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Corrections and Update for: Precision spectroscopy of molecular hydrogen ions: an introduction

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I. CORRECTIONS

Main Text

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Section 2.3.5: The effect of finite nuclear size

The expression

$$\langle \delta(\mathbf{r}_e) \rangle_{at.u.} = Z_{nuc}^2 / (\pi n^3)$$

11 is from Bethe and Salpeter's book *The quantum mechanics of one- and two-electron atoms*, eq.(3.46), that has a typo.
12 The exponent of Z_{nuc} should be 3.

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Supplemental material

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Section C.1

15 The statement "There is no dependence on v since g_l does not appear if $N = 0$ " is incorrect. There is a dependence
16 on v even when $N = 0$, through $g_e(v, N = 0)$.

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II. COMMENTS AND UPDATES

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Section D

19 The discussion can be made more compact by noting [1] that the Zeeman effect on the hyperfine structure of para-
20 H_2^+ (i.e. zero total nuclear angular momentum, $I = 0$) is actually analogous to the case discussed by Breit and Rabi
21 in 1931. The original Breit-Rabi formula is for an atom in a magnetic field, with total electronic angular momentum
22 $\mathbf{J} = 1/2$ (for example, a single electron in a state with zero orbital angular momentum) and arbitrary nuclear spin \mathbf{I} .
23 For a calculation, see Ramsey's book on molecular beams, Chapter III.4.2 or Millman *et al* [2], where also the case of
24 $J > 1/2$ is briefly presented.

In para- H_2^+ , we instead have an electron spin \mathbf{s}_e , $s_e = 1/2$ and an arbitrary even rotational angular momentum \mathbf{N} ,
 $N = 0, 2, 4, \dots$. For this case, in the basis described in the main paper, we can recast the explicit hamiltonians into a
general form valid for any N , m_F :

$$H_{\text{spin}}(v, N \text{ even}) = c_e(v, N) \begin{pmatrix} -(N+1)/2 & 0 \\ 0 & N/2 \end{pmatrix},$$
$$H_{\text{Zeeman}}(v, N \text{ even}, m_F) = \frac{\mu_B B}{2N+1} \begin{pmatrix} m_F(g_e - (2N+2)g_l) & \sqrt{(N+1/2)^2 - m_F^2} (g_e - g_l) \\ \sqrt{(N+1/2)^2 - m_F^2} (g_e - g_l) & -m_F(g_e + 2Ng_l) \end{pmatrix}. \quad (1)$$

25 Note that $g_e = g_e(v, N)$, $g_l = g_l(v, N)$, and $g_e < 0$.

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The eigenvalues of the 2×2 matrix $H_{\text{tot}} = H_{\text{spin}}(v, N \text{ even}) + H_{\text{Zeeman}}(v, N \text{ even}, m_F)$ provide a closed-form expression of the energies of the two states with given m_F , where m_F takes on the values $-(N - 1/2), \dots, N - 1/2$. These two states correspond to the electron spin oriented approximately parallel and antiparallel to the external magnetic field. The energies of the two stretched states $m_F = \pm(N + 1/2)$ are simply the values of the lower diagonal element of H_{tot} .

As a function of magnetic field strength, the ordering of the states having the electron's magnetic moment antiparallel to \mathbf{B} , i.e. the high-energy group, changes. To see this mathematically, consider first the limit of small magnetic field. Then the energies of all states are just the diagonal elements of $H_{\text{spin}} + H_{\text{Zeeman}}$. The high-energy group's energies are given by the lower diagonal matrix element. Since $g_e < 0$, the highest-energy state in that group is $m_F = N + 1/2$, one of the stretched states, while the lowest-energy state in the same group is $m_F = -N - 1/2$.

Actually, the energy of the $m_F = N + 1/2$ stretched state is

$$\begin{aligned} E(m_F = N + 1/2) &= -\mu_B B(g_e + 2Ng_l)/2 + Nc_e/2, \\ &= \mu_B B(|g_e| - 2Ng_l)/2 + Nc_e/2, \end{aligned} \quad (2)$$

for any value of B .

Now consider the limit of very large magnetic field. A Taylor expansion of the eigenvalues shows that the high-energy solution is asymptotically

$$(|g_e| - (2m_F - 1)g_l)\mu_B B/2 + (m_F - 1/2)c_e/2, \quad (3)$$

for arbitrary $m_F \neq -(N + 1/2)$. (The stretched state with $m_F = -(N + 1/2)$, belongs to the low-energy group when B is large, see Fig. 2 in the Supplemental Material.)

When the rotational Zeeman energy term in (3) dominates over the spin energy term, i.e. when $B > c_e/(2\mu_B g_l)$ (e.g. 2.9 T for $v = 1$) the energy (3) is maximized for the smallest m_F for which there are two solutions, $-N + 1/2$, and it is then larger than the stretched-state energy, eq.(2). Actually, then the ordering of energies is, from highest to lowest: $m_F = -N + 1/2, -N + 3/2, \dots, N + 1/2$. In other words, the sequence is opposite to the regime of low and moderate magnetic fields, displayed in Fig. 2.

This discussion is relevant for experiments in Penning traps, where B can be 4 T or larger.

Updates on new scientific results

- High-resolution spectroscopy of H_2 in Rydberg states, allowing the determination of vibrational energy differences and spin-rotation couplings: [3]. (Earlier results are found in the dissertation of M. Beyer cited therein.)
- Laser spectroscopy of H_2^+ : [4]

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56 (2024). arXiv:2401.09194.
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