

QED calculations of H₂ molecule

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Do we need QED for H₂?

Dissociation energy of H₂

Year	Experiment	Theory	Δ
1926	$35.2(19) \times 10^3$ ^a		-0.9×10^3
1927		24×10^3 ^{a,b}	-12×10^3
1927	35.3×10^3 ^a		-0.8×10^3
1928		28.3×10^3 ^{a,b}	-7.8×10^3
1929	$36.19(32) \times 10^3$ ^a		0.07×10^3
1931		30.4×10^3 ^{a,b}	-5.7×10^3
1933		$36\ 104(105)$ ^a	-14
1934	36 100(40)		-18
1935	36 116(6)		-2
1960		$36\ 113.1$ ^c	-5.0
1961	$36\ 113.05(30)$		-5.02
1962		36 091	-27
1964		36 114.2	-3.9
1966		36 117.5	-0.6
1968		36 117.4	-0.7
1969	$36117.5(20)$ ^d		-0.6
1969	$36\ 118.3$ ^e		0.2
1970	$36\ 118.6(5)$		0.5
1972		36 117.8	-0.3
1975		36 118.0	-0.1
1978		36 117.92	-0.15
1983		36 118.01	-0.06
1986		36 118.088	0.018
1987		36 118.074	0.004
1992	$36\ 118.11(8)$		0.04
1993	$36\ 118.06(4)$		-0.01
1993		36 118.049	-0.021
1993		36 118.060	-0.010
1995		36 118.069	-0.001
2004	$36\ 118.062(10)$		-0.008
2009	$36\ 118.06962(37)$ ^d		0
2009		$36\ 118.0695(10)$	-0.0001

Source:
Faraday Discuss.
150, 51 (2011)

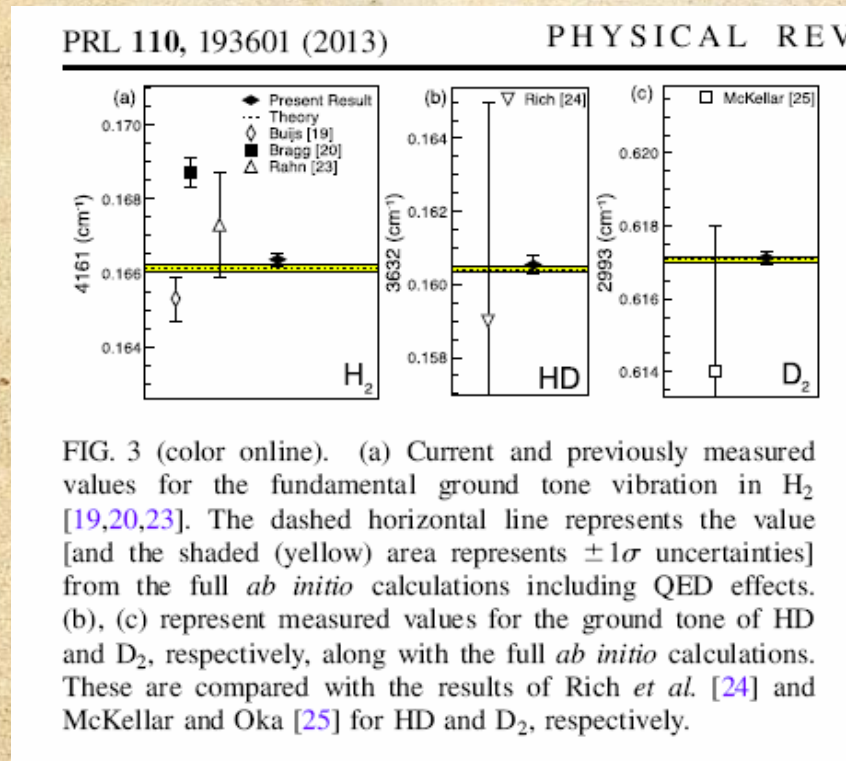
An order of magnitude
in precision every
14 years

QED : **-0.1964 (9)**

Theory:
J. Chem. Theor. Comput.
5, 3039 (2009)

H₂: accurate test of QED in molecules

Measurement of the fundamental ground tone vibration (rotationless vibrational splitting) in H₂, HD, and D₂ [Amsterdam, W. Ubachs group, 2013]



Accurate test of QED in chemically bound systems

QED (H₂): $-0.02145(9) \text{ cm}^{-1}$ 100 times larger than the experimental error

Theory: K. Pachucki, J. Komasa 2013

Spectroscopy of H_2 : bounds on fifth forces

$$V(r_{12}) = \alpha_G e^{-r_{12}/\lambda}$$

Search for an additional interaction between particles at a given length scale $\lambda \leftrightarrow$ search for deviation from the Newtonian law of gravity.

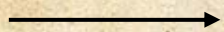
- Gravitational experiments: $10^{-2} \text{ m} < \lambda < 10^6 \text{ km}$
- Casimir force experiments: $10^{-7} \text{ m} < \lambda < 10^{-4} \text{ m}$
- Spectroscopy of H_2 : chemical bond distance length scale

PRL 110, 193601 (2013): H_2 constraint $\alpha_G < 6 \times 10^{-8} \text{ eV}\cdot\text{A}$ for $\lambda \gg R = 0.74 \text{ \AA}$

QED: from atoms to simple molecules

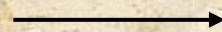
Atomic hydrogen

\vec{r}_{1A}



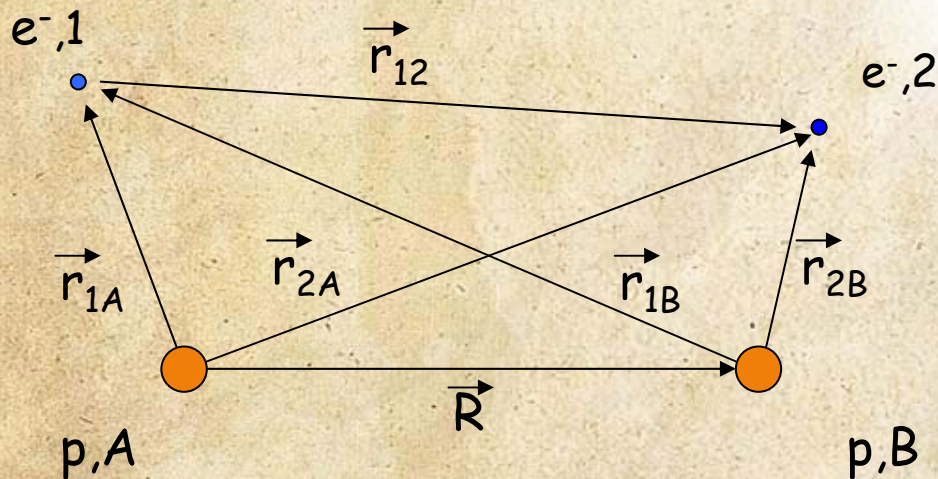
Atomic helium

\vec{r}_{1A} \vec{r}_{2A} \vec{r}_{12}



Molecular hydrogen

\vec{r}_{1A} \vec{r}_{2A} \vec{r}_{12} \vec{r}_{2A} \vec{r}_{2B} \vec{R}



Energy levels of light molecules: QED theory

Perturbative expansion in two parameters

$\alpha \approx 1/137$ is the fine-structure constant

$\beta = m/M$ is the electron-to-nucleus mass ratio $\approx 10^{-3}$ for H_2

$$E(\alpha, \beta) = \begin{array}{cccc} E_{\text{BO}} & + & \alpha^2 E_{\text{REL}} & + & \alpha^3 E_{\text{QED}} & + & \alpha^4 E_{\text{HQED}} & + & \dots \\ + & & + & & + & & & & \vdots \\ \beta E_{\text{AD}} & & \alpha^2 \beta E_{\text{REL}}^{\text{rec}} & & \alpha^3 \beta E_{\text{QED}}^{\text{rec}} & & & & \\ + & & \vdots & & \vdots & & & & \\ \beta^2 E_{\text{NA}} & & & & & & & & \\ \vdots & & & & & & & & \end{array}$$

"usual" chemistry

E_{BO} – the Born-Oppenheimer energy

βE_{AD} – adiabatic correction

$\beta^2 E_{\text{NA}}$ – nonadiabatic correction

$\alpha^2 E_{\text{REL}}$ – relativistic correction

$\alpha^3 E_{\text{QED}}$ – the leading QED correction

$\alpha^4 E_{\text{HQED}}$ – higher order QED correction

Nonrelativistic theory

Schroedinger equation:

$$[H - E] |\phi\rangle = 0$$

$$H = H_{\text{el}} + H_{\text{n}}$$

$$H_{\text{el}} = - \sum_a \frac{\nabla_a^2}{2 m_e} + V$$

Diatomic molecules, coordinate system origin at the bond midpoint:

$$H_{\text{n}} = - \frac{\nabla_R^2}{2 \mu_{\text{n}}} - \frac{\nabla_{\text{el}}^2}{2 \mu_{\text{n}}} - \left(\frac{1}{M_B} - \frac{1}{M_A} \right) \vec{\nabla}_R \cdot \vec{\nabla}_{\text{el}}$$

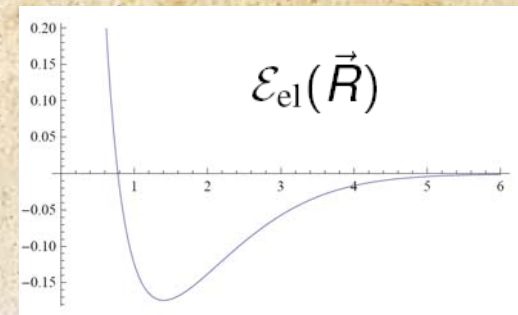
$$\vec{R} = \vec{R}_A - \vec{R}_B \qquad \frac{1}{\mu_{\text{n}}} = \frac{1}{M_B} + \frac{1}{M_A} \qquad \vec{\nabla}_{\text{el}} \equiv \frac{1}{2} \sum_a \vec{\nabla}_a$$

Adiabatic approximation

$$\phi_a(\vec{r}, \vec{R}) = \phi_{\text{el}}(\vec{r}) \chi(\vec{R})$$

Born-Oppenheimer energy:

$$[H_{\text{el}} - \mathcal{E}_{\text{el}}(\vec{R})] |\phi_{\text{el}}\rangle = 0$$

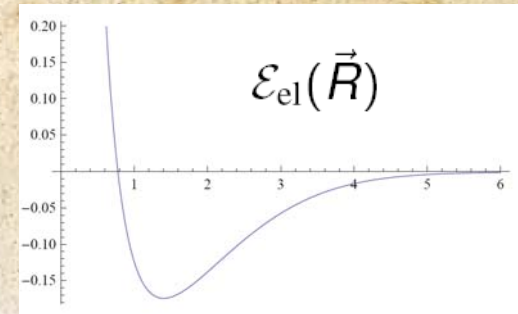


Adiabatic approximation

$$\phi_a(\vec{r}, \vec{R}) = \phi_{\text{el}}(\vec{r}) \chi(\vec{R})$$

Born-Oppenheimer energy:

$$[H_{\text{el}} - \mathcal{E}_{\text{el}}(\vec{R})] |\phi_{\text{el}}\rangle = 0$$



Adiabatic correction:

$$[H_n + \mathcal{E}_{\text{el}}(\vec{R}) + \mathcal{E}_a(\vec{R}) - E_a] |\chi\rangle = 0$$

$$\mathcal{E}_a(\vec{R}) = \langle \phi_{\text{el}} | H_n | \phi_{\text{el}} \rangle_{\text{el}}$$

$$\left[-\frac{1}{2R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_n R^2} + \mathcal{E}_{\text{el}}(R) + \mathcal{E}_a(R) \right] \chi_J(R) = E_a \chi_J(R)$$

Beyond the adiabatic approximation

[K. Pachucki and J. Komasa, *J. Chem. Phys.* **130** 164113 (2009)]

Radial nonadiabatic Schroedinger equation:

$$\left[-\frac{1}{R^2} \frac{\partial}{\partial R} \frac{R^2}{2 \mu_{\parallel}(R)} \frac{\partial}{\partial R} + \frac{J(J+1)}{2 \mu_{\perp}(R) R^2} + \mathcal{V}(R) \right] \chi_J(R) = E \chi_J(R)$$

where

$$\mathcal{V}(R) = \mathcal{E}_{\text{el}}(R) + \mathcal{E}_{\text{a}}(R) + \delta \mathcal{E}_{\text{na}}(R)$$

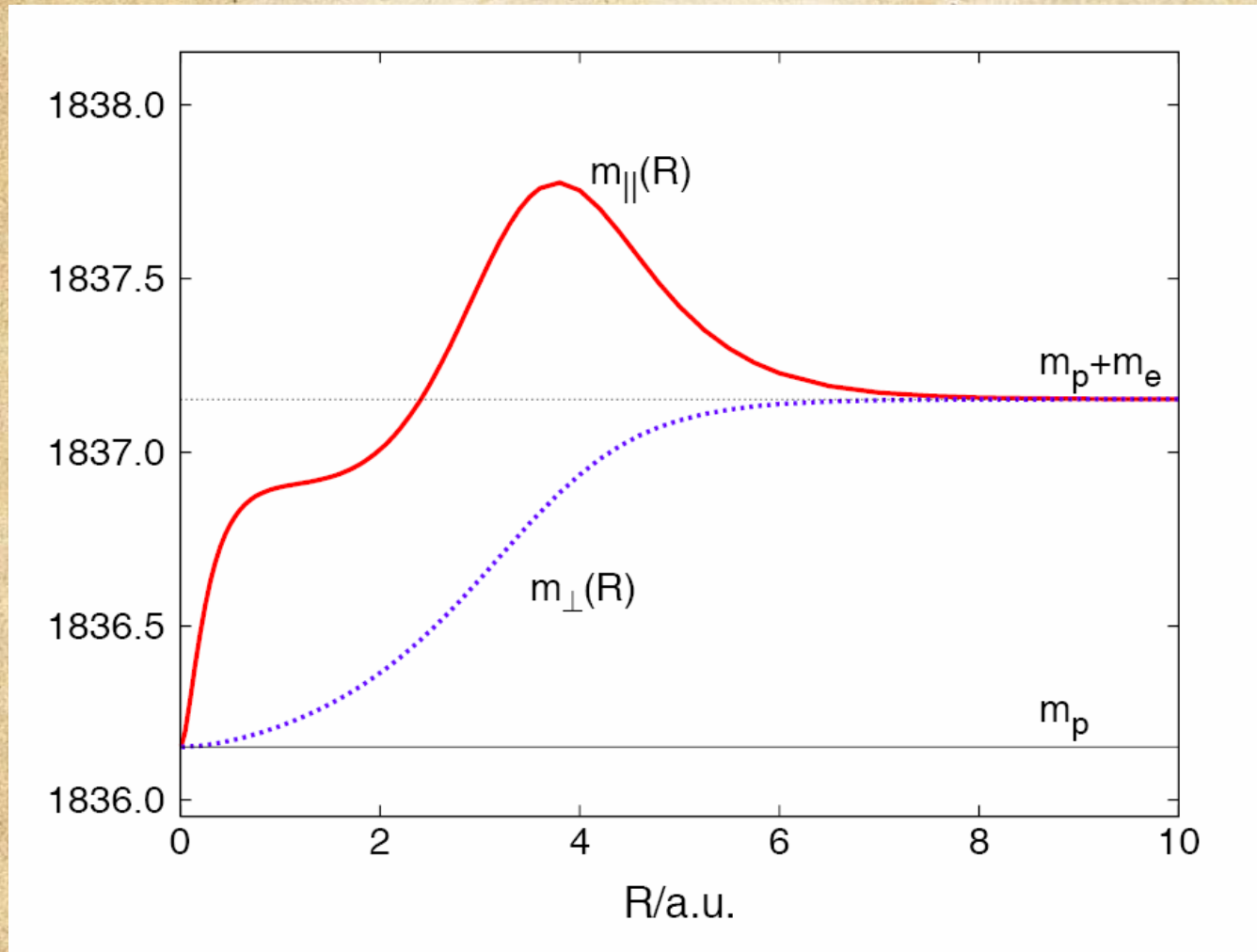
is a nonadiabatic potential energy function

Effective R-dependent nuclear masses:

$$\frac{1}{2 \mu_{\parallel}(R)} \equiv \frac{1}{2 \mu_{\text{n}}} + \mathcal{W}_{\parallel}(R) \qquad \frac{1}{2 \mu_{\perp}(R)} \equiv \frac{1}{2 \mu_{\text{n}}} + \mathcal{W}_{\perp}(R)$$

$$\mathcal{W}_{\parallel}(R) = \frac{1}{\mu_{\text{n}}^2} \left\langle \vec{n} \cdot \vec{\nabla}_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \vec{n} \cdot \vec{\nabla}_R \phi_{\text{el}} \right\rangle_{\text{el}}$$
$$\mathcal{W}_{\perp}(R) = \frac{1}{\mu_{\text{n}}^2} \frac{(\delta^{ij} - n^i n^j)}{2} \left\langle \nabla_R^i \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \nabla_R^j \phi_{\text{el}} \right\rangle_{\text{el}}$$

Effective nuclear masses in H_2



Relativistic correction ($\sim \alpha^2$)

Expectation value of the Breit-Pauli Hamiltonian on the nonrelativistic wave function:

$$\begin{aligned}\mathcal{E}_{\text{REL}} &= \sum_a \left[-\frac{1}{8} \langle \Psi | p_a^4 | \Psi \rangle + \sum_l \frac{Z_l \pi}{2} \langle \Psi | \delta(\vec{r}_{al}) | \Psi \rangle \right] \\ &+ \sum_{a>b} \left[\pi \langle \Psi | \delta(\vec{r}_{ab}) | \Psi \rangle + \frac{1}{2} \left\langle \Psi \left| \vec{p}_a \frac{1}{r_{ab}} \vec{p}_b + \vec{p}_a \cdot \vec{r}_{ab} \frac{1}{r_{ab}^3} \vec{r}_{ab} \cdot \vec{p}_b \right| \Psi \right\rangle \right] \\ &+ \frac{2\pi}{3} \sum_l Z_l \frac{r_{\text{ch}}^2(l)}{\lambda_e^2} \left\langle \Psi \left| \sum_a \delta(\vec{r}_{al}) \right| \Psi \right\rangle\end{aligned}$$

Leading QED correction ($\sim \alpha^3$)

Expectation values on non-local and singular operators need to be calculated

Bethe logarithm:

$$\ln k_0 = \frac{\langle \phi_{el} | \vec{\nabla} (H_0 - \mathcal{E}_0) \ln [2 (H_0 - \mathcal{E}_0)] \vec{\nabla} | \phi_{el} \rangle}{\langle \phi_{el} | \vec{\nabla} (H_0 - \mathcal{E}_0) \vec{\nabla} | \phi_{el} \rangle}$$

Regularized $1/r_{12}^3$ operator:

$$\langle \phi_{el} | P(r_{12}^{-3}) | \phi_{el} \rangle = \lim_{a \rightarrow 0} \langle \phi_{el} | \theta(r_{12} - a) r_{12}^{-3} + 4\pi (\gamma + \ln a) \delta(\mathbf{r}_{12}) | \phi_{el} \rangle$$

Higher-order QED correction ($\sim \alpha^4$)

- An open challenge.
- Very difficult to calculate, known only for H, He and H_2^+ .
- Involves even more singular operators.
- Choice of the basis for representation of the wave function is important.

Wave function

Schroedinger equation is solved by variational principle.

Wave function is represented by a linear combination of basis functions

$$\phi_{el} = \sum_{k=1}^K c_k (1 + \hat{P}_{12})(1 \pm \hat{i}) \psi_k(\mathbf{r}_1, \mathbf{r}_2)$$

Choice of the basis functions:

- Explicitly correlated basis set. Includes explicitly all interparticle distances \vec{r}_{1A} \vec{r}_{2A} \vec{r}_{12} \vec{r}_{2A} \vec{r}_{2B}

- Cusp condition fulfilled ?

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \text{const} + O(r_{12})$$

Explicitly correlated basis sets

Explicitly correlated Gaussians (ECG)

$$\psi_k = \exp(-\alpha r_{1A}^2 - \beta r_{1B}^2 - \gamma r_{2A}^2 - \delta r_{2B}^2 - \lambda r_{12}^2)$$

Positive: fast, stable, all integrals are calculated analytically

Negative: cusp condition is not fulfilled \Rightarrow slow convergence, thousands of nonlinear parameters to be optimized

Explicitly correlated exponentials

$$\psi_k = \exp(-\alpha r_{1A} - \beta r_{1B} - \gamma r_{2A} - \delta r_{2B} - \lambda r_{12})$$

Positive: cusp condition is fulfilled \Rightarrow potentially much more powerful than ECG. The most general two-center two-electron basis.

Negative: how to calculate integrals with such functions???
Haven't been used so far due to overwhelming technical difficulties.

Master two-center integral

A problem: integral to be calculated analytically:

$$f(r) = r \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-w_1 r_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}}{r_{12} r_{1A} r_{1B} r_{2A} r_{2B}},$$

Previously: expansions in r , spherical-wave expansions of r_{12} ...

K. Pachucki, Phys. Rev. A 86, 052514 (2012):

$$f(r) = \int_0^{-\infty} dt e^{tr} \frac{1}{2\sqrt{\sigma}} \left[\theta(t_1 - t) \ln |\beta_{0,0}| + \theta(t_2 - t) \ln |\beta_{3,3}| - \theta(t_3 - t) \ln |\beta_{3,1} \beta_{3,3}| - \theta(t_4 - t) \ln |\beta_{0,1} \beta_{0,0}| \right],$$

$$\beta_{i,j} = \frac{\sqrt{\sigma} - \gamma_{i,j}}{\sqrt{\sigma} + \gamma_{i,j}}, \text{ where } \sigma \text{ and } \gamma_{i,j} \text{ are polynomials}$$

Integral over t remains to be evaluated numerically.

Other two-center integrals

Integrals with additional **positive** powers of r 's can be calculated from $f(r)$ and its derivatives over r by recurrence relations.

Integrals with additional **negative** powers of r 's can be calculated by numerically integrating $f(r)$ over the nonlinear parameters:

$$\left\langle \frac{1}{r_{1A}^2} \right\rangle = \int_0^\infty dq \left\langle \frac{e^{-q r_{1A}}}{r_{1A}} \right\rangle$$

Difficulties: numerical instabilities

First calculations with exponential basis

K. Pachucki and V. A. Yerokhin, Phys. Rev. A 87, 062508 (2013):

TABLE I. Nonrelativistic energy of the ground electronic Σ_g^+ state of the H_2 molecule for two internuclear distances r , in a.u.

N	$r = 1.4$		$r = 14.0$	
	E	δE	E	δE
2	-1.173 468 555		-0.999 999 778 930	
4	-1.174 125 505	-0.000 783 527	-1.000 000 480 057	-0.000 764 402 260
8	-1.174 373 774	-0.000 248 268	-1.000 000 942 482	-0.000 000 462 425
16	-1.174 469 553	-0.000 095 779	-1.000 000 955 376	-0.000 000 012 893
32	-1.174 474 880	-0.000 005 327	-1.000 000 958 807	-0.000 000 003 430
64	-1.174 475 260	-0.000 000 379	-1.000 000 959 559	-0.000 000 000 934
	-1.174 475 714 220 ^a		-1.000 000 960 680 791 ^b	

^aJames-Coolidge basis with $N \approx 20\,000$ [7].

^bExplicitly correlated asymptotic basis with $N \approx 20\,000$ [7].

TABLE II. Expectation value of the operators r_{12}^{-2} and r_{1A}^{-2} for the ground electronic Σ_g^+ state of the H_2 molecule for two internuclear distances r , in a.u.

N	$r = 1.4$		$r = 14.0$	
	$\langle r_{12}^{-2} \rangle$	$\langle r_{1A}^{-2} \rangle$	$\langle r_{12}^{-2} \rangle$	$\langle r_{1A}^{-2} \rangle$
8	0.51 8 482	1.604 12	0.005 155 876	1.002 558 4
16	0.51 7 917	1.601 65	0.005 155 881	1.002 555 5
32	0.51 7 948	1.601 73	0.005 155 882	1.002 562 3
64	0.51 7 934	1.601 70	0.005 155 882	1.002 563 1
	0.51 7 913 ^a	1.597 56 ^a		

^aGaussian basis with $N \approx 1200$ [13].

Conclusion

Theory of H_2 molecule reached a very high level of sophistication. Excellent agreement between theory and experiment.

Modern experiments require calculations of higher-order QED Corrections in H_2 .

Towards calculations of $m\alpha^6$ corrections:

Proof-of-principle calculations with exponential two-center two-electron basis set are reported.

Basis set yields a very compact representation of the wave Function, but is difficult to work with.

Theory versus Experiment: current status

Dissociation energy in H₂ and D₂

Component	D_0/cm^{-1}
E_{BO}	36112.5927(1)
$+\beta E_{AD}$	+5.7711(1)
$+\beta^2 E_{NA}$	+0.4340(2)
$+\alpha^2 E_{REL}$	-0.5318(5)
$+\alpha^3 E_{QED}$	-0.1948(3)
$+\alpha^4 E_{HQED}$	-0.0016(8)
E	36118.0696(11)

	D_0/cm^{-1}	
	H ₂	D ₂
Experiment (1993) ²	36 118.06(4)	36 748.32(7)
Experiment (2004) ³	36 118.062(10)	36 748.343(10)
Experiment (2009/10) ^{4,5}	36 118.069 62(37)	36 748.362 86(68)
Theory (2009) ⁶	36 118.069 6(11)	36 748.363 4(9)
Difference	0.000 0(12)	0.000 5(11)

Theory: Pachucki,
Komasa
J. Chem. Phys. 130,
164113 (2009)

²E. E. Eyler, N. Melikechi, *Phys. Rev. A* **48**, R18 (1993);

³Y. Zang *et al.*, *Phys. Rev. Lett.* **92**, 203003 (2004);

⁴Liu, Salumbides, Hollenstein, Koelemeij, Eikema, Ubachs, Merkt, *JCP* **130**, 174306 (2009)

⁵Liu, Sprecher, Jungen, Ubachs, Merkt, *JCP* **132**, 154301 (2010);

⁶Piszczatowski, Lach, Przybytek, Komasa, Pachucki, Jeziorski, *JCTC* **5**, 3039 (2009)