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# Corrections and Updates 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

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

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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#### *Appendix*

18 In Table I,  $h_{s22}(1)$  and  $h_{s1010}(1)$  contain a typo. In those two expressions, replace " $\mathcal{E}_{1-2}$ " by " $\mathcal{E}_{1+2}$ ".  
19 I thank C. König (MPIK) for pointing out to me that the previous form of  $H_{\text{spin}}(1)$  leads to different eigenvalues  
20 than those I obtained with the code used in various own publications.

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## II. COMMENTS AND UPDATES

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### *Section D*

23 The discussion can be made more compact by noting [1] that the Zeeman effect on the hyperfine structure of para-  
24  $\text{H}_2^+$  (i.e. zero total nuclear angular momentum,  $I = 0$ ) is actually analogous to the case discussed by Breit and Rabi  
25 in 1931. The original Breit-Rabi formula is for an atom in a magnetic field, with total electronic angular momentum  
26  $\mathbf{J} = 1/2$  (for example, a single electron in a state with zero orbital angular momentum) and arbitrary nuclear spin  $\mathbf{I}$ .  
27 For a calculation, see Ramsey's book on molecular beams, Chapter III.4.2 or Millman *et al* [2], where also the case of  
28  $J > 1/2$  is briefly presented.

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In para- $\text{H}_2^+$ , 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  $N$ ,  $m_F$ :

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

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

30 The eigenvalues of the  $2 \times 2$  matrix  $H_{\text{tot}} = H_{\text{spin}}(v, N \text{ even}) + H_{\text{Zeeman}}(v, N \text{ even}, m_F)$  provide a closed-form expres-  
 31 sion 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  
 32 two states correspond to the electron spin oriented approximately parallel and antiparallel to the external magnetic  
 33 field. The energies of the two stretched states  $m_F = \pm(N+1/2)$  are simply the values of the lower diagonal element  
 34 of  $H_{\text{tot}}$ .

35 As a function of magnetic field strength, the ordering of the states having the electron's magnetic moment an-  
 36 tiparallel to  $\mathbf{B}$ , i.e. the high-energy group, changes. To see this mathematically, consider first the limit of small  
 37 magnetic field. Then the energies of all states are just the diagonal elements of  $H_{\text{spin}} + H_{\text{Zeeman}}$ . The high-energy  
 38 group's energies are given by the lower diagonal matrix element. Since  $g_e < 0$ , the highest-energy state in that group  
 39 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

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

40 for any value of  $B$ .

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

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

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

45 When the rotational Zeeman energy term in (3) dominates over the spin energy term, i.e. when  $B > c_e/(2\mu_B g_l)$   
 46 (e.g. 2.9 T for  $v = 1$ ) the energy (3) is maximized for the smallest  $m_F$  for which there are two solutions,  $-N+1/2$ ,  
 47 and it is then larger than the stretched-state energy, eq.(2). Actually, then the ordering of energies is, from highest  
 48 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  
 49 and moderate magnetic fields, displayed in Fig. 2.

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

## 51 Updates on new scientific results

- 52 • High-resolution spectroscopy of  $\text{H}_2$  in Rydberg states, allowing the determination of vibrational energy differences  
 53 and spin-rotation couplings: [3]. (Earlier results are found in the dissertation of M. Beyer cited therein.)
- 54 • Laser spectroscopy of  $\text{H}_2^+$ : [4]

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