Wpływ efektów QED na widmo i geometrię molekuł

Bogumił Jeziorski

Pracownia Chemii Kwantowej, Wydział Chemii
Uniwersytet Warszawski

Seminarium Czwartkowe

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Chemistry up to about 1900:

Science of the nature of matter and its transformations

Chemistry after about 1900:

Science of the nature of matter and its transformations

– but the meaning of matter restricted to substances made of atoms and molecules, disregarding the matter within the atomic nuclei

Quantum Chemistry (born in 1927):

Science of making theoretical predictions of properties of molecules, their chemical reactivity (reaction rates) and physical properties of substances built from atoms and molecules.

Two citations on the use of mathematics in chemistry

> *Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry.... if mathematical analysis should ever hold a prominent place in chemistry – an aberration which is happily almost impossible – it would occasion a rapid and widespread degeneration of that science*

Auguste Comte, Cours de philosophie positive, 1830

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I rather expect that we shall someday find a mathematico-mechanical explanation for what we now call atoms which will render an account of their properties

August Kekule, 1867

Two citations on computations in chemistry

The underlying physical laws necessary for mathematical theory of a large part of physics and for the whole of chemistry are completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble.

Paul A. M. Dirac, 1929

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Paul A. M. Dirac, 1929

At the end of 21st century more than half of the research effort in chemistry will be computational

Henry F. Schaefer III, 2000

Content of the Lecture:

I shall show how accurately quantum chemistry predicts:

- The dissociation energy of the prototypical chemical bond of molecular hydrogen
- Rovibrational spectrum of the hydrogen molecule
- The interation potential for the prototypical van der Waals attraction of helium atoms
- The bond length and the dissociation energy of the enigmatic helium dimer

and what role the effects of quantum electrodynamics play in making these predictions

Determination of the dissociation energy of H_2 – a historical perspective

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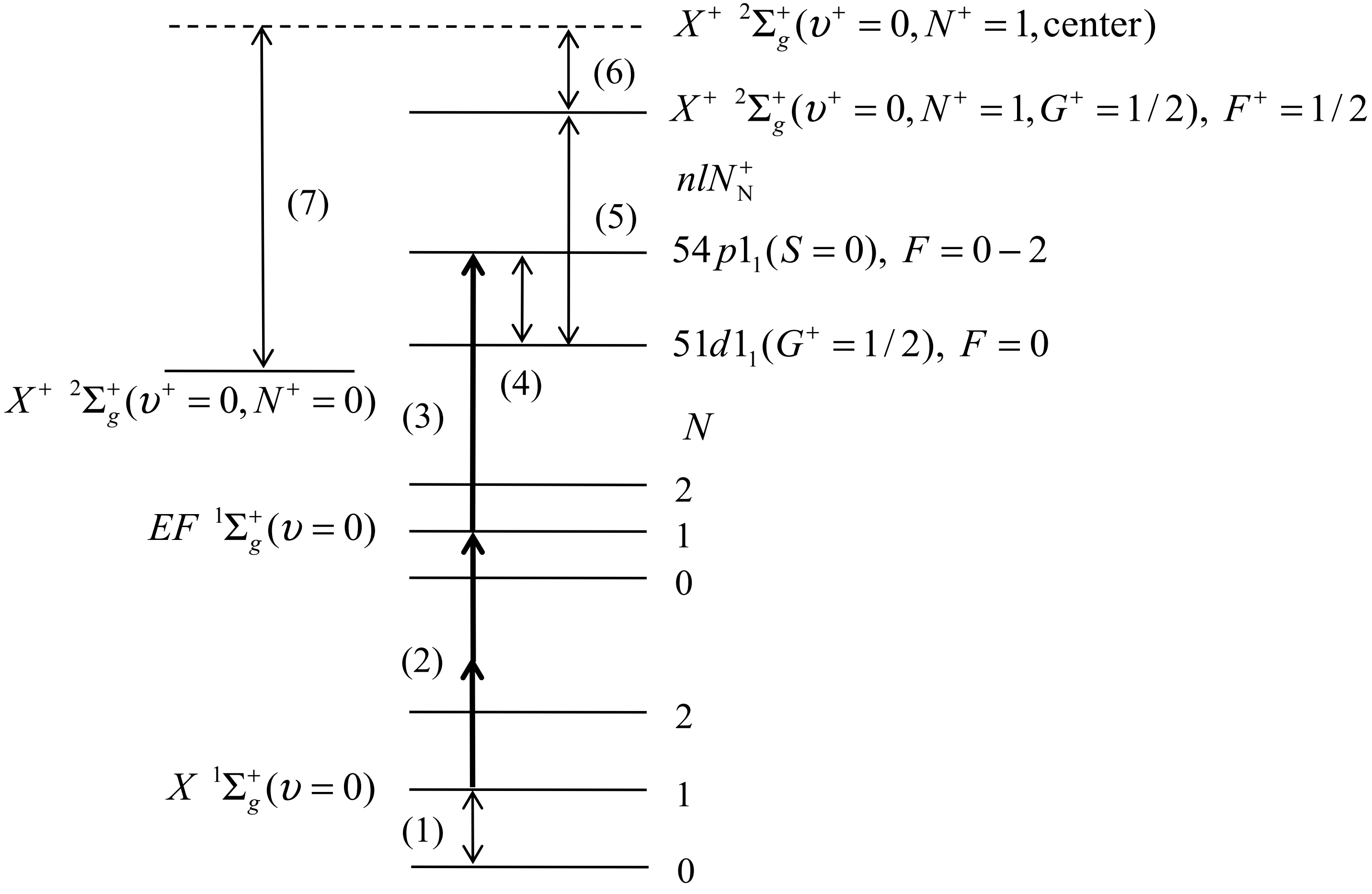
2009	36118.0696(4)	Liu et al (Ubachs and Merkt groups)

Zürich-Amsterdam experiment – ionization energy of H_2



$X^+\ {}^2\Sigma_g^+(v^+ = 0, N^+ = 1, \text{center})$

(6)

$X^+\ {}^2\Sigma_g^+(v^+ = 0, N^+ = 1, G^+ = 1/2),\ F^+ = 1/2$

nlN_{N}^+

(7)

(5)

$54p1_1(S = 0),\ F = 0 - 2$

$51d1_1(G^+ = 1/2),\ F = 0$

(4)

$X^+\ {}^2\Sigma_g^+(v^+ = 0, N^+ = 0)$

(3)

N

2

$EF\ {}^1\Sigma_g^+(v = 0)$ 1

0

(2)

2

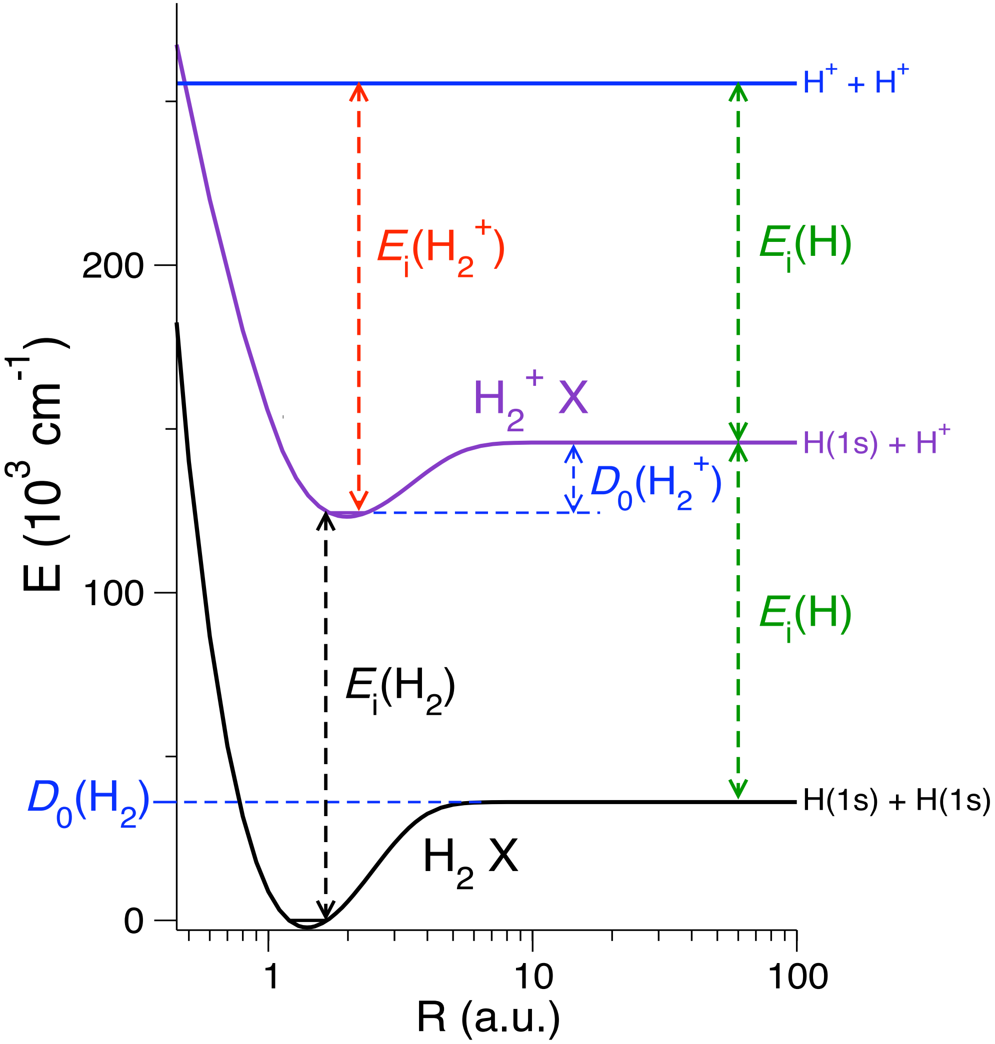
$X\ {}^1\Sigma_g^+(v = 0)$ 1

(1)

0

J. Liu, E.Salumbides, U, Hollenstein, J. Koelemeij, K. Eikema, W. Ubachs, F, Merkt, JCP 130, 174306 (2009)

Zürich-Amsterdam experiment – dissociation energy of H_2



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Experimental data - challenge for theory

$$D_0(\mathrm{H}_2) = 36118.0696(4)\ \mathrm{cm}^{-1}\quad [1]$$

$$D_0(\mathrm{D}_2) = 36748.343(10)\ \mathrm{cm}^{-1}\quad [2]$$

$$\Delta J(1 \to 0) = 118.48684(10)\ \mathrm{cm}^{-1}\ [3]$$

$$\Delta v(1 \to 0) = 4161.1660(3)\ \mathrm{cm}^{-1}\ [4]$$

[1] J. Liu at al, 2009 (Wim Ubachs and Frederic Merkt groups)

[2] Y. P. Zhang, 2004 (Ed Eyler group)

[3] D. E. Jennings et al, 1984

[4] M. Stanke et al, 2009

Schrödinger-Coulomb equation for N particles

$$\left(-\frac{1}{2}\sum_{i=1}^{N}\frac{\nabla_i^2}{m_i}+\sum_{i<j}^{N}\frac{Z_iZ_j}{r_{ij}}\right)\Psi = E\,\Psi$$

where $Z_i = -1$ and $m_i = 1$ when i labels an electron.

The Schrödinger-Coulomb equation:

- is mathematically rigorous (essentially self-adjont operator on the left)
- with a small number of "material parameters" (Z_i's and m_i's) is has an enormous predictive power. Predicts e.g:
  - spectra of all molecules
  - all thermochemistry
  - rates of all chemical reactions

One more citation:

“Je mehr ich über den physikalischen Teil der Schrödingerischen Theorie nachdenke, desto abscheulicher finde ich ihn. Was Schrödinger über Anschaulichkeit seiner Theorie schreibt dürfte wohl kaum eine sinngemässe, in a.W. ich finde es Mist”

Werner Heisenberg, in a letter to Pauli, June 1926

Born–Oppenheimer potential for the $X^1\Sigma_g^+$ state of H_2

The Born–Oppenheimer potential was represented as

$$V(R) = e^{-\beta R^2 - \gamma R}(R^{-1} + \sum_{n=0}^{16} b_n R^n) + (\sum_{n=0}^{2} a_n R^n + a_3 R^{\frac{5}{2}})\, e^{-2R} - \sum_{n=6}^{26} f_n(\eta R) \frac{C_n}{R^n}$$

where

$$f_n(x) = 1 - e^{-x}(1 + x + x^2/2! \cdots x^n/n!)$$

is the Tang-Toennies damping function. The linear parameters a_0 and a_1 are fixed by forcing the correct short-range behaviour

$$V(R) = \frac{1}{R} + E_{\mathrm{He}} - 2E_{\mathrm{H}} + O(R^2)$$

The 3 nonlinear and the remaining 19 linear parameters are fitted to reproduce over 100 data points computed Pachucki.

The error of this BO potential is less than 5 $\times 10^{-5}$ cm^{-1}

Nonrelativistic theory (Schrödinger equation)

Born-Oppenheimer energy	36112.5927(1)
Adiabatic correction	5.7711(1)
Nonadiabatic correction	0.4339(2)
Total nonrelativistic	36118.7978(2)
Bubin et al, 2009†	36118.79774(1)
Experiment	36118.0696(4)
Missing relativity effects	$-0.7282(4)$

†From 4-particle variational calculations employing 10,000-term Gaussian basis (from Adamowicz group)

Relativity: Dirac-Coulomb equation

This is a naive generalization of the Schrödinger equation obtained by adding the Coulombic interelectronic repulsion to the sum of one-electron Dirac Hamiltonians $\hat{h}_{\rm D}$

$$\hat{H}_{\rm DC} = \sum_{i}^{N} \hat{h}_{\rm D}(i) + \sum_{j<j}^{N} \frac{1}{r_{ij}}$$

This equation forms a basis for relativistic quantum chemistry but it suffers from the following pathologies:

- **$\hat{H}_{\rm DC}$ has only continuous spectrum from $-\infty$ to ∞ (no bound states).**
- **Physical states are modeled by Feshbach-type resonances with unphysical width of the order of $Z^3\alpha^3$ [1]**
- **Ground state is unstable, has a finite lifetime**
- **Elimination of the width by Feshbach (Sucher) projection is not unique**
- **Wrong mass dependence of the α^2 relativistic correction even for the hydrogen atom**

[1]**G. Pestka, M. Bylicki, J. Karwowski, J. Phys. B39, 2979 (2006); B40, 2249 (2007)**

Nonrelativistic QED (Caswell, Lepage, Pachucki)

In nonrelativistic QED the energy of a quantum system is expanded in powers of the fine-structure constant α

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \cdots,$$

where $E^{(0)}$ is the nonrelativistic energy, and $E^{(k)}$ are expressed in terms of expectation values of certain operators with nonrelativistic wave functions or in terms of nonrelativistic response functions. For instance

$$\alpha^2 E^{(2)} = \langle H_{\mathrm{BP}} \rangle = \langle H_{\mathrm{mv}} \rangle + \langle H_{\mathrm{D1}} \rangle + \langle H_{\mathrm{D2}} \rangle + \langle H_{\mathrm{OO}} \rangle + \langle H_{\mathrm{SO}} \rangle + \langle H_{\mathrm{SS}} \rangle$$

where H_{BP} is the complete Breit-Pauli Hamiltonian including electron-nucleus terms proportional to $\alpha^2(m_{\mathrm{e}}/m_{\mathrm{p}})^n$, n=1,2,3 (so called recoil terms).

When the recoil terms are neglected and the adiabatic wave functions are used to compute expectation values, the $\alpha^k E^{(k)}$ corrections can be expressed as radial expectation values of the relativistic intertomic potentials

$$V_{\mathrm{int}}(R) = V_0(R) + \alpha^2 V_2(R) + \alpha^3 V_3(R) + \alpha^4 V_4(R) + \cdots$$

α^3 QED Correction

When recoil effects of the order of $\alpha^3(m_\mathrm{e}/m_\mathrm{p})^n$ are neglected the $\alpha^3 E^{(3)}$ QED corrections is

$$\alpha^3\frac{16}{3}\left(\frac{19}{30}-2\ln\alpha-\ln K\right)\langle\delta(r_{1a})\rangle+\alpha^3\left(\frac{164}{15}+\frac{14}{3}\ln\alpha\right)\langle\,\delta(r_{12})\rangle-\alpha^3\frac{7}{6\pi}\langle P(r_{12}^{-3})\rangle$$

where $P(r_{12}^{-3})$ is the distribution defined by

$$\left\langle\psi|P(r_{12}^{-3})|\psi\right\rangle=\lim_{a\to 0}\left\langle\psi|\theta(r_{12}-a)\,r_{12}^{-3}+4\pi\,(\gamma+\ln a)\,\delta(r_{12})|\psi\right\rangle,$$

and $\ln K$ is the infamous Bethe logarithm (in full nonadiabatic form)

$$\ln K=\frac{\langle\psi\,|\,\mathrm{j}\,(\hat{H}-E^{(0)})\ln\left[\,(\hat{H}-E^{(0)})/\mathrm{Ry}_\infty\right]\mathrm{j}\,\psi\rangle}{\langle\psi\,|\,\mathrm{j}\,(\hat{H}-E^{(0)})\,\mathrm{j}\,\psi\rangle}\,.$$

$\mathrm{j}=-\mathrm{p}_1/m_e-\mathrm{p}_2/m_e+\mathrm{p}_a/m_p+\mathrm{p}_b/m_p$ is the electric current operator.
We developed an adiabatic adiabatic approximation to $\ln K$, defined as

$$\ln K^{\mathrm{ad}}=\frac{\langle\,\ln K^{\mathrm{el}}(R)\,D_1(R)\,\rangle}{\langle\,D_1(R)\,\rangle}$$

where $D_1(R)=\langle\delta(r_{1a})\rangle_{\mathrm{el}}$ and $\ln K^{\mathrm{el}}(R)$ is the electronic Bethe logarithm.

α^3 QED Correction - continued

At large R we found the following asymptotic expansions

$$\langle\psi_{\rm el}|P(r_{12}^{-3})\psi_{\rm el}\rangle = \frac{1}{R^3} + \frac{6}{R^5} + \frac{75}{R^7} + \mathcal{O}(R^{-8})$$

and

$$\ln K^{\rm el}(R) = \ln K_{\rm H} + \frac{L_6}{R^6} + \mathcal{O}(R^{-8})$$

with $L_6 = 2.082773$ a.u., which are useful in fitting $V_3(R)$ with analytic functions.

One may ask how accurate this adiabatic approximation to $\ln K$ is. To check this we evaluated $\ln K^{\rm ad}$ for H_2^+ and compared it with the nonadiabatic value obtained recently by V. Korobov (PRA, 73, 204502 (2006). The results are:

$\ln K^{\rm ad}$	3.01276
$\ln K$, from Korobov	3.01225
$\ln K^{\rm ad} + \ln \mu/m_{\rm e}$	3.01222

where $\mu = m_{\rm e} m_{\rm p}/(m_{\rm e} + m_{\rm p})$ is the electron proton reduced mass.
Our recommended value of $\ln K$, for H_2 is 3.0183(1).
The H atom value of $\ln K$ is 2.984128555.

One-loop α^4 QED contribution and other corrections

For atoms the one-loop contribution represents over 80% of the total α^4 QED correction. Therefore only this contribution

$$\alpha^4 E^{(4)}_{\mathrm{one-loop}} = 4\pi\,\alpha^4\,(\frac{427}{96} - 2\ln 2)\,\langle\delta(\mathrm{r}_{1a})\rangle$$

was computed.

We also included the finite nuclear size (2.14 fm) correction for deuterium, equal to -0.0002 cm^{-1}.

For H_2 this correction is less than 0.0001cm^{-1}

Results of calculations. Dissociation energies of H_2 and D_2

		H_2	D_2
α^0	Nonrelativistic	36118.7978(2)	36749.0910(2)
α^2	Mass-velocity	4.4273(2)	4.5125(2)
	1-el. Darwin	-4.9082(2)	-4.9873(2)
	2-el. Darwin	-0.5932(1)	-0.5993(1)
	Breit	0.5422(1)	0.5465(1)
	Total α^2	-0.5319(3)	-0.5276(3)
$\alpha^2\, m_e/m_p$	Estimate	0.0000(4)	0.0000(2)
α^3	1-el. Lamb shift	-0.2241(1)	-0.2278(1)
	2-el. Lamb shift	0.0166(1)	0.0167(1)
	Araki-Sucher	0.0127(1)	0.0128(1)
	Total α^3	-0.1948(2)	-0.1983(2)
$\alpha^3\, m_e/m_p$	Estimate	0.0000(2)	0.0000(1)
α^4	One-loop term	-0.0016(8)	-0.0016(8)
Total theory		36118.0695(10)	36748.3633(9)
Expt.	Eyler, 2004	36118.062(10)	36748.343(10)
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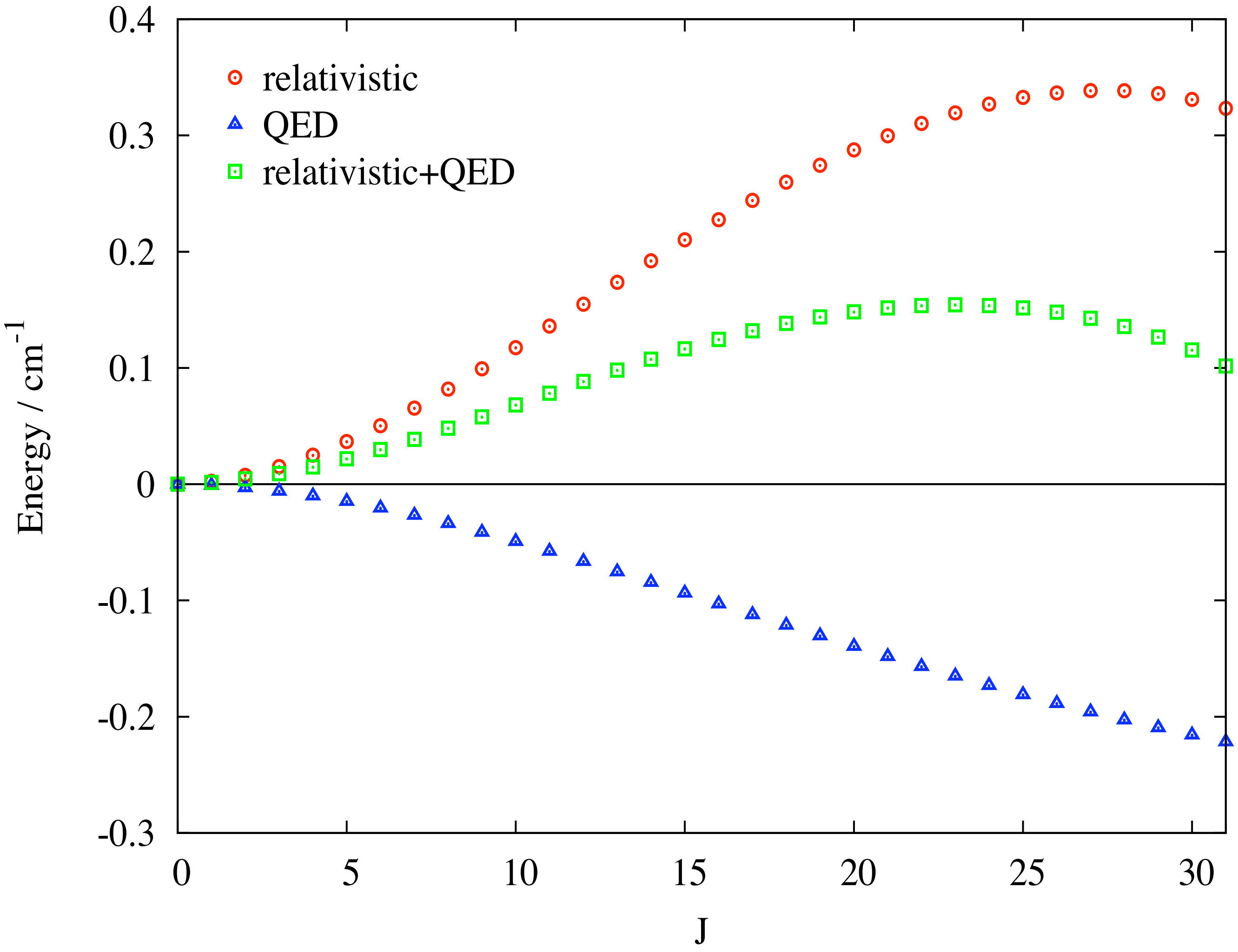
Expt.	Merkt&Ubachs, 2010	36118.0696(4)	36748.3629(6)

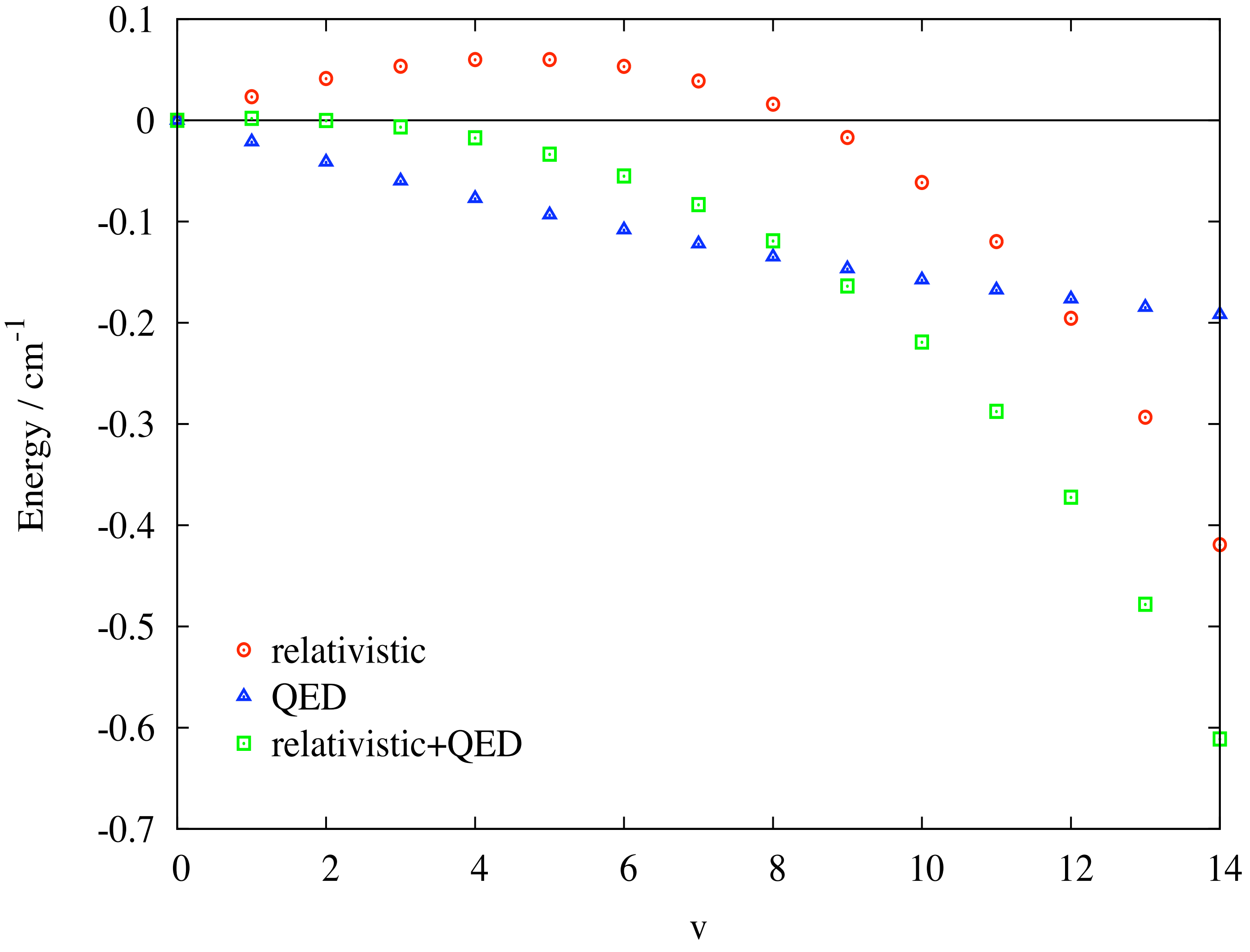
Lowest rotational an vibrational energy intervals for H_2

		$J = 0 \to 1$	$v = 0 \to 1$
α^0	Born-Oppenheimer	118.55558(2)	4163.4035(1)
	Adiabatic	-0.06365(4)	-1.4029(1)
	Nonadiabatic	-0.00667(8)	-0.8365(2)
	Total α^0	118.48526(9)	4161.1641(2)
α^2	Mass-velocity	0.02713(4)	0.5347(2)
	1-el. Darwin	-0.02383(4)	-0.4994(2)
	2-el. Darwin	-0.00160(2)	-0.0391(1)
	Breit	0.00088(2)	0.0279(1)
	Total α^2	0.00258(6)	0.0235(3)
α^3	1-el. Lamb shift	-0.00109(2)	-0.0231(1)
	2-el. Lamb shift	0.00004(1)	0.0011(1)
	Araki-Sucher	0.00002(1)	0.0007(1)
	Total α^3	-0.00103(3)	-0.0213(2)
α^4	One-loop term	-0.00001(1)	-0.0002(2)
Total theory		118.48680(11)	4161.1661(5)
Experiment	Jennings, Stanke	118.48684(10)	4161.1660(3)

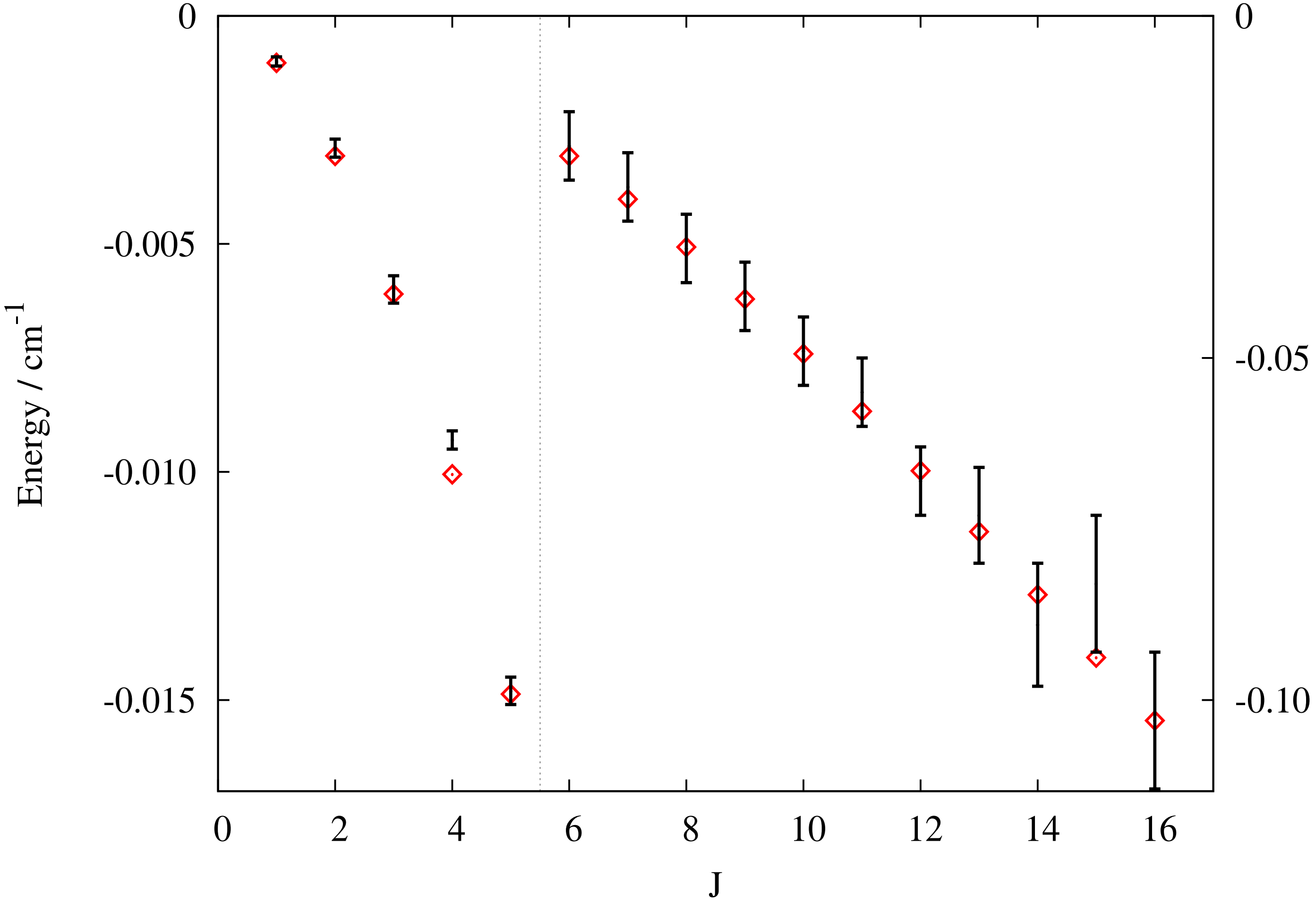
J dependence of the relativistic and QED contributions to the rotational excitation energies at v=0.



Vibrational quantum number dependence of the relativistic and QED contributions to the excitation energies at J=0.



QED contributions to the rotational excitation energies at v=0. Comparison of the present theoretical calculations (open diamonds) with the experimental data of the Amsterdam group (W. Ubachs). The extent of the vertical bars shows the experimental uncertainties.



Take home message from the H_2 study

1. One can do QED calculations for a molecule
2. If thoroughly done, such calculations can be competitive in accuracy with most sophisticated high-resolution spectroscopy measurements
3. The conventional Dirac-Coulomb or Dirac-Coulomb-Breit equations are not useful for this purpose.
4. No long-range nuclear force seen.

Collaboration in the work on molecular hydrogen:

Grzegorz Łach – University of Warsaw

Jacek Komasa – Poznań University

Krzysztof Pachucki – University of Warsaw

Konrad Piszczatowski – University of Warsaw

Michał Przybytek – University of Warsaw

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