Dalgarno's contributions and also on some recent developments.

1. Motivation

One of the most precisely measured physical quantities is the hyperfine transition frequency 1 420 405.751 766 7(10) kHz of the energy splitting of the $1S_{1/2}$ state of the hydrogen atom, where the quantity in parentheses is the corresponding total error, ± 1 mHz, based on an extrapolation to a maser bulb of infinite size.¹ The corresponding precision of the sum of the theoretically calculated terms is about 1 kHz and further precision will depend on future progress in calculations of proton structure dependent terms.²⁻⁴

For the hydrogen molecular ion H_2^+ progress in the theory of the hyperfine structure (hfs) has only this year (2009) achieved⁵ the level of precision better than 10 kHz. In this short paper, I discuss how Alex Dalgarno's attention has nurtured progress through a few well-timed studies over a time span of almost four decades.

In describing the hfs of the atom, the simple Fermi contact formula based on the interaction between the electron and the proton magnetic moments and taking account of the proton-electron reduced mass gives about 1 420.5 MHz, and inclusion of QED non-recoil terms³ get the theoretical value to within 45 kHz of the experimental value. Mass scaling in the Fermi contact term indicates that over 1 MHz of the H atom hfs is attributable to the reduced mass between the proton and the electron and a similar

contribution can be expected for H_2^+ .

Nevertheless, as of the late 70's, theoretical calculations for ortho- H_2^+ in the $N = 1$ rotational state still overestimated the Fermi contact term compared to experiment by ⁶ 400 kHz. This discrepancy indicated that the treatment of reduced mass effects was not complete.

2. An introduction to the early oeuvre

When I started at ITAMP, Alex and I were able to build a collaboration through our shared interests in the study of the long-range interactions between an electron and an ion. I had worked with Larry Spruch at New York University on their applications to the Rydberg states of the He atom. We decided to look at the descriptions of the Rydberg states of the hydrogen molecule, which were being studied experimentally by Steve Lundeen and associates.⁷ It was clear that ultimately so-called non-adiabatic effects (non-local coupling of electron and nuclear wave functions through momenta) would have to be addressed.^{8,9} Within a week of my arrival, Alex had already generously shared his folder on H_2^+ , containing papers he had accumulated in anticipation of some sort of investigation.

Our project benefited from the resources and visitors to the Institute. For example, Professor Yuri Demkov visited and shared of his findings of exact solutions for certain high nuclear charge one electron diatomic molecular ions.¹⁰ Later, Alex would occasionally during our meetings pop into his back office and emerge with one of his reprints from the years between 1954-1960 that was relevant to the molecular ion. And so we progressed from simple variational approximations,¹¹ to adiabatic effects,¹² to asymptotic expressions,¹³ to the hfs.¹⁴ Actually, his student Paul Kalaghan had already combined these into one in the early 70's for his thesis working with Alex on the hfs^{15,16} of H_2^+ , but we decided it was worth a reinvestigation because of the discrepancy discussed in the Introduction and to support on-going experiments by Lundeen and his group. Eventually, the hfs results were presented in 1990 at a meeting in Monterey,¹⁷ written up,¹⁸ and refined¹⁹ and published alongside an experimental paper.^{20,21} We had improved the agreement with experimental values for the Fermi contact electron-nuclear spin coupling constants to around 50 kHz—the expected level for a complete treatment of leading order reduced mass effects (including non-adiabatic couplings).

3. Undergraduate collaborators

During this period, through participation in an undergraduate research initiative sponsored by the Smithsonian Astrophysical Observatory, Dave Bacon from Caltech worked with Alex and I on calculations of the spectra of H_2^+ , and later Marianne (Vieira) Spurrier from Rochester worked with Alex, N. Balakrishnan, and I on calculating collisional deexcitation rates for H_2 with He. In 1997, while still in his first undergraduate year, Jake Taylor from Harvard started research with Alex, Zong-Chao Yan, and I on calculations of the energies and electric dipole polarizability of H_2^+ , which had been measured by Lundeen and associates.²² Jake's work provided a highly accurate nonrelativistic polarizability value.

4. Present status

Vladimir Korobov visited ITAMP in 2000 for in the program on wave functions and QED effects in few-electron atoms. Shortly thereafter, he completed a calculation of the polarizability of H_2^+ and found, surprisingly, that relativity accounted for only about 1/5 of the difference between experiment and non-relativistic theory.²³ Yan, Zhang, and Li also calculated the non-relativistic polarizability and found good agreement with Korobov.²⁴

The nuclear spin-spin tensor interaction contributes to the hfs spectra of H_2^+ and the coupling constants were tabulated by Carrington and Brown.²⁵ Korobov, Hilico, and Karr²⁶ performed a complete calculation of the hfs by including nonadiabatic effects and by using a comprehensive Hamiltonian derived within the Breit-Pauli approximation. Their variational calculations of the hfs coupling constants are highly precise and definitive. In addition, in a parallel development Zong-Chao Yan and his collaborators have also carried out calculations of the hfs²⁷ of H_2^+ . Their values are in harmony with Korobov *et al.*²⁶ This year (2009), Korobov, Hilico, and Karr⁵ pushed the theory of the hfs to the level of 10 kHz by including—in addition to nonadiabatic effects—QED and proton structure terms. In summary, the highest accuracy solutions for H_2^+ have resulted from the use of variational basis sets in Hyleraas coordinates through methods similar to those used with great success for few-electron atomic systems like He.

The most valuable high precision measurements of the hfs of the low-lying states of H_2^+ are those on the $v = 4$ to 8 levels carried out by Jefferts,²⁸ and those for the $v = 0, N = 1$ state by Fu *et al.*²¹ However, additional experimental data is still desirable.

Recently, new data on H_2^+ and its isotopologues have begun to appear.

Osterwalder *et al.*²⁹ obtained the hfs parameters of H_2^+ using a multi-channel quantum defect theory analysis of measured Rydberg levels of H_2 and Cruse *et al.*³⁰ applied the methodology to D_2^+ using Rydberg states of D_2 . Spectra of rovibrational transitions in the ground electronic state of trapped HD^+ ions (sympathetically cooled with Be^+ ions) have been obtained.³¹ Rotational cooling of HD^+ by superelastic collisions with electrons has been reported by the Heidelberg TSR storage ring collaboration.³² An experimental effort to measure two-photon transitions between the $v = 0$ and $v = 1$ levels of the ground electronic state of H_2^+ in an ion trap is in progress.³³

There are as of yet unexplored experimental possibilities such as the antimatter version³⁴ of H_2^+ , anti- H_2^+ (which might also be denoted $\overline{\text{H}_2^+}$ or $\overline{\text{H}_2}$) and there has been no measurement of the hfs of the low-lying rovibrational states of the D_2^+ molecular ion sufficient to measure the nuclear quadrupole moment of the deuteron.

More complicated related molecular ions appear in astrophysical environments. In 1973 Alex and associates estimated the radiofrequency spectrum of H_2D^+ and there are estimates of the hfs³⁵ though the hfs of H_2D^+ and of HD_2^+ has not yet turned out to be a useful diagnostic in radioastronomy.³⁶ Recent experimental work using a cryogenic multipole ion trap has provided Doppler width resolved center frequencies of the lowest transitions,³⁷ of the molecular ions H_2D^+ and HD_2^+ , though sub-Doppler measurements would be required to resolve the calculated hfs.

Through his attention to the problem in the periods ending in 1960, 1972, and 1992, Alex played a characteristic and unheralded role in advancing the understanding of the hydrogen molecular ion's hfs. Three particles never had it so good.

References

1. L. Essen, R. W. Donaldson, M. J. Bangham and E. G. Hope, *Nature* **229**, p. 110 (1971).
2. J. M. Jauch and F. Rohrlich, *The theory of photons and electrons: the relativistic quantum field theory of charged particles with spin one-half* (Springer-Verlag, New York, 1976).
3. J. Sapirstein and D. Yennie, Theory of hydrogenic bound states, in *Quantum Electrodynamics*, ed. T. Kinoshita (World Scientific, Singapore, 1990).
4. M. I. Eides, H. Grotch and V. A. Shelyuto, *Theory of light hydrogenic bound states* (Springer, New York, 2007).
5. V. I. Korobov, L. Hilico and J.-P. Karr, *Phys. Rev. A* **79**, p. 012501 (2009).
6. R. D. Ray and P. R. Certain, *Phys. Rev. Lett.* **38**, p. 824 (1977).

7. W. G. Sturuss, E. A. Hessels, P. Arcuni and S. R. Lundeen, *Phys. Rev. Lett.* **61**, p. 2320 (1988).
8. S. R. Lundeen, *Phys. Rev. Lett.* **62**, p. 3009 (1989).
9. D. M. Bishop, *Phys. Rev. Lett.* **62**, p. 3008 (1989).
10. Y. N. Demkov, *Pis'ma Zh. Eksp. Teor. Fiz.* **7**, p. 101 (1968), [*JETP Lett.* **7**, 76 (1968)].
11. A. Dalgarno and G. Poots, *Proc. Phys. Soc., London, Sect. A* **67**, 343 (1954).
12. A. Dalgarno and R. McCarroll, *Proc. Roy. Soc. London, Ser. A* **237**, p. 383 (1956).
13. A. Dalgarno and A. L. Stewart, *Proc. Roy. Soc. London, Ser. A* **238**, 276 (1956).
14. A. Dalgarno, T. N. L. Patterson and W. B. Somerville, *Proc. Roy. Soc. London, Ser. A* **259**, p. 100 (1960).
15. P. M. Kalaghan, The hyperfine spectrum of the hydrogen molecular ion H_2^+ , PhD thesis, Harvard University 1972.
16. P. M. Kalaghan and A. Dalgarno, *Phys. Lett.* **38A**, p. 485 (1972).
17. J. F. Babb, *Bull. Am. Phys. Soc.* **35**, p. 1177 (1990).
18. J. F. Babb and A. Dalgarno, *Phys. Rev. Lett.* **66**, 880 (1991).
19. J. F. Babb, *Phys. Rev. Lett.* **75**, p. 4377 (1995).
20. J. F. Babb and A. Dalgarno, *Phys. Rev. A* **46**, p. R5317 (1992).
21. Z. W. Fu, E. A. Hessels and S. R. Lundeen, *Phys. Rev. A* **46**, p. R5313 (1992).
22. P. L. Jacobson, D. S. Fisher, C. W. Fehrenbach, W. G. Sturuss and S. R. Lundeen, *Phys. Rev. A* **56**, p. R4361 (1997), ; *ibid.* **57** (1998), p. 4065E.
23. V. I. Korobov, *Phys. Rev. A* **63**, p. 044501 (2001).
24. Z.-C. Yan, J.-Y. Zhang and Y. Li, *Phys. Rev. A* **67**, p. 062504 (June 2003).
25. J. M. Brown and A. Carrington, *Rotational spectroscopy of diatomic molecules* (Cambridge University Press, Cambridge, 2003). pp. 969-972, cited as A. Carrington and D. I. Gammie (1999), unpublished work.
26. V. I. Korobov, L. Hilico and J.-P. Karr, *Phys. Rev. A* **74**, p. 040502 (2006).
27. Z.-X. Zhong, Z.-C. Yan and T.-Y. Shi, *Phys. Rev. A* **79**, p. 064502 (2009).
28. K. B. Jefferts, *Phys. Rev. Lett.* **23**, p. 1476 (1969).
29. A. Osterwalder, A. Wüest, F. Merkt and C. Jungen, *J. Chem. Phys.* **121**, 11810 (2004).
30. H. A. Cruse, C. Jungen and F. Merkt, *Phys. Rev. A* **77**, p. 042502 (2008).
31. J. C. J. Koelemeij, B. Roth, A. Wicht, I. Ernsting and S. Schiller, *Phys. Rev. Lett.* **98**, p. 173002 (2007).
32. D. Shafir, S. Novotny, H. Buhr, S. Altevogt, A. Faure, M. Grieser, A. G. Harvey, O. Heber, J. Hoffmann, H. Kreckel, L. Lammich, I. Nevo, H. B. Pedersen, H. Rubinstein, I. F. Schneider, D. Schwalm, J. Tennyson, A. Wolf and D. Zajfman, *Phys. Rev. Lett.* **102**, p. 223202 (2009).
33. J. P. Karr, F. Bielsa, T. Valenzuela, A. Douillet, L. Hilico and V. I. Korobov, *Can. J. Phys.* **85**, 497 (2007).
34. H. Dehmelt, *Phys. Scr.* **T59**, p. 423 (1995).
35. P. Jensen, I. Páidarová, V. Špirko and S. P. A. Sauer, *Molec. Phys.* **91**, 319 (1997).
36. T. Amano, *Philos. Trans. R. Soc. London, Ser. A* **364**, 2943 (2006).

37. O. Asvany, O. Ricken, H. S. P. Müller, M. C. Wiedner, T. F. Giesen and S. Schlemmer, *Phys. Rev. Lett.* **100**, p. 233004 (2008).