Laboratoire Kastler Brossel
Physique quantique et applications

QED corrections for simple molecules

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- VaQuM2020: Variational Methods for Quantum Many-body sysyems

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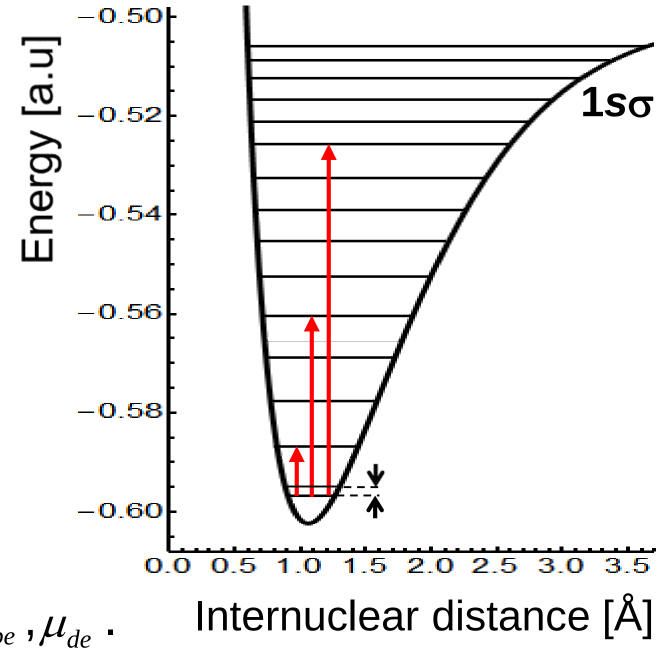
HMI and fundamental constants

Dependence of ro-vibrational transition frequencies on fundamental constants :

$$\nu = c\boxed{R_\infty}\left[\underbrace{\varepsilon_{nr}(\boxed{\mu_{ne}})}_{\text{Schrödinger}} + \underbrace{\alpha^2 F_{QED}(\alpha)}_{\text{Relativistic and QED corrections}} + \underbrace{\sum_n A_n^{fs}(\boxed{r_n}/a_0)^2}_{\text{Nuclear finite size correction}}\right]$$

<u>Vibrational</u>: $\varepsilon_{nr} \propto \sqrt{m_e/m_r}$

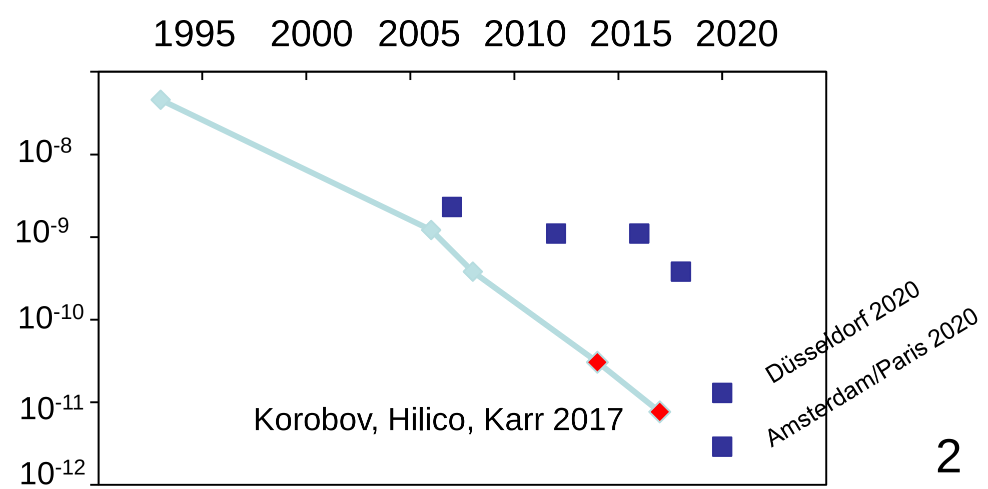
<u>Rotational</u>: $\varepsilon_{nr} \propto m_e/m_r$



$\Rightarrow$ Spectroscopy of H_2^+/HD^+ can be used to determine μ_{pe}, μ_{de} .

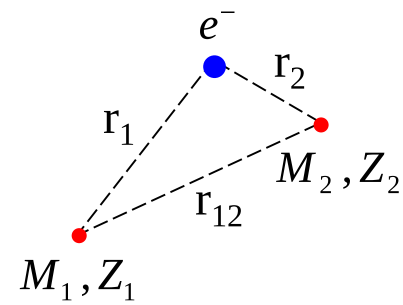
W.H. Wing, G.A. Ruff, W.E. Lamb Jr., J.J. Spezeski, PRL **36**, 1488 (1976)

- <u>Experiments</u> reach very recently a few **10^{-12}** using Doppler-free schemes
- <u>Theoretical</u> accuracy of <u>spin-averaged</u> vibrational transitions = **7.5 10^{-12}**
- However, the exp analysis requires the hyperfine structure calculations!



The three-body Schrödinger equation and variational expansion

$$H\psi = E\psi \qquad H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{p^2}{2m_e} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \frac{Z_1 Z_2}{r_{12}}$$



- Expansion on a basis set $\psi = \sum_{i=1}^{N} c_i \psi_i$

$\Rightarrow$ Eigenvalue problem $\mathbf{H}c = \varepsilon \mathbf{S}c$

$$\begin{cases} H_{ij} = \langle \psi_i | H | \psi_j \rangle & \text{Hamiltonian matrix} \\ S_{ij} = \langle \psi_i | \psi_j \rangle & \text{overlap matrix} \end{cases}$$

Hylleraas-Undheim-MacDonald theorem: $\boxed{\varepsilon_n \geq E_n}$

- How to choose the basis functions ψ_i?

  - fast convergence of energy vs basis size N

  - **as simple as possible** in order to have simple analytical expressions for matrix elements

  - correct behavior at small electron-nucleus distances (Kato cusp condition) is important for relativistic/QED corrections.

- 3-body variational expansion

Separation of radial and angular variables:

$$\boxed{\psi_{LM}^{\Pi}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l_1 + l_2 = L \text{ or } L+1} \mathcal{Y}_{LM}^{l_1 l_2}(\mathbf{r}_1, \mathbf{r}_2) F_{l_1}(r_1, r_2, r_{12})}$$

C. Schwartz, Phys. Rev. **123**, 1700 (1961)

Radial wavefunctions:

$$\boxed{F(r_1, r_2, r_{12}) = \sum_{n=1}^{N} \left(C_n \,\mathrm{Re}\left(e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}}\right) + D_n \,\mathrm{Im}\left(e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}}\right)\right)}$$

V.I. Korobov, Phys. Rev. A **61**, 064503 (2000)

- Exponents generated pseudo-randomly in several intervals.

Status of HD$^+$ hyperfine structure theory

LKB

$$H_{\mathrm{eff}} = \underbrace{E_1(\mathbf{L}\cdot\mathbf{s}_e)}_{\text{Spin-orbit}} + \underbrace{E_2(\mathbf{L}\cdot\mathbf{I}_p) + E_3(\mathbf{L}\cdot\mathbf{I}_d)}_{\text{Nuclear spin-rotation}} + \underbrace{E_4(\mathbf{I}_p\cdot\mathbf{s}_e) + E_5(\mathbf{I}_d\cdot\mathbf{s}_e)}_{\text{Spin-spin Fermi contact interaction}}$$

$$\left.\begin{aligned}
&+E_6\left\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_p)]\right\}\\
&+E_7\left\{2\mathbf{L}^2(\mathbf{I}_d\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_d)]\right\}\\
&+E_8\left\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{I}_d) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d) + (\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{I}_p)]\right\}
\end{aligned}\right\}\text{Spin-spin tensor interactions}$$

$$+E_9\left\{\mathbf{L}^2\mathbf{I}_d^2 - \frac{3}{2}(\mathbf{L}\cdot\mathbf{I}_d) - 3(\mathbf{L}\cdot\mathbf{I}_d)^2\right\}\text{Deuteron Quadrupole moment}$$

✓ Calculations at the Breit-Pauli level (~α^2 relative accuracy)

D. Bakalov, V.I. Korobov, S. Schiller, PRL 2006

(L=1,v=0) Unit: MHz	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
	31.9846	-3.134[-02]	-4.809[-03]	924.629	142.146	8.6111	1.3218	-3.057[-03]	5.666[-03]
	2			1		3			

✓ Higher-order corrections to E_4, E_5

V.I. Korobov, J.C.J. Koelemeij, L. Hilico, J.-Ph. Karr, PRL 2016 (H_2^+)

My work is here

➢ Next step: $(Z\alpha)^2$ relativistic correction to E_1 ; then E_6, E_7

Hyperfine structure calculations and results

➢ HD^+

Theoretical work

- The spin-orbit coefficient E_1 in kHz
  - ✓ M.Haidar, Z.-X. Zhong, V. I. Korobov, and J.-Ph. Karr, Phys. Rev. A 101, 022501, 2020.
  - ✓ V.I.Korobov, J.-Ph. Karr, M. Haidar, Z.-X. Zhong, arXiv:2006.02691, 2020.

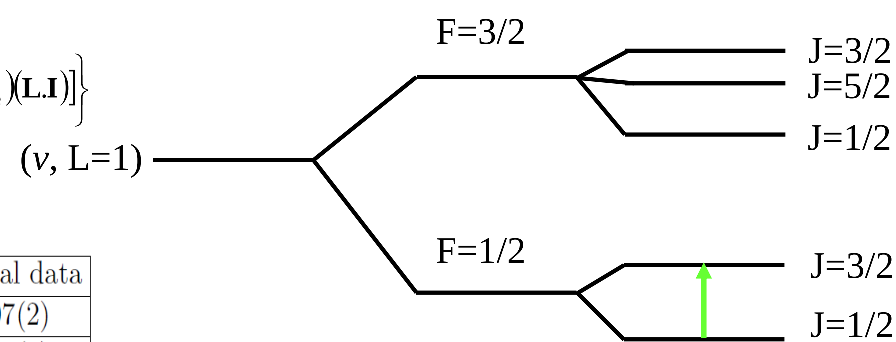
(L,v)	$E_1^{(BP)}$	U_{1b}	U_{2b}	U_{5a}	ΔE_{so}	ΔE_{so-ret}	$\Delta E_{so-so}^{(1)}$	$\Delta E_1^{(6)}$	E_1(this work)
(1,0)	31 984.645	1.170	-2.736	0.021	2.087	0.263	0.313	**1.118**	31 985.76
(1,6)	22 643.474	0.834	-2.097	0.044	1.509	0.181	0.219	**0.689**	22 644.16
(3,0)	31 627.353	1.156	-2.694	0.019	2.043	0.260	0.308	**1.093**	31 628.45
(3,9)	18 270.577	0.680	-1.732	0.043	1.161	0.146	0.182	**0.481**	18 271.06

Experimental result

- At Amesterdam: 2 hyperfine lines: (L=3, v = 0) ⟶ (L=3, v = 9)
  - ✓ S. Patra, et al (Submitted to Science), 2020
- At Düsseldorf: 6 hyperfine lines: (L=0, v = 0) ⟶ (L=1, v = 0)
  - ✓ S. Alighanbari, et al, *Nature 581,* (2020)

➢ H_2^+

$$H_{eff} = b_F(\mathbf{I}.\mathbf{s}_e) + c_e(\mathbf{L}.\mathbf{s}_e) + c_I(\mathbf{L}.\mathbf{I}) + \frac{d_1}{(2L-1)(2L+3)}\left\{\frac{2}{3}\mathbf{L}^2(\mathbf{I}.\mathbf{s}_e) - [(\mathbf{L}.\mathbf{I})(\mathbf{L}.\mathbf{s}_e) + (\mathbf{L}.\mathbf{s}_e)(\mathbf{L}.\mathbf{I})]\right\}$$
$$+ \frac{d_2}{(2L-1)(2L+3)}\left\{\frac{1}{3}\mathbf{L}^2\mathbf{I}^2 - \frac{1}{2}(\mathbf{L}.\mathbf{I}) - (\mathbf{L}.\mathbf{I})^2\right\}$$



In kHz

Preliminary

(L,v)	[1]	new calculation	experimental data
(1,4)	15.371049	15.371397	15.371407(2)
(1,5)	14.381189	14.381507	14.381513(2)
(1,6)	13.413169	13.413451	13.413460(2)

- RF spectroscopy experiments

S.C. Menasian, PhD Thesis (1973)

[1] V.I. Korobov, J.C.J. Koelemeij, L. Hilico, J.-Ph. Karr, PRL **116**, 043001 (2016)