

# Symmetry breaking in covalent chiral bond $H_2$ , according to accurate vibrational levels from Kratzer bond theory

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**Abstract.** *Symmetry breaking in  $H_2$ , quantified with Kratzer bond theory, leads to vibrational levels with errors of only 0,00008 %. For quanta, 0,0011 % errors are smaller than with any ab initio QM method. Chiral behavior of covalent bond  $H_2$  implies bonding between left- and right-handed atoms  $H_R$  and  $H_L$  or between hydrogen  $H$  and antihydrogen  $\bar{H}$ . This generic  $H_2$  asymmetry is given away by a Hund-type Mexican hat curve, invisible in QM.*

## I. Introduction

Symmetry breaking (SB) at low energy in neutral, stable, small quantum systems is important. H and  $H_2$ , the simplest but most abundant systems in the Universe [1], being prototypical for atomic and molecular spectroscopy [2], are therefore prototypical for SB at the eV-level. Unfortunately, bound state H QED [3] and  $H_2$  QM theories [4-6] are complex: QM relies on parameters and hundreds of terms in the wave function to get at observed  $H_2$  levels [7]. The lack of an analytical potential energy function (PEF)[8] for  $H_2$  in [4-6] is also unfortunate: this PEF (i) may disclose the long sought for simple low parameter universal function (UF) behind all shape-invariant potential energy curves (PECs) [2,8-11] and (ii) may, eventually, disclose SB in  $H_2$ . Hence, a simpler  $H_2$  bond theory is of interest for SB but only if it is more accurate than QM, which is problematic. In fact, QM [6] may be the most precise  $H_2$  theory, consistent with observed data [12], it overlooks SB. A recent Kratzer  $H_2$  bond theory [13] gave errors of 3,4  $cm^{-1}$ , comparable with those of 3,2  $cm^{-1}$  in earlier QM [4]. Whereas their large errors vanish with non-adiabatic corrections [5-6], the 3,4  $cm^{-1}$  errors in [13] vanish with an equally simple, parameter free chiral Kratzer theory, as we show here. Being more precise for  $H_2$  than any ab initio QM theory available, this theory for the chemical bond deals analytically with symmetry breaking in  $H_2$ , which is difficult, if not impossible with ab initio QM.

## II. Dunham and Kratzer oscillators for (too) symmetrical $H_2$

The standard 4 particle ( $a^-, A^+$ ;  $b^-, B^+$ ) Hamiltonian  $\mathbf{H}$  or classical energy E for  $H_2$

$$E=\mathbf{H}=\frac{1}{2}p_a^2/m_a+\frac{1}{2}p_b^2/m_b+\frac{1}{2}p_A^2/m_A+\frac{1}{2}p_B^2/m_B-e^2/r_{aA}-e^2/r_{bB}-e^2/r_{bA}e^2/r_{aB}+e^2/r_{ab}+e^2/r_{AB} \quad (1a)$$

where all symbols have their usual meaning, led to vibrational energies [13]

$$E_{\text{vib}}=\Delta\mathbf{H}=(E-2E_H)\approx f^2\hbar^2/(mr_{AB}^2)\pm A_r e^2/r_{AB}=B/r^2\pm A_r e^2/r \quad (1b)$$

With the B-term positive, the  $A_r$ -term can only be negative for  $H_2$  to be stable. Scaling by  $\Delta\mathbf{H}_0=-$

$\frac{1}{2}A_r e^2/r_0$  gives Kratzer oscillator  $K(r_0/r)$  in variable  $r_0/r$  [14]

$$K(r_0/r)+1=\Delta\mathbf{H}/(-\frac{1}{2}A_r e^2/r_0)+1=(r_0/r)^2-2r_0/r+1=(1-r_0/r)^2 \quad (1c)$$

analytically and conceptually different from JWKB and Dunham potentials in variable  $r/r_0$  [15].

Dunham's  $V_D(r/r_0)$  and Kratzer's  $V_K(r_0/r)$  potentials are respectively

$$V_D(r) = a_0(1-d)^2=(1-r/r_0)^2 \quad (1d)$$

$$V_K(1/r) = a_0(1-1/d)^2=a_0(1-r_0/r)^2=(a_0/r^2)V_D(r) \quad (1e)$$

With  $U(r)=\sum a_n(r-r_0)^n$ , Dunham's oscillator (1d) relates to the JWKB-approximation. Kratzer's (1e) refers naturally to turning points  $(e^2/r_0)(r_0/r_1-r_0/r_2)$  in PECs, as disclosed by RKR-methods [16-18]. In [13], deviations from  $r_0$  in  $r=r_0+\Delta$ ,  $r/r_0=1+\Delta/r_0=1+\delta$  are quantized with vibrational number  $v$  using  $\delta=qv$ . Equally distributed in perfectly symmetric  $H_2$ , these deviations generate [13]

$$\delta=r/r_0-1=\Delta/r_0 =^{1/2}\Delta/r_0-(-^{1/2}\Delta/r_0)=^{1/2}qv-(-^{1/2}qv)=qv \quad (1f)$$

$$q=\omega_e/a_0=2\omega_e/(e^2/r_0)=\omega_e/(^{1/2}k_e r_0^2)=\omega_e/(^{1/2}D_{ion})=4410,172/78844,913=0,05591(1g)$$

where  $\omega_e$  is the fundamental frequency,  $a_0$  the first order Dunham coefficient,  $D_{ion}=e^2/r_0$  the ionic bond energy and force constant  $k_e=e^2/r_0^3$  [13]. The advantage over [4-6] is that  $H_2$  characteristics in (1g) all derive directly from atom mass  $m_H$  and its classical radius, defined as [13]

$$r_H=[3m_H/(4\pi\Gamma_H)]=0,7365.10^{-8} \text{ cm} \quad (1h)$$

for density  $\Gamma_H=1$  [13,19]. Kratzer's potential (1c) in inverse  $r_0/r$  or

$$\delta_K=r_0/r_1-r_0/r_2=1/(1-^{1/2}\Delta/r_0)-1/(1+^{1/2}\Delta/r_0)=qv/(1-^{1/4}q^2v^2) \quad (1i)$$

led to level results for  $H_2$ , 30 times more accurate than Dunham's (1f) [13].

Since the term in  $A_r$  in (1b) must be  $<0$ , Coulomb law for an ion pair with reduced mass  $\mu_{HH}=^{1/2}m_H$  gives  $E_{HH}=^{1/2}\mu_{HH}v^2-e^2/r$ . Its first derivative  $d/dr$  gives classical radial equilibrium condition

$$^{1/2}m_H v^2 r = e^2 \quad (1j)$$

Using  $m_H$  and  $r_H$  in (1h), velocity  $v$  in (1j) leads to a  $H_2$  fundamental vibrational frequency [13]

$$\omega_H=4410,172 \text{ cm}^{-1} \quad (1k)$$

close to the value  $4401 \text{ cm}^{-1}$  in [7,20]. Since  $3,4 \text{ cm}^{-1}$  errors for symmetric  $H_2$  do not comply with spectroscopic accuracy [13], we now consider a less symmetrical, chiral  $H_2$  model.

### III. Symmetry-breaking from achiral to chiral $H_2$

Following the chemist's symmetry view  $H_2=2H=HH$ , bisecting  $H_2$  line segment  $L=r_0$

$$H_2=\{H_L, C, H_R\} \sim L(0, +^{1/2}, +1) \text{ or } L'(-^{1/2}, 0, +^{1/2}) \quad (2a)$$

implies a bond symmetry  $S_0$ , quantified by the ratio of equal parts (proportions), i.e.  $S_0=^{1/2}/^{1/2}=1$ , valid for any  $r_{AB}>$  or  $<r_0$ . Deviations  $\delta<0$  or  $\delta>0$  from  $^{1/2}r_0=r_H$  do not alter  $S_0$ , since

$$S_0=^{1/2}(1\pm\delta)/[^{1/2}(1\pm\delta)]=^{1/2}/^{1/2}=1 \quad (2b)$$

remains valid, however large  $\delta$ .  $H_L$  at the left and  $H_R$  at the right of the center call for back-front or mirror-symmetry in  $H_2$ . The frame is left-handed for  $H_L$  and right-handed for  $H_R$  (or vice versa) but  $S_0$  typifies a too symmetrical, achiral unit  $H_2$ , although using  $H_L H_R$ ;  $H_R H_L$  is superfluous, if  $H_L=H_R$  [10]. As in QM, there is no need for less symmetrical or chiral  $H_2$ , for which  $H_L \neq H_R$  and  $S \neq 1$ .

Theoretically, sign-conjugated deviations  $\gamma$  from achiral part  $p_a=^{1/2}$  always give generic unequal parts

$$p_\gamma=p_{R,L}=p_\pm=^{1/2}(1\pm\gamma)=p_a(1\pm\gamma)=p_L+p_R \quad (2c)$$

The ratio of chiral parts  $p_L/p_R$  returns an intrinsic, generic  $H_2$  left-right asymmetry (chirality<sup>1,2,3</sup>)

<sup>1</sup> Difference  $\gamma$  is a *continuous chirality measure* (CCM) [21].

<sup>2</sup> Left and right are formalized with Dirac's  $\gamma^5$  [22]. Dimensionless left and right properties  $P$  are  $P_L=^{1/2}p(1-\gamma_L)$  and  $P_R=^{1/2}p(1+\gamma_R)$ , with  $|\gamma_L|=|\gamma_R|$ , implying that *centers of chiral systems are not exactly in the middle*.

$$S_C=(1-\gamma)/(1+\gamma) \quad (2d)$$

equal to  $S_0$  only if asymmetry effect  $\gamma=0$ . Complementarity  $p_R=1-p_L$  or  $x_2=1-x_1$  gives

$$1=x_1+x_2=p_L+p_R=x_1+(1-x_1)=p_L+(1-p_L)=p_R+p_L=1/2(1+\gamma)+1/2(1-\gamma)=1 \quad (2e)$$

For parts not equal to  $1/2$ , an axial view is needed. Parallel  $\perp$ ,  $\Gamma$  or anti-parallel  $\perp$ ,  $\Gamma$  states in 3D  $H_2$  view (1h) use all intra- and inter-atomic separations  $r_{Aa}$ ,  $r_{Bb}$ ,  $r_{AB}$ ,  $r_{ab}$ ,  $r_{Ab}$  and  $r_{Ba}$  in (1a). For  $X_2$  bonds, reduced axial and radial parts are  $|1/2|$  and  $|1|$ . At  $r_0=2r_H$ , hypotenuse  $h=r_{Ab}=r_{Ba}$  for axial  $H_2$  states  $e^2/r_{Ab}$  and  $e^2/r_{Ba}$  in (1a) in reduced form is equal to

$$h/(2r_H)=h'=(1/2r_H)\sqrt{(4r_H^2+r_H^2)}=1/2\sqrt{5} \quad (2f)$$

invariantly giving away the square root of 5 by definition. Upon bisection, its 2 equal parts

$$1/2h'=1/4\sqrt{5}=0,55901699>1/2 \quad (2g)$$

are larger than achiral value  $1/2$  by exactly 0,059026994 or  $1/0,059026994$  ( $\approx 17$ ), commensurate with (1g). Classically, axial states (2f) use Euclidean division [19] (see Section V) and may well lead in a generic way to  $\gamma$ -effects related to  $\sqrt{5}$ , overlooked thus far in all  $H_2$  theories, including QM.

#### IV. Formal Kratzer bond theory for symmetry breaking in chiral $H_2$

In theory, the effect of non-zero  $\gamma$  on the  $H_2$  structure is easily quantified with oscillators (1g)-(1h).

(a) Linear Dunham variable  $\delta$  (1f) is  $\gamma$ -invariant: achiral and chiral cases are degenerate

$$\text{achiral: } qv=+1/2qv+1/2qv=1/2qv -(-1/2qv)=qv \quad (3a)$$

$$\text{chiral: } qv=+1/2(1+\gamma)qv+1/2(1-\gamma)qv=1/2qv+1/2qv=1/2qv -(-1/2qv)=qv \quad (3b)$$

(b) With inverse Kratzer variable  $\delta_K$  (1i), this  $\gamma$ -degeneracy is lifted since

$$\text{achiral: } 1/(1-1/2qv) - 1/(1+1/2qv)=qv/(1-1/4q^2v^2) \quad (3c)$$

$$\text{chiral: } 1/[1-1/2(1+\gamma)qv] - 1/[1+1/2(1-\gamma)qv]=qv/[1-\gamma qv-1/4(1-\gamma^2)q^2v^2] \quad (3d)$$

The formal effect of non-zero  $\gamma$  (symmetry breaking) in  $H_2$  in a Kratzer variable is

$$qv/[(1-1/4q^2v^2)-\gamma qv+1/4\gamma^2q^2v^2]=[qv/(1-1/4q^2v^2)]/[1-\gamma qv(1-1/4\gamma qv)/(1-1/4q^2v^2)] \quad (3e)$$

The ratio of achiral (3b) and (3c) gives harmonic mean  $(1-1/4q^2v^2)=(1+1/2qv)(1-1/2qv)$ , the reason why Kratzer's oscillator outperforms Dunham's by a factor 30 [9,13]. Since harmony improves  $H_2$  results [13], other harmonies, including those with  $\gamma$  as in (3e), must be inventoried (see Section VI).

#### V. Euclidean $H_2$ symmetry

Axial states in Section III are either parallel or anti-parallel. Parallel boat structure (4a)

$$(L) \quad \begin{array}{c} \triangle \\ \text{r}_H \quad \text{r}_H \\ \text{2r}_H \end{array} \quad (R) \quad \text{and} \quad (L) \quad \begin{array}{c} \triangle \\ \text{r}_H \quad \text{r}_H \\ \text{2r}_H \end{array} \quad (R) \quad (4a)$$

contains 2 rectangular triangles, one left-, the other right-handed (or vice versa). Since these cannot coincide without leaving the paper plane, chirality applies (mirror, perpendicular to the paper).

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<sup>3</sup> In Heitler-London theory [24], permutation, achieved with two-center functions  $\psi_{AB}$  and  $\psi_{BA}$ , leads to exchange forces, responsible for bonding, whereby chiral behavior is not considered.

Chair structures are achiral, not chiral, unless L- and R-parts are unequal ( $S \neq 1$ ). Unlike (4a), the 2 triangles in a chair can be made to coincide by in-plane rotation. With different sizes, a perspective will displace them in front and back of the mirror in the paper plane.

In either case, Euclidean division of  $AC = r_{Ab} = r_{Ba} = AB + AC = a + b = a(1+k)$  and number  $k = b/a$ , gives

$$AB/BC = BC/AC; a/b = b/(a+b) \text{ or } 1/k = k/(1+k) \quad (4b)$$

This brings in  $k^2 - k - 1 = 0$  and solutions  $k = \frac{1}{2}(1 \pm \sqrt{5})$ . Golden ratio  $k = b/a$  obeys phi-numbers<sup>4</sup>

$$\varphi = 1/\Phi = \frac{1}{2}(1 + \sqrt{5}) \quad (4c)$$

in line with (2f)-(2h) [19]. Strangely enough, (4c) is not the only solution possible.

Table 1 Phidias-Euclid and Dirac schemes for complementary chiral parts in  $H_2$

|                        | Phidias-Euclid                              | Complementarity               | Dirac I   | Dirac II <sup>a</sup>   |
|------------------------|---|-------------------------------|---|---|
| Left part $x_L$        | 1   | x                             | $\frac{1}{2}(1-\gamma)$                         | $\frac{1}{2}-\gamma'$   |
| Right part $x_R$       | k   | 1-x                           | $\frac{1}{2}(1+\gamma)$                         | $\frac{1}{2}+\gamma'$   |
| Unit                   | 1+k   | 1                             | 1   | 1   |
| Ratio's                | $1/k = k/(1+k)$                             | $x/(1-x) = 1-x$               | $(1-\gamma)/(1+\gamma) = \frac{1}{2}(1+\gamma)$ | $(\frac{1}{2}-\gamma')/(\frac{1}{2}+\gamma') = \frac{1}{2}+\gamma'$ |
| Quadratic              | $k^2 - k - 1 = 0$                           | $x^2 - 3x + 1 = 0$            | $\gamma^2 + 4\gamma - 1 = 0$                    | $\gamma'^2 + 2\gamma' - \frac{1}{4} = 0$                            |
| Solutions <sup>b</sup> | $k = \varphi = \frac{1}{2}(1 \pm \sqrt{5})$ | $x = (3/2)(1 \pm \sqrt{5}/3)$ | $\gamma = -2(1 \pm \frac{1}{2}\sqrt{5})$        | $\gamma' = -(1 \pm \frac{1}{2}\sqrt{5})$                            |
| Values <sup>c</sup>    | +1,618; -0,618                              | +2,618; +0,382                | -4,236; +0,236                                  | -0,118; +2,118  |
| With inverse           | $k = 1 + 1/k$                               | $x = 3 - 1/x$                 | $\gamma = 1/\gamma - 4$                         | $\gamma' = 1/(4\gamma) - 2$   |

a) Dirac I solution  $\frac{1}{2}(1 \pm \gamma)$  transforms in  $\frac{1}{2} \pm \frac{1}{2}\gamma = \frac{1}{2} \pm \gamma'$ , with handedness  $\gamma = 2\gamma'$  (see solutions for  $\gamma$  and  $\gamma'$ ).

b) Interchanging  $x_R$  and  $x_L$  gives different quadratics and solutions:  $k^2 + k - 1$ ,  $x^2 + x - 1 = 0$  and  $\gamma^2 - 4\gamma - 1 = 0$ . A permutation of parts leads to 4 rather than 2 solutions of type  $\pm a(1 \pm b\sqrt{5})$ , not given in the Table.

c) Only 3 decimals given, based on  $\sqrt{5} = 2,236067978... \approx 2,236$

Alternatives, all containing  $\sqrt{5} = 2\varphi - 1$ , are in Table 1. The 4 different scale factors for units are  $\frac{1}{2}$ , 1,  $3/2$  and 2; the 3 different coefficients for  $\sqrt{5}$  are 1,  $1/3$  and  $\frac{1}{2}$ . The last 3 Columns apply for unit 1; Phidias-Euclid recipe in Column 2 treats one part as if it were the unit. Choices are difficult by relations between linear  $k$ ,  $x$ ,  $\gamma$  and inverse  $1/k$ ,  $1/x$ ,  $1/\gamma$  (see last row). Table 1 does not single out a *best* solution. Rather than solving the wave equation for Hamiltonian (1a), we test all solutions possible by plugging them in (1l)-(1m) and looking at the results obtained.

## VI. Ionic chiral Kratzer bond theory for $H_2$ with left-right asymmetric $H_L$ and $H_R$

Of all possible combinations in Table 1, only parts  $x_{RL}$ , based on  $\sqrt{5}$  as in (2f) and (4c) and equal to

$$x_{RL} = x_{\pm} = p(1 \pm \gamma) = (2/3)(1 \pm \frac{1}{2}/\varphi) = (2/3)(1 \pm \frac{1}{2}\Phi) \quad (5a)$$

invariantly related to Euclid's golden number

$$\Phi = 1/\varphi = 2/(1 + \sqrt{5}) = \frac{1}{2}(\sqrt{5} - 1) = 0,618033989... \quad (5b)$$

reproduce  $H_2$  levels within greater precision than QM (see below). Plugging (5a) in (3f) gives

$$\begin{aligned} \delta_K = r_0(1/r_a - 1/r_b) &= 1/[1 - (1 + \frac{1}{2}\Phi)q\varphi/3] - 1/[1 + (1 - \frac{1}{2}\Phi)q\varphi/3] \\ &= (2/3)q\varphi/[1 - \Phi q\varphi/3 - q^2\varphi^2(1 - \frac{1}{4}\Phi^2)/9] = (2/3)q\varphi/[1 - 0,206011q\varphi - 0,100501q^2\varphi^2] \quad (5c) \end{aligned}$$

whereby internal  $H_2$  asymmetry is assessed with Euclid's recipe involving axial states.

<sup>4</sup> Phi-numbers appear in mathematics (Fibonacci series...), physics, chemistry, biology, architecture, arts [25].

As in [13], multiplying (5c) with 1,5 to correct for Euclidean factor 2/3 in (5a) and (5c) returns

$$\delta'=1,5\delta_K=qv/(1-0,206011qv-0,100501q^2v^2) \quad (5d)$$

the parameter free chiral Kratzer variable, we use below for fitting  $H_2$  levels [7]. The chiral version  $v_\gamma$  of the conventional vibrational quantum number  $v$  is an effective quantum number

$$v_\gamma=\delta''=\delta'/q=1,5\delta_K/q=qv/(1-0,206011qv-0,100501q^2v^2) \quad (5e)$$

close to  $v/[1-(qv/5)(1+1/2qv)]$ . Fitting with (5e) gives coefficients smaller by  $q$ , see (6b) below.

## VII. Results

### VII.1 $H_2$ levels and bond energy $D_e$

Fitting the 14  $H_2$  levels [7] with (5d) using a quartic through the origin gives

$$E_\delta=-4864,602868\delta^4+18697,327977\delta^3-54425,081623\delta^2+76533,833034\delta \text{ cm}^{-1} \quad (6a)$$

with goodness of fit  $R^2=0,999999999997$ . As in [13], the term in  $\delta$  has the correct value, close to  $a_0$  in (1g). A fit with (5e) leads to the more familiar quartic in  $v$  (similar to that in  $(v+1/2)$  [13])

$$E_v=-0,047618v_\gamma^4+3,272089v_\gamma^3-170,279673v_\gamma^2+4280,902374v_\gamma \quad (6b)$$

The main advantage of (6a) [13] is that the  $H_2$  bond energy  $D_e$  is given by the intercept, appearing when level energies are plotted versus complementary variable

$$x=1-b\delta=1-1,5,0,92762998107\delta=1-1,391444972\delta \quad (6c)$$

for this makes the linear Coulomb term in  $\delta$  in (6a) vanish exactly. The same factor 1,3914 also appears for the H spectrum as  $r_H/r_B=1,3915\dots$ , where  $r_B$  is the Bohr length, and close to  $9\varphi/4$  [19].

For achiral  $H_2$ ,  $D_e$  is  $36146,44 \text{ cm}^{-1}$  [13]. For chiral  $H_2$  (6c),  $D_e$  appears in a closed form quartic

$$E_x=-6569,703251x^4+2855,209522x^3-32395,749724x^2+36110,244712 \text{ cm}^{-1} \quad (6d)$$

$$=-[6569,703252x^4-2855,209522x^3+310,220306x^2]-32085,529418x^2+D_e \text{ cm}^{-1} \quad (6e)$$

mathematically equivalent to and as precise as (6a). Fig. 1 illustrates the effect on levels of adjusted and complementary variables (6c). The quartic in (6d) exposes the asymmetrical chiral nature of  $H_2$ , although this contribution is relatively small. Fig. 2 shows the Hund-type  $H_2$  Mexican hat curve

$$(D_e-E_x)-32085,529418x^2=6569,703252x^4-2855,209522x^3+310,220306x^2 \quad (6f)$$

It exposes new critical points, due to left-right asymmetric, chiral  $H_2$ . Fig. 2 also shows the curve for terms in  $x^3$  and  $x^4$  in (6d). Fig. 3 zooms in on these new critical points for  $H_2$ , given away by its vibrational spectrum but invisible in QM, and which typify symmetry breaking in  $H_2$ .

### VII.2 Precision of parameter free chiral Kratzer bond theory: comparison with *ab initio* QM

Level errors of  $0,015 \text{ cm}^{-1}$  give a precision of  $8,6 \cdot 10^{-7} \%$ , see Table 2. With  $0,05 \text{ cm}^{-1}$  errors for Dabrowski data [7], the constraint of spectroscopic accuracy is met. 4<sup>th</sup> and 6<sup>th</sup> order fits with  $qv$  give errors of  $7,15 \text{ cm}^{-1}$  and  $0,24 \text{ cm}^{-1}$ , 475 and 17 times larger than a 4<sup>th</sup> order fit with (5d).

Table 3 for  $\Delta G(v+1/2)$  includes errors of all *ab initio* QM methods available [4-6,26-28]. Error ratios (%) vary from 40,3 for 1975 QM [4] to 1,8 for 1995 QM with many correction terms [6]. Recent QM methods [27,28] are less precise (see last row).

## VIII. Discussion

(i) The centuries old problem [2, 9-11] with ionic and covalent energies  $D_{\text{ion}}$  and  $D_e$  is solved. With (6c)-(6d),  $D_e$  is generated analytically by Coulomb's ionic bond energy  $D_{\text{ion}}$ , securing the  $\text{H}_2$  bond is stable [13]. In an effortless way, with an ionic Coulomb view and with (6a)-(6c),  $D_e$  amounts to

$$D_e = 36110,244711 \text{ cm}^{-1} \quad (7a)$$

Although slightly lower than  $36118,3 \text{ cm}^{-1}$  in [20], the deviation of  $8 \text{ cm}^{-1}$  is only 0,022 %. A similar difference appears between  $\omega_e = 4410,1722 \text{ cm}^{-1}$  in (1g) and  $4401,213 \text{ cm}^{-1}$  in [20]. This result is also important for the distinction between  $D_{\text{ion}}$  and  $D_e$  as a scaling aid the molecular constants and in the search for the universal function (UF) [2,8-11] (see Introduction).

(ii) The unprecedented precision in this work derives from only one parameter free variable (5c) and only 3 terms in  $x^2$ ,  $x^3$  and  $x^4$  in (5g). This analysis outperforms QM [4-6, 26-28], although all these QM methods are highly parameterized and use hundreds of terms in the  $\text{H}_2$  wave function.

(iii) Of all QM methods in Table 3, Wolniewicz's method [6] may be the best [12], it is still 2 times less precise than ours. Wolniewicz used relativistic, adiabatic and non-adiabatic corrections with ab initio QM in a BO-approximation [6]. These corrections, as well as QM itself, are all avoided in a simple chiral Kratzer approach, which, nevertheless, remains the more precise (see Table 3).

(iv) Errors for  $\text{H}_2$  quanta in Table 3 are of the same order as the standard H Lamb shift. Hence, our results call for new determination of  $\text{H}_2$  levels with a precision of  $0,001 \text{ cm}^{-1}$  or better. These may settle problems with  $P_{1/2}$  or  $S_{1/2}$  states for the  $\text{H}_2$  ground state and confirm the quality of our results.

(v) Although simple first principles chiral Kratzer  $\text{H}_2$  bond theory uses only hydrogen mass  $m_{\text{H}}$  as input, new critical points emerge, invisible in and never exposed with ab initio QM (see Fig. 2-3).

(vi) Whereas the potential in the JWKB-approximation starts off with linear  $k(r_1-r_2)$  as in a Dunham expansion, it is evident from all Coulomb terms in (1a) and from RKR-procedures that a potential in inverse  $r$  or  $1/r$ , say  $e^2/r_1 - e^2/r_2 = (e^2/r_0)(r_0/r_1 - r_0/r_2)$  seems superior.

(vii) A chiral  $\text{H}_2$  bond must be interpreted with CP [13]. Reminding (1c) and the  $A_r$ -term, constant  $A_r$  implies that  $\text{H}_2$  geometry is fixed. This excludes coordinate dependent P-effects but points to intra-atomic charge inversion C, for only a term in  $A_r < 0$  can make  $\text{H}_2$  stable [10,23]. Then, our results provide with signatures for natural antihydrogen- or  $\underline{\text{H}}$ -states [10,23,29,30]. The common sense idea [10] that  $\text{H}_2$  consists of  $\text{H}_L\text{H}_R$  and  $\text{H}_R\text{H}_L$  (or of  $\underline{\text{H}}\underline{\text{H}}$  and  $\underline{\text{H}}\underline{\text{H}}$ ) is given away by Hund-type Mexican hat curves for  $\text{H}_2$  (Fig. 2-3). To make sense [29,30], also the H line spectrum must exhibit left-right asymmetry, point to  $\text{H}_R$ - and  $\text{H}_L$ -states or to H- and  $\underline{\text{H}}$ -states through the intermediary of a similar H Mexican hat curve for natural atom H, which is exactly what we observed [29,30].

(viii) The rigor of ab initio QM, often contra productive and inconclusive, can be avoided with less rigorous density functional theory (DFT) [10], seemingly in line with density  $\Gamma$  in (1h). Coefficient 1,391.. in (5f) for  $\text{H}_2$  bond densities also appears identically for H atom density [19].

(ix) Using (5a) and (5b), generic asymmetry  $S_C$  in (2d) for  $\text{H}_2$ , is now related quantitatively to

$$S_c \sim (1 - \frac{1}{2}\Phi) / (1 + \frac{1}{2}\Phi) = 0,690983 / 1,309017 = 0,527864 \quad (7b)$$

as given away by the H<sub>2</sub> vibrational spectrum [7], the backbone of the H<sub>2</sub> PEC.

## IX. Conclusion

Conceptually simple ionic Kratzer chiral bond theory is accurate for the prototypical and simplest quantum oscillator in nature: covalent bond H<sub>2</sub>. *Asymmetrical, chiral* H<sub>2</sub> binds hydrogen (H-state) to antihydrogen ( $\bar{H}$ -state). Wave equation and wave functions are not needed, since the first principles of old quantum theory suffice [13]. This simpler theory proves more accurate than any ab initio QM H<sub>2</sub> theory available. Unlike QM or QED, low energy symmetry breaking or left-right asymmetry in both H and H<sub>2</sub>, eventually leads to even more accurate, analytical solutions than hitherto believed.

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Table 2. Experimental [7] and theoretical vibrational energy levels of H<sub>2</sub> (cm<sup>-1</sup>)

| v  | E <sub>v,0</sub> [7] | This work | Difference |
|----|----------------------|-----------|------------|
| 0  | 0,00                 | 0,000     | 0,000      |
| 1  | 4161,14              | 4161,143  | -0,003     |
| 2  | 8086,93              | 8086,943  | -0,013     |
| 3  | 11782,36             | 11782,321 | 0,039      |
| 4  | 15250,31             | 15250,317 | -0,007     |
| 5  | 18491,92             | 18491,917 | 0,003      |
| 6  | 21505,78             | 21505,799 | -0,019     |
| 7  | 24287,91             | 24287,950 | -0,040     |
| 8  | 26831,16             | 26831,128 | 0,032      |
| 9  | 29124,09             | 29124,081 | 0,009      |
| 10 | 31150,47             | 31150,442 | 0,028      |
| 11 | 32887,13             | 32887,155 | -0,025     |
| 12 | 34302,20             | 34302,206 | -0,006     |
| 13 | 35351,36             | 35351,358 | 0,002      |
| 14 | 35973,38             | 35973,377 | 0,003      |

average difference 0,0151 cm<sup>-1</sup> (8,6.10<sup>-7</sup>%)

Table 3. Experimental and theoretical quanta for H<sub>2</sub> and differences ε (Exp-Theo in cm<sup>-1</sup>)

| v                         | Quanta ΔG(v+1/2) |                  | Differences <sup>a)</sup> in this work and in 7 QM studies from 1975 to 2008 as referenced |         |         |         |         |           |          |          |
|---------------------------|------------------|------------------|--|---------|---------|---------|---------|-----------|----------|----------|
|                           | Exp [7]          | <i>This work</i> | <i>This work</i>   | 1975[4] | 1983[5] | 1993[6] | 1995[6] | >1995[26] | 2006[27] | 2008[28] |
| 0                         | 4161,14          | 4161,143         | -0,002   | -0,94   | -0,04   | -0,027  | -0,027  | -0,023    | -0,024   | -0,0241  |
| 1                         | 3925,79          | 3925,800         | -0,010   | -0,88   | -0,07   | -0,052  | -0,046  | -0,047    | -0,049   | -0,0484  |
| 2                         | 3695,43          | 3695,379         | 0,051  | -0,74   | 0,01    | 0,029   | 0,041   | 0,038     | 0,035    | 0,0354   |
| 3                         | 3467,95          | 3467,996         | -0,046   | -0,69   | -0,07   | -0,037  | -0,026  | -0,033    | -0,036   | -0,0357  |
| 4                         | 3241,61          | 3241,600         | 0,010  | -0,50   | 0,02    | 0,036   | 0,046   | 0,033     | 0,029    | 0,0301   |
| 5                         | 3013,86          | 3013,881         | -0,021   | -0,48   | -0,02   | -0,001  | 0,009   | -0,009    | -0,012   | -0,0116  |
| 6                         | 2782,13          | 2782,152         | -0,022   | -0,38   | -0,02   | -0,024  | -0,006  | -0,031    | -0,036   | -0,0340  |
| 7                         | 2543,25          | 2543,178         | 0,072  | -0,20   | 0,08    | 0,043   | 0,075   | 0,041     | 0,037    | 0,0388   |
| 8                         | 2292,93          | 2292,953         | -0,023   | -0,12   | -0,03   | -0,067  | -0,020  | -0,063    | -0,067   | -0,0644  |
| 9                         | 2026,38          | 2026,361         | 0,019  | 0,15    | -0,05   | -0,030  | 0,029   | -0,026    | -0,028   | -0,0258  |
| 10                        | 1736,66          | 1736,712         | -0,052   | 0,27    | -0,15   | -0,108  | -0,047  | -0,116    | -0,118   | -0,1156  |
| 11                        | 1415,07          | 1415,052         | 0,018  | 0,69    | 0,08    | -0,043  | -0,006  | -0,093    | -0,092   | -0,0906  |
| 12                        | 1049,16          | 1049,152         | 0,008  | 1,11    | -0,06   | 0,038   | 0,021   | -0,090    | -0,087   | 0,0444   |
| 13                        | 622,02           | 622,019          | 0,001  | 1,70    | 0,30    | 0,164   | 0,064   | -0,078    | -0,068   | -0,2021  |
| Error in cm <sup>-1</sup> |                  |                  | 0,025  | 0,632   | 0,071   | 0,050   | 0,033   | 0,036     | 0,051    | 0,0572   |
| Error in %                |                  |                  | 0,0011   | 0,0424  | 0,0059  | 0,0037  | 0,0019  | 0,0033    | 0,0032   | 0,0044   |
| Ratio % with this work    |                  |                  | 1  | 40,3    | 5,6     | 3,5     | 1,8     | 3,1       | 3,0      | 4,2      |

a) all decimals as given in published data



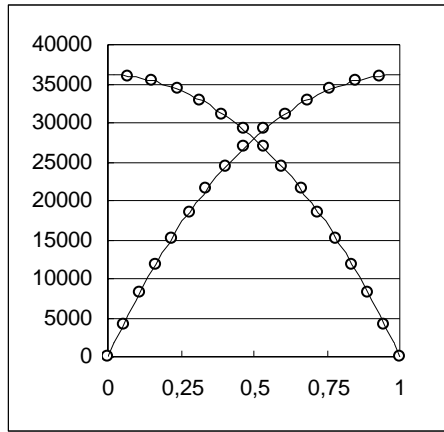


Fig. 1 Levels  $E_{v,0}$  versus Euclidean  $b\delta$  (left to right) and complementary  $x=1-b\delta$  (right to left), with  $D_e$  as natural intercept

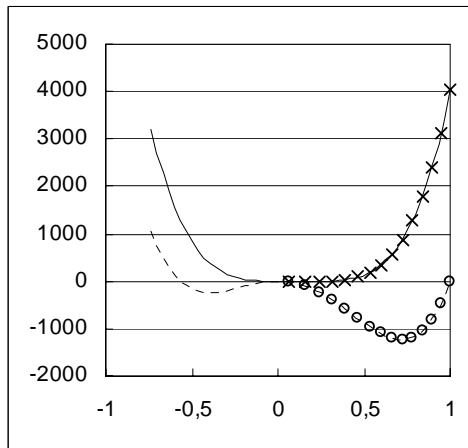


Fig. 2  $H_2$  Mexican hat curves: eqn (6f) (full line x) and  $D_e(1-x^2)-E_{v,0}$  (dashed line o), both quartics extrapolated to the left

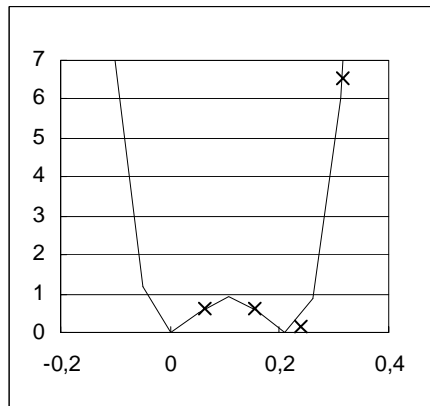


Fig. 3 Zooming in on the lower part of the  $H_2$  Mexican hat curve, eqn. (6f)